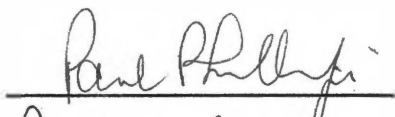
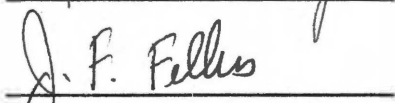
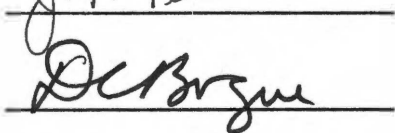


To the Graduate Council:

I am submitting herewith a dissertation written by Zhuomin Ding entitled "The Study Of The Kinetics Of Crystallization Of Polymers During Rapid Cooling And Computer Modeling Of Melt Spinning Process." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Polymer Engineering.


Joseph E. Spruiell, Major Professor

We have read this dissertation
and recommend its acceptance:

Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

**THE STUDY OF THE KINETICS OF CRYSTALLIZATION OF
POLYMERS DURING RAPID COOLING
AND
COMPUTER MODELING
OF THE MELT SPINNING PROCESS**

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Zhuomin Ding

May, 1996

ACKNOWLEDGEMENTS

The author would like to express his appreciation to his major professor and advisor, Professor Joseph E. Spruiell, for his guidance, support and encouragement throughout the course of this work.

The author also would like to thank Professors P. J. Philips, D. C. Bogue, and J. F. Fellers, for serving on his committee and for their advice and suggestions during this work.

Special thanks are extended to Exxon Chemical Company for their support of this work and for supplying the polymers and some characterization of the polymers.

The author acknowledges the help provided by the electronics and machine shops, and his fellow students and friends. Special thanks go to Mr. Fumin Lu., Dr. Sam He and Mr. Manho Kim.

Finally, the author wishes to express his deepest gratitude to his family and his wife for their support and love.

ABSTRACT

A new technique based on Light Depolarizing Microscopy (LDM) for the study of nonisothermal crystallization of polymers was developed in this research. The cooling rates applied in this technique are not constant, and the polymer is cooled down by a cooling medium with constant temperature. The cooling rates applied in this dissertation ranged up to 2500 °C/min and the technique has a potential ability to reach much higher cooling rates. The temperature measurement was introduced into the LDM technique by using a thermocouple directly embedded in the polymer. A second light sensor was also introduced in the LDM technique to follow the light scattering effect caused by the numerous nuclei created under high cooling rates. This information is necessary in order to correct for the light scattering effect. The developed technique includes a VCR system used for the measurements of spherulite growth during crystallization under high cooling rates. Two light intensities, temperature, and spherulite growth can be simultaneously measured in the developed technique.

A heat transfer analysis for the considered sample assembly used in the developed technique was carried out to check the influence of temperature distribution along the direction perpendicular to the sample plane. It was found that for a sample thickness less than 150 μm and cooling rates up to 2500 °C per minute the temperature distribution in the sample can be neglected. This heat transfer analysis thus supplies a basis for the believe that the temperature measurement in the technique is well controlled. Based on the heat transfer analysis, a cooling rate function (CRF) has been suggested for quantitatively describing the cooling condition applied in the experiments.

An optical analysis for the developed system was also made to supply the theoretical base for the technique. A new equation and a new quantity to correct for the

light scattering effect encountered in the experiment were proposed based on this analysis. The proposed equation and quantity were successfully used in correction of the light scattering effect and was verified by numerous experiments. The optical analysis includes a potential ability to handle measurements of crystallization under orientation.

A power law nucleation rate function was proposed to analyze the kinetic data obtained by the technique. Based on the proposed nucleation function, the Avrami equation was derived and the Avrami index and rate constant were found to have new meaning. According to the nucleation function, various kinetic equations for nonisothermal crystallization appearing in the literature were found to be different forms of the Avrami equation. According to this new analysis the Avrami index can be separated into geometric and nucleation indexes, and from the crystallization constant, a nucleation rate constant can be calculated. The nucleation index and nucleation rate constant are the two parameters which determine the power law nucleation rate function. The nucleation function can thus be determined from the Avrami index and crystallization rate constant obtained through the usual Avrami analysis for the experimental kinetic data. From the determined nucleation function, the nucleation density as a function of time can be computed. Also through the power law nucleation rate function, the theoretical base for application of the Avrami equation to the nonisothermal kinetic data obtained through the developed technique was established.

The developed technique and theories were applied to six isotactic polypropylenes. Both overall crystallization rates and growth rates were studied during nonisothermal crystallization at rapid cooling rates. The growth rates in isothermal crystallization were also examined for the six iPPs to help understand the data obtained by the developed technique and supply the bridge connecting the technique to the traditional kinetic studies.

Important experimental facts discovered by the technique include the following. The growth rate is constant with time during nonisothermal crystallization under rapid cooling rates. The growth rate measured by the technique is well connected to the data obtained under isothermal condition; i.e., the data obtained by both the new technique and by the established isothermal crystallization method composed one picture describing the crystallization kinetics by growth rate. These facts suggest that the crystallization kinetic data obtained from the experiments can be explained by a local isothermal crystallization mechanism. The growth rate study by the technique thus extended the temperature range of growth rate studies to a much lower and wider range important to the understanding of crystallization occurring in polymer processing. The differences of the growth rates for different materials were found to be small in the examined range of molecular weight and molecular weight distributions. For the small possible difference in growth rate, for materials with different molecular weight and polydispersities, at high crystallization temperature, materials with lower molecular weight or broader polydispersity exhibit a higher growth rate, but these trends were found to be reversed in the lower crystallization temperature range. A possible mechanism has been suggested to explain these phenomena. Another important fact is that the overall crystallization rate is higher for materials which can produce higher nucleation rates during crystallization. The reason for materials producing higher nucleation rate may be attributed to a higher molecular weight and/or broader molecular weight distributions, or simply caused by different levels of nucleating impurities existing in the materials.

Equations describing the temperature dependence of nucleation rate constant and crystallization induction time were suggested according the experimental results obtained.

The crystallization kinetics data obtained for the six polypropylenes were used in developing an improved model for the melt spinning process. Other improvements in the melt spinning model included replacing the Newtonian viscosity equation by a

generalized power law equation based on the data obtained in shear experiments for nine iPPs with different molecular weight and polydispersity, and introducing the dependence of molecular weight and polydispersity into the model. The improved model has been tested for variation in molecular weight, polydispersity, and spinning conditions including spinning speeds, melt temperature, ambient temperature, and mass throughput. Among these, the results from variation of molecular weight and polydispersity are most difficult to obtain and understand, and these results have been carefully discussed through key parameters such as crystallization onset stress, onset temperature, crystallization rate constant, Avrami index, nucleation rate constant, final birefringence, final crystallinity, final orientation functions and so on. By these tests, the model was found to give satisfactory simulations of the melt spinning process.

TABLE OF CONTENTS

PAGE

Chapter 1 INTRODUCTION

1

Chapter 2 FUNDAMENTAL BACKGROUND AND LITERATURE REVIEW

		4
2.1.	Basic Concepts Of Polymer Crystallization	4
2.1.1.	Basic Structural And Morphological Concepts.....	4
2.1.2.	Basic Concepts Of Isothermal Polymer Crystallization Kinetics	6
	Overall crystallization rate ——— nucleation and growth phenomena	6
	Growth rate theory	10
	Nucleation	13
	Expression of crystallization rate constant k	14
2.1.3.	Typical Methods Of Studying Crystallization Kinetics In Polymers	15
	Calorimetry.....	15
	Dilatometry.....	18
	Light Depolarizing Microscopy (LDM).....	18
	Other methods.....	21
2.2.	Quiescent Nonisothermal Crystallization	22
2.2.1.	Prior Studies And Methods Analysis Of Nonisothermal Crystallization In Polymers.....	22
2.2.2.	Major Experimental And Analytical Problems In The Analysis Of Nonisothermal Crystallization.....	25
2.3.	Crystallization In The Presence Of Molecular Orientation	25
2.3.1.	Prior Studies And Attempts To Analyze The Influence Of Molecular Orientation.....	25
	General characteristics	25
	Flow-induced crystallization	27

	Stress-induced crystallization	29
	Kinetic equation including the orientation effect	32
2.4.	Prior Studies Of The Crystallization Of Isotactic Polypropylene...	36
2.4.1.	Structure And Morphology.....	36
2.4.2.	Isothermal Crystallization Kinetics.....	42
2.4.3.	Nonisothermal Quiescent Crystallization Kinetics.....	46
2.4.4.	Influence Of Molecular Orientation.....	48
2.5.	Review of Computer Simulation Of Melt Spinning Process	48

Chapter 3

METHOD FOR THE STUDY OF THE QUIESCENT NON-ISOTHERMAL CRYSTALLIZATION UNDER RAPID COOLING RATES

		51
3.1.	Introduction	51
3.2.	Material Studied And Equipment	52
3.2.1.	Hot Stage System	52
3.2.2.	Temperature Measurement	55
3.2.3.	Sample Assembly	56
3.2.4.	Light Intensity Measurement	56
3.2.5.	Spherulite Diameter Measurement	56
3.3.	Analysis Of The Heat Transfer Problem.....	56
3.4.	Factors Affecting Light Intensity Measured	67
3.4.1.	Effect Of Sample Thickness On The Light Intensity.....	67
3.4.2.	Evidence Of Light Scattering Effect In LDM Method (Under High Cooling Rates)	69
3.4.3.	Correction For The Light Scattering Effect.....	73
3.5.	Results	76
3.5.1.	Temperature	76
3.5.2.	Light Intensities	78
3.5.3.	Spherulite Diameter Measurement	82
3.5.4.	Relative Relationships Between I , I_0 , R , T , And Spherulite Growth	91
3.6.	Preliminary Conclusions Concerning The Technique And Its Application To Polypropylene Crystallization Studies	92

Chapter 4

INTERPRETATION OF CRYSTALLIZATION KINETICS USING A POWER LAW NUCLEATION FUNCTION

		95
4.1.	Introduction	95
4.2.	Nucleation Rate Function And Derivation Of The Avrami Equation	95
4.3.	Significance Of The Nucleation Rate Function	101
4.4.	Relationships Between Various Nonisothermal Kinetic Equations	103
4.5.	Kinetic Analysis	108
4.5.1.	Introduction	108
4.5.2.	Material And Experimental	109
4.5.3.	Parameters Directly Collected From Experimental Data	111
4.5.4.	Discussion Of The Parameters Directly Collected From Experimental Data	121
4.5.5.	Parameters Based On Kinetic Theories	127
4.5.6.	Discussion Of The Parameters Based On Kinetic Theories ...	133
4.6.	Nucleation Density	137
4.7.	Comparison With The Results From Other Research (Growth Rate)	139
4.8.	Conclusions Concerning The Use Of The Nucleation Rate Function	143

Chapter 5

QUIESCENT NONISOTHERMAL CRYSTALLIZATION OF ISOTACTIC POLYPROPYLENES

		146
5.1.	Introduction	146
5.2.	Materials and Experimental.....	147
5.3.	Preliminary Characterization Of The Materials	151
5.4.	Results	153
5.4.1.	Crystallization Plateau Temperature, Induction Time And Onset Temperature	153
5.4.2.	Crystallization Half Time	153
5.4.3.	Growth Rate Measurements	162
5.4.4.	Relative Nucleation Densities	173
5.4.5.	Avrami Index And Crystallization Rate Constant	173

5.4.6.	Calculation of Nucleation Rate Constant and Nucleation Densities	181
5.5.	Discussion	185
5.5.1.	Growth Rate	185
	Discussion of growth rate	185
	Mechanism of crystal growth	187
5.5.2.	Discussion Of The Crystallization Induction Time	188
5.5.3.	Discussion Of Overall Crystallization Rate	190
	Discussion on the material characteristics	190
	Crystallization half-time	191
	Avrami index, nucleation rate constant and nucleation rate	192
	Mechanism of nucleation	195
5.5.4.	Discussion Of The Crystallization Plateau Temperature	196
5.6.	Conclusions	197

Chapter 6

COMPUTER MODELING OF THE MELT SPINNING PROCESS

		199
6.1.	Introduction	199
6.2.	Description Of The Model	200
6.2.1.	Crystallization Kinetic Equation	200
6.2.2.	Crystallization Induction Time t_0	202
6.2.3.	Avrami Index, Crystallization Rate Constant And Nucleation Rate Function	203
6.2.4.	Final Crystallinity X_c And Crystalline Orientation Factor f_c ..	206
6.2.5	Energy Balance	207
6.2.6.	Elongational Viscosity	208
6.3.	Parameter Adjustment	212
6.4.	Extension Of The Model To Materials With Various Molecular Weight And Molecular Weight Distributions	215
6.4.1.	Viscosity	216
6.4.2.	Constants In The Equation For Nucleation Rate Constant	218
6.4.3.	Constants In Crystallization Induction Time t_0	219
6.4.4.	Constants In The Equation Related To Crystallization Half Time	219

6.4.5.	Constants In The Equation Related To Final Crystallinity X_c ..	221
6.4.6.	Constants In The Equation Related To Crystalline Orientation Factor	221
6.5.	Description Of The Calculation Procedure	221
6.6.	Simulation Results	229
6.6.1.	Relationships Between Various Profiles	229
6.6.2.	Influence Of Change In Molecular Weight.....	231
	Predicted results	232
	Discussion of influence of molecular weight	238
	Parameters related to crystallization	
	onset: t_1 , t_0 , T_{on} , σ_{on} and X_{on}	242
	Crystallization kinetic parameters: n , N_c , and k	245
	Final orientation and crystallinity	249
6.6.3.	Change In Molecular Weight Distribution	249
	Predicted results	249
	Discussion of the simulated profiles	253
	Parameters related to crystallization	
	onset: t_1 , t_0 , T_{on} , σ_{on} , and z_{on}	261
	Crystallization kinetic parameters: n , N_c , and k	265
	f_c and f_a , X_c , and Δn	267
6.6.4.	Variation In Spinning Conditions	270
6.7.	Necking Phenomenon	270
6.8.	Conclusion Remarks	271

Chapter 7

	CONCLUSIONS AND RECOMMENDATIONS ..	274
7.1.	Summary Of Major Conclusions	274
7.2.	Recommendations For Future Research	278
	LIST OF REFERENCES	281
	APPENDIXES	291

Appendix A

NUMERICAL SOLUTION FOR THE PARTIAL DIFFERENTIAL EQUATIONS FOR THE NONISOTHERMAL PROCESS

		292
A.1.	Temperature Of $\Theta_i^j = \Theta_1^j$, At $\xi_i = \xi_1$ For $j=1, 2, 3, \dots$, i.e., At B.C. 1	296
A.2.	Temperature Of $\Theta_i^j = \Theta_2^j, \Theta_3^j, \dots, \Theta_{I-1}^j$ at $0 < \xi_2, \xi_3, \dots, \xi_{I-1} < 1$, For $j = 1, 2, 3, \dots$ ($j=0$ Is Initial Condition.)	299
A.3.	Temperature Of $\Theta_i^j = \Theta_I^j$, At $\xi_i = \xi_I$ For $j=1, 2, 3, \dots$, i.e., At B.C. 2	300

Appendix B

ANALYSIS OF THE LIGHT INTENSITY AS A FUNCTION OF CRYSTALLINITY AND MOLECULAR ORIENTATION IN THE LIGHT DEPOLARIZING MICROSCOPY

		313
B.1.	Introduction	313
B.2.	Light Intensity From An Oriented Single Crystal	313
B.2.1.	Generalized Retardation Equation	316
B.2.2.	Refraction Index On The Equivalent Optical Axis	319
B.2.3.	The Propagation Direction Of Ordinary Ray	328
B.2.4.	Propagation Direction Of Extraordinary Ray	328
B.2.5.	Some Relations	331
B.2.6.	Generalized Light Transmission Equation	332
B.3.	Light Intensity Equation For A Crystalline Sample	335
VITA		342

LIST OF TABLES

TABLE	PAGE
2.1. Theoretical Values Of The Avrami Index, n	8
2.2. Unit Cells of Isotactic Polypropylene	36
2.3. Type Of Spherulites And Their Birefringence Value [Padden And Keith (1959, 1966), Samuels And Yee (1972)]	38
2.4. Refractive Indexes Along Unit Cell Axes	40
3.1. The Estimated Maximum Cooling Rate For Three Different Sample Thickness For LDPE	64
4.1. Regressive Constants In Hoffman-Lauritzen Equation For The Experimental Data Of Growth Rate Obtained By Different Researchers	141
5.1. Isotacticities Estimated By FTIR For All Six Isotactic Polypropylenes	148
5.2. Crystallization Temperature, Melting Temperatures And Crystallinities Determined By DSC For All iPPs	152
5.3. Summary Of The Regressive Constants And Coefficients For Crystallization Half Time, Crystallization Rate Constant, And Nucleation Rate Constant.	161
5.4. Summary Of Regressive Constants, K_g And $\ln(G_0)$, In The Hoffman-Lauritzen Equation And Square Of Regressive Coefficient, r^2 , For All Six iPPs.	167
5.5. Avrami Index, Nucleation Index And Value Of B-Function For The Six Considered Materials	177
6.1. Materials Studied and Regressive Constants In the Viscosity Equation	217
6.2. Regressive Constant In The Equation For Nucleation Rate Constant ..	220

LIST OF FIGURES

FIGURE	PAGE
2.1. Summary of the previous melt spinning model [Patel, Bheda and Spruiell (1991)]	50
3.1. Experimental system.	53
3.2. Hot stage system.	54
3.3. Sample assembly used in the experiments.	57
3.4. Schematic diagram of the light depolarizing microscope.	58
3.5. Temperature distribution in a slab at various time which is cooled down a flowing air in a temperature = 0°C. The heat transfer coefficient h_a is 70 (W/M ² K)	61
3.6. Temperature distribution in a slab at various time which is cooled down a ice water. The heat transfer coefficient h_a was assumed to be 500 (W/M ² K), or CRF = 0.908 (1/sec).	62
3.7. Comparison of the cooling curves calculated by the complex model, equation (3.1)- (3.4), at $x = 0$, and the simplified model, equation (3.6), at various cooling rates.	66
3.8. Light intensity measured from the slow cooled and quenched samples versus sample thickness after light compensation was made. I_0 was kept at $3.07 \cdot 10^{-12}$ (w/cm ²) when the light path was half open, without analyzer and with one glass slide and one glass cover in light path.	68
3.9. Light intensity, light intensity without analyzer, and relative light intensity versus time.	70
3.10. Light intensity without analyzer, temperature and spherulite radius versus time for CRF = 0.600 (1/sec).	71
3.11. Light intensity, I , as a function of the light intensity without analyzer, I_0' , for samples with different crystallinity levels (sample thickness = 0.15 [mm]).	74
3.12. Cooling curves for PP at five different cooling rates.	77
3.13. Fitting the cooling curve to obtain CRF.	79
3.14. Average cooling rate before crystallization versus CRF.	80
3.15. Light intensity without analyzer versus time at various cooling rates.	81
3.16. Light intensity versus time at various cooling rates.	83
3.17. Relative light intensity versus time at various cooling rates.	84
3.18. Relative crystallinity versus time at five cooling rates.	85

FIGURE	PAGE
3.19. Relative crystallinity versus temperature at various cooling rates	86
3.20. Relative light intensity versus temperature at various cooling rates	87
3.21. Spherulite radius versus time measured at two cooling rates indicated in the figure.	88
3.22. Light intensity, temperature and spherulite radius versus time for CRF = 0.600 (1/sec)	90
3.23. Temperature and relative light intensity versus time at CRF=0.074 (1/sec)	93
4.1. Examples of temperature versus time obtained in nonisothermal crystallization experiments at various cooling rates for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	113
4.2. Examples of relative crystallinity versus time obtained in nonisothermal crystallization experiments at various cooling rates for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	114
4.3. Plateau temperature, T_p , versus heat transfer coefficient, h_a , at all applied cooling rates in the experiments for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	115
4.4. The growth rate, G , versus crystallization temperature at all applied cooling rates in the experiments for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	116
4.5. Hoffman-Lauritzen plot for the growth rates plotted in Figure 4.4	117
4.6. Crystallization induction time and crystallization onset temperature at different cooling rates for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	119
4.7. The crystallization half time versus crystallization plateau temperature at different cooling rates for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	120
4.8. $\ln(1/t_{1/2})$ versus $\frac{1}{T\Delta T f}$ for the data plotted in Figure 4.7.	122
4.9. Relating crystallization induction time to the crystallization onset temperature according to Equation (4.37) for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	126
4.10. Avrami plot, $\ln\ln\left(\frac{1}{1-\theta}\right)$ versus $\ln(t)$, for runs at different cooling rates for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	128

FIGURE	PAGE
4.11. Avrami index obtained for all examined cooling rates versus crystallization plateau temperature for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	130
4.12. Crystallization rate constant, k , obtained for all examined cooling rates versus crystallization plateau temperature for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	131
4.13. $\ln(k)+U^*/R(T - T_s)$ versus $\frac{1}{T\Delta T_f}$ for the data plotted in Figure 4.12.	132
4.14. Nucleation rate constant, N_c , versus crystallization plateau temperature for all examined cooling rates for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	134
4.15. $\ln(N_c)+U^*/R(T - T_s)$ versus $\frac{1}{T\Delta T_f}$ for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	135
4.16. Nucleation density versus time at various cooling rates for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$	138
4.17. A comparison of growth rates among results from different researches indicated in the figure.	140
4.18. A comparison of predictions for the growth rate as function of crystallization temperature by Hoffman-Lauritzen equations, for Regime III, obtained in Figure 4.17.	142
5.1. Average cooling rate versus heat transfer coefficient applied in the experiments.	150
5.2. Crystallization plateau temperature T_p versus heat transfer coefficient h_a for all six materials considered.	154
5.3. Crystallization induction time and crystallization onset temperature versus cooling rates, described by heat transfer coefficient, for all six materials.	155
5.4. Relating crystallization induction time to the crystallization onset temperature according to Equation (4.37).	156
5.5. The crystallization half time obtained directly from θ - t plot, $t_{1/2}$ (circles), and calculated from crystallization rate constant and Avrami index, $t_{1/2,cal}$ (squares), versus plateau temperature, T_p , for six considered iPPs.	157
5.6. A comparison of crystallization half time versus plateau temperature among the six examined iPPs.	159
5.7. $\ln(1/t_{1/2})+U^*/R(T-T_s)$ versus $\frac{1}{T\Delta T_f}$ for the data plotted in Figure 5.6	160

FIGURE	PAGE
5.8. Growth rates measured under iso- and nonisothermal crystallization for six considered materials, individually plotted.	163
5.9. Measured growth rates and regressive curves for all six materials.	164
5.10. Hoffman-Lauritzen plot of growth rates for the six considered materials, separately plotted.	165
5.11. Hoffman-Lauritzen plot of growth rates for the six considered materials, comprehensively plotted.	166
5.12. Comparison of the effect of molecular weight (MW) on the growth rate, G: (a) narrow breath ; and (b) broad breath.	168
5.13. Comparison of the effect of molecular weight distribution on the growth rate: (a) high MW, (b) medium MW, and (c) low MW	169
5.14. Growth rate versus molecular weight at different crystallization temperature for broader MWD materials, Resin #3, 5, and 6.	171
5.15. Growth rate versus polydispersities at different crystallization temperature for medium MW materials, Resin #9 and 5.	172
5.16. Measured relative nucleation density for all six considered iPPs	174
5.17. Avrami index, n , versus crystallization plateau temperature, T_p under various cooling-rates for six considered iPPs.	176
5.18. The crystallization rate constant, k , obtained directly by Avrami analysis (triangles) and through crystallization half time (circles) versus plateau temperature, T_p , at various cooling rates for six considered iPPs.	178
5.19. The crystallization half time calculated from crystallization rate constant and Avrami index, $t_{1/2,cal}$, versus the one obtained directly from θ -t plot, $t_{1/2}$, for six considered iPPs.	179
5.20. Crystallization rate constant k versus crystallization plateau temperature T_p for the six considered iPPs.	182
5.21. Nucleation rate constant N_c versus crystallization plateau temperature T_p for the six considered iPPs.	183
5.22. Calculated nucleation density versus time for materials with different MW and broad MWD at crystallization temperature = 96 °C.	184
5.23. Final nucleation density calculated according to equation (4.40) using data given in Tables 5.3 - 5.5	186
6.1. Fitting the energy balance equation to the experimental temperature measured in quiescent nonisothermal crystallization under a rapid cooling rate.	209

FIGURE	PAGE
6.2. Magnitude of complex viscosity versus angular frequency at experimental temperature = 180 °C for the nine considered iPPs.	210
6.3. Example of fitting the simulated result to the experimental birefringence to adjust model parameters C_{IO} , C_{NO} , and n for Resin #6, $M_w = 136060$ and $M_w/M_n = 3.8$. Spinning conditions: melt temperature = 210 °C, diameter of spinneret = 0.0764 mm, ambient temperature = 30 °C, spinning length = 220 cm, and the take-up velocities are specified in the plot.	214
6.4. Flow diagram of the calculation procedure of the model of the melting spinning process.	222
6.5. Calculated birefringence, diameter, temperature, crystallinity, and nucleation density versus distance from spinneret at various spinning speeds for iPP spinning speed = 5700 m/min, $M_w = 141790$, $M_w/M_n = 2.8$, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.68 g/min.	230
6.6. Calculated birefringence versus distance from spinneret at various molecular weight for iPP. Polydispersity is held at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	233
6.7. Calculated temperature versus distance from spinneret at various molecular weight for iPP. Polydispersity is held at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	234
6.8. Calculated diameter versus distance from spinneret at various molecular weight for iPP. Polydispersity is held at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	235
6.9. Calculated crystallinity versus distance from spinneret at various molecular weight for iPP. Polydispersity is held at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	236
6.10. Calculated nucleation density versus distance from spinneret at various molecular weight for iPP. Polydispersity is held at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min. ...	237
6.11. Calculated elongational viscosity versus distance from spinneret at various molecular weight for iPP. Polydispersity is held at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	239
6.12. Calculated stress versus distance from spinneret at various molecular weight for iPP. Polydispersity is held at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	240

FIGURE	PAGE
6.13. Crystallization onset temperature, T_{on} , onset position, z_{on} , and onset stress, σ_{on} , as functions of molecular weight. Polydispersity was held at 3.8 and spinning speed is 2000 m/min.	241
6.14. crystallization induction time, t_0 , and time needed to cool down polymer from its melt temperature to equilibrium melting temperature, t_1 as functions of MW.	243
6.15. Temperature and stress in the polymer stream on the spinline as functions of time for materials with various molecular weight.	244
6.16. Avrami index, n , nucleation rate constant, N_C and crystallization rate constant, k , as functions of molecular weight.	246
6.17. Nucleation rate described power law nucleation rate function versus time for materials with various molecular weight.	248
6.18. Crystalline orientation function, f_C , amorphous orientation function, f_a , final crystallinity, X_C , and final birefringence, Δn , as functions of molecular weight.	250
6.19. Calculated birefringence versus distance from spinneret at various polydispersity for iPP. Mw = 170000, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	251
6.20. Calculated temperature versus distance from spinneret at various polydispersity for iPP. Mw = 170000, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	252
6.21. Calculated diameter versus distance from spinneret at various polydispersity for iPP. Mw = 170000, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	254
6.22. Calculated crystallinity versus distance from spinneret at various polydispersity for iPP. Mw = 170000, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	255
6.23. Calculated nucleation density versus distance from spinneret at various polydispersity for iPP. Mw = 170000, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	256
6.24. Calculated stress versus distance from spinneret at various polydispersity for iPP. Mw = 170000, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	258

FIGURE	PAGE
6.25. Calculated elongational viscosity versus distance from spinneret at various polydispersity for iPP. $M_w = 170000$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.	259
6.26. Crystallization induction time, t_0 , and time needed to cool the polymer from its melt temperature to its equilibrium melting temperature, t_1 , as functions of MWD.	262
6.27. Crystallization onset temperature, T_{on} , onset position, z_{on} , and onset stress, σ_{on} , as functions of molecular weight distribution. Weight average molecular weight was held as 170000 and spinning speed is 2000 m/min.	263
6.28. Temperature and stress in the polymer stream on the spinline as functions of time for materials with various molecular weight distribution.	264
6.29. Avrami index, n , nucleation rate constant, N_c and crystallization rate constant, k , as functions of polydispersity.	266
6.30. Nucleation rate described power law nucleation rate function versus time for materials with various polydispersity.	268
6.31. Crystalline orientation-function, f_c , amorphous orientation function, f_a , final crystallinity, X_c , and final birefringence, Δn , as functions of polydispersity.	269
A.1. Sample assembly and its coordinate system for the heat transfer analysis.	293
A.2. Variables used in the numerical solution of non-isothermal heat transfer problem for a slab.	306
A.3. Specific heat of LDPE (From [EPSE]).	307
A.4. Specific volume of LDPE.	308
A.5. Thermal conductivity of LDPE.	309
A.6. Cooling curve for a sample cooled down in air.	310
A.7. Cooling curve for a sample quenched in ice-water.	312
B.1. Coordinate system adopted for the optical analysis of light depolarization by a single crystal. The stage plane of LDM is parallel to xy-plane.	315
B.2. A polarized light ray, thick with arrow is birefracted by a lamella, KLMN.	317
B.3. Separating of incident ray into ordinary and extraordinary rays by a lamella KLMN.	320

FIGURE	PAGE
B.4. C - C section view of Figure B.3.	321
B.5. A incident ray (polarized) in F'G'FG plane is birefracted by a lamella (KLMN is a plane in the lamella). The ordinary ray is vibrating in O'O"W'W" plane and the extraordinary ray is vibrating in KLMN plane.	323
B.6. Relations between the directions of electrical field vectors and propagation of the extraordinary and ordinary rays.	324
B.7. Determine the direction of extraordinary ray by Huygens principle.	325
B.8. Relations between directions of lamellar optical axis, vibration of electrical field of extraordinary and ordinary, and the propagation direction of incident, extraordinary and ordinary rays.	327
B.9. Separating the amplitude of electrical field of incident ray into the ones of extraordinary and ordinary rays.	333
B.10. The amplitudes of electrical field of extraordinary and ordinary rays are separated into components on the directions of polarizer and analyzer.	334

NOMENCLATURE

c	light velocity in vacuum.
C	Light scattering constant.
C_d	Drag coefficient.
C_I	Temperature coefficient for crystallization induction time.
C_{IO}	Orientation parameter for crystallization induction time.
C_k	Temperature coefficient for crystallization rate constant,
C_N	Temperature coefficient for nucleation rate constant.
C_{NO}	Orientation parameter for nucleation rate constant.
C_p	Heat capacity.
C_{t12}	Temperature coefficient for crystallization half time.
D	Filament diameter.
d_e	distance which extraordinary ray goes through the crystal
d_o	distance which ordinary ray goes through the crystal
E_a	amplitude of the transmitted light wave in analyzer direction
E_e	amplitude of extraordinary ray, the light wave in direction of the equivalent optical axis
E_{ea}	amplitude of light wave of the component of E_e in direction cross to the equivalent optical axis
E_{ep}	amplitude of light wave of the component of E_e in the direction of the equivalent optical axis
E_i	amplitude of the incident light wave
E_p	amplitude of the light wave in direction cross to the equivalent optical axis.
E_o	amplitude of ordinary ray, the light wave in the direction cross to the equivalent optical axis
E_{oa}	amplitude of light wave of the component of E_o in direction cross to the equivalent optical axis
E_{op}	amplitude of light wave of the component of E_o in direction of the equivalent optical axis
f_a	Orientation function in the amorphous phase.
f_c	Orientation function in the crystalline phase.
g	Acceleration due to gravity.
G	Linear growth rate of spherulites.
h	Heat transfer coefficient.
h_a	Heat transfer coefficient of the air.

I	light intensity (with analyzer).
I_i	light intensity of incident light
I_a	light intensity emerging from analyzer
I_0	Light intensity without analyzer.
k	Thermal conductivity, crystallization rate constant.
K_g	Temperature coefficient for growth rate.
n	Avrami index, absolute refractive index.
n'	Avrami geometric index
n_a	refractive index in direction of optical axis
n_b	refractive index vertical to the direction of optical axis
n_e	refractive index for ordinary ray, in direction of the equivalent optical axis
n_o	refractive index for ordinary ray, vertical to the direction of the equivalent optical axis.
N_c	Nucleation rate constant.
$\dot{N}$	Nucleation rate.
m	Nucleation index.
R	Universal gas constant, relative light intensity.
t	Time.
t_0	Crystallization induction time.
t_1	Time when temperature equals to the equilibrium melting temperature.
$t_{1/2}$	Crystallization half time.
t_{on}	Crystallization onset time.
T	Temperature, crystallization temperature, plateau temperature, temperature in the polymer stream.
T_1	Temperature of the cooling medium.
T_a	Ambient temperature.
T_c	Crystallization temperature.
T_g	Glass transition temperature.
T_m	Melting temperature.
T_m°	Equilibrium melting temperature.
T_{on}	Crystallization onset temperature.
T_p	Crystallization plateau temperature.
T_s	$= T_g - 30$ (K).
U^*	Activation energy for segmental jump rate.

v	the speed of light in a medium
V	Filament velocity.
v_e	velocity of extraordinary ray
v_o	velocity of ordinary ray
W	Mass throughput rate.
X_c	Final crystallinity.
z	Distance from spinneret.
$\dot{E}$	Elongational rate.
δ	frequency difference
ΔH	Heat of fusion.
Δn	Birefringence.
$\dot{\gamma}$	Shear rate.
η	Shear viscosity.
η_0	Zero shear viscosity
η_e	Elongational viscosity
λ	wave length
$\lambda\delta$	path difference ($2\pi\delta$ ` phase difference).
θ	Relative crystallinity, the angle between extraordinary ray and the optical axis
ρ	Polymer density.
σ	Stress.
σ_{on}	Crystallization onset stress.
τ	Time.

Chapter 1

INTRODUCTION

Crystallization kinetics has mostly been studied isothermally in order to understand basic molecular mechanisms. The most widely used techniques in isothermal kinetic study are dilatometry [Bekkedahl (1949, 1967)], Differential Scanning Calorimetry (DSC) [Godovsky and Slonimsky (1974), Mancarella and Martuscelli (1977), Monasse and Haudin (1986)] and Light Depolarizing Microscopy (LDM) [Magill (1960, 1961, 1962)]. By LDM, the spherulite growth rates can also be determined. Kinetics of quiescent isothermal crystallization in polymers like PE and PP was generally studied at relatively low supercooling because, at the low cooling rates available, crystallization had already begun before the temperature in the polymer could reach a lower value. The prediction of crystallization under high supercooling is usually obtained by extrapolation of the data obtained in a narrow temperature range at high temperature.

Though a few kinetic studies of nonisothermal crystallization have been carried out, and a few publications have dealt with nonisothermal, quiescent crystallization, the cooling rates were far from those used in polymer processing, being generally less than 100 °C per minute. The DSC and LDM again were employed in the nonisothermal kinetic studies [Maglio, Martuscelli, Palumbo and Soldati (1976), Jeziorny (1978), Hay and Mills (1982), Hammami (1990), Chan and Isayev (1992)]. The cooling rates in polymer processing are usually very high (several thousands °C/min.), and are often accompanied by molecular orientation. For a better understanding of the crystallization kinetics under polymer processing conditions, one needs to study the crystallization under higher cooling rates with and without the presence of molecular orientation.

The basic thesis of the present dissertation is that improved methods (both experimental and analytical) of studying nonisothermal crystallization are necessary and possible. The dissertation's objectives are to (1) develop an improved experimental technique for studying crystallization of polymers under nonisothermal quiescent conditions, (2) develop appropriate analytical tools for analyses of the data from the experimental technique, (3) apply the technique and analysis to a series of polypropylene resins of differing molecular weight and molecular weight distribution, (4) extend of the technique and analysis to describe the orientation influenced crystallization that occurs during melt spinning and (5) incorporate the latter results into a mathematical model of the melt spinning process.

The research described in Chapter 3 was carried out in order to develop a technique of studying nonisothermal crystallization during rapid cooling with conditions close to those met in polymer processing. The primary concern of the research in Chapter 3 is to develop the experimental technique for studying nonisothermal quiescent crystallization. In order to be useful the technique must be capable of crystallization kinetics studies at cooling rates as high as several thousand °C per minute.

The limitation of the DSC and LDM methods apparently comes from the difficulty of creating a fast and constant cooling condition. Because optical-electron response is theoretically quick and sensitive enough to follow very rapid and small changes of crystallization in a thin film, which is the usual sample for the optical microscope, a modified LDM technique was selected to be used in the quiescent component of the proposed research. To create a high cooling rate in LDM, the following consideration was made for the quiescent and nonisothermal crystallization. Most crystallization that occurs during processing does not occur under constant cooling rates, and the constant cooling rates are not necessary for the kinetic study, if the temperature in the sample can be measured simultaneously as the light intensity is being recorded. In

our studies we carried out studies with a constant temperature of cooling medium (but not constant cooling rate). This procedure allows quick change in temperature, and also matches the cooling condition frequently encountered in polymer processing. For these reasons, the selected technique adopts a gas, with constant temperature, as cooling medium to create a rapid and nonisothermal cooling process. The developed technique also extends the experimental range of the growth rate studies to much lower crystallization temperatures than were previously available.

A power law nucleation rate function is proposed in Chapter 4 for the analysis of the experimental data obtained by the developed technique. Based on the proposed function, a method of analysis of the data is described, and the analysis is illustrated by application to interpret the data for a specific polypropylene resin. Based on the nucleation rate function, nucleation rate constant and nucleation index are defined. A method to separate them from the crystallization rate constant and the Avrami index is described. The nucleation density, can thus be calculated through the obtained nucleation rate function.

Chapter 5 applies the developed LDM technique and kinetic analysis developed in Chapter 4 to the study of the crystallization kinetics of six isotactic polypropylenes (iPP). These studies included the overall crystallization rate and growth rate. The results of Chapter 5 are applied in the computer simulation of the melt spinning process.

The computer modeling of melt spinning is described in Chapter 6. This model involves more than studying crystallization kinetics under orientation. Basically, three new aspects have been introduced into the model previously developed by Patel and Spruiell (1991): (1) new crystallization kinetic equations that include the influence of molecular orientation and a description of nucleation rate, (2) a generalized power law viscosity equation, and (3) the dependence of the model on molecular parameters.

Chapter 2

FUNDAMENTAL BACKGROUND AND LITERATURE REVIEW

2.1. Basic Concepts Of Polymer Crystallization

2.1.1. Basic Structural and Morphological Concepts

Polymer molecules sometimes possess the ability to crystallize, but the crystalline solids are usually only semi-crystalline. Therefore, for polymeric materials, there are differences of degree of crystallinity, size and shape of the crystallites (i.e. morphology) which affect the properties of the polymer. The morphology is affected by processing conditions like rate of cooling, presence of orientation and the temperature during crystallization. Other factors include the tacticity, molecular weight and molecular weight distribution, degree of branching, comonomer content, and presence of any additives such as nucleating agents.

Polymer molecules have conformations of the form of zig-zags or helices. PE molecules in zig-zag form pack into an orthorhombic unit cell with $a = 7.418$, $b = 4.946$, and $c = 2.546 \text{ \AA}$ with the c axis being the chain direction. The extension of a single crystal in the chain direction is only about $100 \text{ \AA}$, but it is much larger in the lateral direction. That is, the single crystals formed by polymer molecules are in the form of lamellae in which the chains run through the thickness direction and fold back and forth on themselves. There are two extreme models for molecular chains to form lamella: adjacent reentry model [Keller (1957)], and switchboard model [Flory (1962)]. Current understanding is that molecules in a lamella crystallized from polymer dilute solution will fold themselves according to the adjacent reentry model, but it is believed that crystallization from melt produces lamellae with structures in between the switchboard

and adjacent reentry models having tie-molecules and cilia. The extent of the adjacent reentry folds is dependent on the cooling rate for crystallization, the flexibility of the molecules, and the stress. The more rigid the molecules, or the higher the cooling rate, the fewer adjacent reentry folds will be formed and the lamellae formed will contain many more cilia and tie-molecules.

There is a regime theory [Hoffman, Davis and Lauritzen(1976), Hoffman (1982)] which describes how the lamellae are formed by molecules. In regime I, there are few growing centers on the growth front. The lamellae grow layer by layer of molecular stems. A layer is essentially formed by folding molecules stem by stem onto the previous formed layer. In regime II, the growth still goes layer by layer, but many more growing centers fill one layer simultaneously. In regime III, new growing centers are prolific and form before the previous layer is filled. Several layers are being filled up simultaneously in this case. Molecules crystallizing from the dilute solution, usually follow the regime I scheme, from concentrated solution or melt, regime I, II, or III. In the crystallization from melt at high supercooling or high cooling rate as in quenching, the crystal growth will likely follow regime III scheme and for low supercooling or low cooling rate process, regime II. For some polymers, regime I can occur in crystallization from melt.

The shape of the grown lamellae are different when crystallized from solution than when crystallized from the melt. The width and length of the solution crystallized lamellae are similar to and they look like plates. The simplest aggregation of lamellae in polyethylene is a pyramid which is composed by four {110} lamellae. When the preparation condition or the characteristics of the polymer changes, the resultant crystals may have different habit such as truncated lozenge which is a hollow pyramid with 4 {110} and 2 {100} fold domains, true lozenge that is flat, not pyramidal and consists of 4 {110} corrugated fold surface domains, and dendrite crystals [Bassett and Keller (1962)]. The lamellae formed from melt generally look like a lath which is narrow in width and

long in length. It may be twisted or non-twisted along the longitude of the lath. The aggregation of such lamellae is generally called a spherulite [Hoffman, Davis and Lauritzen (1976)]. The laths in spherulites are necessarily branched so that the space in the spherulite can be filled. There is amorphous material between lamellae within the spherulite. For polymer crystallization under stress, row nucleated structure has been observed, in which the crystals are nucleated on a central backbone and grow in directions perpendicular to it. A similar structure, called a shish-kebab, which consists of a central backbone with lamella overgrowth in directions perpendicular to the direction of the backbone, is also obtained from a stirred solution. Deformed spherulites, ellipsoidal in shape, may also be formed during crystallization from oriented melt.

2.1.2. Basic Concepts of Isothermal Polymer Crystallization Kinetics

2.1.2.1. Overall crystallization rate — nucleation and growth phenomena

Even though a knowledge of the linear growth rate and the primary nucleation rate could be used to calculate the overall crystallization rate, the experiments and theory about bulk crystallization are very important because the nucleation information can rarely be obtained; the impingement effect is difficult to be incorporated, and processes of secondary crystallization occur which cause additional complications. Because the measurement of the bulk crystallization rate includes comprehensive information on all those aspects, the analysis of the data becomes also quite complicated.

The first effort to describe bulk crystallization quantitatively in terms of nucleation and linear crystal growth rate was made by Kolmogoroff (1937), Johnson and Mehl (1939) and Avrami (1939, 1940, 1941). The kinetic equation was named after Avrami which was initially developed for metals and is a most popular kinetic equation for overall crystallization. The Avrami equation reads

$$\theta = 1 - \exp\{-k t^n\} \quad (2.1)$$

where θ is fraction of transformed phase, k is the crystallization rate constant, and n is the Avrami index which is related to the nucleation mechanism and geometry of crystal growth. The Avrami equation was originally derived according to statistical methods. Attempts to simplify its derivation were made by several authors [Evans (1954), Morgen (1954), Mandelkern (1964)]. Evans (1954) applied the Poisson distribution function in the derivation of the Avrami equation and made the derivation more acceptable. The equation was subsequently modified by Mandelkern (1964) to include some aspects of incomplete crystallization encountered in polymer crystallization. However, the Avrami equation describes the behavior of metallic systems more closely than that of polymeric materials. The idea of a two-phase system is implicit in the model. In the original derivation several approximations were introduced during the derivation. The isovolume assumption was eliminated by introducing the weight fraction concept which replaced the original volume fraction in the equation [Morgen (1954), Mandelkern (1964)]. However, the isokinetic assumption is still kept in the derivation. The equation is not able to account for secondary crystallization and crystal perfection, nor the details of the impingement effect. Based on the original theory the Avrami index, n , can be explained in terms of the nature of the nucleation and growth process as indicated in Table 2.1. In actual application the equation overpredicts the experimental data during the late stage of crystallization, fractional Avrami index is often obtained, and the Avrami index can not always be explained by crystal geometry. The Avrami equation describes overall crystallization which includes nucleation rate and linear growth rate (of, frequently, spherulites). The nucleation rate describes the number of nuclei created per unit time per unit volume. The linear growth rate describes the change in length of lamellae per unit time. Because the lamellae grow approximately in the direction of the radius of

Table 2.1. Theoretical Values Of The Avrami Index, n

Crystal growth	Nucleation	Avrami index
Fibril	Instantaneous	1
	Sporadic	2
Disc	Instantaneous	2
	Sporadic	3
sphere	Instantaneous	3
	Sporadic	4
Sheaf	Instantaneous	5
	Sporadic	6

spherulites, the growth rate also refers to the rate of increase of the radius of spherulites. Both nucleation rate, $\dot{N}$, and growth rate, G , are included in crystallization rate constant, k , in the Avrami equation. The $\dot{N}$ and G are related to k through the equation

$$k = \frac{A_g \dot{N} G^{n-1}}{n}$$

where A_g is a constant related to the growth geometry. For example, for a three dimensional growth of spherical crystals, $A_g = 4\pi/3$. Assuming that the nucleation is constant with time and by experimentally determining k , n and G , nucleation rate can be calculated from the crystallization rate constant. The time when crystallinity equals 1/2 is called crystallization half-time, $t_{1/2}$. Substituting $\theta = 1/2$ and $t = t_{1/2}$ into the Avrami equation, a relation between crystallization rate constant and crystallization half-time is obtained, that is,

$$k = \frac{\ln(2)}{(t_{1/2})^n}$$

According to this equation, the crystallization half-time also describes the overall crystallization rate.

Other attempts to improve the Avrami equation were to introduce items or factors to account for the secondary crystallization [Banks, Gordon, Roe and Sharples (1963), Hillier (1965), Dietz (1981), Velisaris and Seferis (1986)]. Banks et al suggested that isothermal crystallization was generally divided into two stages: the initial part of the isotherm is the primary crystallization stage and the last part, the secondary crystallization. They applied the Avrami equation to the two crystallization stages, respectively, and two sets of values for k and n were obtained. Another extreme method of treating the primary and secondary crystallization was introduced by Velisaris and Seferis (1986). They suggested that the secondary crystallization occurs simultaneously

with primary crystallization and the kinetic equation is a linear combination of two Avrami equations with different pairs of k and n values. A more reasonable way to include the secondary crystallization into the kinetic equation was introduced by Hillier (1965). In his analysis, the secondary crystallization begins at a certain time after the primary crystallization begins, and the secondary crystallization was superimposed onto the primary crystallization. The shortcoming of Hillier's approach is that primary and secondary crystallization ended at the same time when all crystallization is finished and the impingement effect was not considered (mathematical difficulties). By properly modifying Hillier's equation and/or calculation, this approach could work better. Dietz (1981) has introduced a factor into the original kinetic equation to correct for the effect caused by secondary crystallization. His approach is more empirical, and lacks any theoretical base.

All the attempts to improve the original Avrami equation ignored an important point: whether the Avrami equation (or modified one) can precisely describe the nucleation behavior. The nucleation rate may possibly dramatically affect the bulk crystallization rate, and variation in nucleation rate may be far more significant in controlling the bulk crystallization kinetics than other possible variables. The impingement effect is also neglected since the exponential form more or less covers this problem. The nucleation rate can approximately be constant in isothermal crystallization, while the impingement can never be avoided. This effect must necessarily be included in the kinetic equation if it is desired to have one equation to describe the whole crystallization process.

2.1.2.2. Growth rate theory

For a lamella growing from solution, assuming isothermal steady state, Hoffman (1964) has shown that the crystal growth is controlled by secondary nucleation and the

growth rate, G , of polymer crystallization may be expressed by:

$$G = G_0 \exp\left[-\frac{\Delta U}{kT}\right] \exp\left[-\frac{\Delta F^*}{kT}\right] \quad (2.2)$$

where G_0 is the preexponential factor which is independent of temperature, ΔF^* is the energy change for formation of the critical nucleus, ΔU is the activation energy for segmental jumping, or the barrier which a segment has to overcome to be attached to the crystal growing surface, and k is the Boltzman constant.

In melt, spherulites also grow at a constant rate at a given temperature [Price(1952), Keller, Lester and Morgan (1954), Mandelkern (1964)]. The temperature dependence of the growth rate was found to be consistent with crystal growth controlled by secondary nucleation [Mandelkern (1958)]. This fact suggested that, from a molecular point of view, spherulite growth resembles the single crystal growth from solution. With the recognition that spherulites are formed by the growth of lamellae in the radial direction, the chain-folded lamella growth theory developed for solution grown crystals was directly used to describe the growth of spherulites from melt [Hoffman (1964), Hoffman and Lauritzen (1961)]. It is envisaged that the spherulite growth rate is proportional to the lateral growth rate of a lamella so that it follows equation (2.2).

Hoffman, Davis and Lauritzen (1976) and recently Hoffman [Hoffman (1982)] have revised the secondary nucleation theory and introduced regimes to the polymer crystallization. Depending on the relative rate of the nucleation, i , at which the first stem is deposited on the crystal surface, and lateral growth rate, g , at which the stems are deposited onto the crystal surface to form a molecular layer after the first stem has been deposited, there are three regimes: regime I, II, and III. In regime I, the nuclei are sporadically deposited on the substrate, the stem spreading rate, g , is much greater than the nucleation rate, i . Therefore, $G \propto i$. In regime II, many nuclei form on the

substrate, but crystal growth is still layer by layer. The increased nucleation rate makes $i \approx g$ and $G \propto (i g)^{1/2}$ in regime II. In regime III the $i \gg g$, and $G \propto i$ again.

The energy for segments jumping, ΔU , in equation (2.2) may be estimated by WLF equation [Hoffman and Weeks (1962), Susuki and Kovacs (1970), Hoffman, Davis and Lauritzen (1976)] which gives: $-\frac{\Delta U}{kT} = -\frac{U^*}{R(T-T_\infty)}$, where U^* is related to the activation energy for segmental jumping (usually a universal value of $U^* = 1500$ cal/mol can be used.) T_∞ is the critical temperature below which there is no possibility for a segment to transmit, $T_\infty \approx T_g - 30$ K. The energy change of formation of a critical nucleus can be calculated according to the secondary nucleation theory [Hoffman (1964)]:

$$\Delta F^* = 4 b_0 \sigma \sigma_e / \Delta G, \quad \text{for regime III}$$

$$\Delta F^* = 2 b_0 \sigma \sigma_e / \Delta G, \quad \text{for regime II}$$

where $\Delta G = \frac{\Delta T f \Delta H}{T_m}$ is the free energy change when a unit volume of crystal forms from liquid; f is the factor to correct the heat of fusion as temperature is lowered, $f = \frac{2T}{T+T_m}$; b_0 is the thickness of single layer crystal formed by stems; σ is the side surface free energy and σ_e is the end surface free energy of the formed crystal; T_m is the equilibrium melting point; and ΔH is the heat of fusion. According to the regime theory, a constant K_g is defined as,

$$K_g = \frac{4 b_0 \sigma \sigma_e T_m}{k \Delta H} \quad \text{in regime I and III}$$

and

$$K_g = \frac{2 b_0 \sigma \sigma_e T_m}{k \Delta H} \quad \text{in regime II}$$

Therefore $\frac{\Delta F^*}{kT} = -\frac{K_g}{T \Delta T f}$ and equation (2.2) may be written as:

$$G = G_0 \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{K_g}{T \Delta T f}\right] \quad (2.3)$$

The first exponential factor in this equation describes the diffusion of segments as a function of temperature, and the second, the nucleation of the segments. According to equation (2.3), at high temperature the growth rate increases with decrease in temperature and it is a nucleation controlled process. At lower temperature the growth rate decreases with decrease in temperature and it is a diffusion controlled process.

In application, equation (2.3) is usually in the form of

$$\ln G + \frac{U^*}{R(T-T_\infty)} = \ln G_0 - \frac{K_g}{T \Delta T f} \quad (2.4)$$

In the plot of $\ln G + \frac{U^*}{R(T-T_\infty)}$ against $\frac{1}{T \Delta T f}$, the slope of regime II is half of that for regime I or III.

2.1.2.3. Nucleation

The nucleation theory is an important but less theoretically understood part in crystallization theory and it is also difficult to be experimentally verified. According to Turnbull(1952), Cormia, Price and Turnbull (1962), Price(1969), and Hoffman, Davis and Lauritzen (1976), the heterogeneous and homogenous nucleation rates may be expressed as (cylindrical nucleus is considered),

$$(\dot{N})_{\text{heter}} = (N_0)_{\text{heter}} \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{8\pi\sigma^2\sigma_e}{kT} \frac{1}{\Delta G}\right] \quad (2.5)$$

$$(\dot{N})_{\text{homo}} = (\dot{N}_0)_{\text{homo}} \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{8\pi\sigma^2\sigma_e}{kT} \frac{1}{\Delta G^2}\right] \quad (2.6)$$

where $\Delta G = \frac{\Delta T f \Delta H}{T_m}$. The heterogeneous nucleation rate equation refers to a process in which the molecules form crystal by depositing themselves onto certain substrates. Such procedures are called secondary nucleation if one deals with crystal growth. The equation of growth rate G is, therefore, formed based on the heterogeneous nucleation rate equation. If equation (2.5) is used in that sense, it may be a proper expression for a nucleation rate. For a primary nucleation process, the name heterogeneous nucleation rate is confusing because a heterogeneous nucleation is time independent and the nucleation rate is zero after the nuclei are formed in the initial stage of crystallization. Thus, for time independent nucleation, it is better to use the concept of nucleation density. For this purpose, if one integrates equation (2.5) and (2.6) at a given temperature (to understand more easily, it is assumed that the crystallization is isothermal and the nucleation is time independent) to give equations like,

$$(N)_{\text{heter}} = (N_0)_{\text{heter}} \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{8\pi\sigma^2\sigma_e}{kT} \frac{1}{\Delta G}\right] \quad (2.7)$$

$$(N)_{\text{homo}} = (N_0)_{\text{homo}} \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{8\pi\sigma^2\sigma_e}{kT} \frac{1}{\Delta G^2}\right] \quad (2.8)$$

where $(N)_{\text{heter}}$ and $(N)_{\text{homo}}$ are temperature-dependent, $(N_0)_{\text{heter}}$ and $(N_0)_{\text{homo}}$ are constant. The homogeneous equation is retained because it is possible that a time-independent nucleation may proceed homogeneously. By equation (2.7), one is now able to talk about the temperature dependence of heterogeneous nucleation.

2.1.2.4. Expression of crystallization rate constant k

Cebe (1988) has assumed that k is determined mainly by the temperature dependence of growth rate and not by the rate of nucleation. She has expressed the k as:

$$k = k_0 \exp\left[-\frac{nU^*}{R(T-T_\infty)}\right] \exp\left[-\frac{n8\pi\sigma^2\sigma_e T_m}{k\Delta H} \frac{1}{T\Delta T f}\right] \quad (2.9)$$

By the relations of $K(T) = [k(T)]^{1/n}$ and $k = \ln(2) \left(\frac{1}{t_{1/2}}\right)^n$, equation (2.9) can be transformed to express Nakamura constant, K [Patel (1991)], and $\frac{1}{t_{1/2}}$ [Hoffman and Weeks(1962), Wunderlich (1976), Archambault and Prud'homme (1980), Lambert (1988), Phillips and Kao(1986)] as function of temperature, respectively, which are similar to equation (2.9).

2.1.3. Typical Methods Of Studying Crystallization Kinetics In Polymers

2.1.3.1. Calorimetry

Since heat of fusion is proportional to the crystallinity in the polymer sample, one is able to monitor the crystallization process by measuring the released heat during crystallization. The heat releasing rate during crystallization can be detected by Differential Scanning Calorimetry (DSC). DSC is used in studying both isothermal [Mueller and Martin (1964), Godovsky and Slonimsky (1974), Mancarella and Martuscelli (1977), Monasse and Haudin (1986)] and nonisothermal crystallization kinetics [Maglio, Martuscelli, Palumbo and Soldati (1976), Jeziorny (1978), Hay and Mills (1982)].

For isothermal experiments the heat release or absorption rate is plotted against time, and for nonisothermal crystallization, against temperature. The relative crystallinity during isothermal or nonisothermal crystallization can be calculated by [Hay and Mills (1982)],

isothermal

$$\frac{X_c}{(X_c)_\infty} = \frac{\int_0^t \left[\frac{dH}{dt}\right] dt}{\int_0^\infty \left[\frac{dH}{dt}\right] dt}$$

nonisothermal

$$\frac{X_c}{(X_c)_\infty} = \frac{\int_{T_{on}}^T \left[\frac{dH}{dt} \right] \frac{1}{dT/dt} dT}{\int_{T_{on}}^{T_e} \left[\frac{dH}{dt} \right] \frac{1}{dT/dt} dT}$$

According to Gray (1986), the heat generating rate caused by crystallization in polymer, $\frac{dH}{dt}$, can be expressed by the following equation,

$$\frac{dH}{dt} = -\frac{dq}{dt} + (C_s - C_r) \frac{dT_p}{dt} - RC_s \frac{d^2q}{dt^2}$$

where $\frac{dq}{dt}$, which is a quantity recorded by DSC, is the heat flow rate from the compensatory heating element to the polymer sample, C_s is the heat capacity of sample and sample container (because the thermocouple is embedded in the sample holder, its heat capacity must be considered), C_r is the heat capacity of the reference material, $\frac{dT_p}{dt}$ is the temperature change rate of the sample holder which is measured by the thermocouple, R is the heat resistance from the sample to the thermocouple which includes the heat transfer resistance of sample, sample container and part of the sample holder, which can experimentally be determined by material with sharp transition (crystallization), $\frac{d^2q}{dt^2}$ is the slope of the recorded DSC curve — $\frac{dq}{dt}$ against time. Therefore, the heat change rate of the sample, $\frac{dH}{dt}$, involves the sum of three terms. The first is the signal measured from the zero signal line, the second is the baseline displacement due to heat capacity difference between sample and reference, and the third is the thermal lag caused by the heat transfer resistance from sample to the thermocouple. According to Gray the thermal lag can be corrected graphically. Such correction is however referring to the correction for the time and the magnitude of heat change rate. Such a correction is not usually done in practice, probably because at the end of the peak, the corrected heat flow rate will have the opposite sign as measured heat flow rate has and this is unacceptable. This suggests that there exist problems in Gray's analysis. There

also exists a temperature correction for the sample, since the measured temperature is that of the sample holder. According to Gray the sample temperature, T_s , can be calculated by,

$$\frac{dq}{dt} = (T_p - T_s)/R \quad \text{or,} \quad T_s = T_p - R \frac{dq}{dt}$$

The correction for the sample temperature requires the calculation for every measured temperature according to measured $\frac{dq}{dt}$ - time curve. Apparently, after such correction, the T_s did not retain a linear relationship with time, and constant cooling rate experiments no longer exist. The constant cooling rate experiments in that case refer to that of the sample holder. Although the analysis led to nonconstant cooling rates in the sample, this may be the real situation in the so-called constant cooling rate in non-isothermal crystallization or even in isothermal crystallization measured by DSC. Realizing that there is a temperature difference between the sample holder and the sample, Monasse and Haudin (1986) introduced an empirical equation $T_s = -0.107 \frac{dT_p}{dt} + T_p$, where $\frac{dT_p}{dt}$ is in [$^{\circ}\text{C}/\text{min.}$] for polypropylene to transform the holder temperature to sample temperature. Their experiments were carried out under cooling rates less than $80^{\circ}\text{C}/\text{min.}$, and at that cooling rate they found that the temperature difference between T_p and T_s was 8.5°C . This difference exists between the bottom surface of the sample and the temperature measuring point. Through theoretical analysis they also found that the temperature difference within the sample can be neglected for sample thickness of the order of $300\text{ }\mu\text{m}$. For material without heat generation during cooling, such temperature correction is acceptable under certain cooling rates. However, a crystallization process will delay the cooling process further so that the correction employed by Monasse and Haudin may still not results in the real sample temperature. Thus, there are difficulties in measuring crystallization kinetics by DSC, and these difficulties are made more serious as cooling rate increases.

2.1.3.2. Dilatometry

In addition to the determination of thermal expansivity of solids and liquids, the dilatometer has been used in the study of phase transitions because the specific volume is linearly related to crystallinity of a polymer sample [(Bekkedahl (1949, 1967))]. The level change of the confining liquid in the capillary multiplied by the cross-sectional area of the capillary gives the volume change of the sample and confining fluid. After correction for volume change with temperature of the confining liquid, the volume change of the sample with temperature can be calculated in the case of nonisothermal crystallization. The relative crystallinity is calculated according to the following equation,

$$\theta = \frac{V_0 - V}{V_0 - V_\infty}$$

where V_0 and V_∞ are the initial and final volumes of the sample, V is the volume of the sample during crystallization. For measurement in nonisothermal crystallization the cooling rate is limited to less than 0.5 °C/min. A faster cooling rate may cause a lag of temperature between sample and bath. For isothermal crystallization, the supercooling is also low because it takes time to bring down the temperature of the sample and the dilatometer. Before the temperature of the sample reaches the desired value, the crystallization has already begun. Therefore, dilatometry is not suitable for the study of the fast rates of crystallization which occur either in nonisothermal crystallization at high cooling rate, or isothermal crystallization with relatively large supercooling.

2.1.3.3. Light Depolarizing Microscopy (LDM)

The method of following polymer crystallization by measuring the intensity of light depolarization was first introduced by Magill [1960, 1961, 1962]. He suggested that

the theoretical base of the light depolarizing method is that the depolarized light intensity is proportional to the volume fraction of crystalline phase in the sample:

$$I = k' X_c \quad (2.10)$$

where k' is a constant and X_c is the crystallinity of a sample. From equation (2.10), the equation to calculate the relative crystallinity from the measured depolarized light intensity was derived which is widely used in the LDM approach:

$$\frac{X_c}{(X_c)_\infty} = \frac{I - I_0}{I_\infty - I_0} \quad (2.11)$$

where X_c and $(X_c)_\infty$ are the crystallinity at time t and $t = \infty$, respectively; I_0 and I_∞ are the depolarized light intensities at $t = 0$ and $t = \infty$. He assumed that the depolarized light intensity is proportional to the volume of spherulites. The shape of crystalline entity was implied to be disk-like in his paper.

Stein et al (1966) has given a more detailed theoretical analysis for the light depolarizing method. For a single crystal with its uniaxial optic axis in a plane perpendicular to the light path, and at an angle θ to the vertical direction, the depolarized light intensity may be expressed as:

$$I = I_0 \cos^2(2\theta) \sin^2(\delta/2) \quad (2.12)$$

where δ is the retardation defined by :

$$\delta = \frac{2\pi l (n_1 - n_2)}{\lambda} \quad (2.13)$$

where l is the thickness of the crystal in the direction of the light beam, n_1 is the refractive index parallel to the optic axis, and n_2 is the refractive index perpendicular to

the optic axis. If there is a collection of N crystals randomly arranged, the depolarized light intensity could be calculated by:

$$I = \frac{I_0 NA}{A_0} \langle \cos^2(2\theta) \rangle_{av} \sin^2(\delta/2) \quad (2.14)$$

where A_0 is the area of sample under the field of the microscope, A is the area of a crystal, and $\langle \cos^2(2\theta) \rangle_{av}$ is related to the orientation of crystal. If the crystals are randomly oriented $\langle \cos^2(2\theta) \rangle_{av} = 1/2$; if their optic axes are aligned in the vertical direction $\langle \cos^2(2\theta) \rangle_{av} = 1$. Equation (2.14) can only be established when one takes the shape of the crystals as cylindrical with the height being the sample thickness, l , all cylinders being parallel to the light beam, and the optic axes being in the plane perpendicular to the light beam.

A further theoretical analysis of the light depolarizing method was carried out by Binsbergen (1970). For the first time an explicit description was given to the studied element, "pile" in his paper, which is composed of crystals in the shape of cubes. The way these elements are integrated to a whole sample was also described. A plane-polarized light was supposed to transmit through a specimen which has parallel, flat surfaces. The specimen is perpendicular to the incident light beam and contains randomly located and randomly oriented birefringent crystallites, either in contact with each other or dispersed in a non birefringent matrix. The depolarized light intensity from the sample was obtained by adding together the ones produced by all the piles. This gives,

$$I = I_0 \frac{4\pi(\Delta n)^2}{15\lambda^2} X_c w l \quad (2.15)$$

where w is the edge of the cubic crystal, l is the sample thickness, λ is the wave length of the applied light, I_0 is the intensity of the incident light and the Δn is the birefringence of the crystal.

LDM has been used in studying kinetics of both isothermal and nonisothermal crystallization. The supercooling reached by LDM in isothermal crystallization can be much greater than for dilatometry. In the prior application of LDM in nonisothermal crystallization, the highest cooling rate is less than 100 °C/min. The upper limit of higher cooling rate was caused by the hot stage being unable to create a constant cooling rate higher than that value.

The temperature usually measured in LDM is that of the air surrounding the heating element. The temperature description in LDM is typically much worse than in DSC because the heating element is much larger in LDM and there is also a greater air layer and cover glasses between sample and heating elements (if the hot stage is saturated by the flowing N₂, the situation will be much worse). Because the huge mass difference between sample and heating elements and complicated layers (air or glass), there is little chance for crystallization heat to affect the measured temperature. The constant cooling rate in LDM can only refer to the one of the hot stage.

2.1.3.4. Other methods

Infrared spectra [Cobb and Burton (1953)] can be used to study the crystallization kinetics if a proper crystalline band can be found and used to indicate the occurrence of crystallization. Small Angle Light Scattering (SALS) was reported to be used in the kinetic studies [Baranov(1970), Misra and Stein (1972), Stein and Misra (1973), Mandelkern, Clotin and Benson (1981)] which is sometimes called "real-time SALS" [Culberson (1993)]. The real-time SALS can produce 3-5 images of the scattering pattern per second and provides a means of simultaneously measuring the rate of spherulite growth and the overall rate of quiescent crystallization. X-ray diffraction can be used in kinetic study [Mamedov and Nurieve(1968)], if a position sensitive detector is used to record the entire diffraction pattern as a function of time. Other techniques such as

density balance [Magill(1962)] and density gradient [Keller, Lester and Morgen (1954)], NMR [Peterlin and Roechl (1963)], electrical resistivity [Warfield(1965)], and small angle X-ray scattering [Vignaud(1986)] have been used to monitor the overall transformation process since they all are indicators of the phase change associated with the ordering of polymer molecules.

2.2. Quiescent Nonisothermal Crystallization

2.2.1. Prior Studies And Methods Of Analysis Of Nonisothermal Crystallization In Polymers

Ziabicki (1967) introduced a so-called kinetic crystallizability, G_C , which was intended to be used to characterize the ability of a polymer to crystallize, in a theoretical treatment of melt spinning. His basic assumption was that crystallization follows a first order kinetic equation,

$$\frac{d\theta}{dt} = K(1 - \theta)$$

where K is a crystallization rate constant. Ziabicki described its temperature dependence by an empirical equation,

$$K(T) = K_{\max} \exp \left\{ -4 \ln 2 \cdot \frac{(T - T_{\max})^2}{D^2} \right\} \quad (2.16)$$

where D is the half width of the K verses T curve, $K_{\max}$ is the maximum value of the K , and $T_{\max}$ is the temperature corresponding to $K_{\max}$. The G_C is defined and calculated by,

$$G_C = \int_{T_g}^{T_m} K(T) dT = \left(\frac{\pi}{\ln 2} \right)^{1/2} K_{\max} \frac{D}{2}$$

The $K_{\max}$ and D can be determined by DSC under nonisothermal conditions according to Jeziorny (1978). The kinetic crystallizability does not dynamically describe the crystallization process, nor does it give or collect any information related to $\theta - t$, or $\theta - T$ relation during crystallization.

Based on earlier isokinetic assumptions and using Avrami theory as a basis, Nakamura et al (1972, 1973) derived equations to describe transformation processes with variable nucleation and growth rates. The Nakamura equation reads,

$$\frac{X_c}{(X_c)_{\infty}} = 1 - \exp \left[- \left(\int_0^t K(T) dt' \right)^n \right] \quad (2.17)$$

where n is the Avrami index, $K(T)$ is the nonisothermal crystallization rate function (Nakamura constant), which is related to the isothermal crystallization rate constant, $k(T)$, by,

$$K(T) = [k(T)]^{1/n} \quad (2.18)$$

Nakamura derived his equation from the following equation, which is more general in form,

$$\frac{X_c}{(X_c)_{\infty}} = \int_0^t \dot{\theta}_{\text{iso}} [T(t'), \theta(t)] dt' \quad (2.19)$$

where $\dot{\theta}_{\text{iso}} [T(t'), \theta(t)]$ is the increase rate of relative crystallinity obtained from the analysis of isotherms at temperature T and crystallinity θ . Patel and Spruiell (1991) suggested a differential form for the Nakamura model:

$$\frac{d\theta}{dt} = n K(T)(1-\theta) \left[\ln \left(\frac{1}{1-\theta} \right) \right]^{(n-1)/n} \quad (2.20)$$

where $\theta = \frac{X_c}{(X_c)_\infty}$ is the relative crystallinity. The Avrami index in this equation must necessarily be evaluated by isothermal experiment. Patel and Spruiell (1991) have suggested that the Nakamura equation may be more satisfactory for computing nonisothermal crystallization than other existing models.

Ozawa (1971) has proposed another nonisothermal kinetic equation, which has been adopted by several authors [Eder and Wlochowicz(1983), Monasse and Haudin (1986), Hammami (1990), Hammami and Mehrotra (1993)], under the assumption that the sample is cooled at constant rate. The Ozawa equation is,

$$\theta = 1 - \exp\left\{-\frac{K'(T)}{\alpha^n}\right\} \quad (2.21)$$

or in the form of

$$\ln[-\ln(1-\theta)] = \ln [K'(T)] - n \ln |\alpha| \quad (2.22)$$

where $K'(T)$ is called the cooling function of nonisothermal crystallization at temperature T , α is the cooling rate, and n is the Avrami index. According to this equation, the plot of $\ln[-\ln(1-\theta)]$ vs. $\ln |\alpha|$ has a slope n and intercept $\ln [K'(T)]$. This approach requires values of relative crystallinity at a fixed temperature for different cooling rates.

Dietz (1981) also introduced a kinetic equation for nonisothermal crystallization which is

$$\frac{X_c}{(X_c)_\infty} = \int_0^t n k t^{n-1} (1-\theta) \exp\left(\frac{-a\theta}{1-\theta}\right) dt' \quad (2.23)$$

in which the exponential factor, $\exp\left(\frac{-a\theta}{1-\theta}\right)$, is to correct for secondary crystallization. This equation comes directly from equation (2.19) which was suggested by Nakamura except that one more factor has been added into the equation.

Without any derivation, Kamal and Chu (1983) proposed another nonisothermal kinetic equation,

$$\frac{X_c}{(X_c)_\infty} = 1 - \exp\left\{-\int_0^t n k t^{n-1} dt'\right\} \quad (2.24)$$

All the kinetic equations were used to analyze the experimental data collected from nonisothermal crystallization process by DSC, LDM or dilatometry. None of the kinetic models could fit or predict the experimental data in an entirely satisfactory manner even under low cooling rate conditions.

2.2.2. Major Experimental And Analytical Problems In The Analysis Of Nonisothermal Crystallization

In all previous studies, the cooling rates were too low ($< 100^\circ\text{C}/\text{min.}$) compared to the conditions applied in polymer processing. Because of the existing hot stage for LDM and the structure of the DSC, it has not been possible to increase the cooling rate further. The potential problems existing in the available kinetic models can be understood after the relationships among the equations describing these models are understood (see Chapter 3).

2.3. Crystallization In The Presence Of Molecular Orientation

2.3.1. Prior Studies And Attempts To Analyze The Influence Of Molecular Orientation

2.3.1.1. General characteristics

Crystallization of a polymer while being deformed (strained) has the following characteristics compared to crystallization under quiescent condition:

(1) Strain causes macromolecules to have a lower entropy but change little in enthalpy.

(2) The melting temperature $T_m = \frac{\Delta H}{\Delta S}$ increases, and, therefore, the supercooling of crystallization increases. The crystallization in a strained system occurs at higher temperature than in quiescent system.

(3) The nucleation rate is greatly enhanced and, therefore, the overall crystallization rate is increased. At a given temperature a deformed macromolecule may crystallize under a larger supercooling and therefore is subjected to a greater driving force for nucleation and crystallization. The extended chain is also kinetically more ready to approach the final conformation existing in the crystalline state. For both thermodynamic and kinetic reasons, deformation enhances nucleation and crystallization (Wunderlich (1976)).

(4) The linear growth rate increases only slightly due to deformation. Andrews et al (1971) found that the effect on the linear crystal growth rate of cis-1,4-Poly(2-methylbutadiene), by measuring the lamellae growing from fibrous nuclei, is small. Increasing the linear deformation of a thin film from 50% to 250% increases the growth rate by only 25% and the maximum of the curve of crystal growth rate versus temperature was almost unchanged. The linear growth rate of lamellae under strain is therefore not much different from quiescent melt. The increase of linear growth rate was attributed to the increase in melting point caused by deformation. However Andrews et al (1971) pointed out that the correction of melting temperature for deformation leads to too high a temperature for the maximum rate of crystallization and does not lead to quantitative agreement between experimental and predicted data.

(5) The increase of supercooling due to deformation will also decrease lamellar thickness at a given crystallization temperature. This has been reported by Kobayashi and

Nagasawa (1970) who worked on polyethylene with crystallization from melts under shear.

(6) Deformed spherulites, cylindrites and shish-kebab structures are the three usual morphological forms found in strained systems. Cylindrites are highly oriented along the strain direction and exhibit lamellae growing radially oriented from primary nuclei more or less aligned in rows parallel to the strain. This produces an entity similar to a spherulite, but with cylindrical symmetry. Shish-kebabs are similar to cylindrites except that the term usually refers to entities formed from solution rather than the melt. The row nuclei of cylindrites or shish-kebabs contain more or less extended chains. The crystallization proceeds by epitaxial overgrowth of folded chain lamellae onto the row nuclei. If the lamellae grow radially from the central row nucleus and are densely packed, cylindrites are produced. If they are not densely packed or spaced, the shish-kebab morphology will be obtained. In the case of very large spacing of nuclei, deformed spherulites (rotational ellipsoid) can develop with their short axis in strain direction. For polymers crystallizing from melts, the morphology changes from spherulitic to deformed spherulite [Samuels(1974), Dees and Spruiell (1974)], shish-kebabs and cylindrites [Andrews (1962), Katayama, Amano and Nakamura (1968), Mackley and Keller (1973), Dees and Spruiell (1974)] as deformation increases. Polymer crystallizing in the stirred solution or flowing fluid produces fibrillar nuclei which are along the flow direction and permits epitaxial overgrowth of lamellae which are oriented normally to the flow direction. Thus, shish-kebab structure is obtained with a long, thin central nucleus called shish and irregularly spaced, twisted lamellae called kebabs.

2.3.1.2. Flow-induced crystallization

In flow-induced crystallization, the crystallization exists in part of the fluid (polymer solution or melt) which is in the region near to a certain substrate. The main

part of the fluid, which is flowing, has little crystallization and continues to flow after crystallization begins in the limited region. In this category, one basically deals with shear flow, such as polymer solution flowing in a tube or being mechanically stirred, or melts flowing in Couette viscometer (concentric cylinder geometry) with larger gap, and crystallization occurs on certain substrates whose surface has zero flow velocities, or jet-stretching (flowing melt into two mutually opposed orifices to create a pure shear) [Mackley and Keller (1973)], or shear between plates [George and Tucker (1975)]. The molecule deposited on the substrate is highly oriented because free chain ends are dragged by flowing fluid and straightened along the flow stream. Crystallization temperature in studies of flow-induced crystallization is usually kept constant. Flow-induced crystallization is usually studied in dilute solution (Rietveld and McHugh 1985, McHugh and Blunk 1986) and sometimes in melts [Kobayashi and Nagasawa (1970)].

Early work on crystallization from stirred solution has shown stirrer speed needs to be higher than a critical value to obtain fibrillar crystalline habit and above this critical speed the crystallization rate increases with the stirring speed [Pennings and Pijpers (1970)]. The growth rate was also studied in tubular [Pennings (1977), Pennings, Zwijnenburg and Lagveen (1973), Zwijnenburg and Pennings (1975), McHugh, Vaughn and Ejike (1978), McHugh, Ejike and Silebi (1979), Rietveld and McHugh (1985), McHugh and Blunk (1986)] or concentric cylinder geometry [Zwijnenburg and Pennings (1975)] with seeding techniques. The growth rate was found to increase with flow velocity and decrease with temperature. It has been suggested that the local flow phenomena may play an important role in the growth process.

The kinetic equation analogous to the one derived from rubber elasticity theory is improperly used in flow induced crystallization because in addition to crystallization thermodynamics, molecular transport, molecular orientation, and flow kinematics are important to the flow-induced crystallization and must be considered [McHugh (1982)].

The kinetic data of flow-induced crystallization from solution, measured by polarized light illumination technique, was obtained by McHugh and his coworkers (Rietveld and McHugh 1985, McHugh and Blunk 1986). The crystalline and amorphous phase orientation function, and the diameter of the fiber were assumed to be constant during crystallization. The Avrami equation was employed in their data analysis. The experimental data can be best fit by Avrami equation and the Avrami index was found to be 2 or 2.5.

2.3.1.3. Stress-induced crystallization

In stress-induced crystallization, the crystallization evenly exists throughout the material and the whole fluid is rapidly solidified after crystallization begins. The materials studied could be linear or crosslinked. The kinetic equation derived from rubber elasticity theory is often used in this category.

Stress-induced crystallization was initially investigated using samples of a slightly crosslinked polymer system under uniaxial tension because the deformation of melts is difficult to maintain throughout the crystallization. Early studies have been carried out on *cis*- and *trans*-polyisoprene and *trans*-polychloroprene (Gent 1954, 1955, 1965 and 1966, Treloar 1941). The crystallization was followed by the stress decay and linked at zero extension to dilatometric data. It was found that the crystallization onset and half-time decrease with increase of extension ratio. The increase in crystallization rate with extension was attributed to corresponding increase of equilibrium melting temperature and, hence, degree of supercooling. The Avrami index, n , was found to be reduced from a quiescent value of 3 to 1 (Gent 1954) or 2 (Gent 1966). A later study on *cis*-polyisoprene (Kim and Mandelkern 1968), by dilatometry and stress decay, verified these early findings over a wide range of crystallization temperatures and extension ratios. They found that the degree of crystallization increases with the extension ratio.

The Avrami equation was applied in isothermal strain-induced crystallization in rubber. It was found that in the Avrami plot, a linear relation held up to a relatively high level of crystallinity. The usual deviation from the Avrami expression under quiescent condition occurs at a relative crystallinity about 0.1, while for the deformed samples, the whole crystallization range could be fitted. The Avrami index was independent of crystallization temperature. It approached from 3.55, at elongation ratio = 1, to an asymptotic limit of about 1 as the elongation ratio increases to 6. For large deformation when $n=1$, the crystallization consists of either one-dimensional growth from predetermined nuclei activated at $t=0$ or will be essentially a sporadic nucleation process. The nature of the major nucleation and growth processes are independent of temperature at a constant elongation ratio. Change in the Avrami index indicates change in nucleation and growth process. Kawai, Iguchi and Tonami (Kawai, Iguchi and Tonami 1967) examined the crystallization of uniaxially stressed crosslinked polyethylene melts and reported an enhancement in crystallization rate as the elongation ratio was increased. Change in the Avrami index was reported on biaxial deformation of cis-1,4-polyisoprene, in which n decreases from 3 to 0.7 (Oono, Miyasaka and Ishikawa 1973). In crosslinked polyethylene, $n \approx 1$ for extension ratio from 2 to 5 (Kawai, Matsumoto, Kato, and Maeda 1968). For crosslinked LDPE the Avrami index changes from 5-6 for undeformed state to 1-2 for deformed state (Phillips and Kao 1986).

The stress-induced crystallization of uncrosslinked system is usually studied in the melt state under extension condition in the form of fiber or film (uniaxial orientation), shear between parallel plates [Haas and Maxwell (1969), Wereta and Gogos (1971), Fritzsche et al (1976),], shear in Couette viscometer or concentric-cylinder type viscometer (narrow gap) in which the polymer crystallizes throughout the melt [Fritzsche et al (1974,1976), Sherwood et al (1978)], shear in dilatometer [Thiel (1975)] or annealing oriented material under strain or applied strain rate. Haas and Maxwell (1969)

examined polyethylene and found that at low stresses, increasing undercooling and molecular weight produced a more rapid crystallization. However, at high stresses this behavior was reversed. It was also observed that the application of stress greatly increased the nucleation process.

Lagasse and Maxwell (1969) analyzed the crystallization onset or induction time of the crystallization of polyethylene. They found that the low molecular weight material showed a critical value of shear rate below which the induction time was constant, and high molecular weight samples showed decreasing induction time with increasing shear rate and decreasing temperature.

Thiel (1975) imposed shear in a dilatometer at a later stage of the crystallization in his study of shear-induced crystallization of poly(ethylene oxide) and found the crystallization rate was more rapid than when imposing stress in the early crystallization stage. The Avrami index was found to be as high as 16, if the Avrami equation is employed in the data analysis.

Fritzsche et al (1974, 1976) have found values of n as high as 9 in crystallizing poly(ethylene oxide) in which shear was continuously imposed in a concentric cylinder type dilatometer during the crystallization rate measurement. They also observed that the induction time was reduced and the transformation rate was accelerated by shear. n also increased with increasing temperature at constant shear rate. An increase of Avrami index with increase in strain rate has been attributed to the break up of crystalline aggregates that act as nuclei for further crystallization.

Increase of the Avrami index from the quiescent value of 3 to a value greater than 5 and decrease of induction time with increasing shear rate for poly(ethylene oxide) and poly (ϵ -caprolactone) sheared in a concentric cylinder type dilatometer was also reported by Sherwood et al (1978). Again the Avrami equation was used in their data analysis.

The kinetics of strain-induced crystallization of poly(ethylene terephthalate) has been studied by annealing the oriented amorphous polymer. The crystallization was found to be much faster than for unstrained material [Smith and Steward (1974), Alfonso, Verdoni and Wasiak (1978), Gupta, Motz and Schultz (1983), Hamidi, Abhiraman and Asher (1983)]. They found that the higher the molecular orientation, the shorter the crystallization half time and the Avrami index decreases from 3 to about 1.

Crystallization rates in melt spinning are often high because of molecular orientation [Dees and Spruiell (1974), Katayama, Amano and Nakamura (1968)].

2.3.1.4. Kinetic equation including the orientation effect

The kinetic equation for crystallization rate applied in the case of orientation-induced crystallization has frequently been the Avrami equation as mentioned several times above. Nobody has ever tried to modify this equation to meet the needs of orientation induced crystallization. Effort has been made, however, to introduce the orientation effect to the rate constant k which is expressed as a function of temperature under quiescent condition. The earliest significant theoretical work to account for the crystallization rate constant in strained systems came from Kobayashi and Nagasawa (1970). Ziabicki (1974) has presented a phenomenological analysis of orientation phenomena and has discussed the kinetic equations in regard to molecular orientation within the crystallizing polymeric systems.

Based on rubber elasticity theory, a few researchers tried to include the orientation effect into the kinetic equation [Ziabicki (1976), Yeh and Hong (1979), Yeh, Hong, and Krueger (1979), Zhou (1988), Zhou and Spruiell (1989), Katayama and Yoon (1985), Patel, Bheda and Spruiell (1991), Patel and Spruiell (1991)]. The strain-effect is incorporated into the kinetic equation through thermodynamic functions.

In rubber elasticity theory which was originally developed by Kuhn [(1936), (1946), Grun and Kuhn (1942)] and later improved by Treloar (1943, 1946, 1975), and Flory (1943, 1969), four equations which are important to kinetics of polymer crystallization are given as follows.

The entropy difference caused by simple extension:

$$\Delta S = -\frac{1}{2} k N \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \quad (2.25)$$

where k is Boltzman constant, N is the number of chains (a chain is defined as a molecular section connecting two crosslink points) per unit volume of the material, λ is extension ratio, and T is temperature. The stress and extension ratio in simple extension are related by

$$\sigma = k N T \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (2.26)$$

The birefringence equation expressed as a function of extension ratio as

$$\Delta n_a = n_1 - n_2 = \frac{2\pi}{45} \frac{n_0^2 + 2}{n_0} (a_{//} - a_{\perp}) N \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (2.27)$$

where n_1 and n_2 are refractive indices parallel and perpendicular to the extension direction. n_0 is an average refractive index of material, $n_0 = (n_1 + 2 n_2)/3$. $a_{//}$ and $a_{\perp}$ are the components of the bond polarizability parallel to and perpendicular to bond direction. According to equation (2.26) and (2.27), the stress optical relation thus reads,

$$\sigma = \left[k T / \left(\frac{2\pi}{45} \frac{n_0^2 + 2}{n_0} (a_{//} - a_{\perp}) \right) \right] \Delta n_a \quad (2.28)$$

The free energy of the system under strain or molecular orientation, ΔG , is the difference of the one for crystallization in the isotropic state, ΔG_{iso} , and the one caused by molecular orientation, ΔG_{or} :

$$\Delta G = \Delta G_{iso} - \Delta G_{or} \quad (2.29)$$

Similarly, one has expressions for enthalpy and entropy,

$$\Delta S = \Delta S_{iso} - \Delta S_{or} \quad (2.30)$$

$$\Delta H = \Delta H_{iso} - \Delta H_{or} \quad (2.31)$$

Yeh and Hong (1979) assumed that $\Delta H_{or} \approx 0$, Therefore, $\Delta H \approx \Delta H_{iso}$, thus

$$\Delta G - \Delta G_{iso} \approx -T (\Delta S - \Delta S_{iso})$$

By equation (2.30), it changes to,

$$\Delta G = \Delta G_{iso} + T \Delta S_{or} \quad (2.32)$$

where ΔS_{or} is the entropy difference between oriented melt and isotropic melt which is given by rubber elasticity theory, equation (2.25). The relation between ΔS_{or} and orientation is thus connected by extension ratio, λ , through equation (2.25) and (2.27). Ziabicki (1976) assumed that any function, F , can be expanded in a power series of orientation factor, f , as,

$$F(f) = F(f=0) + a_1 f + a_2 f^2 + \dots \approx F(f=0) + a_2 f^2 \quad (2.33)$$

Based on symmetry arguments he deleted the linear term in the series. Equation (2.33) was adopted by Katayama and Yoon (1985); they argue that,

$$\Delta S_{or} \propto \Delta n_a^2, \text{ or, } \Delta S_{or} = A' \Delta n_a^2 = A f_a^2 \quad (2.34)$$

where A' or A is constant. By equation (2.34) and $\Delta G_{iso} = \Delta H_{iso} \Delta T / T_m$, equation (2.32) may then be written as,

$$\Delta G = \Delta H_{iso} \Delta T / T_m + A T f_a^2 \quad (2.35)$$

An assumption used to incorporate the strain effect into the kinetic equations is that the strain effect only affects the factor containing ΔG . Substituting equation (2.35) into (2.5) and (2.3), Katayama and Yoon (1985), Zhou (1988), Zhou and Spruiell (1989), Patel, Bheda and Spruiell (1991), Patel and Spruiell (1991)] obtained the nucleation and growth rate expression under strain of

$$\dot{N} = \dot{N}_0 \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{C_1'}{T \Delta T f + C_1'' T^2 f_a^2}\right] \quad (2.36)$$

$$G = G_0 \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{C_2'}{T \Delta T f + C_2'' T^2 f_a^2}\right] \quad (2.37)$$

Apparently encouraged by the appearance of above equations, they gave the rate constant, k , under strain the form of,

$$k = k_0 \exp\left[-\frac{U^{*'}}{R(T-T_\infty)}\right] \exp\left[-\frac{C_3'}{T \Delta T f + C_3'' T^2 f_a^2}\right] \quad (2.38)$$

or,

$$\left(\frac{1}{t_{1/2}}\right) = \left(\frac{1}{t_{1/2}}\right)_0 \exp\left[-\frac{U^*}{R(T-T_\infty)}\right] \exp\left[-\frac{C_3'}{T \Delta T f + C_3'' T^2 f_a^2}\right]. \quad (2.39)$$

The expression for growth rate G may be more suitable than the nucleation rate expression, because only the heterogeneous expression was used for nucleation, and for primary nucleation that expression may be invalid. Proper expressions for time dependent nucleation rate should come from equation (2.6), and for time independent nucleation, from equation (2.7) or (2.8).

Ziabicki (1976) on the other hand, directly applied equation (2.33) to obtain $F = \ln k$, without help from rubber elasticity theory, and he obtained the ratio of rate constant under strain and rate constant under isotropic state, k_0 , as,

$$k/k_0 = \exp (A f_a^2) \quad \text{or,} \quad k = k_0 \exp (A f_a^2) \quad (2.40)$$

2.4. Prior Studies Of The Crystallization Of Isotactic Polypropylene

2.4.1. Structure And Morphology

There are three kinds of unit cells, α , β , and γ , which are summarized in Table 2.2, for polypropylene crystals, and one smectic structure. The forms of crystal, α , β or γ , and their quantities in bulk polymer samples can be determined by the X-ray diffraction pattern according to Turner, Aizilewood and Beckett (1964). The existence of smectic form and its quantity can also be determined by X-ray diffraction [Farrow (1965), Gezovich, and Geil (1968), Zannetti, Celotti, Fochera, and Francesconi (1969)].

There are four types, I, II, III and IV, of spherulites for α and β crystal forms according to Padden and Keith (1959, 1966). Type I and II spherulites have the α form, and type III and IV, have the β form. The division of the types are according to the form of crystal and the birefringence of the spherulites. The birefringence of a spherulite, Δn_s , is defined as,

$$\Delta n_s = n_r - n_t \quad (2.41)$$

where n_r and n_t are the radial and tangential refractive indexes of the spherulite. According to this definition, a spherulite is positive if $n_r > n_t$; negative if $n_r < n_t$. Table 2.3 lists the types of spherulites and the birefringence values for α and β spherulites.

Table 2.2. Unit Cells of Isotactic Polypropylene

Phase	Unit cell	a(Å)	b(Å)	c(Å)	α	β	γ
α -form	monoclinic	6.67	20.94	6.50	90°	99.3°	90° [a]
β -form	hexagonal	19.08	19.08	6.50	90°	90°	120° [b]
γ -form	orthorhombic	8.54	9.93	42.41	90°	90°	90° [c]
γ -form	triclinic	6.54	21.4	6.50	89°	99.6°	99° [d]

[a] Turner, Aizilewood and Beckett (1964)

[b] Samuels and Yee (1972)

[c] Bruckner and Meille (1989), and Meille, Bruckner and Porzio (1990)

[d] Morrow and Newman (1968)

Table 2.3. Type Of Spherulites And Their Birefringence Value [Padden And Keith (1959, 1966), Samuels And Yee (1972)]

Type	n_r	n_t	$\Delta n_s \times 10^{-3}$	Form
I			3	α
II	1.5093	1.5115	-2.2	α
III	1.496	1.059	-6.5	β
IV	1.496	1.496~1.519	-3 ~ -21*	β

* There are alternatively arranged black and yellow stripes in type IV spherulite. -3 is in dark strip and -21, in yellow stripe.

There are also different refractive indexes along the axes of the unit cell: n_c is index of refraction along the direction of the molecular chain and n_a is index of refraction along the a-axis of the unit cell. For simplification, a crystal is often taken as having one optical axis (this is true for hexagonal crystals), so that the refractive index along the b-axis is approximately equal to n_a . Table 2.4 gives n_a and n_c values for α and β spherulites. The value of n_r and n_t can be calculated by the following equations (assuming c is in tangential direction):

$$n_r = X_c n_a + (1 - X_c) n_{am} \quad (2.42)$$

$$n_t = X_c n_c + (1 - X_c) n_{am} \quad (2.43)$$

where n_{am} is the refractive index of amorphous phase in spherulites, 1.4707. X_c is the crystallinity of the spherulite calculated from density.

The α form crystal is usually obtained when the crystallization temperature is higher than 130 °C, or less than 80 °C, and the β form may be produced between 80 to 130 °C according to Padden and Keith (1959, 1966). The quantity of produced β form crystal depends on preparation method and molecular weight of the sample. The type I spherulites of α form crystal may be formed in the lower temperature range which is above 130 °C, and type II spherulites of α form crystal may be formed at higher temperature range above 130 °C. In the temperature range producing α form, a mixed type, I and II, of spherulites may also be produced. Type III spherulites are formed at lower temperature range in which β form can be produced, and the type IV is formed at higher temperature in that range. Quenching can produce α form spherulite or smectic structure [Gezovich and Geil, (1968)]. γ form of crystal is prepared under special preparation condition, especially under elevated pressure [Campbell (1991)].

Table 2.4. Refractive Indexes Along Unit Cell Axes

	n_a	n_c
α form	1.515	1.544
β form	1.506	1.536

There are two kinds of lamellae which compose spherulites. One is usually encountered in which molecular chains are perpendicular to the folding surface. The other is the one which exists in γ form crystals, with the chains 50° to the folding surface and the chains in adjacent folding planes cross with an angle of 100° between them (the stems are not perpendicular to the folding surface and the stems in a unit cell are not parallel to each other) [Campbell (1991)]. According to Sauer, Morrow and Richardson (1964), an α form lamella is a lath like rectangular crystal, with a-axis being parallel to long dimension of the crystal, b-axis is almost in the width direction, and c-axis is perpendicular to the fold surface. The growth direction of the long lath like lamella is along a-axis. The lamella in β form is also a lath like rectangular crystal, but may be twisted along the a-axis which is still parallel to long dimension of the crystal. In such a lamella both b- and c-axes rotate around the a-axis, which is the growth direction, periodically or randomly [Samuels and Yee (1972)].

There are two kinds of branches, besides the lamellae growing radially, which occur in spherulites. The growth direction of the first kind of branch has a small angle to the lamellae that grow along the radius. This kind of branch exists in all types of spherulites. It is necessary for such branches to fill the space when the size of spherulite increases. The growth direction of another kind of branch, edged-on lamellae, has large angles to the radial-growing lamella. For α form crystal, the angle between second kind of branch and radial-growing lamella is around 80° [Mandelkern(1958), Banks, Gordon, Roe and Sharples(1963)], and for γ form, around 40° [Campbell (1991)]. The structure of branches is the same as radial-growing lamellae with a-axis parallel to the longest dimension of the lamella. According to Padden and Keith (1966), lamellae grow in radial direction first and form the framework of a spherulite. Then, the branches with large angle to the radial lamellae start to grow. If a lot of edged-on lamellae developed during the crystallization process, the quantity of the lamellae with 80° to the radius is much

more than those parallel to it, so that the resulting spherulite, type I, is positive. If the amount of the edged-on lamellae is not much, the resulting spherulite, type II, is negative. There also seems to be a state existing between the two extreme conditions. This is evidently the reason for the formation of mixed type (of I and II) spherulite.

2.4.2. Isothermal Crystallization Kinetics

Griffith and Ranby (1959) fit the Avrami equation to data, dilatometrically measured, by pre-choosing Avrami index $n=3$ for iPP (DP =10,000), and found that when temperature increases from 133 to 155 °C crystallization rate constant k decreases from $5.82 \cdot 10^{-4}$ to $4.23 \cdot 10^{-11}$.

Marker, Hay, Tilley, Early and Sweet (1959) studied isothermal kinetics of iPP (intrinsic viscosity = 1.74-2.74 dl/g), using dilatometry with crystallization temperature being 123 - 136°C. The Avrami equation was employed in their data analysis. They found that $n=3$ and k changes from $2.69 \cdot 10^{-8}$ to $3.72 \cdot 10^{-12} \text{ sec}^{-3}$ as crystallization temperature increases. The growth rate of spherulites was constant at a given temperature and it decreases from 0.48 to 0.023 μ/sec as crystallization temperature increased. They also found that the number of nuclei increased rapidly to a constant value at an early stage of crystallization (the nucleation time is about 100 seconds at 129°C).

Falkai (1959,1960) measured the nucleation and growth rate of iPP (intrinsic viscosity = 1.28 dl/g), separately at various crystallization temperatures. He found that the overall crystallization described by the Avrami equation, in which $n=3$ was used, described those data well. The variation of the growth rate with temperature was examined and the growth rate which is constant at a given temperature decreases from $1.8 \cdot 10^{-3}$ to $2.7 \cdot 10^{-5} \text{ [cm/min.]}$ with increase in crystallization temperature from 122 to 145 °C. The growth rate G and the crystallization temperature was related by an equation of the form $\log(G) = 0.225 - 5.06 \cdot 10^4 / T\Delta T$. The heterogeneous nucleation

density decreases, from $2.36 \cdot 10^{-6}$ to $0.47 \cdot 10^{-6} [1/\text{cm}^3]$ with increase in crystallization temperature from 122 to 145 °C. The bulk crystallization followed by dilatometry can also be described by the Avrami equation. Avrami index was found to be 3 at various crystallization temperatures (127.5-145 °C).

The light depolarization measurement has been introduced by Magill (1962) to follow the crystallization of iPP with intrinsic viscosity being 1.5 dl/g (corresponding to $M_w = 1.96 \cdot 10^5$). The crystallization temperature applied in his experiments were in the range 99- 140°C. He observed that the crystallization rate constant measured by light depolarization measurement had the same magnitude as values derived from the dilatometer, and the nucleation was predetermined above 115°C, and sporadic below this temperature.

Parrini and Corrieri (1963) studied the influence of the molecular weight distribution on crystallization kinetics of iPP ($M_w = 181,000 - 493,000$ and $M_w/M_n = 1.33-11$). The crystallization was followed by dilatometry. Crystallization temperature was from 130 to 160 °C). They found that the crystallization rate is lower for samples having a very narrow distribution compared with polydisperse samples at the same crystallization temperature. Nucleation was found to be predetermined when crystallization temperature is below 150°C. At temperature above 150°C, the nucleation is mainly sporadic. Sporadic nucleation was more easily achieved for samples with narrow molecular weight distribution. Avrami equation was used in their research and n was found to increase from 3 to 4 as temperature increased. Broad molecular weight distribution tends to give lower n than samples with narrow molecular weight distribution. Molecular weight does not affect the n in their studied range. However, the samples with broad molecular weight distribution have much larger k than samples with narrow molecular weight distribution.

Hoshino, Meinecke, Powers and Stein (1965) have dilatometrically studied the overall crystallization rate of PP. The crystallization behavior was considered in relation to the stereoregularity of the sample. The combined results of studies of the crystallization of polypropylene by optical microscopy and by x-ray diffraction are consistent with a two stage process of crystallization. The first stage is radial growth of spherulites which can be described by Avrami equation with $n=3.9$. The nuclei produced in this stage were predetermined but did not all start at once. The second process was a secondary crystallization within the spherulite. The local process was also describable by an Avrami equation with $n=1.8$. The rate of secondary crystallization decreases also as crystallization temperature increases. The overall crystallization rate decreases for the less tactic fractions, but the secondary crystallization increases as tacticity of the samples becomes lower.

The light depolarization measurement and dilatometry was applied in the measurement of kinetics of isothermal crystallization of nucleated polypropylene [Binsbergen and Lange (1970)]. A nonlinear regression analysis was used in fitting the measured data into the Avrami equation. The nucleation density is highly dependent on the temperature of crystallization. The nucleation is essentially instantaneous and the density increases by a factor of 10 with an increase in the supercooling of 4°C. The material used in his experiment has intrinsic viscosity of 2.9 dl/g. The temperature range of his experiments was 125 to 149°C. The very slow crystallization showed an Avrami index n of somewhat less than 3, for fast ones it tends to give values considerably higher than 3, sometimes 5 to 6. The intermediate rate gives $n=3$.

Using infra-red spectroscopy, Wlochowicz and Eder (1981) analyzed the isothermal crystallization kinetics, bulk crystallization and growth rate, of iPP (intrinsic viscosity =1.64, crystallization temperature : 95-142 °C). They found that n was about 3 and the nucleation is predetermined.

Research on the kinetics of the isothermal crystallization by spherulite growth measurement has also been made by Lovinger, Chua and Gryte (1977), Goldfarb (1978), Wlochowicz and Eder (1981), and Martuscelli, Silvestre and Abate (1982). Clark and Hoffman (1984) applied the regime theory to the iPP spherulite growth data and concluded that a regime II to III transition occurs at a crystallization temperature of 137 °C ($\Delta T = 48$ K).

Recent research [Hammami (1990), $M_w = 150,200 - 257,100$, Campbell (1991), $M_w = 83,000$, under supercooling less than 70 °C] not only show the constant growth rate in isothermal crystallization for iPP, but also confirmed that it exhibits a regime II to III transition near 137 °C [Campbell (1991)]. The growth rate related to crystallization temperature follows Hoffman-Lauritzen equation, equation (2.3). The growth rates, nucleation rates, morphology, rate constant and Avrami index are dependent on the tacticity, impurity, and molecular weight of the materials [Hammami (1990)]. The higher the molecular weight, the slower the crystallization rate of the polymer. The tacticity and copolymerization effects are more prominent than those of the molecular weight. Homopolymers crystallize faster than copolymers. The nucleation density is observed to be far more sensitive to the crystallization temperature than to the time in isothermal crystallization. The nucleation density is inversely proportional to the degree of undercooling. The nucleation was found to be heterogeneous. The final crystallinity increases with increase in crystallization temperature. The Avrami equation was used to analyze the bulk crystallization kinetics. The Avrami index increases from two to four when crystallization temperature decreases from above 135 °C to 128 °C. The decrease in Avrami index at high temperature was attributed to disk-like crystalline entities formed during the experiment because the size of the spherulites were much larger than the thickness of the sample in LDM approach [Hammami (1990)]. The index close to four was explained by the possible time dependent nucleation, though the nucleation density

measurement revealed the nucleation is time independent. Both equation (2.7) and (2.8) were tried to fit the nucleation density data [Hammami (1990)]. It was found that the homogeneous nucleation density, equation (2.8), fit the experimental data better than the other did. The crystallization rate constant increases as crystallization temperature decreases, which follows equation (2.9) [Hammami (1990), Campbell (1991)].

2.4.3. Nonisothermal Quiescent Crystallization Kinetics

Few researches have been reported on the nonisothermal crystallization of polypropylene.

Ozawa's approach has been used by Monasse and Haudin (1986) in their kinetic analysis of the nonisothermal crystallization of iPP ($M_w = 450,000$ and $M_n = 56,000$) using DSC at constant cooling rate in the range from 0.3 to 80°C/min. A transition from a sporadic to instantaneous nucleation is found about 122°C. Avrami index was found to be 4 in the sporadic nucleation range and 3 in instantaneous nucleation range. Eder and Wlochowicz (1983) also applied Ozawa equation in their research. Their material had $[\eta] = 2.48\text{-}2.72$ dl/g, and they used the DSC to follow the crystallization under cooling rate: 0.5 - 10 °C/min.. They found n ranging from 3.3 to 2.6 and suggested predetermined nucleation and three dimensional growth of the crystallites in their experiments.

Wu, Dann, Cheng and Wunderlich (1988) using a modified DSC investigated polypropylene crystallization under quench conditions (cooling rates up to 10,000 deg/min and only the temperature of crystallization was recorded). They reported that even at these fast cooling rates, polypropylene crystallized on cooling between 77 to 7 °C, no fully amorphous material was produced, and no initial stage crystallization to the condis state could be proven by quenching after partial crystallization. Similar experiments were done by Piccarolo, Saiu, Brucato and Titomanlio (1992) in which they

quenched iPP ($M_w = 476,00$ and $M_n = 79,300$) at a cooling rate higher than $4800\text{ }^\circ\text{C/min}$ and the sample temperature was followed during crystallization. At such cooling rates, the resultant samples were essentially smectic. When cooling rates were below a few tens of $^\circ\text{C/sec.}$, only α -form monoclinic crystal was obtained.

Hammami (1990) studied iPP with various molecular weight using DSC and LDM technique. He observed that the effect of molecular weight on the crystallization rates is not as pronounced as in the case of isothermal studies because of the overwhelming effects of temperature on the crystallization rates. Nakamura equation, (2.17) or (2.20), (in which the value of $n = 3$ was obtained from isothermal crystallization), Ozawa equation, equation (2.22), and Ziabicki equation, equation (2.16), have been used in his kinetic analysis. He found that the Nakamura equation can give better descriptions of the experimental results than the other two equations. The equation predicts the experimental curves well except towards the end of the crystallization.

Kim et al (1991) using DSC and LDM studied iPP ($M_n = 4.18 \cdot 10^4$ and $M_w = 2.32 \cdot 10^5$) nonisothermal crystallization kinetics under cooling rates 0.5 to $16\text{ }^\circ\text{C/min}$. They applied another non-isothermal kinetic equation proposed by Tobin (1974) and Choe and Lee (1989) which reads,

$$\frac{d\theta}{dt} = k_1(T)(1-\theta)^2 t^2 + k_2(T)^2(1-\theta)^2 \int_0^t (t-\tau)^2 [1-\theta(\tau)]^2 d\tau$$

where k_1 is the rate constant for crystal growth on heterogeneous nuclei and k_2 the rate constant for crystal growth on homogeneous nuclei, and found the kinetic equation worked well. The nucleation was supposed to be mixed heterogeneous and homogenous, or heterogeneous alone in their analysis.

In DSC measurement, following Khanna (1990), Zhang et al (1994) suggested the use of $(T_{in} - T_{1/2})/\beta$ to characterize crystallizability of the polymer in nonisothermal

crystallization, where β is cooling rate, T_{in} is crystallization initial temperature, and $T_{1/2}$ is the temperature where 50% area under the peak has been reached. They found that nucleating agents are more efficient in PP-PE copolymer than in PP homopolymer.

2.4.4. Influence Of Molecular Orientation

Little is known about this. Katayama and Yoon (1985), Zhou (1988), Zhou and Spruiell (1989), Patel (1991), and Patel and Spruiell (1991) have applied equation (2.38) in the simulation of melt spinning process in which the equation was simultaneously and numerically solved together with mass balance, heat balance, and rheological equation according to measured diameter, birefringence, spinning stress and temperature along the spinline. In their calculation the Avrami index was chosen to be 1 - 2.4 because of the existence of the molecular orientation. The crystalline entity of PP formed under uniaxial extension was reported to be in shapes of ellipsoid of revolution, not spherulitic, with its rotational axis (minor axis) parallel to the extension direction [Samuels (1974), Dees and Spruiell (1974)].

2.5. Review of Computer Simulation Of Melt Spinning Process

Melt spinning is the most common method to produce continuous filaments from polymers. Spinning modeling allows one to predict the physical properties of the spun yarn from a knowledge of the spinning conditions and polymer properties. The earliest computer simulation of the melt spinning process was introduced by Kase and Matsuo [Kase and Matsuo (1965, 1967)] for PET melt spinning process. The spinning speed applied in their model is low (< 750 m/min) so that the complexity from crystallization can be avoided. The effects of gravity, inertia, and air drag were also neglected because of the low spinning speed applied. Later Hamana, et al [Hamana, et al (1969)] introduced the effects of gravity, inertia, and air drag into spinning model which is applied to PET

and nylon 6 spun at the spinning speed less than 900 m/min. Similar work was done by George [George (1982)] for PET with the applied spinning speeds up to 3500 m/min, but still no crystallization was included into the model.

The description of the crystallization in spinning model was first introduced by Shimizu, Okui, and Kikutani [Shimizu, Okui, and Kikutani (1985)]. The crystallization kinetic equation used in their model was basically the one suggested by Nakamura. The crystallization term was also included in the energy balance equation. The energy balance equation applied in their model was first suggested by Battacharya and Moutsoglou [Battacharya and Moutsoglou (1982)]. In the model suggested by Shimizu, Okui, and Kikutani, they introduced an empirical equation to correct for the effect of crystallinity on the viscosity. They developed the model for PET with melt spinning speed up to 9000 m/min. Very similar work, for PET, was also done by Katayama and Yoon [Katayama and Yoon (1985)] at the same time.

The melting spinning model was introduced into our lab by Zieminski and Spruiell (1988), which was similar to that described by Shimizu, et al [Shimizu, Okui and Kikutani (1985)] applied for Nylon-66. Later, Patel, Bheda and Spruiell (1991) [Patel, Bheda and Spruiell (1991)] modified the model and applied it for Nylon-6. They suggested the differential form of the Nakamura crystallization kinetic equation to replace the integral one previously used in the model created by Zieminski and Spruiell (1988). Hajji, et al (1992) applied the model to polypropylene in the simulation of the spun bonding process. The previous melt spinning model in our lab was the one finalized by Patel, Bheda and Spruiell (1991), which is summarized in Figure 2.1.

PREVIOUS MODEL

Continuity Equation:
$$W = \frac{\pi D^2}{4} \rho V$$

Momentum Balance:
$$\frac{dF_{rheo}}{dz} = W \frac{dV}{dz} + \frac{1}{2} \rho_a C_d V^2 \pi D - \frac{W g}{V}$$

Energy Balances

[Battacharya et al (1982)]:

$$\frac{dT}{dz} = -\frac{D\pi h_a}{C_p W} (T - T_1) + \frac{\rho_c \Delta H}{\rho C_p} X_c \frac{d\theta}{dz}$$

Viscosity and Constitutive Equations

Constitutive Equations:
$$\frac{dV}{dz} = \frac{\sigma}{\eta_e (T, \theta)}$$

Viscosity:
$$\eta_e (T) = A \cdot \exp \left[\frac{B}{T} \right]$$

Shimizu et al(1985):
$$\eta_e (T, \theta) = \eta_e (T) \exp \{ a_3 \theta^{b_3} \}$$

Birefringence Orientation:
$$\Delta n_a = C_{op} \sigma \text{ and } f_a = \frac{\Delta n_a}{\Delta n_a^0}$$

$$\Delta n = (1 - \theta) \Delta n_a + \theta f_c \Delta n_c^0$$

Crystallization Kinetics:
$$\frac{d\theta}{dt} = \frac{nK}{V} (1 - \theta) \left[\ln \left(\frac{1}{1 - \theta} \right) \right]^{\frac{n-1}{n}}$$

$$K (T, f_a) = [\ln (2)]^{\frac{1}{n}} \left(\frac{1}{t_{1/2}} \right)_0 \exp \left\{ \frac{-U^*}{R (T - T_s)} \right\} \exp \left\{ \frac{-C_3}{T \Delta T f + C T^2 f_a^2} \right\}$$

Figure 2.1. Summary of the previous melt spinning model [Patel, Bheda and Spruiell (1991)]

Chapter 3

METHOD FOR THE STUDY OF THE QUIESCENT NON-ISOTHERMAL CRYSTALLIZATION UNDER RAPID COOLING RATES

3.1. Introduction

This chapter describes the experimental techniques for the study of the quiescent nonisothermal crystallization under rapid cooling rates. The kinetic analysis for the experimental results will be discussed in the next chapter, Chapter 4.

The technique was developed based on light depolarizing microscopy, LDM, to study the nonisothermal crystallization of polymers at average cooling rates up to 2500 °C per minute. The experimental quantities that are measured in this technique include the temperature, the light intensity, and spherulite diameter. For such a purpose, a sample chamber, heating and cooling system, and data collecting systems were developed.

The polymer temperature, light intensity with analyzer, light intensity without analyzer, diameter of spherulites (by VCR technique) can simultaneously be measured in this technique. The two light intensities are measured because of the light scattering effect caused by numerous nuclei under the fast cooling condition.

The relationship between sample thickness and measured light intensity was also examined to understand the importance of control of the sample thickness in sample preparation. The potential higher cooling rate has not been tried because the presently adopted cooling condition is easily applied and under these cooling rates a lot of information needs to be analyzed and understood. Further experiment will include using thinner sample thickness (less than 150 μm) to get much higher cooling rates, and experimental investigation of the nucleation behavior. Though the starting material for the research is PP, the preliminary experiments about LDPE and HDPE also revealed very interesting phenomena by the new technique.

The theoretical analysis of the heat transfer for the considered sample under experimental conditions has been made according to basic principles in chemical engineering, to ensure that the crystallization does indeed take place under known and controlled conditions. Theoretical analysis of the light depolarization method has also been suggested. Such an analysis is inevitable especially when the scattering effect has experimentally been found so strong that it has to be corrected before the data can be used in the kinetic analysis. For the purpose of the further study of strain-induced crystallization, the analysis attempts to include the orientation effect.

3.2. Material Studied And Equipment

The material studied in this chapter was iPP resin having a MFR of 18, $M_w = 226,200$ and a polydispersity of 5.87.

The whole experimental system is composed of a light depolarizing microscope, hot stage system, light intensity measurement unit, temperature measurement unit, and spherulite diameter measurement system, see Figure 3.1.

3.2.1. Hot Stage System

The hot stage system is designed to hold, heat and cool the sample. The hot stage system is shown in Figure 3.2. The sample chamber has six inlets: two for heating, two for cooling, and two for exhausting. The doubled inlets are designed to improve the uniformity of heating or cooling. The sample is heated and cooled in the same place without being transferred. The sample system works as described below.

Nitrogen is introduced from a tank and goes through the first solenoid valve which will be used to cut the air to stop heating but without cooling. The second solenoid valve allows the air to go either to the cooling line or to the heating line on which there is

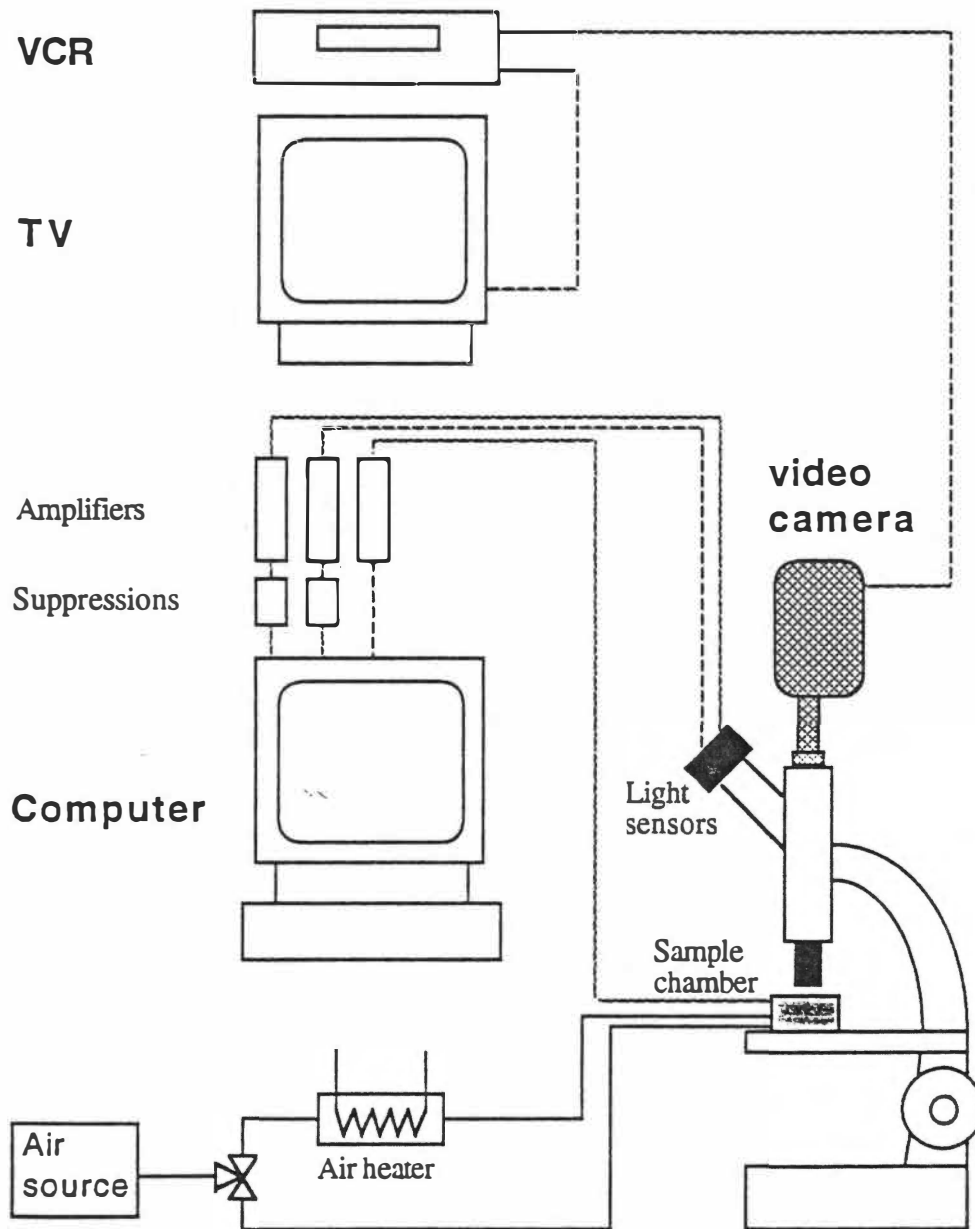


Figure 3.1. Experimental system.

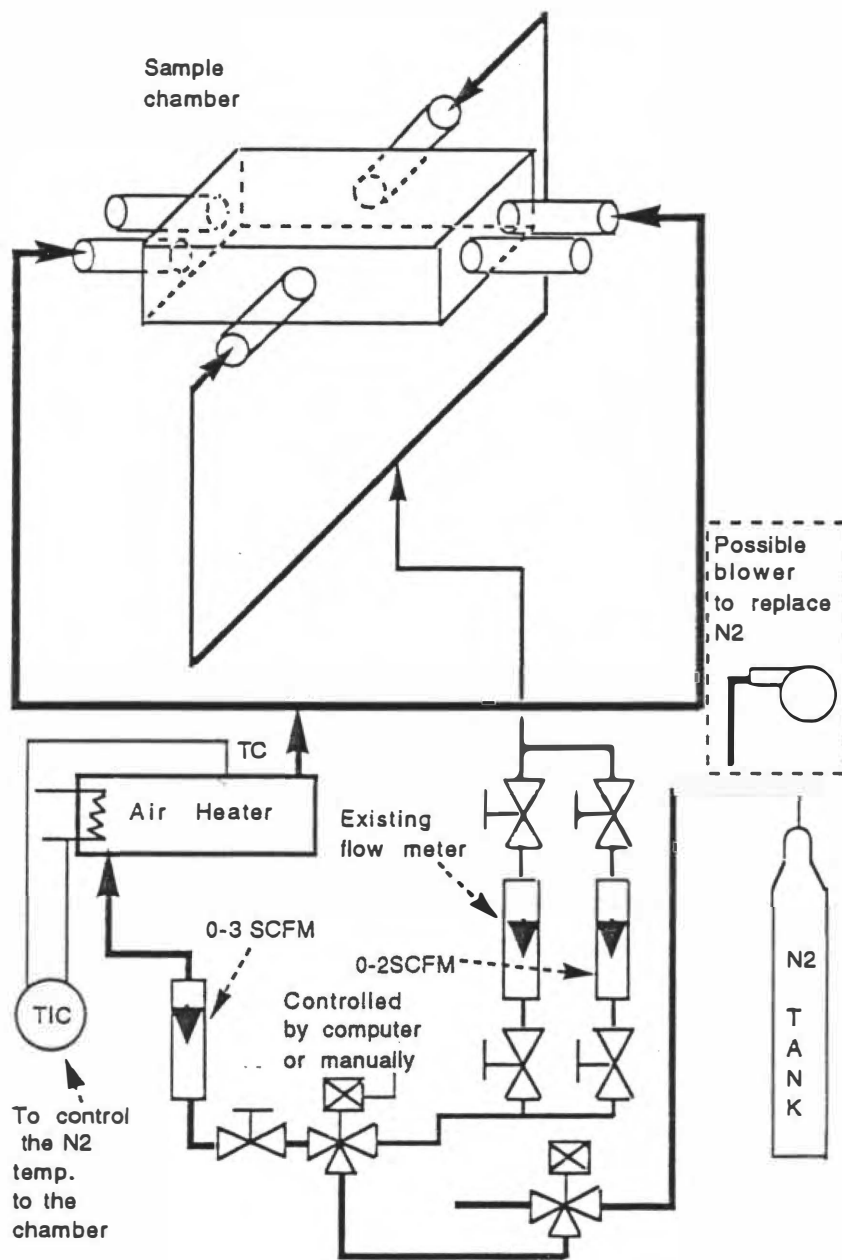


Figure 3.2. Hot stage system.

a heat exchanger to heat the air to the desired temperature. This valve is able to switch the air from heating to cooling without time interval. After the sample heat up and stabilization is completed, cooling air is turned on, and the system is designed to start to collect the data automatically from a given temperature (190 °C for PP). The flow meter in the heating line is to set up the heating rate. The two flow meters in the cooling line control and measure the cooling air flow rate so as to make the cooling condition repeatable. Because of the large variation of the cooling rate, two flow meters with different ranges were selected. The air temperature is controlled by a temperature controller. The two solenoid valves are controlled by computer to create different cooling conditions. Tubing before the heater is flexible since the temperature is low there. This flexible tubing is to separate the possible vibration caused by the air source and allow the hard Teflon tubing to contract and expand freely by properly fixing the heater. The cooling rate of the sample is controlled by the air flow rate.

3.2.2. Temperature Measurement

The temperature measuring system was originally built up by He and Bogue (1992). Some modifications for the temperature measurement system have been made for more convenient operation such as temperature real time display, automatic trigger of the data collecting procedure, and so on. The crystallization temperature was measured by an iron-constantan thermocouple which is directly inserted into the polymer. The thermocouple is 76.2 μm in diameter. It takes 0.08 sec (response time) for the thermocouple to change 63% of temperature from 427°C to 38°C when it is placed in air at a flow rate of 18.3 m/sec. The signal from thermocouple is sent into an IBM PC after being amplified. It may be possible to obtain and use smaller thermocouples. This would allow the use of thinner samples and even faster cooling rates.

3.2.3. Sample Assembly

The examined polymer is in the shape of film and has a thickness of 150 μm . The sample was sandwiched between two cover classes which have a thickness of 150 μm , see Figure 3.3. Both ends of the sample assembly are fixed in the sample chamber.

3.2.4. Light Intensity Measurement

The light intensities with and without analyzer are simultaneously measured as shown in Figure 3.4. The analyzer was moved to a position just before one of the two photodiodes which are placed at the two eye-pieces of the microscope. The two signals from the photodiodes are sent to the IBM PC computer after they are suppressed and amplified.

3.2.5. Spherulite Diameter Measurement

A video camera, which is mounted on the microscope, VCR and TV are employed to record the process of spherulite growth. 60 frames of image per second can be obtained by the system. The spherulite diameter is measured on the TV screen.

3.3. Analysis Of The Heat Transfer Problem

The considered heat transfer problem occurs in the quiescent non-isothermal crystallization. A rapid cooling or quenching process is to be considered in the heat transfer analysis. The non-isothermal quiescent crystallization encountered in our experiments is an unstable heat transfer process with the third kind of boundary condition. The selection of boundary condition is based on the consideration that during cooling, the temperature on the sample surface reaches that of the cooling medium gradually, not instantaneously. With such boundary condition the heat transfer equation is generally more difficult to solve.

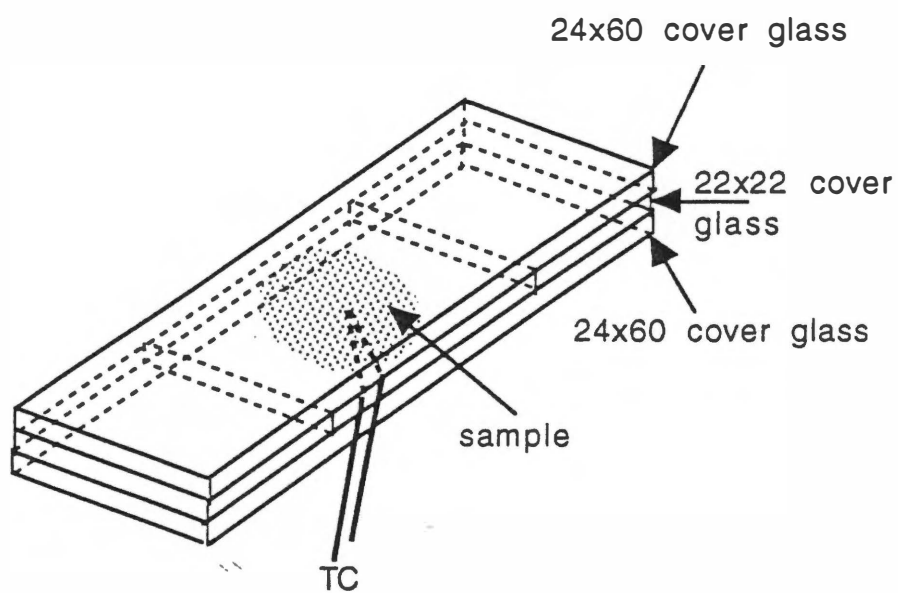


Figure 3.3. Sample assembly used in the experiments.

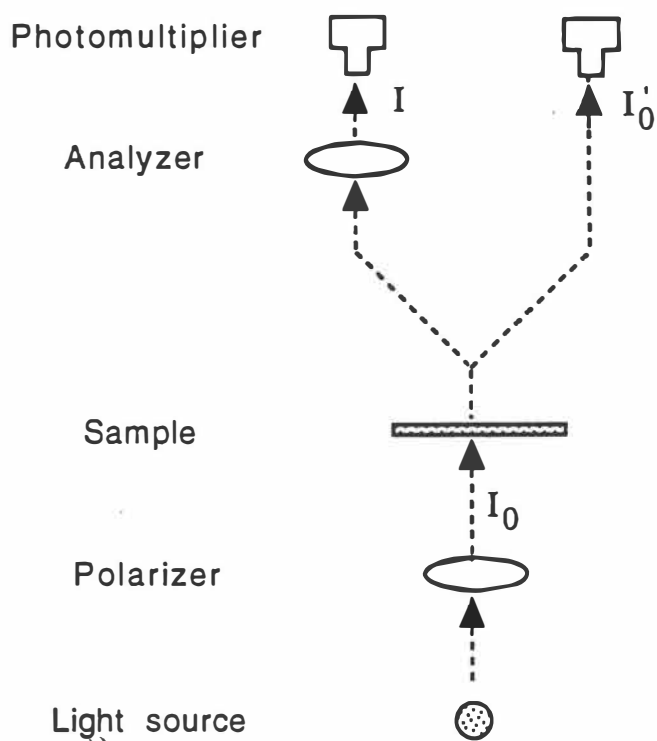


Figure 3.4. Schematic diagram of the light depolarizing microscope.

According to heat transfer theory, the governing equation for the one dimensional heat transfer from a slab is,

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) \quad (3.1)$$

where ρ is the density of the polymer, C_p is the specific heat of the polymer, and k thermal conductivity of the polymer. x represents the direction of the heat transfer. In the calculation, the ρ , C_p and k are all considered to be variable during cooling, and C_p also covers the heat released from crystallization. The initial and boundary conditions for the considered problem are:

$$\text{I.C.:} \quad T(x,0) = T_0 \quad (3.2)$$

$$\text{B.C. 1:} \quad \frac{\partial T(0,t)}{\partial x} = 0 \quad (3.3)$$

$$\text{B.C. 2:} \quad \frac{\partial T(b,t)}{\partial x} = -\frac{H_{ga}}{k} [T(b,t) - T_1] \quad (3.4)$$

where T_0 is the initial temperature of the sample, $T(0,t)$ and $T(b,t)$ are the temperature at the center and surface of the sample respectively. T_1 is the temperature of cooling medium. H_{ga} may be called the overall heat transfer coefficient of the air and glass and is defined as,

$$\frac{1}{H_{ga}} = \frac{1}{k_g/l_g} + \frac{1}{h_a} \quad (3.5)$$

where k_g is the thermal conductivity of the glass and l_g is the thickness of cover glass, h_a is the heat transfer coefficient of the air, $h_a = k_a/l_a$, l_a is the thickness of air layer in which the temperature is higher than T_1 , and k_a is the thermal conductivity of the air. The calculation shows that the temperature distribution in the sample along the direction,

x , perpendicular to the sample plane can be neglected when the average cooling rate applied in the experiment is less $3000^{\circ}\text{C}/\text{min}$ and when the sample thickness is less than $200\text{ }\mu\text{m}$.

Figure 3.5 shows a numerical solution for the considered heat transfer problem. The conditions for that solution are: sample thickness is 0.2 mm , the thickness of either cover glass is 0.15 mm , and heat transfer coefficient of air $h_a = 70\text{ [W/(M}^2\cdot\text{K)]}$ which corresponds to $\text{CRF} = 0.154\text{ (1/sec)}$ (CRF will be defined below). These conditions are analogous to the ones applied in collecting experimental data. Figure 3.5 shows that the temperature distribution in the sample along the direction perpendicular to the sample plane can be neglected at any time. The temperature gradient mainly exists in the air boundary layer, though there is a small gradient in the cover glass as well. Therefore, when the thickness is less than $200\text{ }\mu\text{m}$ and the cooling intensity, represented by h_a , is less than $70\text{ [W/(M}^2\cdot\text{K)]}$, the sample will be evenly cooled according to this calculation. In this example, it took less than 5 sec for temperature to drop from 150 to 50°C (average cooling rate is $1200^{\circ}\text{C}/\text{min}$).

As an examination of the capability of the model to reflect large temperature distribution in the sample, the sample was assumed to be quenched in ice-water. Figure 3.6 gives the result for such calculation under the condition of sample thickness is 0.2 mm , $h_a = 500\text{ [W/(M}^2\cdot\text{K)]}$, or $\text{CRF} = 0.908\text{ (1/sec)}$. It shows that there is still a large temperature gradient in the boundary layer, but the temperature distributions in the sample at various time can not be neglected in this case. This result also tells us that the neglect of temperature gradient is limited by cooling intensity. The temperature gradient in the sample can be neglected only under moderately high cooling condition. It took about half second to allow the temperature to cool from 150 to 50°C . The average cooling rate for this case is about $16,000^{\circ}\text{C}/\text{min}$.

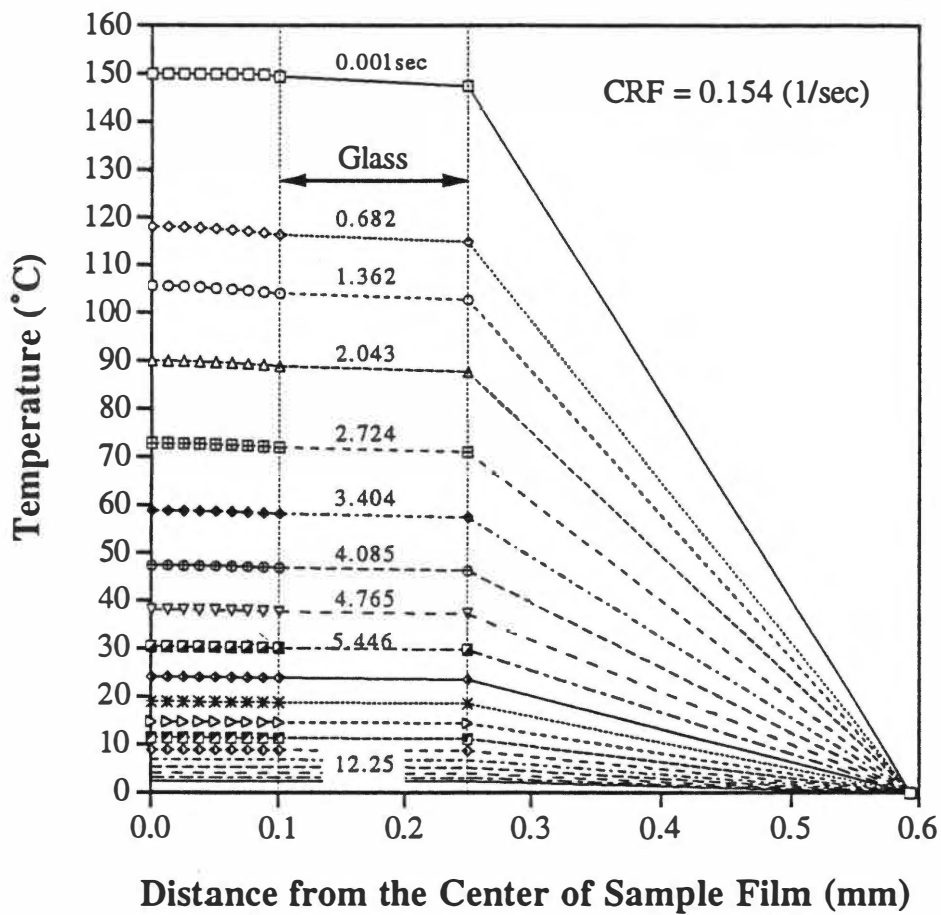


Figure 3.5. Temperature distribution in a slab at various time which is cooled down a flowing air in a temperature = 0°C. The heat transfer coefficient h_a is 70 (W/M²K).

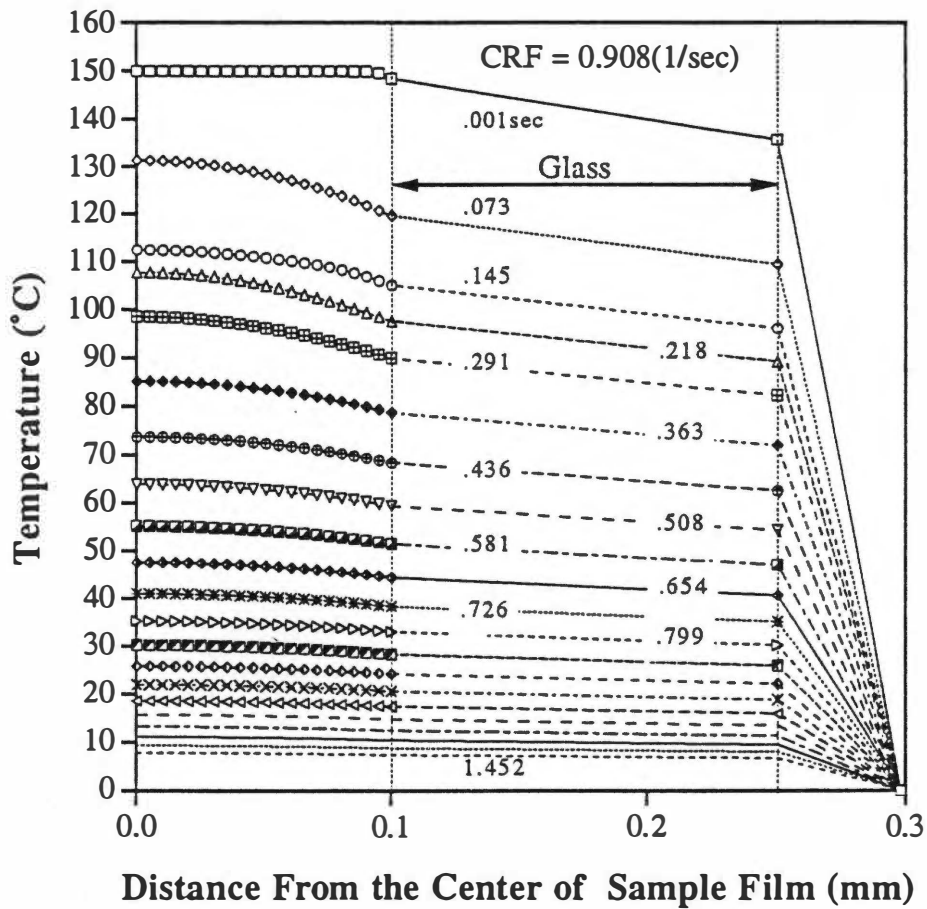


Figure 3.6. Temperature distribution in a slab at various time which is cooled down a ice water. The heat transfer coefficient h_a was assumed to be 500 (W/M²K), or CRF = 0.908 (1/sec).

It is apparent that with thinner sample thickness, one may reach higher cooling rates without worrying about the temperature distribution in the sample. The criteria that determines if a temperature distribution in a cooling object can be neglected or not can be quantitatively given by the calculation of Biot number. Based on the calculation of the Biot number the maximum cooling rate for three different sample thicknesses for LDPE was estimated and given in Table 3.1.

Considering that the heat conductivity of PP will not be too far from LDPE and the selection of the value of the heat conductivity of LDPE was conservative, the estimated maximum cooling rate that would give an approximately even temperature distribution in the sample is also a good approximation for PP. More precise result needs to use the heat conductivity as function of temperature for PP by numerical calculation.

According to the above analysis, the heat transfer equation may be simplified. The simplified model could be derived as follows.

The heat transferred into the film is 0. The heat transfer out of the film is equal to $Hga(T - T_1)$. The net change of the heat in the film caused by heat transfer is, therefore,

$$0 - A Hga(T - T_1) = - A Hga(T - T_1)$$

The heat change rate within the film is equal to $V \frac{\rho C_p dT}{dt}$. The heat change rate should equal to heat net change caused by heat transfer:

$$V \frac{\rho C_p dT}{dt} = - A Hga(T - T_1) \quad (3.6)$$

where V is the volume of the considered object. The initial condition for this heat transfer problem is :

$$T(0) = T_0 \quad (3.7)$$

Equations (3.6) and (3.7) compose the simplified heat transfer problem. If C_p and ρ are

Table 3.1. The Estimated Maximum Cooling Rate For Three Different Sample Thickness For LDPE

Sample Thickness [μm]	h_{max} [W/(m ² •K)]	h_{max} [cal/(cm ² •°C)]	Max. avg. Cooling Rate [°C/min.]	CRF [1/sec]
50	1171	$27.98 \cdot 10^{-3}$	13290	0.739
150	340	$8.136 \cdot 10^{-3}$	3816	0.21
200	251	$6.006 \cdot 10^{-3}$	2799	0.153

* for LDPE: $k = 0.24$ [W/(m²•K)], $k_g = 0.8$ [W/(m²•K)]

constants, Equation (3.6) and (3.7) can be solved analytically. Here, however, $\rho = \rho(T)$ and $C_p = C_p(T)$. Therefore, the present problem can only be solved by numerical approximation.

There are several well established procedures to obtain the numerical solution of equation (3.6) and (3.7). The results in this research are solved by fourth-order Runge-Kutta procedure. The results are given in Figure 3.7. In Figure 3.7, the solid lines are the results calculated by the simplified model and the dotted lines are the values in the center of the sample calculated by the complex model, equations (3.1) - (3.4). Figure 3.7 tells us that the results calculated by the simplified and the complex models are almost the same. Therefore the simplified model can be used to describe the temperature change in the considered sample within the range of cooling rates where the temperature distribution through the sample thickness is negligible.

In the calculation, the crystallization effect was included in the heat capacity. Such an approach can not handle variation of crystallization temperature and crystallinity. The heat released during crystallization does not change with different cooling rates. Hence, a more elegant way to treat the crystallization heat is to exclude the crystallization heat from heat capacity and introduce a separate term in the heat transfer equation. The following is the recommended way to treat this problem.

If ΔH is the heat of fusion, X (by volume) is the absolute crystallinity and ρ_c is crystalline density, the crystallization effect may be introduced to equation (3.6) as,

$$\frac{dT}{dt} + (A Hga/\rho C_p V) (T - T_1) = [(\rho_c/\rho) \Delta H/C_p] \frac{dX}{dt} \quad (3.8)$$

Assuming $Hga/\rho CV$ will not change much, and $(\rho_c/\rho) \approx 1$ during crystallization, one may simplify equation (3.8) to,

$$\frac{dT}{dt} + \frac{Hga}{\rho CV} (T - T_1) = \frac{\Delta H}{C_p} \frac{dX}{dt} \quad (3.9)$$

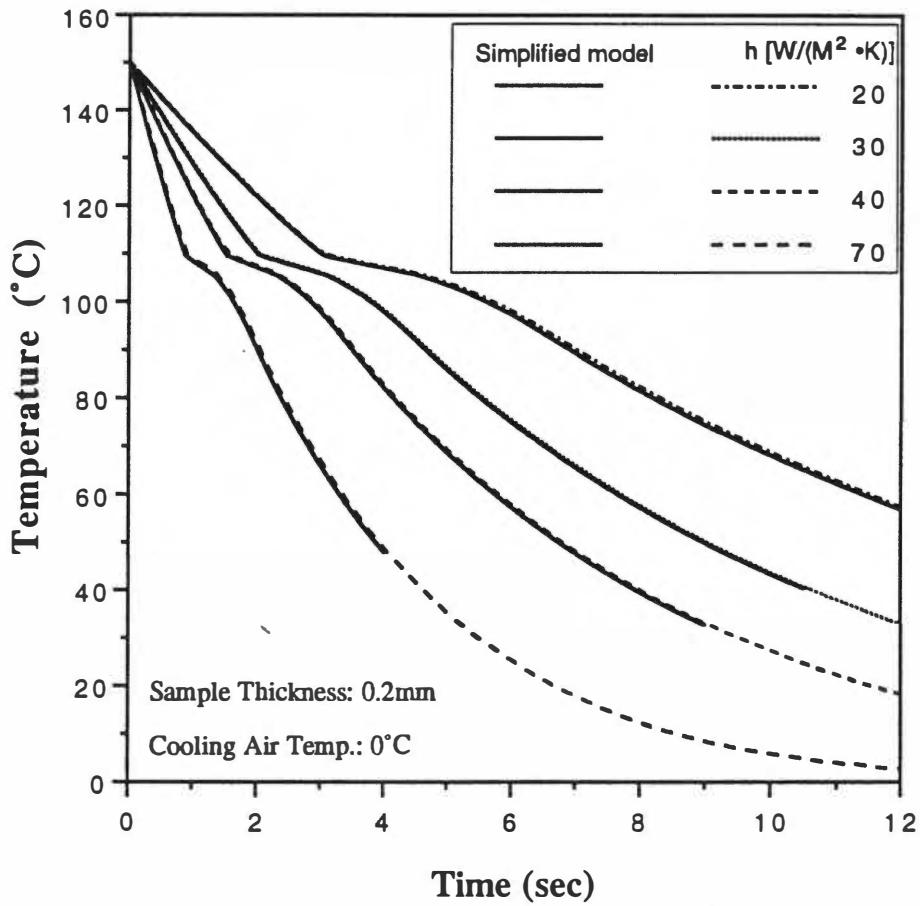


Figure 3.7. Comparison of the cooling curves calculated by the complex model, equation (3.1)- (3.4), at $x = 0$, and the simplified model, equation (3.6), at various cooling rates.

$\frac{dX}{dt}$ can be calculated from the measured temperature-time data according to above equation. The significance of equation (3.9) is not that it can be used to calculate the temperature according to crystallization behavior. Instead, it may be used to obtain the crystallization information from the temperature.

3.4. Factors Affecting Light Intensity Measured

3.4.1. Effect Of The Sample Thickness On The Light Intensity

To examine the influence of sample thickness on the measured light intensity, light intensity was measured for samples with different thickness at the same crystallinity. It was found that the measured light intensity is influenced by the effect of light scattering caused by crystallites in the sample. The measured light intensity varies irregularly to the sample thickness if the intensity of the light source, I_0 , is fixed. Such scattering effect can be compensated by increasing the intensity of the source light. By removing the analyzer from the light path, I_0 can be measured without a sample in the light path. After the sample is placed in the light path, one may keep I_0 at the same level as without a sample in the light path by increasing the intensity of light source. In this way the scattering effect can be compensated. The relationship between light intensity and sample thickness after correction for scattering effect is given in Figure 3.8. The correction for light scattering for each point in Figure 3.8 was made individually. The light intensity and sample thickness displays linear relationship after the light scattering correction was made. The slow cooled samples in Figure 3.8 were prepared by keeping them in the film press and naturally cooled down from 200°C to room temperature. The whole cooling process is about ten hours, so that the crystallinity in that sample was high (The density of that sample is 0.912 g/cm²). Figure 3.8 also gives the situation of the samples with

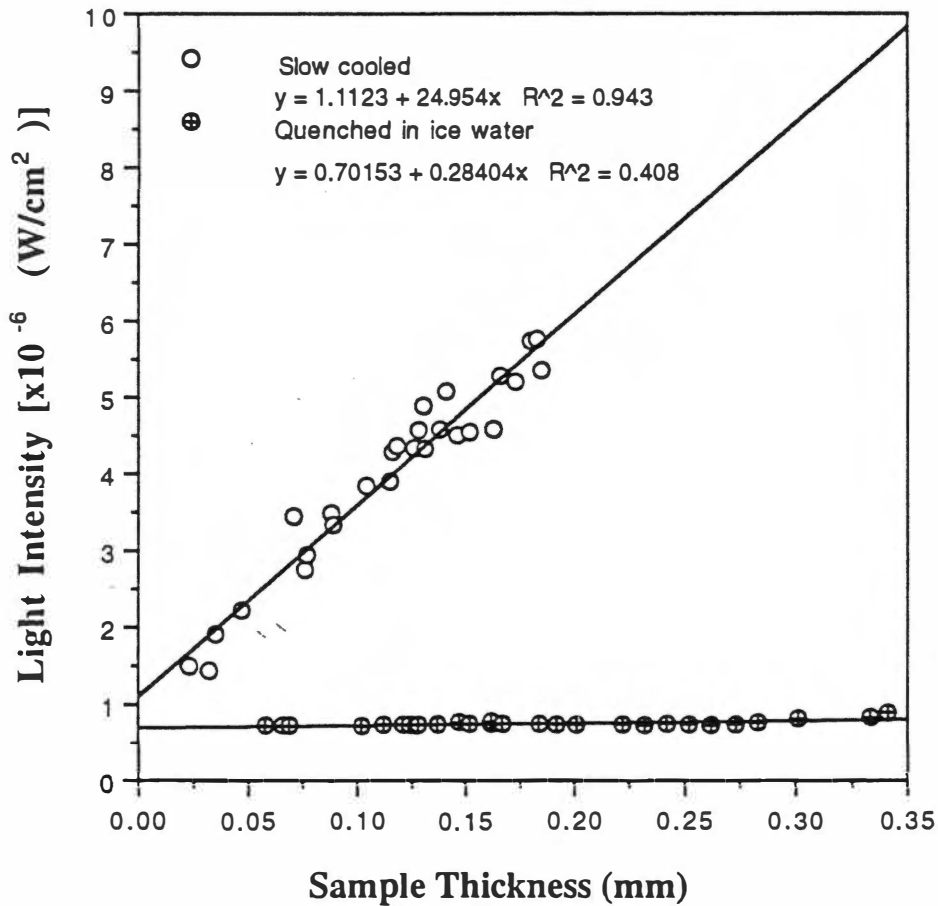


Figure 3.8. Light intensity measured from the slow cooled and quenched samples versus sample thickness after light compensation was made. I_0 was kept at $3.07 \cdot 10^{-12}$ (W/cm^2) when the light path was half open, without analyzer and with one glass slide and one glass cover in light path.

low crystallinity which were prepared by quenching the samples in ice water .

3.4.2. Evidence Of Light Scattering Effect In LDM Method (Under High Cooling Rates)

It was found that in the early stages of crystallization, the light intensity measured under high cooling rates drops first before it increases with increase in crystallinity in the sample. Figure 3.9 gives such an example (CRF, the light intensity without analyzer and the relative light intensity in Figure 3.9 will be discussed later). The following consideration was made to explain this phenomenon. If there were no scattering effect in the LDM method, the intensity transmitted through the sample and before the analyzer should maintain constant before, during and after crystallization. By removing the analyzer from the light path, one is able to measure this intensity which will be called light intensity without analyzer, I_0' (The term light intensity is now specifically used for the intensity measured with analyzer which is denoted as I). Figure 3.9 gives such a result which shows the light intensity without analyzer drops first and recovers later during the crystallization. This is the evidence of the existence of light scattering effects during crystallization.

The change of spherulite radius was plotted in the same figure as I_0' and temperature in Figure 3.10. Spherulite-b in that figure was chosen from earliest produced nuclei and the diameter measurement for spherulite-a lasted until almost completion of impingement. From Figure 3.10 we can see that the reduction in I_0' the scattering effect is related to the growing spherulites. It is apparent that the scattering effect will be related to nucleation density, size of spherulites, and impingement of spherulites.

There are two reasons responsible for the reduction in light intensity in the early stage of crystallization. One is the light scattering effect from spherulites and the other is existence of a certain level of the leaked light. The leaked light is a result from polarizers

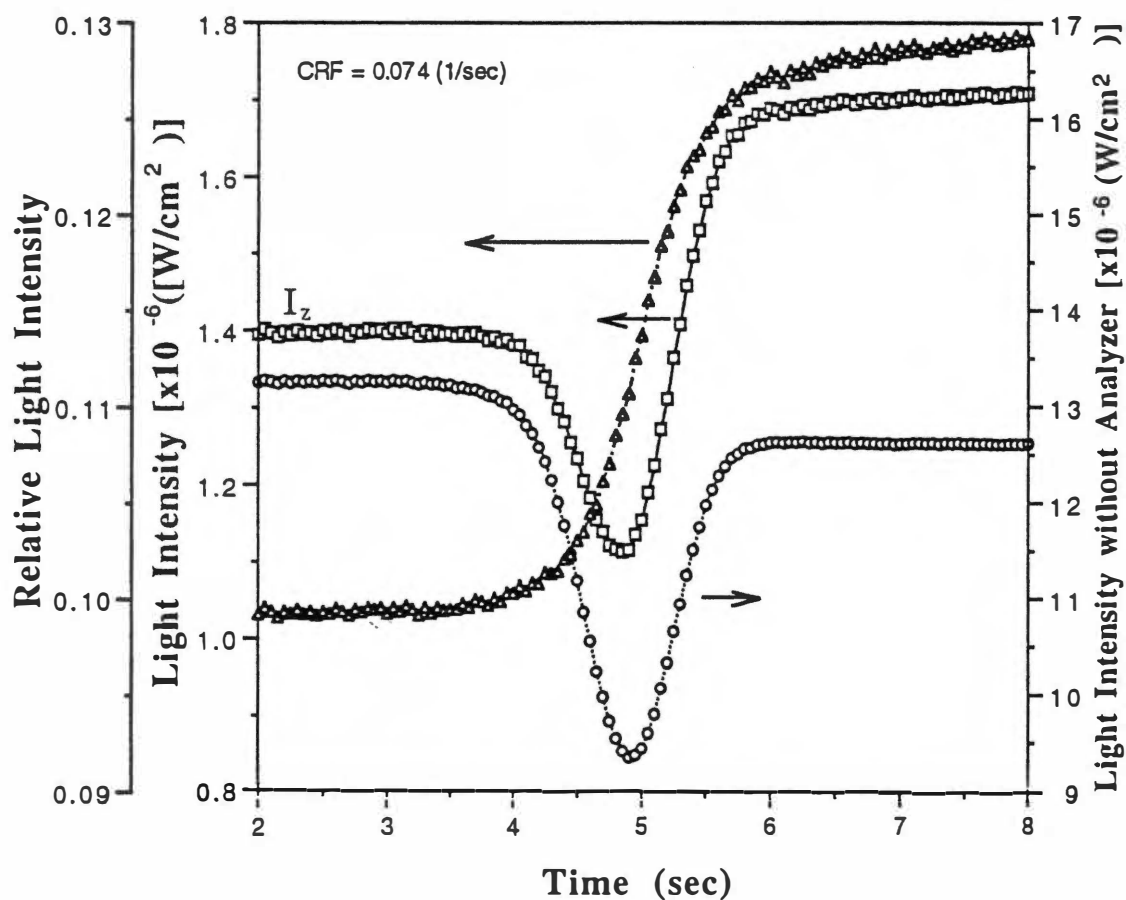


Figure 3.9. Light intensity, light intensity without analyzer, and relative light intensity versus time.

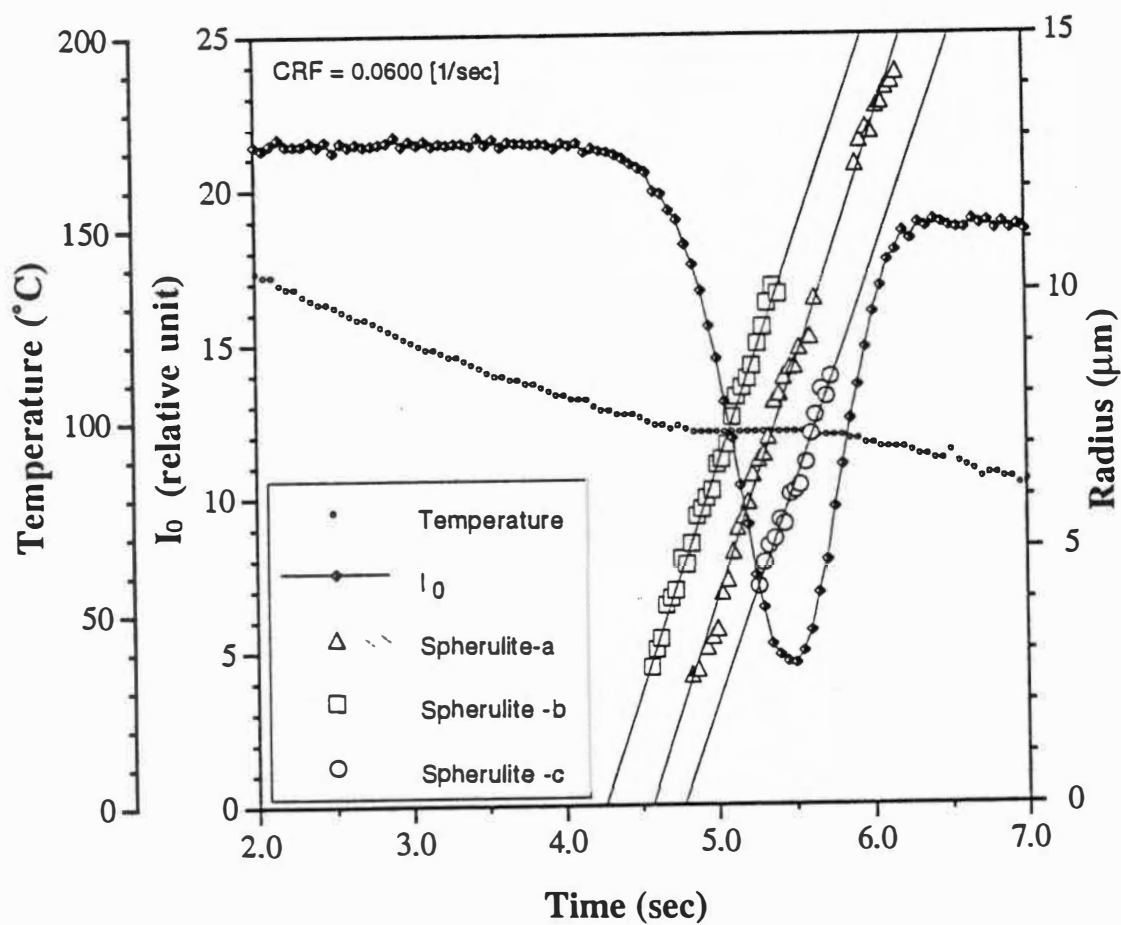


Figure 3.10. Light intensity without analyzer, temperature and spherulite radius versus time for CRF = 0.600 (1/sec).

that are practical, not ideal. For two crossed ideal polarizers, no light could transmit through the second polarizer, but for real polarizers some light passes the analyzer. The scattering effect is related to the number and size of the spherulites in the sample. The measured light intensity is a comprehensive result of the scattering effect, which causes the light intensity to decrease, and the depolarizing effect of spherulites, which enhances the measured light intensity. At an early stage of the crystallization, the small spherulites scatter light more than they depolarize it. Therefore, the light intensity drops first. The minimum of the intensity curve corresponds to maximum scattering effect. After the minimum point the scattering effect decreases because the spherulites become larger. The light intensity without analyzer describes the scattering effect without the complication of depolarization. The increase of the I_0' after the minimum point of the curve is related to the size of the spherulites, and at the later stage, the impingement of spherulites. The impingement of the spherulites has a very important effect on the scattered light because the interface between two spherulites does not scatter light much. The impinged spherulites are united as if they are in one spherulite. Therefore, after impingement is completed, the scattering effect reduces to a minimum. A slightly lower level of I_0' after impingement compared to the melt state is caused by the two phase structure in the spherulite, and spherulite-spherulite interfaces. The light intensity with analyzer reflects the characteristics of both the light intensity without analyzer, which describes the scattering effect in the crystallization early stage, and the relative light intensity, which is a quantity that describes the depolarizing effects only (defined later) in the crystallization stage. The point at which the light intensity starts to drop represents the onset of crystallization. That the light intensity approaches to the final value indicates that the crystallization is approaching completion.

3.4.3. Correction For The Light Scattering Effect

In crystallization under fast cooling rates, the nucleation density is high and the sizes of the resultant spherulites are small. This will create strong light scattering during crystallization. The scattering effect must be corrected before the light intensity can be used to describe the overall crystallization rate. The method to correct for the light scattering effect is developed and described here.

The incident light (before the sample), I_0 , represents the intensity of the light source. The measured light intensity without analyzer (with sample), I_0' , is equal to:

$$I_0' = I_0 - I_s \quad (3.10)$$

where I_s is the intensity of scattered light. it is assumed that the reduction of the light intensity without analyzer, I_0' , caused by scattering during crystallization and measured under constant intensity of the light source, I_0 , is equivalent to the one caused by variation of I_0 without light scattering during the same process. By this assumption, I_0 in equation (B.59) can be replaced by I_0' , and the equation can be written as,

$$I = I_0' (1 - \bar{d} f^* X_c + R_0) + C \quad (3.11)$$

where I_0' is the light intensity without analyzer. $\bar{d}$ is the average lamellar thickness. f^* is an orientation related function. X_c is dynamic absolute crystallinity [$X_c = X_c(t)$]. R_0 and C are constants. If the sample thickness, lamellar thickness, crystallinity and orientation are fixed, equation (3.11) can be written as:

$$I = (\text{constant}) I_0' + C \quad (3.12)$$

This equation means that the measured light intensity with analyzer is a linear function of the light intensity without analyzer under the mentioned condition. This relationship is supported by Figure 3.11.

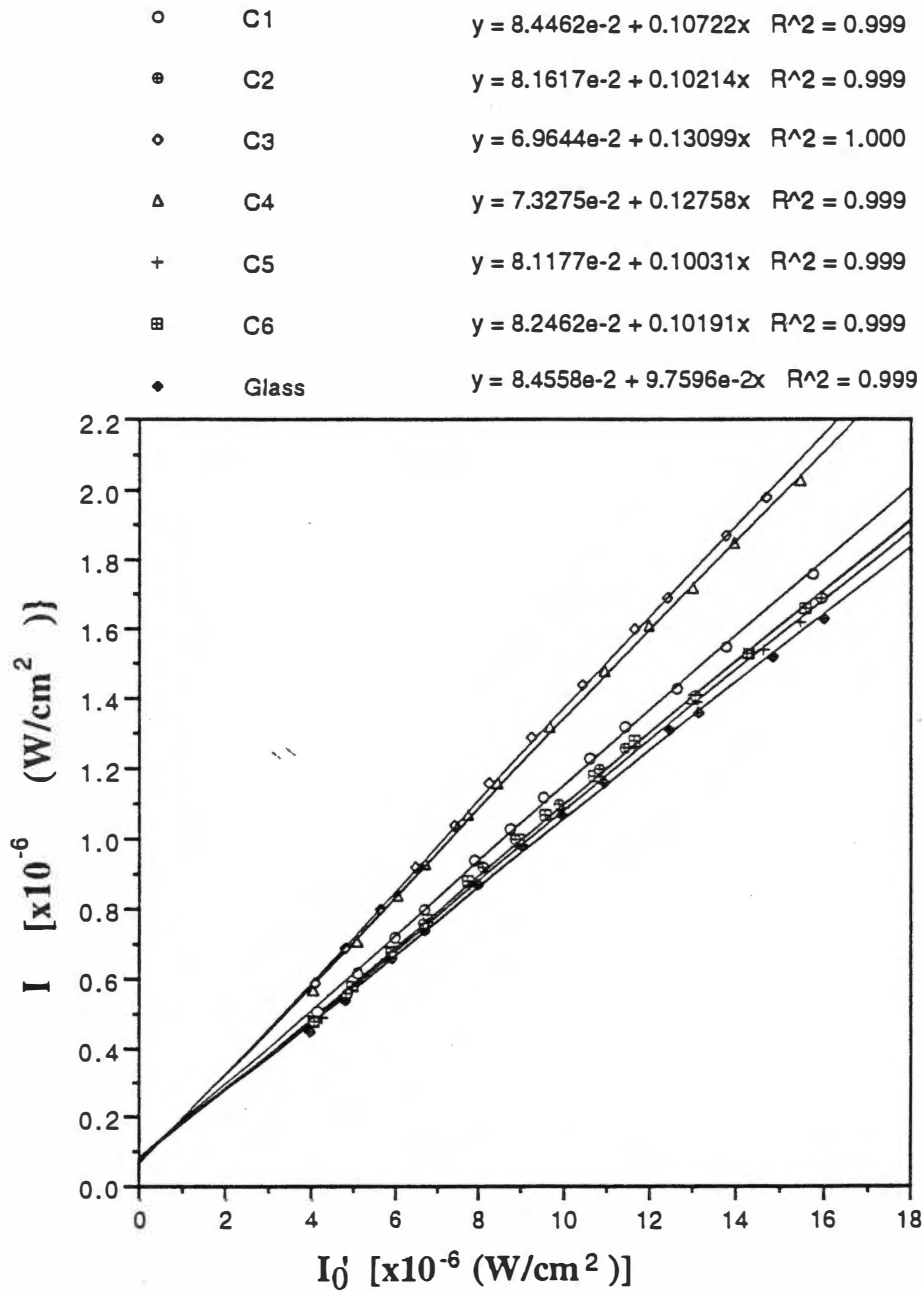


Figure 3.11. Light intensity, I , as a function of the light intensity without analyzer, I_0' , for samples with different crystallinity levels (sample thickness = 0.15 [mm]).

Six film samples (Sample C1 to C6) with different crystallinities were prepared and the thickness was controlled at 0.15 mm. For each sample, the light intensities with and without analyzer were measured under the same conditions, except for temperature, as in nonisothermal experiments. By varying the intensity of the light source, I_0 , a set of data, I and I_0' for each sample was obtained. For each curve in Figure 3.11, I is linearly related to I_0' as expected from equation (3.12). The reason that there is an intercept for each curve is that the photo diode accepts a certain amount of light from the surroundings, and is also related to the zeroing of the system. The existence of the intercept also explains the significance of constant C in equation (3.11). According to eq. (3.11), the different slope in Figure 3.11 is caused by different crystallinity in each sample, as the sample thicknesses and orientation factors are the same for each sample. Since the experimental conditions are the same as in non-isothermal experiments, the average intercept of these curves, $C = 0.078773 \times 10^{-6} \text{ (w/cm}^2\text{)}$ (the intercept for glass was excluded from the average.), in Figure 3.11 can be used in the nonisothermal experiments. This is the way to determine the constant C in equation (3.12). For new materials or a new experimental condition such as new I_0 , change of sample thickness, or change of magnitude of the objective lenses, everything must be repeated to get a new value for C .

The correction for the scattering effect becomes apparent if equation (3.11) is rewritten as:

$$\frac{I-C}{I_0'} = 1 - \bar{d} f^* X_c + R_0 \quad (3.13)$$

Define the left side of the equation as relative light intensity, R , that is,

$$R = \frac{I-C}{I_0'} \quad (3.14)$$

R is now only a function of crystallinity, orientation, and sample thickness. The scattering effect is thus excluded from the relationship between R and l , f^* and X_c . An example of the scattering correction is given in Figure 3.9. The relative intensity in Figure 3.9 is obtained by applying equation (3.14) to the data in the same figure. Figure 3.9 shows that this approach for scattering correction produces the required monotonic change of the relative light intensity with time as crystallinity increases in the sample.

3.5. Results

3.5.1. Temperature

Figure 3.12 gives the cooling curves for runs with different cooling rates. For a given cooling rate the temperature drops fast at first because the temperature difference between the polymer and the cooling medium is large. After the initial drop in temperature, there is a plateau which results from the heat of crystallization liberated during crystallization. After the plateau, the rate of temperature change is low, primarily because of the lower temperature difference between polymer and cooling medium. Finally, the temperature in the polymer approaches that of the cooling medium.

Since it is difficult to use air flow rates to describe the cooling rate for the considered system, a way to quantitatively describe the cooling rate applied needs to be defined. Assuming that k_g and k_a are constant in the cooling process, and, ρ and C_p are nearly constant with change in the temperature before crystallization, one may have an analytical expression for the developed heat transfer equation for the simplified model, equation (3.6):

$$T - T_s = (T_0 - T_s) \exp\{ -CRF t \} \quad (3.15)$$

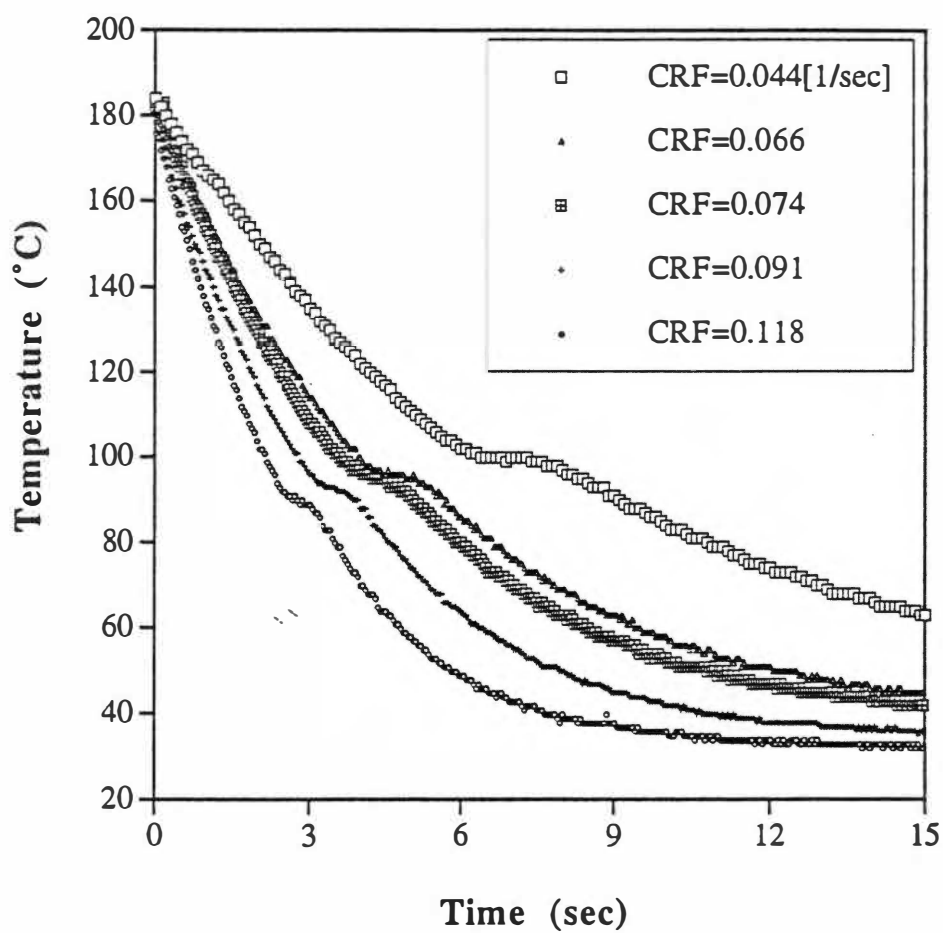


Figure 3.12. Cooling curves for PP at five different cooling rates.

where CRF is defined as $CRF = H_{ga} / V\rho C_p$, which may be called the cooling rate factor. From equation (3.15), one can see that CRF has a unit of (sec^{-1}). The cooling intensity is related to the thickness of air layer, l_a , in which the temperature is higher than T_s . The higher the cooling rate, the thinner the boundary air layer. Other parameters in CRF are independent of the cooling rate. The good fitting of the measured temperature indicates that equation (3.15) was correctly developed so that CRF can be accepted to describe the cooling rate.

CRF can directly be obtained by fitting equation (3.15) to the measured temperature before crystallization. Figure 3.13 gives examples to obtain the values of CRF for the data given in Figure 3.12. Temperatures given in Figure 3.13 can also be approximated by straight lines. That is, an average cooling rate before crystallization can approximately be found so as to get some idea for the magnitude of cooling rates represented by CRF. The obtained average cooling rates were plotted against CRF in Figure 3.14. As shown in Figure 3.14, the highest average cooling rate is about 2200 $^{\circ}\text{C}/\text{min}$.

3.5.2. Light Intensities

The light intensity without analyzer for runs with various cooling rates is shown in Figure 3.15. The figure shows that the I_0' peak becomes deeper as cooling rates increase, indicating that the higher the cooling rate, the higher is the nucleation rate in crystallization and the stronger is the light scattering. The width of the I_0 peak gives the duration of spherulite growth. As cooling rate increases the spherulite growth period becomes shorter. This is a result of two contributions: the higher nucleation rate and faster growth rate as cooling rate increases. Both factors accelerate the rate for spherulites to fill the space in a sample. It is the increased nucleation density that results in strong

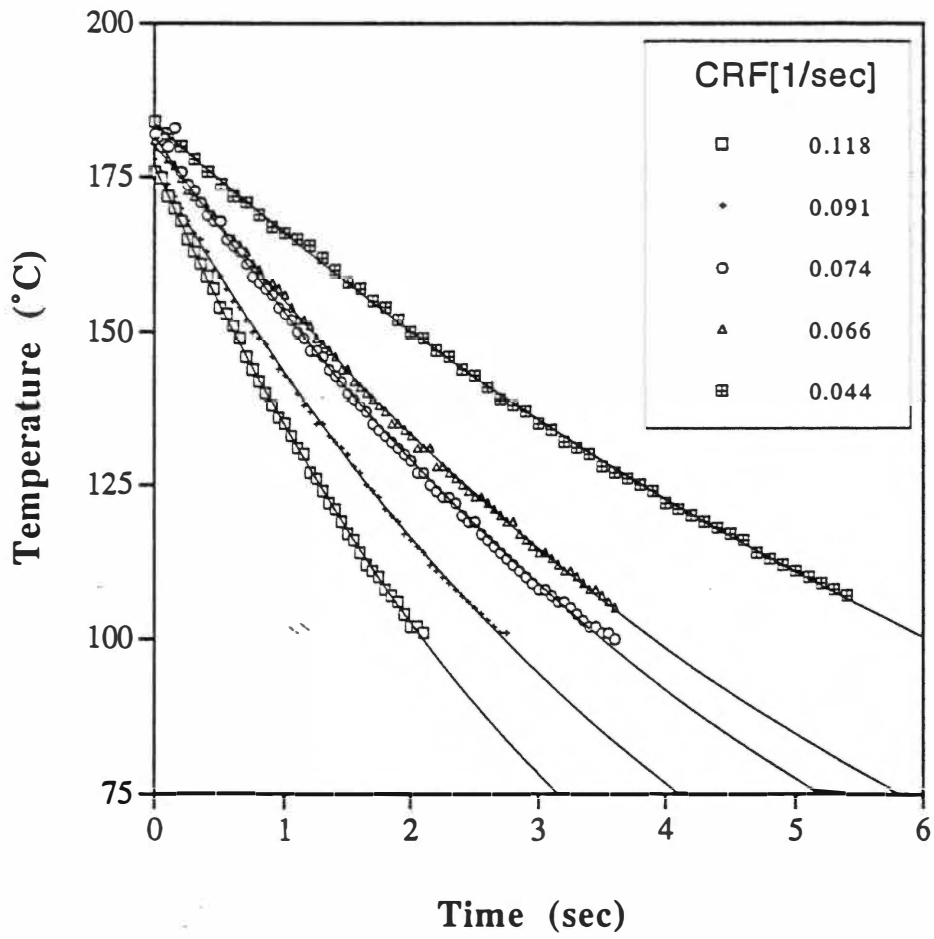


Figure 3.13. Fitting the cooling curve to obtain CRF.

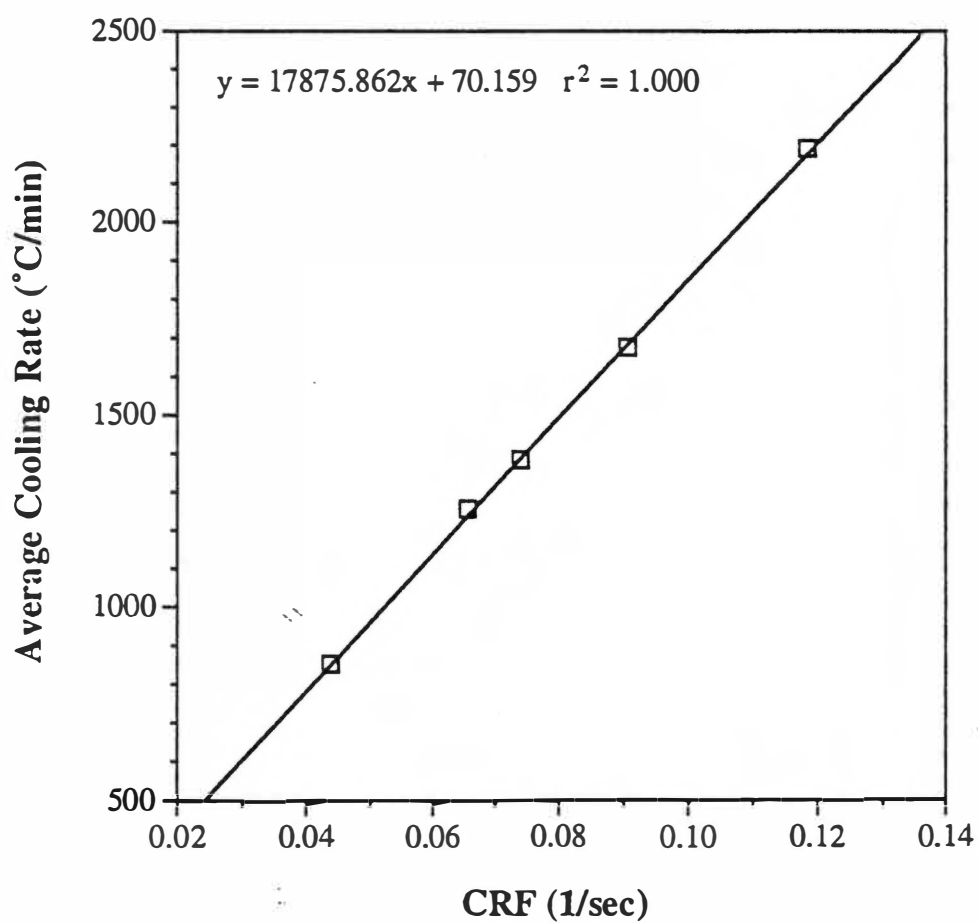


Figure 3.14. Average cooling rate before crystallization versus CRF.

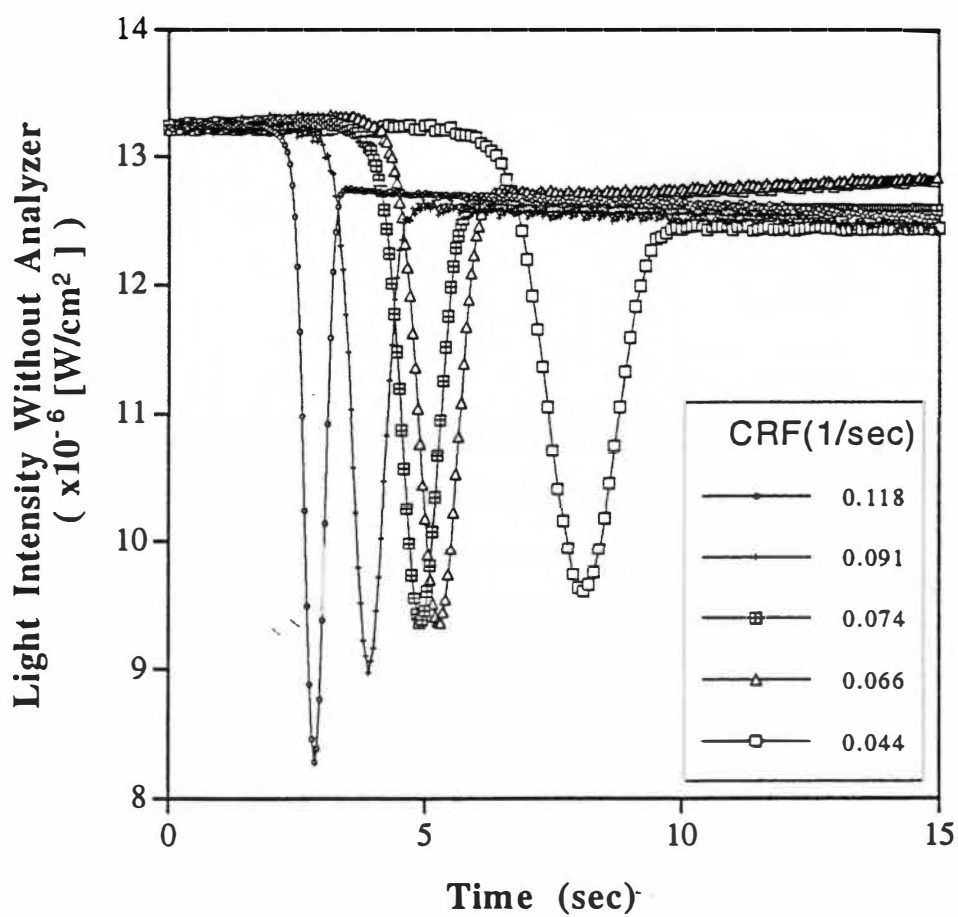


Figure 3.15. Light intensity without analyzer versus time at various cooling rates.

scattering when crystallization occurs under high cooling rates. The slight difference in the final values of I_0' may be attributed to morphological differences, especially crystallinity differences.

Figure 3.16 gives the measured light intensity for the same runs in Figure 3.15. The scattering and depolarizing effects are comprehensively reflected in the light intensity. Figure 3.17 shows the relative light intensity, R , as a function of time. The R was obtained by combining data in Figure 3.15 and 3.16. This is the plot which excludes the scattering effect from the light intensity and gives only the depolarizing effect. According to equation (7.20), the relative light intensity, R , is linearly related to crystallinity. Figure 3.17 shows that before crystallization occurs, there is an induction time after the temperature drops below the equilibrium melting point. The induction time gets shorter as the cooling rate increases. After crystallization begins, the crystallinity develops rapidly and gets close to the final value within a very short time. The period of rapidly increasing crystallinity becomes shorter as the cooling rate increases. After that rapid change, there is a slower process for the crystallinity to reach the final value. The final values of R decrease as cooling rate increases. This indicates that the final crystallinity decreases with increase in cooling rate.

The relative crystallinity plotted against time is given in Figure 3.18. The kinetic analysis will be made on this kind of plot in Chapter 4. The relative light intensity and relative crystallinity plotted against temperature are given in Figure 3.19 and 3.20, respectively. It is clear that the onset temperature for crystallization decreases with increase in cooling rate, and that the primary crystallization temperature range narrows.

3.5.3. Spherulite Diameter Measurement

The spherulite radius measured under two similar cooling rates are plotted against time in Figure 3.21. The figure tells us at once that the spherulite growth rates which are

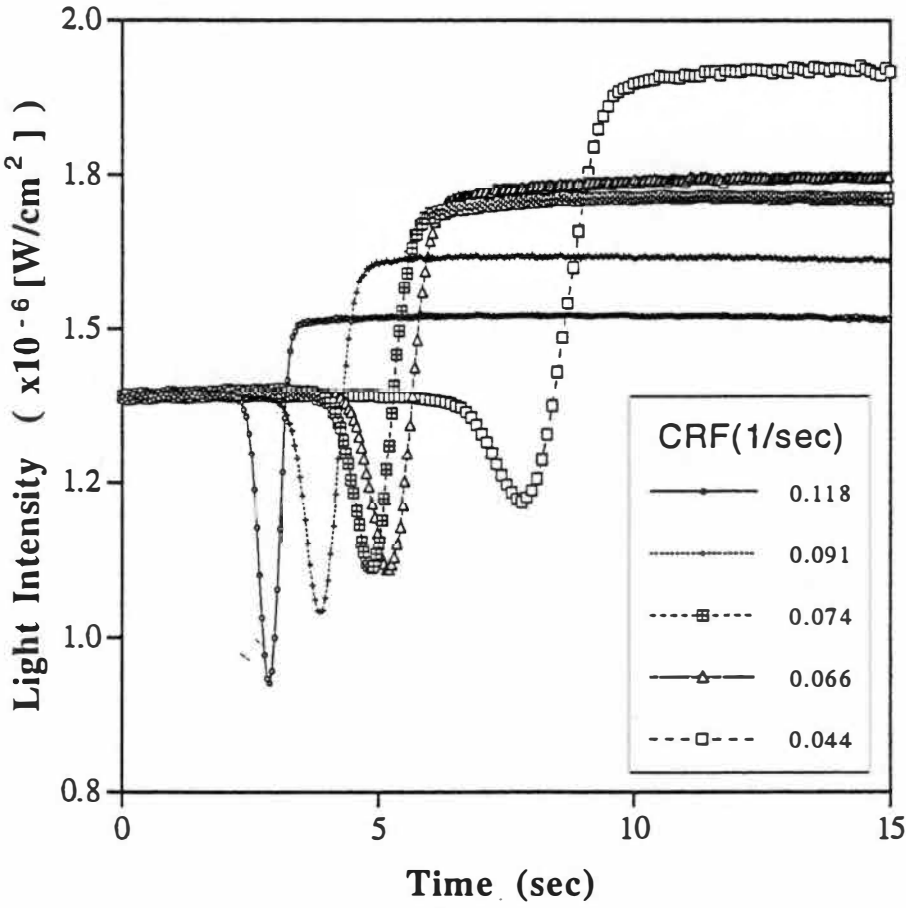


Figure 3.16. Light intensity versus time at various cooling rates.

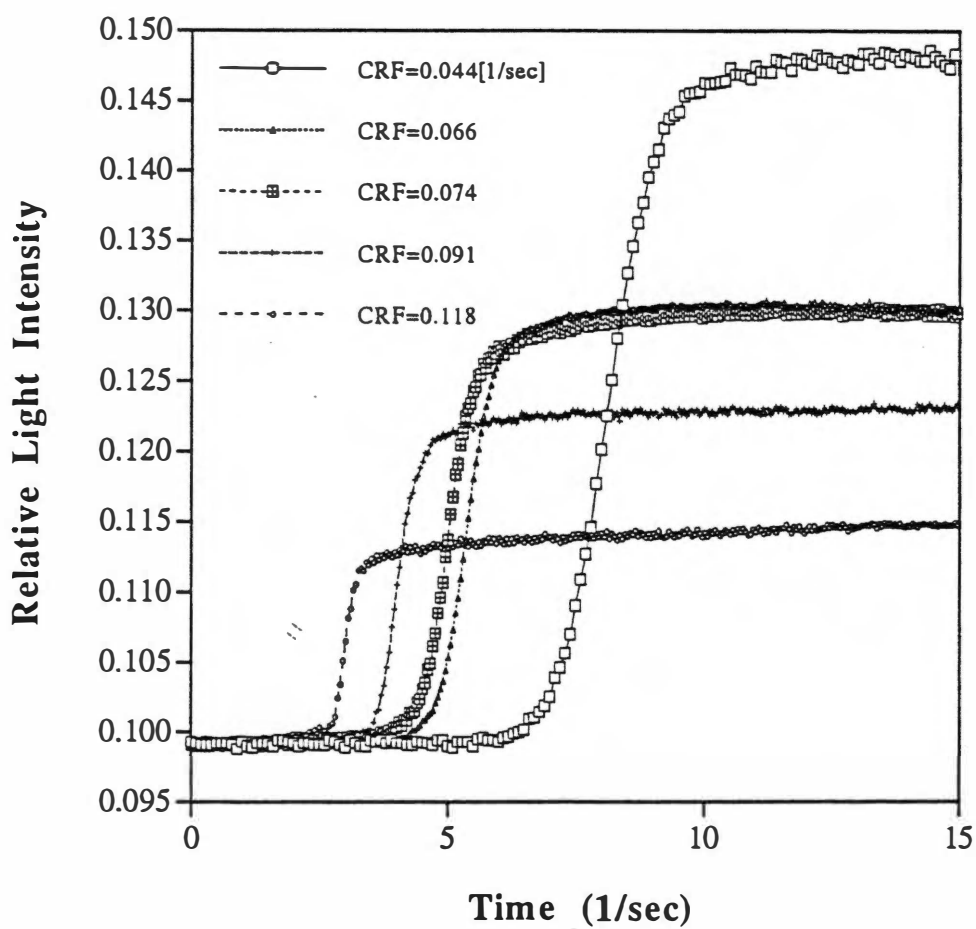


Figure 3.17. Relative light intensity versus time at various cooling rates.

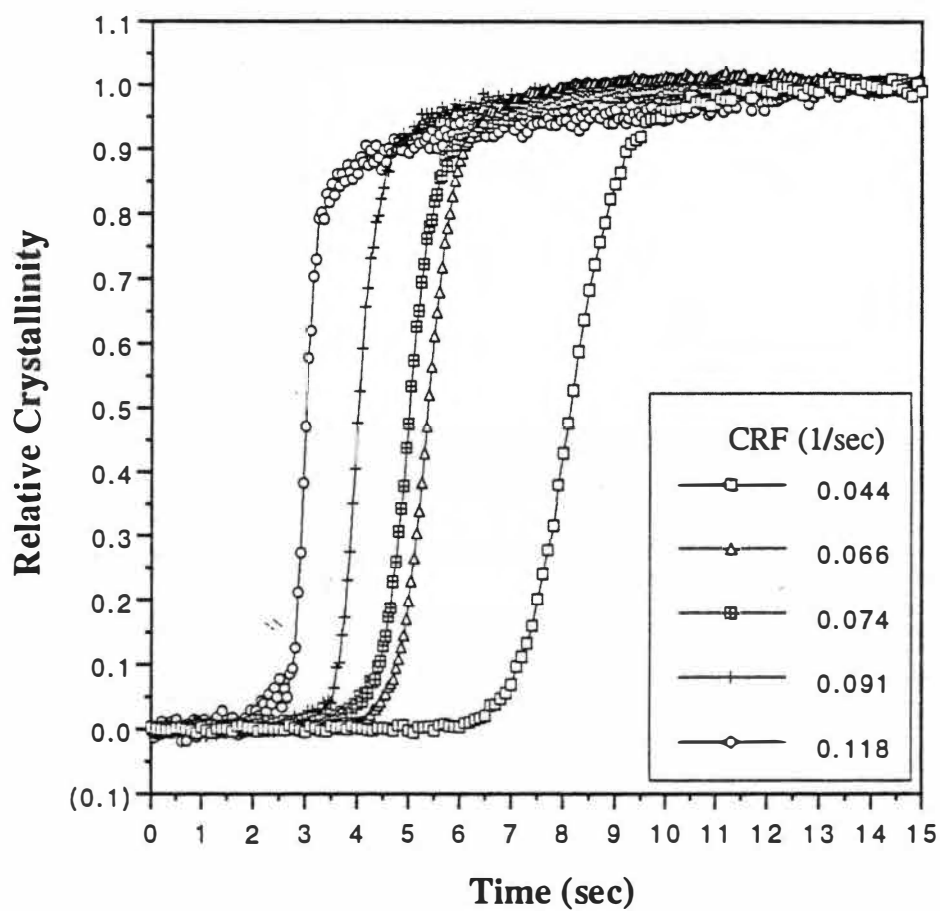


Figure 3.18. Relative crystallinity versus time at five cooling rates.

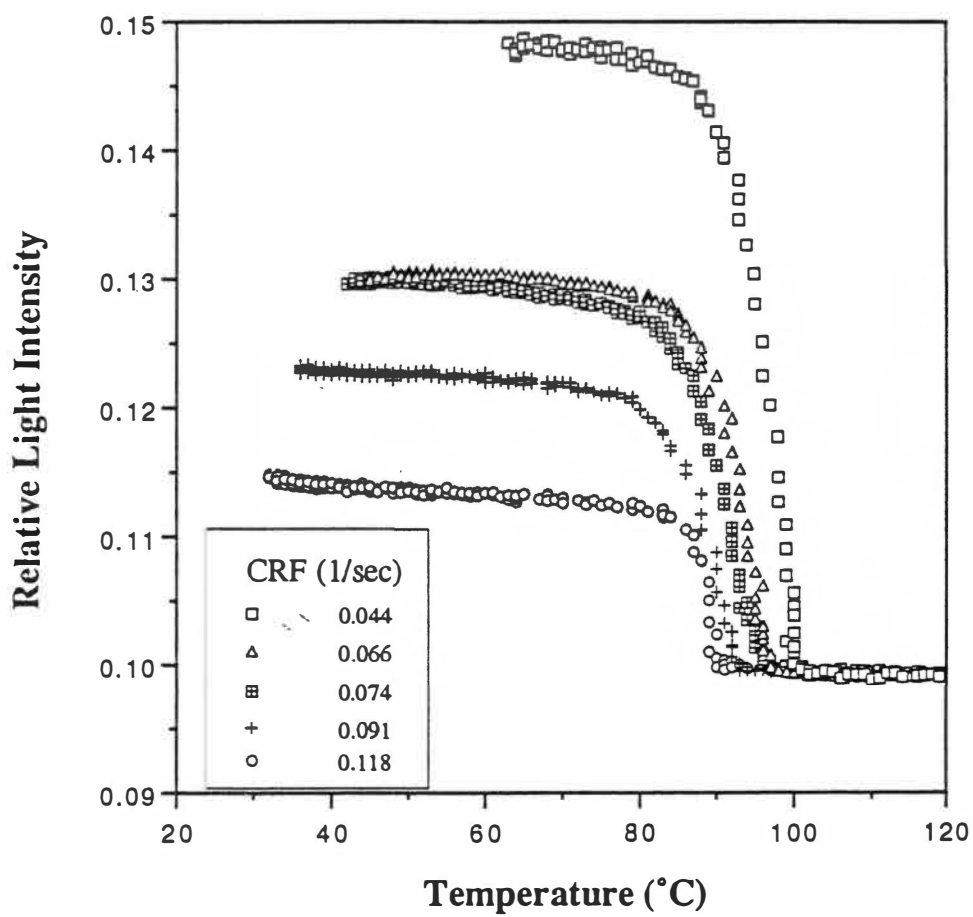


Figure 3.19. Relative light intensity versus temperature at various cooling rates.

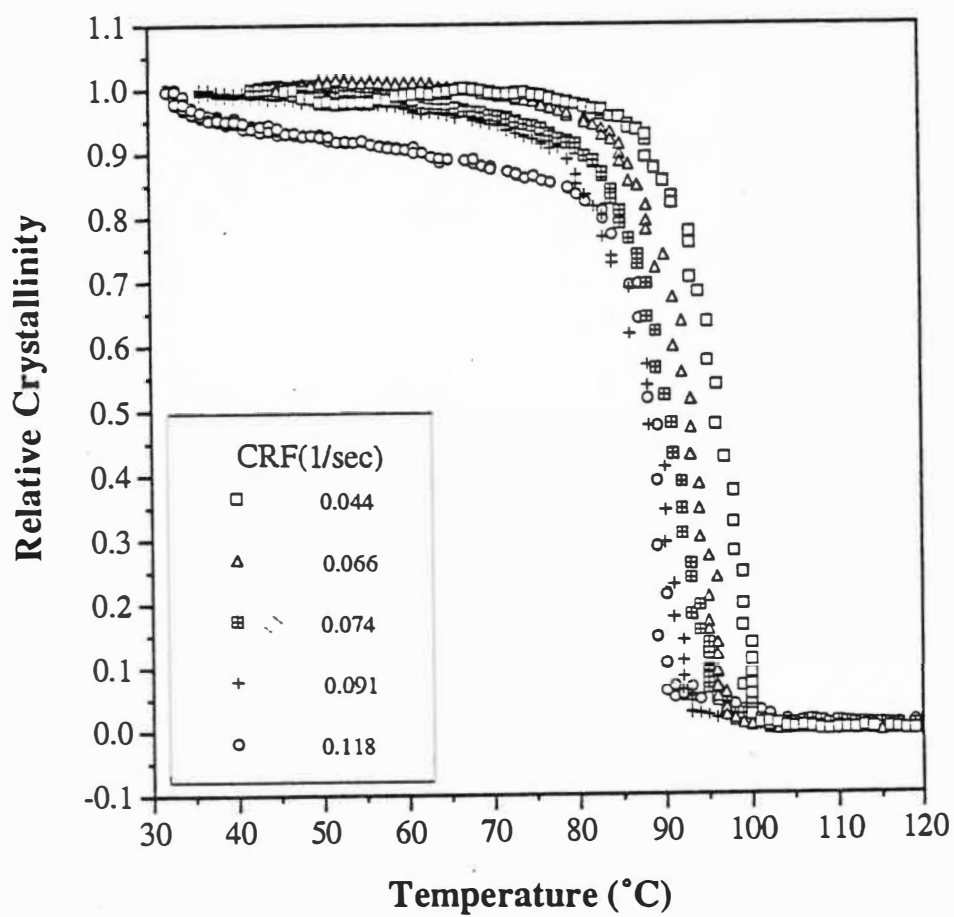


Figure 3.20. Relative crystallinity versus temperature at various cooling rates.

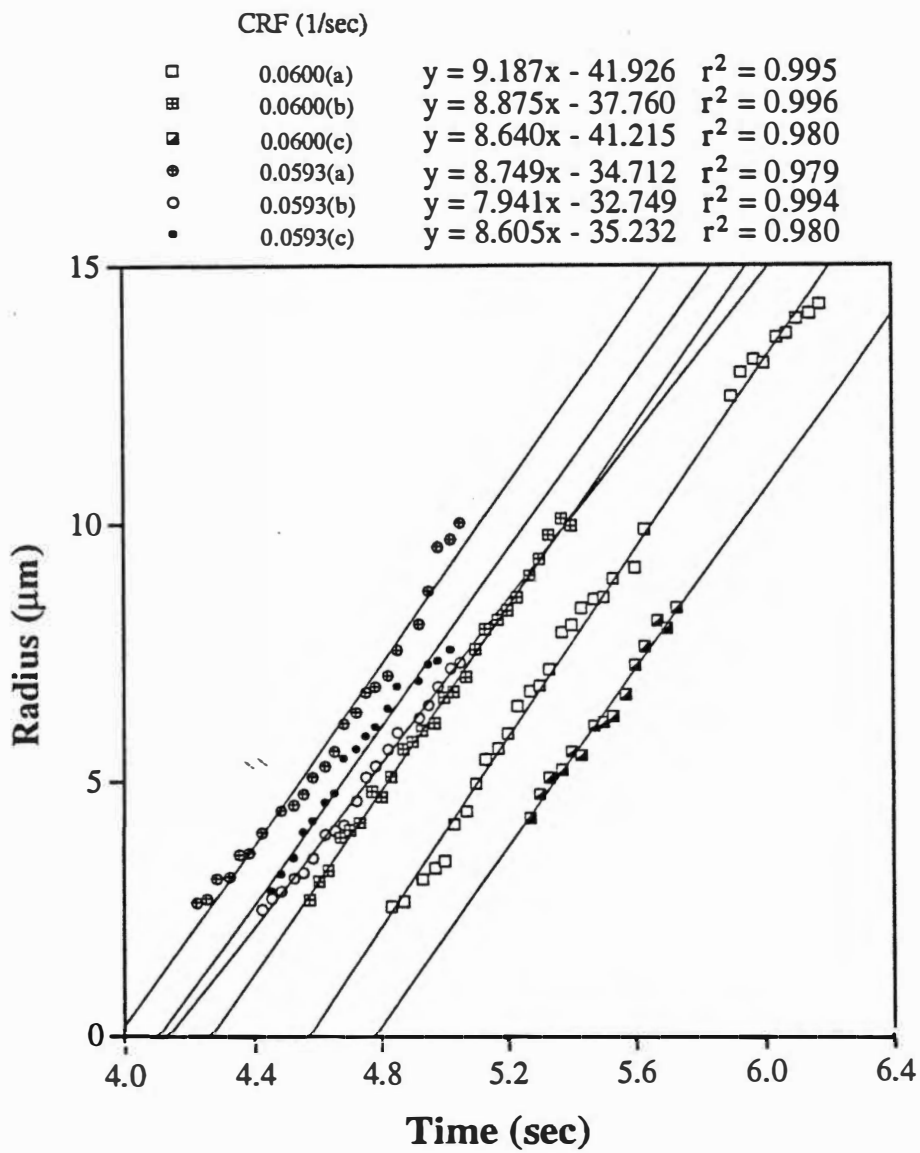


Figure 3.21. Spherulite radius versus time measured at two cooling rates indicated in the figure.

the slopes of the radius versus time plots, are constant during the crystallization, which is highly non-isothermal. Since the measured radii cover almost the whole spherulite growth region, the growth rate is constant through the growing process of spherulites. The data in Figure 3.21 shows that there are different growth rates existing in the same cooling process. One curve in the figure has an apparently different slope from the others, and the other five curves have almost the same slopes. This suggests that there are two growth rates for the six randomly chosen spherulites in the selected crystallization process. The curves with low slopes appear before and after curves with large slopes. This tells us that the different growth rate is not caused by different temperature, since the earlier the spherulite nucleated, the higher the temperature would be expected to be when it is nucleated. Different types of spherulites or lattice structure might be the reason for the different growth rates obtained.

Figure 3.22 shows graphically the relationships between the plateau temperature and the growth of spherulites. From this figure, one can see that the plateau temperatures are closely related to the growth of spherulites. Generally, the appearance of the temperature plateau is later than the nucleation of the first spherulite at the onset of crystallization in the system. The plateau temperatures also end somewhat before the spherulites stop growing. The plateau temperature could not last for the whole region in which spherulites are growing. The constant spherulite growth rate might, therefore, be attributed to a local constant crystallization temperature.

Figure 3.22 also illustrates the relationship between the growth of spherulites and overall crystallization. By extrapolating radius versus time to zero radius the time at which the spherulite was nucleated could be determined. The crystallization onset time can be related to the point where the light intensity starts to deviate from the base line which is the method used to determine the crystallization onset time (I_0) is better than

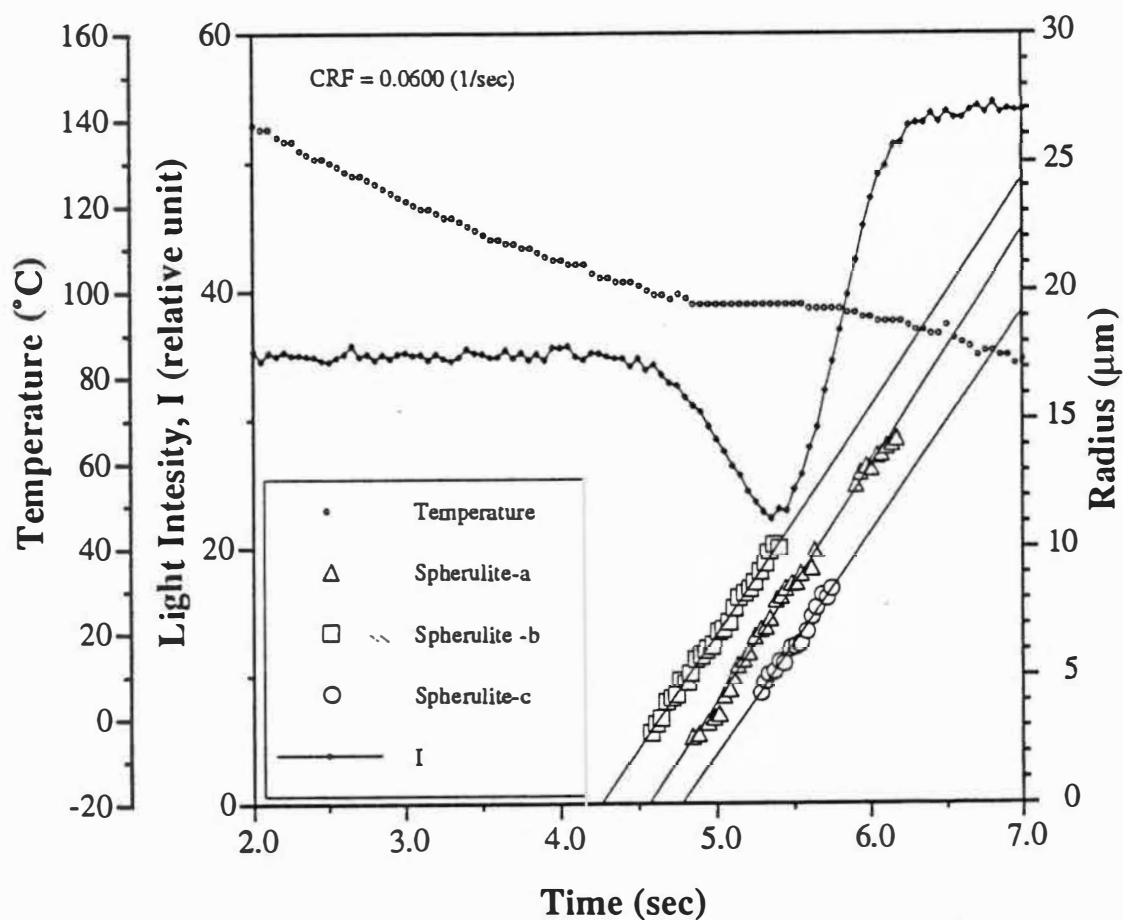


Figure 3.22. Light intensity, temperature and spherulite radius versus time for CRF = 0.600 (1/sec).

I in this use). Since the measured spherulites were chosen among the ones created at onset of crystallization and the ones that complete their impingement at the end of primary crystallization, Figure 3.22 shows that the spherulite growth only lasts a short period. The growth of the spherulite is the reason for the dramatic increase in light intensity which corresponds to the main region for crystallinity to increase. The long and slow period for crystallinity to approach the final value begins after the impingement of spherulites is completed, and can only be attributed to the secondary crystallization.

The relationship of growth rates versus plateau temperatures will be given and discussed in Chapter 4.

3.5.4. Relative Relationships Between I , I_0 , R , T , And Spherulite Growth

The relationship between light intensity with and without analyzer for $CRF = 0.074$ (1/sec) was given in Figure 3.9. The drop of the two intensities begins almost at the same time since both reflect the scattering effect. For light intensity with analyzer, the reduction of intensity in the early stages of crystallization occurs also because there is little depolarizing effect for tiny nuclei. The I reaches its minimum value at about the same time as I_0' because of the light scattering effect.

Figure 3.9 also gives the relationship between relative light intensity and light intensity without analyzer with respect to time. From Figure 3.9 one can see that the light scattering effect occurs in the region in which the relative intensity is rapidly changing. After the scattering peak is ended, the relative intensity increases continuously and slowly. Recalling that the impingement is completed around the end of the scattering peak, the further slow increase of the relative intensity appears to be caused by the secondary crystallization.

Fig. 3.23 gives an example of the relationship between temperature and the relative crystallinity as functions of time. The temperature plateau mainly exists at the

location corresponding to the rapid increase of crystallinity which is between the onset time and point 1 in Figure 3.23. The point 1 represents the beginning of the occurrence of dramatic impingement among spherulites according to the information obtained by the VCR system. The location of the temperature plateau indicates again that the dominant crystallization region is between the crystallization onset and the point 1. After the crystallization begins, the temperature reaches the plateau temperature gradually. This corresponds to the fact that the instantaneous crystallization rate takes time to increase. By combining the information from light intensity and video camera technique, it was found that impingement in the early stage, before point 1 in Figure 3.23, is not severe. The severe impingement started very late and lasted only a very short time (from point 1 to 2). Therefore, the further increasing of the relative crystallinity after the impingement is completed is apparently caused by secondary crystallization.

3.6. Preliminary Conclusions Concerning The Technique And Its Application To Polypropylene Crystallization Studies

A new technique which is based on light depolarizing microscopy has been developed for studying nonisothermal crystallization kinetics under rapid cooling conditions. It is necessary to correct for light scattering in the kinetic studies using LDM technique. The introduced relative light intensity can successfully be used to correct for light scattering effect and to describe the development of crystallinity in the sample. The cooling rate in the developed technique can be quantitatively described by CRF.

There is a plateau in the cooling curve for iPP. The plateau temperature decreases as cooling rate increases.

For iPP, the ultimate crystallinity decreases as cooling rate increases, but the crystallization rate increases with cooling rate.

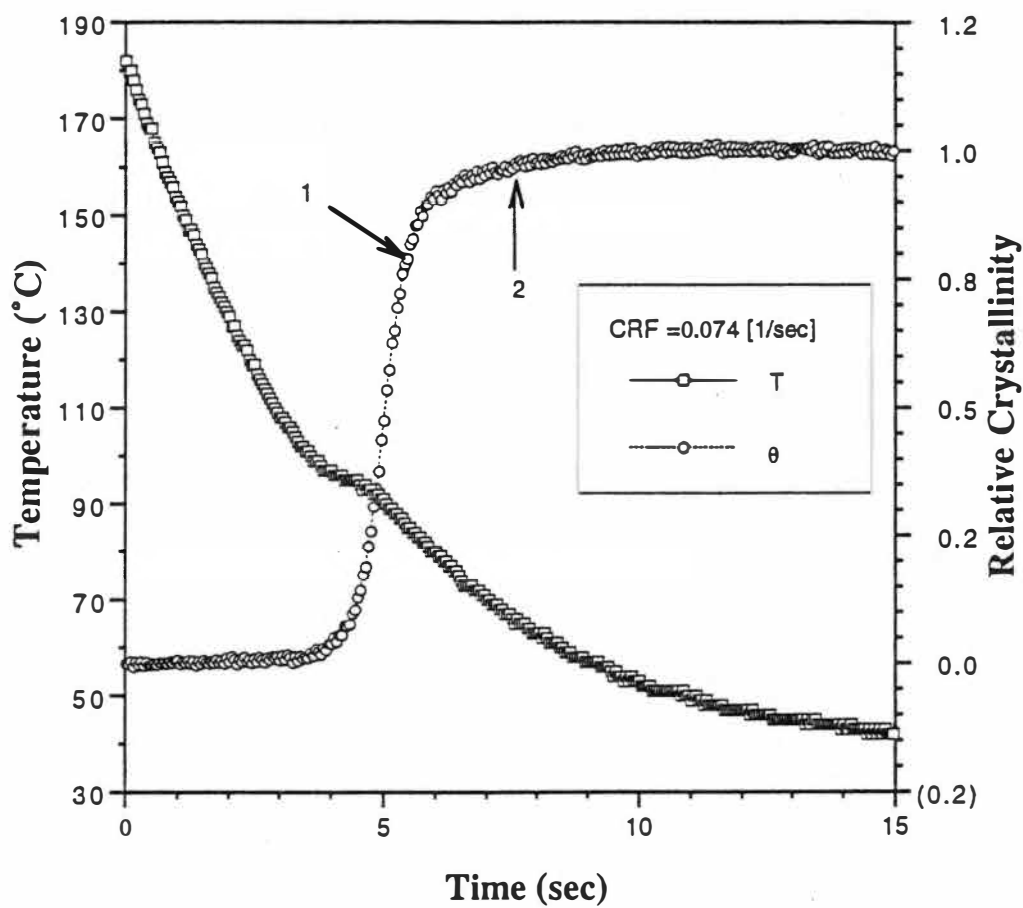


Figure 3.23. Temperature and relative light intensity versus time at $CRF=0.074$ (1/sec).

The spherulite growth rate is constant with time for a given CRF. The growth rate increases with increase of cooling rate and hence with decreasing plateau temperature. This will be described quantitatively in Chapter 4 and 5.

The spherulite growth region is limited to a short time interval which corresponds to the appearance of the plateau in the cooling curve and the region in which the bulk crystallinity dramatically increases.

The reduction in light intensity at an early stage of crystallization indicates that a large number of nuclei are produced during crystallization at high cooling rates.

Chapter 4

INTERPRETATION OF CRYSTALLIZATION KINETICS USING A POWER LAW NUCLEATION FUNCTION

4.1. Introduction

In this chapter, the kinetic analysis will be given of the data collected. In the preliminary kinetic analysis, it was found that the Avrami equation worked well for the interpretation of the data collected. A further understanding of the Avrami equation became necessary. In the process of understanding the crystallization kinetics, a function to describe the nucleation rate was found to be desirable. Such a function is suggested below and is incorporated into the derivation of the Avrami equation. Analysis for the various reported nonisothermal kinetic equations according to the nucleation rate function has also been carried out in this chapter.

Using one of the iPPs studied and described in more detail in Chapter 5, the kinetic analysis, including the calculation of nucleation density according to the suggested nucleation rate function, is demonstrated in this chapter.

4.2. Nucleation Rate Function And Derivation Of The Avrami Equation

The Avrami equation has been used in not only isothermal crystallization but also in nonisothermal and, sometimes, in orientation-induced crystallization. It is, therefore, important to understand every parameter in that equation. A new derivation presented below aims at supplying a deeper understanding of the equation.

In all previous derivations carried out by various researchers, the first step of the derivation is not clear. To clarify this one needs to carefully define what is the basis of the nucleation rate. Three different bases can be used to define the nucleation or nucleation density: volume of whole material, volume of untransformed amorphous material which

does not include the amorphous material in the transformed entity such as spherulites, and volume of all amorphous material which includes the untransformed melt and the amorphous part in the transformed entity. The nucleation density with whole material as its base is physically more understandable and is a quantity used to describe the experimentally measured data. The nucleation rate using untransformed volume as base is more suitable to describe the nucleation behavior because the nucleation occurs only in the untransformed part. The quantity using whole amorphous material as base is apparently related to secondary crystallization and crystal perfection because it deals with amorphous material in the transformed part. All six quantities can be transformed to each other through algebraic manipulation.

We define equation (4.1) as a nucleation rate function that describes the nucleation rate, $\dot{N}$, using the volume of untransformed material as base,

$$\dot{N} = N_c \cdot (1 + m) \cdot t^m \quad (4.1)$$

where N_c is a nucleation rate constant that is a temperature dependent, but time independent and has the unit of $[\#/(sec^{m+1} \cdot cm^3)]$, m is called the nucleation index which is part of the Avrami index as will be discussed below, and t is crystallization time. The nucleation rate function uses time as the independent variable to describe the time dependence of nucleation. The units of $\dot{N}$ are number of nuclei per sec per cm^3 .

Assuming isovolume during crystallization and constant Avrami index, one is able to neatly derive the Avrami equation with transformation being described by volume fraction by using the nucleation rate function, equation (4.1). Such derivation is now presented as follows.

The number of nuclei created during time τ to $\tau + d\tau$ is given by

$$V_m \dot{N} d\tau \quad (4.2)$$

where V_m is the volume of untransformed material. The volume transformed, V_{sp} , which is semi-crystalline, during that period is then equal to

$$dV_{sp} = v(t, \tau) V_m \dot{N} d\tau \quad (4.3)$$

where $v(t, \tau)$ is interpreted as the average volume of a transformed entity (spherulite) per nucleus which was nucleated at time τ and calculated at time t . Prior to impingement this quantity can be calculated using relatively simple and appropriate assumptions. An important point to keep in mind, however, is that $v(t, \tau)$ will actually be affected by impingement, though this effect is usually ignored. By using the relationship of $V = V_{sp} + V_m$ and $\theta = V_{sp} / V$, where θ is volume fraction of the transformed material, equation (4.3) may be changed to

$$d\theta = v(t, \tau) (1 - \theta_v) \dot{N} d\tau \quad (4.4)$$

After moving $(1 - \theta)$ from right to left side, integrating the equation from $t = 0$ to t , and solving for θ , one obtains the exponential form naturally,

$$\theta = 1 - \exp\left\{-\int_0^t v(t, \tau) \dot{N} d\tau\right\} \quad (4.5)$$

If we assume that the crystal grows with constant linear velocity G in n' dimensions (n' is not necessarily a whole number), equation (4.5) may be written as (ignoring impingement),

$$-\ln(1 - \theta) = \int_0^t A_g \left[\int_{\tau}^t G dy \right]^{n'} \dot{N} d\tau \quad (4.6)$$

$$= A_g G^{n'} \int_0^t [t - \tau]^{n'} \dot{N} d\tau \quad (4.7)$$

where A_g is a constant which depends on the geometric shape of the spherulite growth front. Substituting equation (4.1) into equation (4.7), one has,

$$\begin{aligned}
 \ln(1-\theta) &= -A_g \int_0^t (t - \tau)^{n'} G^{n'} N_c (1 + m) \tau^m d\tau \\
 &= -A_g N_c G^{n'} \int_0^t (t - \tau)^{n'} (1+m) \tau^m d\tau
 \end{aligned}$$

Integrating it by parts,

$$\begin{aligned}
 \ln(1-\theta) &= -A_g N_c G^{n'} \int_0^t (t - \tau)^{n'} d\tau^{m+1} \\
 &= -A_g N_c G^{n'} \left\{ \tau^{m+1} (t - \tau)^{n'} \Big|_0^t - \int_0^t (t - \tau)^{n'-1} \tau^{m+1} (-1) n' d\tau \right\} \\
 &= -n' A_g N_c G^{n'} \int_0^t (t - \tau)^{n'-1} \tau^{m+1} d\tau \\
 &= -n' A_g N_c G^{n'} t^{m+1+n'} \int_0^1 x^{m+2-1} (1 - x)^{n'-1} dx
 \end{aligned}$$

where the integration is defined to be the B-function:

$$B(m+2, n') = \int_0^1 x^{m+2-1} (1 - x)^{n'-1} dx \quad (4.8)$$

Finally,

$$\begin{aligned}
 \ln(1-\theta) &= -N_c t^{m+1} [n' A_g G^{n'} t^{n'} B(m+2, n')] \\
 &= -N_c n' A_g G^{n'} B(m+2, n') t^{n'+m+1}
 \end{aligned} \quad (4.9)$$

The Avrami equation, crystallization rate constant and Avrami index are thus given by,

$$\theta = 1 - \exp\{-k t^n\} \quad (4.10)$$

$$k = N_c n' A_g G^{n'} B(m+2, n') \quad (4.11)$$

$$n = n' + m + 1 \quad (4.12)$$

n' is called geometric index because it is related to the shape or growth dimension.

The isokinetic assumption made by Avrami was not used in the derivation. From the derivation procedure, one can see that the Avrami equation includes the description of

part of secondary crystallization which maintains a constant density of spherulites formed, but does not reflect the lamella thickening or other secondary crystallization processes which might cause further increase of density of the spherulites. The influence of spherulite impingement due to overgrowth before the occurrence of severe impingement can be included in the Avrami geometric index, n' . The assumption of a constant Avrami index is only suitable for the crystallization which occurs before the severe impingement stage. It is, in fact, impossible for a single equation (with single pair of n and k) to describe the whole bulk crystallization process. This is because during a certain time period the impingement is so severe that it reduces the crystallization rate very much compared to the stage before severe impingement. During the severe impingement stage, the growth and nucleation of crystals are overwhelmed by the impingement effect so that the kinetic analysis loses its meaning. After impingement, only the secondary crystallization and crystal perfection process remain. It seems that a complete kinetic equation must at least account for three effects: nucleation and growth, secondary crystallization, and impingement. For the purpose of practical kinetic analysis, data from the early stage of crystallization supplies information of temperature or cooling rate dependence for growth rate and nucleation rate. It is difficult to get this information from the impingement stage. For theoretical prediction of crystallinity, one may use the equation fixed by the data obtained from the early crystallization stage to approximate the value of crystallinity at the late stage of crystallization.

The B-function in equation (4.10) to (4.12), has a definite value for a given crystallization process and can generally be solved through numerical integration. For three dimensional growth with impingement considered, the geometric constant A_g is approximated as for a sphere, $A_g \approx 4\pi/3$. This value for A_g is adopted throughout for further discussion in this research.

The impingement of spherulites causes a reduction in the Avrami index. In the present studies, such reduction in the Avrami index was included in the geometric index, or the geometric index describes the actual shapes of crystalline entities. The geometric index or the reduction in the geometric index caused by impingement was assumed to be constant. How much reduction in the geometric index could be caused by impingement? The problem may be tackled using computer simulation. For lack of such information, a value of 2 for three dimensional growth will be assumed to get nucleation index from Avrami index, n , which can be obtained by Avrami analysis of the experimental data.

Now consider a few special cases. For crystallization with time independent nucleation, $m=-1$, $B(-1+2, n') = B(1, n')$. $B(1, n')$ can be calculated as

$$B(1, n') = \int_0^1 (1-x)^{n'-1} dx = - \int_0^1 (1-x)^{n'-1} d(1-x) = - \frac{1}{n'} (1-x)^{n'} \Big|_0^1 = \frac{1}{n'}$$

Therefore,

$$\ln(1-\theta) = -N_c A_g G^{n'} t^{n'} \quad (4.13)$$

For crystallization with constant nucleation rate, $m = 0$, it can be calculated that $B(2, n') = \frac{1}{(n'+1)n'}$. Therefore,

$$\ln(1-\theta) = -N_c A_g G^{n'} \frac{1}{(n'+1)} t^{n'+1} \quad (4.14)$$

Assuming the impingement effect is neglected, that is $n'=3$ for three dimensional growth, $n'=2$, for two dimensional growth, and $n'=1$ for one dimensional growth, Equation (4.13) and (4.14) reduce to kinetic equations traditionally obtained. From this we can see that equations (4.10) to (4.12) not only includes all the cases described by equation (4.13) and (4.14), but also includes the case for fractional Avrami index and any kind of nucleation behavior. It is therefore a general kinetic equation for bulk crystallization.

By using the weight of the material to describe the transformation process, the isovolume assumption can be eliminated in the derivation. The procedure is similar to the above derivation from equation (4.4) through (4.12). $\theta_w = W_{sp}/W$ will be used as weight fraction of the transformation instead, where W_{sp} is the weight of the transformed material. The nuclei produced during time τ to $\tau + d\tau$ is now equal to $W_m \dot{N} d\tau$. Therefore,

$$\begin{aligned} dW_{sp} &= \dot{N} \cdot (W_m/\rho_a) \cdot d\tau \cdot w(t, \tau) \\ d\theta_w &= (1/\rho_a) \dot{N} (1 - \theta_w) \cdot d\tau \cdot w(t, \tau) \\ \frac{1}{1 - \theta_w} d\theta_w &= (1/\rho_a) \dot{N} \cdot d\tau \cdot v(t, \tau) \rho_s \end{aligned}$$

finally,

$$\theta_w = 1 - \exp\{-k_w t^n\} \quad (4.15)$$

$$k_w = \frac{\rho_s}{\rho_a} N_c n' A_g G^{n'} B(m+2, n') \quad (4.16)$$

$$n = n' + m + 1 \quad (4.17)$$

Because of the existence of equation (4.15), the isovolume assumption is automatically eliminated.

4.3. Significance Of The Nucleation Rate Function

The power law nucleation rate function simulates the nucleation rate from $t = 0$ to the end of crystallization, or describes the distribution of the nucleation rate with respect to time. The function is mathematically time dependent all the time, or treats all kinds of nucleation as being time dependent. The power law nucleation function describes the manner of nucleation by using the proper combination of m and N_c . The m determines the shape and magnitude of the function, and N_c is related to the magnitude of the function along the time axis. In the special case of time independent predetermined nuclei, the nucleation rate function is infinite at $t = 0$ and zero elsewhere.

The function simulates the manner of the nucleation by a distribution. From the nucleation rate function point of view, the time dependent and time independent nucleation are divided according to the nucleation index. The time independent nucleation only exists when m is less than 0. When $m = -1$, only time independent nucleation exists. When $-1 < m < 0$, both time independent and time dependent nucleation occur in the crystallization. When $0 \leq m < \infty$, only time dependent nucleation exists. For $-1 < m < 0$, the function describes nucleation for the case that has an infinite nucleation rate at $t=0$ while time dependent nucleation drops gradually to a certain value as time elapses. For $0 < m < 1$, the function describes that the time dependent nucleation increases as time elapses. When $m > 1$, time dependent nucleation rate increases with time at a faster and faster rate the higher is the value of m .

From the experimental point of view, time independent nucleation refers to a process in which nuclei are produced over a short time interval $t = 0 \sim 0+\delta t$. Compared to the total crystallization time, δt is very small and the nuclei produced during δt can be approximately looked at as forming at $t = 0$. Any nucleus produced outside δt is time dependent nucleation. Now, when m is close to -1, there exists only time independent nucleation from the experimental point of view. When m is not close to -1 but still negative, both time independent and time dependent nucleation occur. When $m > 1$, many nuclei are produced during δt ; both time independent and time dependent nucleation exist. When $0 \leq m \leq 1$ basically only time dependent nucleation exists.

By the introduction of the power law nucleation function, one attributes all deviations of the usual Avrami index for a specific geometric shape to the variation of the nucleation rate. It includes the impingement effect in the geometric index. It admits the growth rate is constant. The derivation of equation (4.10) tells us that to obtain the form of $-\ln(1-\theta) = k t^n$, one does not necessarily assume $\dot{N} = \text{constant}$. It is also possible to reach this equation by assuming that nucleation rate is a power law function of time. This may

explain why the simple Avrami equation works in non-isothermal crystallization. If one “assumes” the nucleation rate is constant in both isothermal and non-isothermal crystallization, and we use the kinetic equation in the form of $-\ln(1-\theta) = kt^n$, we may unconsciously deal with some kind of non-constant nucleation rate, especially when the “n” value can not be explained by the geometry of the crystal. In this case the nucleation rate varies and only the N_C in the power law function may remain constant. It is now clear that the Avrami equation can always be integrated if the nucleation rate is described by a power law function. Therefore, equation (4.10) is very general if one understands the index of the time is composed of n' for crystal growth and m for nucleation.

4.4. Relationships Between Various Nonisothermal Kinetic Equations

To illustrate relationships between various nonisothermal crystallization kinetics equation, the traditional Avrami equation will be derived first according to the method described above. For convenience, the volume based relative crystalline fraction will be used.

Start from equation (4.5) that is,

$$\theta = 1 - \exp\left\{-\int_0^t v(t, \tau) \dot{N} d\tau\right\} \quad \text{or,} \quad -\ln(1-\theta) = \int_0^t v(t, \tau) \dot{N} d\tau \quad (4.5)$$

and assuming that the crystal grows with constant linear velocity G in $(n-1)$ dimensions (n is not necessarily a whole number), equation (4.5) may be written as,

$$-\ln(1-\theta) = \int_0^t A_g \left[\int_{\tau}^t G dy \right]^{n-1} \dot{N} d\tau \quad (4.18)$$

$$= A_g G^{n-1} \int_0^t [t - \tau]^{n-1} \dot{N} d\tau \quad (4.19)$$

Assuming $\dot{N}$ is constant which is generally considered in isothermal crystallization (and which is the natural result from the definition of the nucleation rate), equation (4.19) can be integrated to give the Avrami equation:

$$\theta = 1 - \exp\{-k t^n\} \quad (4.20)$$

where k is the crystallization rate constant, which is

$$k = \frac{A_g G^{n-1} \dot{N}}{n} \quad (4.21)$$

The isokinetic assumption made by Avrami is implied in the derivation since both growth rate G and nucleation rate $\dot{N}$ are assumed constant in the derivation.

The relationships among various nonisothermal equations can now be derived as follows. Starting from equation (4.18), we may write

$$\theta = 1 - \exp\left\{-A_g \int_0^t \left[\int_{\tau}^t (G/\dot{N}(y)) \dot{N}(y) dy\right]^{n-1} \dot{N}(\tau) d\tau\right\}$$

Introducing the isokinetic assumption of Avrami, $G/\dot{N}$ is constant with time and the equation changes to

$$\theta = 1 - \exp\left\{A_g (G/\dot{N})^{n-1} \int_0^t \left\{\int_{\tau}^t d\left[\int_0^y \dot{N}(x) dx\right]\right\}^{n-1} \dot{N}(\tau) d\tau\right\}$$

After several integration steps,

$$\theta = 1 - \exp\left\{\frac{A_g (G/\dot{N})^{n-1}}{n} \left[\int_0^t \dot{N}(x) dx\right]^n\right\} \quad (4.22)$$

$$= 1 - \exp \left\{ \left[\int_0^t \left(\frac{AG^{n-1} \dot{N}}{n} \right)^{1/n} dx \right]^n \right\}$$

Substituting equation (4.21) and using $K = k^{1/n}$, one reaches the Nakamura equation, equation (2.12). From the derivation, one learns that by the isokinetic assumption, $\dot{N}$ must also be a constant, because G is constant. Therefore, K in the Nakamura equation is also a constant. By these conditions, the Nakamura equation, changes to the Avrami equation, equation (4.20), at once.

The Avrami equation, equation (4.20), may have two possible differential forms:

$$\frac{d}{dt} [-\ln(1-\theta)] = \frac{d}{dt} [k t^n] \quad \Rightarrow \quad \frac{d\theta}{dt} = n k t^{n-1}(1-\theta) \quad (4.23)$$

$$\frac{d}{dt} [-\ln(1-\theta)]^{1/n} = \frac{d}{dt} [k^{1/n} t] \quad \Rightarrow \quad \frac{d\theta}{dt} = n K(T)(1-\theta) \left[\ln \left(\frac{1}{1-\theta} \right) \right]^{(n-1)/n} \quad (4.24)$$

The differential equation (4.24) is the so-called differential Nakamura equation, equation (2.15). This tells us that Nakamura equation is another form of the Avrami equation. If one integrates equation (4.23), there are two possible results,

$$\int_0^{\theta(t)} d\theta = \int_0^t n k t^{n-1}(1-\theta) dt \quad \Rightarrow \quad \theta = \int_0^t n k t^{n-1}(1-\theta) dt \quad (4.25)$$

$$\int_0^{\theta(t)} \frac{1}{(1-\theta)} d\theta = \int_0^t n k t^{n-1} dt \quad \Rightarrow \quad \theta = 1 - \exp \left\{ - \int_0^t n k t^{n-1} dt \right\} \quad (4.26)$$

Comparing Dietz equation, equation (2.18), with equation (4.25), one can see at once that Dietz equation is another form of Avrami equation except that a correction factor for secondary crystallization has been added into it. Consequently, k in Dietz equation must be a constant also. Equation (4.26) is exactly the Kamal equation, equation (2.19), which is now obtained from Avrami equation. Similarly, k needs to be constant in the Kamal

equation according to the Avrami equation. It is very clear now that most of the available nonisothermal kinetic equations, except the Ozawa equation, are essentially equivalent to the Avrami equation but in different form. The reason that people prefer the integral form is that they can allow k (or K) to become a variable after the integral symbol because k (or K) must be a variable under nonisothermal condition. In doing this, they ignore the fact that k (or K) is required to be constant by the derivation. Why do these models more or less work in kinetic analysis with mistakes present in them? The answer is related to the nucleation rate. The application of the power law nucleation rate function explains that the Avrami equation, equation (4.10), still works in nonisothermal crystallization under very high cooling rates. According to the nucleation rate function, the resultant kinetic equation (4.10) still keeps its original form, but index n is split into two parts: n' and m . Equation (4.10) can then be changed to

$$\theta = 1 - \exp\{-k t^{n'+m+1}\} = 1 - \exp\{-k t^{m+1} t^{n'}\} = 1 - \exp\{-k' t^{n'}\} \quad (4.27)$$

where k is constant, n' is related to the shape of crystal, and m is related to the nucleation rate. $k' = k t^{m+1}$ is crystallization rate constant which is now time dependent. Going back to the original question and using the Kamal model as an example one can see the problem. Before the Kamal model can be used to analyze the nonisothermal crystallization data, index n must be chosen, such as for spherulitic growth and time dependent nucleation, $n = 4$. The problem is that in actual crystallization the index is most probably different from the chosen value ($n = 4$). Such difference is exactly described by the power law nucleation rate function approach. By choosing $n = 4$, people unconsciously include time dependent factors into the k and made it to be k' which is just like the conversion made in equation (4.27). The Nakamura and Dietz equations have the same problem in that one needs to choose an n as does the Kamal equation, so that similar change of rate constant also existed in their approaches. In a word, the selection of a value of the Avrami index might help to correct

the mistake by including the time dependence of nucleation rate in the crystallization rate constant. Therefore, these approaches still work in an empirical sense. The problem of unsatisfactorily functioning of the models comes from the selection of the value of n and lack of understanding of the crystallization process. With proper choice of n value, Nakamura, Kamal, and Dietz equations must work well in the early crystallization stage in which both secondary crystallization and spherulite impingement can be neglected. It is also clear that instead of including a time dependent factor into the rate constant as was done in the Nakamura, Kamal, and Dietz equation, the Avrami equation is preferred to be used directly because one is able to obtain the index from the nonisothermal experimental data and avoid arbitrarily selecting a value for it.

The Ozawa equation may be derived by substituting cooling rate $\alpha = dT/dt$ into equation (4.6),

$$\begin{aligned}
 \theta &= 1 - \exp \left\{ A_g \int_0^t \dot{N} \left(\int_{T(\tau)}^{T(t)} G(T) \frac{1}{\alpha} dT \right)^{n-1} d\tau \right\} \\
 &= 1 - \exp \left\{ A_g \int_{T(0)}^{T(t)} \dot{N} \left(\int_{T(\tau)}^{T(t)} G(T) \frac{1}{\alpha} dT \right)^{n-1} \frac{1}{\alpha} dT \right\} \\
 &= 1 - \exp \left\{ \frac{A_g \int_{T(0)}^{T(t)} \dot{N} \left[\int_{T(\tau)}^{T(t)} G(T) dT(y) \right]^{n-1} dT(\tau)}{\alpha^n} \right\} \quad (4.28)
 \end{aligned}$$

Let,

$$K' = A \int_{T(0)}^{T(t)} \dot{N} \left[\int_{T(\tau)}^{T(t)} G(T) dT(y) \right]^{n-1} dT(\tau) \quad (4.29)$$

Substituting equation (4.29) into equation (4.28), the Ozawa equation is obtained. From equation (4.29), one can see that to get a constant intercept, $\ln(K')$ by equation (2.17),

nucleation rate or rate constant k must only depend on temperature, not the cooling rates, and Avrami index must necessarily be constant for different experiments with different cooling rates. Both points are approximately true only under low cooling rate experiments and if the cooling rate does not change too much in a given range. Under high cooling rates the nucleation rates and crystallization rate constant will depend highly on the cooling rate. At a given temperature, if cooling rates are different for different experiments, the nucleation rate or rate constant will no longer be the same. And also the Avrami index will change because of the change of the nucleation rate according to the power law nucleation rate function. Thus, Ozawa's approach may be used only under low cooling rates and with narrow variation in cooling rates.

4.5. Kinetic Analysis

4.5.1. Introduction

The experimental data obtained was analyzed by using the Avrami equation. The application of the Avrami equation to nonisothermal crystallization is based on the assumption that the temperature during crystallization does not change too much during crystallization because of the heat released from crystallization, and the temperature during crystallization can be represented by a crystallization plateau temperature. The crystallization plateau temperature determines crystallization half time, crystallization rate constant and, therefore, Avrami index which are the kinetic parameters used in the Avrami equation. Because from the Avrami index and crystallization rate constant, the nucleation rate can be calculated, the plateau temperature also determines the nucleation rate for a crystallization with given cooling rate. Because the Avrami equation can well fit the experimental relative crystallinity versus time curves, and the experimental growth rate is constant with the time, the argument that the usage of the single value for each kinetic

parameter, which is determined by the plateau temperature, to the whole crystallization region, in which the temperature varies, but not much, is acceptable.

The applied Avrami equation was derived using a power law nucleation rate function in section 4.2. The resultant equations are summarized as follows:

$$\text{Crystallization:} \quad \theta = 1 - \exp\{-kt^n\} \quad (4.30)$$

$$n = n' + m + 1 \quad (4.31)$$

$$k = N_c n' \frac{4\pi}{3} G^{n'} B(m+2, n') \quad (4.32)$$

$$B(m+2, n') = \int_0^1 x^{m+2-1} (1-x)^{n'-1} dx \quad (4.33)$$

$$\text{Nucleation Rate:} \quad \dot{N} = N_c (m+1) t^m \quad (4.34)$$

where the n in equation (4.30) is the usual Avrami index. According to the above derivation, it may be split into geometric index n' and nucleation index m , equation (4.32). In equation (4.32) G is growth rate and $B(m+2, n')$ is called B-function which is defined by equation (4.33). The nucleation rate function is defined by equation (4.34), in which N_c is called the nucleation rate constant.

4.5.2. Material And Experimental

In the present discussion, the technique of analysis will be discussed in detail for one of the resins studied, namely Resin #3. This resin has a Melt Flow Rate (MFR) of 18, a polydispersity of 4.8 and a weight average molecular weight of 210,850. The results for the other five resins are presented in Chapter 5.

The equipment and technique used for nonisothermal crystallization was described in Chapter 3. The sample thickness used is 150 μm . The cooling condition applied in this chapter will be described by one of three measures: crystallization plateau temperature,

CRF or heat transfer coefficient of the air, h_a . The relationship between crystallization plateau temperature and heat transfer coefficient will be given later. The reason to introduce heat transfer coefficient is that h_a is independent of the thickness and other properties of the cover glass which is used to support the polymer, while CRF is related to the properties of the cover glass. The introduction of h_a makes the results comparable to data obtained under other circumstances, such as the data collected from the spinline. The relationship between h_a and CRF can be obtained by fitting an equation similar to equation (3.8) to the curves of temperature and time obtained from our experiments. Such an example will be given in Chapter 6. The h_a in ($\text{cal}/\text{cm}^2 \cdot \text{sec} \cdot \text{K}$) is related to CRF in ($1/\text{sec}$) for experimental conditions specified by Chapter 3 according to equation (4.35),

$$h_a = 3.7113 \cdot 10^{-2} \cdot \text{CRF} + 2.8853 \cdot 10^{-4} \quad (4.35)$$

In the growth rate studies, the same system has been used as for bulk crystallization rate studies for the measurement of growth rate in the nonisothermal crystallization process. Isothermal experiments were also carried out to extend the range of the growth rate measurement to higher temperature. The reason for using the isothermal procedure in the high temperature range of crystallization is that such a thermal history during crystallization is similar to the one encountered in the procedure of nonisothermal crystallization adopted in this research. In the nonisothermal crystallization under rapid cooling, the crystallization temperature during spherulite growth is basically maintained constant. Such a procedure can be obtained for crystallization at temperature higher than about 116°C by isothermal crystallization. The reason that the isothermal crystallization was adopted to extend the crystallization to a higher temperature is to obtain the constant growth rate under high temperature. The growth rate found in the nonisothermal crystallization at low temperature is constant. We have use similar procedure to make the data comparable. If the nonisothermal crystallization procedure is used to measured the growth rate at high

temperature, the growth rate might change during crystallization, because when crystallization temperature is greater than 116 °C, the crystallization temperature in a nonisothermal crystallization can be varied by a nonisothermal procedure because of the low release rate of crystallization heat.

The highest crystallization temperature, represented by plateau temperature in nonisothermal crystallization, that can conveniently be reached in the nonisothermal crystallization for the applied equipment is about 116 °C. The low limit of the crystallization temperature for nonisothermal crystallization is determined by the readability of the image recorded by the VCR. For extremely high cooling rate, the numerous nuclei produced in the crystallization make it difficult to follow the growth rates and prevent one from reaching a lower crystallization temperature for a given material. The lowest crystallization temperature in the isothermal crystallization is about 118°C. This limit can be improved by using a cooling procedure in which the cooling rate is high before crystallization and maintained constant after crystallization begins. The upper temperature applied in the present isothermal crystallization experiment is 138 °C.

The sample thickness in the isothermal growth rate measurement is also 150 µm. The sample is heated at 200 °C for 2 minutes before it is transferred to another hot stage of which the temperature is kept at a desired crystallization temperature for isothermal crystallization. In nonisothermal crystallization, the heating is continued for 1 minute after the temperature has exceeded 190 °C. The ending temperature is about 230 °C when 1-minute heating time is reached, and cooling is begun at that point.

4.5.3. Parameters Directly Collected From Experimental Data

Parameters directly collected from experimental data include Growth rate, G , crystallization induction time, t_0 , crystallization temperature (or plateau temperature), T_p , and crystallization half time, $t_{1/2}$. Some examples of the experimental data. temperature, T ,

and relative crystallinity, θ , for collection of the kinetic parameters are given in Figure 4.1 and 4.2 respectively.

The crystallization plateau temperature is directly read from the cooling curves such as the ones given in Figure 4.1. The plateau temperature, T_p , versus heat transfer coefficient, h_a , at all applied cooling rates in the experiments is given in Figure 4.3. This figure also specifies the range and each value of applied cooling rates. According to Figure 4.3, the crystallization plateau temperature decreases as cooling rate increases. The lowest plateau temperature for the fastest cooling rate is about 92 °C, and the highest one for the slowest cooling rate is about 113 °C. Data in Figure 4.3 is obtained from all the crystallization rates. The plateau temperatures obtained for growth rate measurements have a similar temperature range and fall on a similar curve to Figure 4.3 (not shown).

The growth rate, G , versus crystallization temperature is given in Figure 4.4. Both iso- and nonisothermal data are plotted in Figure 4.4. The T in Figure 4.4 refers to the crystallization plateau temperature for nonisothermal crystallization and crystallization temperature for isothermal crystallization. The same symbol is adopted for both iso- and nonisothermal data, but the symbol for isothermal data is smaller than the one for nonisothermal data. From Figure 4.4 one can see at once that growth rate obtained in iso- and nonisothermal crystallization are reasonably smoothly connected, and both iso- and nonisothermal data fell on the same curve. The nonisothermal data are more scattered than for the isothermal data. As shown in Figure 4.4, the growth rate increases as crystallization temperature decreases.

The growth rate data shown in Figure 4.4 is plotted according to the Hoffman-Lauritzen equation, equation (2.3), in Figure 4.5. Figure 4.5 further demonstrates the similarity between the isothermal and nonisothermal crystallization in the present research. Again the iso- and nonisothermal growth rate data for the considered material are well

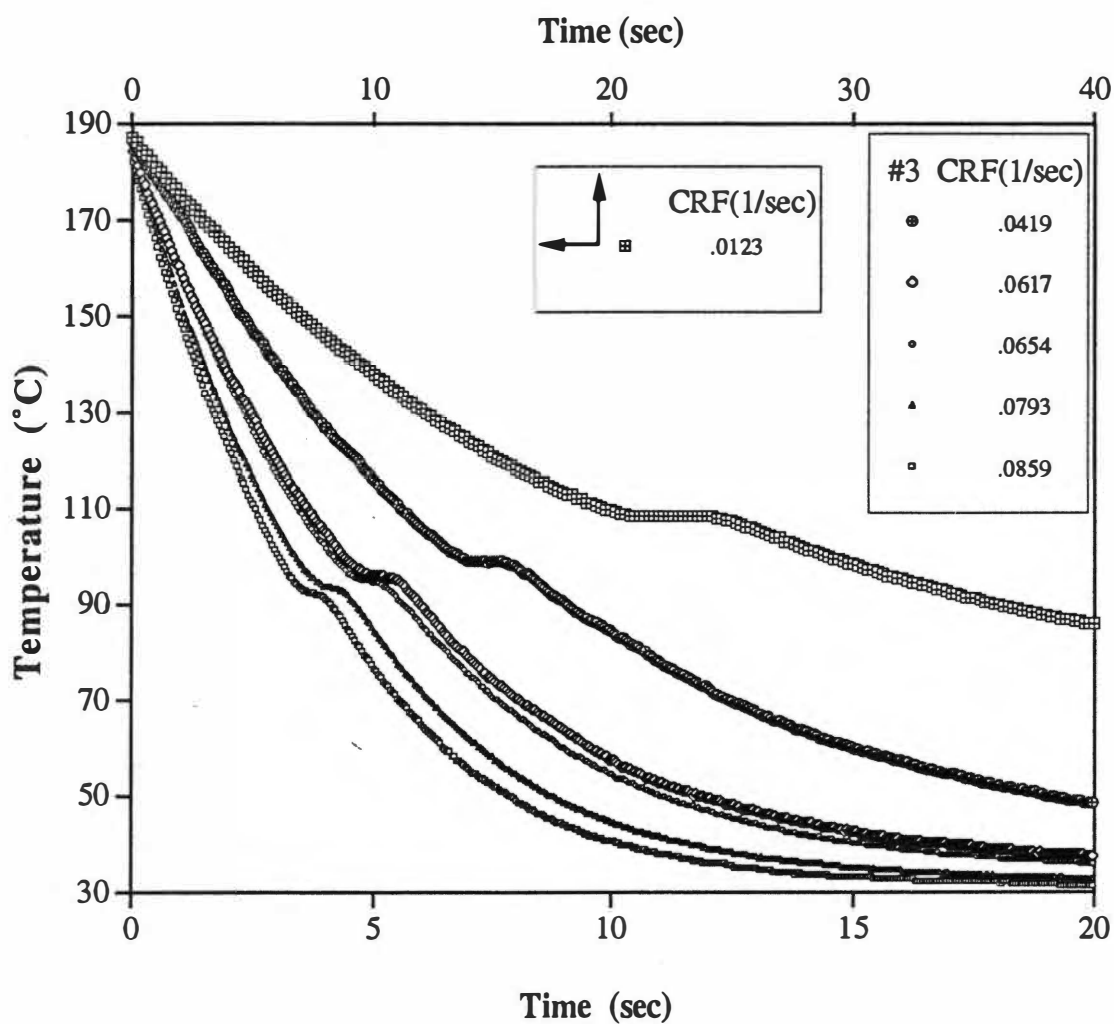


Figure 4.1. Examples of temperature versus time obtained in nonisothermal crystallization experiments at various cooling rates for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

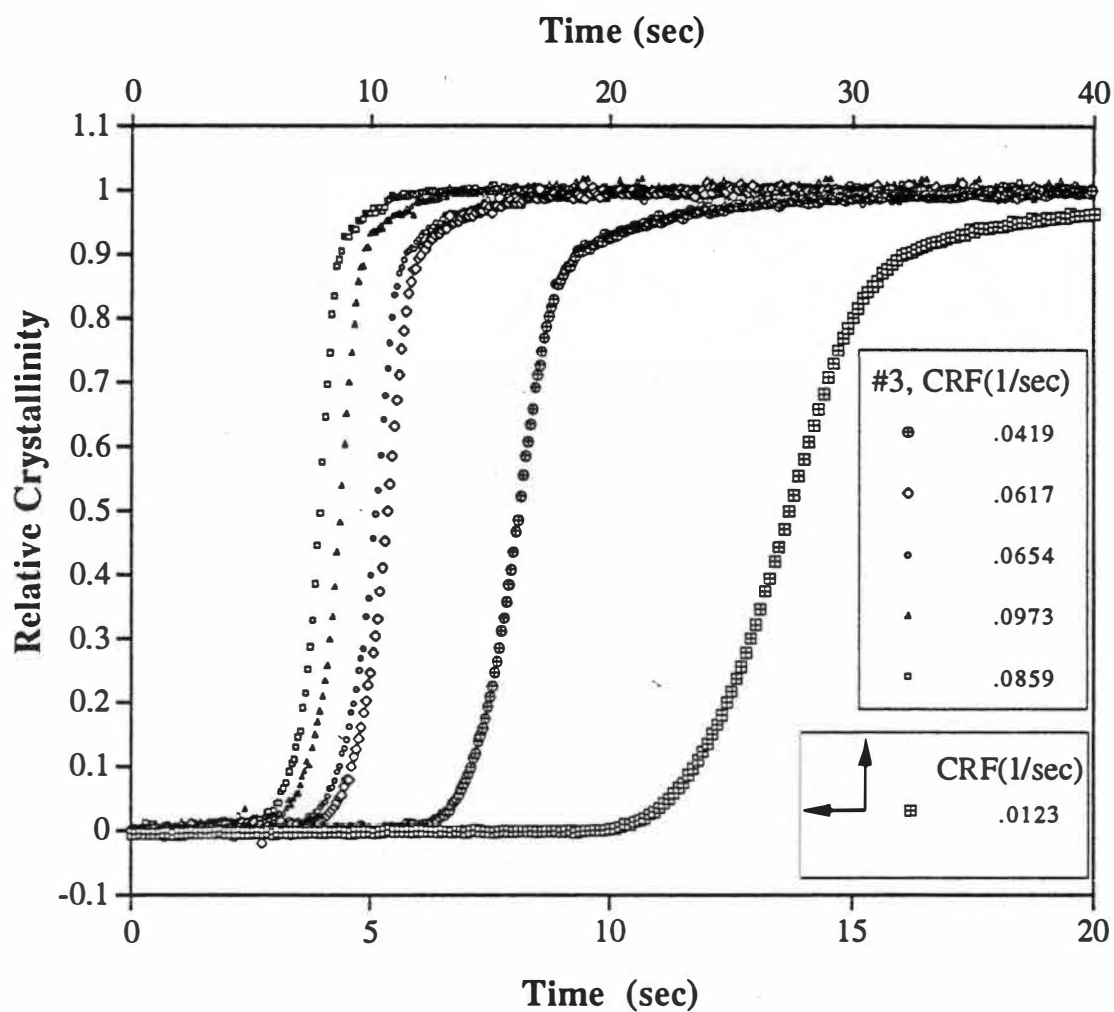


Figure 4.2. Examples of relative crystallinity versus time obtained in nonisothermal crystallization experiments at various cooling rates for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

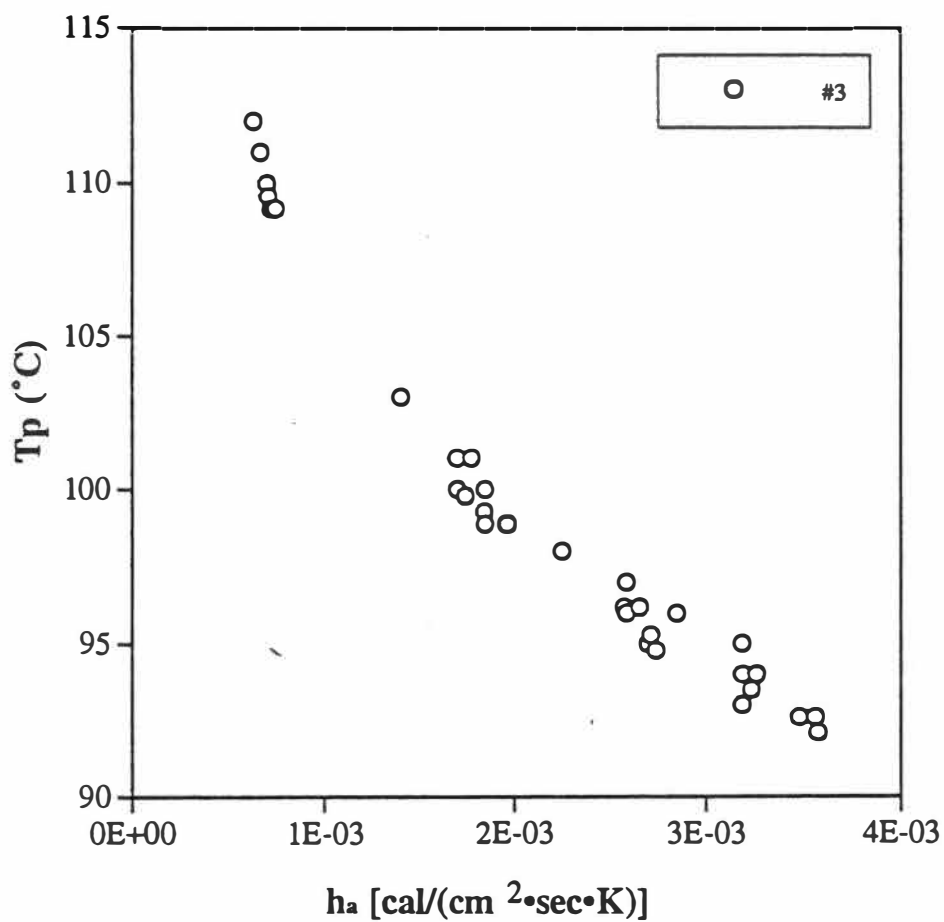


Figure 4.3 Plateau temperature, T_p , versus heat transfer coefficient, h_a , at all applied cooling rates in the experiments for iPP. MFR = 18. $M_w/M_n = 4.8$ and $M_w = 210,850$.

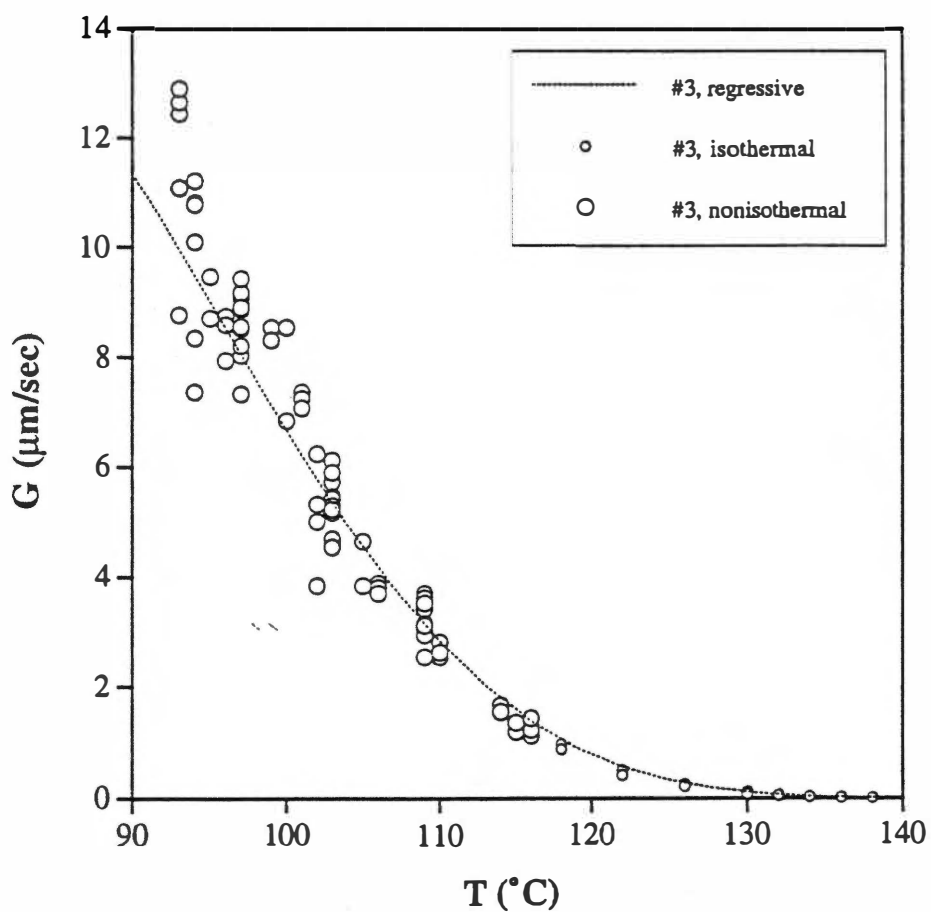


Figure 4.4 The growth rate, G , versus crystallization temperature at all applied cooling rates in the experiments for iPP. $MFR = 18$, $M_w/M_n = 4.8$ and $M_w = 210,850$.

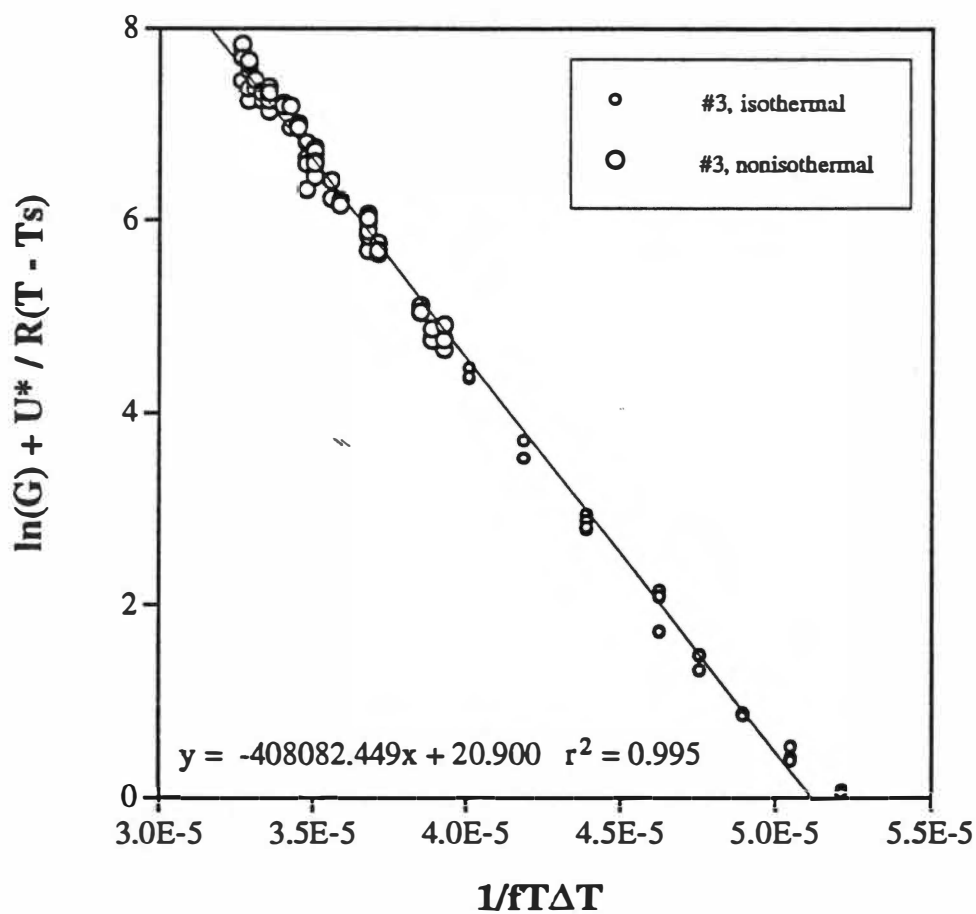


Figure 4.5. Hoffman-Lauritzen plot for the growth rates plotted in Figure 4.4.

connected and they fell on one straight line. The values of K_g and $\ln G_0$ are 408,082 (K^2) and 20.90 [$\ln(\mu\text{m}/\text{sec})$] respectively.

The time required for the temperature to drop from the melt temperature to the equilibrium melting point is denoted as t_1 . The time when crystallization begins is the crystallization onset time, t_{on} . The time from t_1 to t_{on} is the crystallization induction time, $t_0 = t_{\text{on}} - t_1$.

The crystallization induction time and crystallization onset temperature at different cooling rates for the considered material are given in Figure 4.6. The crystallization induction time was obtained from the light intensity without analyzer as described in Chapter 3. Both crystallization induction time and crystallization onset temperature decrease as cooling rate increases. Thus, the crystallization induction time decreases as crystallization temperature decreases. The crystallization onset temperature was collected at crystallization onset after crystallization induction time was determined. The crystallization onset temperature is more scattered than the data for crystallization induction, but still linearly related to the heat transfer coefficient.

Crystallization half time, $t_{1/2}$, is the time for crystallinity to reach 1/2 of the final value. Crystallization half time can be directly obtained from relative crystallinity versus time curves as shown in Figure 4.2. Crystallization onset time has been extracted from the crystallization half time presented in this research. That is, the crystallization half time starts at time equals crystallization onset time and proceeds until the relative crystallinity equals 0.5. The crystallization half time obtained for crystallization at different cooling rates is plotted against crystallization plateau temperature for the considered iPP in Figure 4.7. As shown in Figure 4.7, the crystallization half time decreases as crystallization temperature decreases or the cooling rate increases.

The crystallization half time can be related to crystallization temperature according to the equation (4.36):

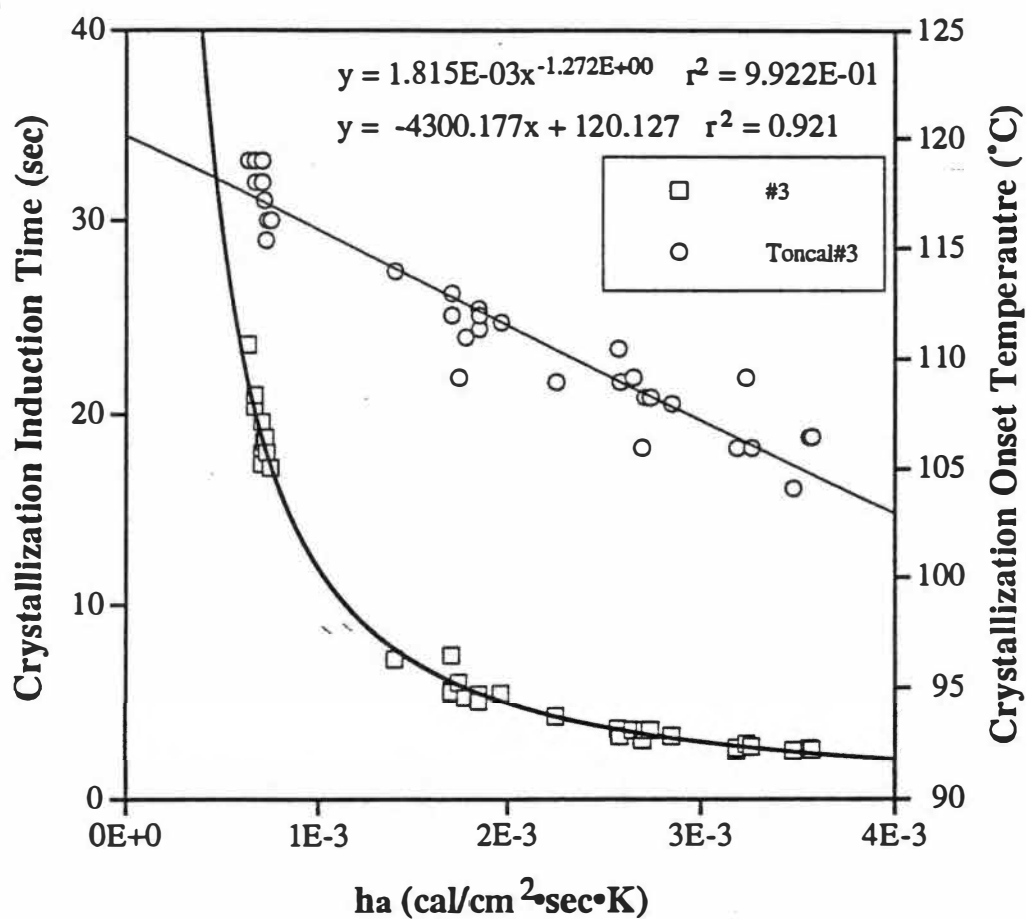


Figure 4.6. Crystallization induction time and crystallization onset temperature at different cooling rates for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

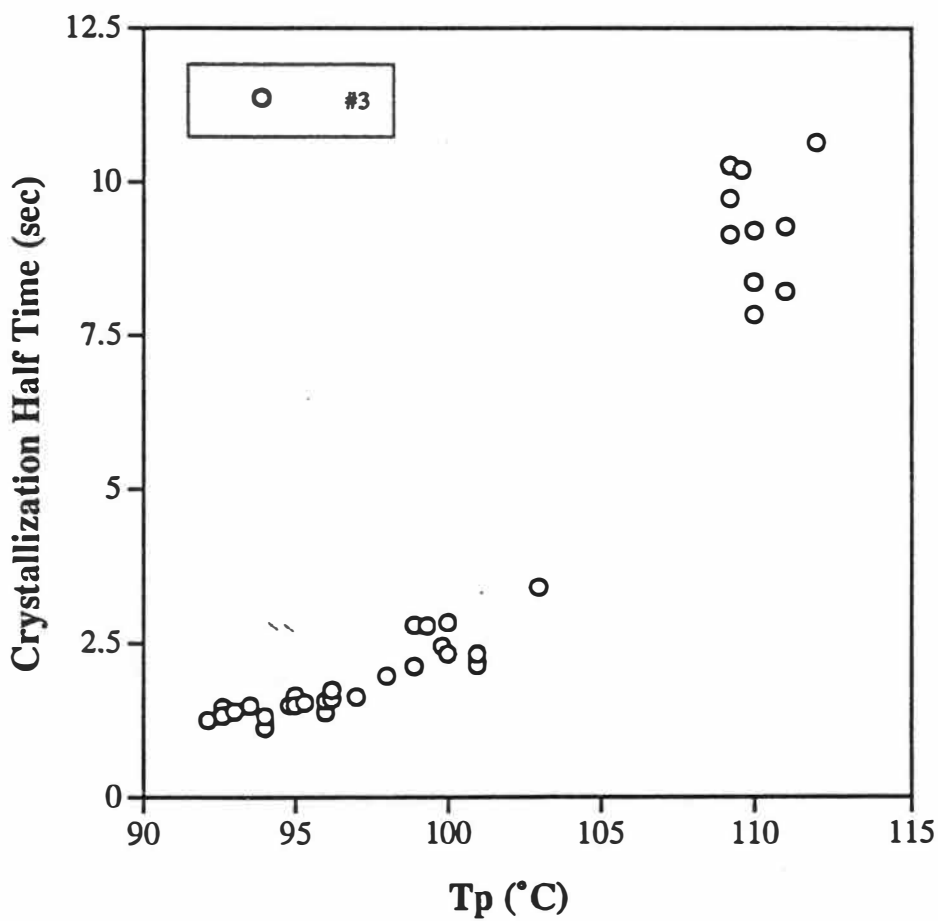


Figure 4.7. The crystallization half time versus crystallization plateau temperature at different cooling rates for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

$$\frac{1}{t_{1/2}} = \left(\frac{1}{t_{1/2}}\right)_0 \exp\left(\frac{U^*}{R(T - T_s)}\right) \exp\left(\frac{C_{t12}}{T\Delta T f}\right) \quad (4.36)$$

Replacing the crystallization temperature by the plateau temperature, the data in Figure 4.7 are plotted in Figure 4.8 according to equation (4.36). From Figure 4.8 one can see that the data falls on a straight line and follows equation (4.36) well. The constants C_{t12} and $\ln\left[\left(\frac{1}{t_{1/2}}\right)_0\right]$ were found to be $5.601 \cdot 10^5$ (K²) and 23.32 [ln(1/sec)], respectively.

4.5.4. Discussion Of The Parameters Directly Collected From Experimental Data

The scattered growth rates shown in Figure 4.4 are caused by slightly different growth rates occurring for different spherulites in the same experimental run. The procedure to collect the diameter data from the TV screen is that most of the spherulites that are in focus will be measured, the number of such spherulites is around three per run. After the data is collected the growth rate is calculated and no further averaging or correction is needed for the obtained data. It was also found that different growth rates for different spherulites also exists in isothermal crystallization. Because the magnitude of the growth rate for the isothermal crystallization is small such a scatter in the data is not evident in Figure 4.4. It seems that the lower the crystallization temperature, the more variation in growth rate in the same experimental run. The reason for the existence of the different growth data in the same experimental run is unknown. The fact given by Figure 4.4 that both growth rates obtained by iso- and nonisothermal crystallization fell on one curve supports the argument for a constant growth rate in nonisothermal crystallization. The figure also suggests a way to extend the kinetic study to the low crystallization temperature region by applying the presently developed technique. From the figure one can see that the nonisothermal data extend the growth rate data to a much wider

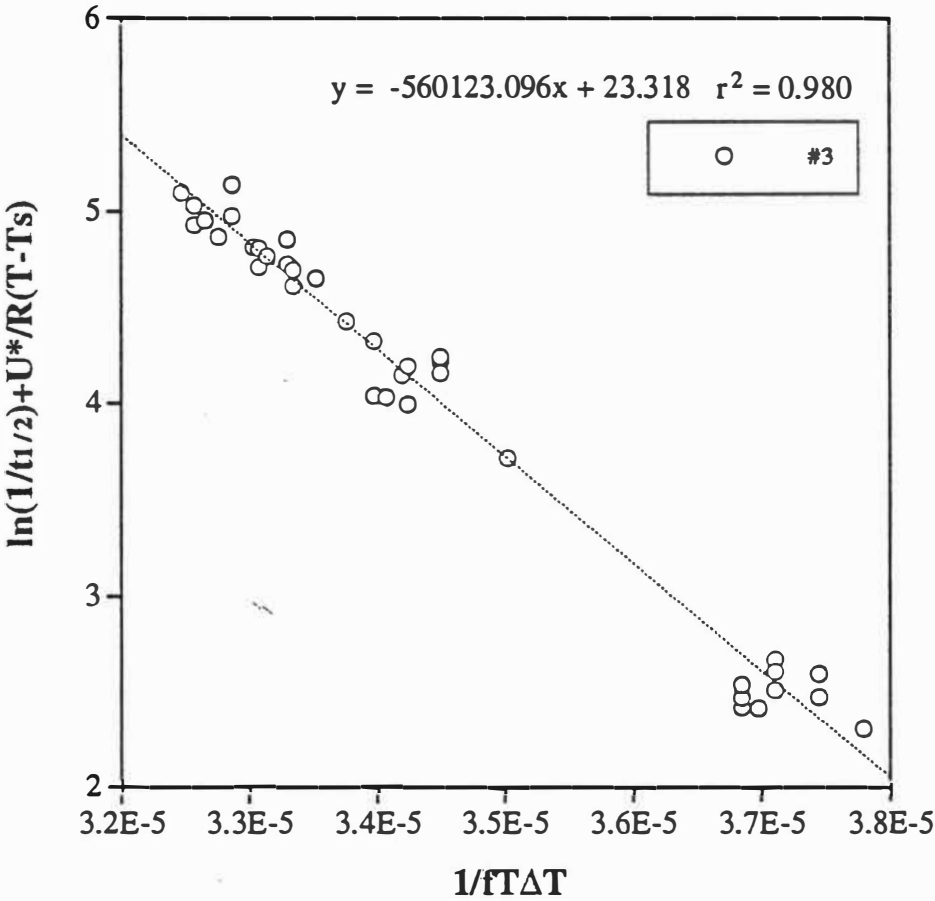


Figure 4.8. $\ln(1/t_{1/2})$ versus $\frac{1}{T\Delta T f}$ for the data plotted in Figure 4.7.

temperature range. With data covering such a wider range, the regression made for the experimental data is more reliable, otherwise it is dangerous to extrapolate from isothermal data, which only covers a narrow temperature range, to the data for a low crystallization temperature.

Figure 4.5 reveals that nonisothermal data not only follows the Hoffman-Lauritzen equation, but also is described by the same equation as the isothermal data. The nonisothermal data gives the data in the lower crystallization temperature range and the isothermal data describes the growth in the higher crystallization temperature range. The nonisothermal data expands the growth rate data to much lower crystallization temperature and provides more reliable values of G_0 and K_g by regressing the Hoffman-Lauritzen equation to the experimental data over the wider temperature range.

It is noticed that at crystallization temperature 138 °C the data points are slightly above the regressive curve. This is most probably caused by the regime transition (III to II) at a temperature around 138 °C [Clark and Hoffman (1984)]. Measurements were not made for the present samples at temperatures above 138 °C, but the literature is clear that a regime transition occurs at about this temperature. Such a regime transition results in a different slope in the Hoffman-Lauritzen plot. The present data indicate that regime III exists over the entire range studied here with the possible exception of a point or two at the high temperature end of the plot.

In the Avrami analysis, it is critical to correctly determine the crystallization onset time. When crystallization onset time varies a little bit, the slope and interception in the Avrami plot will differ considerably for the same set of experimental data. This is especially true in nonisothermal crystallization when the cooling rate applied in the experiment is high, because the crystallization time is short. It is, however, difficult to determine it in both DSC and traditional LDM. Therefore, the idea of whole range fitting [Binsbergen and de Lange (1970)] to the $\theta - t'$ curve was suggested to obtain the crystallization onset time, Avrami

index and crystallization rate constant in a single nonlinear regression. Unfortunately, many combinations of these three parameters allow a reasonable fit of the Avrami equation to the $\theta - t'$ curve. This makes a statistical regression procedure difficult to converge in the calculation and prevents us from obtaining a reasonable crystallization onset time by the nonlinear regression procedure.

In the present technique, the light intensity without analyzer, I_0 , is measured which is sensitive to crystallization in the early stage of crystallization. Because I_0 detects the light scattering from crystallites, and the small crystallites at the beginning of the crystallization mainly scatter light, I_0 drops quickly when crystallization starts. The beginning of the deviation of I_0 from the base line is then selected as crystallization onset time for the present work. This method has been verified by video camera technique and gives consistent results for data from numerous experiments under various cooling conditions.

The crystallization onset time is the time when the first batch of nuclei are created. The crystallization induction time therefore reflects the rate of nucleation of that first batch of nuclei. The shorter the crystallization induction time the faster the rate of creation of nuclei in the system. The reason that this rate is reflected by crystallization induction time instead of crystallization onset time is that the driving force to create nuclei begins to appear in the system for a temperature equal to the equilibrium melting point, at which the crystallization induction time begins. A higher cooling rate makes it possible to reach a lower crystallization temperature. This produces a higher driving force to produce nuclei. The great driving force produces nuclei in less time. That is why the crystallization induction time decreases as crystallization temperature decreases or cooling rate increases.

Motivated by the phenomenon that the induction time reflects the rate of nucleation of the first batch of the nuclei, its reciprocal describing such a rate, and analogous to the temperature dependence of crystallization rate constant, we introduce the following

equation to relate crystallization onset temperature to the reciprocal of crystallization induction time, $\frac{1}{t_0}$, for quiescent crystallization:

$$\frac{1}{t_0} = \left(\frac{1}{t_0}\right)_0 \exp\left[\frac{-C_I}{T \Delta T f}\right] \quad (4.37)$$

where $\left(\frac{1}{t_0}\right)_0$ and C_I are constants determined by the quiescent experiments. According to equation (4.37), the crystallization onset time and temperature given in Figure 4.6 are plotted in Figure 4.9. From Figure 4.9 one can see that this way of relating crystallization induction time to crystallization onset temperature can be accepted. From the slope and interception, $C_I = 478,910 \text{ [K}^2\text{]}$ and $\ln\left[\left(\frac{1}{t_0}\right)_0\right] = 16.267 \text{ [ln(1/sec)]}$ are obtained. The significance of equation (4.37) is to produce a theoretical relationship to predict the crystallization induction time. This is extremely important to the computer model for any kind of process which deals with crystallization.

It is well known that the reciprocal of the crystallization half time represents the overall crystallization rate. Therefore the overall crystallization rate increases as cooling rate increases, as the crystallization half time decreases with increase in cooling rate. However the crystallization half time does not supply detailed information on the crystallization: whether the change of crystallization rate is caused by change of growth rate or nucleation rate. However, the crystallization half time is a parameter which is directly collected from experiment without relying on any theoretical treatment, and consequently, it is a very important parameter to describe the crystallization rate. With information from growth rate, as well as overall crystallization rate, it is possible to get information about nucleation rate. Actually, this is one of the major aspects of this chapter and will be discussed in detail.

The existence of a temperature plateau indicates that the rate of energy release during crystallization is higher than the rate at which energy is carried away by the cooling medium. The reasons why the crystallization temperature decreases with increase in cooling

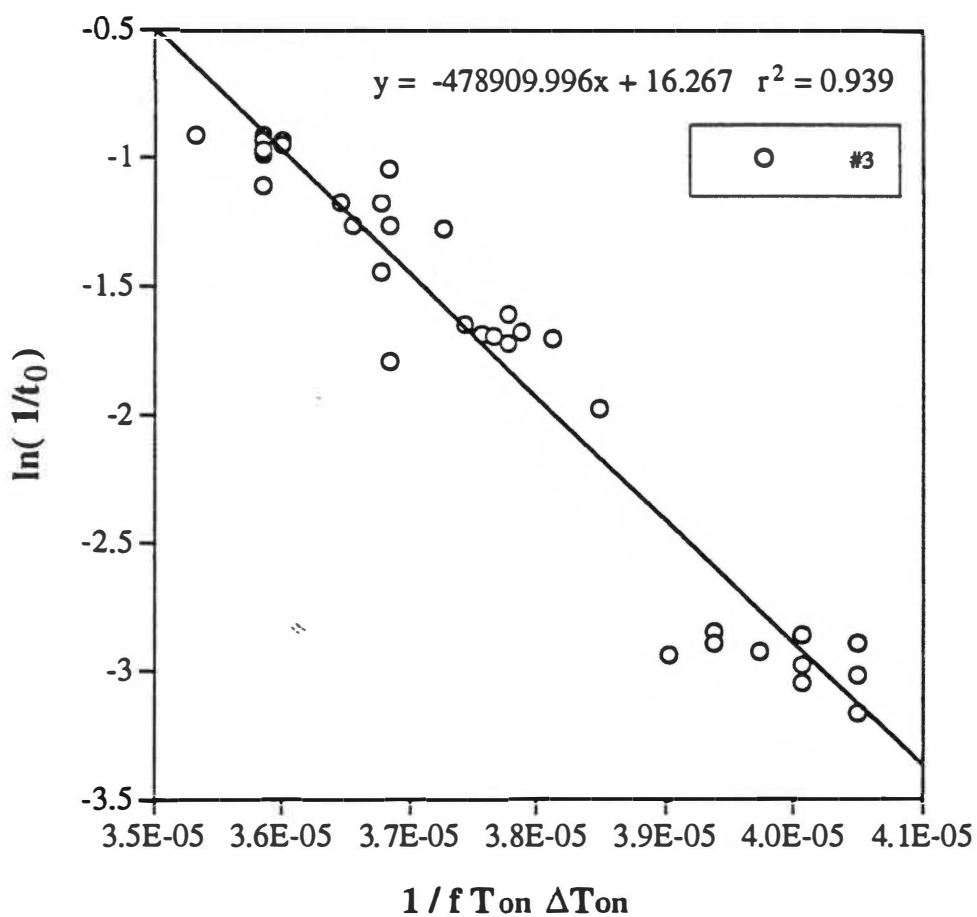


Figure 4.9 Relating crystallization induction time to the crystallization onset temperature according to Equation (4.37) for iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

rate are that the crystallization onset moves to a lower temperature, lower crystallinity is developed and heat is carried away at a greater rate due to the higher cooling rates applied. As cooling rate increases, the rate at which energy is carried away by the cooling medium increases faster than does the rate of energy release due to the crystallization. Even though the crystallization rate increases with increase in cooling rate, a higher cooling rate results in a lower crystallinity.

4.5.5. Parameters Based On Kinetic Theories

Further analysis based on application of kinetic theories to the obtained dynamic relative crystallinity data produces several more crystallization kinetic parameters. Two such parameters are the Avrami index and crystallization rate constant. Using the concept of power law nucleation function, the Avrami index can be separated into geometric and nucleation index, and from crystallization rate constant, one may further calculate nucleation rate constant. These parameters are based on the derived Avrami equation. Data for nucleation rate is very difficult to measure experimentally. But the overall crystallization rate and growth rate can be readily determined by experiment as has been shown. These two parameters contain the information about nucleation rate, and it can be extracted with the power law nucleation rate theory.

The procedure to obtain the nucleation index, m , and nucleation rate constant is to obtain the Avrami index, n , and crystallization rate constant, k , first, and then calculate m from n and N_c from k . The n and k are obtained by fitting Avrami equation 4.30 to the data of relative crystallinity and time in the plot of $\ln\ln\left(\frac{1}{1-\theta}\right)$ versus $\ln(t)$ that may be called the Avrami plot. An example of such a plot is given in Figure 4.10. The time in Figure 4.10 starts from crystallization onset, that is, the induction time has been extracted from it. The curves in Figure 4.10 are similar to the ones encountered in treatments of isothermal

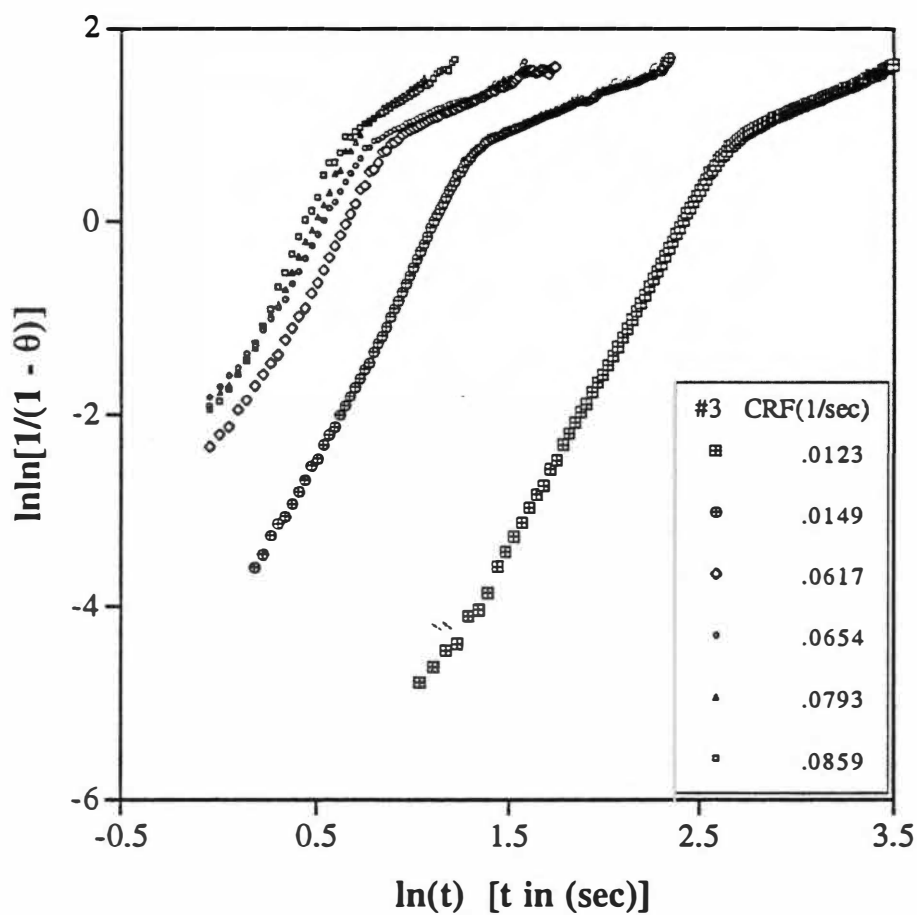


Figure 4.10. Avrami plot, $\ln \ln\left(\frac{1}{1 - \theta}\right)$ versus $\ln(t)$, for runs at different cooling rates for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

data. There are two sections with different slopes for a curve of $\ln\ln(\frac{1}{1-\theta})$ versus $\ln(t)$ in Figure 4.10. The section with smaller slope corresponds to the period following impingement of spherulites (lamella thickening and, possibly, some secondary crystallization). The section with larger slope corresponds to the all crystallization process. The first section for crystallization exists in the location where the crystallization temperature plateau occurs, or is the region in which the crystallinity dramatically increases due to spherulite growth. The Avrami index and crystallization rate constant are obtained for the section of primary crystallization. The slope of that section gives the Avrami index and its intercept is $\ln(k)$.

The values of Avrami index obtained for all examined cooling rates are given in Figure 4.11. As shown in Figure 4.11, the obtained Avrami indexes for the considered iPP all fall in a scattered band between 3 and 4. There is no tendency for the Avrami index to change as cooling rates vary. An average Avrami index for data presented in Figure 4.11 is 3.58.

The crystallization rate constant, k , is given in Figure 4.12. As shown in Figure 4.12, the crystallization rate constant increases as cooling rate increases, though data is more scattered at high cooling rates. Using equation (2.24), which is rewritten as equation (4.38),

$$k = k_0 \exp\left(\frac{U^*}{R(T - T_s)}\right) \exp\left(\frac{C_k}{T\Delta T f}\right) \quad (4.38)$$

the data given in Figure 4.12 is plotted in Figure 4.13. From Figure 4.13 we can see that the data falls on a straight line though it is scattered. The constants C_k and $\ln(k_0)$ in equation (4.38) are obtained from Figure 4.13 which equal to $1.691 \cdot 10^6$ (K^2) and 59.32 [$\ln(1/\text{sec}^n)$].

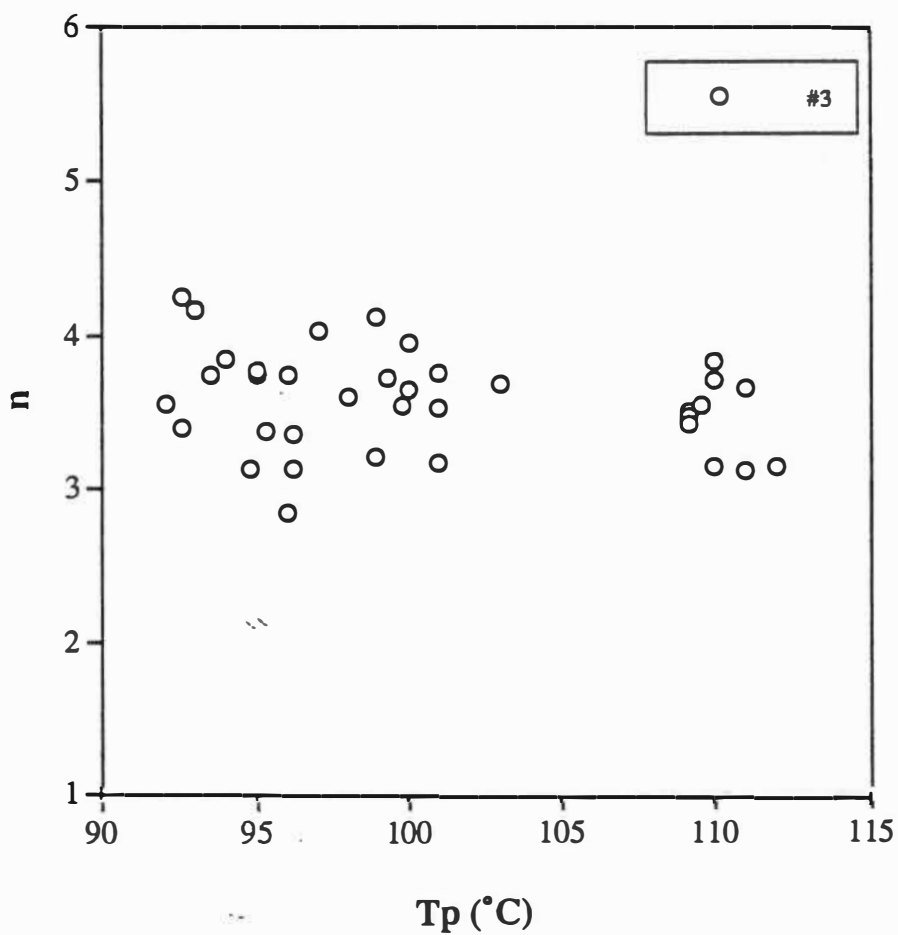


Figure 4.11. Avrami index obtained for all examined cooling rates versus crystallization plateau temperature for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

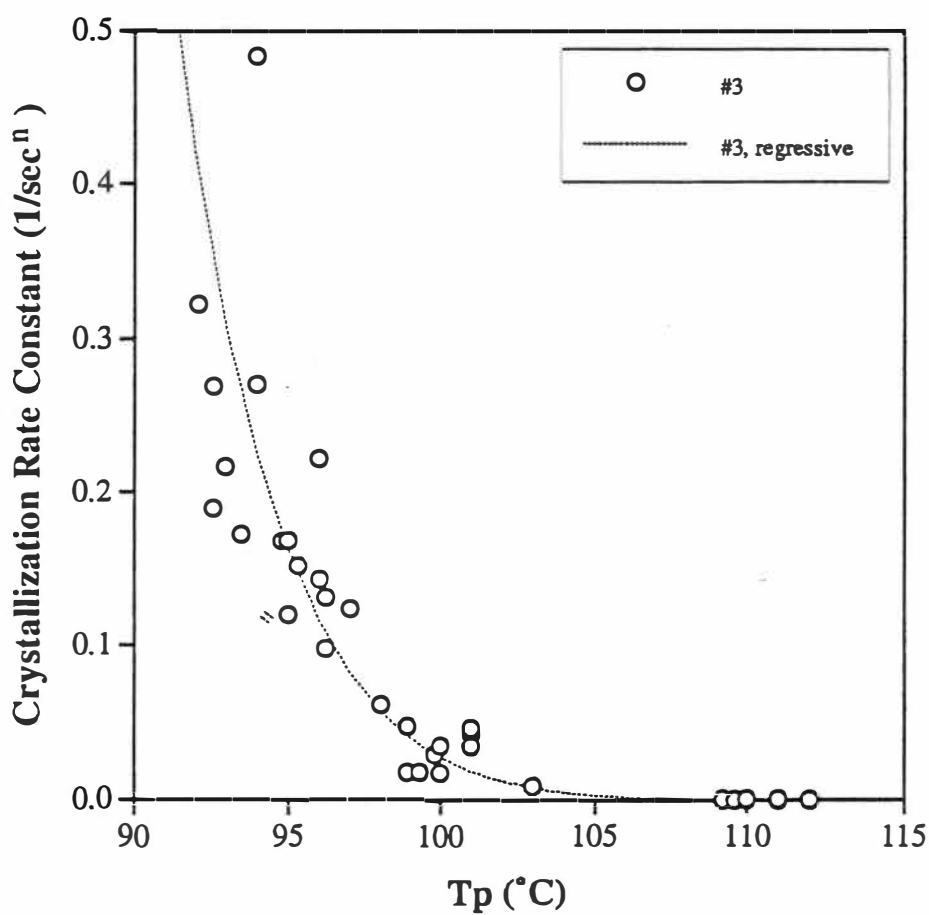


Figure 4.12. Crystallization rate constant, k , obtained for all examined cooling rates versus crystallization plateau temperature for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

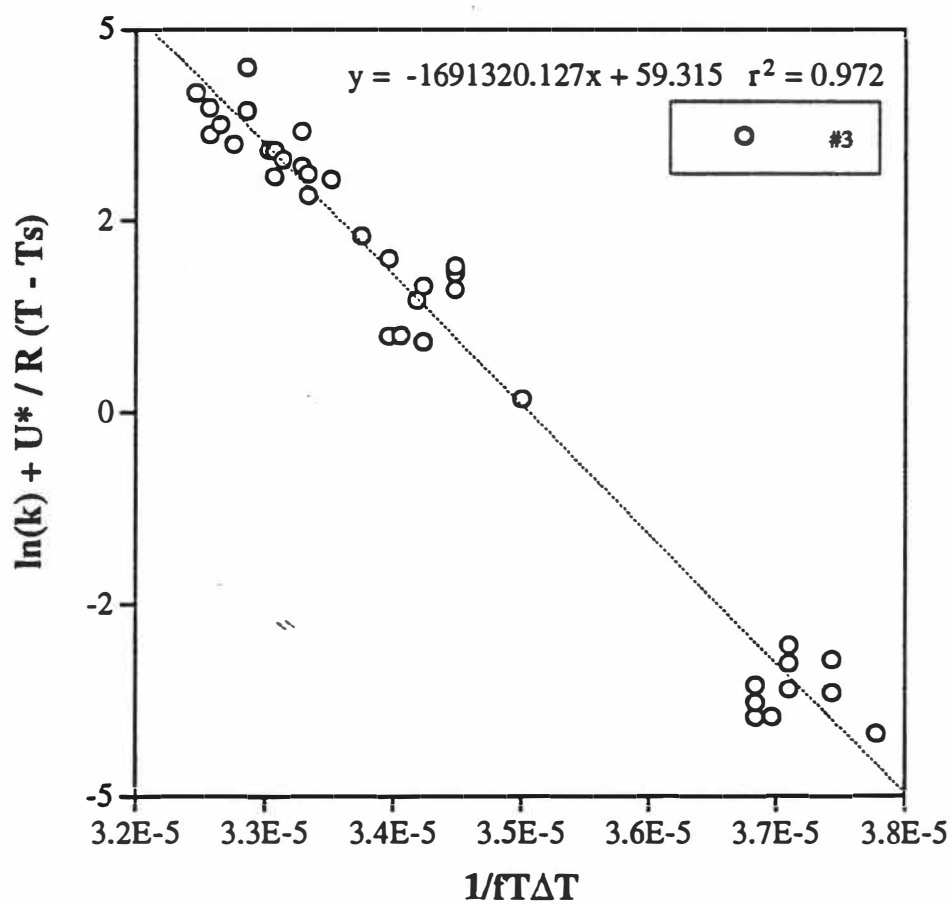


Figure 4.13. $\ln(k) + U^*/R(T - T_s)$ versus $\frac{1}{T\Delta T}$ for the data plotted in Figure 4.12.

After the Avrami index and crystallization rate constant are obtained, the nucleation rate constant, N_c , and nucleation index, m , can be calculated. By assuming geometric index equals 2 (discussed below) and the Avrami indices given in Figure 4.11, the nucleation indexes are calculated for each individual run for the considered iPP according to equation (4.31). The nucleation rate constant, N_c , is calculated according to equation (4.32) by using experimental growth rate data shown in Figure 4.4, nucleation index and geometric index. Obtained nucleation rate constants are given in Figure 4.14. As shown in Figure 4.14, the nucleation rate constant increases as cooling rates increases, but the data looks more scattered than does the crystallization rate constant, see Figure 4.12.

Analogous to the crystallization rate constant, the temperature dependence of the nucleation rate constant may be described by the following equation:

$$N_c = (N_c)_0 \exp \left\{ \frac{U^*}{R(T - T_s)} \right\} \exp \left\{ \frac{C_N}{T\Delta T f} \right\} \quad (4.39)$$

Figure 4.15 is a plot according to equation (4.39) using the data given in Figure 4.14. It can be seen at once that the nucleation rate constant can well be related to the crystallization plateau temperature by equation (4.39). The regressive constants, C_N and $\ln[(N_c)_0]$ are $1.118 \cdot 10^6 \text{ (K}^2\text{)}$ and $54.48 \{ \ln[\# / (\text{sec}^{m+1} \cdot \text{cm}^3)] \}$, respectively.

4.5.6. Discussion Of The Parameters Based On Kinetic Theories

Avrami index includes information about the growth geometry, impingement, and nucleation. For spherulitic growth, the corresponding Avrami geometric index is 3. When impingement exists, the Avrami geometric index is less than 3, and it is possibly less than 2. The reduction of Avrami geometric index depends on the degree of impingement. This, in turn, is related to nucleation rate and the confinement caused by the container holding the polymer during crystallization. If the sample geometric shape, which for LDM is the

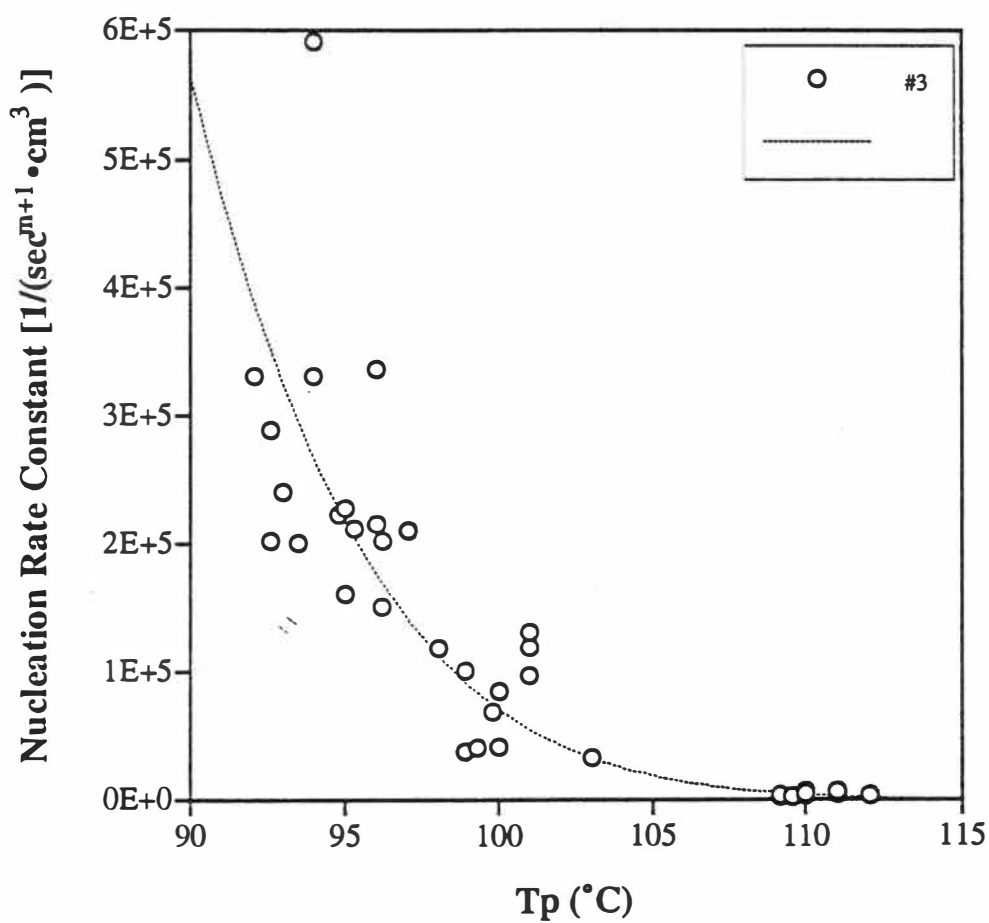


Figure 4.14. Nucleation rate constant, N_c , versus crystallization plateau temperature for all examined cooling rates for the considered iPP. MFR = 18, M_w/M_n = 4.8 and M_w = 210,850.

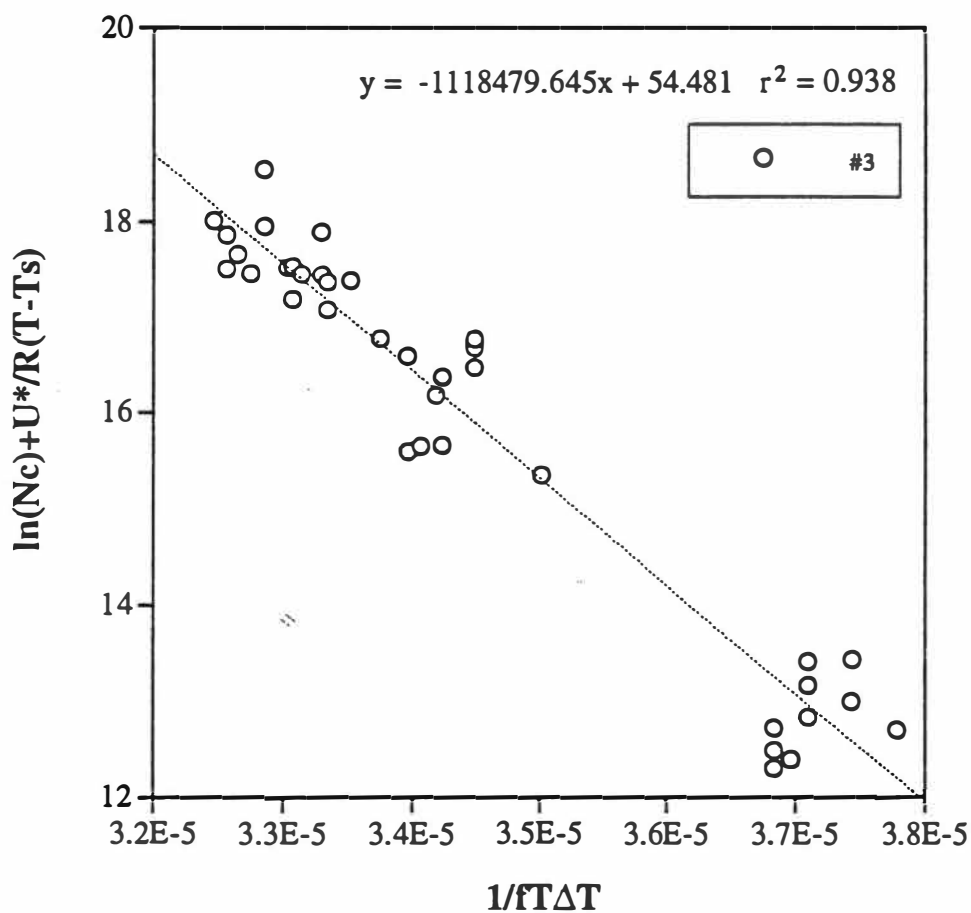


Figure 4.15. $\ln(N_c) + U^*/R(T - T_s)$ versus $\frac{1}{T\Delta T f}$ for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210,850$.

sample thickness, is kept the same for all experiments, the degree of impingement is determined by the rate of the nucleation. For a process with higher nucleation rate, larger reduction in geometric index will be observed. Such reduction might possibly be much less than 3. There is no direct relation available that correlates the nucleation rate and the reduction in geometric index caused by impingement. It seems that the difficulty of measuring nucleation rate has prevented us from obtaining this information. This problem, however, can be solved by a computer simulation. For the convenience of discussion, it is assumed that the geometric index remains constant at 2 for all the cases in this research after the impingement effect has been considered.

The Avrami index also includes the component of nucleation rate controlled by the nucleation index. The relationship between nucleation index and the distribution of the nucleation rate has been discussed previously. The nucleation rate thus affects the Avrami index through the effect of impingement which affects the geometric index, and the time dependence of nucleation rate which is described by the nucleation index. It seems that the detailed information of the effect of nucleation rate on the Avrami index can only be obtained by computer simulation of crystallization. This kind of research needs to be done in the future.

The fact that the Avrami index is independent of cooling rate, Figure 4.11, suggests that the manner of the nucleation, or the relative amount of time dependent and time independent nucleation is basically independent of cooling rate. The nucleation rate increases with cooling rate because the nucleation rate constant increases with increase in cooling rates, Figure 4.14. Further, the reason that the overall crystallization rate described by crystallization half time increases with cooling rate, Figure 4.7, is because both nucleation rate and growth rate increase with increases in cooling rate.

Based on the interpretation described here, the scattered Avrami index is likely caused by fluctuation in nucleation rate from run to run for a given cooling rate. The

scattered crystallization constants are caused by fluctuation in nucleation rate and possibly also due to some variation of growth rate under the same cooling condition.

4.6. Nucleation Density

The nucleation rate is described by the nucleation rate function, equation (4.34). It is, however, of interest to describe the nucleation in terms of nucleation density which is an experimentally measurable quantity, and one which is readily visualized. To calculate the nucleation density as a function of time, $N(t)$, from the nucleation rate function, equation (4.40) is introduced,

$$N(t) = \int_0^t N_c \cdot (1 + m) \cdot \tau^m (1 - \theta) \cdot d\tau \quad (4.40)$$

Using N_c and m , obtained previously, and experimentally measured relative crystallinity, θ , $N(t)$ can be calculated according to equation (4.40). Examples of this calculation are given in Figure 4.16. Please note that the examples given in this chapter are all from the same six runs; different results from the six runs are plotted in different places throughout this chapter. The plots include Figure 4.1, 4.2, 4.3, 4.10, and 4.16. In Figure 4.16, the value of N_c and m used for each of the six different cooling rates are from the individual runs. It should be noted that either Avrami index or nucleation rate constant obtained at different cooling rates is somewhat scattered around an average value, see Figure 4.11 and 4.14. This variation in the values of m and N_c causes some variability in the curves showing the development of nucleation density with time. In general, as shown in Figure 4.16, the curves of nucleation density for higher cooling rates begin earlier, increase faster, and reach higher final values in a shorter time. This tells us the nucleation rate is faster for runs carried out at higher cooling rates. The difference in nucleation rate at different cooling rates is largely caused by difference in nucleation rate constant as the nucleation index is basically constant at different cooling rates.

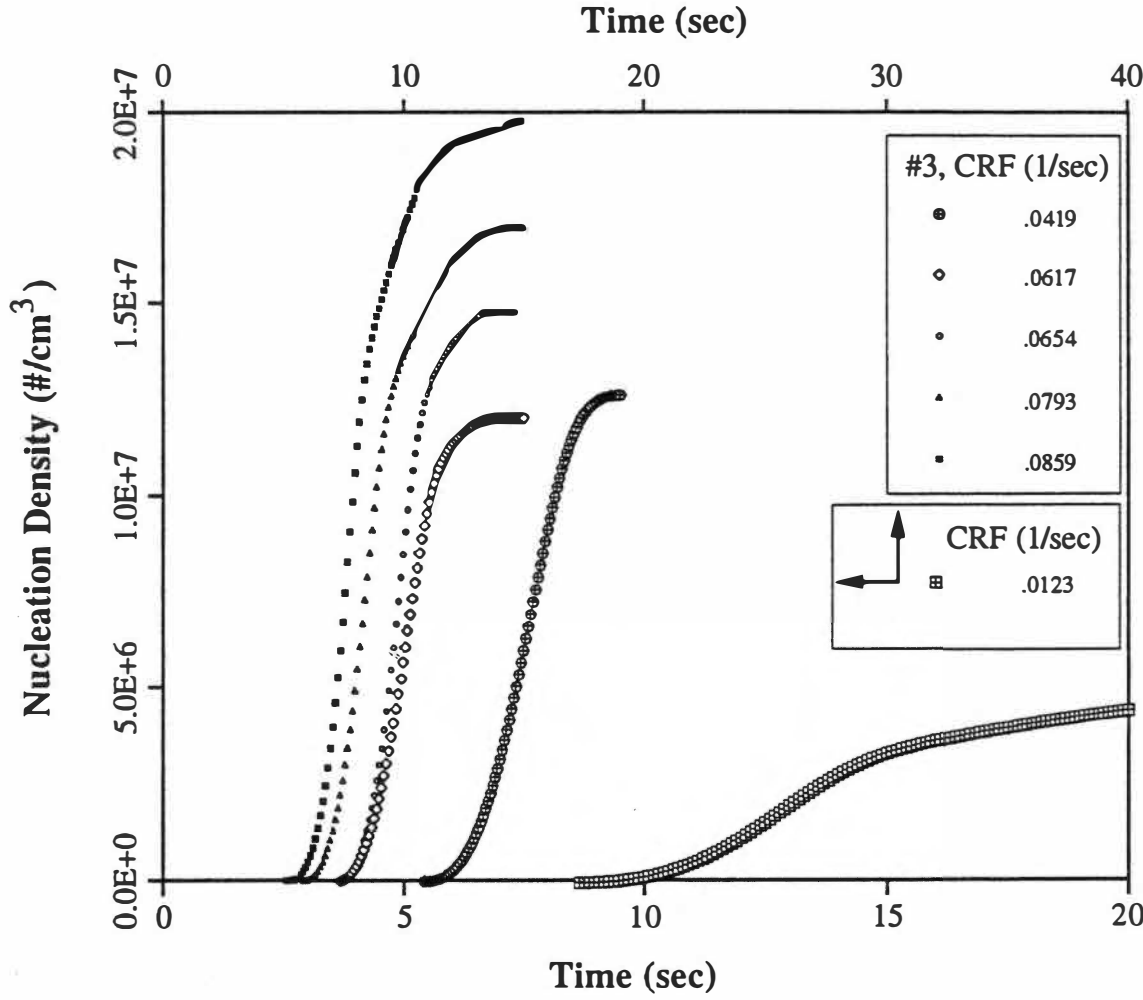


Figure 4.16. Nucleation density versus time at various cooling rates for the considered iPP. MFR = 18, $M_w/M_n = 4.8$ and $M_w = 210.850$.

4.7. Comparison With The Results From Other Research (Growth Rate)

In order to compare our results with those of previous investigations, the growth rates obtained in the present research are plotted in the form of a Hoffman-Lauritzen plot with the isothermal data from Hammami's and Campbell's works [Hammami(1990), Campbell (1991)] in Figure 4.17. The constants in the Hoffman-Lauritzen equation obtained for each material are summarized in Table 4.1. From Figure 4.17 we can see that compared with Regime III data from Hammami and Campbell, our data, including the data measured under high cooling rates also belongs to Regime III, but our data covers a much wider temperature range. There is not much difference between our isothermal data and Campbell's Regime III data for $M_w = 83,000$. However, because of the small difference in slopes between the curves for the two data sets, one may expect a difference when extrapolating Campbell's data to lower crystallization temperature range. Also one may notice that the different material in Regime III exhibits different slope, K_g , though they are not large, see also Table 4.1. Comparing the K_g value in Regime III, one has the following sequence: present work > Campbell's ($M_w = 83,000$) > Campbell's ($M_w = 151,000$) > Hammami's ($M_w = 127,000$).

Figure 4.18 gives the comparison between the present measured data and that predicted by the Hoffman-Lauritzen equations obtained in Figure 4.17. In Figure 4.17 Campbell's data is plotted by using the equations belonging to regime III. From Figure 4.18 one can see that the experimental growth rates obtain under high cooling rate can not be predicted by the equations for isothermal growth rates from previous researches. It is not clear whether this is due to real differences between the growth rates of the materials used due to such factors as variation of isotacticity, or due simply to inability to extrapolate data taken in a narrow, high temperature range to lower temperatures.

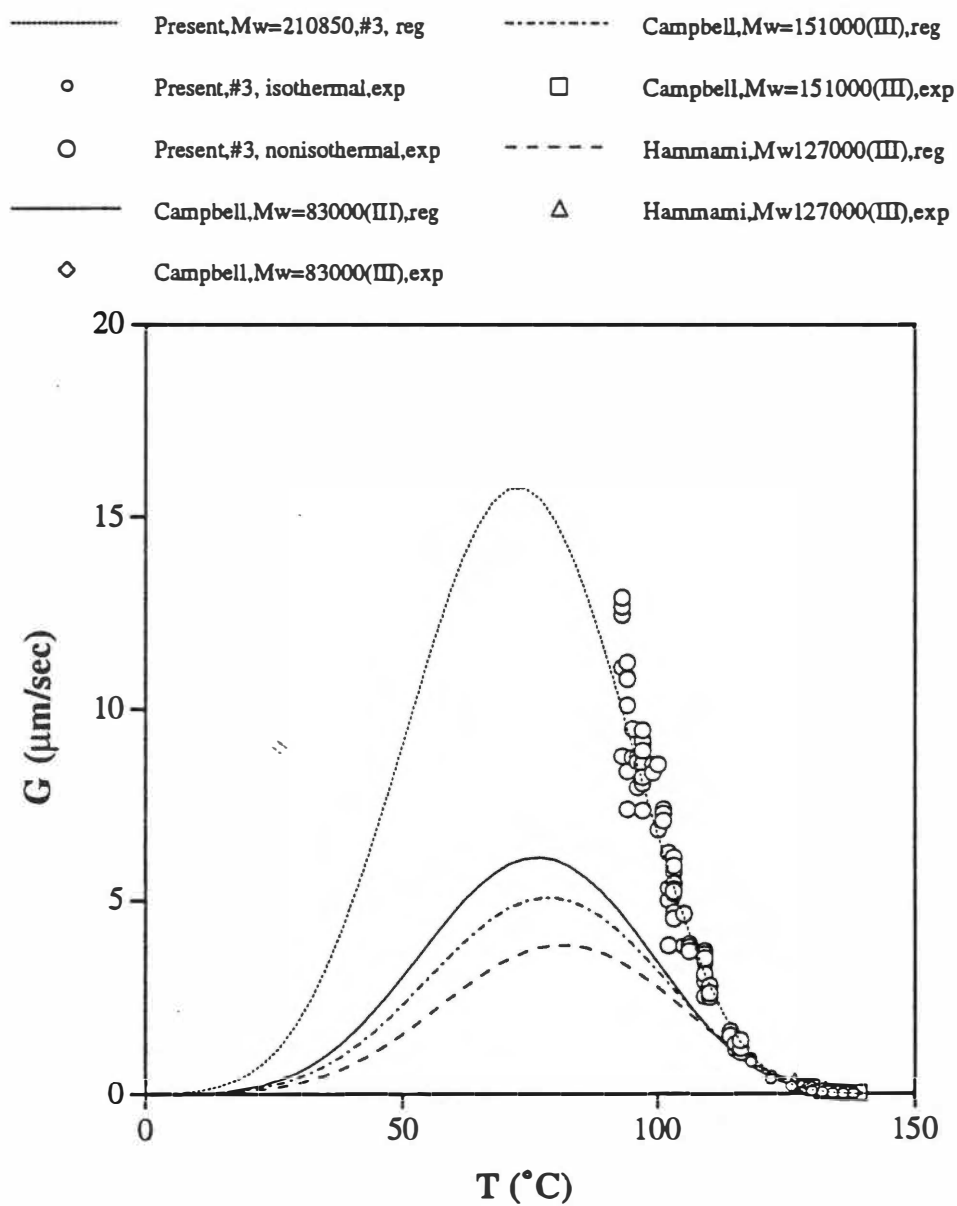


Figure 4.17. A comparison of growth rates among results from different researches indicated in the figure.

Table 4.1. Regressive Constants In Hoffman-Lauritzen Equation For The Experimental Data Of Growth Rate Obtained By Different Researchers

Researchers	Mw	Regime	K_g (K^2)	$\ln G_0$ [$\ln(\mu\text{m}/\text{sec})$]	r^2
Present Work	210,850	III	408082	20.900	0.995
Campbell	83,000	II	167447	8.750	0.982
Campbell	83,000	III	349246	18.212	0.935
Campbell	151,000	II	186448	10.024	0.970
Campbell	151,000	III	320210	17.153	0.974
Hammami	127,000	III	285585	15.830	0.998

○	present, Mw=210850, #3, isothermal	$y = -408082.449x + 20.900 \quad r^2 = 0.995$
○	present, Mw=210850, #3, nonisothermal	
◆	Campbell, Mw=83000 (II)	$y = -167447.145x + 8.750 \quad r^2 = 0.982$
◇	Campbell, Mw=83000 (III)	$y = -349245.942x + 18.212 \quad r^2 = 0.935$
⊠	Campbell, Mw=151000 (II)	$y = -186448.396x + 10.024 \quad r^2 = 0.970$
□	Campbell, Mw=151000 (III)	$y = -320209.954x + 17.153 \quad r^2 = 0.974$
△	Hammami, Mw=127000 (III)	$y = -285585.477x + 15.830 \quad r^2 = 0.998$

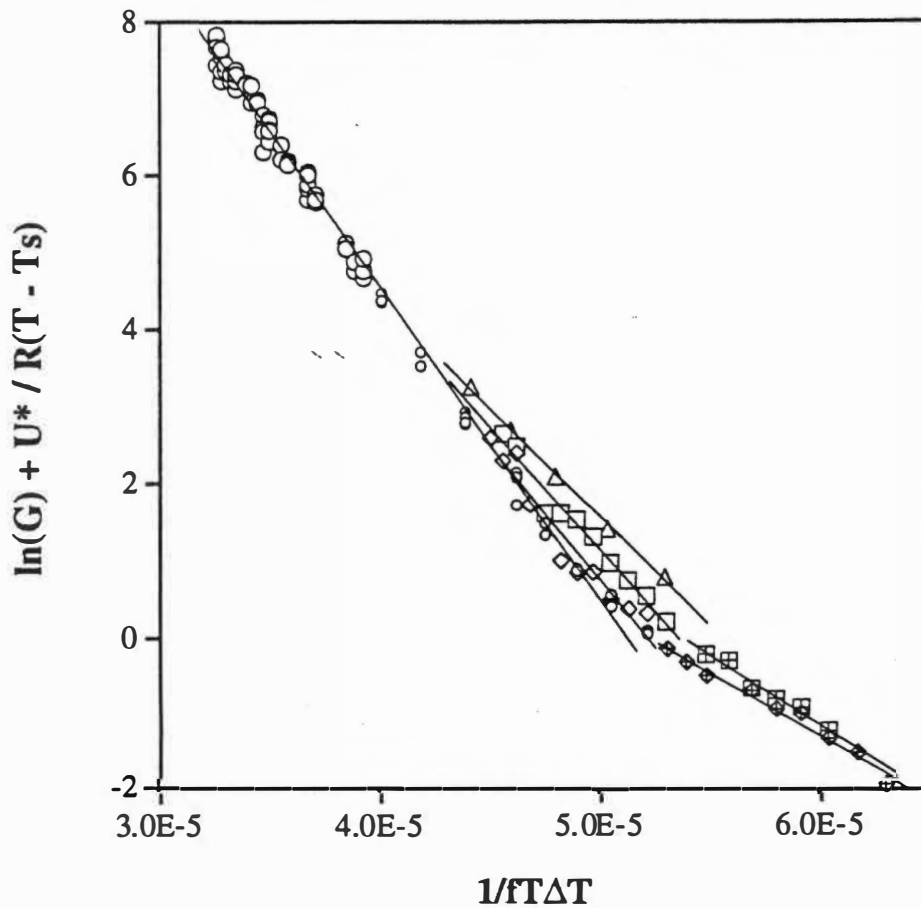


Figure 4.18. A comparison of predictions for the growth rate as function of crystallization temperature by Hoffman-Lauritzen equations, for Regime III, obtained in Figure 4.17.

4.8. Conclusions Concerning The Use Of The Nucleation Rate Function

A nucleation rate function is proposed to explain and describe the crystallization kinetic data. The proposed nucleation rate function gives the parameters in the Avrami equation new meanings. By using the nucleation rate function and the experimentally observed constant growth rate, the Avrami equation was more properly derived. Also by use of the nucleation rate function, various nonisothermal kinetic equations were shown to be special cases of the Avrami equation. The proposed nucleation rate function is a general function which includes all kinds of nucleation behavior. This made the derived Avrami equation general and suitable for crystallization with any type of nucleation rate. The Avrami index in the derived Avrami equation can be fractional, and the present analysis explains why this is often observed experimentally.

Growth rate obtained under isothermal and nonisothermal crystallization in the present research are well connected and can be described by one Hoffman-Lauritzen equation. This suggests that the growth rates measured in nonisothermal conditions using the present developed technique and under isothermal conditions appear to represent the same thing, but in different temperature range. This also suggested that the constant growth rate observed in the nonisothermal crystallization can be explained by a locally isothermal process. The present research extended the growth rate measurement to a much lower temperature range. The measured growth rates at temperatures below 116 °C down to 90 °C remain in crystallization regime III. The growth rate increases as crystallization temperature decreases in the temperature range 90 - 138 °C.

The overall crystallization rate characterized by crystallization half time increases as cooling rate increases (down to crystallization temperature 90°C).

The Avrami equation is applicable in the kinetic analysis to the data collected in the nonisothermal crystallization under rapid cooling conditions, at least in the primary crystallization stage. Such an application is based the assumption that the crystallization temperature can be represented by the plateau temperature and a single value for both the crystallization rate constant and the nucleation rate constant, can be used for the whole crystallization region. The Avrami plot showed a decrease in slope in the range where impingement occurs, similar to that observed for isothermal data. This would seem to indicate the presence of secondary crystallization. The Avrami index was independent of cooling rate in the range of cooling rates examined. The obtained Avrami index for primary crystallization was found to be between 3 and 4 with an average value of 3.58.

The crystallization rate constant defined by equation (4.32) is constant with time in a given crystallization process and increases as cooling rate increases due to the applied cooling conditions and resulting temperature of crystallization. Even though both Avrami index and crystallization rate constant are constant with time, the nucleation rate which may be described by the proposed nucleation rate function is a function of time. In the present examples, the nucleation rate decreases with time as the nucleation density saturates at some final value.

By introduction of the concept of nucleation rate function, it was shown that the nucleation rate constant can be separated from crystallization rate constant, and the nucleation index can be separated from the Avrami index. To separate the nucleation rate constant from the Avrami index, the reduction to the geometric index caused by impingement must be known. No information is available about the nucleation rate and the impingement effect. Further research needs to be done to find the relationship between geometric index and nucleation rate. By making a reasonable assumption about the geometric index, the nucleation rate was shown to increase with increase in cooling rate. The increase in nucleation rate as cooling rate increased was caused by increase in

nucleation rate constant. The temperature dependence of nucleation rate constant could be described by an equation similar to the one for crystallization rate constant.

For the present material, there was no significant difference in the Avrami index for crystallization under different cooling conditions. Assuming the geometric index is the same under different cooling condition, the nucleation index is independent of the cooling condition, or the manner of nucleation remains the same under different cooling conditions. Because the nucleation rate constant increases as cooling rate increases, the overall nucleation rate increases as cooling rate increases. The increase of the overall crystallization rate is caused by both increase in the nucleation rate and increase in the growth rate when cooling rate increases.

Chapter 5

QUIESCENT NONISOTHERMAL CRYSTALLIZATION OF ISOTACTIC POLYPROPYLENES

5.1. Introduction

This chapter applies the described technique and the approach described in Chapter 4, of using nucleation rate function and the Avrami equation derived by using the nucleation rate function to analyze the data for several polypropylene resins. The purpose of the research described in this chapter is to comprehensively test the new technique and approach through measurements on various materials, and to supply crystallization kinetic data for the melt spinning model described in Chapter 6. Materials with different molecular weight and polydispersity levels were chosen for this purpose. From among the available nine iPPs, which include three different levels of MW, in each of which there are three different levels of polydispersity, two extremes of polydispersities in each molecular weight level were selected to test the new technique. The results turned out quite convincing with respect to the validity of the technique. Thus no further tests for additional materials were necessary to verify the technique. The research was then changed toward application of the results in the spinning model which requires information about the molecular parameter dependence of the materials. This chapter deals with the influence of molecular parameters on the crystallization behavior of isotactic polypropylenes.

To effectively extract the nucleation rate from the bulk crystallization, the spherulite growth rate for each of the individual materials considered has experimentally been determined in addition to the overall crystallization rate. The purpose of the growth rate studies is also to compare the differences in MW and MWD without worrying about influences from nucleating impurities. Further, in order to ensure that the major effects observed were due to molecular weight and polydispersity differences, and not to

differences in isotacticity, FTIR and DSC techniques were employed to estimate the isotacticities.

5.2. Materials and Experimental

The resins studied in the experiments are isotactic propylene homopolymers, which are listed in Table 5.1. The materials are divided into three groups according to their molecular weight (MW). High MW: Resin #1 (narrow) and Resin #3 (broad); Medium MW: Resin #9 (narrow) and Resin #5 (broad); and low MW: Resin #8 (narrow) and Resin #6 (broad). The molecular weight and polydispersity data were supplied by Exxon Chemical Company.

The isotacticity data given in Table 5.1 was determined here. The method of estimating the isotacticity in the materials, which was proposed by Luongo (1960), was described by Williams (1995). However, in order to avoid the effect of the sample thickness, the reflection mode was applied in the present research. The sample thickness used for this purpose was 0.5 mm. The samples were prepared from pellets in a film press at 200 °C. The resin was preheated for 1 minute before being pressed. The pressure and temperature were maintained for 1 minute, then, the polymer was removed from the press and cooled down in the atmosphere. Further details of the technique and the results are presented in the next section of this chapter.

The isotacticity was also studied by DSC following Burfield, et al [Burfield, Patrick and Doi (1990)]. In the present studies, the ultimate crystallinity, the crystallinities obtained by heating and cooling the samples, and crystallization and melting temperatures have been determined. A first heating run was obtained by heating the polymer from 50 to 200 °C at a rate of 20 °C/min. After being maintained at 200 °C for 3 minutes, the first cooling run at a rate of 20 °C/min was made which is called the "cooling run" in the discussion below.

Table 5.1. Isotacticities Estimated By FTIR For All Six Isotactic Polypropylenes

Resin	MFR	Mn	Mw	Mz	$\frac{Mw}{Mn}$	$\frac{Mz}{Mw}$	A ₉₉₅ (Area of band 995 cm ⁻¹)	A ₉₇₄ (Area of band 974 cm ⁻¹)	$\frac{A_{974}}{A_{995}}$	Iso- tacticity (%)
#1	16N	55350	171810	317840	3.1	1.85	0.058	0.0736	1.268	91
#3	18B	44090	210850	704070	4.8	3.3	0.0213	0.0253	1.189	93
#9	35N	49930	141790	251270	2.8	1.8	0.1598	0.1852	1.159	93
#5	42B	40480	162680	479130	4.0	3.0	0.0335	0.0374	1.115	94
#8	78N	42170	118920	199980	2.8	1.7	0.162	0.1849	1.142	93
#6	75B	34490	136060	408280	3.8	3.0	0.0881	0.105	1.192	93

The second heating run at the same condition as the first one is called the "heating run". From the crystallization onset temperature obtained in the cooling run, a temperature for isothermal crystallization was selected by adding 7 °C to the crystallization onset temperature. The same sample was heated up again with a rate of 20 °C/min to 200 °C. After being maintained at that temperature for three minutes, the polymer was cooled down to the selected isothermal crystallization temperature at a rate of 100°C/min. The sample was allowed to crystallize and anneal at the chosen crystallization temperature for 15 minutes. With the selected crystallization temperature, the crystallization is completed within 4 minutes, and the sample was annealed for greater than 10 minutes. This crystallization procedure is called the "annealed run". The sample was heated again from 50 to 200 °C with a rate of 20 °C/min to determine the ultimate crystallinity created by the annealing run from the heat of fusion.

The crystallization of the six chosen iPPs have been studied under rapid cooling, the bulk crystallization rate being measured by following the intensities of the depolarized light as described in Chapter 3. The applied cooling intensity and corresponding average cooling rate of the experiments are given in Figure 5.1.

The relative nucleation densities of the samples were estimated by directly counting the number of nuclei under the field of microscope, 150x205 μm in size. The measured nucleation density quantitatively describes the visual picture seen by the eye. The counted nuclei include only the focused ones and do not include the ones covered by spherulites on top of them. This method gives a more correct description of relative nucleation density when nucleation rate is high or the size of the spherulites is small since they cover fewer spherulites below them. The spherulites counted basically represent the final relative nucleation density in the sample, but the method is only an estimation of the relative nucleation density in the samples.

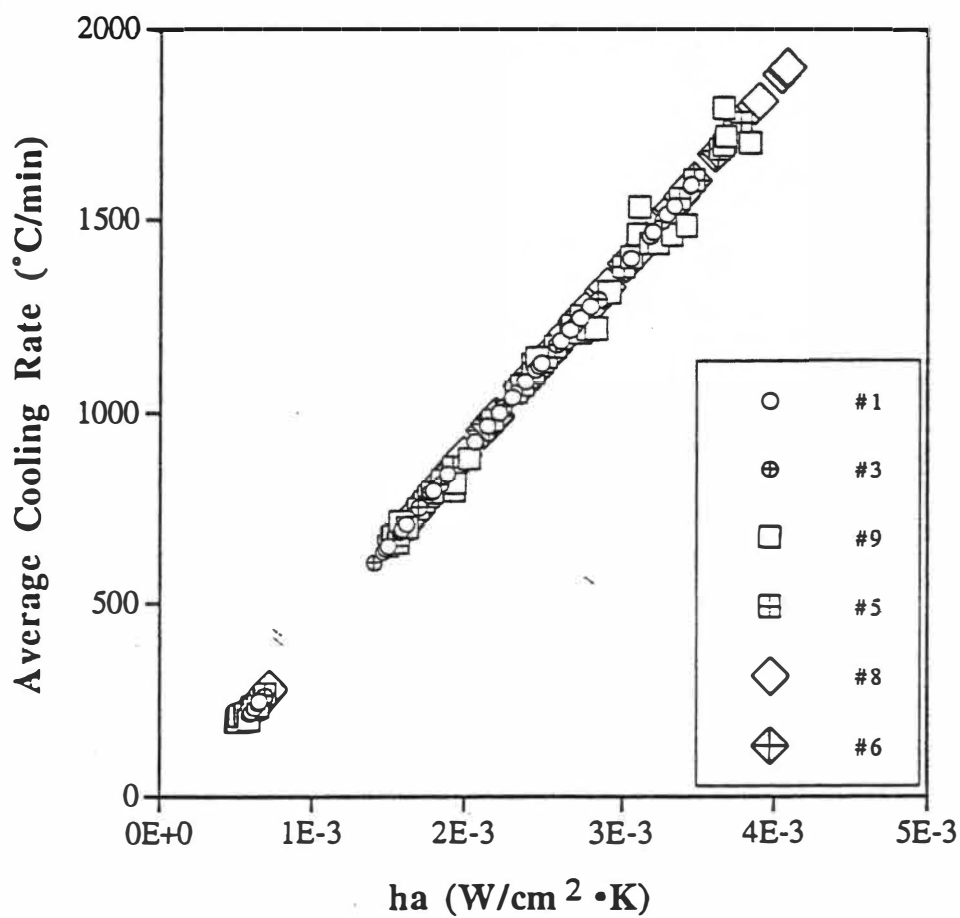


Figure 5.1. Average cooling rate versus heat transfer coefficient applied in the experiments.

5.3. Preliminary Characterization Of The Materials

The isotacticities estimated by FTIR for all six iPPs are given in Table 5.1. The isotacticity listed in Table 5.1 was calculated from the area ratio of the band at 974 cm^{-1} to that at 995 cm^{-1} according to the calibration described by Williams (1995). Because of slight differences in experimental technique between the present measurements and those of Williams, it was found that the band area ratio for Resin #9 (named as MT - iPP in Williams's work) was not precisely the same in the two cases. Consequently, a conversion factor of 1.581/1.159 has been applied in order to use her calibration equation to obtain the isotacticity for the present materials. The results are listed in Table 5.1. The estimated precision of these relative isotacticities is ± 1 to 2 percent. The difference in isotacticity among all six materials studied in the present research is small and probably not significant according to the FTIR result shown in Table 5.1.

The results from DSC measurement are given in Table 5.2. The purpose of the DSC studies is also to examine the isotacticity of the materials. For this purpose the crystallinity measured for samples after they were annealed is important. The annealed crystallinity developed in the samples reflects the regularity of molecular chains in the sample. For isotactic homopolymer this regularity is isotacticity. From the value of annealed crystallinities listed in Table 5.2 we can see that the difference of the isotacticity among all six materials is not significant according to DSC measurement. One also may notice that the difference of the crystallinity determined from cooling runs is small, while the crystallization temperature does exhibit difference that are outside the standard deviation for a given material. It appears that these effects are probably due to differences in molecular weight or nucleating impurities in the samples as discussed below, rather than due to differences in isotacticity.

Table 5.2. Crystallization Temperature, Melting Temperatures And Crystallinities Determined By DSC For All iPPs

Sample	Cooling (20°C/min)			Heating (20°C/min)			Heating (20°C/min) After samples being annealed		
	T _c (°C)	ΔH (J/g)	X _c	T _m (°C)	ΔH (J/g)	X _c	T _m (°C)	ΔH (J/g)	X _c
#1	105.2	98.0	0.594	162.8	92.3	0.559	164.7	106.5	0.645
#3	109.9	99.2	0.601	163.1	98.2	0.595	166.6	104.7	0.635
#9	104.1	96.4	0.584	165.1	89.7	0.544	165.6	107.4	0.651
#5	109.6	99.9	0.605	162.7	98.6	0.598	165.4	108.7	0.659
#8	109.4	100.0	0.606	160.2	102.1	0.619	163.6	107.1	0.649
#6	103.8	99.9	0.605	157.9	94.9	0.575	161.3	107.1	0.649

5.4. Results

5.4.1. Crystallization Plateau Temperature, Induction Time And Onset Temperature

The plateau temperatures are given in Figure 5.2, all decreasing as cooling rate increases. Excluding Resin #8, the higher MW resins exhibit higher crystallization plateau temperature at the same cooling rate. Generally, the influence of MW seems greater than the influence of MWD, but the effect of the latter is inconsistent. Resin #8 has the highest T_p of the six considered iPPs. The reasons for this are not immediately obvious, but it will be shown that this is related to the presence of excessive adventitious nuclei in the sample. The variations of nucleation rate for all the samples will be compared.

Figure 5.3 gives the measured crystallization induction time for the six iPPs. Surprisingly, all induction times fall on a single curve, decrease as cooling rate increases. Crystallization onset temperatures are plotted also in Figure 5.3, which reduce as cooling rate increases, and tends to fall on one curve, although there is substantial scatter.

The crystallization onset time and temperature given in Figure 5.3 are plotted according to equation (4.37) in Figure 5.4. All data fall approximately on one curve. Equation (4.37) can reasonably relate induction time to onset temperature for all materials. From the slope and intercept, $C_I = 403965 \text{ [K}^2\text{]}$ and $\ln[(\frac{1}{t_0})_0] = 13.435$ are obtained. The values of C_I and $\ln[(\frac{1}{t_0})_0]$ can be used for various iPP because both relationships of t_0 versus h_a and T_{on} versus h_a are independent of the material characteristics.

5.4.2. Crystallization Half Time

The crystallization half-times for all materials are given in Figure 5.5. The circles were determined directly from experimental relative crystallinity versus time data by finding

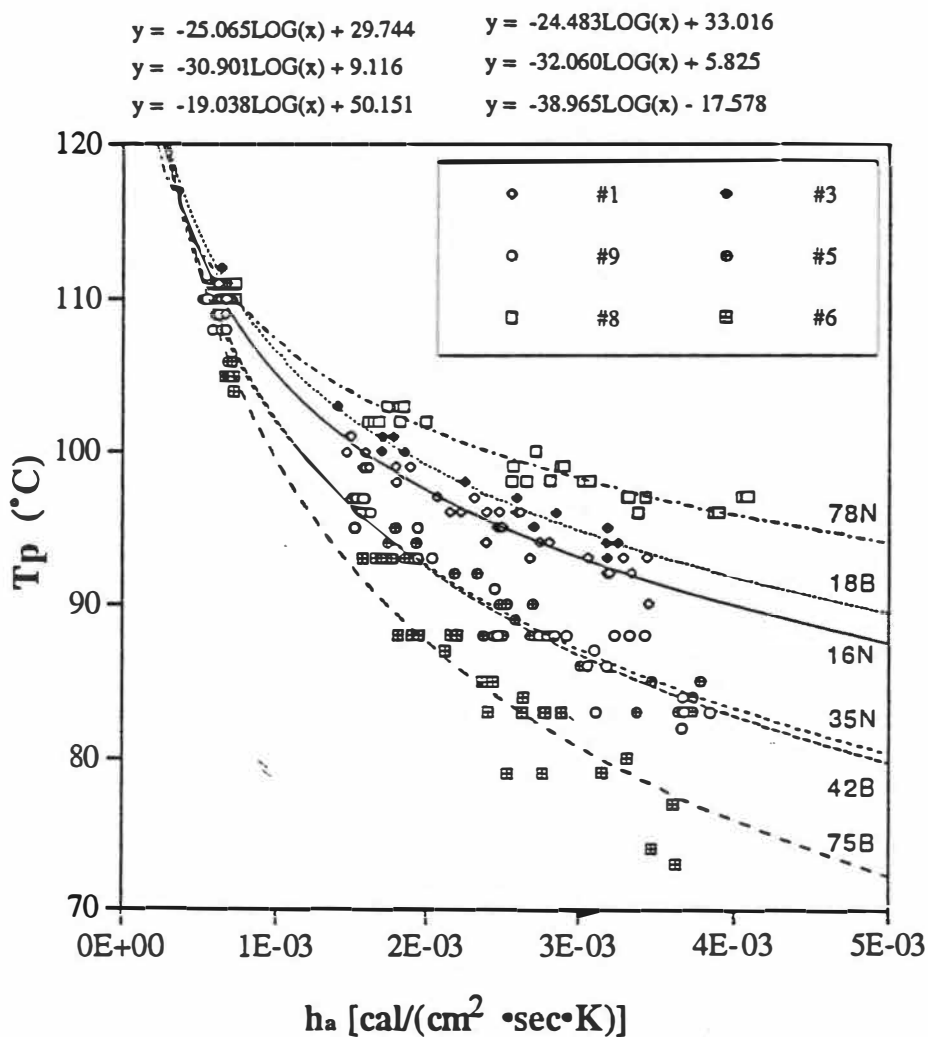


Figure 5.2. Crystallization plateau temperature T_p versus heat transfer coefficient h_a for all six materials considered.

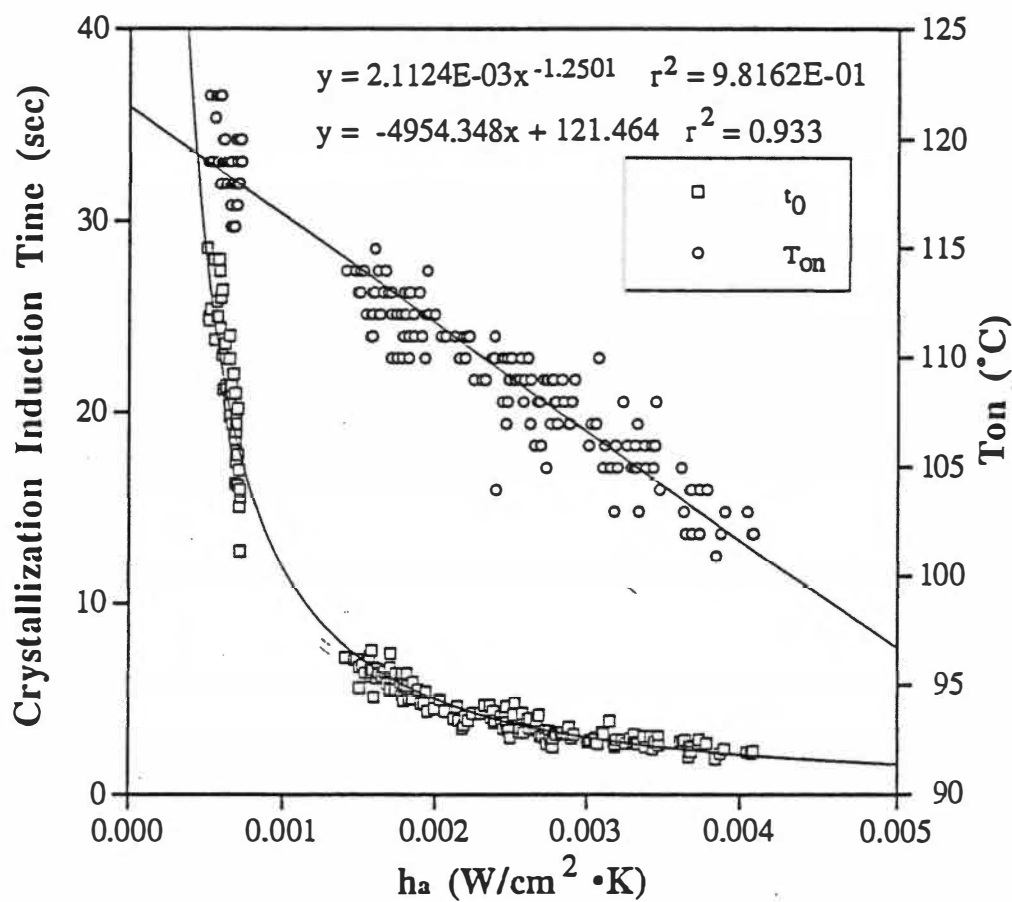


Figure 5.3. Crystallization induction time and crystallization onset temperature versus cooling rates, described by heat transfer coefficient, for all six materials.

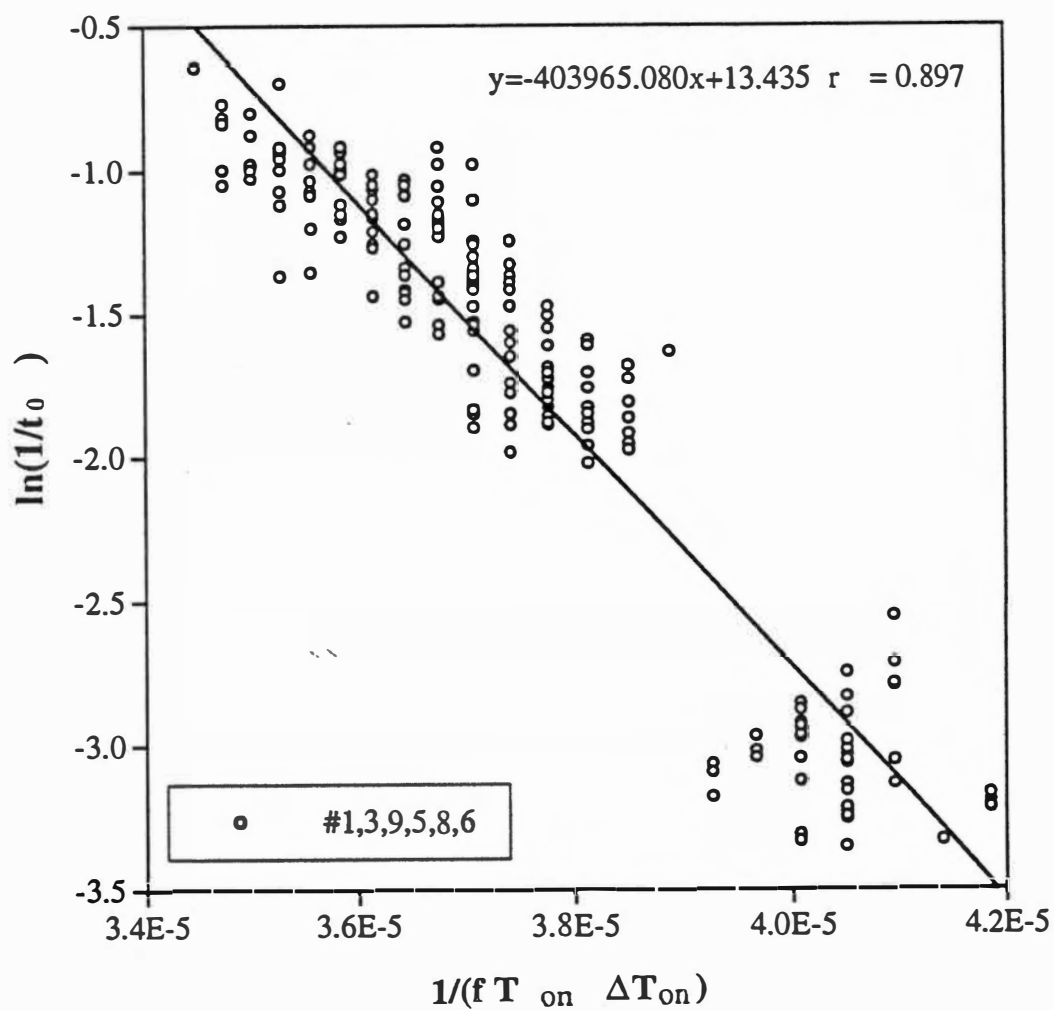


Figure 5.4. Relating crystallization induction time to the crystallization onset temperature according to Equation (4.37).

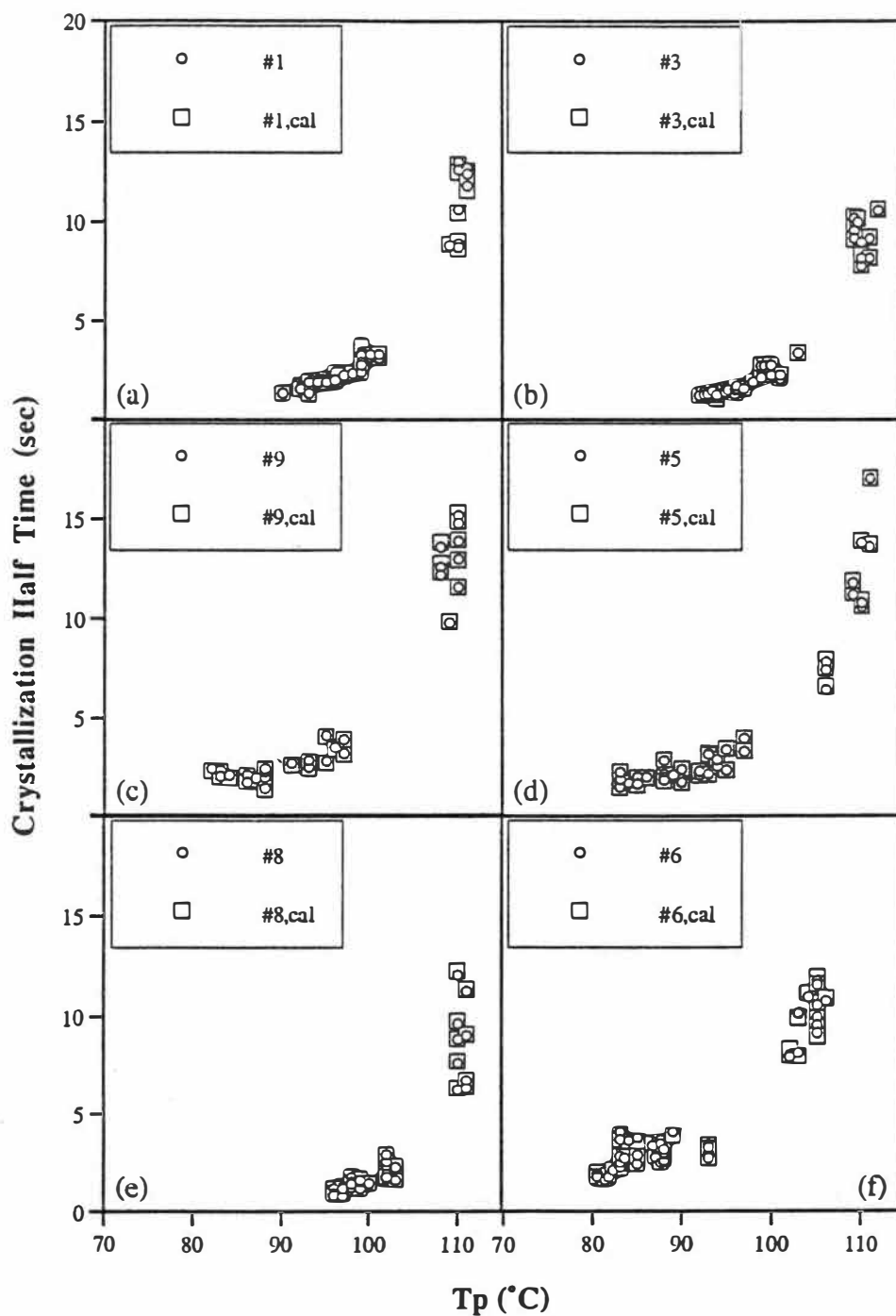


Figure 5.5. The crystallization half-time obtained directly from θ -t plot, $t_{1/2}$ (circles), and calculated from crystallization rate constant and Avrami index, $t_{1/2,cal}$ (squares), versus plateau temperature, T_p , for six considered iPPs.

the time when relative crystallinity reaches 50%. The squares were calculated from the Avrami index and the crystallization rate constant as described below. The fact that the two results are essentially identical demonstrates the internal consistency of the data and the Avrami analysis. The crystallization half-time decreases as cooling rate increases for all six resins. The data for each sample lies on a reasonably smooth curve, though there are substantial differences between the curves for the different samples. A better comparison between crystallization half-time for the six materials is given in Figure 5.6, in which half-time is plotted on a log scale against plateau temperature. From Figure 5.6 we can see that, except Resin #8, the higher the molecular weight, the shorter is the crystallization half-time. For materials with broad MWD in the highest MW group, Resin #1 and #3, the curve for broad MWD, Resin #3, is below the one for narrower material, Resin #1. Whereas, for medium MW materials, the broad one, Resin #5, is a little bit above the narrow one, Resin #9. The curve for Resin #8, occupies the highest position in the figure despite the fact that it has low MW and narrow MWD.

The half-time can be related to temperature according to the equation (5.2):

$$\frac{1}{t_{1/2}} = \left(\frac{1}{t_{1/2}}\right)_0 \exp\left(\frac{U^*}{R(T - T_s)}\right) \exp\left(\frac{C_{t12}}{T\Delta T f}\right) \quad (5.2)$$

Replacing the crystallization temperature by the plateau temperature, the data in Figure 5.6 are plotted in Figure 5.7 according to equation (5.2). From Figure 5.7 one can see that the data for each material falls on its own straight line and follows equation (5.2) well. The line of highest crystallization rate for Resin #8 is above all other curves and has largest slope and intercept. As the half-time decreases, the curves in Figure 5.7 tend to have decreasing values in both slope and intercept. The regression constants are given in Table 5.3.

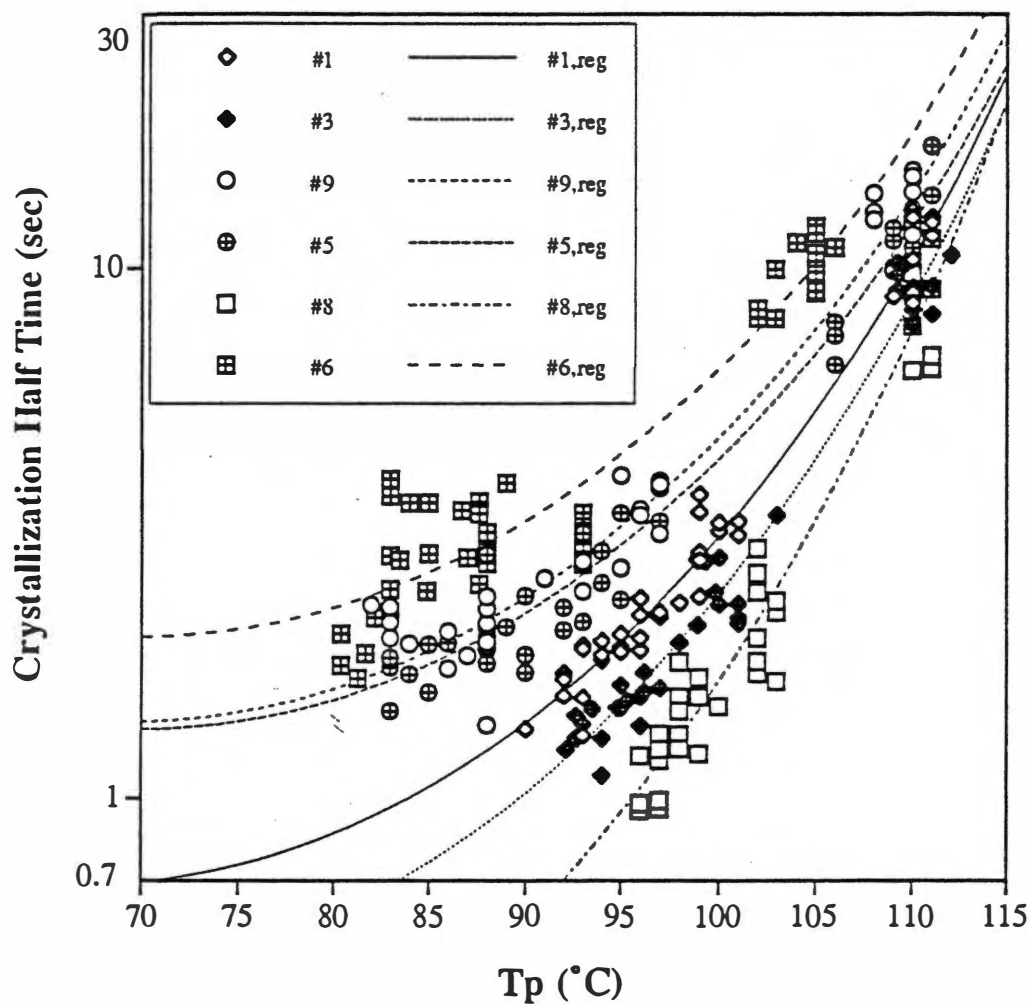


Figure 5.6. A comparison of crystallization half-time versus plateau temperature among the six examined iPPs.

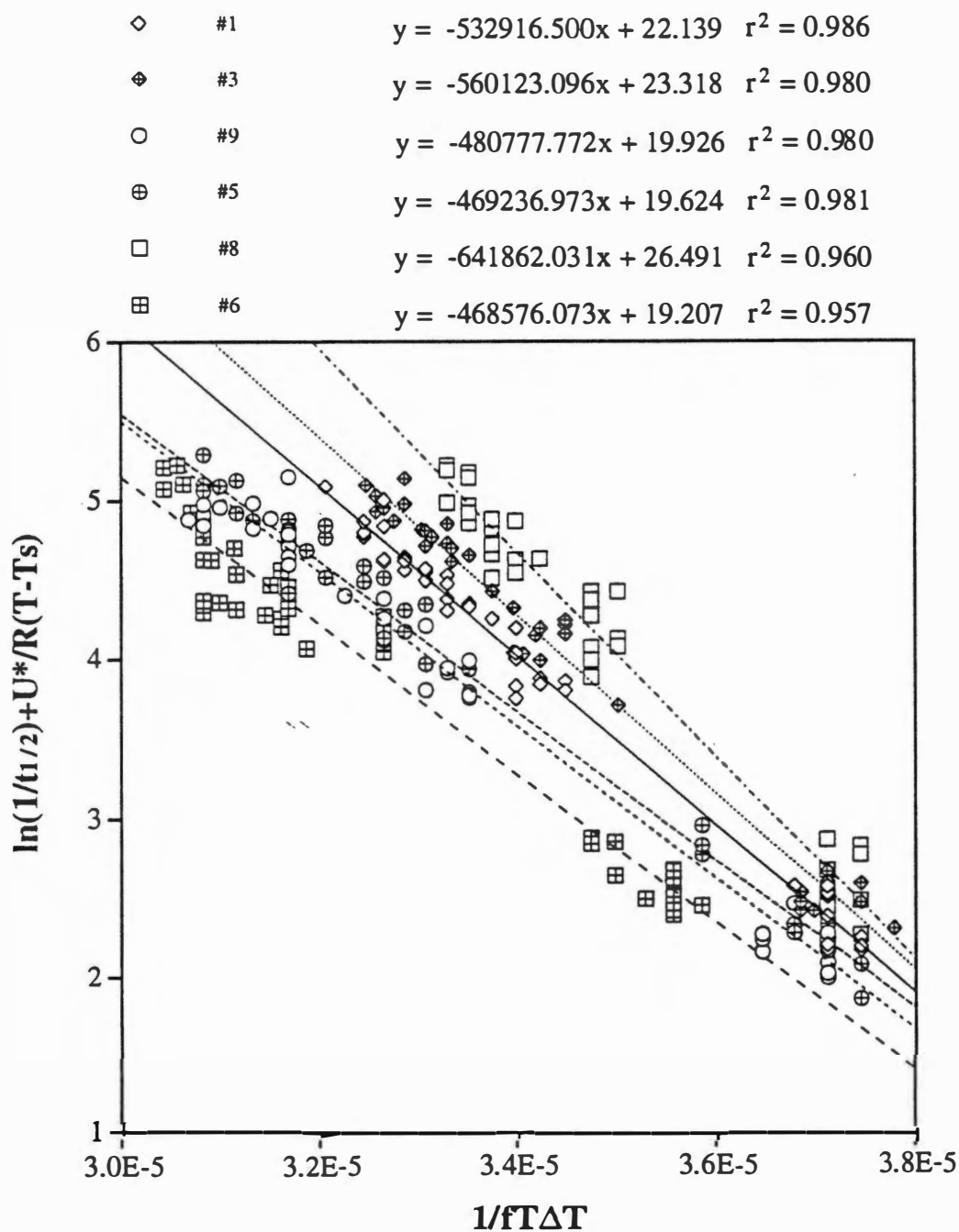


Figure 5.7. $\ln(1/t_{1/2}) + U^*/R(T-T_s)$ versus $\frac{1}{T\Delta T f}$ for the data plotted in Figure 5.6.

Table 5.3. Summary Of The Regressive Constants And Coefficients For Crystallization Half-time, Crystallization Rate Constant, And Nucleation Rate Constant

Resin	C_{t12} $\cdot 10^5(K^2)$	$\ln\left(\frac{1}{t_{1/2}}\right)_0$	$r^2(t_{1/2})$	C_k $\cdot 10^5(K^2)$	$\ln(k)_0$	$r^2(k)$	C_N $\cdot 10^5(K^2)$	$\ln(N_c)_0$	$r^2(N_c)$
#1	5.329	22.139	0.99	16.824	57.845	0.98	10.668	52.112	0.95
#3	5.475	22.956	0.99	16.711	58.853	0.98	10.921	53.828	0.96
#9	4.808	19.926	0.98	9.781	34.153	0.97	4.672	30.799	0.89
#5	4.692	19.624	0.98	13.039	43.862	0.97	8.336	42.845	0.93
#8	6.419	26.491	0.96	24.821	87.287	0.95	19.201	83.674	0.91
#6	4.364	18.127	0.96	10.598	34.506	0.91	6.635	35.944	0.82

5.4.3. Growth Rate Measurements

The measured spherulite growth rates for materials are given in Figure 5.8, both isothermal and nonisothermal data being plotted. Figure 5.8 shows that the observed behavior of growth rate as a function of temperature described in Chapter 4 for Resin #3, is also true for the other five materials. Figure 5.9 puts all the experimental growth rate data together, and basically shows us that there is little difference in growth rate for the samples.

The growth rate data shown in Figure 5.9 are plotted in Figure 5.10 according to the Hoffman-Lauritzen equation, equation (2.3). Again the isothermal and nonisothermal growth rate data for each materials is well connected and they fall on one straight line. To compare the materials, curves in Figure 5.10 are put together in Figure 5.11. It appears that there are, at most, small differences in growth rate among the materials. The differences existing among the materials are thus given by the difference in slope and intercept of the Hoffman-Lauritzen equation in Figure 5.11 or K_g and $\ln(G_0)$, given in Table 5.4.

To carefully compare the difference in growth rate caused by material characteristics, the data are now plotted according to the given polydispersity, M_w/M_n , with variation of MW in Figure 5.12, and given MW with variation in polydispersity in Figure 5.13. From Table 5.1 we can see that variation of M_z is quite consistent with variation of M_w/M_n , i.e., the examination of effects of M_w/M_n can result in similar conclusions as examination of M_z for these materials. Figure 5.12 shows that the materials with high MW, Resin #1 and #3 have slower growth rate than the ones with medium MW, Resin # 9 and #5, and low MW, Resin #8 and #6. The difference is more evident for the groups with narrow molecular weight distribution, Figure 5.12-(a). The difference becomes larger when crystallization temperature is higher. There are no significant differences in growth rate between materials with medium and low MW.

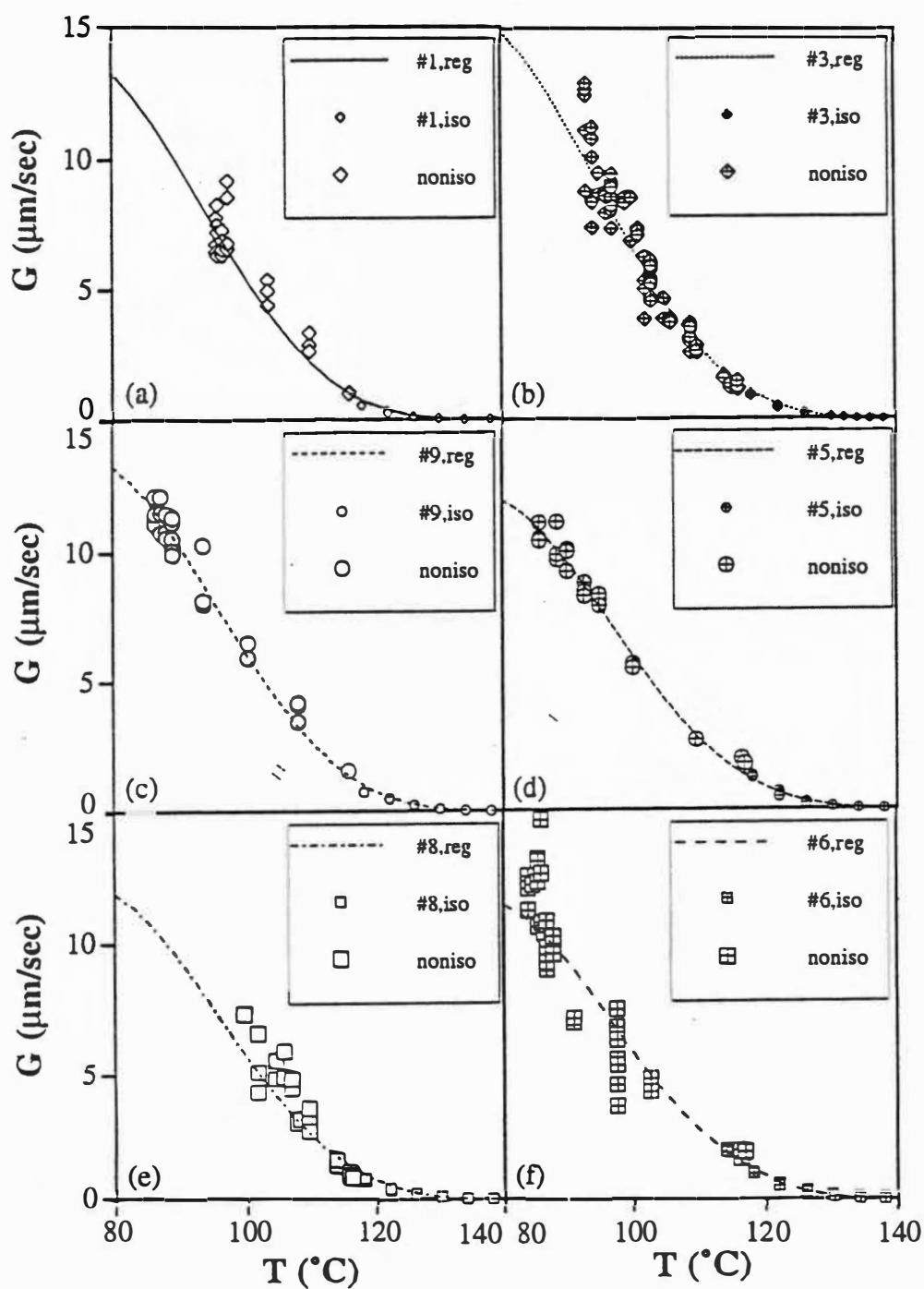


Figure 5.8. Growth rates measured under iso- and nonisothermal crystallization for six considered materials, individually plotted.

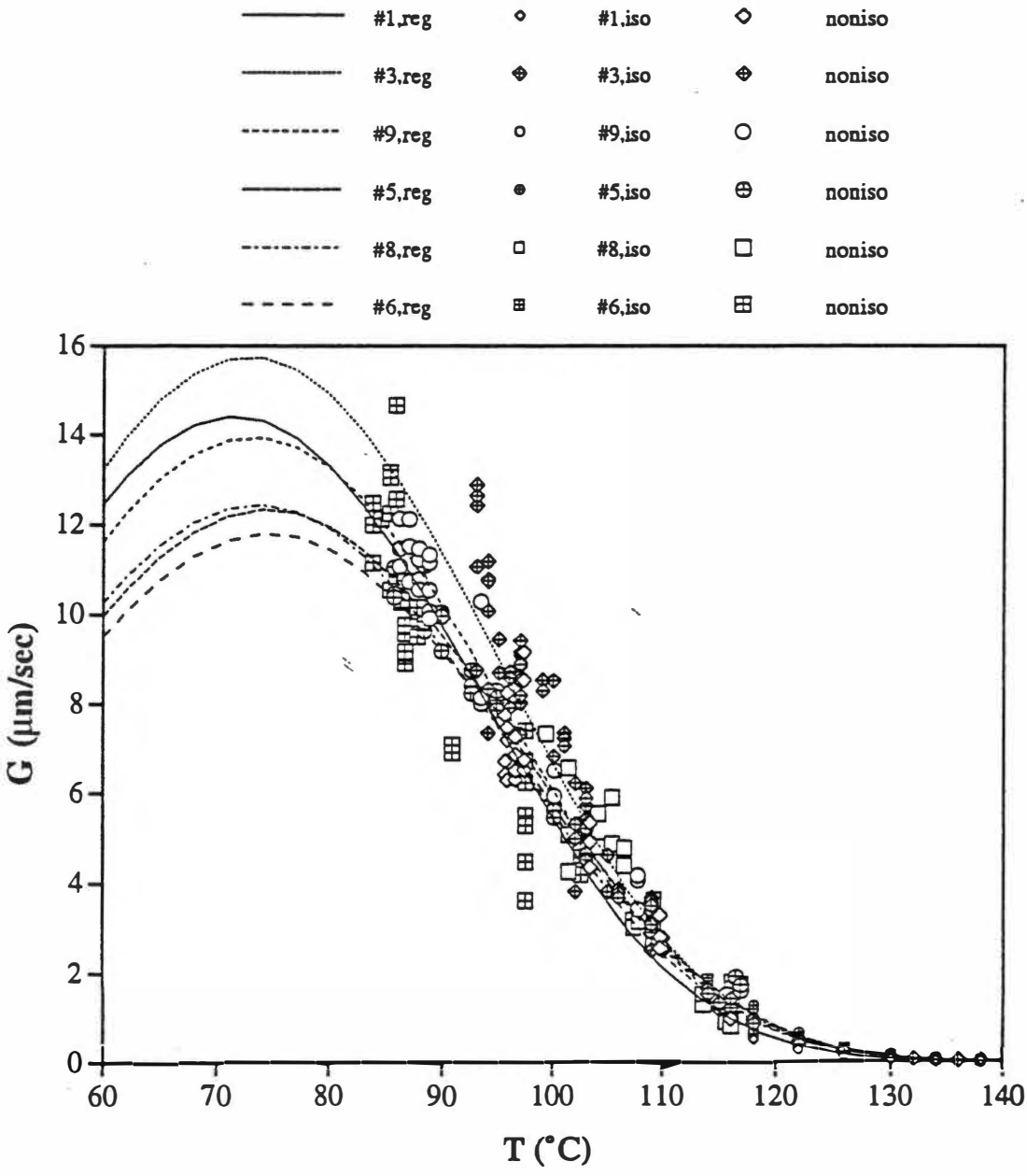


Figure 5.9. Measured growth rates and regressive curves for all six materials.

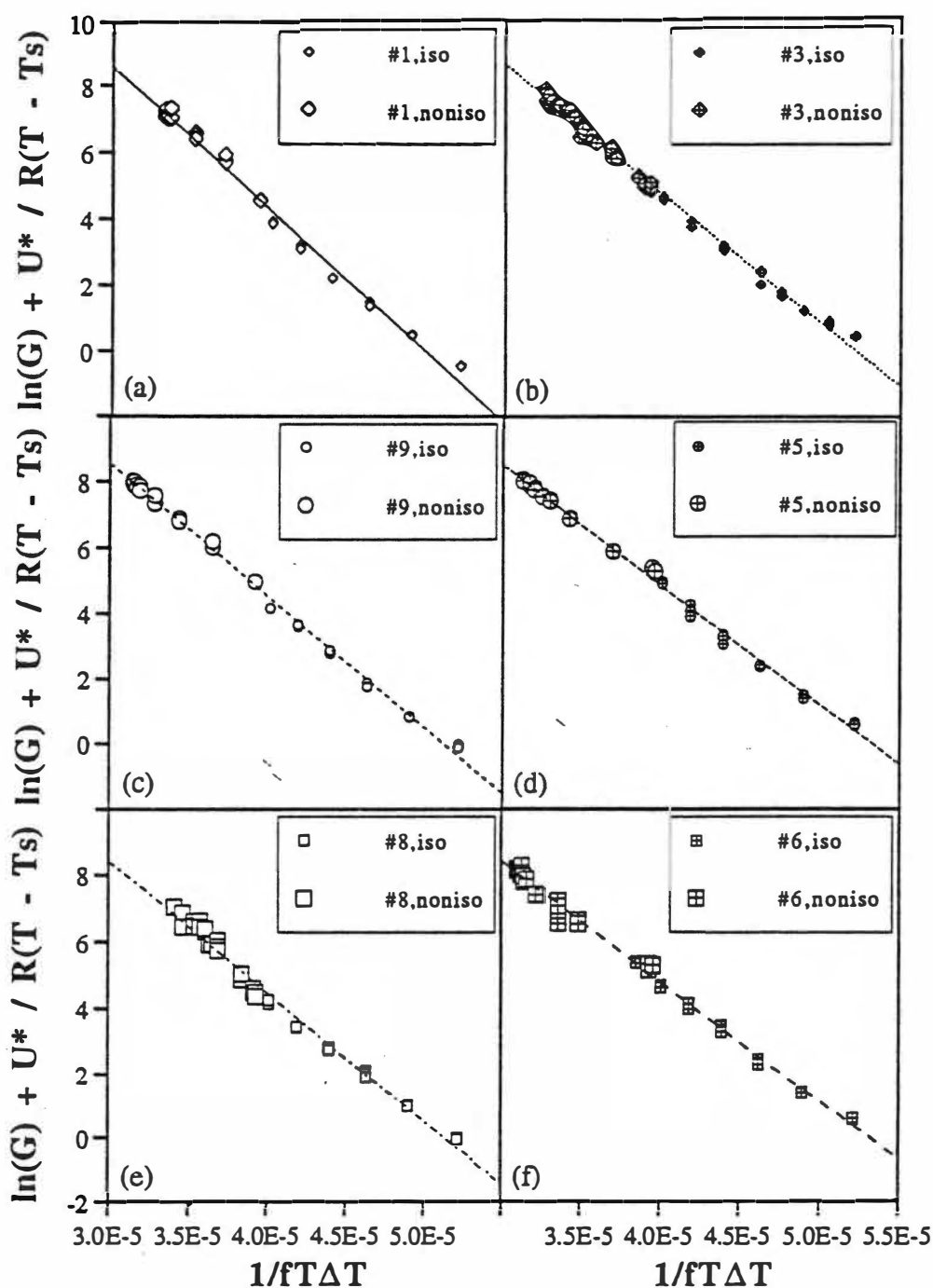


Figure 5.10. Hoffman-Lauritzen plot of growth rates for the six considered materials, separately plotted.

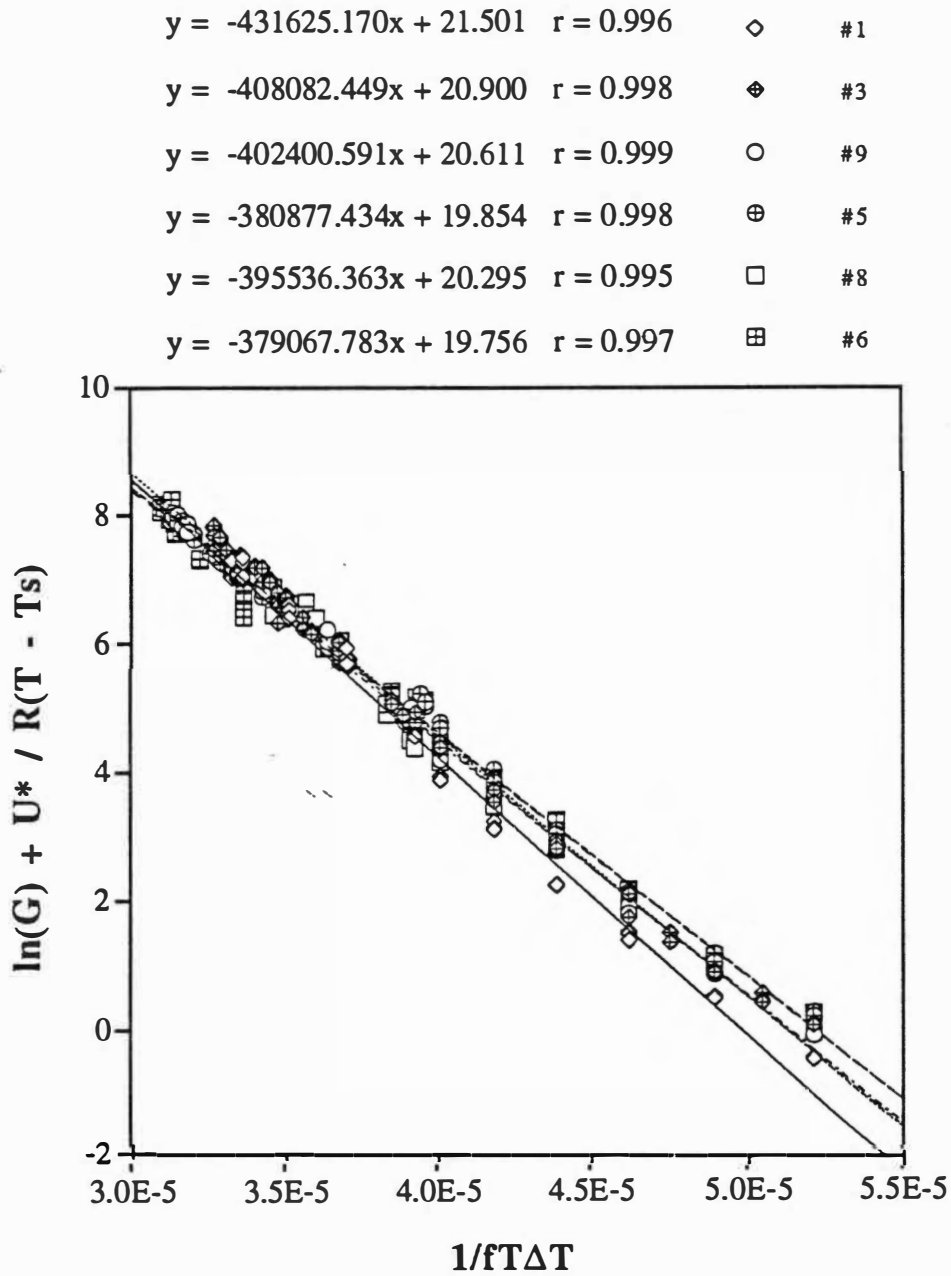


Figure 5.11. Hoffman-Lauritzen plot of growth rates for the six considered materials, comprehensively plotted.

Table 5.4. Summary Of Regressive Constants, K_g And $\ln(G_0)$, In The Hoffman-Lauritzen Equation And Square Of Regressive Coefficient, r^2 , For All Six iPPs.

Resin	MFR/MWD	K_g (K^2)	$\ln(G_0)[\ln(\mu\text{m}/\text{sec})]$	r^2
#1	16N	431625	21.501	0.992
#3	18B	408082	20.900	0.995
#9	35N	402401	20.611	0.998
#5	42B	380877	19.854	0.996
#8	78N	395536	20.295	0.989
#6	75B	379068	19.756	0.994

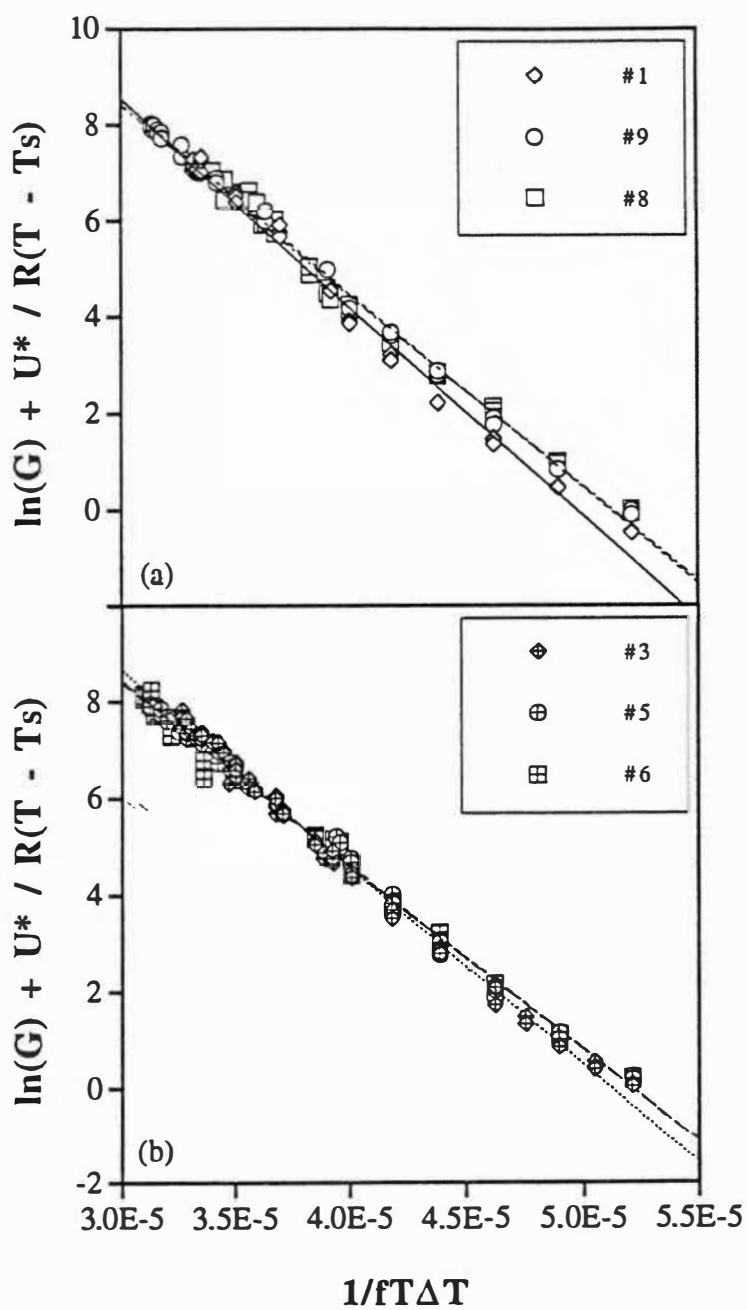


Figure 5.12. Comparison of the effect of molecular weight (MW) on the growth rate, G : (a) narrow breath; and (b) broad breath.

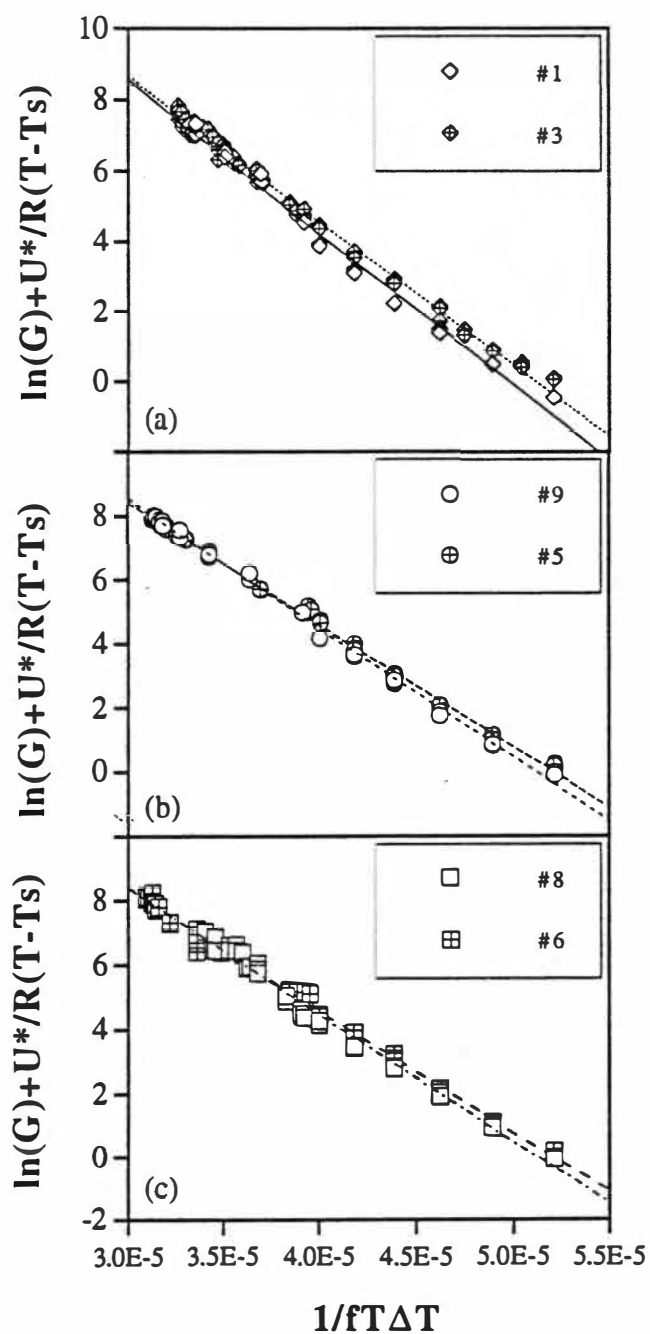


Figure 5.13. Comparison of the effect of molecular weight distribution on the growth rate: (a) high MW, (b) medium MW, and (c) low MW.

Figure 5.13 shows the effect of molecular weight distribution on the growth rate. Generally, the curve for the samples with wide breadth is located above the ones with narrow distribution, and the distance becomes larger in the high crystallization temperature range. This difference is more evident at high M_w level, Resin #1, 3, see Figure 5.13-(a).

The Hoffman-Lauritzen plots of Figures 5.12 and 5.13 actually display or emphasize the difference at low values of growth rate, i.e., isothermal data. The nonisothermal data or high value of growth rate at low crystallization temperature is compressed by the nature of the plot and show little difference in growth rate for different materials in this lower temperature range. To compare the possible difference at low temperatures Figure 5.9 needs to be reexamined.

Also shown in Figure 5.9 are the locations of the regression curves obtained from the Hoffman-Lauritzen plots. The comparison of the difference in growth rates can now be made using the regressive curves, by which the random fluctuation is statistically removed. Please note that when the difference in growth rate is discussed, only the range covering the experimental data is used. Such a range refers to the crystallization temperature from 80 to 138 °C. To clearly examine the difference in growth rate for different material, growth rate data from Figure 5.9 at temperatures of 80, 89, 98, 107, 116, 125, and 134 °C, will be plotted against M_w and M_w/M_n at constant temperatures. These plots are shown in Figures 5.14 and 5.15, and are designed to show the difference in growth rate at different temperatures. To clearly examine the difference both at low and high temperature, both linear and logarithmic scales are used. For comparison of growth rate at high value at low temperature, the linear plot is better, and for lower value at high temperature, the logarithmic scale is clearer.

The comparison of the growth rate at different crystallization temperature with different MW at broad MWD, Resins #3, 5, and 6, is given in Figure 5.14. One can see at

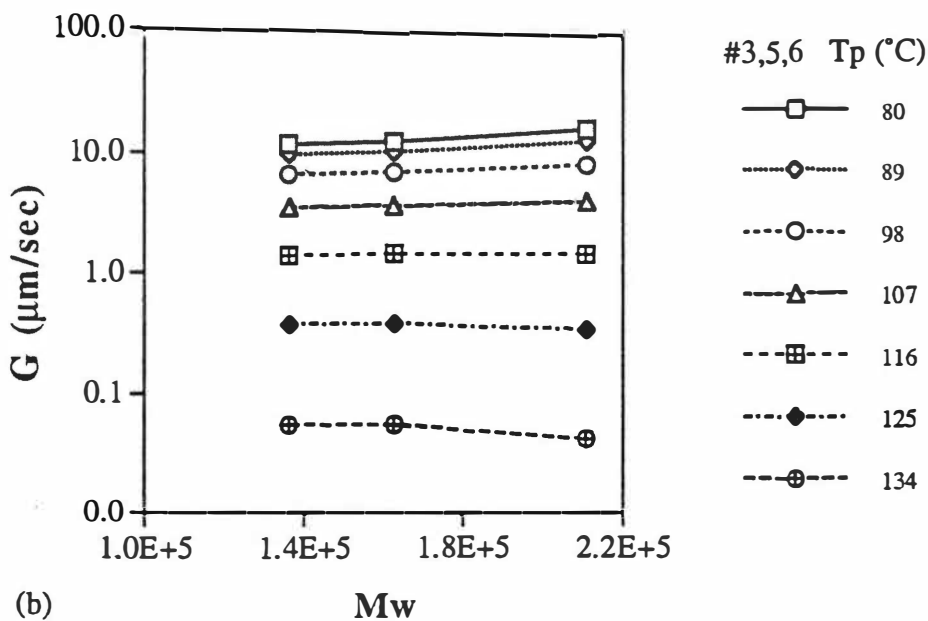
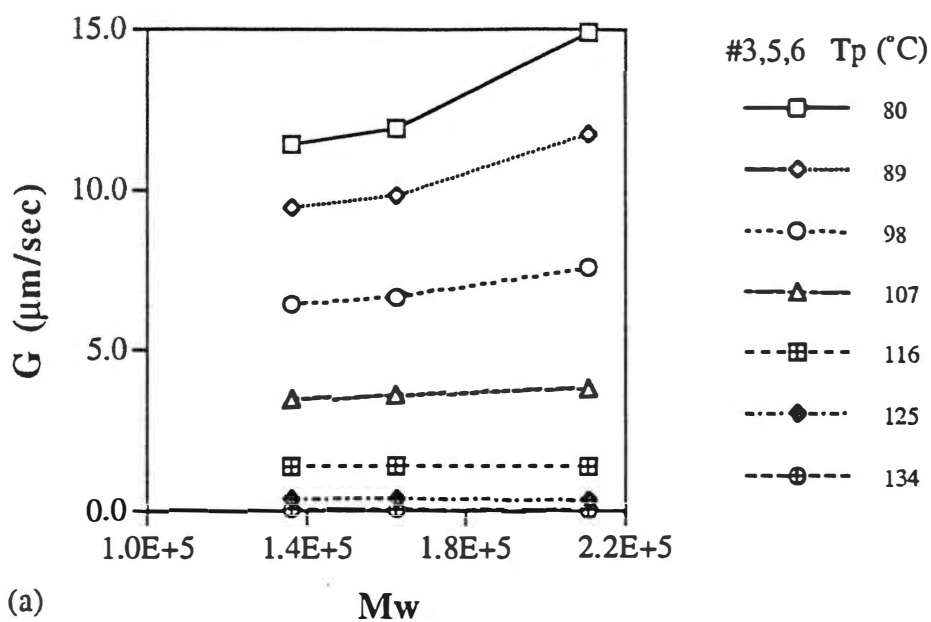


Figure 5.14. Growth rate versus molecular weight at different crystallization temperature for broader MWD materials, Resin #3, 5, and 6.

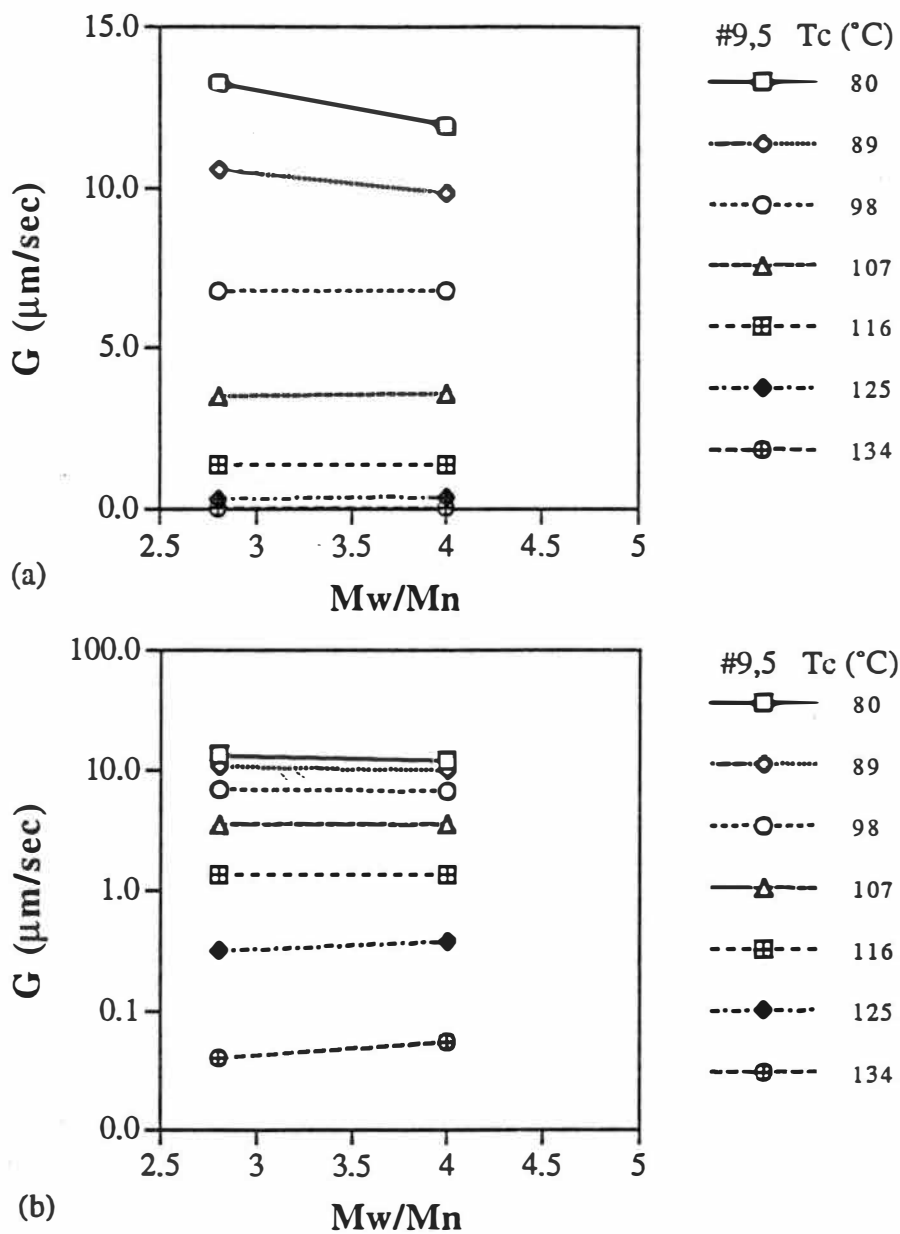


Figure 5.15. Growth rate versus polydispersities at different crystallization temperature for medium MW materials. Resin #9 and 5.

once that at lower crystallization temperature the growth rate increases with increase in MW, Figure 5.14 - (a), while at higher temperature, it decreases with MW, see Figure 5.14 - (b). The transition temperature is around 116°C. Similar trends were found when the narrow materials, Resins #1, 9, and 8 were compared.

Figure 5.15 compares the difference in growth rate with polydispersity at medium MW level, Resins #9, and #5. As shown in Figure 5.15, the growth rate increases with increase in breadth in the high crystallization temperature range. In the low crystallization temperature range, the growth rate decreases with increase in breadth. The transition temperature is about 107 °C for material with medium MW. Similar situation can be found for materials with low MW with transition temperature about 107 °C. The materials with high MW, Resins #1 and 3, exhibits the same trend that increase in MWD increases the growth rate at both low and high temperatures.

5.4.4. Relative Nucleation Densities

The measured relative nucleation density for the various materials are given in Figure 5.16. As shown in Figure 5.16, Resin #8 has the highest relative nucleation density among the six materials at a given crystallization temperature. The materials in the highest MW group, Resins #3 and 1, exhibit nucleation densities significantly higher than for medium and low MW group, but lower than for Resin #8. There is little difference between the medium and the low MW group except for Resin #8. The differences between materials with different MWDs but similar MW are also small.

5.4.5. Avrami Index And Crystallization Rate Constant

Even though the crystallization half-time relates to the crystallization plateau temperature well, one still needs Avrami index, crystallization rate constant, or nucleation

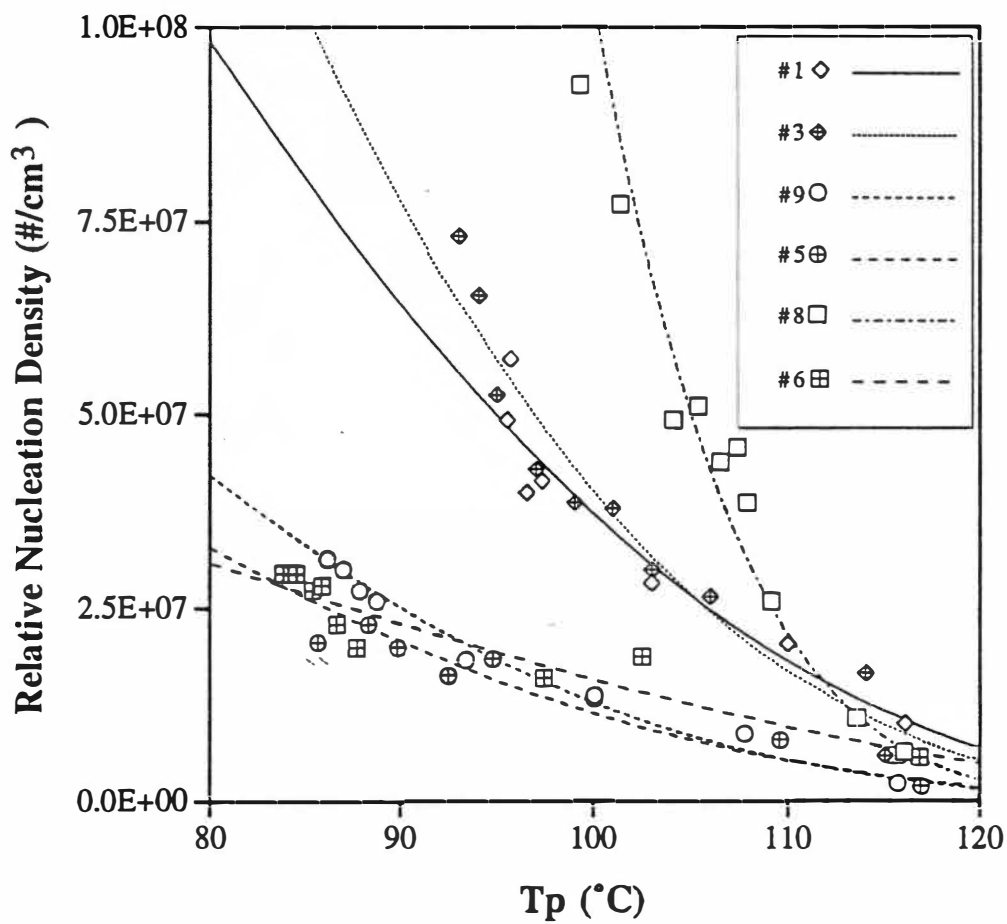


Figure 5.16. Measured relative nucleation density for all six considered iPPs.

rate from bulk crystallization experiments so that we can use the Avrami equation to simulate crystallization processes.

The Avrami indexes for all iPPs are given in Figure 5.17. From Figure 5.17, one can see that the values of Avrami index are scattered from run to run at different cooling rates for an individual material, but there is no significant trend for Avrami index to vary with applied cooling rates for any of the materials. Under these conditions it seems reasonable to average the values of Avrami index for each resin, the result of which is summarized in Table 5.5. As shown in Figure 5.17 and Table 5.5, The average Avrami index varies between materials. There is no big difference in Avrami index among Resin #1, #3, #5, and #6. Resin #8 has significantly higher value of Avrami index, and Resin #9 has a small Avrami index.

The crystallization rate constants for all materials are given in Figure 5.18. The triangles represent the results obtained directly from the intercept of the Avrami plot. The origin of the circles will be discussed below. Generally, the rate constant determined by the Avrami analysis increases as cooling rate increases or the plateau temperature decreases for all polymers.

A relationship exists between the crystallization rate constant, Avrami index and crystallization half-time. This relationship is

$$\ln(2) = k \cdot t_{1/2}^n \quad (5.1)$$

With the Avrami index and crystallization rate constant in Figure 5.17 and 5.18, this equation gives the crystallization half-times shown as squares in Figure 5.5. A comparison between calculated half-time, $t_{1/2,cal}$, and directly collected from the curves of relative crystallinity versus time, $t_{1/2}$, gives the conclusion that they are essentially identical as shown Figure 5.5. Figure 5.19, in which $t_{1/2,cal}$ was plotted against $t_{1/2}$, further

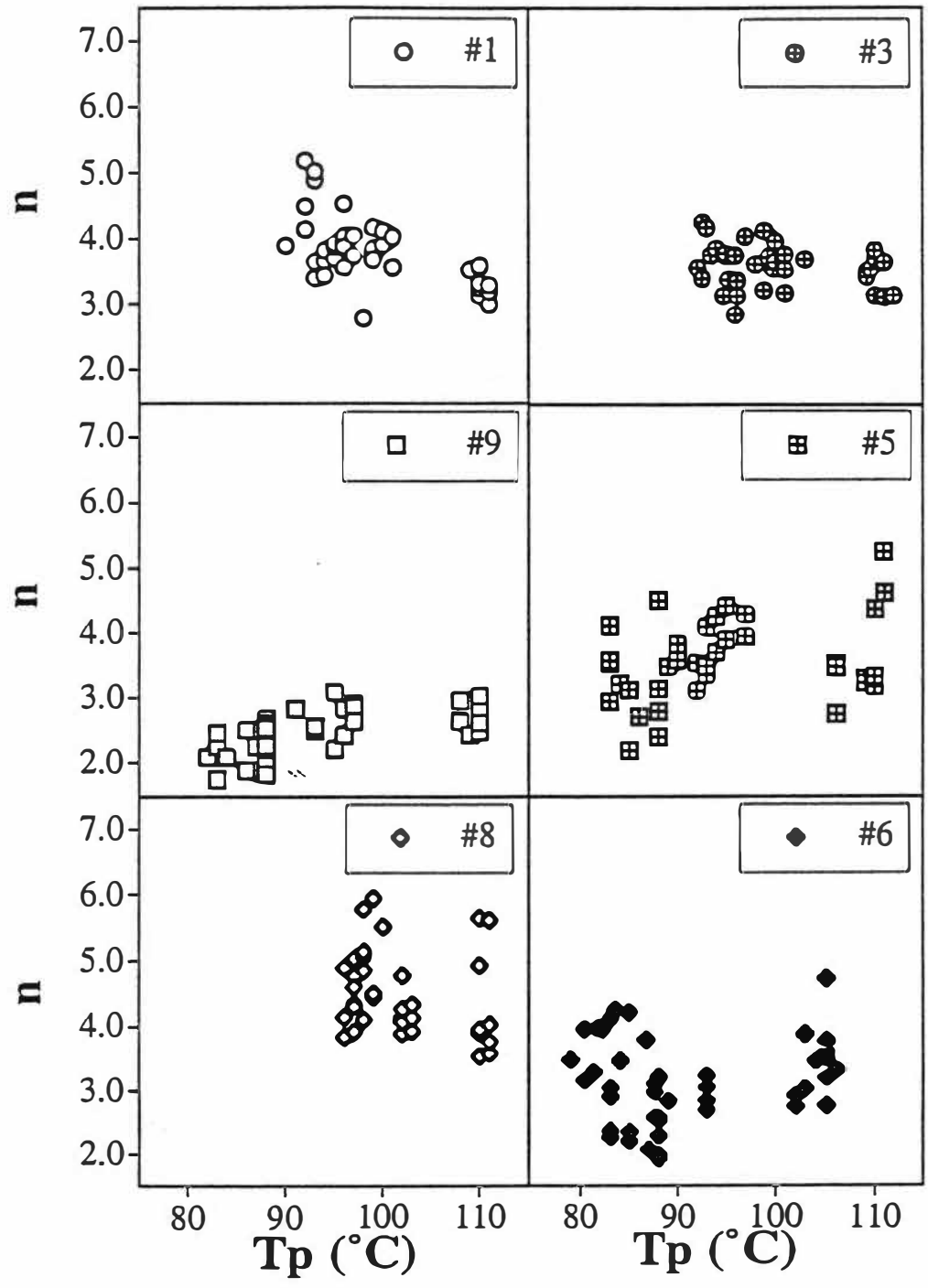


Figure 5.17. Avrami index, n , versus crystallization plateau temperature, T_p under various cooling rates for six considered iPPs.

Table 5.5. Avrami Index, Nucleation Index And Value Of B-Function For The Six Considered Materials

Resin	n(averaged)	m	B(m+2,n')
#1	3.81	0.81	0.09340
#3	3.58	0.58	0.10827
#9	2.49	-0.51	0.26949
#5	3.58	0.58	0.10827
#8	4.49	1.49	0.06381
#6	3.13	0.13	0.14999

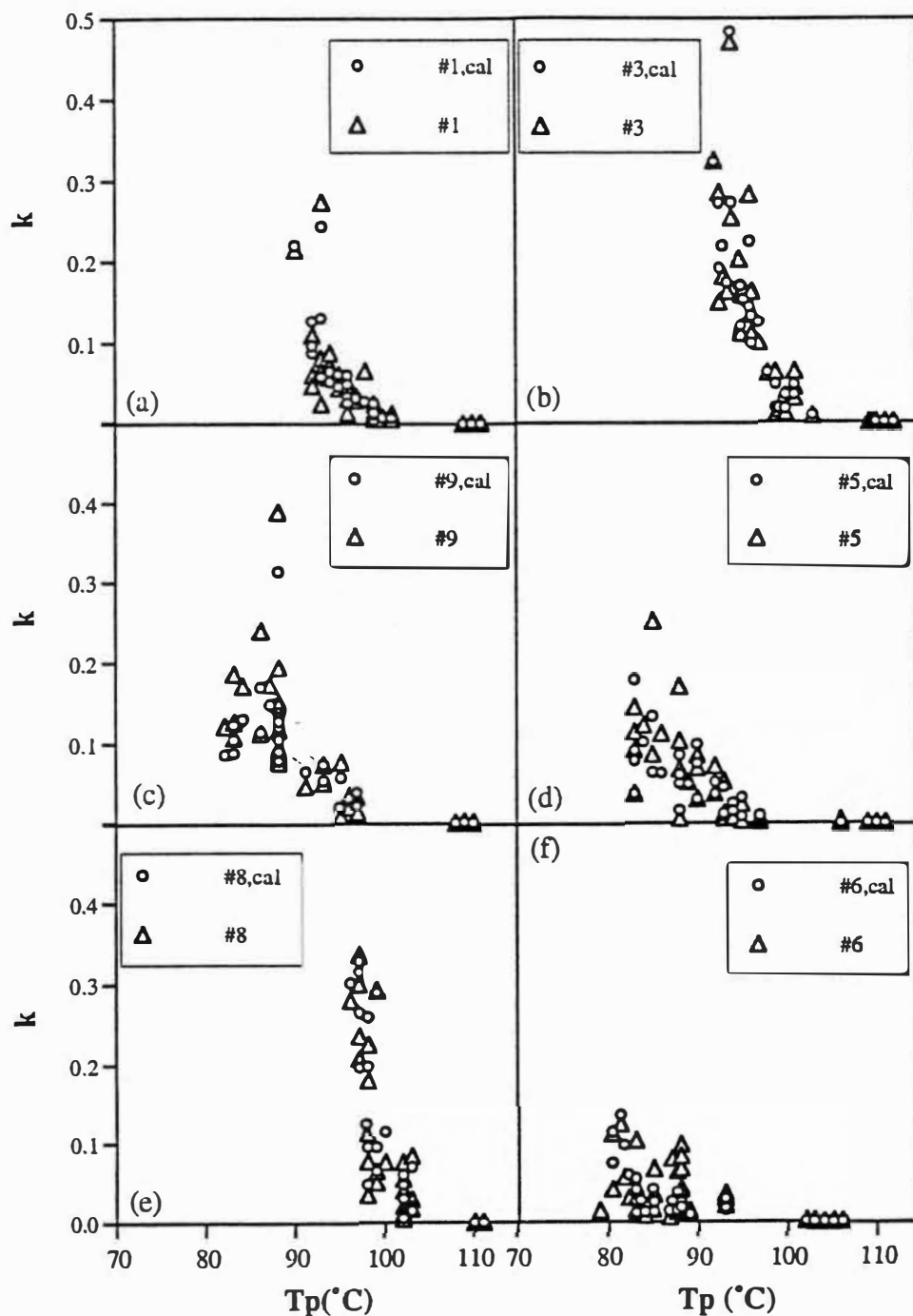


Figure 5.18. The crystallization rate constant, k , obtained directly by Avrami analysis (triangles) and through crystallization half-time (circles) versus plateau temperature, T_p , at various cooling rates for six considered iPPs.

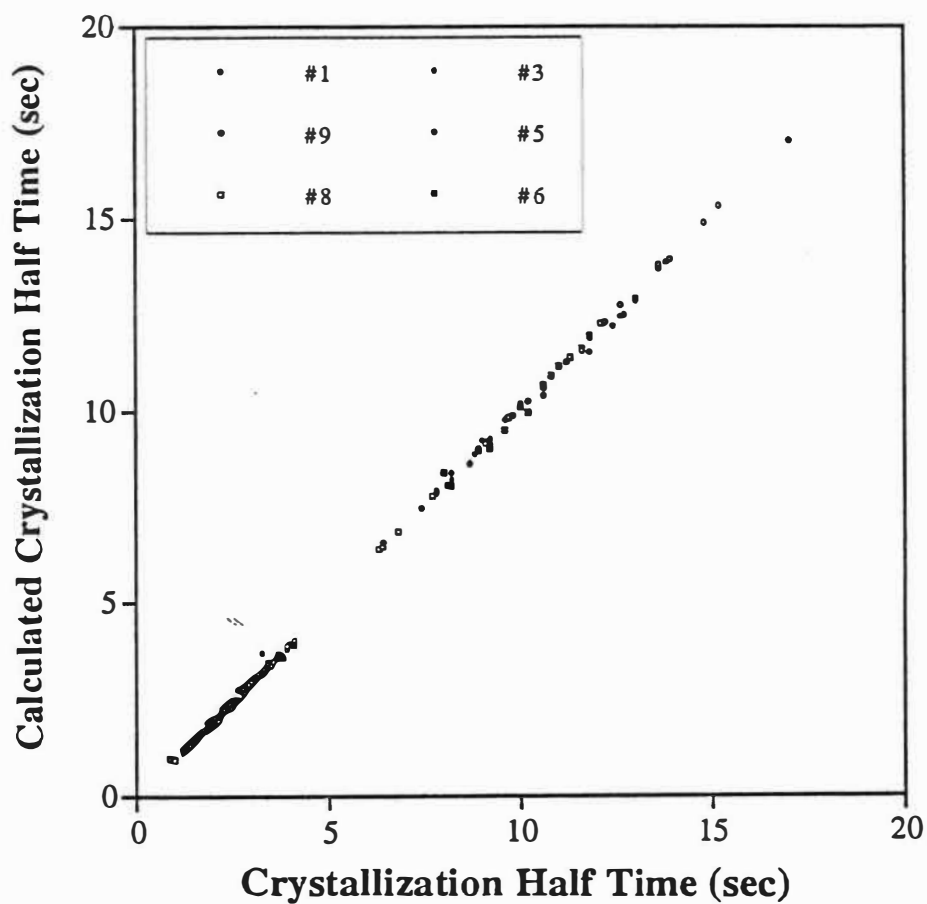


Figure 5.19. The crystallization half-time calculated from crystallization rate constant and Avrami index, $t_{1/2,cal}$, versus the one obtained directly from θ -t plot, $t_{1/2}$, for six considered iPPs.

demonstrates this conclusion. The data points in figure 5.19 fall on a line with slope equal 1 and intercept equal zero. This result clearly shows the internal consistency of the data and indicates that slight variations in Avrami index result in slight variations in crystallization rate constant that compensate each other and give the proper crystallization half-time.

Because the crystallization rate constant obtained by Avrami analysis is scattered for some materials, efforts have been made to obtain less scattered crystallization rate constants in order to further use the information from crystallization rate constant. From the well behaved crystallization half-time, one may use equation (5.1) to back-calculate crystallization rate constant by a proper selection of the Avrami index. One solution to this problem is to obtain the crystallization rate constant based on an averaged Avrami index. The circles in Figure 5.18 give the crystallization rate constant k' that results from this calculation.

From Figure 5.18 one can see that k' is somewhat less scattered than k , especially for Resin #6. k' gives a reasonable trend when cooling rate increases for Resin #6. The calculated crystallization rate constant will be used in comparison of crystallization rate constants for the six materials and in the calculation of the nucleation rate constants described below.

The averaged Avrami index in Table 5.5 which is used in calculation of the calculated crystallization rate constant in Figure 5.18 is averaged over a resin. The other average range that could be chosen is over all resins considered. If such a value were used, the trend for crystallization rate constant and time dependent nucleation will be identical with the case of crystallization half-time when different material is compared. In this case any fluctuation between materials would also be arbitrarily lumped into the time independent nucleation. The overall averaged n would also treat the time dependent nucleation the same for all materials in the averaged range. It is believed that the differences

of Avrami index between materials is real and significant. Consequently, the values of n were only averaged over a given material.

The crystallization rate constants for different materials are plotted against plateau temperature in Figure 5.20. It is not surprising to see that rate constant basically reflects the crystallization rates described by crystallization half-time. The curve of resin #8 occupies the highest and rightmost position in the plot, and the curve moves to the left and down in location when the material has lower MW or narrower MWD, except that the position of resin #9 and #5 are switched with each other. In Figure 5.6, Resin #5 has a shorter crystallization half-time than does Resin #9, while in Figure 5.20, Resin #5 has a smaller rate constant than Resin #9. Such a reversal of the order is exactly caused by the difference in Avrami index. Here the difference in Avrami index is large enough to cause such an effect.

5.4.6. Calculation of Nucleation Rate Constant and Nucleation Densities

The nucleation rate constant was calculated from crystallization rate constant according to equation (4.32). The results are plotted against plateau temperature (Figure 5.21), from which it can be seen that the trend for all materials is similar to that of the crystallization half-time. The highest nucleation rate constant is for Resin #8. The data given in Figure 5.21 was analyzed using equation (4.39). The regressive constants and coefficients for equation (4.39) are summarized in Table 5.3. Generally, the material with higher nucleation rate gives a higher value of C_N and $\ln(N_c)_0$.

Because the nucleation rate was determined through the suggested nucleation rate function, equation (4.34), use of the function to compute nucleation densities will be briefly examined. An illustration of the way that calculated nucleation density varies with time is presented in Figure 5.22. This comparison is made among three materials with different molecular weight, all with broad molecular weight distribution. The specific resins

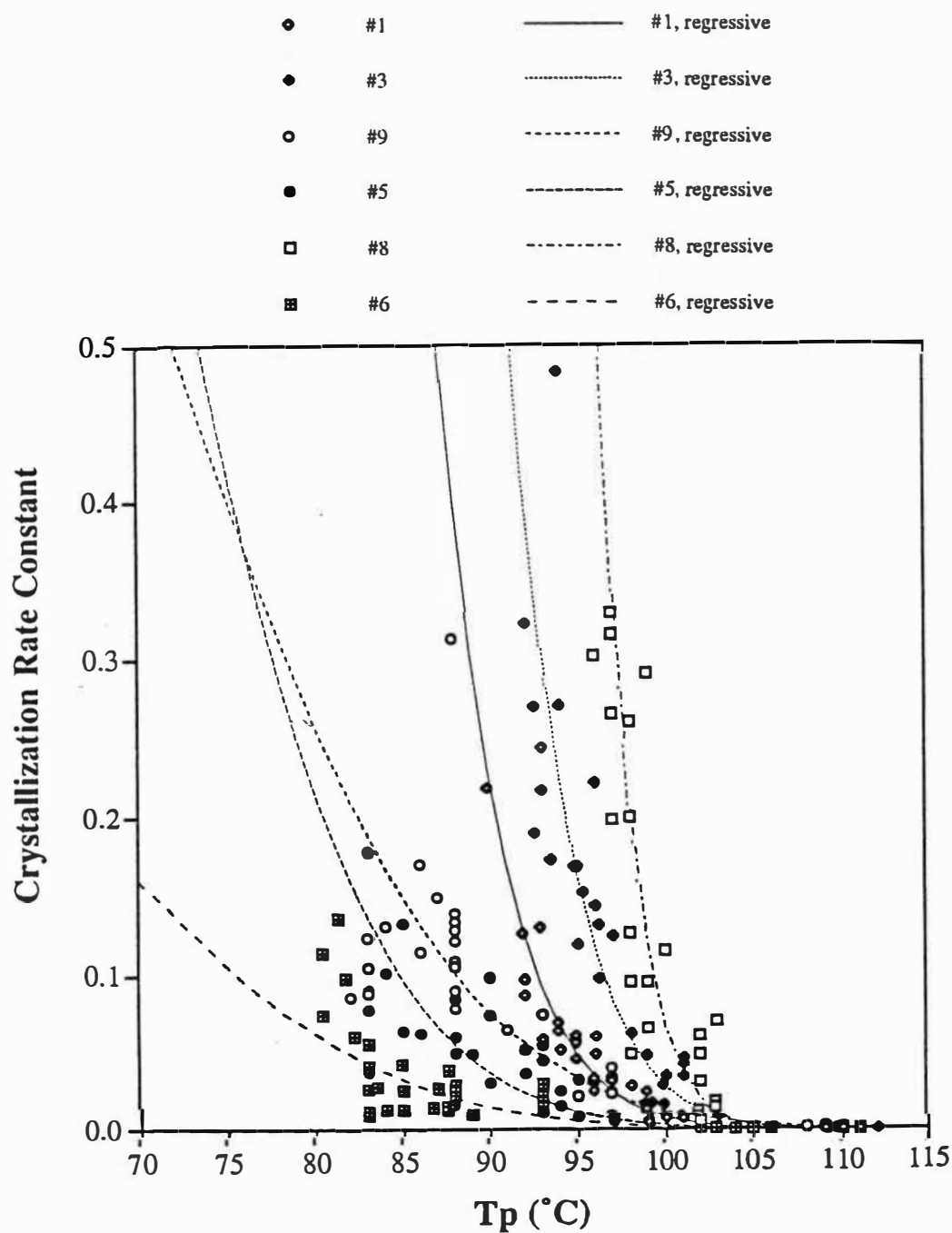


Figure 5.20. Crystallization rate constant k versus crystallization plateau temperature T_p for the six considered iPPs.

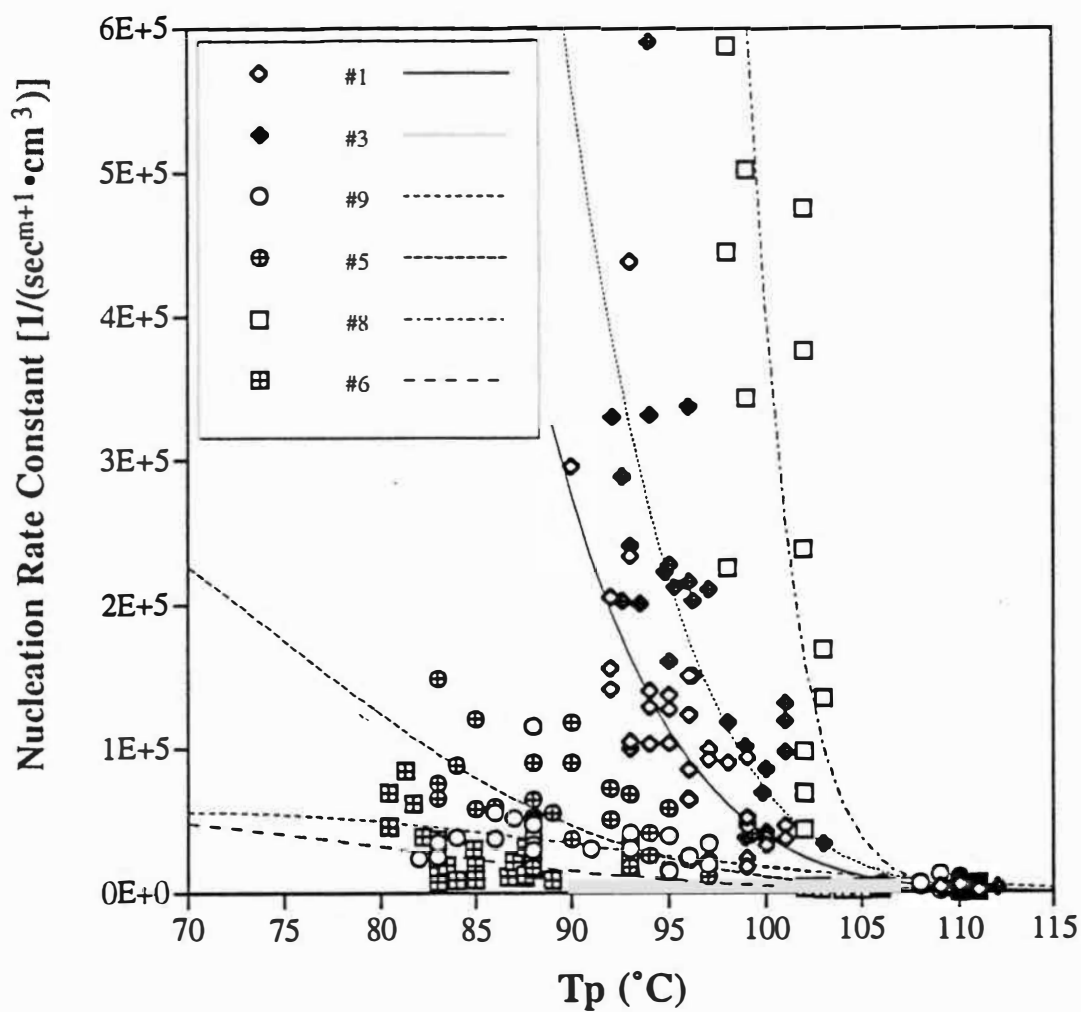


Figure 5.21. Nucleation rate constant N_C versus crystallization plateau temperature T_p for the six considered iPPs.

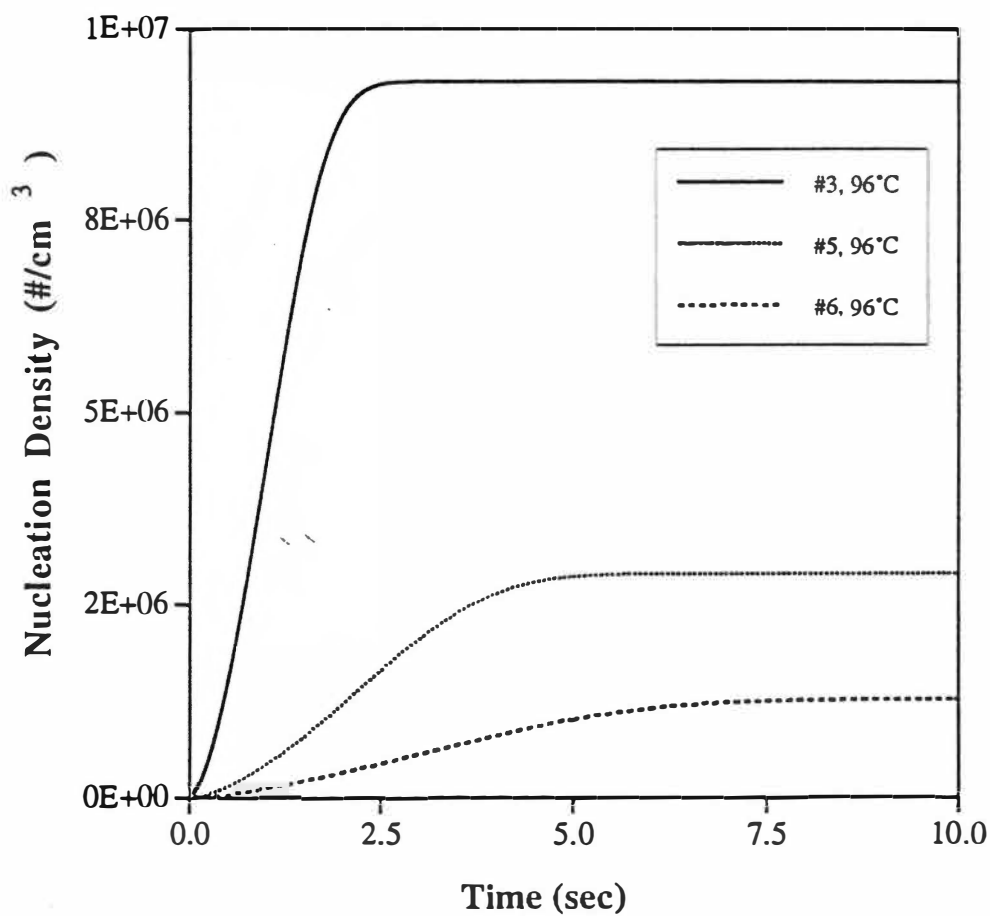


Figure 5.22. Calculated nucleation density versus time for materials with different MW and broad MWD at crystallization temperature = 96 °C.

are Resin #3, high MW and broad, #5 medium MW broad and #6, low Mw broad. The nucleation density in Figure 5.22 is calculated using the averaged m given in Table 5.5 and regressive $N_c(T)$, equation (4.39). From Figure 5.22 one can see that the higher the molecular weight the faster is the increase in nucleation density; it reaches a higher final value in a shorter time. The increase in nucleation density when molecular weight increases is caused by increase in nucleation rate constant because the Avrami indexes are similar among these materials.

Figure 5.23 shows the final nucleation density (the upper asymptotes of the curves shown in Figure 5.22) calculated for each material as a function of temperature in the temperature range where experimental data were collected. These results clearly show that the nucleation density is a strong function of both crystallization temperature and resin. According to this interpretation, Resin #8 has the highest nucleation density of any of the resins at any crystallization temperature, followed by Resins #3, #1, and #5. Resins #6 and #9 have nearly equal densities which are the lowest of all the resins studied. The order of the nucleation densities is largely controlled by the values of the nucleation rate constant, N_c . It is also of interest to compare the nucleation densities computed from the nucleation rate function, Figure 5.23 to the relative nucleation densities estimated from direct experimental observation of the number of spherulites present in the microstructures of the these materials, Figure 5.16. The similarity is striking.

5.5. Discussion

5.5.1. Growth Rate

5.5.1.1. Discussion of growth rate

It is noted that at crystallization temperature 138 °C the data points are above the regressive curve for all six materials. This is likely caused by the regime transition (III to

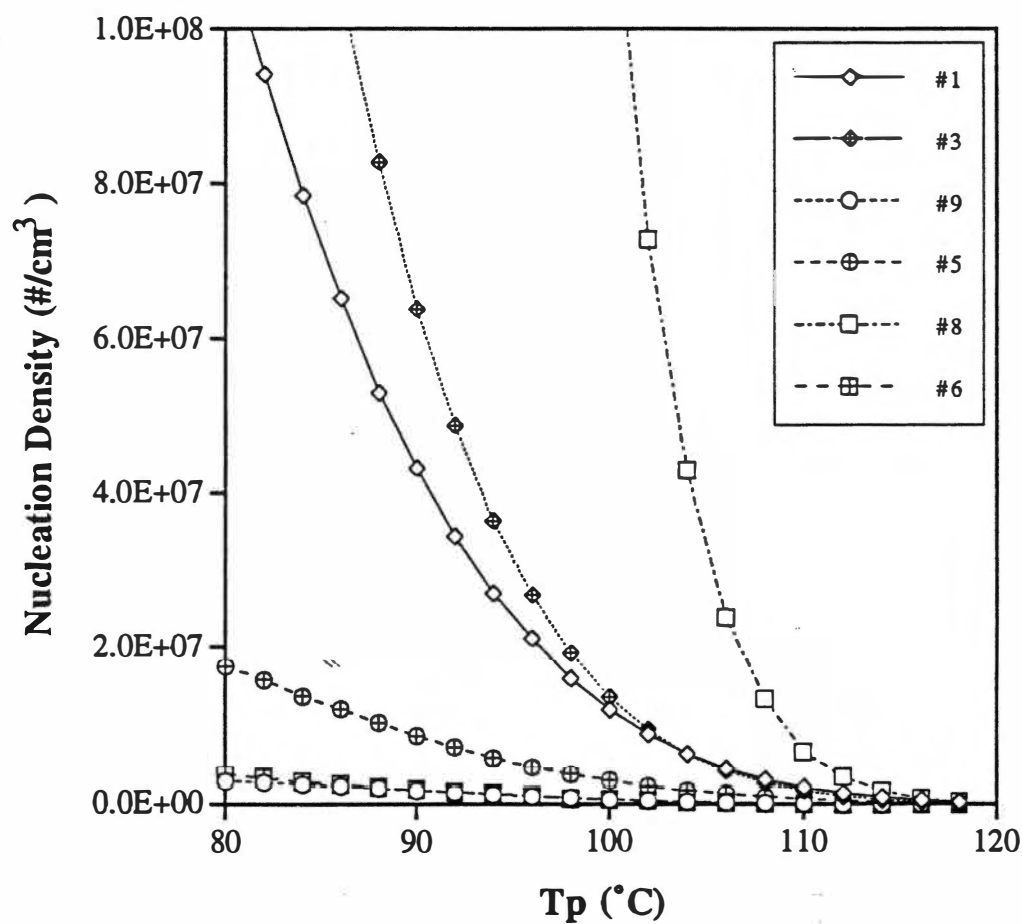


Figure 5.23. Final nucleation density calculated according to equation (4.40) using data given in Tables 5.3 - 5.5.

II) at temperature around 138°C [Clark and Hoffman (1984)]. The present data indicate that regime III exists over the entire range studied here with the possible exception of a point or two at the high temperature end of the plot.

The observed small differences in growth rates may be caused by differences in molecular parameters. In the absence of any indication that significant differences in isotacticity may cause these differences, the effects are ascribed to the influence of MW and MWD. A word of caution is necessary here. Since the differences in growth rates among the resins are very small, and the isotacticities are not known with extremely high precision, it is possible that such differences in isotacticity do, in fact, cause the observed differences in growth rates. However, the observed trends seem more consistent with molecular weight and MWD effects. Generally, the lower the MW at given MWD, or the broader the MWD at given MW, the faster the growth rate at high crystallization temperature range. This trend is reversed at low crystallization temperature range. A possible mechanism can be suggested as follows.

5.5.1.2. Mechanism of crystal growth

It is clear that the research deals with crystal growth in regime III in which many growth centers are created to complete a layer of stems at a growing front. In regime III the rate of surface nucleation (the rate of the first stem incorporating onto the growing surface of crystal) is much faster than the rate of lateral growth (adding more stems onto the growing center). The lateral growth rate involves reptation motion of molecular chains; and the rate of surface nucleation needs only attach the first stem onto the crystal surface and it is not controlled by reptation motion — nonreptation controlled. The rate of reptation motion is determined by the length of molecular chain or molecular weight. The longer the molecular chain, the slower is the reptation motion. The surface nucleation rate is determined by the probability to find a regular chain section (stem) nearby the crystal

growing surface that needs little movement to incorporate into the crystal lattice. A longer molecular chain supplies a higher probability of finding such stems because fewer chain ends are present in the melt. The molecular parameter dependence of growth rate depends on the result from the two competitive mechanisms: reptation controlled and nonreptation controlled mechanisms. At high crystallization temperature, the growth is reptation controlled. The number of stems involved in the lateral growth is large. In such a case, materials with lower MW exhibit a faster growth rate. At low crystallization temperature, the surface nucleation dominates the growth process and the growth is nonreptation controlled. The high MW materials, thus, give the higher growth rates at lower temperature.

At lower MW level and higher crystallization temperature, spherulite growth is more reptation mechanism controlled and less nonreptation controlled. At low crystallization temperature, the growth is nonreptation mechanism controlled. By this argument, as MW increases, the transition temperature for the reversal of the trend of molecular parameter dependence of growth rates should increase.

5.5.2. Discussion Of The Crystallization Induction Time

In quiescent crystallization, the onset of crystallization is suggested to be caused by heterogeneous nucleation in the present work. This argument is motivated by the following consideration. If the onset of crystallization were caused by homogeneous nucleation, nucleating impurity or material would not function during the crystallization. Because, first, in such a case, the nuclei would be easier formed by the melted molecular chains rather than by incorporating them onto the existing heterogeneous nuclei in the crystallization onset; and, second, after crystallization begins this trend would be maintained so that there would be little chance for molecules to grow on the nucleating impurity. The onset of the

crystallization is, hence, led by heterogeneous nucleation. For a given nucleating material, the onset of the crystallization only depends on the driving force for the heterogeneous nucleation, that is, the supercooling of the crystallization. Therefore, all crystallization induction times fall on a single curve. The heterogeneous nucleation explains that the crystallization induction time is independent of the molecular weight and molecular weight distribution, but its independence of the number of adventitious nuclei requires further consideration. The onset of the nucleation deals with the appearance of the first batch of the nuclei. The number of nuclei in that batch doesn't matter to the crystallization onset. Therefore, the amount of the nucleating agent does not affect the onset time, and samples that have varying amounts of adventitious nucleating agents exhibit the same crystallization onset time. This is emphasized by the fact that the t_0 of Resin #8 falls on the same curve in Figure 5.3 as all other resins; one can see that the amount of the nucleating impurity does not affect the onset of the nucleation. This means that increasing the relative amount of the nucleating impurity only creates more growing centers at the onset of the crystallization.

The isotacticities among the six samples were checked by FTIR and DSC. Both techniques give the same conclusion that there are no significant differences in isotacticities among the considered materials. That the crystallization induction times of all six materials are independent of MW and MWD gives a third experimental evidence for similar isotacticities of the six iPPs. Williams (1995), using the present technique, recently showed that differences occurred in the induction times for resins with substantial difference in isotacticity or for resins containing an ethylene comonomer.

The crystallization onset temperature is also independent of MW or MWD, or nucleating agent. Because the driving force to nucleate is realized through change in temperature, the crystallization onset temperature must be uniquely determined by the cooling rate.

5.5.3. Discussion Of Overall Crystallization Rate

5.5.3.1. Discussion on the material characteristics

Before we start to discuss the effect of molecular parameters on the crystallization rate, it is admitted that an increase in nucleation rate may be caused by two possible reasons in this research: nucleating impurities and molecular parameters. The nucleating materials are expected to have much stronger influence on the crystallization rate than the molecular parameters. In the present results, there exist differences in nucleation rate among the iPPs. No nucleating agent has been purposely added to these materials. However, among these materials, Resin #8 appears to contain a certain kind of adventitious nucleating material which may be introduced by using different catalyst for this resin from the ones for the other five iPPs. Thus, one may say that Resin #8 is apparently different from the other materials and contains a significant amount of adventitious nucleating material. One can not say that there are no nucleating materials in the other five resins. In fact, most nucleation in polymers appears to be heterogeneous. But the content of nucleating material appears much higher in Resin #8 than in the other resins. It is, of course, possible that differences in the amount of nucleating material exist among the other resins, and the complete variation in crystallization behavior could be largely ascribed to these differences. However, all the other resins were prepared by similar techniques and involved a washing step that removed most of the catalyst residues and other contaminants that might nucleate the crystallization. Based on this information it was assumed for the following discussion that the differences in nucleation rates are caused by differences of molecular parameters among them. Such an assumption actually has been supported by experimental evidence. It is noticed that experimental data for the overall crystallization in this chapter shows trends with respect to MW or MWD except for Resin #8. The growth rate data also shows a slight dependence on the MW and MWD. Though, the difference of growth rate caused by MW and MWD is

small and reverse in trend as crystallization temperature changes, the growth rate data still reflects the influence of MW and MWD existing in the materials, not the influence from other factors such as nucleating impurities. Further, a similar trend with the MW and MWD is found in the overall crystallization studies as is observed with growth rate data. Therefore, it is possible that the different nucleation rate is caused by molecular parameters not by nucleating material for Resin #1, 3, 9, 5 and 6. The overall crystallization rate of Resin #8 is out of the order suggested by both growth rate and overall crystallization rate. Therefore, the influence of the nucleating material has been introduced to explain the observed phenomena. The extremely fast crystallization rate for Resin #8, seems clearly to be caused by nucleating impurities.

5.5.3.2. Crystallization half-time

The crystallization half-time describes the overall bulk crystallization rate which quantitatively describes how fast the material can crystallize. Unlike the derivative of the relative crystallinity which describes the instantaneous crystallization rate at any given time, the crystallization half-time is the best parameter to characterize the overall crystallization rate of a crystallization process for a material. Such a parameter is comparable between different materials. This ability of the crystallization half-time to track the overall crystallization results from the fact that the crystallization half-time combines information from nucleation, growth rate, impingement and even the secondary crystallization for the whole crystallization period and neglects the detailed information about the individual quantities.

From Figure 5.6 one can see that the molecular weight has a significant influence on the crystallization half-time. The materials with higher MW exhibit a smaller crystallization half time which means faster overall crystallization rates. The influence of MWD on the overall crystallization is much weaker than that of MW, especially for the

medium MW group. The extraordinarily high overall crystallization rate of Resin #8 caused by the adventitious nucleating material suggests that the nucleating material has a stronger influence on overall crystallization rate than either MW or MWD. Combining information from growth rates which are only slightly influenced by MW and MWD, the increase in overall crystallization rates caused by MW, MWD, or nucleating materials can thus be largely attributed to increase in nucleation rates.

5.5.3.3. Avrami index, nucleation rate constant and nucleation rate

In order to interpret the difference between the Avrami index, the power law nucleation rate function described in Chapter 4 was used. The high value of nucleation index of Resin #8 tells us that the heterogeneous nucleation has become time dependent. Because of $m > 1$, the nucleation of the Resin #8 is especially time dependent and very fast. According to the power law nucleation rate theory this means that, physically, a large number of nuclei are continuously being created during crystallization. The negative value of the nucleation index for Resin #9 means the time dependent nucleation rate is decreasing with time and the time independent nucleation plays an important role in the total nucleation process. Compared to the other five materials, resin #9 has a large amount of time independent nucleation (relative to the number of nuclei created time dependently) because the nucleation index is about -0.5. The number of nuclei created at the beginning of the crystallization is much greater than the amount of nuclei created time dependently. The reason for this is unknown.

From Table 5.5, we can see that the material which is capable of producing higher nucleation density has a higher value of nucleation index. This is especially true for Resin #8. Generally speaking, materials in the higher MW group exhibit higher nucleation index. But the MWD dependence of the nucleation index in low MW group has been disturbed by the nucleation impurity in Resin #8. From Figures 5.16, 5.22 and 5.23 we can see that the

nucleation density exhibits the MW dependence. The difference of nucleation density caused by different MW level appears to be evident between high MW, Resins #1 and 3, and medium and low MW groups. The adventitious nucleating impurity in Resin #8 caused a large difference in nucleation density which is the highest one among the six materials. The differences due to MWD appear minor. The comparison between the nucleation density values calculated from the nucleation rate function analysis, Figure 5.23, and the experimentally measured relative nucleation densities, Figure 5.16, indicates that the nucleation rate function analysis leads to reasonable nucleation densities that have the same general trend as the experimental observations. Thus, we may conclude that the nucleation rate function analysis is an important contribution. It seems that nucleation index confirms, more or less, the differences that existed in the nucleation density. A more precise description of the nucleation rate by nucleation rate function requires better understanding of the reduction in geometric index caused by impingement, so that separation of the geometric growth index and nucleation index can be performed more accurately. It would also help to improve the method of determining the crystallization onset time to improve the Avrami analysis and to obtain more consistent Avrami index.

From the data of crystallization half-time, one observes that small random differences in the Avrami index and crystallization rate constant are balanced by crystallization half-time through equation (5.1). Because n' is assumed the same, m is changed when n is changed. Because G does not change much for different material, N_c is changed when k is changed. Further all samples are observed to produce spherulites on crystallization. Therefore, the balance made by crystallization half-time is actually between the nucleation index and nucleation rate constant. When m changes, the shape of the nucleation distribution function or the relative amount of the time-dependent and time-independent nucleation changes. That is to say, there exists a certain equivalency between time-dependent and time-independent nucleation. Different nucleation distribution can

produce the same value of crystallization half-time. It is the distribution of growing centers with respect to time that affects the overall crystallization rate. For the same number of nuclei produced during crystallization, they increase the overall crystallization rate much more if they are produced early in the crystallization process than if they are produced gradually throughout the crystallization process. The observed phenomenon that the overall crystallization rate described by crystallization half-time is well related to cooling rate but the obtained Avrami index is more scattered when cooling rate changes might be explained by the effect of nucleation on the overall crystallization rate. The fewer nuclei produced time-independently, the more nuclei produced in a time-dependent manner with the effect of crystallization on the overall crystallization rate maintains the same at a given cooling rate. The effect of the nucleation on the overall crystallization is a function of the cooling rate. The scattering of Avrami index caused by fluctuation in time-dependent nucleation comes from the difficulty of experimentally controlling the thermal history of the sample precisely the same for each run, and therefore inability to precisely control the amount of time-independent and time-dependent nucleation from run to run.

In spite of the data scatter, one can deduce that the increase of crystallization rate is essentially caused by increase in the nucleation rate constant as cooling rate increases for the present samples. The manner of the nucleation, or the relative amount of time-dependent and time-independent nucleation is basically independent of cooling rate. Of course, there is also a contribution to the overall crystallization rate caused by the change in growth rate of the spherulites with increase in the cooling rate. Higher cooling rates lead to lower crystallization temperature and faster growth rates as previously discussed.

The nucleation rate constant for Resin #8 is high because of the presence of adventitious nucleating material as previously discussed. The nucleation rate constants exhibit a dependence on the MW and MWD. The higher the molecular weight, the higher the nucleation rate constant is. The broad MWD material gives the higher nucleation rate

constant for the high MW group, Resin #1 and #3. As in the crystallization half-time, for medium MW group, the effect of the MWD is not large.

Because the growth rate does not change much with respect to the materials considered, the total crystallization rate described by crystallization half-time is higher when nucleation rate is higher for a material. Generally, if the differences in overall crystallization rate are attributed to the MW or MWD, not the existence of nucleating materials as we assumed before, the MW has relatively big impact on the nucleation rate. Increasing the MW can effectively increase nucleation rate and therefore the crystallization rate. The MWD has relatively weak influence on the nucleation rate and crystallization rate. The influence of MW or MWD on the total nucleation rate is largely caused by their effect on nucleation rate constant. The presence of nucleating material has a big influence on both nucleation rate constant and nucleation index, so that it substantially increases the nucleation rate and, therefore, the crystallization rate.

5.5.3.4. Mechanism of nucleation

The suggested nonreptation controlled mechanisms for growth rates are also suitable for nucleation in which no reptation is necessary to create a nuclei, and it is nonreptation controlled. The nucleation may more frequently start from stems of high MW chains because it give more chance to find chain sections, folded and/or unfolded, to form nuclei. There is no reptation movement necessary for nucleation because reptation movements are aimed at a site where part of the chain has attached. In the absence of a nucleus, no such site is present. The nucleus is formed when enough chain sections are neatly packed together. The chain sections forming nuclei may be folded chain stems and/or individual stems from different molecules. Thus the longer the chain the higher the possibility of finding the neatly packed chain section because of less chain ends. The material with higher MW gives, therefore, the higher nucleation rate. The material with

broader breath has some longer chains compared with material with the same MW but narrower breath. Those long chain molecules supply high chance to create nuclei. Therefore, materials with broad breath may exhibit higher nucleation rate than does narrower breath materials.

5.5.4. Discussion Of The Crystallization Plateau Temperature

The trend of crystallization plateau temperature with cooling rate is consistent with the one of crystallization half-time and nucleation rate constant. Resin #8 has the highest crystallization temperature because it contains the nucleating impurities. The value of the crystallization plateau temperature is determined by crystallization rate and ultimate crystallinity developed in the sample. The crystallization rate in this chapter refers to the relative crystallization rate or phase transition rate. In the transformed phase there are crystalline and amorphous regions. The crystallization heat is related to the amount of crystalline material. The heat generation rate is related to the rate of formation of the absolute amount of crystalline material, which is the product of $d\theta/dt$ and ultimate crystallinity. It is worth pointing out that the heat generation rate is directly related to instantaneous crystallization rate not to the overall crystallization rate described by crystallization half-time. However, if the overall crystallization rate is high, it gives a higher value of maximum $d\theta/dt$, but not necessarily the higher $X_c \cdot d\theta/dt$, which also depends on the absolute crystallinity. In all, the value of the plateau temperature is related to $X_c \cdot d\theta/dt$. Usually the X_c will not change too much for the same kind of material. The $d\theta/dt$ plays an important part in determining the value of plateau temperature because its variation in magnitude is large for different material. According to this argument, the material with high crystallization rate has a higher crystallization plateau temperature, because the starting point, the crystallization onset temperature is uniquely determined by cooling rate. All the characteristics of the influence of MW, MWD and nucleating substance on the

crystallization rate are thus carried into the crystallization temperature because the plateau temperature is essentially determined by crystallization rate. The trends of the T_p versus h_a with respect to MW or MWD are therefore analogous to the ones for crystallization half-time.

5.6. Conclusions

The isotacticities of the six considered materials were quite similar. This was supported by the evidences from FTIR and DSC measurements.

The crystallization onset time was independent of MW, MWD and adventitious nucleating material, and determined only by cooling rates applied. The reason for this was attributed to the crystallization onset being caused by heterogeneous nucleation. The crystallization induction times of all six materials were related to crystallization onset temperature by a single equation which is useful in determination of crystallization onset under strain.

There are no large differences on the growth rates of the considered materials with different molecular weight and molecular weight distribution. However, there exists some small difference in growth rates among these materials. In the high crystallization temperature range, the growth rate decreased slightly as molecular weight increased, and increased as the breadth of the molecular weight distribution increased. In the low crystallization temperature range these trends were reversed.

The crystallization half-time was used to compare the overall crystallization rate. The overall crystallization rate in nonisothermal crystallization may be affected by molecular weight and slightly by molecular weight distribution when the existence of nucleating material was assumed to be absent or of similar amounts. The increase in molecular weight or distribution breadth increased the overall crystallization rate. The dependence of the overall crystallization rate on the MW and MWD was attributed to nucleation. When MW

and, possibly, MWD increased, high crystallization rate was ascribed to a high nucleation rate in the crystallization because the growth rate was not strongly affected by molecular parameters. The adventitious nucleating material can significantly increase nucleation rate in the crystallization. Therefore, the nucleating agent can effectively increase the overall crystallization rate.

The materials with higher MW tend to give a higher value of the Avrami index and nucleation rate constant. The dependence of the Avrami index and nucleation rate constant on MWD is not as strong as on MW among the six considered materials. The existence of adventitious nucleating materials results in a high value of the Avrami index and nucleation rate constant. The reason for the unusual low Avrami index for Resin #9 is unknown. Further understanding of the Avrami analysis is required to obtain less scattered values of Avrami index to describe the kinetics parameters of the materials more precisely.

The crystallization plateau temperature displays a similar dependence to the material parameters as crystallization half-time. This is because the value of the plateau temperature is mainly determined by crystallization rate.

Chapter 6

COMPUTER MODELING OF THE MELT SPINNING PROCESS

6.1. Introduction

One approach to study crystallization under strain is to simulate the melt spinning process in which the molecules are uniaxially oriented along the filament axis. The influence of the molecular orientation to crystallization can thus be found out by fitting the simulated profiles to the ones obtained by on-line measurement from the spinline. The present research is based on the model for melt spinning in our laboratory introduced by Zieminski and Spruiell [Zieminski and Spruiell (1988)] and later modified by Patel, Bheda, and Spruiell [Patel, Bheda, and Spruiell (1991)]. Because the flow behavior of the melt on the spinline strongly affects the molecular orientation, the viscosity equation in the present model has also been improved to get a closer description of the polymer crystallization under strain. The significance of this research goes beyond the study of the crystallization under strain, but improves the mathematical modeling of the melt spinning process. In addition to that, an improved computer simulation of the melt spinning process was developed that can simulate the important differences due to molecular weight variations.

Melt spinning of polymeric filaments is a complex, dynamic process. Under steady state conditions, the temperature and filament diameter changes along the spinline and induces changes in the molecular orientation and crystallinity. To describe such a process one needs continuity, momentum and energy balances, an equation relating parameters such as stress or strain to molecular orientation, a rheological constitutive equation, and crystallization kinetics equations. The proper form of the constitutive equation, and crystallization kinetics equations are not well established and likely depend on the material

being spun. In order to solve these equations one needs expressions for the heat capacity, density, and various other materials parameters and coefficients that appear in the chosen equations. Among these, the materials parameters that describe the viscosity and crystallization kinetics are the most difficult to experimentally determine. For lack of a proven relationship and ease of evaluating the constants, earlier work [Zieminski and Spruiell (1988), Patel, Bheda, and Spruiell (1991)] has often assumed an “apparent elongational viscosity” from data obtained from the spinline. Although this gave useful results for polymers that do not exhibit a strong dependence of viscosity on strain rate, it has limited applicability to the spinning of polymers with higher molecular weights and broader molecular weight distributions. Likewise, improved crystallization kinetics expressions and data are needed to describe the influence of factors such as the effect of molecular weight and molecular weight distribution on the stress-induced crystallization.

The improvement made in the present model is in the description of crystallization and viscosity for processing polymer under strain. The model takes advantage of the recently developed technique [Ding and Spruiell (1994)] described in Chapters 3 and 4 for studying quiescent nonisothermal crystallization under rapid cooling conditions which are similar to conditions occurring during polymer processing. By use of that technique the kinetic parameters were related to the resin characteristics such as molecular weight and molecular weight distribution for the case of quiescent crystallization and then applied in the model.

6.2. Description Of The Model

6.2.1. Crystallization Kinetic Equation

The Avrami equation, equation (6.1), was employed in the present model. This equation is the same one as expressed by equation (4.30). To express the equation directly

used in the model, the crystallization induction time t_0 , and the time when the temperature in the polymer stream is equal to the equilibrium melting temperature, t_1 , were included in the equation. The t in equation (6.1) is the elapsed time starting at the distance from spinneret, $z = 0$.

$$\theta = 1 - \exp\{-k(t - t_1 - t_0)^n\} \quad (6.1)$$

The differential form, which is expressed by equation (6.2), of equation (6.1) is necessary for it to be applied in the model.

$$\frac{d\theta}{dt} = nk(t - t_1 - t_0)^{n-1}(1 - \theta) \quad (6.2)$$

The procedure of the computer simulation is essentially to solve differential equations. The above form of the Avrami equation is the one required in the solutions of computer simulations. However, t_0 , k , and n are unknown under strain conditions. To obtain these parameters, the integrated form of the Avrami equation has to be placed in the model. The differential form of the Avrami equation, equation (6.2), is required while simultaneously solving the energy balance equation. The derivation of Equation (6.2) is based on the application of the power law nucleation function in the derivation of the Avrami equation. Equation (6.2) also includes the crystallization induction time which is critically important to the crystallization kinetics under strain.

The effect of molecular orientation is realized through its influence on nucleation rate and crystallization onset in the present model. The reason that the Avrami equation can be used to describe the nonisothermal crystallization and also the effect of strain is that one treats the k and n as constants for both quiescent and strained nonisothermal crystallization. According to the nucleation rate function, it is not necessary for the nucleation rate to be constant when k and n are constant. The variation of the nucleation rate is realized through

t^m in which the exponential of t is constant during crystallization. Such an application of the Avrami equation is based the description of nucleation rate by a power law function, see Chapter 4. The orientation effect for the crystallization under strain is reflected in the nucleation rate which is embedded in the rate constant k , Avrami index n , and crystallization induction time t_0 .

6.2.2. Crystallization Induction Time t_0

For a strained system, the orientation helps molecular nucleation and adds more driving force for the system to crystallize. Therefore, the strain on the spinline leads to a much shorter crystallization induction time. The suggested way to incorporate the orientation effect into t_0 is analogous to the orientation dependence of the crystallization rate constant. The strain effect may be introduced into the induction time expressed by equation (4.37) as:

$$\frac{1}{t_0'(T, f_a)} = \left(\frac{1}{t_0}\right)_0 \exp\left[\frac{-C_I}{T\Delta T f + C_{IO} T^2 f_a^2}\right] \quad (6.3)$$

where C_{IO} is an adjustable constant which accounts for the strain effect, $\left(\frac{1}{t_0}\right)_0$ is the

preexponential constant for induction time, f_a is the orientation factor in the amorphous phase, T is the crystallization onset temperature. The $\left(\frac{1}{t_0}\right)_0$ and C_I are determined by

quiescent experiment using equation (4.37) as was done in Chapters 4 and 5. The method of determining the C_{IO} in equation (6.3) will be discussed in section 6.2.3 of this chapter. Equation (6.3) expresses the crystallization induction time as a function of the given temperature and orientation in the polymer stream. To distinguish the crystallization induction time in the spinline where the temperature and the molecular orientation are changing, a prime has been added to the crystallization induction time under given temperature and orientation in equation (6.3). The crystallization induction time on the

spinline is denoted as t_0 (without prime) in this chapter. Even though C_I can be universally applied to various homo-iPP, the value of C_{IO} has material dependence. Different from the quiescent condition, there is flow existing in the melt for crystallization under strain. Materials with different molecular weight and molecular weight distribution give different response to the applied strain, so that the crystallization onset varies with the material characteristics.

The primary difficulty of calculating the crystallization induction time on the spinline is that both temperature and orientation in the polymer stream are changing along the spinline. One is unable to directly use the t_0' and the cooling rate relation obtained under quiescent crystallization. One possible approach to tackle this problem is to construct the following equation to superimpose the effects of temperature and molecular orientation on the spinline:

$$\int_{t(T_m^0)}^{t(T_{on})} \frac{1}{t_0(T, f_a)} dt = 1 \quad (6.4)$$

The crystallization onset can be determined if one substitutes equation (6.3) into equation (6.4) :

$$\int_{t(T_m^0)}^{t(T_{on})} \left(\frac{1}{t_0}\right)_0 \exp\left[\frac{-C_I}{T\Delta Tf + C_{IO}T^2f_a^2}\right] dt = 1 \quad (6.5)$$

where $t(T_m^0) = t_1$ and $t(T_{on}) = t_{on} = t_1 + t_0$. Equation (6.5) includes both thermal and orientation effects in it.

6.2.3. Avrami Index, Crystallization Rate Constant And Nucleation Rate Function

The nucleation rate function applied in the model is in the form of

$$\dot{N} = N_c(1+m)(t - t_0 - t_1)^m \quad (6.6)$$

where N_c is nucleation rate constant and m is nucleation index which is related to the Avrami index n by :

$$n = n' + m + 1 \quad (6.7)$$

where n' is the geometric index. The time dependent part in the nucleation rate function is $(t - t_0 - t_1)^m$. The quantity N_c is assumed to be a function of temperature and molecular orientation. Thus for each different spinning condition, the crystallization temperature and orientation are different which produces a different nucleation rate constant. The temperature dependence for different spinning process is obtained by modifying equation (4.39). The item $C_{NO}T^2f_a^2$ was added into equation (4.39) in order to account for the effect of molecular orientation and the nucleation rate constant under strain may then be expressed as:

$$N_c = (N_c)_0 \exp\left\{-\frac{U^*}{R(T - T_\infty)}\right\} \exp\left\{-\frac{C_N}{T\Delta Tf + C_{NO}T^2f_a^2}\right\} \quad (6.8)$$

where $(N_c)_0$ is the preexponential constant for the nucleation rate constant and C_{NO} is the constant which accounts for the orientation effect on the nucleation rate constant under strain.

The crystallization rate constant used in the model is

$$k = N_c n' \frac{4\pi}{3} G^{n'} B(m+2, n') \quad (6.9)$$

where

$$B(m+2, n') = \int_0^1 x^{m+2-1} (1-x)^{n'-1} dx \quad (6.10)$$

The Avrami index is calculated according to equation (6.7) after n' and m are determined. The geometric index n' is assumed to be 2 for crystallization under strain.

Even though the nucleation index can be calculated in quiescent studies, the m is still an adjustable parameter in the spinning model. This is because the nucleation under strain is strongly affected by molecular orientation. The effect of the molecular orientation is not only reflected in the nucleation rate constant to alter the temperature dependence of the nucleation, but also reflected in the time dependence of the nucleation. This means that the Avrami index still describes the nucleation manner on the spinline. The variation of Avrami index with spinning speed will be explained by variation of the manner of nucleation. Unlike the crystallization rate constant, there is no equation which can relate the nucleation index, m , to a variable such as degree of orientation at crystallization onset. The determination of nucleation index is based on an assumption that the crystallization half time is determined only by spinning speed on the spinline, because the nucleation rate and, hence, the crystallization rate under strain is essentially controlled by spinning stress which is uniquely related to spinning speed. An attempt to relate the nucleation index to the crystallization onset stress has been tried because the crystallization onset stress is the result of determination of the crystallization point and such a correlation would save the additional assumption. It was surprising to find that the Avrami index could not be empirically related to either the crystallization stress, or the crystallization onset temperature, either of which characterized the thermal and strain history on the spinline before crystallization. The reason for this is not clear. The assumption that it can be evaluated from crystallization half time has the physical meaning that after crystallization begins, the solidification of highly crystallizable polymer on the spinning line is controlled by crystallization and the solidification rate is characterized by crystallization half time. The whole solidification, however, is still determined by the process before and after crystallization begins. When spinning speed is fixed, the solidification after crystallization is fixed, but the process before crystallization is determined by other conditions. m is thus

obtained after crystallization rate constant is determined because crystallization half time is determined by spinning speed according to an empirical equation:

$$t_{1/2} = \exp\{B_{112}\} V_t^{A_{112}} \quad (6.11)$$

where A_{112} and B_{112} are constants to be determined in the model and V_t is the take-up velocity. It is worth a try to use the relation of crystallization half time as a function of crystallization temperature and orientation at crystallization onset to obtain the crystallization half time under strain first, and then to calculate the Avrami index through crystallization half time and crystallization rate constant. Such an approach can avoid the big assumption for the crystallization half time. This approach is suggested as future work for the spinning model research because it will deal with the determination of all the constants which accounts for orientation in the model and was impossible to complete in the present study.

6.2.4. Final Crystallinity X_c And Crystalline Orientation Factor f_c

The following empirical equations were applied in the model to calculate the final crystallinity and crystalline orientation. The final crystallinity in the fiber is expressed by equation (6.12),

$$X_c = 0.75\{1 - \exp[-(a_{X_c} \sigma_{on} + b_{X_c})]\} \quad (6.12)$$

where σ_{on} is the stress at crystallization onset time obtained by computer simulation using this model, and a_{X_c} and b_{X_c} are regressive constants which can be determined by the experimental crystallinity and simulated stress at crystallization onset time. The simulated crystallization onset temperature can almost equally be related to X_c by another empirical equation. The correlation of the final crystallinity to the stress at crystallization onset gives a little bit better results when various materials are correlated by equation (6.12). It makes

almost no difference whether one uses σ_{on} or T_{on} because either quantity contains both thermal and strain information.

The crystalline orientation factor f_c is given by equation (6.13),

$$f_c = \exp\{B_{fc}\} T_{on}^{A_{fc}} \quad (6.13)$$

Where T_{on} is the crystallization onset temperature which is obtained by computer simulation using the present model. A_{fc} and B_{fc} are the regressive constants. f_c is obtained by fitting the model to the experimentally measured birefringence profiles.

6.2.5 Energy Balance

There is no change for the energy balance equation, equation (6.14), used in the previous model. The equation, however, was verified by fitting the energy balance equation to the cooling curve obtained in the quiescent experiment. The difference between the crystallization rate caused by strain on the spinline and in quiescent crystallization is described by $\frac{d\theta}{dt}$. Therefore, the validity of equation (6.14) can be checked by quiescent experiment. The energy balance equation used in the model is,

$$\frac{dT}{dt} = - \frac{4h_a}{\rho C_p D} (T - T_1) + \frac{\rho_c \Delta H}{\rho C_p} X_c \frac{d\theta}{dt} \quad (6.14)$$

Where D is sample dimension (diameter for fiber and sample thickness for quiescent experiment), T_1 is the temperature of cooling medium, θ is relative crystallinity, and X_c and h_a are final crystallinity in the sample and heat transfer coefficient of the cooling medium, respectively. In the simulation of quiescent crystallization, X_c , h_a and T_1 are the fitting constants. In the spinning model X_c and h_a are described by imperial equations, and T_1 is given as a spinning condition. The polymer density and heat capacity are functions of temperature in the fitting which are the same as used in the spinning model.

In the experiment of quiescent crystallization, both the temperature and the crystallization were directly recorded during the crystallization in which the complexity of the strain effect is absent. We found that the energy balance equation can well fit the experimental temperature. Figure 6.1 shows an example of such fitting.

6.2.6. Elongational Viscosity

The model uses the generalized Cross model [Cross (1965, 1966, 1969, 1979)] to describe the viscous behavior. The cross model is a widely used generalized power law viscosity equation [Bogue (1966), Bogue and While (1970), Patel and Bogue (1989), Liu, Bogue and Spruiell (1995)]. Recently, the Cross model has successfully been used in the mathematical modeling of film blowing [Liu, Bogue and Spruiell (1995)]. The Cross model used in the present model for the elongational viscosity is

$$\eta_e(T, \dot{E}) = \frac{3A_{vis}e^{B_{vis}/T}}{1 + (a_{vis}3A_{vis}e^{B/T}\sqrt{3}\dot{E})^{b_{vis}}} \quad (6.15)$$

where a_{vis} , b_{vis} , A_{vis} , and B_{vis} are model constants. To obtain the model constants for equation (6.15), the viscosity data obtained in shear experiments was used. The shear viscosity versus shear rate supplied for the various resins by Exxon Chemical Company is given in Figure 6.2. It is noticed that in the figure the magnitude of the complex viscosity measured by a parallel-plate oscillatory rheometer was plotted against frequency, rather than the shear viscosity versus shear rate. In the present study the Cox and Merz rule [Cox and Merz (1958)] is implied that says that curves of shear viscosity versus shear rate are often nearly the same as curves of the magnitude of complex viscosity versus frequency. In the discussion in this chapter we only use the terms of shear viscosity and shear rate. Generally, one needs the shear form of Cross model, equation (6.16), to fit the shear data,

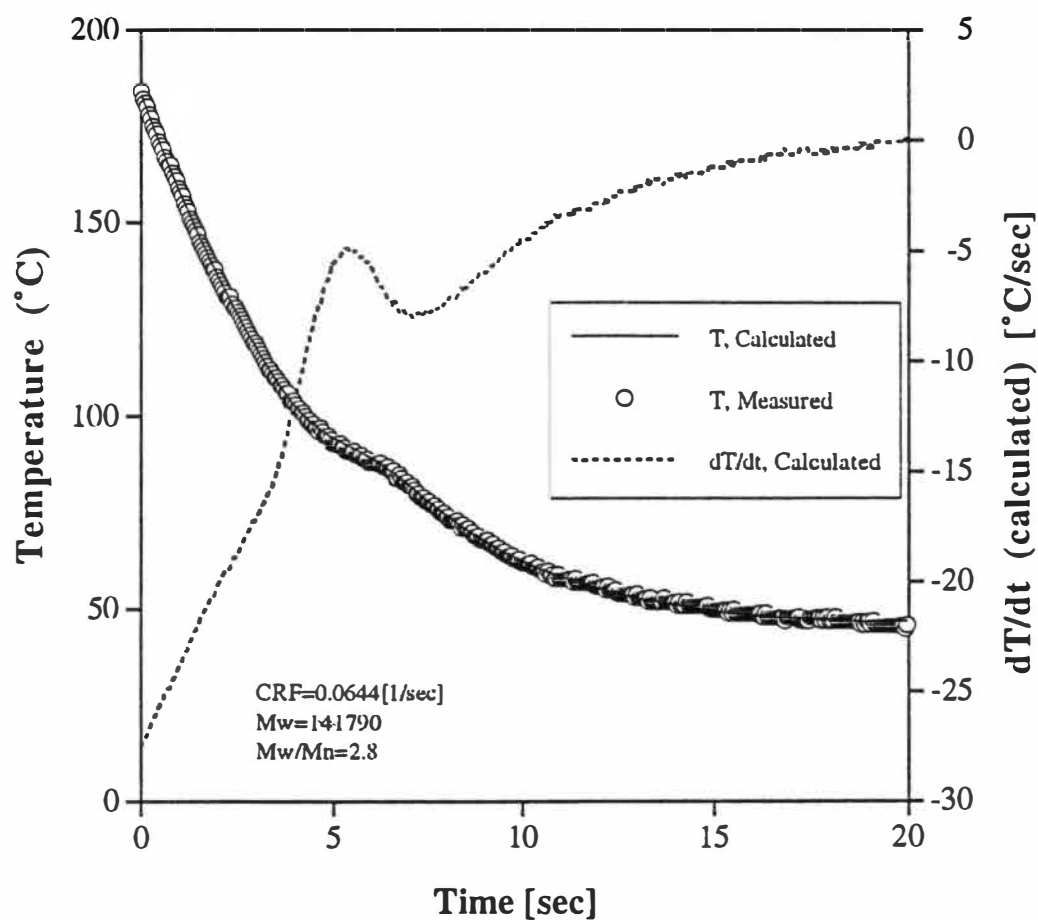


Figure 6.1. Fitting the energy balance equation to the experimental temperature measured in quiescent nonisothermal crystallization under a rapid cooling rate.

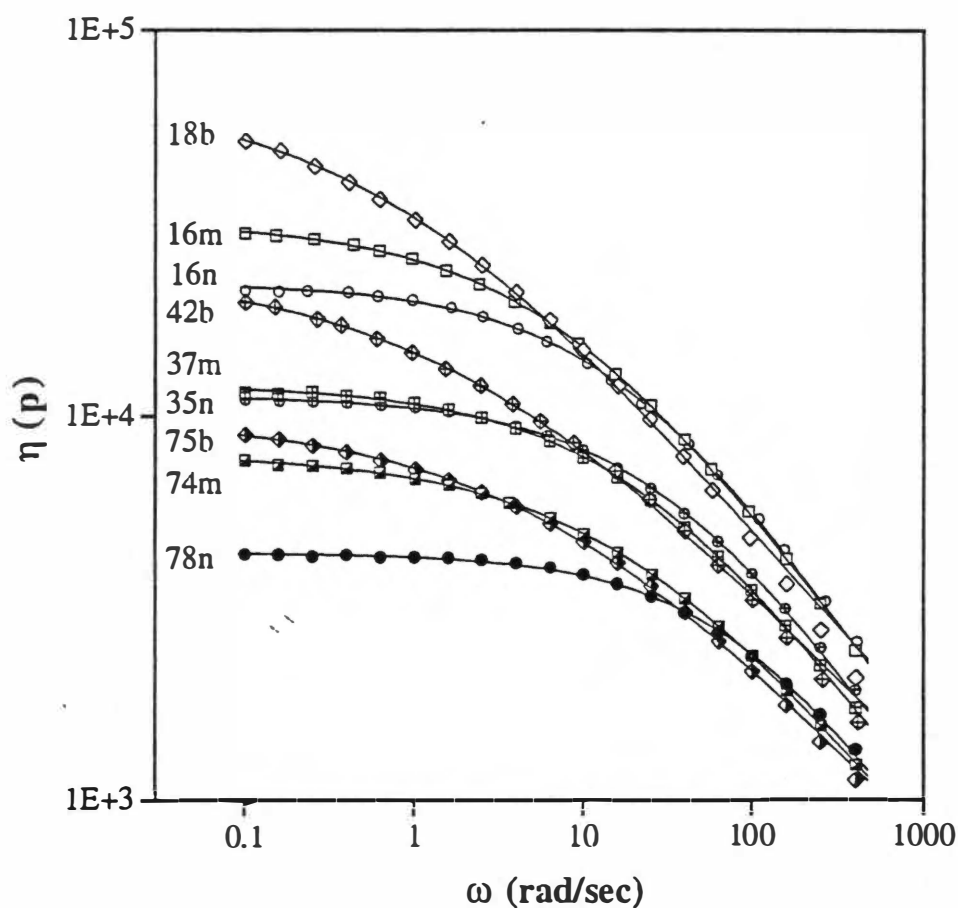


Figure 6.2. Magnitude of complex viscosity versus angular frequency at experimental temperature = 180 °C for the nine considered iPPs.

$$\eta_s(T, \dot{\gamma}) = \frac{\eta_0}{1 + (a_{vis} \eta_0 \dot{\gamma})^{b_{vis}}} \quad (6.16)$$

where η_0 is the zero shear viscosity which is given by equation (6.17),

$$\eta_0(T) = A_{vis} e^{B_{vis}/T} \quad (6.17)$$

The constant a_{vis} , b_{vis} and zero shear viscosity in equation (6.16) were obtained by fitting equation (6.16) to the curve of viscosity verses shear rate at a given temperature. When the zero shear rate viscosity data obtained under different temperature is obtained, equation (6.17) is used to fit the zero shear viscosity versus temperature, and A_{vis} and B_{vis} are thus obtained. The activation energy, B_{vis} , used in the model has value of 11.5 [kcal/mol] ($R = 1.987$ [cal/(mol.K)], $B/R = 11.5 \cdot 10^3 / 1.987 = 5.78762 \cdot 10^3$ [K]) which was supplied by Exxon Chemical Company. With B_{vis} being determined by shear experiments, A_{vis} , a_{vis} and b_{vis} can also directly be determined by spinning experiments which allow calculation of the elongational viscosity by an inversion procedure.

The elongational viscosity can be calculated from the temperature and diameter profiles obtained from the spinline. To obtain the temperature profiles, the regressive equation, usually a polynomial equation, for the diameter profiles needs to be used. Because such regressive equation does not include the die swell effect, but fits the equation to the diameter of the spinneret hole and diameters measured which start from 5 cm for spinneret, errors may be introduced into the calculation. Besides, the temperature and diameter measurements themselves accumulate experimental errors into the calculation of elongational viscosity. The obtained parameters in the viscosity equation were more irregularly related to molecular weight and polydispersity than ones directly obtained from shear viscosity. However, the simulated profiles such as temperature and diameter might be closer to the measured ones by using the parameters fixed through elongational data,

because a fitting procedure to the experimentally measured temperature and diameters has been applied. Compared to the elongational viscosity, the shear viscosity is a directly measured quantity in the experiments, without intermediate experiments and calculations. Less errors could be introduced into the obtained parameters in the viscosity equation. Therefore, A_{vis} , a_{vis} and b_{vis} obtained through shear data can more closely reflect the differences in molecular weights and polydispersities of the materials. However, on the spinline the flow is elongational, the simulated results obtained by using the viscosity equation fixed through shear data might not be good as the one obtained by using the viscosity equation fixed by elongational data. To utilize the strong points from both techniques, the regression of the empirical equation which relates the a_{vis} and b_{vis} to the M_w and M_w/M_n was made on the shear data, and the resultant equation for b_{vis} has been modified by comparing the predicted values for b_{vis} by the equation from the shear data to the b_{vis} from the elongational data. The relationship of $(b_{vis})_{shear}/1.6 = (b_{vis})_{elongational}$ was thus found and applied in the simulation. Similar procedure was carried out for a_{vis} , but there was no significant difference found for values of a_{vis} obtained from the two approaches.

The viscosity is corrected for crystallization according to the equation suggested by Shimizu, et al [Shimizu, Okui and Kikutani (1985)],

$$\eta_e(T, \dot{E}, \theta) = \eta_e(T, \dot{E}) \exp\{a_3 \theta^{b_3}\} \quad (6.18)$$

6.3. Parameter Adjustment

Constant C_N and $(N_c)_0$ in equation (6.8) were determined by quiescent experiment using equation (5.10). The experimental data required for this purpose is described in Chapter 4. C_{NO} in equation (6.1), C_{IO} in equation (6.3) and nucleation index m in equation (6.7) are determined by fitting the simulated birefringence profiles to the

experimental profile obtained from the spinline by on-line measurement. Such experimental data was supplied by Misra, et al [Misra (1994), and Misra, Lu, Spruiell and Richeson (1995)]. The birefringence experimental profile supplies us the information of crystallization onset, increasing rate, ending and orientation along the spinline, and the final value of birefringence. The fitting of the simulated result to the experimental results is a trial and error method, not a statistical one so that the procedure to obtain these parameters is time consuming.

When fitting the simulated results to the experimental birefringence profile, C_{IO} is adjusted according to the onset of rapid increase of birefringence. C_{NO} and m are adjusted together to match the increasing rate of the birefringence. Looking back to the crystallization kinetics results for quiescent crystallization, we know that t_0 , k and n are closely related to each other. Determination of t_0 will strongly affect the value of n . After the fitting was completed, the crystallization half-times were calculated according to the nucleation index obtained. In the completed model, the nucleation index is calculated according to the crystallization half time and crystallization rate constant. For a better adjustment of C_{IO} , C_{NO} and m , various birefringence profiles obtained at different spinning speeds are necessary for each material. The parameters in the present work were adjusted according to two sets of birefringence data obtained at two spinning speeds for each material. An example of the fitting of the simulated results to the experimental birefringence for Resin #6 with $M_w = 136060$ and $M_w/M_n = 3.8$ is given in Figure 6.3, In the example shown, $C_{IO} = 792.7$, $C_{NO} = 3712.2$, $m = 0.12$ for take-up velocity $V_t = 2911$ [m/min] (V in Figure 6.3 is take-up velocity) and $m = 0.181$ for $V_t = 1741$ [m/min]. The spinning conditions are: melt temperature = 210 °C, length of spinline = 220 [cm], diameter of the die = 0.0764 [mm], ambient temperature = 30 °C, and mass throughput = 1.69 [g/min].

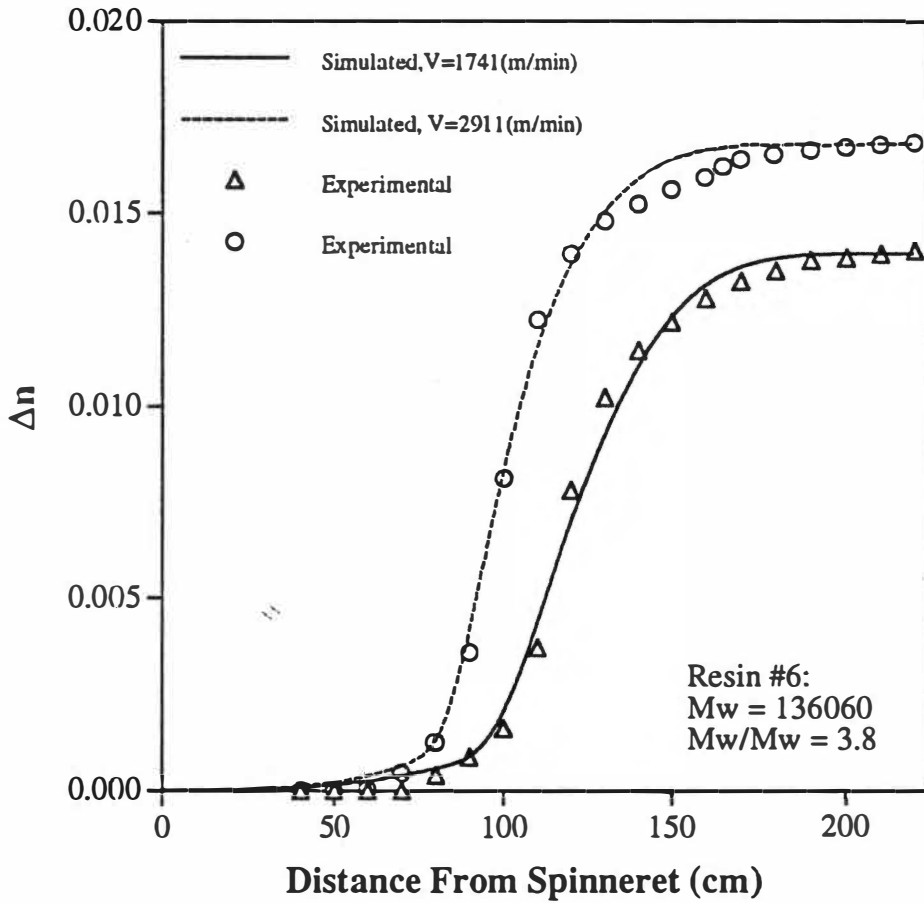


Figure 6.3. Example of fitting the simulated result to the experimental birefringence to adjust model parameters C_{IO} , C_{NO} , and n for Resin #6, $M_w = 136060$ and $M_w/M_n = 3.8$. Spinning conditions: melt temperature = 210 °C, diameter of spinneret = 0.0764 mm, ambient temperature = 30 °C, spinning length = 220 cm, and the take-up velocities are specified in the plot.

The effect of orientation on the crystallization was assumed to be determined by the orientation at crystallization onset in this model. The crystalline orientation was assumed to be constant during crystallization. The crystalline orientation f_c was obtained by fitting the simulated birefringence to the final birefringence measured using the final crystallinity measured off-line. The dependence of f_c on different spinning conditions for each material was found to be described by equation (6.13) in which the dependence of the crystalline orientation on the spinning condition is described by crystallization onset temperature.

The process of adjusting those parameters to fit the simulated results to the experimental birefringence profiles is to determine the strain effect on the crystallization kinetics. Other simulation results such as filament diameter, temperature and stress are not controlled during parameter adjustment. The correct prediction for those variables relies on the correct description of energy balance, viscous behavior and others. It is of course the description of crystallization kinetics that plays the key role in the prediction of other variables. That is why we use the birefringence as criteria to control the model parameter adjustments.

6.4. Extension Of The Model To Materials With Various Molecular Weight And Molecular Weight Distributions

After the model parameters were obtained for each individual material, the constants used in the empirical equations, equation (6.13) for crystalline orientation function, equation (6.12) for final crystallinity, equation (6.11) for crystallization half time, constants used in equation (6.8) for the crystallization rate constant, equation (6.3) for crystallization induction time, and equation (6.15) for elongational viscosity, were correlated to molecular weight and molecular weight distribution. This procedure introduced the molecular parameter dependence into the model.

6.4.1. Viscosity

Equations (6.19) - (6.21) were determined from the experimental measurements made in shear for various homo-iPPs with different molecular weights and molecular weight distributions.

$$A_{vis} = -4.54496 \cdot 10^{-6} M_w + 1.86739 \cdot 10^{-11} M_w^2 + 0.01401 \frac{M_w}{M_n} + 0.25119 \quad (6.19)$$

$$a_{vis} = -4.44115 \cdot 10^{-11} M_w + 1.03599 \cdot 10^{-5} \frac{M_w}{M_n} - 2.25033 \cdot 10^{-5} \quad (6.20)$$

$$b_{vis} = (1.25453 \cdot 10^{-6} M_w - 0.15989 \frac{M_w}{M_n} + 0.98983) \cdot \frac{1}{1.6} \quad (6.21)$$

The comparison of the calculated value by equation (6.19), (6.20) and (6.21) with the fitting value are given in Table 6.1. In Table 6.1 $A_{vis}(\text{shear})$, $a_{vis}(\text{shear})$, and $b_{vis}(\text{shear})$, are the constants obtained individually by fitting to the experimental data. $A_{vis\text{-cal}}$, $a_{vis\text{-cal}}$, and $b_{vis\text{-cal}}$, Are the values calculated according to regressive equations (6.19) - (6.21). $\Delta A_{vis} = |A_{vis}(\text{shear}) - (A_{vis\text{-cal}})|$ and similar equations apply for a_{vis} , and b_{vis} . From Table 6.1 one can see that equations (6.19) - (6.21) can describe the individual fitting constants reasonably well.

The evaluation of the regressions which relate model parameters to MW and MWD may be statistically made by confidence levels or regressive coefficient. The statistical evaluation requires a certain number of samples in a considered test. The present research deals with two independent variables and sometimes the order of an independent variable is higher than one. With only nine experimental points for viscosity, five experimental points for crystallization kinetics and structure parameters, there is not an acceptable number of samples from a statistical point of view, which might result in a poor acceptable confidence. The improvement for the statistical confidence can be effectively made by an increase in the number of samples (resins) in this research. However this is limited by the number of resins available and the large amount of effort required to obtain and analyze the

Table 6.1. Materials Studied and Regressive Constants In the Viscosity Equation

Resin	MFR/MWD	Mw/Mn	Mw	$A_{vis}(shear)$	$A_{vis-cal}$	$\Delta A_{vis}/A_{vis}$
#1	16N	3.1	171810	0.0622	0.0650	0.05
#2	16M	3.5	183980	0.0891	0.0962	0.08
#3	18B	4.8	210850	0.1933	0.1904	0.02
#9	35N	2.8	141790	0.0320	0.0214	0.33
#4	37M	3.7	143850	0.0341	0.0357	0.05
#5	42B	4	162680	0.0673	0.0621	0.08
#6	75B	3.8	136060	0.0280	0.0318	0.14
#7	74M	3.4	132260	0.0225	0.0244	0.08
#8	78N	2.8	118920	0.0124	0.0140	0.13

Resin	$a_{vis}(shear)$	$a_{vis-cal}$	$\Delta a_{vis}/a_{vis}$	$b_{vis}(shear)$	$b_{vis-cal}$	$\Delta b_{vis}/b_{vis}$
#1	2.104E-06	1.982E-06	0.06	0.7068	0.7097	0.00
#2	3.636E-06	5.586E-06	0.54	0.6426	0.6610	0.03
#3	1.791E-05	1.786E-05	0.00	0.5285	0.4869	0.08
#9	2.275E-06	2.073E-07	0.91	0.7002	0.7200	0.03
#4	3.272E-06	9.440E-06	1.89	0.6547	0.5787	0.12
#5	1.647E-05	1.171E-05	0.29	0.4902	0.5543	0.13
#6	1.272E-05	1.082E-05	0.15	0.5049	0.5529	0.10
#7	5.469E-06	6.846E-06	0.25	0.5905	0.6121	0.04
#8	1.821E-06	1.223E-06	0.33	0.7486	0.6913	0.08

data for more resins. Under the limited number of resins, one has to work out a way which can solve the problems. Thus, the correctness of the regressive equation was briefly verified by direct comparison of the predicted values given by the regressive equation to the experimental values. Such an approach provides a direction which leads to us to a point that we can compare the simulated birefringence profiles with the experimental profiles. By this kind of comparison, not only the crystallization parameters, such as C_{IO} , C_{NO} , the Avrami index and so on, can be found, but also the validity of the constants obtained in the procedure that regresses parameters to the MW and MWD can be verified. Because this kind of procedure is not a simple statistical technique, it takes time to finally obtain reasonable values for the related parameters, and it also results in a limited workable range of MW and MWD for the resultant model. The following remarks are thus given to the parameters or coefficients obtained for this chapter: The large number of significant amount of figures retained in the coefficients in equations (6.19) - (6.21) (and subsequent equations in this chapter) are not intended to imply that these values are known to that level of accuracy, but it is only intended to mean that the best fit of data was found with these coefficients.

6.4.2. Constants In The Equation For Nucleation Rate Constant

The coefficients in the equation for nucleation rate constant were found to be given in terms of molecular weight and polydispersities as:

$$C_N = 2.58459M_w - 1.33949 \cdot 10^3 M_w / M_n + 3.67389 \cdot 10^5 \quad (6.22)$$

$$(N_c)_0 = \exp\{2.54865 \cdot 10^{-4} M_w - 2.60195 M_w / M_n + 8.20833\} \quad (6.23)$$

$$C_{NO} = \exp\{3.830616 \cdot 10^{-9} M_w^2 + 0.6426435 M_w / M_n + \\ + 50.24516 - 7.199395 \cdot 10^{-4} M_w - 6.918589 \cdot 10^{-15} M_w^3\} \quad (6.24)$$

The comparison of the calculated values by equation (6.22), (6.23) and (6.24) with the fitting values are given in Table 6.2. It should be pointed out that C_N and $(N_c)_0$ obtained for the model were based on a single growth rate equation (of Resin #3), because other growth rate data were not available at that time, and crystallization rate constant for Resin #6, was directly obtained by Avrami analysis. A more preferred way to obtain equations (6.22) - (6.24) is to use the data given in Chapter 5.

6.4.3. Constants In Crystallization Induction Time t_0

The constants in equation (6.3) for the crystallization induction time, t_0 , were evaluated as follows:

$$C_{IO} = \exp(-1.99120210^{-9}M_w^2 + 1.716287M_w / M_n - 17.68836 + 3.34479210^{-4}M_w + 3.65036110^{-15}M_w^3) \quad (6.25)$$

$$C_I = 4.040 \cdot 10^5$$

$$\ln \left[\left(\frac{1}{t_0} \right)_0 \right] = 13.44$$

6.4.4. Constants In The Equation Related To Crystallization Half Time

The constants in equation (6.11) for crystallization half-time were found to be:

$$A_{t12} = 0.385119 \cdot 10^{-5}M_w - 0.009836914M_w / M_n + -1.4410166 - 6.920791 \cdot 10^{-12}M_w^2 \quad (6.26)$$

$$B_{t12} = -2.055947 \cdot 10^{-5}M_w + 1.123203M_w / M_n + 6.355718 + 2.06265410^{-11}M_w^2 \quad (6.27)$$

Table 6.2. Regressive Constants In The Equation For Nucleation Rate Constant

Resin	MFR	C _N	C _N Calculated	$\Delta C_N/C_N$	$\ln(N_C)_0$	$\ln(N_C)_0$ Calculated	$\frac{\Delta \ln(N_C)_0}{\ln(N_C)_0}$
#1	16N	822389	807295	-0.018	45.746	43.931	-0.040
#3	18B	855738	905920	0.059	47.001	49.457	0.052
#9	35N	695013	730107	0.050	34.343	37.060	0.079
#5	42B	910762	782492	-0.141	44.310	39.262	-0.114
#6	75B	655869	713958	0.089	31.308	32.998	0.054

6.4.5. Constants In The Equation Related To Final Crystallinity X_c

The constants in equation (6.12) were found to be given by

$$a_{X_c} = \exp\{8.215628 \cdot 10^{-5} M_w - 0.228821 M_w / M_n + \\ -21.63389 - 2.571536 \cdot 10^{-10} M_w^2\} \quad (6.28)$$

$$b_{X_c} = 1.820856 \cdot 10^{-6} M_w + 0.3378755 M_w / M_n + \\ -0.487424 + 7.59372910^{-12} M_w^2 \quad (6.29)$$

6.4.6. Constants In The Equation Related To Crystalline Orientation Factor

The constants in equation (6.17) were found to be given by

$$A_{fc} = -44.85633 \cdot 10^{-6} M_w + .5714364 M_w / M_n + \\ +2.317424 + 1.27887910^{-10} M_w^2 \quad (6.30)$$

$$B_{fc} = -4.54496 \cdot 10^{-6} M_w + .01401 M_w / M_n + \\ +0.25119 + 1.86739 \cdot 10^{-11} M_w^2 \quad (6.31)$$

6.5. Description Of The Calculation Procedure

The flow diagram for the present simulation of the melt spinning process is given in Figure 6.4. The input of the model includes take-up velocity V_t , melt temperature T^0 , diameter of spinneret D_0 , length of the spinline L , ambient temperature T_A , mass throughput W , weight average molecular weight M_w and polydispersity M_w/M_n . One also needs to guess a value for the initial rheological force, F_0 .

The calculation can be divided into two stages: calculation before crystallization and after crystallization begins. The first stage deals with calculation without crystallization which includes equations (1) - (7) in Figure 6.4. During this stage, the crystallization onset is determined according to equation (6.4) or equation (10) in Figure 6.4. The integration of

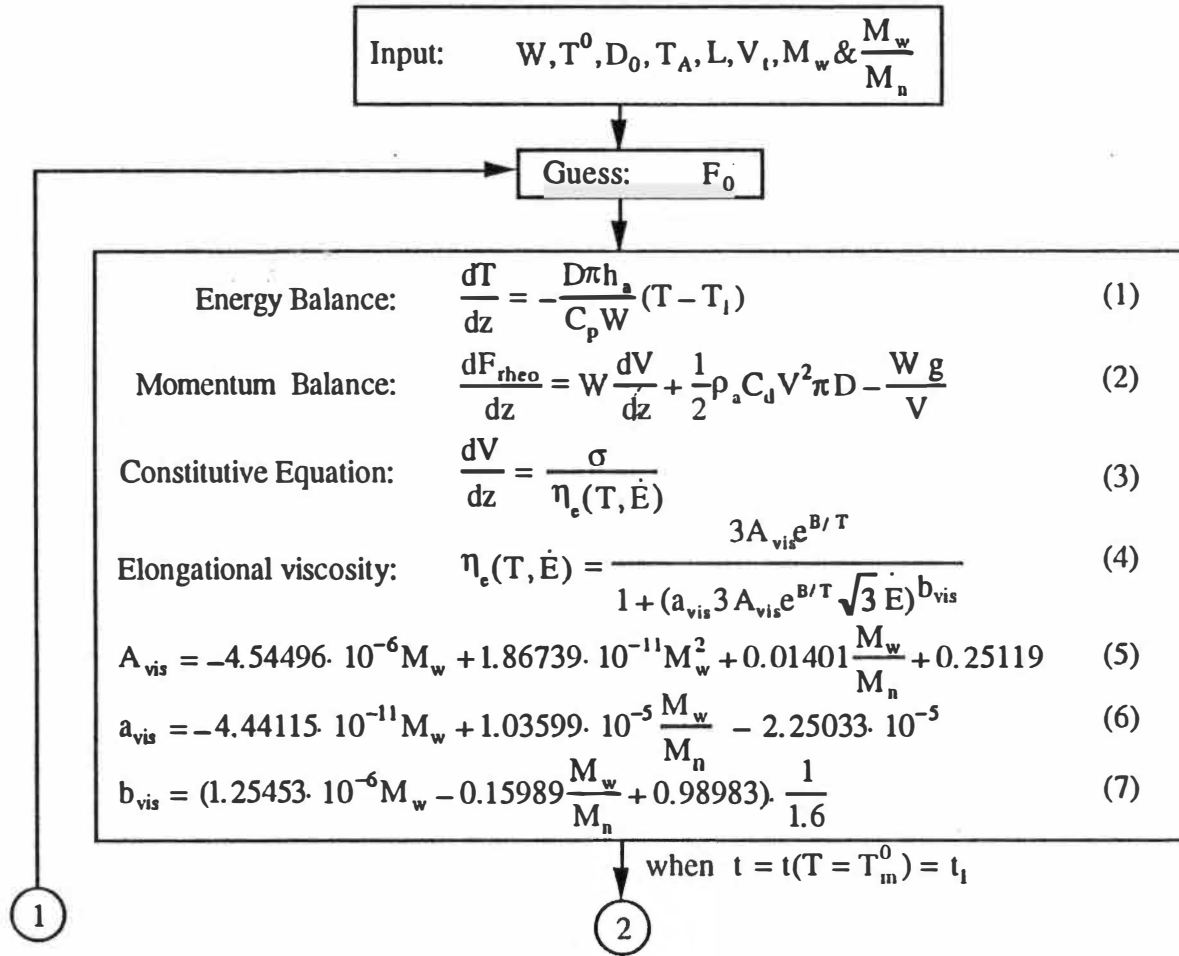


Figure 6.4. Flow diagram of the calculation procedure of the model of the melting spinning process (continued on next page).

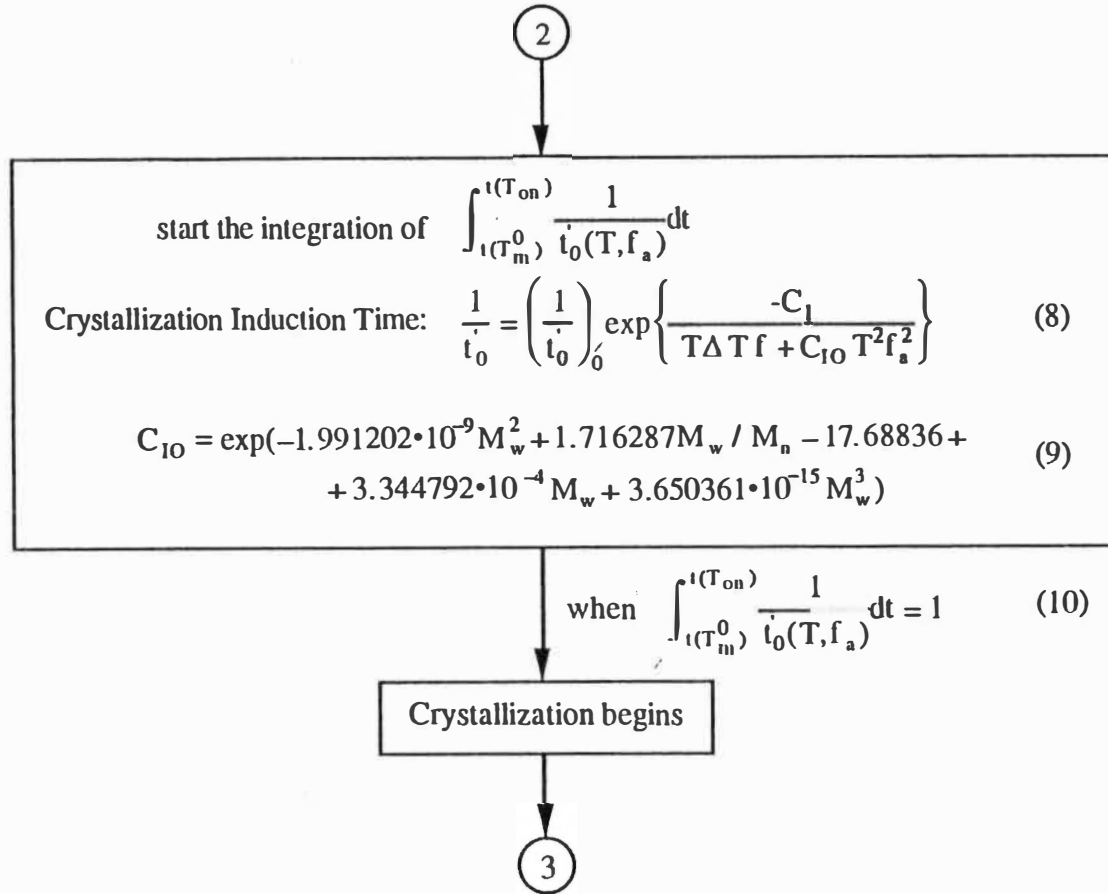


Figure 6.4 (continued — 1) Flow diagram of the calculation procedure of the model of the melting spinning process (continued on next page).

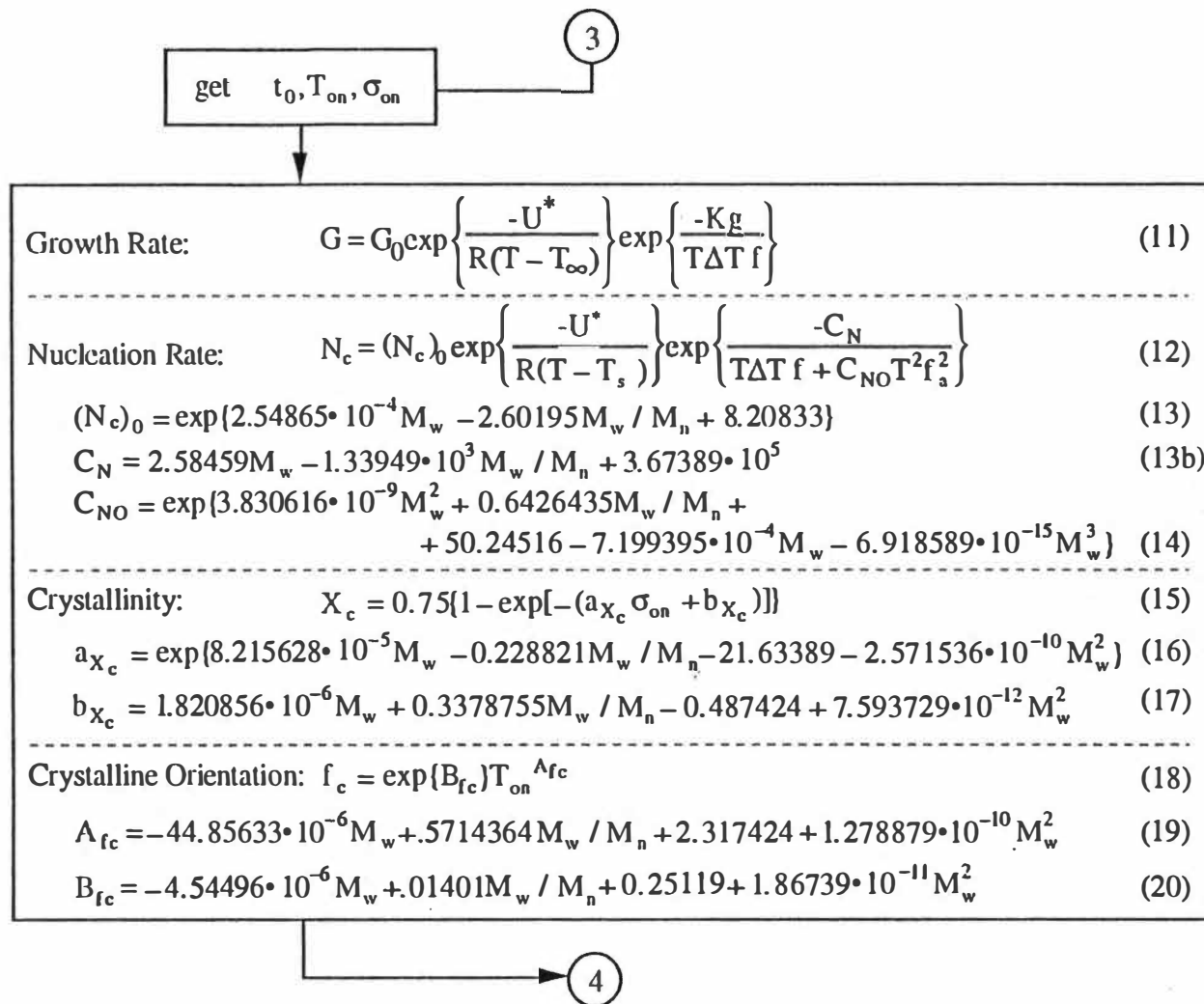


Figure 6.4 (continued — 2) Flow diagram of the calculation procedure of the model of the melting spinning process (continued on next page).

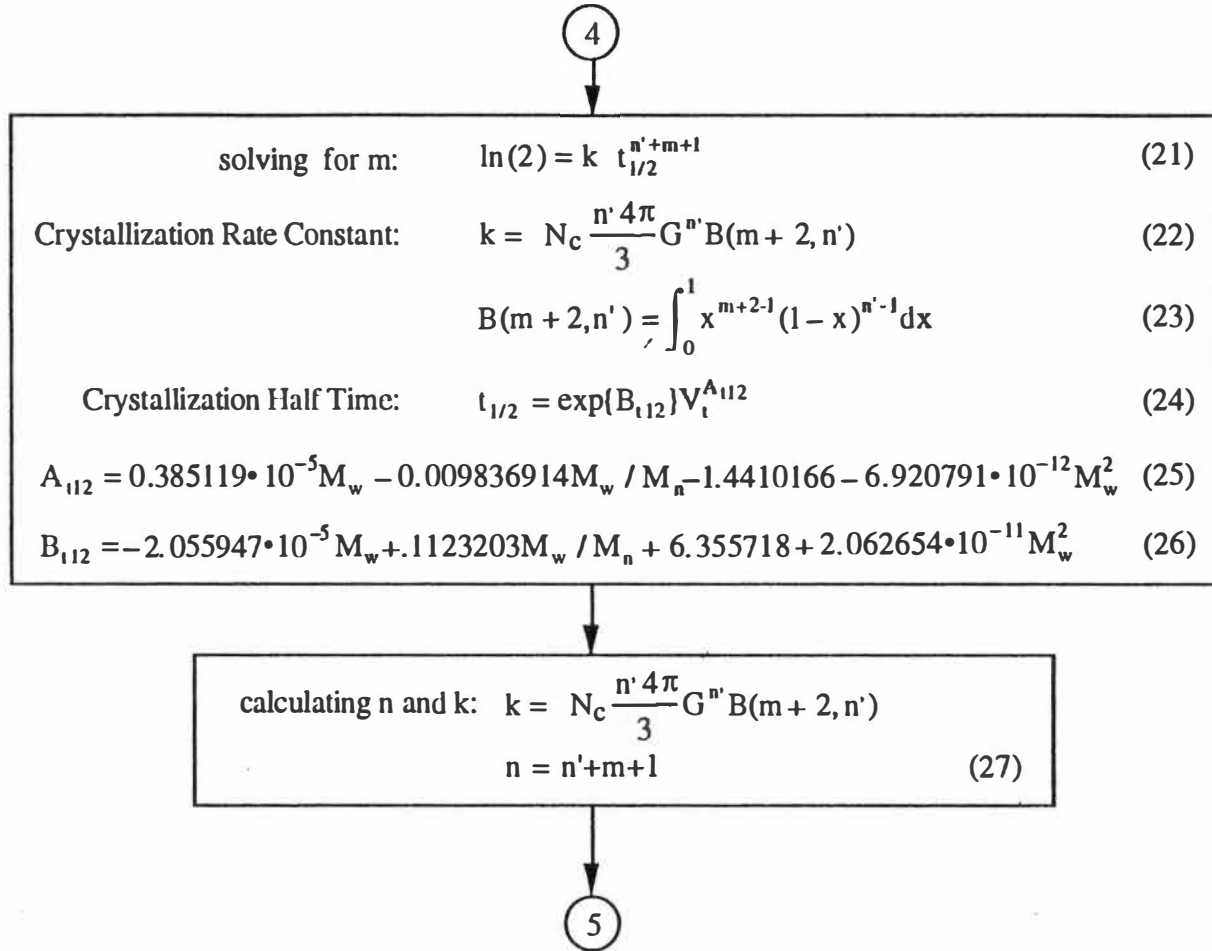


Figure 6.4 (continued — 3) Flow diagram of the calculation procedure of the model of the melting spinning process (continued on next page).

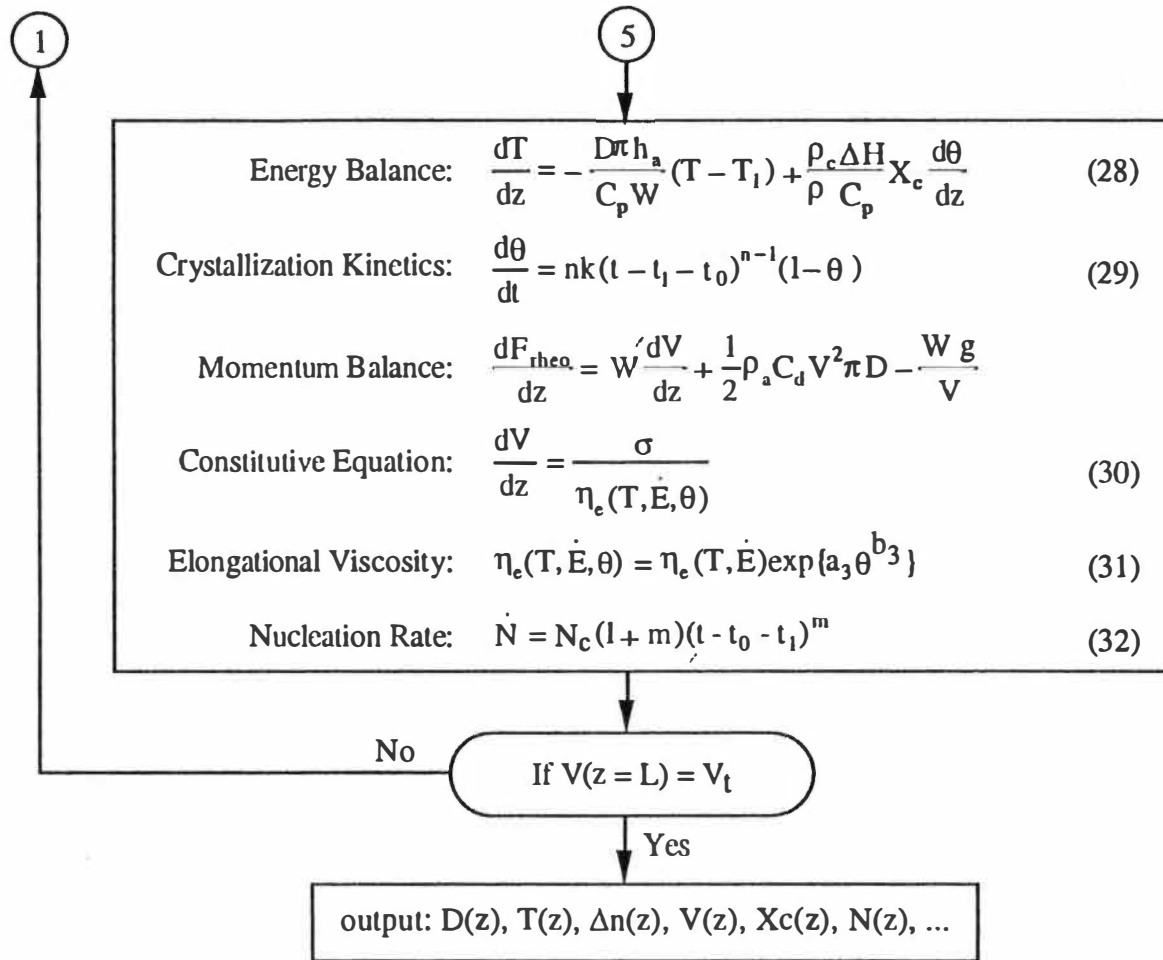


Figure 6.4 (continued — 4) Flow diagram of the calculation procedure of the model of the melting spinning process.

the reciprocal of incubation time in the model starts at $t_1 = t(T=T_m^0)$. The crystallization begins when $\int_{t(T_m^0)}^{t(T_{on})} \frac{1}{t_0(T, f_a)} dt = 1$. The crystallization onset time is $t_{on} = t_1 + t_0$. The induction time is thus calculated by $t_0 = t_{on} - t_1$. The temperature at crystallization onset is called the crystallization onset temperature. The orientation used to calculate the nucleation rate constant under strain in equation (6.8) is also selected at crystallization onset. With those parameters determined, the nucleation rate constant, the growth rate, the final crystallinity in the fiber, and the crystalline orientation can be calculated. Because the crystallization half time is determined by the given take-up speed, the nucleation index can be solved after the growth rate and nucleation rate constant are calculated according to equation (21) in Figure 6.4. The crystallization rate constant and Avrami index are then calculated after the m is obtained. In the calculation, the linear growth rate was assumed not to be a function of the orientation, and the nucleation is a decisive factor for the rate of crystallization under strain.

In the second stage of calculation which includes equation (28) - (32) in Figure 6.4, the crystallization is included in the energy balance equation. The crystallization kinetic equation is also introduced as shown by equation (29) and (32) in Figure 6.4. The elongational viscosity is corrected for crystallinity according to equation (31) in Figure 6.4. The calculated final velocity $V(z = L)$ is compared with the given take-up speed V_t . If $|V(z = L) - V_t|$ is less than a selected limit, say 10 [m/min], the program gives the output such as diameter $D(z)$, temperature $T(z)$ and so on along the spinline z . If $|V(z = L) - V_t|$ is greater than the limit, calculation goes back to the very beginning: a new F_0 will be selected and the calculation will be repeated.

In the selection of F_0 , the program will find an optimum F_0 according to certain evolution scheme which systematically tries to match the boundary condition: the given spinning speed. During the evolution period, because the final spinning speed is changing

before the given value is reached, most of the crystallization kinetic parameters also vary at each evolution process which includes the nucleation rate, crystallization constant and the nucleation index m . The crystallization onset time, the onset temperature and the onset stress also change during the evolution. Each evolution process needs to calculate the integration of reciprocal of crystallization half time to find the crystallization onset time. The final value of the model parameters are found when the final spinning speed matches the given take-up velocity. The process of finding the optimum F_0 in the calculation is therefore time consuming.

The plateau temperature in the cooling curve was firstly selected as the crystallization temperature in the model. Such a selection relies on the plateau temperature as a function of cooling rate characterized by heat transfer coefficient obtained in quiescent crystallization, thermodynamic analysis of the relation of crystallization temperature and melting temperature, and the results (referring to plateau temperature) obtained from the calculation of the model. The main difficulty for such an approach is that the calculation time is very long during adjustment of the parameters related to the orientation, because during the evolution procedure to obtain an optimum F_0 , the plateau temperature is changing as F_0 changes, even though the plateau temperature is predicted before crystallization. The change of plateau temperature results in a change of all parameters which are determined by plateau temperature. This causes the required computer time to obtain the optimum value of F_0 to be very long. This also creates a problem for parameter adjustment in the case of multiple materials. To reduce the complexity of parameter adjustment, the crystallization onset temperature is selected as the crystallization temperature in the present model. Such a selection needs no theoretical analysis or calculation to obtain the crystallization temperature because the crystallization temperature is found when the crystallization onset is found. It is, therefore, the determination of crystallization onset that becomes critically important.

6.6. Simulation Results

6.6.1. Relationships Between Various Profiles

For a better understanding and easier discussion of the obtained results, the relationships between profiles of birefringence, temperature, diameter, crystallinity and nucleation density will be discussed first. Figure 6.5 gives those profiles which are plotted against distance from the spinneret. It is because we mainly use those profiles to discuss and demonstrate the simulation results that we discuss the relationships before we discuss anything else. It is possible however, other profiles, such as viscosity, velocity gradient, stress, and so on, may be introduced to understand points otherwise difficult to understand.

The results in Figure 6.5 were obtained for material with $M_w = 141790$, $M_w/M_n = 2.8$ under the spinning speed = 5700 m/min, melt temperature = 210 °C, ambient temperature = 30°C, and mass throughput = 1.68 g/min. The crystallization begins at the distance from the spinneret $z = 74$ cm for this specific case. The crystallinity increases rapidly and approaches the final value at $z = 125$ cm. The nucleation density increases very rapidly at the crystallization onset and more quickly approaches the final value than does the crystallinity. There is recalescence in the temperature profile which is apparently caused by the heat released from crystallization according to the crystallinity and temperature profile given by Figure 6.5. At crystallization onset, the little heat generated by the small amount of crystallinity only slows down the rate of temperature decrease. As the rate of crystallization increases, the temperature starts to reincrease. At the maximum of the reheat-up of the temperature, almost 80% of the final crystallinity has been transformed. After the temperature reheat-up, the temperature continuously drops again because the crystallization

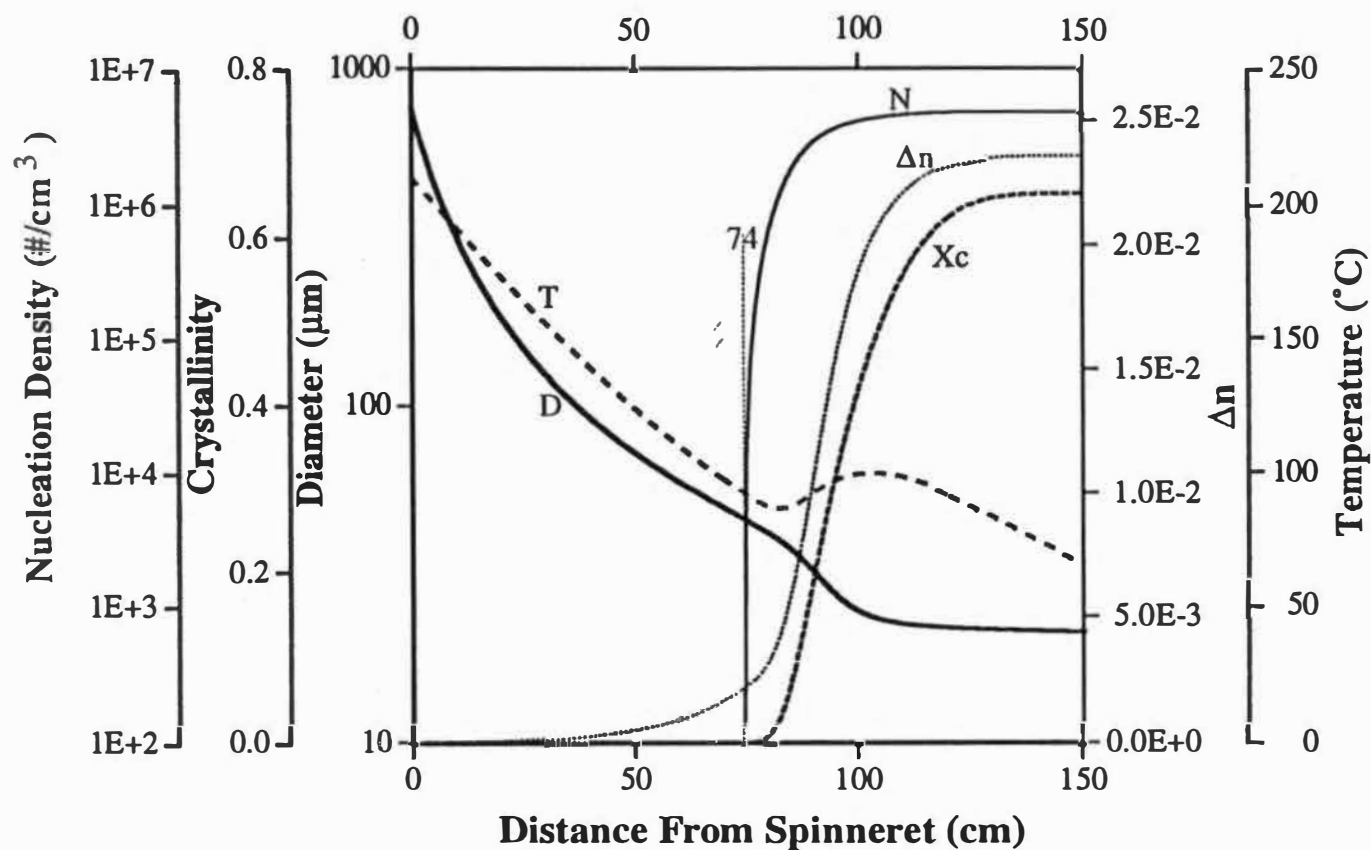


Figure 6.5. Calculated birefringence, diameter, temperature, crystallinity, and nucleation density versus distance from spinneret at various spinning speeds for iPP spinning speed = 5700 m/min, $M_w = 141790$, $M_w/M_n = 2.8$, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.68 g/min.

approaches the end. The location of the reheat-up of the temperature is at the main region of crystallinity development.

As indicated by Figure 6.5, the birefringence profile is basically divided into three parts: in the first part, the birefringence increases slowly, which corresponds to the development of some molecular orientation before crystallization; in the second part the birefringence increases fast, which corresponds to the development of crystallization on the spinline; in the last part, the crystallization is almost complete and birefringence is gradually approaching the final value. The fast increase region for birefringence is related to the rapid increase in crystallinity according to the birefringence and crystallinity profiles given by Figure 6.5. The increase in birefringence with increase of crystallinity is because of the oriented nucleation and growth of the oriented crystalline phase. This produces large quantities of oriented molecules compared to the case of the oriented amorphous phase. The birefringence in filaments is decided by the degree of molecular orientation in each phase and the crystallinity.

There is faster draw down in the diameter profile during the earlier crystallization region, which will be discussed in more detail later in this chapter. The diameter approaches the final value as crystallinity approaches its ultimate value.

6.6.2. Influence Of Change In Molecular Weight

In this section the influence on the simulation results of changing the molecular weight at constant polydispersity is illustrated. The weight average molecular weight examined for this purpose is from 110,000 to 230,000. For the purpose of this illustration, the polydispersity is held constant at $M_w/M_n = 3.8$, and the spinning conditions are chosen as follows: spinning speed = 2000m/min, melt temperature = 210 °C, Ambient temperature = 30 °C, and mass throughput = 1.6 g/min.

6.6.2.1 Predicted results

Figure 6.6 gives birefringence profiles for materials with various molecular weights. As shown in Figure 6.6, the profile for higher MW has a earlier start of the fast increase in birefringence, a higher increase rate for the fast increase region of birefringence, and approaches to a higher final value than does the one for lower MW .

The simulated temperature profiles for this example are presented in Figure 6.7. Figure 6.7 shows that the curve for higher molecular weight displays a sharper temperature reheat-up and the position of the reheat-up in temperature shifts closer to the spinneret.

The diameter profiles given in Figure 6.8 display an extraordinary feature. The diameter draw down is slower near the spinneret for materials with higher molecular weight, and later drops faster to approach the final diameter. The diameter profiles for different molecular weight therefore exhibit a crossover with each other. However, the draw down, in all, is faster for materials with higher molecular weight than for lower MW materials because the diameter for higher MW material approaches the final value sooner than does the low MW material.

Figure 6.9 gives the crystallinity profiles for different molecular weight. The crystallinity starts to develop closer to the spinneret, increases faster and reaches a higher final value for higher molecular weight materials. The lower final crystallinity value for $M_w = 230,000$, is possibly caused by the parameters in the model not being perfectly adjusted, or change of the MW is out of the workable range at the given polydispersity.

Figure 6.10 gives profiles of nucleation density along the spinline. The nucleation density increases faster and reaches a higher final value for materials with higher MW than for the lower MW materials.

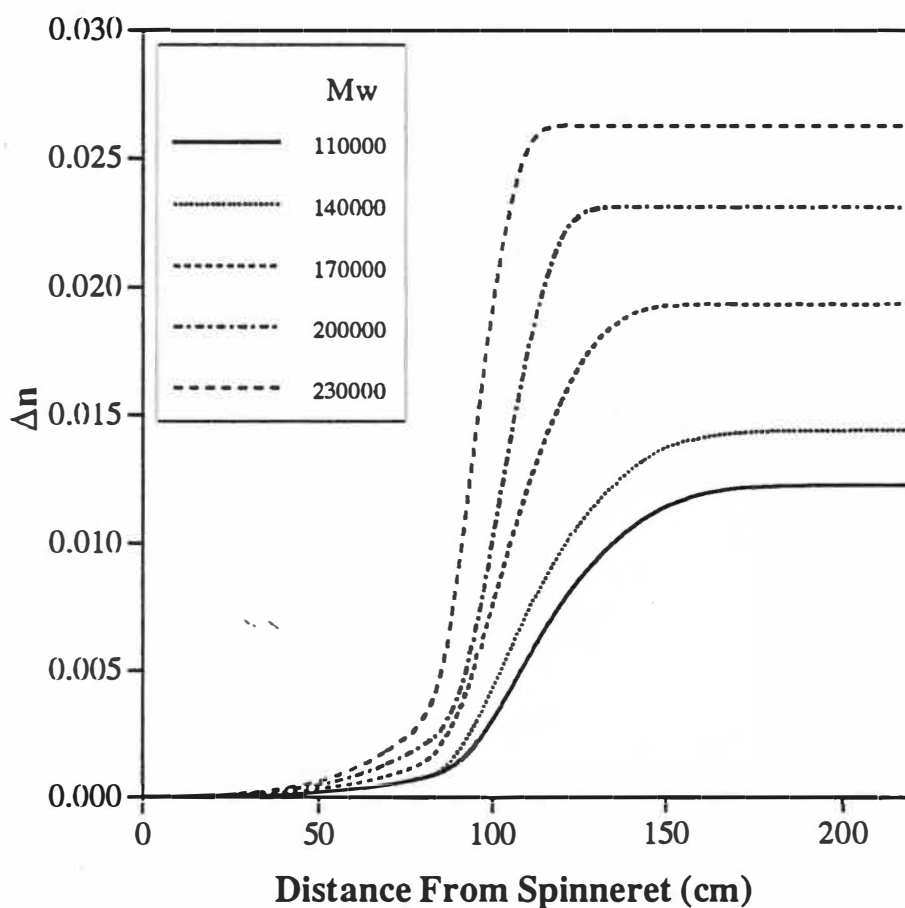


Figure 6.6. Calculated birefringence versus distance from spinneret at various molecular weight for iPP. Polydispersity is held constant at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

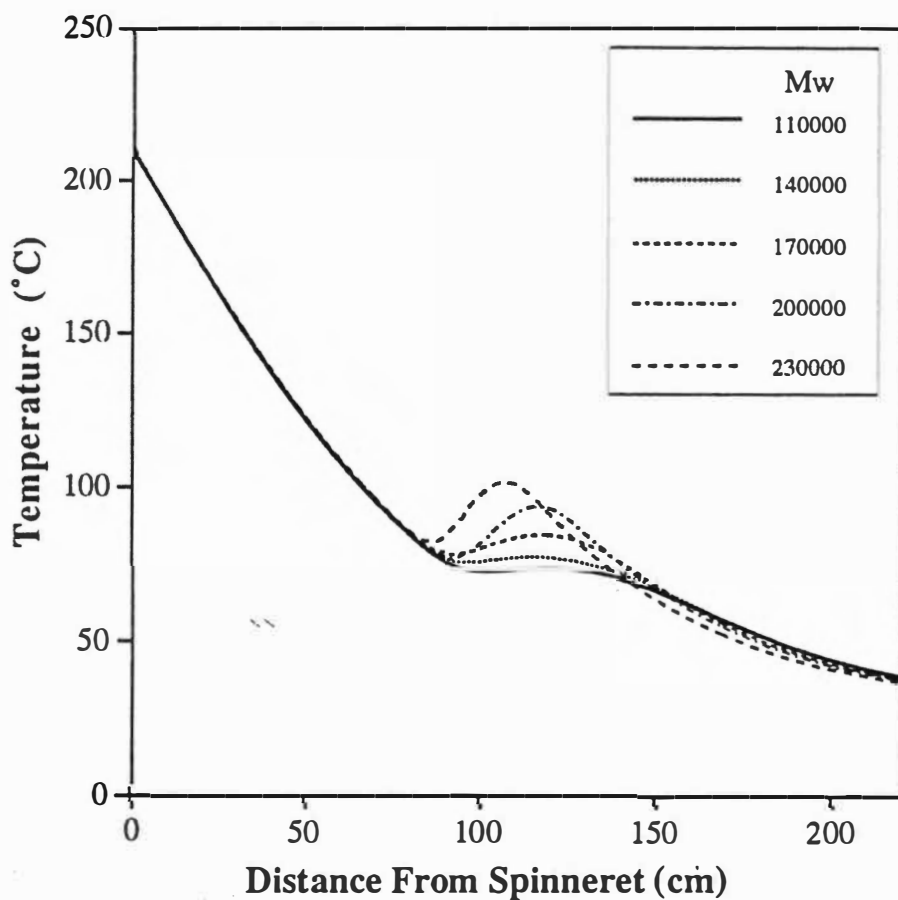


Figure 6.7. Calculated temperature versus distance from spinneret at various molecular weight for iPP. Polydispersity is held constant at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210°C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

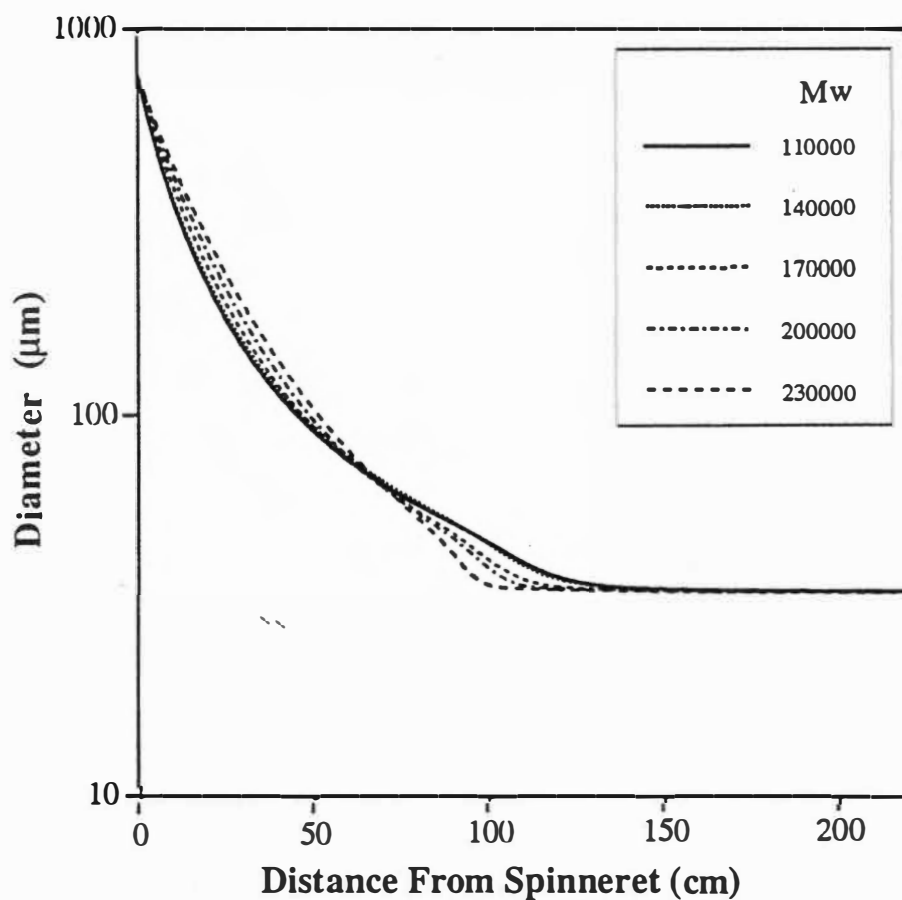


Figure 6.8. Calculated diameter versus distance from spinneret at various molecular weight for iPP. Polydispersity is held constant at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210°C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

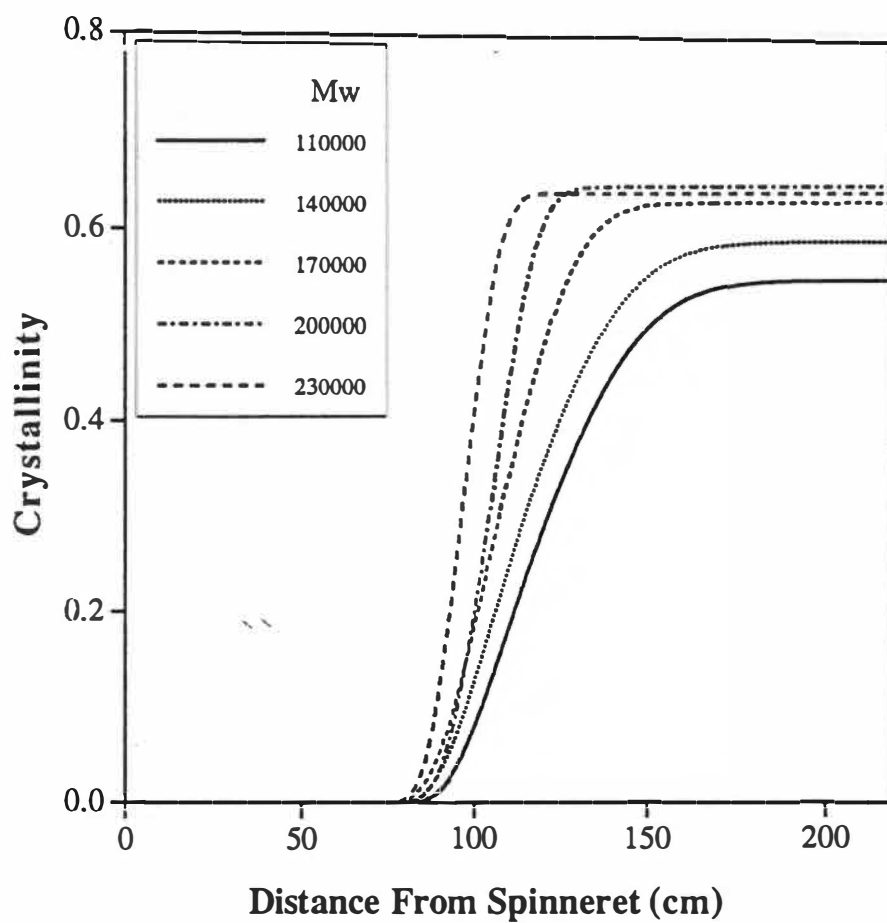


Figure 6.9. Calculated crystallinity versus distance from spinneret at various molecular weight for iPP. Polydispersity is held constant at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210°C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

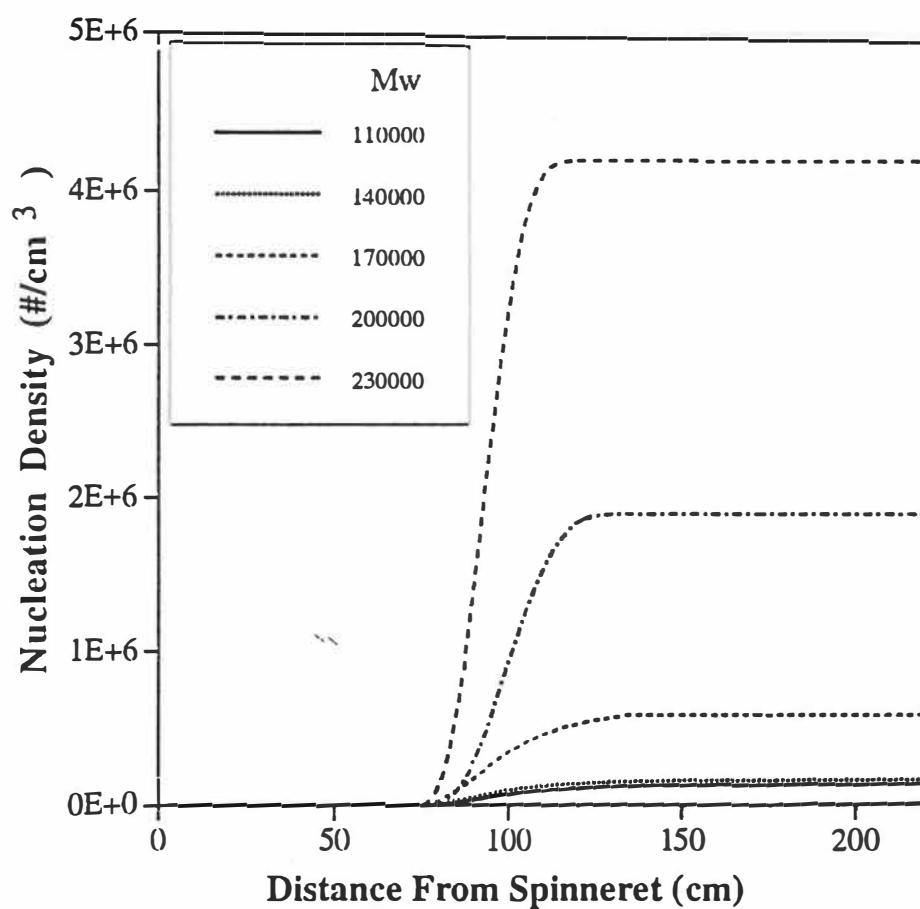


Figure 6.10. Calculated nucleation density versus distance from spinneret at various molecular weight for iPP. Polydispersity is held constant at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210°C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

6.6.2.2. Discussion of influence of molecular weight

The key point in the variation of MW is that increase in MW increases the viscosity at each point along the spinline, as shown in Figure 6.11. In Figure 6.11, the elongational viscosity for materials with various MW were plotted against distance from spinneret. The shape of the viscosity will be discussed later in this section. Figure 6.11 shows that the material with higher molecular weight has a higher elongational viscosity along the spinline. Because of the higher viscosity, the stress along the spinline also has higher value for the materials with higher MW as show by Figure 6.12 in which the stress along the spinline is plotted against distance from spinneret. In Figure 6.12, the curves for material with higher molecular weight are above the ones with lower molecular weight before crystallization. The higher stress gives a higher molecular orientation along the spinline, and high molecular orientation triggers off the crystallization onset closer to the spinneret, or at a smaller crystallization onset distance, z_{on} , Figure 6.13, and induces a higher crystallization rate for materials with higher MW, Figure 6.9. The higher crystallization rate gives a sharper reheat-up of temperature in Figure 6.7 which occurs closer to the spinneret. Both the closer distance to the spinneret and the higher crystallization rate result in a shorter draw down zone and more compressed deformation region on the spinline for materials with higher MW.

A crossover point in the diameter profile shown in Figure 6.8 would seem to be necessary. If the profiles for materials with higher molecular weight were all located on the left side of the ones with low molecular weight, this would imply that the thinning rate is faster all the time for materials with higher molecular weight. Especially when one considers the thinning process near the spinneret, the higher viscosity of material with higher molecular weight would be expected to reduce the thinning rate. The faster thinning in the region near the spinneret reveals the lower viscosity for lower molecular weight

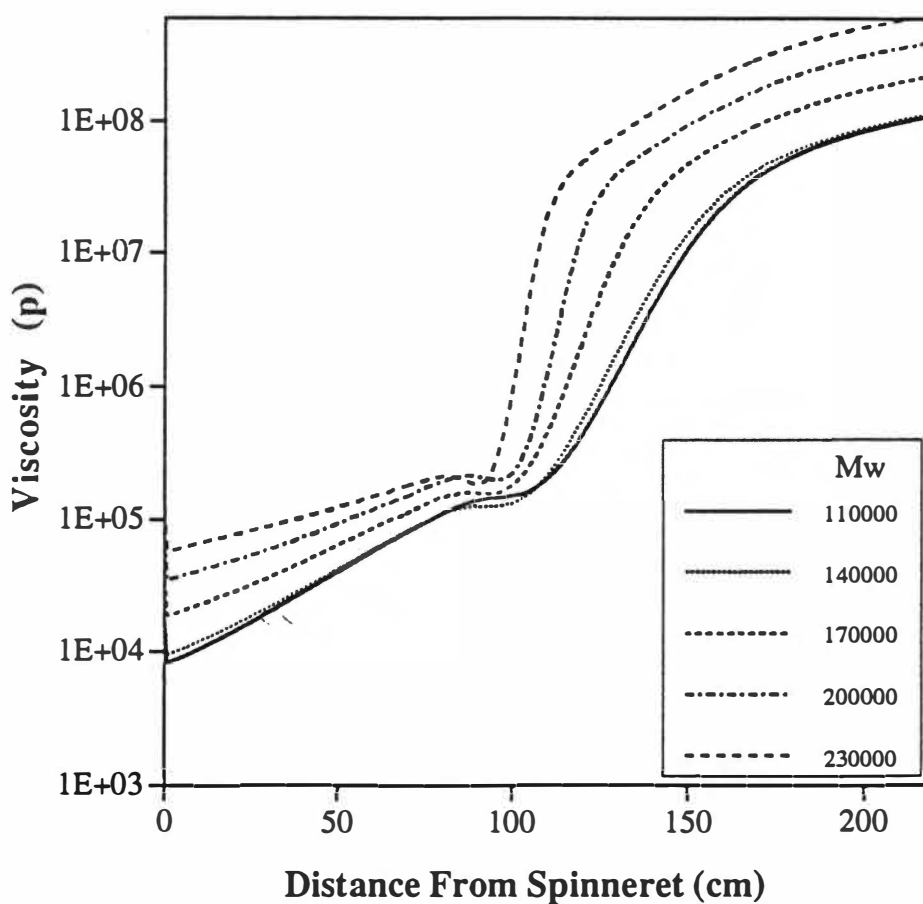


Figure 6.11. Calculated elongational viscosity versus distance from spinneret at various molecular weight for iPP. Polydispersity is held constant at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210°C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

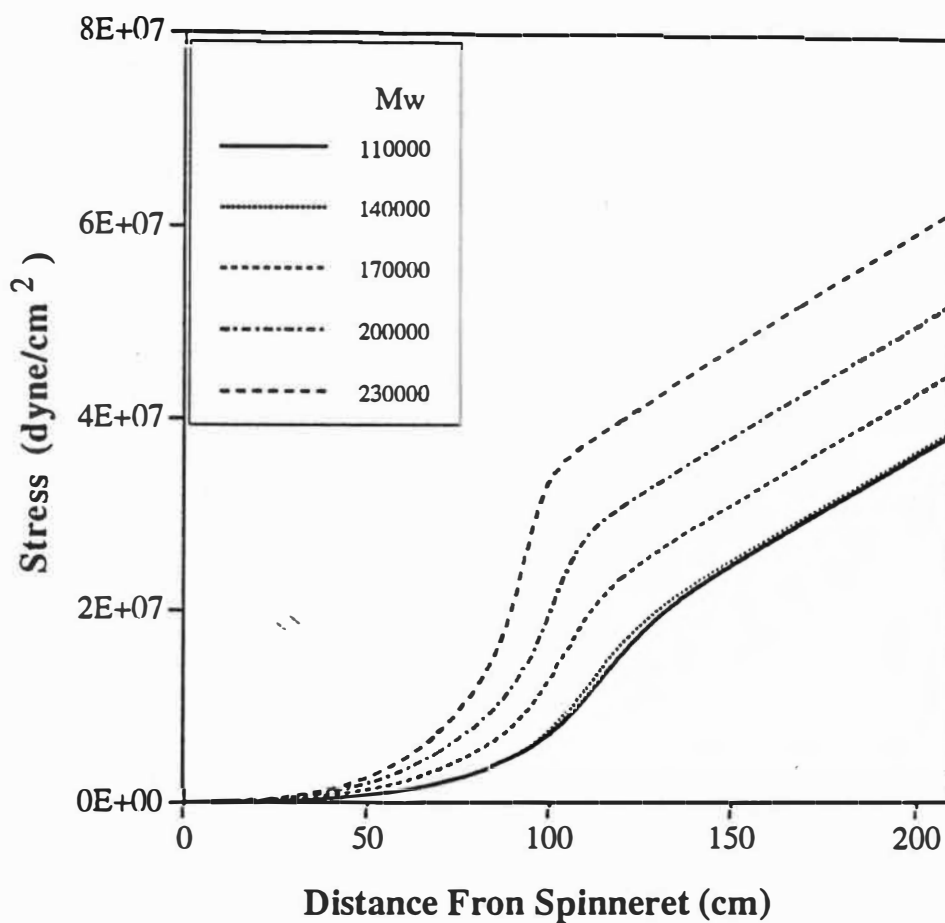


Figure 6.12. Calculated stress versus distance from spinneret at various molecular weight for iPP. Polydispersity is held constant at $M_w/M_n = 3.8$, spinning speed = 2000 m/min, melt temperature = 210°C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

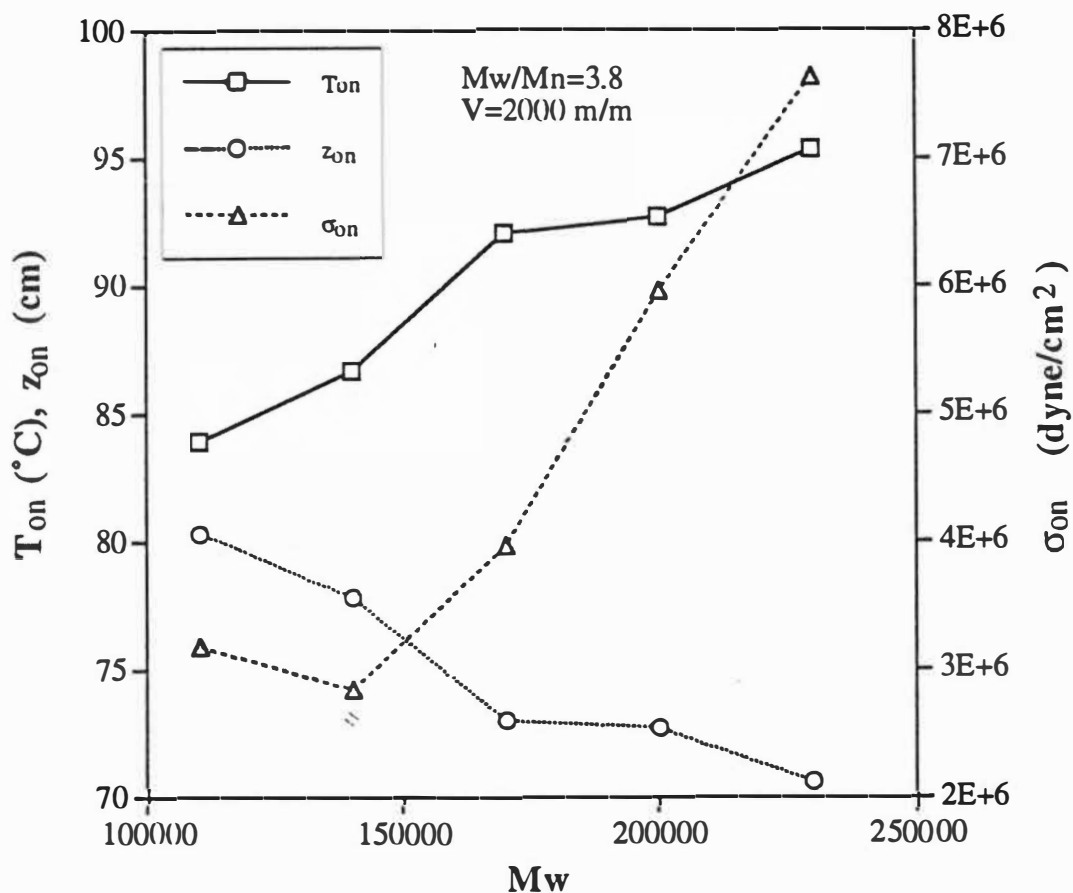


Figure 6.13. Crystallization onset temperature, T_{on} , onset position, z_{on} , and onset stress, σ_{on} , as functions of molecular weight. Polydispersity was held constant at 3.8 and spinning speed is 2000 m/min, melt temperature = 210°C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

material. Though there is a faster thinning process in the early deformation stage for materials with lower MW, the later onset of crystallization under lower stress delays the ending of the draw down. The draw down region for materials with lower MW is therefore longer than the one with higher MW. For material with higher MW, though there is a slower draw down near the spinneret, it has to have a rapid draw down in the later stage to reach the final diameter within a shorter draw down region. Therefore, the crossover in diameter profile for materials with different MW is necessary.

The higher crystallization rate is caused by the higher nucleation rate. Since the stress is higher, the nucleation rate is faster for materials with higher MW. With higher nucleation rate, the higher molecular weight material reaches a higher final nucleation density with a faster rate of increase.

6.6.2.3. Parameters related to crystallization onset: t_1 , t_0 , T_{on} , σ_{on} and X_{on}

Figure 6.13 shows that the higher molecular weight leads to higher onset temperature and stress, T_{on} and σ_{on} . Also, the location of the crystallization onset on the spinline shifts closer to the spinneret as molecular weight increases. In spite of this, both the crystallization induction time, t_0 , and the time needed to cool down the polymer from its melt temperature to its equilibrium melting temperature, t_1 , increase with increasing molecular weight as shown in Figure 6.14. Figure 6.15 explains the reason for this unexpected behavior. The left ends of the horizontal straight lines in Figure 6.15 represent the t_1 , the right ends, the t_{on} , the length of them is t_0 , and the levels of them, the crystallization onset stress. If one draws a vertical line through the right end of each of these lines, the point where it crosses the temperature curve locates crystallization onset temperature. As indicated by Figure 6.15, the lower the molecular weight, the faster the

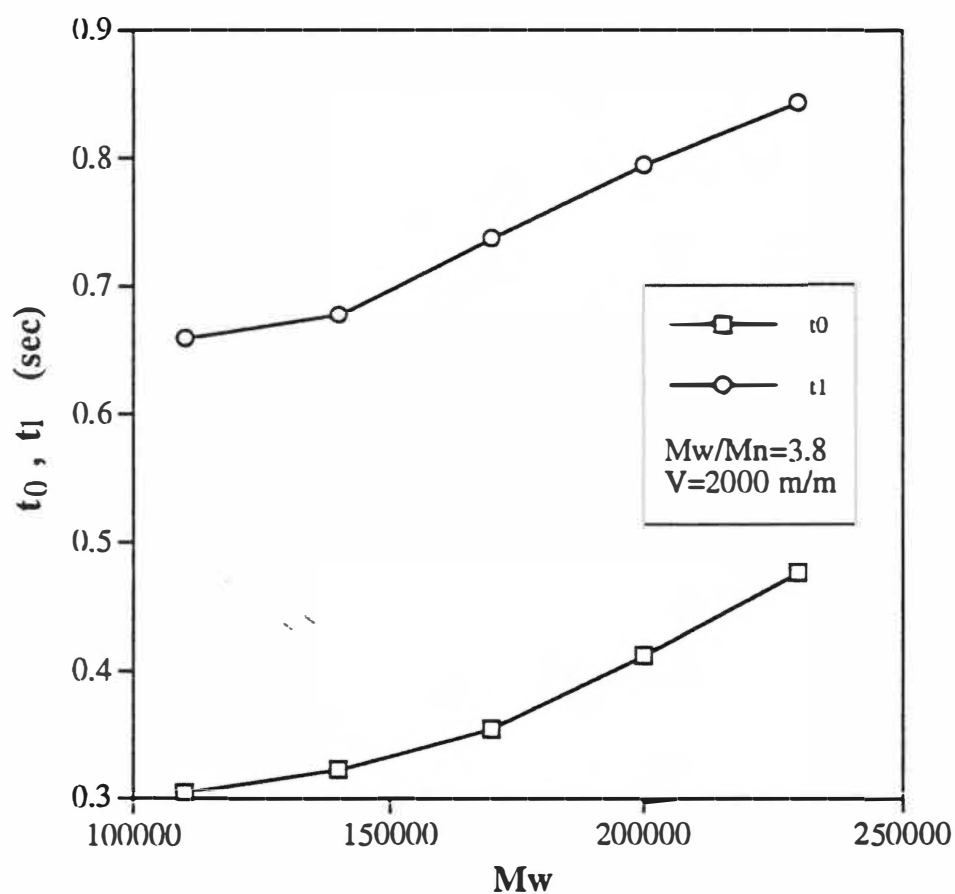


Figure 6.14. crystallization induction time, t_0 , and time needed to cool down polymer from its melt temperature to equilibrium melting temperature, t_1 as functions of MW.

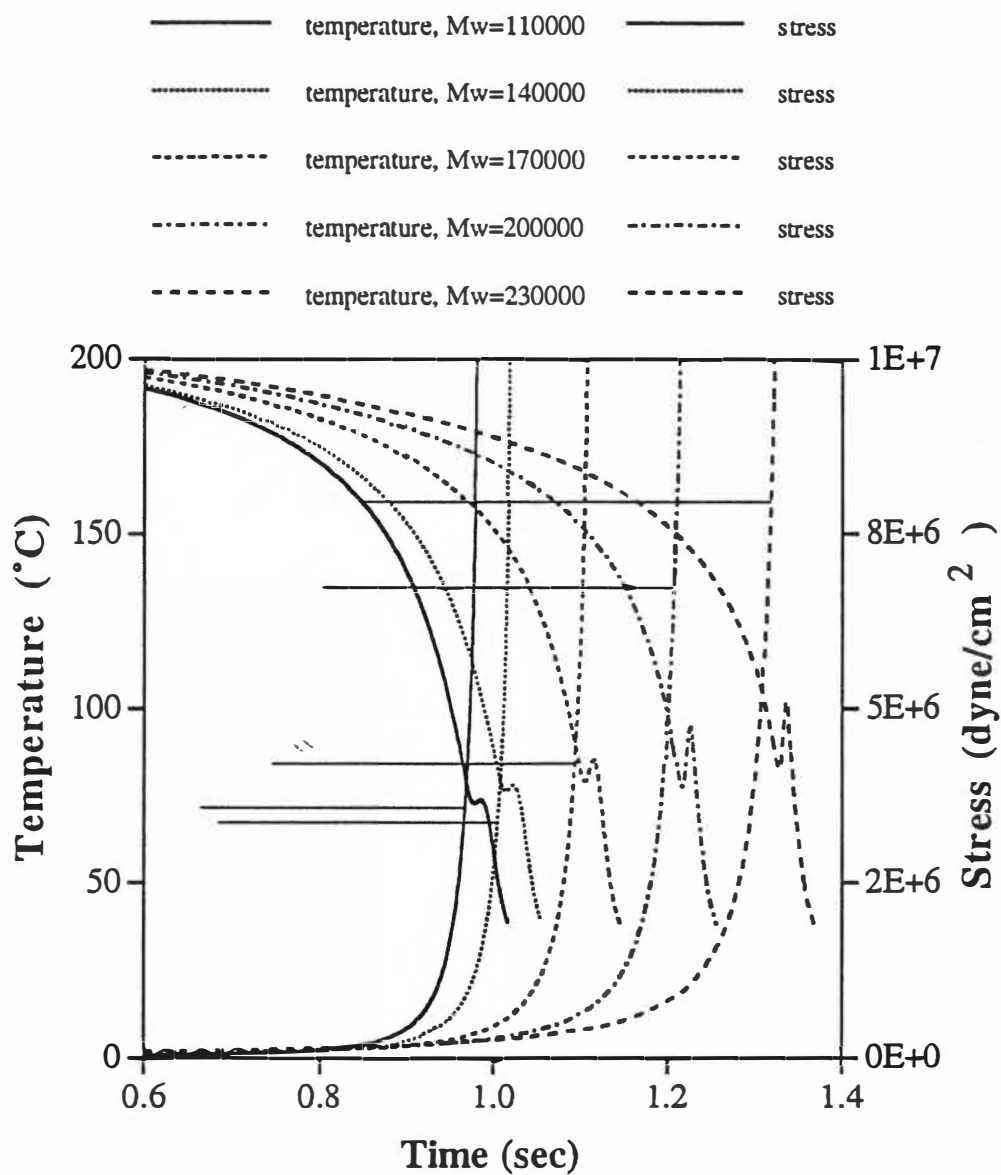


Figure 6.15. Temperature and stress in the polymer stream on the spinline as functions of time for materials with various molecular weight.

cool down of temperature and the faster is the increase of the stress in the polymer. This is because the lower molecular weight gives a lower viscosity at the same temperature, and the polymer is easier to deform before crystallization. The thinning process is faster in the upper part of the spinline with decreasing molecular weight. This results in the faster cool down of the polymer temperature. The cooling curve is therefore shifted to the left in Figure 6.15 when molecular weight decreases. This produces the lower values of both t_1 and t_0 as molecular weights decreases.

The variation of cooling rate and stress development in the spinning process combine to give a higher driving force for crystallization at a given temperature for the higher molecular weight samples, which results in a higher onset temperature for crystallization as molecular weight increases.

The higher deformation rate and faster cooling rate result in a faster stress build-up for material with lower molecular weight in spite of the lower viscosity. These effects combining to give a shorter induction time for material with lower molecular weight. But because of the lower viscosity of the lower molecular weight material, the crystallization onset stress is lower and crystallization does not proceed until the sample reaches a lower temperature than for the case of the higher molecular weight materials. Undoubtedly, the strain thinning effect also contributes to the observed behavior.

6.6.2.4. Crystallization kinetic parameters: n , N_c , and k

The Avrami index, n , nucleation rate constant, N_c , and crystallization rate constant, k , increase with increasing molecular weight as shown in Figure 6.16.

When the magnitude of Avrami index is considered in relation to the nucleation rate or crystallization rate, care must be taken to realize that a larger Avrami index sometimes means a faster nucleation or crystallization rate and, sometimes, it means a slower

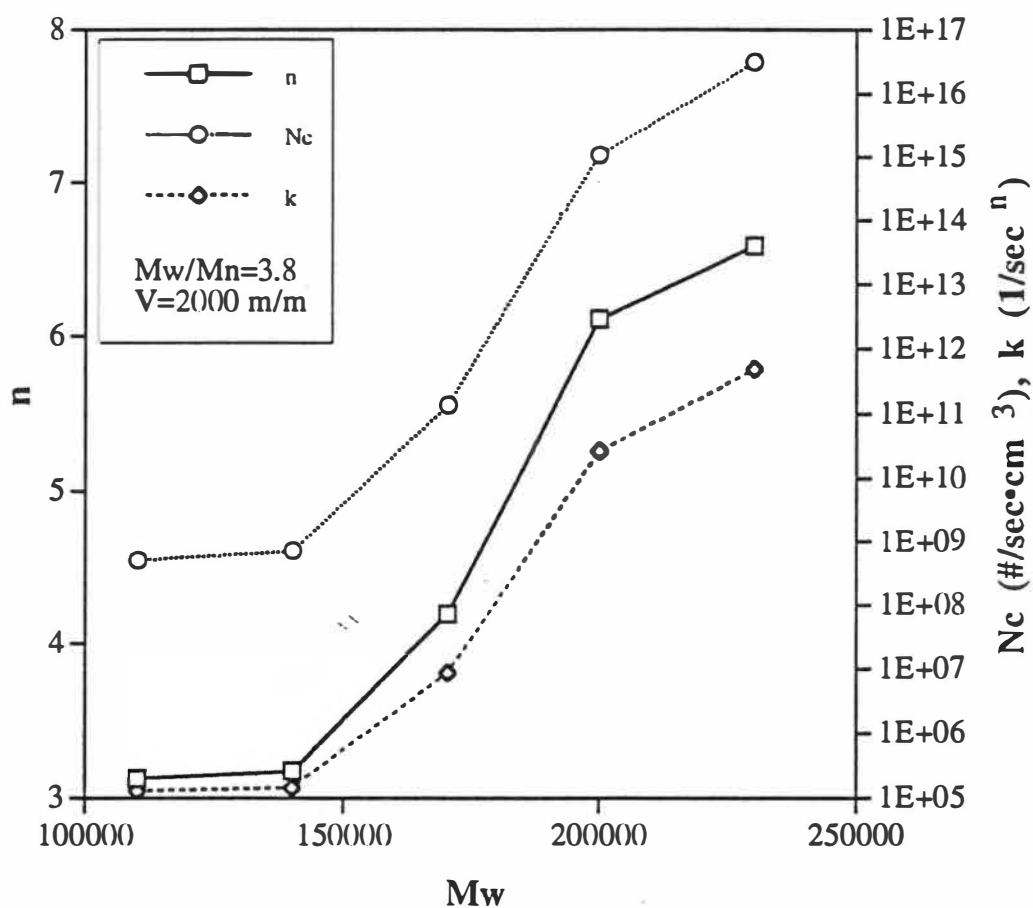


Figure 6.16. Avrami index, n , nucleation rate constant, N_c and crystallization rate constant, k , as functions of molecular weight.

nucleation or crystallization rate. A way to find out the influence of the Avrami index or nucleation index on the overall crystallization rate or the nucleation rate is to plot the overall crystallization rate or nucleation rate against $t-t_0-t_1$ which is denoted as “time” in the following discussion. For this reason, the nucleation rate was plotted against time in Figure 6.17. There exists a cross over point in the curves of nucleation rate versus time when comparing materials with different molecular weight at a small time value (about 0.005 sec). Because the crystallization occurs within 0 - 0.05 seconds in the present research, the nucleation rate essentially follows the rule that higher Avrami index gives higher nucleation rate, Figure 6.17. The increase of n and N_c with increase in molecular weight essentially gives a higher nucleation rate in the considered time frame (about 0.005 - 0.05 seconds). Thermodynamically, the higher crystallization temperature (in the absence of stress) would produce a weaker driving force for nucleation, but higher stress supplies more driving force for nucleation. In the present case the increased stress seems to override the influence of increased temperature and the higher stress results in higher nucleation rate with higher molecular weight. Kinetically, it takes more time to form nuclei at lower crystallization temperature, especially when the stress is lower, so that the nucleation rate is lower when molecular weight is lower. The lower N_c is essentially the direct result from the lower stress at crystallization onset.

Figure 6.16 also shows that the lower molecular weight results in a lower crystallization rate constant. In the considered crystallization temperature range, a decrease in crystallization temperature results in an increase of growth rate. Thus, the lower crystallization constant is primarily caused by the lower nucleation rate constant for lower molecular weight material.

The bulk crystallization rate decreases with decrease of molecular weight, because both k and n are smaller at lower molecular weight.

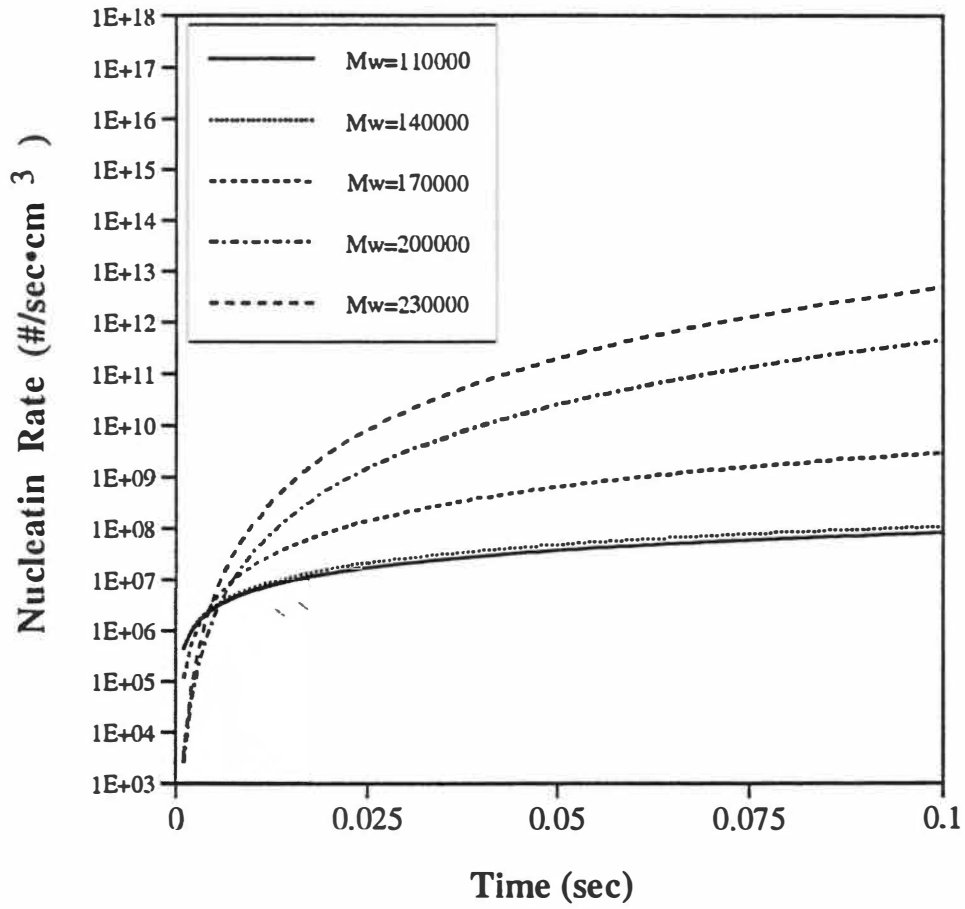


Figure 6.17. Nucleation rate described power law nucleation rate function versus time for materials with various molecular weight.

6.6.2.5. Final orientation and crystallinity

Figure 6.18 shows that the higher the molecular weight, the higher is the orientation in both the crystalline and amorphous regions. This is caused by the higher stress at crystallization for higher molecular weight material.

Both final crystallinity, X_C , and birefringence increase with increase of molecular weight as shown in Figure 6.18. The higher birefringence is a result of the higher crystalline and amorphous orientation.

6.6.3. Change In Molecular Weight Distribution

The polydispersity, M_w/M_n , examined for this purpose is from 3.3 to 4.4. When the polydispersity changes, the molecular weight is held at $M_w = 170000$, and the spinning conditions are: spinning speed = 2000m/min, melt temperature = 210 °C, ambient temperature = 30 °C, and mass throughput = 1.6 g/min.

6.6.3.1. Predicted results

An illustration of the effect of changing the MWD at fixed MW and spinning conditions is now presented. The birefringence for materials with various polydispersity are plotted against distance from the spinneret in Figure 6.19. As shown in Figure 6.19, the profile for materials with broader MWD is above the ones with narrower MWD near the spinneret. The birefringence enters the fast increasing stage earlier and reaches a lower final value with broadening of the MWD. This results in a crossover of the birefringence profile results for samples with different MWD.

The temperature profiles for materials with various MWD are given in Figure 6.20. The temperature plateau for materials with broader MWD starts earlier than the ones with narrower MWD and the plateau becomes less evident as MWD becomes broader.

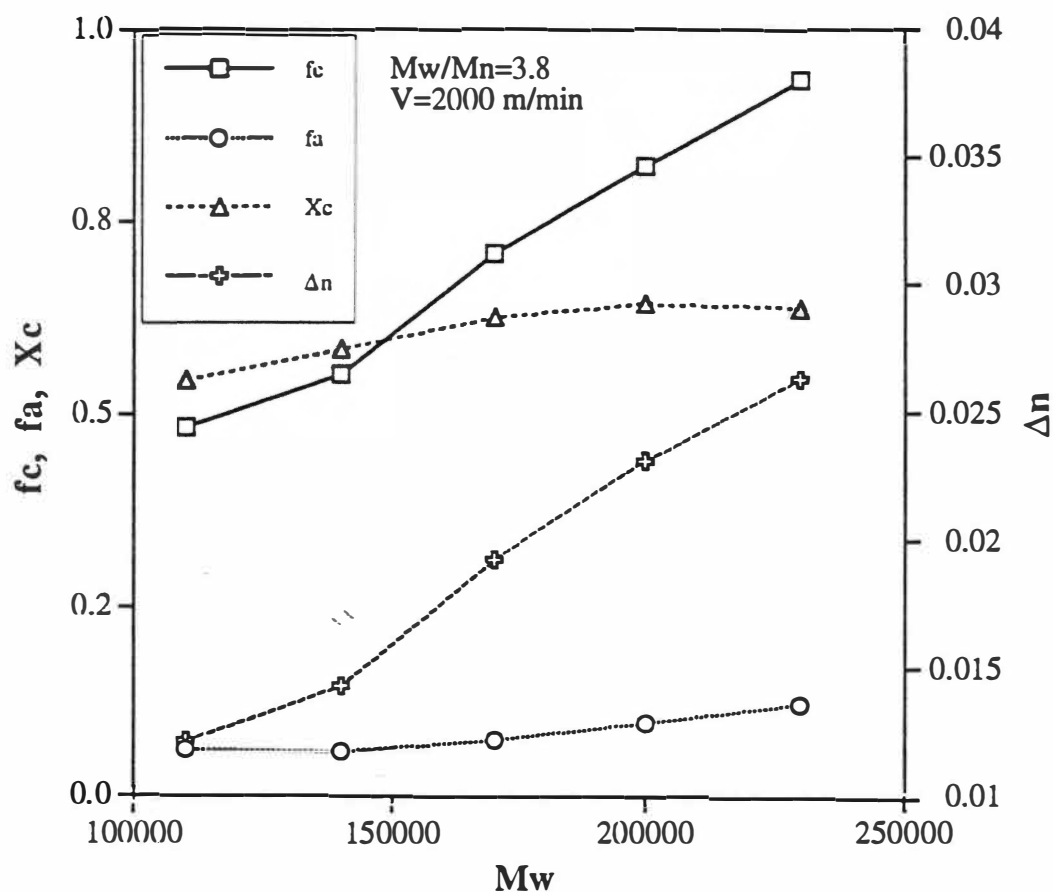


Figure 6.18. Crystalline orientation function, f_c , amorphous orientation function, f_a , final crystallinity, X_c , and final birefringence, Δn , as functions of molecular weight.

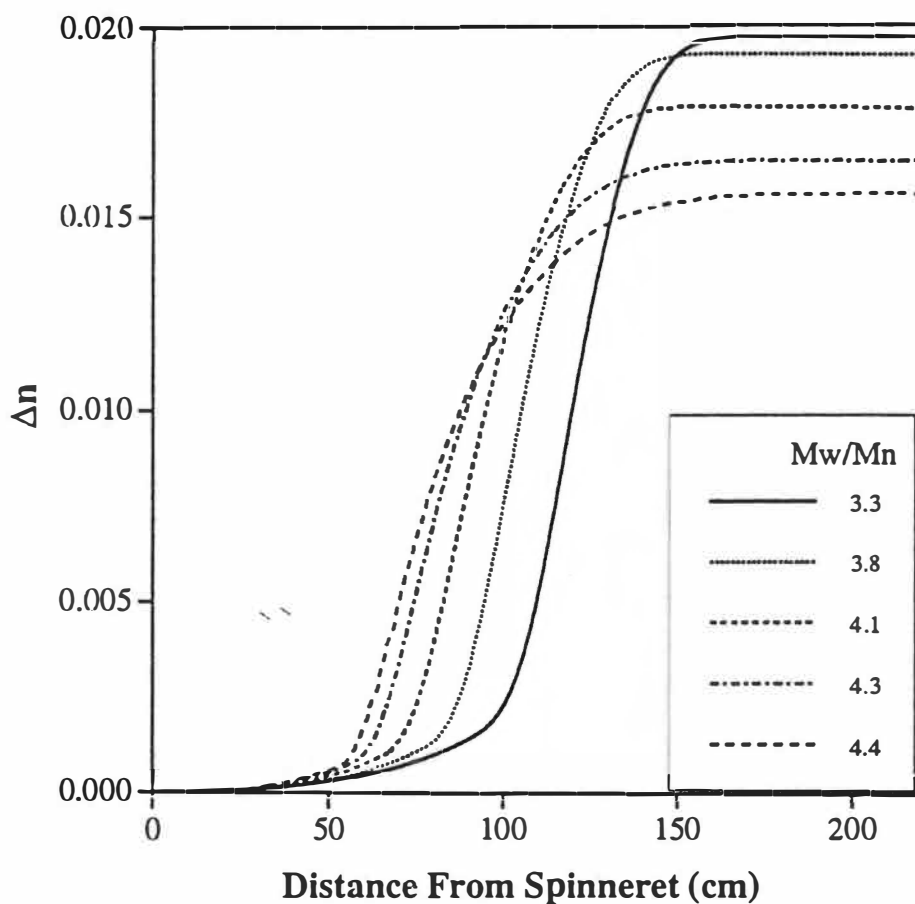


Figure 6.19. Calculated birefringence versus distance from spinneret at various polydispersity for iPP. $M_w = 170000$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

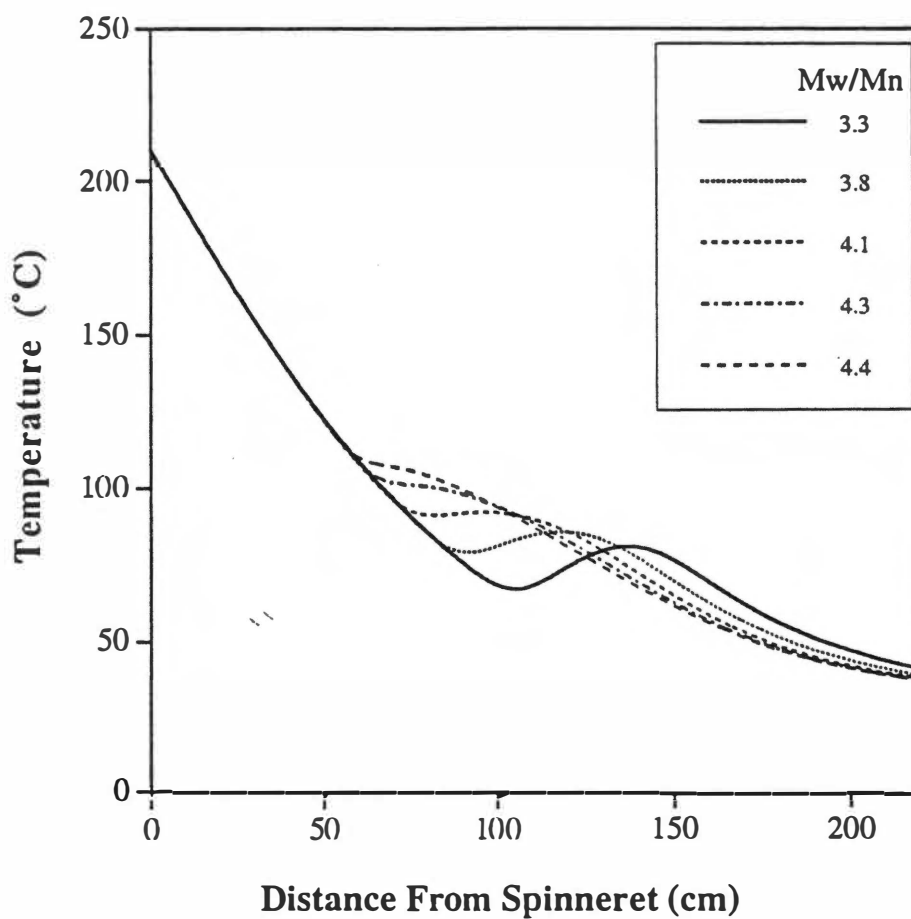


Figure 6.20. Calculated temperature versus distance from spinneret at various polydispersity for iPP. $M_w = 170000$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

Figure 6.21 gives the diameter profiles of the polymer stream on the spinline. The thinning process is faster for broader material as indicated by the figure. The draw down region is shorter for broad materials.

The crystallinity is plotted against distance from the spinneret in Figure 6.22. For material with broader MWD, the crystallization begins earlier, increases with a slower rate, and reaches a little lower final value, which is not much different from the ones for narrower MWD materials.

The development of nucleation density on the spinline is given in Figure 6.23. From Figure 6.23 we can see that the nucleation density for material with broader MWD rises earlier with higher nucleation rate and reaches a higher final value.

6.6.3.2. Discussion of the simulated profiles

We have noticed that when polydispersity gets broader, crystallization begins at a location closer to the spinneret, but the crystallization rate is slower. Presumably, the earlier crystallization onset is caused by the molecules in the high molecular weight tail of the distribution which can more easily be oriented under strain. These long molecules trigger off an early nucleation at higher temperature in the polymer stream. While the remaining small molecules participate in a growth process at higher crystallization temperature that results in a somewhat lower crystallization rate.

The faster increase and higher final value of nucleation density for broader material also results from the long molecular chains in the high MW tail in the MWD. The long chain molecules create more nuclei with faster rate at higher temperature. With a lower growth rate for broader material, and higher nucleation rate, the material has more chance to reach a higher final value of nucleation density. A higher nucleation rate, in this case, does not result a higher rate of progression of crystallization because of the lower growth rate.

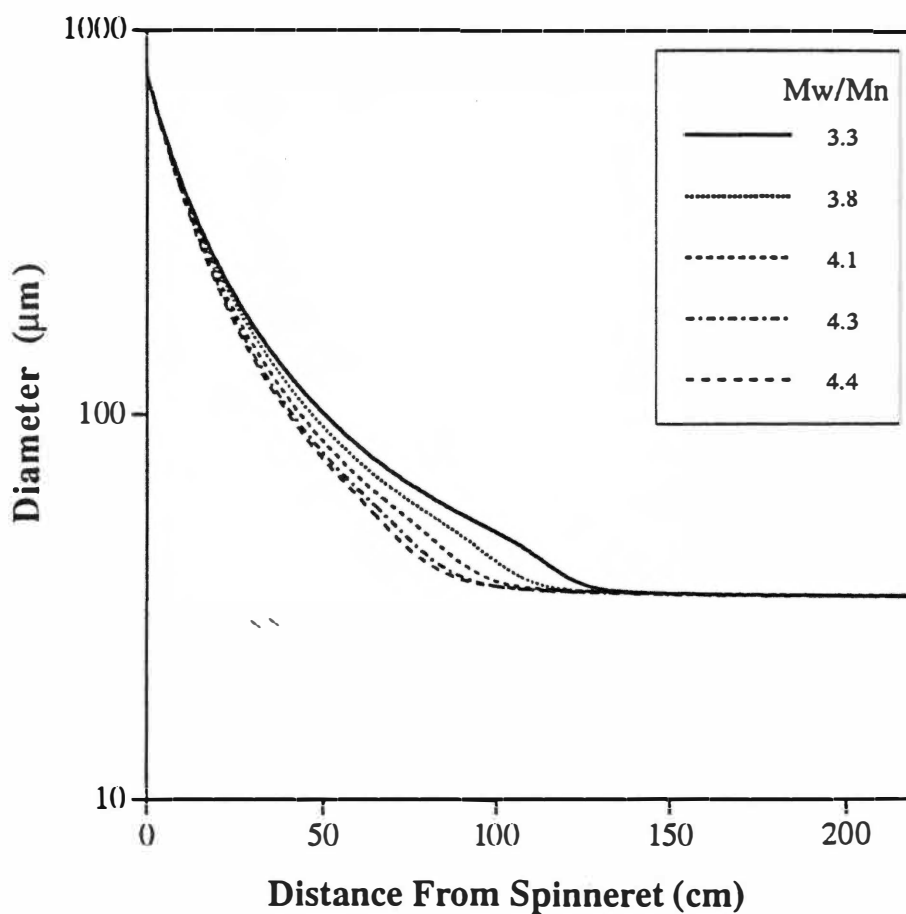


Figure 6.21. Calculated diameter versus distance from spinneret at various polydispersity for iPP. $M_w = 170000$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

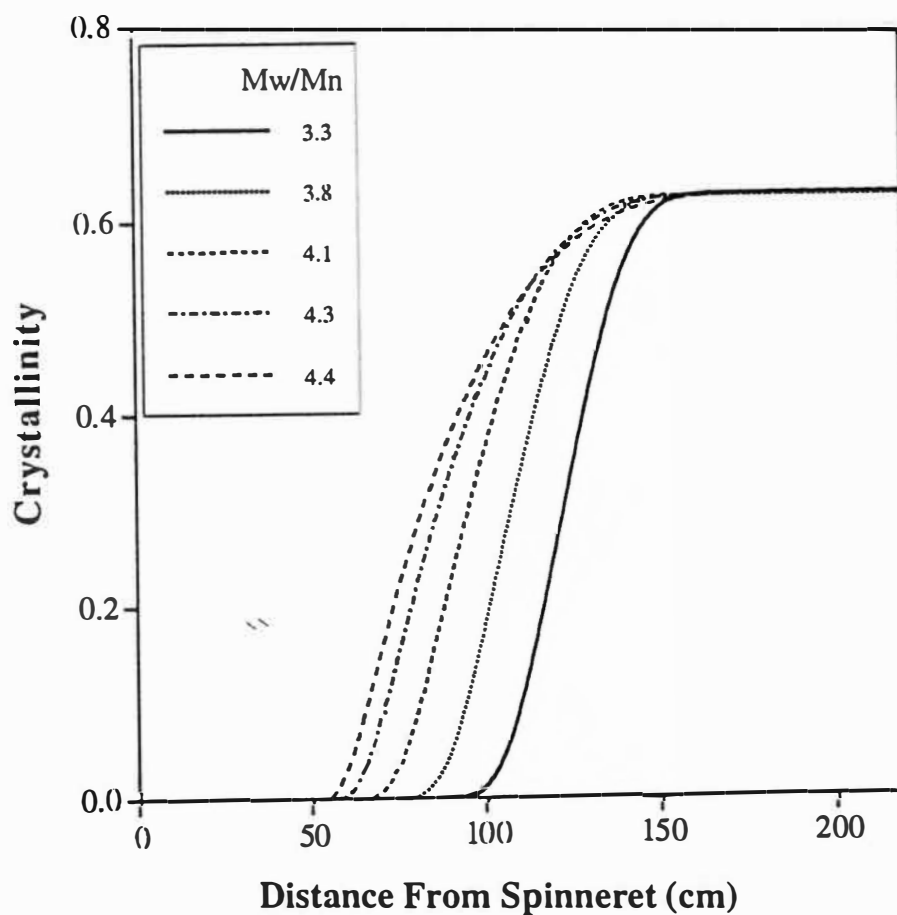


Figure 6.22. Calculated crystallinity versus distance from spinneret at various polydispersity for iPP. $M_w = 170000$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

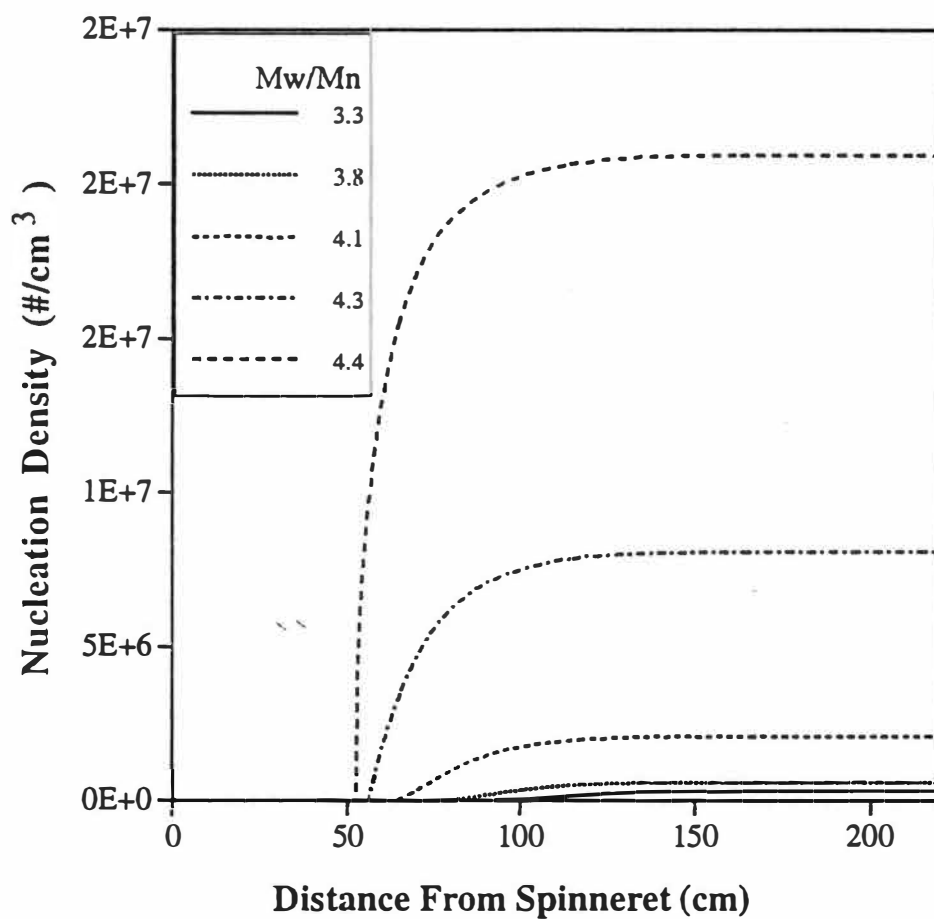


Figure 6.23. Calculated nucleation density versus distance from spinneret at various polydispersity for iPP. $M_w = 170000$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

The higher birefringence near the spinneret before crystallization for broader MWD is attributed to the higher stress at a given distance away from the spinneret. Figure 6.24 gives the calculated stress along the spinline for materials with various polydispersity under conditions specified in the figure. The left ends of the horizontal straight lines in Figure 6.24 indicate the location where the temperature in the polymer stream equals to the equilibrium melting temperature, and the right ends, the crystallization onset time. The levels of these lines represent the stress at crystallization onset. The stress develops more rapidly for material with broader breath as illustrated in Figure 6.24. However the material with broader breath crystallizes at lower stress, and higher temperature. Prior to crystallization the higher birefringence for materials with broader breath is apparently related to the higher stress level in the polymer stream. It is interesting to see that the stress level is not determined by viscosity in this case. Figure 6.25 gives the elongational viscosity along the spinline. From Figure 6.25 we can see that before crystallization the viscosity for materials with different polydispersity are almost identical. This phenomenon suggests that the viscosity on the spinline is essentially controlled by temperature and average MW. The broader breath material should have exhibited more strain thinning effect than materials with narrower breath. But it is not the case. The viscosity behavior during crystallization seems to further support this point. The material with narrower MWD exhibits more reduction in viscosity than others. The reason for this is apparently related to crystallization. When the crystallization rate is fast, Figure 6.22, the reheat-up of temperature is more evident, Figure 6.20, for materials with narrower MWD. The reason for broader material has higher stress along the spinline can now only be attributed to the higher stain rate. A plot, which is not given, shows that is exactly the case. The higher strain rate results from the earlier onset of crystallization. The early onset of the crystallization compressed the deformation region and causes the draw down to occur closer to the spinneret for material with broader distribution.

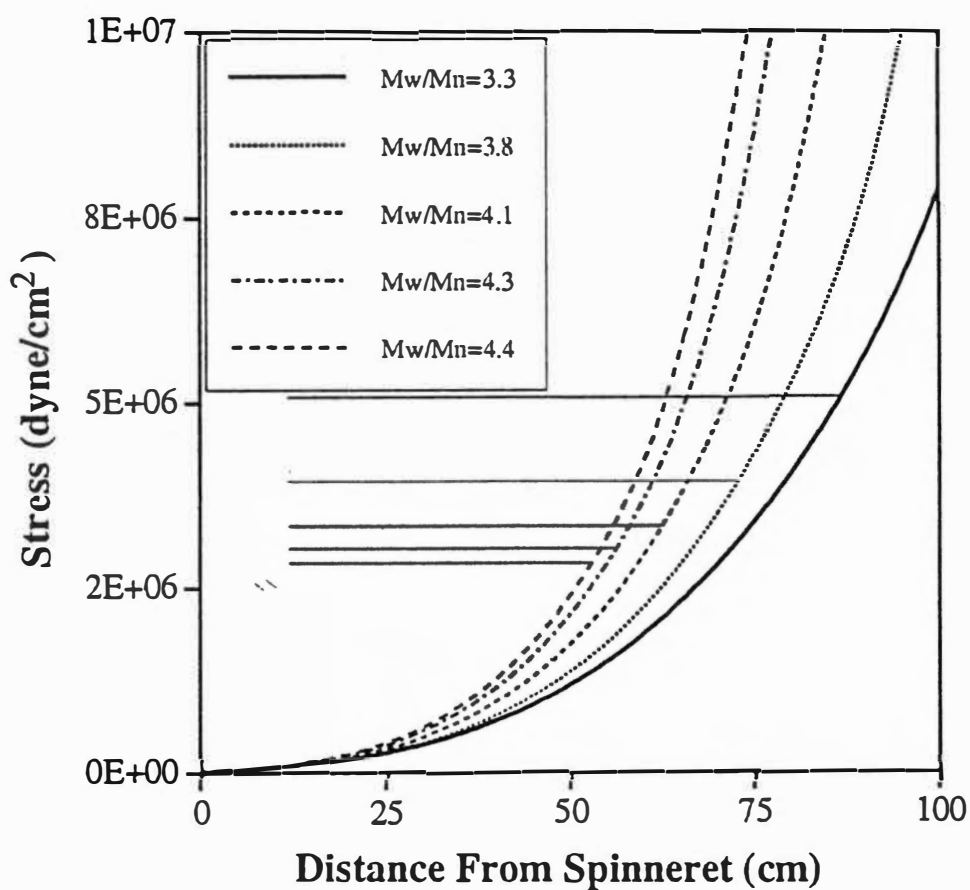


Figure 6.24. Calculated stress versus distance from spinneret at various polydispersity for iPP. Mw = 170000, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

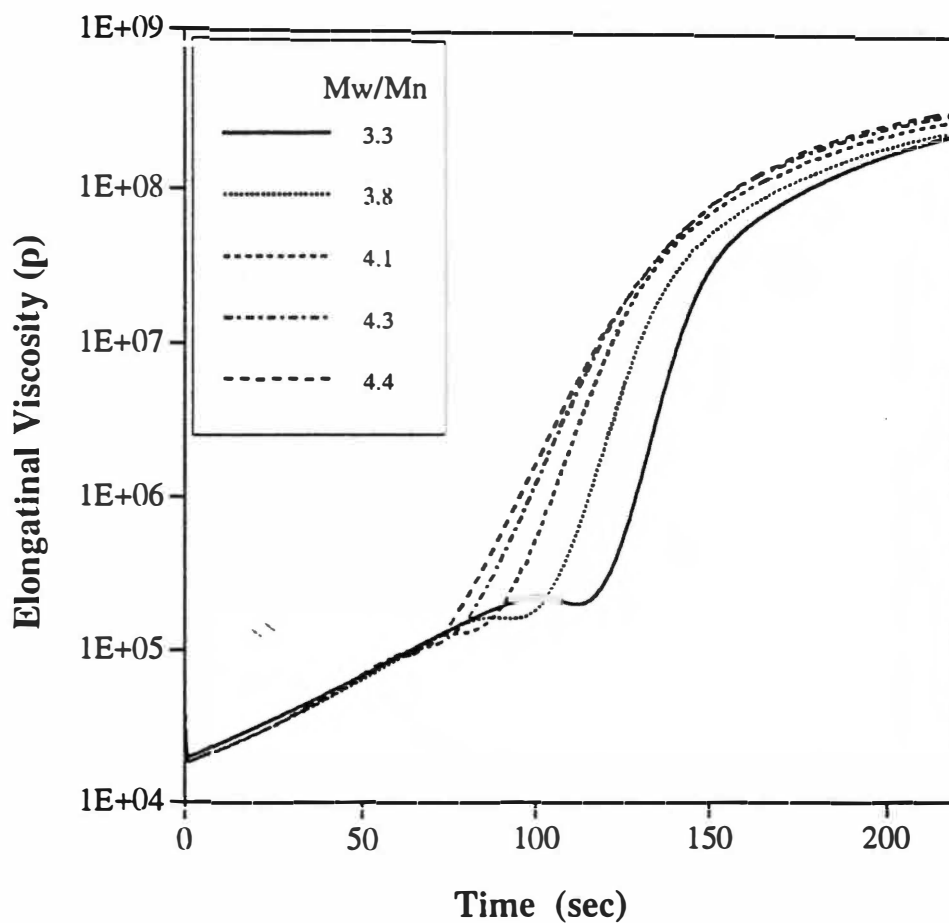


Figure 6.25. Calculated elongational viscosity versus distance from spinneret at various polydispersity for iPP. $M_w = 170000$, spinning speed = 2000 m/min, melt temperature = 210 °C, ambient temperature = 30 °C, mass throughput = 1.6 g/min.

The earlier onset of crystallization results in the earlier jump of birefringence for broader MWD materials. The lower crystallization stress and the slower crystallization rate of broader MWD material is responsible for the slower increase of the birefringence after crystallization begins. The change of the final birefringence with MWD is related to the bimodel orientation model for material with broad MWD [Misra, Lu, Spruiell and Richeson (1995)]. According to their explanation, the long chain molecules at high MW tail orient along the fiber axis and induce nucleation early under low stress and high temperature on the spinline. A portion of the remaining molecules grow in an orientation such that the chains are approximately in the direction perpendicular to the fiber axis. The birefringence is weakened by the orientation in the second direction and its value is therefore low. In the present model, the model parameters, especially the one for crystallization induction time is fixed by experimental data from on-line experiment. Consequently, the model carries the feature of the experimental data that the onset of the crystallization is earlier for material with broader breadth. It also exhibits the feature that lower final birefringence occurs for broader MWD resin. However, the model only describes the orientation value observed by experiment. It does not describe the detailed information of the structure in the fiber. The model only uses a constant crystalline orientation function to describe the crystallization orientation for the whole crystallization process. In reality, for a bimodel orientation biorientation, the crystalline orientation at the onset must be higher than the one observed in the as spun fibers. That is, the crystalline orientation must decrease from the value at crystallization onset to the a lower final value. The model does not reflect this behavior. However, the effect of orientation on the crystallization on the spinline is determined by the amorphous orientation at crystallization onset; the constant crystalline orientation does not affect the description of the crystallization kinetics adopted in the model. Hence, the model, generally speaking, still works well. For the description of the total orientation as described by birefringence, because at crystallization onset the quantity of the crystalline phase is

small, the application of a constant crystalline orientation value will not affect the description of the total orientation much. In the early stage of crystallization, the main contribution to birefringence is from the amorphous part which results from simulated stress and is, therefore, reliable. As for the later stage of the crystallization, the real crystalline orientation does, in fact, drop to a value close to the constant values chosen. Therefore, there is no problem to use a constant crystalline orientation to describe the birefringence in the model. In a word, the model describes the experimentally observed birefringence, not the detailed description of crystalline orientation in the fiber.

Earlier onset of crystallization is responsible for the earlier start of the plateau in the cooling curve for broader MWD in Figure 6.20. The less evident plateau is because the crystallization heat generation rate is slower since the crystallization rate is slower for broader MWD material.

The faster thinning process is caused by compressed draw down region which is caused by the early start of the crystallization for material with broader MWD .

6.6.3.3. Parameters related to crystallization onset: t_1 , t_0 , T_{on} , σ_{on} , and z_{on}

Both crystallization induction time, t_0 , and the time needed to cool the polymer from its melt temperature to its equilibrium melting temperature, t_1 , decreases as MWD broadens as shown in Figure 6.26. Figure 6.27 shows that the temperature at crystallization onset, T_{on} , increases with increasing polydispersity, and the distance from the spinneret at crystallization onset, z_{on} , and stress at crystallization onset, σ_{on} , decrease as polydispersity increases. All these parameters are related to the crystallization onset. Because the key parameter here is the crystallization induction time which deals with time, the following discussion is based on time.

Figure 6.28 gives the temperature and stress in the polymer stream on the spinline

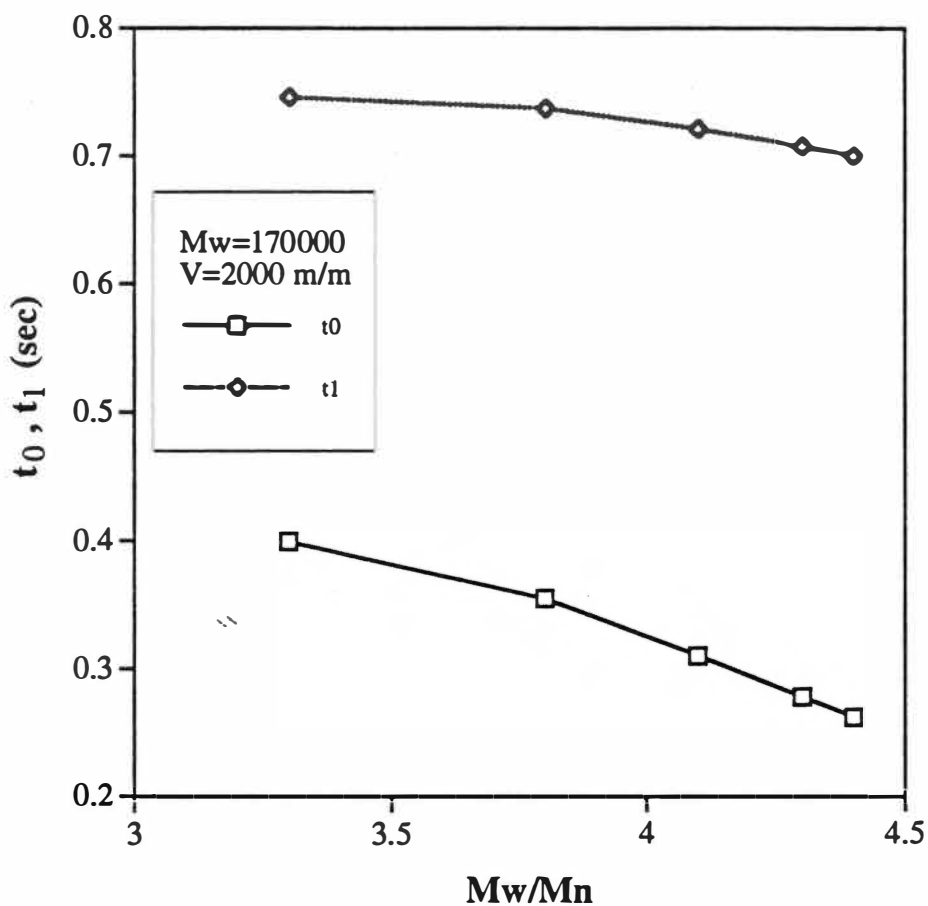


Figure 6.26. Crystallization induction time, t_0 , and time needed to cool the polymer from its melt temperature to its equilibrium melting temperature, t_1 , as functions of MWD.

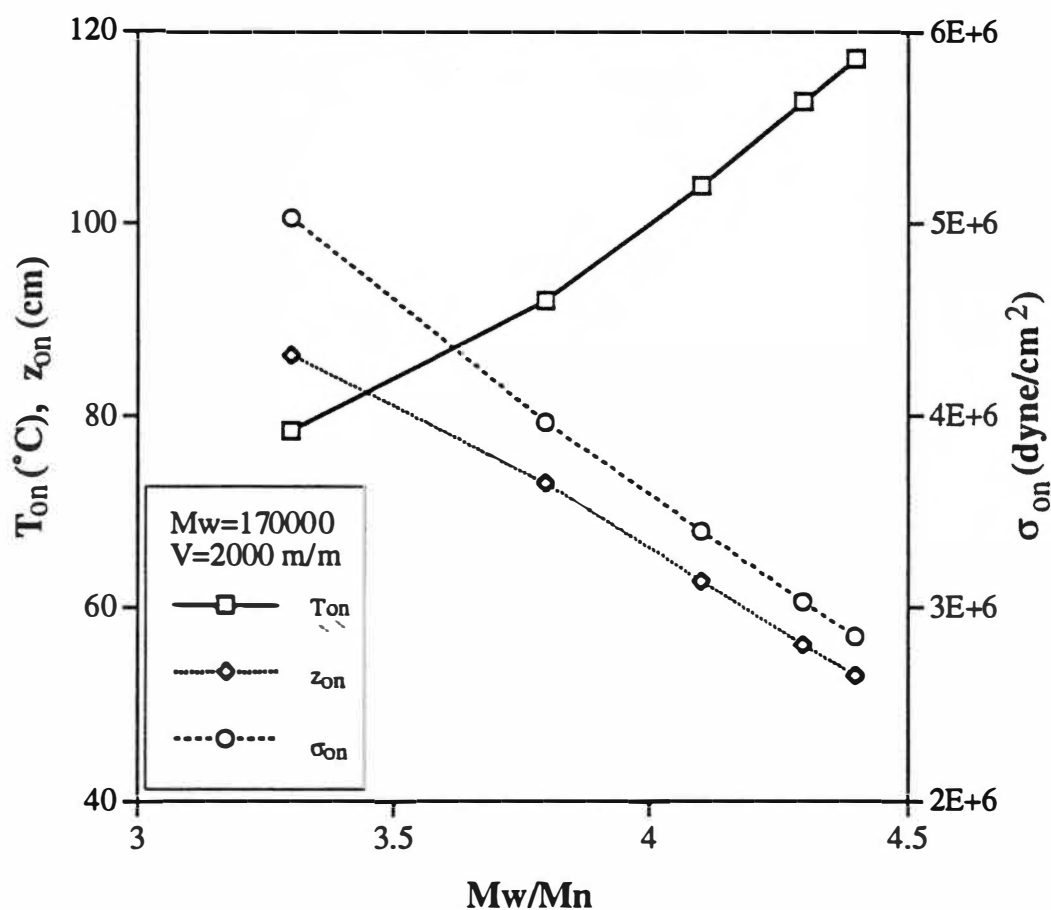


Figure 6.27. Crystallization onset temperature, T_{on} , onset position, z_{on} , and onset stress, σ_{on} , as functions of molecular weight distribution. Weight average molecular weight was held as 170000 and spinning speed is 2000 m/min.

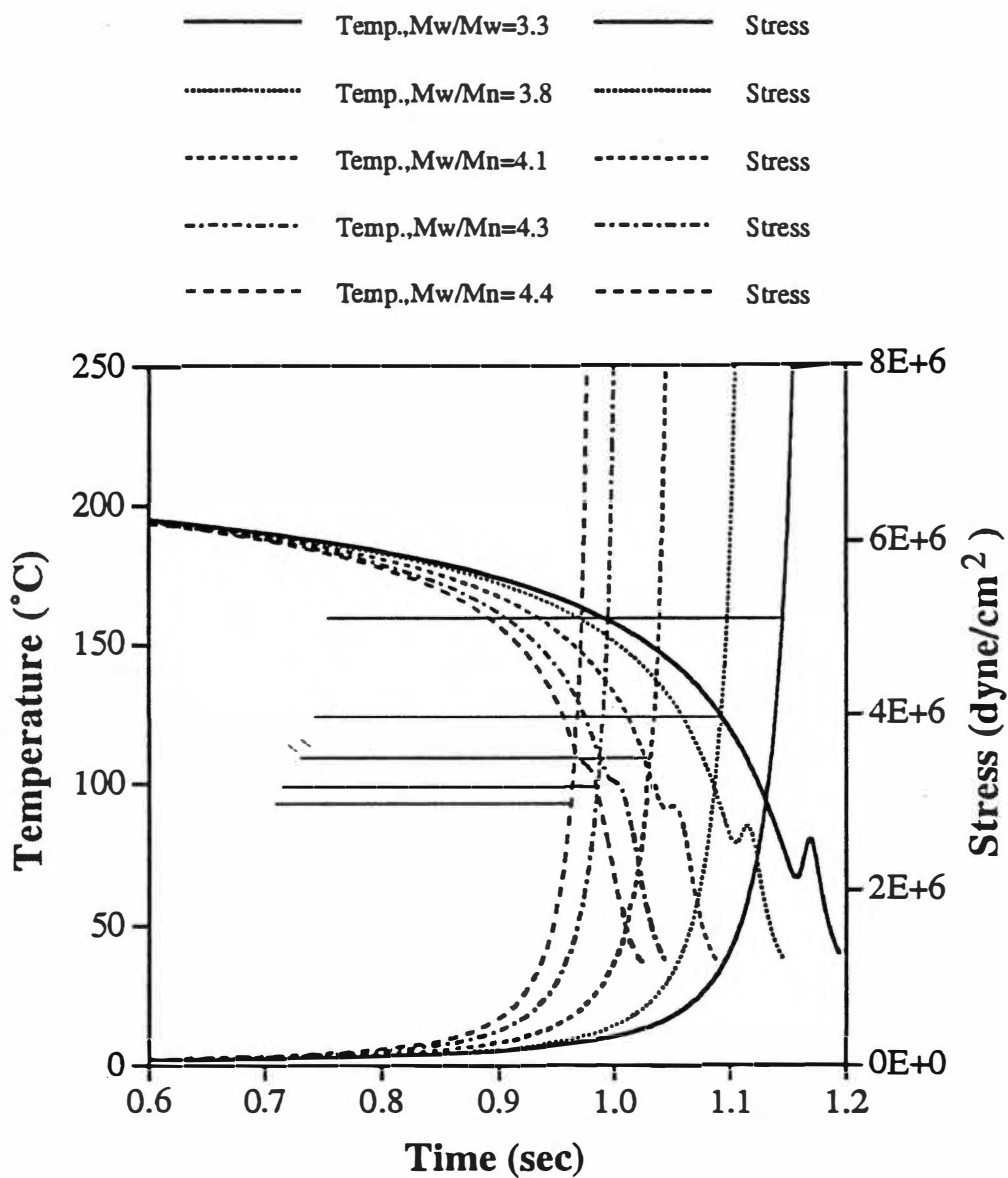


Figure 6.28. Temperature and stress in the polymer stream on the spinline as functions of time for materials with various molecular weight distribution.

as functions of time for materials with various molecular weight. The horizontal lines in Figure 6.28 indicate the length of induction time. The left ends of the lines represent t_1 and the right ends, the crystallization onset. The height of the lines correspond to the stress level at crystallization onset. The crystallization onset temperature can be found by drawing a vertical line passing through the right end of the line.

The stress is determined by velocity gradient and viscosity. The velocity gradient is determined by length of draw down, that is, the crystallization onset. If crystallization begins early and crystallization rate is high, the draw down distance will decrease and the velocity gradient will be high before crystallization. The strain rate becomes higher for material with broader MWD because the strain finishes in a shorter time. Higher strain rate results in the higher rate of development of stress along the spinline.

Because the large molecules in the high MW tail can orient easily, the nucleus forms at higher temperature and lower stress for material with broader MWD. This gives a shorter crystallization induction time.

Because of the early onset of the crystallization, the draw down period is compressed, and the thinning process is accelerated. The thinner polymer stream cools down faster than the thicker one. It takes, therefore, less time for polymer to reach the equilibrium melting temperature, so that the t_1 reduces when MWD becomes broader.

The position of the crystallization onset on the spinline is moved up as polydispersity increases because of the shorter t_1 and crystallization induction time.

6.6.3.4. Crystallization kinetic parameters: n , N_c , and k

Avrami index, n , nucleation rate constant, N_c , and crystallization rate constant, k , decrease with increases in polydispersity, Figure 6.29. Because the geometric index is fixed at 2 for the crystallization under strain for all cases in the model, the discussion of the n refers to the nucleation index, m . With change in molecular weight distribution, the

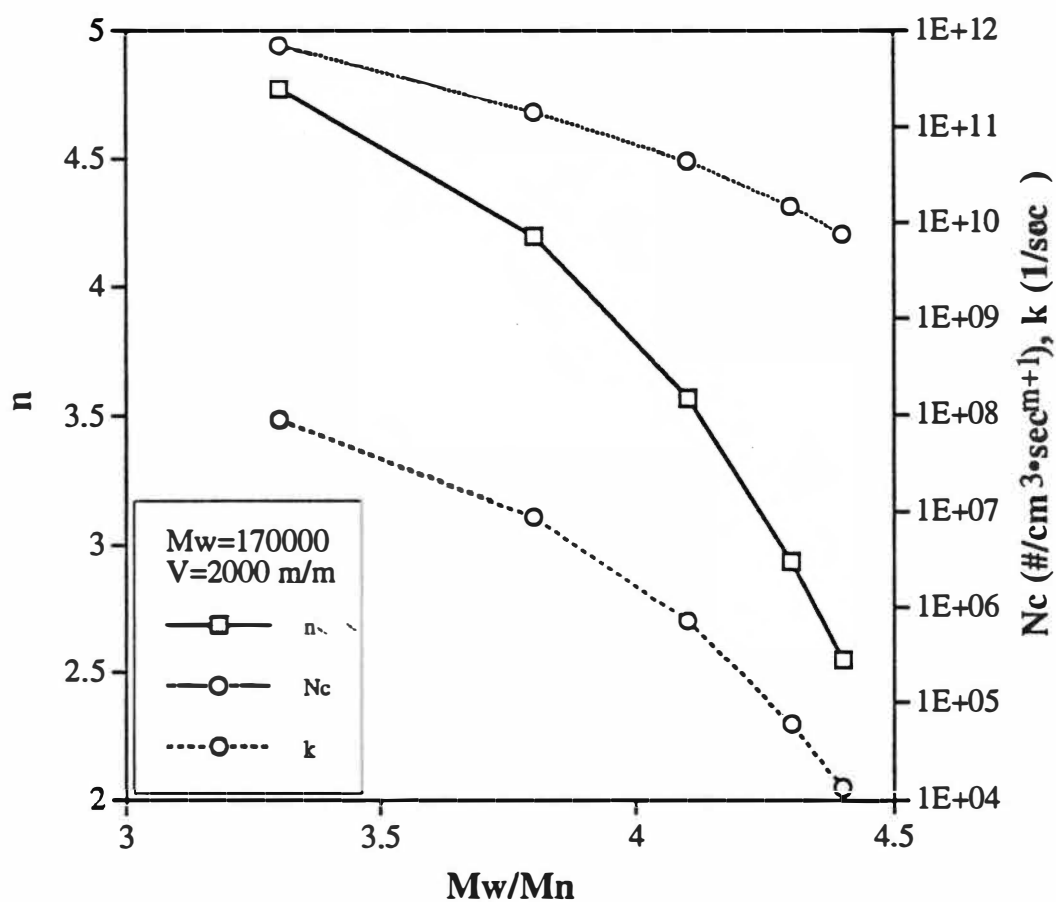


Figure 6.29. Avrami index, n , nucleation rate constant, N_c and crystallization rate constant, k , as functions of polydispersity.

crystallization essentially occurs before the crossover point in Figure 6.30, where the power law nucleation rate was plotted against time. In such a case, the smaller Avrami index means a higher nucleation rate. Therefore, the nucleation rate is higher for broader MWD material which has a smaller Avrami index in Figure 6.28. The decrease in both n and N_c with increase in MWD results in a higher nucleation rate in the considered crystallization period (about 0 - 0.05 seconds which is found in the plot of crystallinity against time, not given here). Because the long chain molecules in the high molecular weight tail of the molecular weight distribution are more easily oriented, the nucleation rate is higher at the lower stress and higher crystallization temperature for material with broader MWD. The combination of a smaller N_c and the smaller Avrami index is required to give a higher nucleation rate.

The rate constant contains information of nucleation and growth rate. Since the crystallization onset temperature increases, the growth rate decreases as polydispersity increases. Both decrease in nucleation rate constant and growth rate results in decrease in crystallization rate constant as polydispersity increases. The combination of a smaller crystallization rate constant and smaller Avrami index gives the slower crystallization rate for material with broader polydispersity, Figure 6.19.

6.6.3.5. f_c and f_a , X_c , and Δn

As shown in Figure 6.31, both crystalline orientation function, f_c , and amorphous orientation function, f_a , in the as-spun filaments decrease as polydispersity increases. The f_c in the model is calculated from birefringence by a two phase model. The value of f_a is calculated according to the stress optical law while the crystallinity is evaluated from the empirical equation which is based on experimental data. Based on the x-ray data of Misra et al. [Misra, Lu, Spruiell and Richeson (1995)], the fraction of the crystals in the secondary

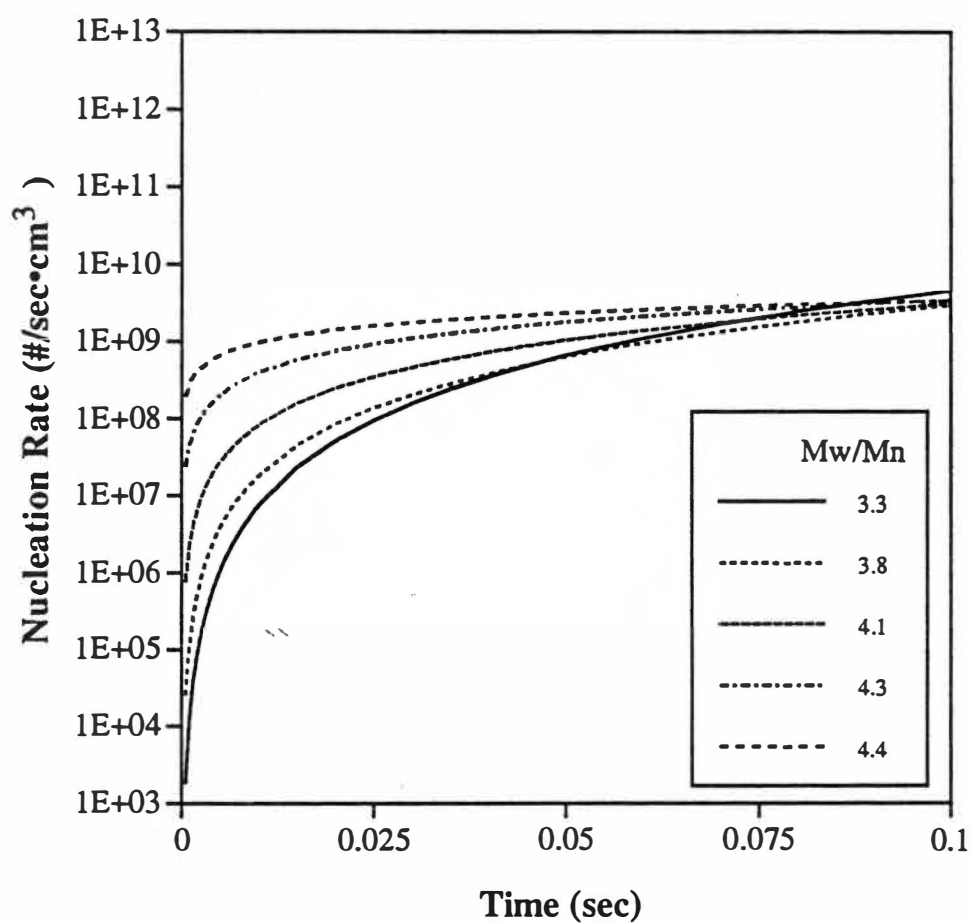


Figure 6.30. Nucleation rate described power law nucleation rate function versus time for materials with various polydispersity.

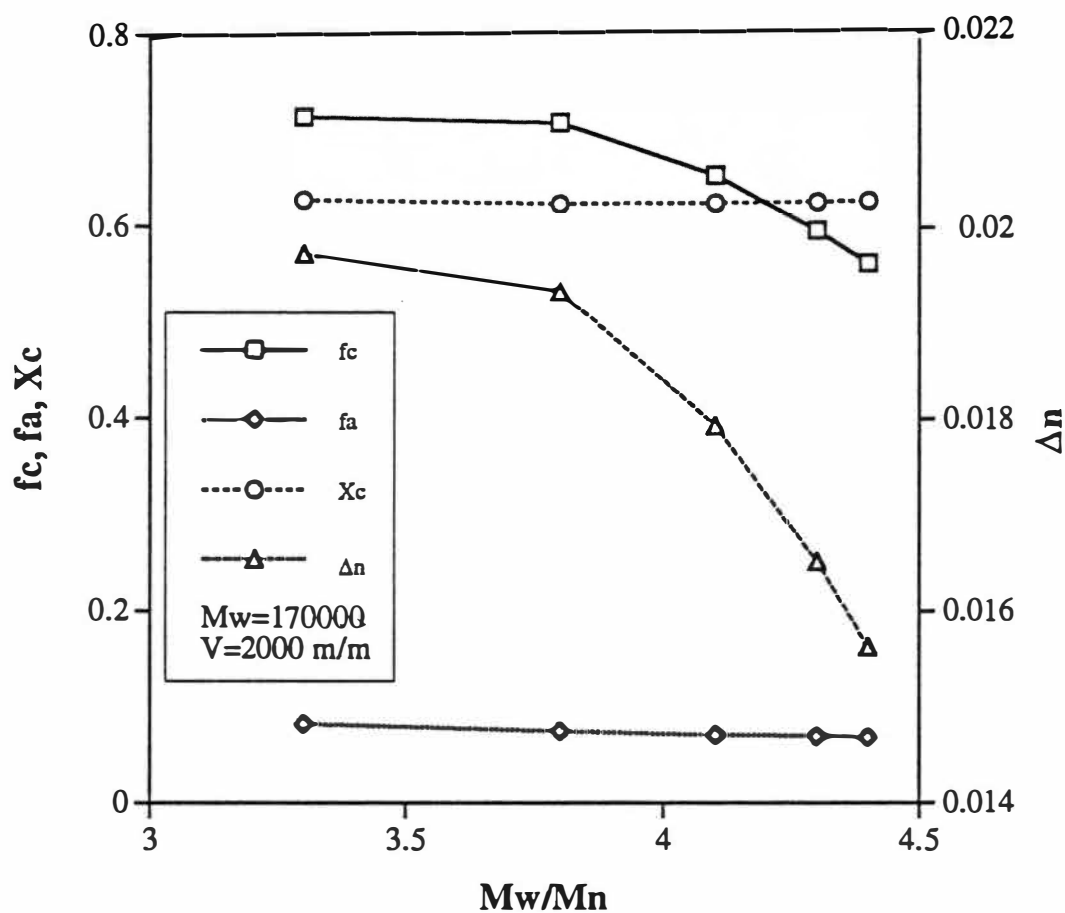


Figure 6.31. Crystalline orientation function, f_c , amorphous orientation function, f_a , final crystallinity, X_c , and final birefringence, Δn , as functions of polydispersity.

orientation with chains nearly perpendicular to the fiber axis, increases with increases if the polydispersity. Thus, the decreases in f_c computed by the model is consistent with the experimental x-ray patterns. The decrease in f_a in the as-spun filaments with increase in polydispersity is simply because the spinning stress at the start of crystallization is lower for material with broader MWD.

The final crystallinity is essentially unaffected by variation in MWD (though there is a very small increase of crystallinity when polydispersity increases, Figure 6.31. This would seem to be related to crystallization temperature.

The decrease of final birefringence with increasing polydispersity, Figure 6.31, is the result of bimodal orientation which has been discussed in detail above.

6.6.4. Variation In Spinning Conditions

The simulation has been further tested by examining the effects of changing spinning speeds, melt temperature, mass throughput and ambient temperature for a given polypropylene resin ($M_w = 141790$, $M_w/M_n = 2.8$). The results seem compatible with experimental data and with earlier versions of the mathematical model. Because these results are quite lengthy, but do not provide any new insights, the detailed simulated data is not presented and discussed here. In general, these results are very straight forward and much easier to interpret than the influences from MW and MWD which have already been discussed. The results of studying the variation of spinning conditions show the model is able to predict the changes caused by change in spinning speed, melt temperature, mass throughput and ambient temperature.

6.7. Necking Phenomenon

It is interesting to notice that under some conditions the model predicts necking in the profile of filament diameter versus distance from the spinneret. There was no attempt to

specifically design the model so as to produce this result. Since the model gives this result, explanation must be made for it.

As displayed in Figure 6.5, the occurrence of necking results from the reduction in viscosity in the crystallization early stage. The reduction in viscosity is basically caused by heat generated from crystallization. The crystallization has two competitive influences to the viscosity. On one hand, crystallization produce heat (of fusion) and reduces the viscosity — temperature effect. On the other hand, crystallites produced can physically block the flow of polymer chains and increases the viscosity — physical blocking effect. In the earlier stage of crystallization, the temperature effect is dominant so that viscosity decreases as crystallization proceeds. After a greater amount of crystallinity has developed, the physical blocking effect become dominant. It causes the viscosity to increase and the draw down slows down and everything stops.

A high heat generation rate caused by high crystallization rate is a necessary condition for a reduction in viscosity. The high cooling rate of filament may raise the required magnitude of crystallization rate and weaken the necking phenomenon.

The existence of strain thinning may reduce the required magnitude of crystallization rate and enhance necking phenomenon. It is possible for necking to occur if the polymer viscosity has no strain rate dependence (Newtonian fluid) as long as the temperature can rise after crystallization begins. However, the strain thinning effect helps the necking to occur and make it observable under moderate crystallization rate. It has been observed that the necking is much more evident in the simulated result if the strain thinning effect is stronger under the same spinning condition.

6.8. Conclusion Remarks

The generalized power law viscosity equation and the crystallization kinetics equations based on a derivation of the Avrami equation in which the nucleation rate was

separated from the Avrami rate constant have been introduced into the model for the melt spinning process to describe the viscous behavior and crystallization kinetics on the spinline for polypropylene. The molecular weight and polydispersity dependence of the model was introduced through coefficients in viscosity and crystallization kinetics equations which were empirically related to the molecular weights and polydispersities based on the experimental data for nine resins obtained from the spinline. In the relationships between coefficients of the viscosity equation, information from both shear and elongational experiments has been utilized. In the relationships between the parameters of crystallization kinetics equations, information from quiescent crystallization studies has been utilized. By comparison to the actual spinline data, kinetics obtained under quiescent condition were modified to account for the influence of stress-induced molecular orientation present in the spinning process.

The resultant model has been tested for variation of molecular weight under given polydispersity and spinning conditions, and variation of polydispersity under given molecular weight and spinning conditions. On these aspects, the birefringence, diameter, temperature, crystallinity, and nucleation density profiles were examined. The variation of spinning conditions, spinning speed, melt temperature, ambient temperature and mass throughput were also tested for the improved model. It was shown that the model can describe, at least qualitatively, most of the aspects of the experimental data for a variety of polypropylenes.

In the examination of the ability of the model, the important parameters, such as crystallization temperature, crystallization stress, orientation factors, final crystallinity, crystallization rate constant, Avrami index, nucleation rate constant, crystallization induction time, as functions of molecular weight and polydispersity have been examined. The results shows that the relationships predicted by the model are generally in agreement

with the ones observed by experiment or that might be expected based on previous discussion in the literature.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

7.1. Summary Of Major Conclusions

Though individual conclusions have been drawn in Chapters 3, 4, 5 and 6, respectively, this chapter summarizes those conclusions and makes recommendations for future research.

A new technique, based on light depolarizing microscopy, which can be used in the study of nonisothermal crystallization kinetics of polymers under cooling rates of several thousands degree C per minute was developed in this research. The applied cooling condition is constant in temperature of cooling medium but not in cooling rates. The cooling rate can be quantitatively described by a Cooling Rate Function (CRF). The CRF is determined by regressing an equation, which results from a heat transfer analysis, to the temperature measured before crystallization. The CRF can be related to crystallization plateau temperature or heat transfer coefficient which also describes the cooling condition applied in the experiments.

The temperature of polymer is measured by a thermocouple which is directly embedded in the polymer. The cooling curves clearly exhibit a plateau resulting from the heat of crystallization that is given up during crystallization. The observed crystallization plateau temperature decreases as cooling rate increases.

The developed technique includes measurements of overall crystallization rate and crystal growth rate. The measurement of overall crystallization rate is carried out by dynamically following changes of light intensity both with and without an analyzer. Light scattering effects caused by numerous nuclei created under rapid cooling conditions was consistently observed; this light scattering causes a problem in the data analysis when only

the intensity with analyzer is used. A second light sensor was introduced to help overcome this problem. A relative light intensity was defined to correct for the light scattering effect, using intensities measured both with and without analyzer. The relative crystallinity needed in the kinetics analysis is calculated from relative light intensity.

A VCR system was introduced into the technique to measure the growth rate of spherulites under cooling conditions similar to the ones applied in the measurement of overall crystallization rate. A constant growth rate was observed in nonisothermal crystallization under rapid cooling conditions. A localized isothermal process was suggested to explain this phenomenon.

A nucleation rate function was proposed to analyze the nonisothermal crystallization data obtained by the developed technique. By the suggested function, The Avrami equation was rederived and the Avrami index in the resultant equation was separated into a geometric index and a nucleation index. A nucleation rate constant was also defined, and it was shown that it can be obtained from the crystallization rate constant obtained from the Avrami analysis. In this procedure, it is necessary to know or assume a value of the geometric growth index.

The Avrami equation was found applicable to the experimental data obtained by the technique. That is, both the Avrami index and crystallization rate constant are constant with the time. The reason for this was attributed to the fact that the time-dependence of the nucleation rate was included in the nucleation rate function. The constant Avrami index and crystallization rate constant describe, actually, a time-dependent nucleation rate process when examined through the suggested nucleation rate function.

Spherulite growth rates were found to be constant with time during the period in which the growth rates could be measured. As most of this period corresponded with the presence of a constant temperature plateau, the constant growth rates were attributed to a localized isothermal growth process.

The growth rates measured by the present technique and by the usual isothermal technique were found to be well connected, and they can be described by a single Hoffman-Lauritzen equation. This supports the argument for the local isothermal process for the spherulite growth behavior investigated.

For a given iPP, the crystallization half-time decreases as cooling rate increases. The Avrami index was independent of the applied cooling rates in the range of conditions investigated, though there was substantial scatter in the data. Crystallization rate constant and nucleation rate constant increase as cooling rate increases. Nucleation rate constant was related to crystallization temperature through a suggested equation, which was also modified to account for molecular orientation and was applied in the spinning model.

Crystallization induction time and onset temperature decrease as cooling rate increases. Both were found to be independent of the molecular weight and MWD. Induction time is related to onset temperature through a proposed equation under quiescent conditions. This equation was modified to describe the crystallization induction time under molecular orientation. Such an equation was applied in the spinning modeling.

Among the six iPPs compared, there are no large differences of growth rates when molecular weight and polydispersity change. The small differences of growth rates show that at high crystallization temperature, lower molecular weight and broader molecular weight distribution increase the growth rates, but the trends reverse at low crystallization temperature. An explanation of these results were given based on chain mobility as function of molecular weight. However, it was not possible to completely rule out slight differences of isotacticity as a source of these results.

When molecular weight increases, the overall crystallization rate described by crystallization half-time increases. It seems that increase of polydispersity will also increase the overall rate of crystallization, but the influence of polydispersity is not as large as that of molecular weight. The introduction of nucleating material can effectively increase the

overall crystallization rate. The increase of overall crystallization rate when material characteristics change or nucleating material exists in the resin was attributed to the increase of nucleation rate because growth rate does not change much at the same time.

The crystallization temperature exhibits similar dependencies on the molecular weight, polydispersity and nucleation material as overall crystallization rate. There are no differences in the measured crystallization induction times between the different iPPs under quiescent conditions. Even the existence of adventitious nucleating material at the levels occurring in the present samples does not change the relationship between crystallization induction time and cooling condition.

For a given material, there was no significant difference in the Avrami index for crystallization under different cooling conditions, and the nucleation rate constant increases as cooling rate increases. Materials with higher MW tend to give higher values of the Avrami index. The dependence of the Avrami index on MWD is not evident among the considered materials. The existence of the significant number of adventitious nuclei results in a large Avrami index. The MW and MWD have an effect on the nucleation rate constant similar to the crystallization half-time.

The Avrami integrated and differential equations, the equations for crystallization induction time and nucleation rate function, were incorporated in the melt spinning modeling. The orientation coefficients in these equations and the Avrami index were found by fitting the simulated birefringence profiles to the experimental profiles. The nucleation behavior on the spinline was described by the proposed nucleation rate function.

A generalized power law viscosity equation was also introduced into the spinning model. The coefficients in the viscosity equation were found by fitting the equation to the shear viscosity data with slight modification to accommodate the observed elongational viscosities.

By repeating the same procedures for viscosity and crystallization kinetics equations for materials with different molecular weights and polydispersities, the dependence of molecular weight and polydispersity of the spinning model was introduced.

The model has been tested for variation in molecular weight and polydispersity at various levels and under different spinning conditions. At the same time, the model was also discussed in terms of crystallization stress, crystallization temperature, crystallization induction time, crystallization rate constant, nucleation rate constant, Avrami index, final crystallinity, and final orientation functions in the as-spun filaments. It was found that the model can, at least, qualitatively reflect most of the trends observed in the spinning experiments.

7.2. Recommendations For Future Research

One of the major areas where lack of understanding exists in crystallization theory and its application is in the phenomenon of nucleation and its proper mathematical description. One reason for this is that the numerous factors affect the nucleation process. Another is that it is quite difficult to study nucleation experimentally due to inadequate methods of following the process as a function of time and temperature. Although the present work provides a new way to shed some light on this subject through application of the power law nucleation rate function, much additional work needs to be done to experimentally quantify the rate of nucleation and the way it varies with time and temperature in order to put the interpretations arrived at through use of the nucleation rate function and the Avrami analysis on a firm basis. One way to proceed with this would be to improve the technique used briefly in this research of directly counting the nuclei observed in the sample. This could be vastly improved by use of image analysis techniques so that the number density of nuclei could be followed with time during the crystallization process. Another possible way to follow the nucleation number density might be to use the light

scattering observation in the intensity measured without analyzer to obtain the results. This would require considerable theoretical development, but might provide the simplest experimental route to the desired data.

It is recommended that the problem of nucleation, growth and impingement of spherulites be studied theoretically using computer simulation of the process to examine specific behaviors in detail. This would supply information that can not be obtained by experiment. In particular, such a simulation would help us to examine the effect of impingement on the geometric growth index and the way this influences our interpretation of experimental data.

It is also recommended that the possibility of following dynamically the absolute crystallinity via the measured relative light intensity be investigated. This appears to be feasible, but was not investigated fully in the present research. If this can be done accurately, it would add considerably to the what we learn from the technique. The absolute crystallinity would be especially valuable for high cooling rate studies of polymers for which the absolute crystallinity is changing rapidly with increasing cooling rate. A potential problem is that different crystalline phases and growth morphologies would be expected to produce different amounts of light transmission. It may be necessary to separate this effect from that of crystallinity per se.

The spinning behavior of polypropylenes are known to be function of isotacticity and copolymer content. The present techniques should be used to extend the model of the spinning process to cover these effects, especially for ethylene copolymers.

The application of the LDM technique to the study of the details of crystallization under strain is recommended. this would be a step further than was done in the present research and might shed considerable light on this important, but poorly understood problem.

Finally, it is recommended that the crystallization kinetics equations used in the spinning model be incorporated into a computer model for the injection modeling process. At present, the treatment of crystallization in injection molding simulations is lacking and badly needed for semicrystalline polymers.

LIST OF REFERENCES

LIST OF REFERENCES

- Alfonso, G. C., Verdoni, M. P. and Wasiak, A., *Polymer*, 19, 711(1978).
- Althen, G and Zachmann, H.G., *Makromol. Chem.* 180,2723 (1979).
- Andrews, E.H, *Proc. Roy. Soc. London* , A270, 232(1962).
- Andrews, E.H,Owen,P.J., and Singh,A., *Proc.Roy.London*, A324,79(1971).
- Archambault, P. and Puld'homme, R.E., *J.Polym.Sci.,Phys.*,18, 35(1980).
- Avrami, M., *J. Chem. Phys.*, 7, 1103 (1939).
- Avrami, M., *J. Chem. Phys.*, 8, 212 (1940).
- Avrami, M., *J. Chem. Phys.*, 9, 177 (1941).
- Banks, W., Gordon, M., Roe, R.J., and Sharples, A., *Polymer*, 4, 61 (1963).
- Baranov,V.G.,*Disc.Faraday soc.*, 49,137(1970).
- Bassett, D. C. and Keller, A., *Phil. Mag.*, 6, 345, (1962).
- Battacharya, A.K. and Moutsoglou, A., *ASME paper No. 82-HT 74* (1982).
- Bekkedahl, N., *J. Res. Nat. Bur. Stand.* 43, 145 (1949).
- Bekkedahl, N., *Rubber Chem.Technol.*,40,35(1967).
- Bheda, J. H. and Spruiell, J. E., *J. Appl. Polym. Sci.*, 39, 447(1990).
- Binsbergen, F. J., *J. Macromol. Sci. B4*, 837(1970).
- Binsbergen, F. J., and de Lange, B. G. M., *Polymer*, 11, 309(1970).
- Blackadder, D.A., Schleinitz,H.M.,*Nature*,200,778(1963).
- Bogue, D.C., *Ind. Eng. Chem. Fund.*, 5, 253(1966).
- Bogue, D.C. and While, J.L., "Engineering Analysis of Non-Newtonian Fluid", NATO
Agardograph, #144(1970).
- Bragato, G. and Gianotti,G., *Eur. Polym.*,19,803(1983).
- Bruckner, S. and Meille, S. V. (1989).

- Burfield, D.R., Patrick, S.T. LOI, and Y. Doi, J. Appl. Polym. Sci., 41, 1095(1990).
- Campbell, R. A., Ph.D. Dissertation, University of Tennessee, (1991).
- Carnahan, B., Luther, H.A. & Wilkes, J.O. *Applied Numerical Methods*, John Wiley & Sons, New York, (1969).
- Chan, T.W. and A.I. Isayev, ANTEC, 1148(1992).
- Choe, C.R. and Lee, K.H., Polym. Eng. Sci., 29, 801(1989).
- Clark, E.J. and Hoffman, J.D., Macromolecules, 17, 878 (1984).
- Cobb, W.H. and Burton, R.L., J. Polym. Sci., 10, 276(1953).
- Cormia, R.L., Price, F.P. and Turnbull, D., Kinetics of crystal nucleation in polyethylene, J. Chem. Phys., 37, 1333 (1962).
- Coulson, J.M. & Richardson, J.F. *Chemical Engineering*, Pergamon Press, New York, (1977).
- Cox, W.P. and Nerz, E.H., J. Polym. Sci., 28, 619(1958).
- Cross, M.M, J. Colloid Sci., 20, 99(1965).
- Cross, M.M, Eur. Polym. J., 2, 99(1966).
- Cross, M.M, J. Appl. Polym. Sci., 13, 765(1969).
- Cross, M.M, Rheol. Acta, 18, 609(1979).
- Culberson, W.T., and Tant, M.R., J. Appl. Polym. Sci., 47, 395 (1993).
- Dees, J.R. and Spruiell, J.E., J. Appl. Polym. Sci., 18, 1503(1974).
- Dietz, W., Colloid and polym. Sci., 259, 413 (1981).
- Ding, Z. and Spruiell, J. E., Soc. Plastics Engineers, Tech. Papers, 40, 1485(1994).
- Ding, Z. and Spruiell, J. E., unpublished results (1994).
- Eder, M. and Wlochowicz, A., Polymer, 24, 1593(1983).
- Elias, H.G., *Macromolecules*, Vol. 1, Plenum press, N.Y. (1977).
- EPSE=*Encyclopedia of Polymer Science and Engineering*, Second Edition, 1986.
- Evans, U.R. Trans. Faraday Soc., 41, 365 (1945).

- Falkai, B. Makromol.Chem.,41, 86(1960).
- Falkai, B. and Stuart,H.A., Kolloid Z.,162,138(1959).
- Farrow, G. F. , J. Appl. polym. Sci., 9, 1227(1965).
- Flory, P.J., J. Am. Chem. Soc., 84, 2857(1962).
- Flory, P.J., Statistical Mechanics of Chain Molecules, Interscience, NY, (1969).
- Flory, P.J. and Rehner, J., J. Chem. 11, 512 (1943).
- Fritzsche, A.K. and Price,F.P., Polym. Eng. Sci.,14,401(1974).
- Fritzsche, A.K., Price,F.P. and Ulrich,R.D., Polym. Eng. Sci.,16,182(1976).
- Gent, A,N.,Trans.Faraday Soc.,50,521(1954).
- Gent, A,N., J.Polym.Sci.,18, 321(1955).
- Gent, A,N., J.Polym.Sci.,A2,3,3787(1965).
- Gent, A,N., J.Polym.Sci.,A2,4,447(1966).
- George, H.H., Polym. Eng. Sci., 22, 292(1982).
- George, W. and Tucker,P., Polym.eng.Sci.,15,451(1975).
- Gezovich, D. M. and Geil, P. H., Polym. Eng. Sci., 8, 202(1968).
- Godovsky, Y. K. and Slonimsky, G.L., J. Polym. Sci., Phys. Ed, 12, 1053 (1974).
- Goldfarb, L., Macromol. Chem., 179,2297(1978).
- Gray, A. P., Proc. Amer. Soc. Symp., Analytical calorimetry, Plenum Press, N.Y. (1986).
- Griffith, J.H. and Ranby,B.G., J.Polym.Sci.,38,107(1959).
- Grun, F. and Kuhn, W., Kolloid-Z, 101, 248 (1942).
- Gupte, K.M., Motz,H. and Schultz,J.M., J.Polym.Sci.,B,21,1927(1983).
- He, X. and Bogue, D. C., UTK (1992).
- Haas, T.W., Maxwell,B., Polym.Eng.Sci.,9,225(1969).
- Hajji, N., Spruiell, J. E., Lu, F.M., Malkan, S., and Richardson, G.C. INDA J. Nonwoven, Vol. 4, No.2, 16(1992).

- Hamana, I., et al, *Melliand Text.*, 50, 499(1969).
- Hamana, I., et al, *Melliand Text.*, 50, 382(1969).
- Hamidi, A., Abhiraman,A.S. and Asher,P.J., *J.Appl.Polym.Sci.*,28,567(1983).
- Hammami, A., MS. Thesis, the University of Tennessee, (1990).
- Hammami, A. and Mehrotra, *Thermochim. Acta*, 215, 197 (1993).
- Hay, J.N., *Br. Polym. J.*, 3, 74 (1971).
- Hay, J. N. and Mills, P.J., *Polymer*, 23, 1380 (1982).
- Hillier, I.H., *J. Polym. Sci. Part A*, 3, 3067 (1965).
- Hoffman, J. D., *SPE Trans.*, 4, 315(1964).
- Hoffman, J.D., *Polymer*, 23, 656 (1982).
- Hoffman, J.D., *Polymer*, 23, 656(1983).
- Hoffman, J.D., Davis, G.T.and Lauritzen, J. I., *Treatise on Solid state Chemistry*, Vol.3, Hannay, N.B., eds., Plenum, N.Y. (1976).
- Hoffman, J.D. and Lauritzen, J.I., *J. Res. Stand. A*, 65, 297 (1961).
- Hoffman, J. D. and Weeks, J.J., *J. Chem. Phys.* 37, 1723 (1962).
- Hoshino, S.Meinecke,E.,Powers,J. and Stein,S. *J.Polym.Sci.*,A,3,3041(1965).
- Jeziorny, A., *Polymer*, 19, 1142 (1978).
- Johnson, W. A. and Mehl, R.T., *Metals Technol. AIME Tech.Publ.*,1089 (1939).
- Kamal, M. R. and Chu, E., *Polym. Eng. Sci.* 23, 1 (1983).
- Kampf, G., *Characterization of Plastics by Physical Methods*, Hanser, New York
- Kase, S. and Matsuo, T., *J. Polym. Sci.*, A3, 2541(1965).
- Kase, S. and Matsuo, T., *J. Appl. Polym. Sci.*, 11, 251(1967).
- Katayama, K., Amano,T. and Nakamura,K., *Koll.Z.Z.Polym.*,226,125(1968).
- Katayama, K. and Yoon, M.G., in *High Speed Fiber Spinning*, Ziabicki, A. and Kawai, H., Ed., Wiley, N.Y., (1985).
- Kawai, T., Matsumoto,T., Kato, M., and Maeda, H., *Kolloid Z.Z.Polym.*, 222,1(1968).

- Keller, A., Lester, G.R. and Morgan, L. B., Phil, Trans. R. Soc., 247, 1 (1954).
- Keller, A., Phil. Mag., 2, 1171(1957).
- Kersten, R.D., *Engineering Differential System*, McGraw-Hill Book Company, New York, (1969).
- Khanna, Y.P. Polym.Eng. Sci.,30,1615 (1990).
- Kim, Y.C., Kim, C.Y. and Kim, S.,C., Polym. Eng. Sci.,31,1009 (1991).
- Kim, H.G., Mandelkern,L., J.Polym.Sci.,A2,6,181(1968).
- Kobayashi, K. and Nagasawa, J., J. Macromol. Sci., B4, 331 (1970).
- Kolmogoroff, A.N., Isvest. Akad. Nauk SSSR Ser. Math., 1,335 (1937).
- Kraus, G., and Gruver, J.T., J. Polym.Sci.,B,10, 2009(1972).
- Kuhn, W., Kolloid-Z, 76, 258 (1936).
- Kuhn, W., J. Polym. Sci., 1, 380 (1946).
- Lagasse, R.R. and Maxwell B., Polym. Eng.Sci.,9,225(1969).
- Lambert, W.S., MS Thesis, University of Tennessee, Knoxville (1988).
- Liu, C.C., Ph.D. Dissertation, University of Tennessee, Knoxville, (1994).
- Liu, C.C., Bogue, D. C., and Spruiell, J. E., "Tubular film Blowing: Part I, On-Line Experimental Studies; Part II, Therital Modeling", Interanl. Polym. Proc., accepted (1995).
- Lovinger, A.J., Chua,J.O. and Gryte, C.C., J.Polym.Sci., Phys.,15,641(1977).
- Luongo,J.P., J. Appl. Polym. Sci., 3, 302(1960).
- Mackley, M.R. and Keller,A.,Polymer,14,16(1973).
- Magill, J. H., Nature, Lond., 187, 770 (1960).
- Magill, J. H., Polymer, 2, 221 (1961).
- Magill, J. H., Nature, Lond., 191, 1092 (1961).
- Magill, J. H., J., Brit., Appl. Phys., 12, 618 (1961).
- Magill, J. H., Polymer, 3, 35 (1962).

- Magill, J.H., Res.Dev.(London), 11, 30 (1962).
- Maglio, G., Martuscelli, E., Palumbo, R., and Soldati, I., Polymer, 17, 185 (1976).
- Mamedov, K.P. and Nuriev, A.D., Soviet Phys. Crystallog. (Eng. Trans.), 12, 605 (1968).
- Mancarella, C. and Martuscelli, E., Polymer, 18, 1240 (1977).
- Mandalken, L., Chem. Rev., 56, 903 (1956).
- Mandelkern, L., *Crystallization of Polymers*, McGraw-Hill, N.Y., (1964).
- Mandelkern, L., In *Growth and Perfection of Crystals*, Dorenus, Roberts, and Turnbull Eds., Wiley, N.Y. (1958).
- Mandelkern, L., Clotin, M. and Benson, R.A., Macromolecules, 14, 22 (1981).
- Marker, L., Hay, P.M., Tilley, G.P., Early, R.M. and Sweet, O.J., J. Polym. Sci., 38, 33 (1959).
- Martuscelli, E., Silvestre, C. and Abate, G., Polymer, 23, 229 (1982).
- McHugh, A.J., Polym. Eng. Sci., 22, 15 (1982).
- McHugh, A.J. and Blunk, R.H., Macromol., 19, 1249 (1986).
- McHugh, A.J., Ejike, E. and Silebi, C.A., Polym. Eng. Sci., 19, 414 (1979).
- McHugh, A.J., Rietveld, J., J. Polym. Sci., Phys., 23, 2359 (1985).
- McHugh, A.J., Vaughn, P. and Ejike, E., Polym. Eng. Sci., 18, 443 (1978).
- Meille, S. V., Bruckner, S. and Porzio, W. (1990).
- Misra, S., M.S. Thesis, University of Tennessee, Knoxville, (1994).
- Misra, S., Lu, F.M., Spruiell, J.E. and Richeson G.C., J. Appl. Polym. Sci., 56, 1761 (1995).
- Misra, A. and Stein, R.S., J. Polym. Sci., Polym. Lett., B10, 473 (1972).
- Morgan, P.W. Phil. Trans. Roy. Soc. Ser. A 247.13 (1954).
- Monasse, B., and Haudin, J.M., Colloid and Polym. Sci., 264, 177 (1986).
- Morrow, D. R., and Newman, B. A., J. Appl. Phys., 39, 4944 (1968).

- Mueller, F.H. and Martin,H., J.Polym.Sci.,C,683(1964).
- Nakamura, K., Watanabe, T., Katayama, K., and Amano, T., J. Appl., Polym. sci. 16, 1077(1972).
- Nakamura, K., Katayama, K., and Amano, T., J. Appl., Polym. sci. 17, 1031(1973).
- Oono, R., Miyasaka,K., and Ishikawa, K., H, J. Polym. Sci.,B,11,1477(1973).
- Ozawa, T., *Polymer*, 12, 150 (1971).
- Padden, F. J., and Keith, H. D., J. Appl. Phys. 30, 1485 (1959).
- Padden, F. J. and Keith, H. D., J. Appl. Phys. 30, 1479(1959).
- Padden, F. J. and Keith, H. D. , J. Appl. Phys. 37, 4013 (1966).
- Parrini, P. and Corrieri,G., Macromol. Chem.,62,83,(1963).
- Patel, R.M., Ph.D Dissertation, University of Tennessee, Knoxville, August, (1991).
- Patel, R. M.and Bogue, D. C., J. Rheol., 33, 607(1989).
- Patel, R. M. and Spruiell, J, E., Polyme. Eng. Sci., 31, 730(1991).
- Patel, R. M., Bheda, J. H., and Spruiell, J. E., J. Appl. Polym. Sci., 42, 1671(1991).
- Pennings, A.J., J.Polym.Symp.,59,55(1977).
- Pennings, A.J. and Pijpers,M.F.J., Macromol.,3,261(1970).
- Pennings, A.J., Zwijnenburg,A. and Lagveen,R., Koll.Z.Z.Polym.,251,500(1973).
- Peterlin, A. and Roechl,E., J:Appl.Phys.,34,102(1963).
- Phillips, P.J., Rep. Prog. Phys. 53, 549(1990).
- Phillips, P.J. and Kao,Y.H., Polymer,27,1679(1986).
- Piccarolo, S., Saiu, M., Brucato,V. and Titomanlio, G., J. Appl.Polym.Sci., 46, 625(1992).
- Price, F. P., J. Am. Chem. Soc., 74, 311 (1952).
- Price, F.P., in *Nucleation*, Zettlemayer, Marcel, and Dekked, N.Y (1969).
- Rietveld, J., Mchugh,A.J., J.Polym.Sci.,Phys.,23,2339(1985).
- Samuels, R. J. *Structured Polymer Properties*. Wiley, N.Y. (1974).

- Samuels, R. J. and Yee, R. Y. , J. Polym. Sci. A2, 10, 385(1972).
- Savelyev, I.V., *Physics*, volume II, English version, Translated by Leib, G.,P442, (1980).
- Sauer, J. A., Morrow, D. R. , and Richardson, G. C., J. Appl. Phys. 36, 3017(1964).
- Sherwood, C.H., Price,F.P., Stein,R.S. and J.Polym.Sci.,Polym.Symp.,63,77(1978).
- Shimizu, J., Okui, N. and Kikutani, T., in High Speed Fiber spinning, Wiley, NY, 173(1985).
- Smith, F.S.and Steward,R.D., Polymer,15,283(1974).
- Spruiell, J. E. and White, J. L., Polym. Eng. Sci., 15, 660(1975).
- Tadmor, Z., *Principles of Polymer Processing*, John Wiley & Sons, New York, (1979).
- Stein, R.S., Erhardt, P., van Aartsen, J. J., Clough, S., and Rhodes, M., J. Polym. Sci., C13, 1(1966).
- Stein, R.S. and Misra,A., J.Polym.Sci. Phys., 11,109(1973).
- Susuki, T. and Kovacs, A. Polym. J., 1. 82 (1970).
- Thiel, M.H.,J.Polym.Sci.,B,13,1097(1975).
- Treloar, L.R.G., Trans.Faraday,Soc., 37,84(1941).
- Tobin, M.C. J. Polym. Sci., Phys. Ed., 14, 2253 (1976).
- Tobin, M.C. J. Polym. Sci., Phys. Ed., 12, 399 (1974).
- Tobin, M.C. J. Polym. Sci., Phys. Ed., 14, 2235 (1974).
- Tobin, M.C. J. Polym. Sci., Phys. Ed., 15, 2269 (1977).
- Treloar, L.R.G., Trans. Faraday Soc., 39, 36 (1943).
- Treloar, L.R.G., Trans. Faraday Soc., 39, 241 (1943).
- Treloar, L.R.G., Trans. Faraday Soc., 42, 83 (1946).
- Treloar, L.R.G., *The Physics of Rubber Elasticity*, 3rd Ed., Oxford, N.Y., (1975).
- Turnbull, D., J. Chem. Phys., 20, 411(1952).
- Turner, A. J., Aizilewood, J. M., and Beckett, D.R., Makromol. Chem., 75, 134(1964).

- Velisaris, C. and Seferis, J., Polym. Eng. Sci., 26, 1574 (1986).
- Vignaud, R. and Schultz, J.M., Polymer, 27, 651 (1986).
- Warfield, R.W. Makromol. Chem., 89, 269 (1965).
- Wereta, A., Jr. and Gogos, C.C., Polym. Eng. Sci., 11, 19 (1971).
- Williams, S.M., Master Degree Thesis, UTK (1995)
- Wlochowicz, A. and Eder, M., Polymer, 22, 1285 (1981).
- Wu, Z.Q., Dann, V.L., Cheng, S.Z.D. and Wunderlich, B., J. Therm. Anal., 34, 105 (1988).
- Wunderlich, B., "Macromolecular Physics", V2, Academic Press, N.Y., (1976).
- Yamamoto, M., White, J.L., J. Polym. Sci., A2, 9, 1399 (1971).
- Yamaura, K., Ide, K., Matsuzawa, S., J. Macromol. Sci., B4, 331 (1970).
- Yeh, G.S.Y. and Hong, K.Z., Polym. Eng. Sci., 19, 395 (1979).
- Yeh, G.S.Y., Hong, K.Z. and Krueger, D.L., Polym. Eng. Sci., 19, 401 (1979).
- Zannetti, R., Celotti, G., Fochera, A. and Francesconi, R., Makromol. Chem., 128, 137 (1969).
- Zhang, R., Zheng, H., Lou, X. and Ma, D., J. Appl. Polym. Sci., 51, (1994).
- Zhou, J., MS. Thesis, the University of Tennessee, (1988).
- Zhou, J. and Spruiell, J.E., in Nonwovens — an advanced Tutorial, Turbak, A.F. and Vigo, T.L., Ed., TAPPI Press, Atlanta, (1989).
- Ziabicki, A., Appl. Polym. Symp., 18, 142 (1967).
- Ziabicki, A. *Fundamentals of Fiber Formation*, Wiley, N.Y., (1976).
- Zieminski, K.F. and Spruiell, J.E., J. Appl. Polym. Sci., 35, 2223 (1988).
- Zwijnenburg, A. and Pennings, A.J., Colloid Polym. Sci., 253, 452 (1975).

APPENDIXES

Appendix A

NUMERICAL SOLUTION FOR THE PARTIAL DIFFERENTIAL EQUATIONS FOR THE NONISOTHERMAL PROCESS

The considered system for the heat transfer analysis is shown in Figure A.1. To solve the heat transfer problem, the following assumptions were made:

- (a) The heat transfer perpendicular to the x-direction is neglected (one dimensional heat transfer assumption). This assumption is reasonable since the thickness of the sample to be examined is $\leq 200 \mu\text{m}$ and the diameter of the sample plane is around 10 mm. The ratio of the width to the thickness of the sample is $10/0.2 = 50$. That is, compared to the thickness, the width of the sample is large enough to be treated as an infinite plane.
- (b) The crystallization effect is included in the specific heat [Tadmor (1979)]. No crystallization term will appear in the heat transfer equation. Such treatment made the mathematics for this heat problem less complicated, while allowing the effect of crystallization to be included in the calculation.
- (c) The dependence of specific heat on temperature is independent of the cooling rate. This assumption is for assumption (b), since only one set of data at one cooling rate is available in the literature. To make the present calculation possible this assumption has to be made. In practice, the crystallization rate might be different at different cooling rate, so that the heat generated by crystallization will be different. The relation between heat capacity and temperature will be changed. This is the subject of the present research which deals with crystallization rate at different cooling rate.
- (d) The thermodynamic parameters of glass and air are approximately constant with temperature.

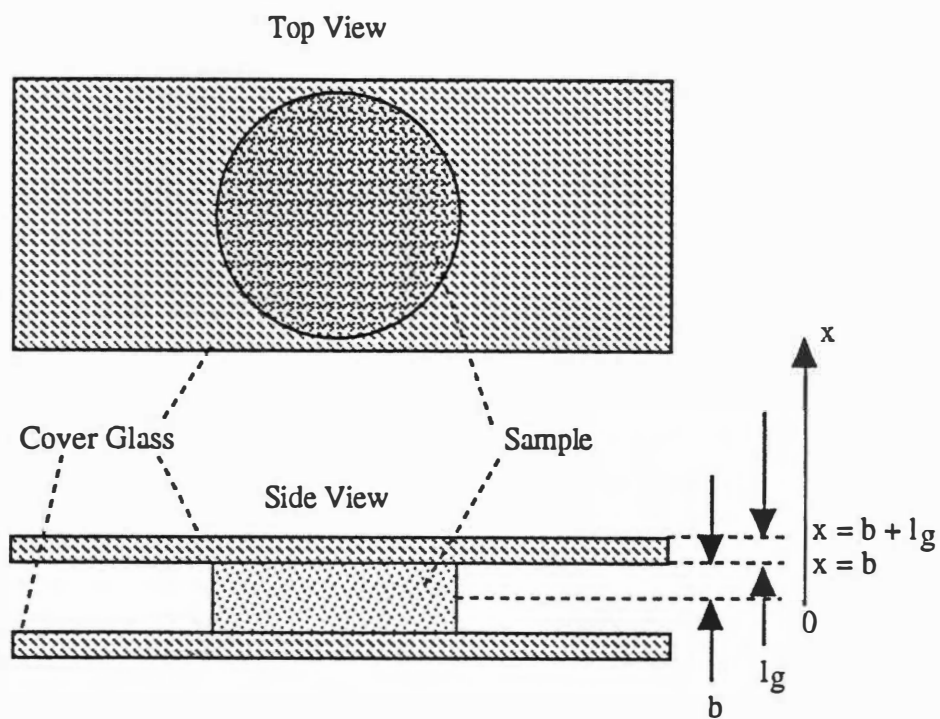


Figure A.1. Sample assembly and its coordinate system for the heat transfer analysis.

According to the basics in chemical engineering, the one dimensional heat transfer for a slab is described by equation (A.1),

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) \quad (\text{A.1})$$

where ρ is the polymer density, C_p is the specific heat of polymer, and k , thermal conductivity of the polymer. If $\rho = \rho_0$, $k = k_0$ and $C_p = C_{p0}$ at $T = T_0$, and let $\rho' = \rho/\rho_0$, $k' = k/k_0$, $C_p' = C_p/C_{p0}$, $\xi = x/b$ (b is half thickness of sample), $\alpha' = \alpha/\alpha_0$, $\Theta = \frac{T-T_1}{T_0-T_1}$, and $\tau = \alpha_0 t/b^2$ (α_0 is the thermal diffusivity at T_0), equation (A.1) can be written in dimensionless variable as:

$$\rho' C' \frac{\partial \Theta}{\partial \tau} = \frac{\partial k'}{\partial \xi} \frac{\partial \Theta}{\partial \xi} + k' \frac{\partial^2 \Theta}{\partial \xi^2} \quad (\text{A.2})$$

where ρ' , C' and k' can be grouped as thermal diffusivity $\alpha' = k' / (\rho' C')$. The initial and boundary conditions for the considered heat transfer problem are:

$$\text{I.C.:} \quad T(x,0) = T_0 \quad (\text{A.3})$$

where T_0 is the initial temperature in the sample when the sample just begins to be cooled. The dimensionless form of the initial condition is,

$$\Theta(\xi,0) = 1 \quad (\text{A.3b})$$

$$\text{B.C. 1:} \quad \frac{\partial T(0,t)}{\partial x} = 0 \quad (\text{A.4})$$

or,

$$\frac{\partial \Theta(0,\tau)}{\partial \xi} = 0 \quad (\text{A.4b})$$

$$\text{B.C. 2: } \frac{\partial T(b,t)}{\partial x} = -\frac{H_{ga}}{k} [T(b,t) - T_1] \quad (\text{A.5})$$

or,

$$\frac{\partial \Theta(1,\tau)}{\partial \xi} = -\frac{H_{ga} b}{k_0 k} \Theta(1,\tau) \quad (\text{A.5b})$$

where B.C. 2 is obtained by the following procedure.

At $x = b$, the heat transferred per unit time and unit area can be calculated by:

$$q = (k_g/l_g)(T_b - T_g) \quad (\text{A.6})$$

where T_g is the temperature at $x = b+l_g$, i.e., at the interface between glass and cooling air, T_b is the temperature at $x = b$, i.e., at the interface between sample and glass, k_g is the thermal conductivity of glass, and k_a is the thermal conductivity of air. At $x = b+l_g$, the heat transferred per unit time and unit area is given by:

$$q = h_a(T_g - T_1) \quad (\text{A.7})$$

where l_g is the thickness of cover glass, h_a is the heat transfer coefficient of air, and T_1 is the temperature of cooling medium. Combining equation (A.6) and (A.7), one has,

$$q\left(\frac{1}{k_g/l_g} + \frac{1}{h_a}\right) = T_b - T_1 \quad (\text{A.9})$$

where $h_a = k_a/l_a$, l_a is the thickness of air layer in which the temperature is higher than T_1 . Therefore, the heat resistance caused by glass and air, $\frac{1}{H_{ga}}$ (H_{ga} may be called the heat transfer coefficient of the air and glass), is:

$$\frac{1}{H_{ga}} \equiv \frac{1}{k_g/l_g} + \frac{1}{h_a} \quad (\text{A.10})$$

Using (A.10), equation (A.9) may be written as:

$$q = H_{ga} (T_b - T_1) \quad (A.11)$$

From the other hand, the heat conducted by the interface of polymer, at $x=b$ (in the polymer), can be described as:

$$q = -k \frac{\partial T}{\partial x} \quad (A.12)$$

Since $\frac{\partial T}{\partial x} < 0$, the minus sign keeps right side of equation (A.12) positive. q in equation (A.11) and (A.12) should be equal. Thus,

$$\frac{\partial T}{\partial x} = -\frac{H_{ga}}{k} [T(b,t) - T_1] \quad (A.13)$$

Where $T(b,t) = T_b$. If $x = b$ is considered equation (A.13) leads to B.C. 2.

The numerical solution for the heat transfer problem in the present research was obtained following Tadmor's approach [Tadmor (1979)]. Different from Tadmor's approach, the present research uses the third kind of boundary condition which is much more difficult to be handled than the constant boundary condition (first kind of condition) used by Tadmor. The numerical solution of the considered heat transfer problem is derived as follows.

A. 1. Temperature Of $\Theta_i^j = \Theta_1^j$, At $\xi_i = \xi_1$ For $j=1, 2, 3, \dots$, i.e., At B.C. 1

This step is to develop the equation to calculate the temperature at the center of the polymer, that is at $i = 1$, or $\xi_i = \xi_1 = 0$. Substitute B.C. 1:

$$\frac{\partial \Theta(\xi_1, \tau_j)}{\partial \xi} = 0 \quad (A.4b)$$

into the Talor's expansion for Θ_0^j at $a = \xi_1$ is (choose $x = \xi_0$):

$$\Theta_0^j = \Theta_1^j + \frac{d\Theta_1^j}{d\xi} (\xi_0 - \xi_1) + \frac{d^2\Theta_1^j}{d\xi^2} \frac{(\xi_0 - \xi_1)^2}{2!} + O[(\xi_0 - \xi_1)^3]$$

one has,

$$\Theta_0^j = \Theta_1^j + \frac{d^2\Theta_1^j}{d\xi^2} \frac{(\xi_0 - \xi_1)^2}{2!} + O[(\xi_0 - \xi_1)^3]$$

$\Rightarrow$

$$\frac{d^2\Theta_1^j}{d\xi^2} = \frac{2}{(\xi_0 - \xi_1)^2} \{ \Theta_0^j - \Theta_1^j \} + O[(\xi_0 - \xi_1)] = \frac{2}{(\xi_0 - \xi_1)^2} \{ \Theta_0^j - \Theta_1^j \} = \frac{2}{(\Delta\xi)^2} \{ \Theta_0^j - \Theta_1^j \} \quad (\text{A.14})$$

where $O[(\xi_0 - \xi_1)]$ was neglected. Equation (A.2) at $i = 1$ is expressed as,

$$\rho' C' \frac{\partial \Theta_1^j}{\partial \tau} = \frac{\partial k'_1}{\partial \xi} \frac{\partial \Theta_1^j}{\partial \xi} + k' \frac{\partial^2 \Theta_1^j}{\partial \xi^2}$$

Substitute B.C. 1, equation (A.4b) and equation (A.14) into it,

$$\frac{\partial \Theta_1^j}{\partial \tau} = k'_1 \frac{1}{\rho'_1 C'_1} \frac{2}{(\Delta\xi)^2} \{ \Theta_0^j - \Theta_1^j \} = \alpha'_1 \frac{2}{(\Delta\xi)^2} \{ \Theta_0^j - \Theta_1^j \} \quad (\text{A.15})$$

Here we met problem. There is no point for $i=0$! There is a difference between $i = I$ and $i = 0$. For $i=I$, the point exists, but no such a point of $i = 0$. This difference causes different problem for solving the third kind of B.C.. The Θ_0^j problem is tackled by the following procedure. If one still choose $a = \xi_1$, but $x = \xi_2$, similarly he can get:

$$\frac{\partial \Theta_1^j}{\partial \tau} = \alpha'_1 \frac{2}{(\Delta\xi)^2} \{ \Theta_2^j - \Theta_1^j \} \quad (\text{A.16})$$

Minus equation (A.15) from equation (A.16) one gets,

$$0 = \Theta_2^j - \Theta_0^j \quad \text{or} \quad \Theta_0^j = \Theta_2^j \quad (\text{A.17})$$

Substitute this into equation (A.15) one obtains:

$$\frac{\partial \Theta_1^j}{\partial \tau} = \alpha'_1 \frac{2}{(\Delta \xi)^2} \{ \Theta_2^j - \Theta_1^j \} \quad (\text{A.18})$$

In fact, we only need to deal with $a = \xi_1$, and $x = \xi_2$. It is not necessary to get equation (A.15). However, if one uses equation (A.29) at $i=1$, all these steps become necessary. Similarly, one may obtain the equation for step $j+1$ as:

$$\frac{\partial \Theta_1^{j+1}}{\partial \tau} = \alpha'_1 \frac{2}{(\Delta \xi)^2} \{ \Theta_2^{j+1} - \Theta_1^{j+1} \} \quad (\text{A.19})$$

By equation (A.18) the right side of equation (A.26), the Crank-Nickolson equation becomes,

$$\begin{aligned} \Theta_1^j + \frac{\Delta \tau}{2} \frac{\partial \Theta_1^j}{\partial \tau} &= \Theta_1^j + \frac{\Delta \tau}{2} \alpha'_1 \frac{2}{(\Delta \xi)^2} \{ \Theta_2^j - \Theta_1^j \} \\ &= \Theta_1^j + \alpha'_1 p \{ \Theta_2^j - \Theta_1^j \} \end{aligned} \quad (\text{A.20})$$

By equation (A.19) the left side of equation (A.26) changes to

$$\begin{aligned} \Theta_1^{j+1} - \frac{\Delta \tau}{2} \frac{\partial \Theta_1^{j+1}}{\partial \tau} &= \Theta_1^{j+1} - \frac{\Delta \tau}{2} \alpha'_1 \frac{2}{(\Delta \xi)^2} \{ \Theta_2^{j+1} - \Theta_1^{j+1} \} \\ &= \Theta_1^{j+1} - \alpha'_1 p \{ \Theta_2^{j+1} - \Theta_1^{j+1} \} \end{aligned} \quad (\text{A.21})$$

Combining (A.20) and (A.21), the Crank-Nickolson equation changes to,

$$\left(\frac{1}{\alpha'_1} - p \right) \Theta_1^j + p \Theta_2^j = \left(\frac{1}{\alpha'_1} + p \right) \Theta_1^{j+1} - p \Theta_2^{j+1} \quad (\text{A.22})$$

A.2. Temperature Of $\Theta_1^j = \Theta_2^j, \Theta_3^j, \dots, \Theta_{I-1}^j$ at $0 < \xi_2, \xi_3, \dots, \xi_{I-1} < 1$, For $j = 1, 2, 3, \dots$ ($j=0$ Is Initial Condition.)

Since this part does not deal with boundary conditions, the derivation of this part follows Tadmor (1976). In terms of finite differences, for τ in j step, equation (A.2) can be written as:

$$\begin{aligned} \rho'_i C'_i \frac{\partial \Theta_i^j}{\partial \tau} &= \left(\frac{k'_{i+1} - k'_i}{\Delta \xi} \right) \left(\frac{\Theta_{i+1}^j - \Theta_i^j}{\Delta \xi} \right) + k'_i \left[\frac{\Theta_{i-1}^j - 2\Theta_i^j + \Theta_{i+1}^j}{\Delta \xi^2} \right] \\ &= \frac{1}{\rho'_i C'_i \Delta \xi^2} \{ k'_i \Theta_{i-1}^j - (k'_{i+1} + k'_i) \Theta_i^j + k'_{i+1} \Theta_{i+1}^j \} \end{aligned} \quad (\text{A.23})$$

In the same way for τ in $j+1$ step, one has:

$$\frac{\partial \Theta_i^{j+1}}{\partial \tau} = \frac{1}{\rho'_i C'_i \Delta \xi^2} \{ k'_i \Theta_{i-1}^{j+1} - (k'_{i+1} + k'_i) \Theta_i^{j+1} + k'_{i+1} \Theta_{i+1}^{j+1} \} \quad (\text{A.24})$$

By Crank-Nickolson method. one has:

$$\Theta_i^{j+1} = \Theta_i^j + \frac{1}{2} \left[\frac{\partial \Theta_i^j}{\partial \tau} + \frac{\partial \Theta_i^{j+1}}{\partial \tau} \right] \Delta \tau \quad (\text{A.25})$$

or,

$$\Theta_i^{j+1} - \frac{\Delta \tau}{2} \frac{\partial \Theta_i^{j+1}}{\partial \tau} = \Theta_i^j + \frac{\Delta \tau}{2} \frac{\partial \Theta_i^j}{\partial \tau} \quad (\text{A.26})$$

By equation (A.24), the left side of equation (A.26) is equal to:

$$\Theta_i^{j+1} - \frac{\Delta \tau}{2} \frac{\partial \Theta_i^{j+1}}{\partial \tau} = \Theta_i^{j+1} - \frac{\Delta \tau}{2} \frac{1}{\rho'_i C'_i \Delta \xi^2} \{ k'_i \Theta_{i-1}^{j+1} - (k'_{i+1} + k'_i) \Theta_i^{j+1} + k'_{i+1} \Theta_{i+1}^{j+1} \}$$

Let $\alpha'_i = k'_i / (\rho'_i C'_i)$ and $p = \Delta\tau / \Delta\xi^2$, the equation changes to

$$\Theta_i^{j+1} - \frac{\Delta\tau}{2} \frac{\partial \Theta_i^{j+1}}{\partial \tau} = \alpha'_i \left\{ -\frac{p}{2} \Theta_{i-1}^{j+1} + \left[\frac{1}{\alpha'_i} - \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} \right) + P \right] \Theta_i^{j+1} - \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} + 1 \right) \Theta_{i+1}^{j+1} \right\} \quad (\text{A.27})$$

Similarly, the right side of equation(A.26) is:

$$\Theta_i^j + \frac{\Delta\tau}{2} \frac{\partial \Theta_i^j}{\partial \tau} = \alpha'_i \left\{ \frac{p}{2} \Theta_{i-1}^j + \left[\frac{1}{\alpha'_i} - \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} \right) - P \right] \Theta_i^j + \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} + 1 \right) \Theta_{i+1}^j \right\} \quad (\text{A.28})$$

Combine (A.27) and (A.28), one finally get,

$$\begin{aligned} \frac{p}{2} \Theta_{i-1}^j + \left[\frac{1}{\alpha'_i} - \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} \right) - P \right] \Theta_i^j + \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} + 1 \right) \Theta_{i+1}^j = \\ = -\frac{p}{2} \Theta_{i-1}^{j+1} + \left[\frac{1}{\alpha'_i} + \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} \right) + P \right] \Theta_i^{j+1} - \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} + 1 \right) \Theta_{i+1}^{j+1} \end{aligned} \quad (\text{A.29})$$

where $\alpha' = k' / (\rho' C')$, $k' = k/k_0$, k_0 is the thermal conductivity at T_0 , $p = \Delta\tau / \Delta\xi^2$. This equation is to calculate the temperature at $\xi_i = \xi_2, \xi_3, \dots, \xi_{I-1}$ (I : $x=0$ to b or $\xi = 0$ to 1 is divided into $I-1$ sections in the numerical calculation. $\xi_I=1$).

A.3. Temperature Of $\Theta_i^j = \Theta_I^j$, At $\xi_i = \xi_I$ For $j=1, 2, 3, \dots$, i.e., At B.C. 2

The purpose of this part is to develop the equation to calculate the temperature at $\xi_i = \xi_I = 1$. Talor's expansion for Θ_{I-1}^j at $i = I$ or $\xi_i = \xi_I$ is:

$$\Theta_{I-1}^j = \Theta_I^j + \frac{d\Theta_I^j}{d\xi} (\xi_{I-1} - \xi_I) + \frac{d^2\Theta_I^j}{d\xi^2} \frac{(\xi_{I-1} - \xi_I)^2}{2!} + O[(\xi_{I-1} - \xi_I)^3]$$

where $\Theta_I^j = \Theta(\xi_I, \tau_j)$, $j = 0, 1, 2, \dots$

$\xi_I = 1$ is correspondent to $x = x_b$

Note: The general form of Taylor's expansion is:

$$f(x) = f(a) + f'(a)(x-a)/1! + f''(a)(x-a)^2/2! + \dots + f^{(n)}(a)(x-a)^n/n! + \dots$$

Here we take $\xi_{I-1} = x$ and $\xi_I = a$ in the expansion of Θ_{I-1}^j , and keep $\Delta\xi = (\xi_I - \xi_{I-1})$.

Therefore,

$$\Theta_{I-1}^j = \Theta_I^j + \frac{d\Theta_I^j}{d\xi} (-\Delta\xi) + \frac{d^2\Theta_I^j}{d\xi^2} \frac{(-\Delta\xi)^2}{2!} + O[(\Delta\xi)^3]$$

or,

$$\frac{d^2\Theta_I^j}{d\xi^2} = \frac{2!}{(\Delta\xi)^2} [\Theta_{I-1}^j - \Theta_I^j + \frac{d\Theta_I^j}{d\xi} (\Delta\xi)] + O[(\Delta\xi)] \quad (\text{A.30})$$

By B.C. 2, equation (A.5b) changes to

$$\frac{d\Theta_I^j}{d\xi} = \frac{-H_{gab}}{k_0 k'} \Theta_I^j \quad (\text{A.31})$$

Neglecting $O[(\Delta\xi)]$, equation (A.30) becomes:

$$\frac{d^2\Theta_I^j}{d\xi^2} \approx \frac{2}{(\Delta\xi)^2} \Theta_{I-1}^j - \frac{2}{(\Delta\xi)^2} \left(1 + \frac{H_{gab}}{k_0 k'} (\Delta\xi)\right) \Theta_I^j \quad (\text{A.32})$$

By equation (A.2),

$$\rho'_I C'_I \frac{\partial \Theta_I^j}{\partial \tau} = \frac{\partial k'_I}{\partial \xi} \frac{\partial \Theta_I^j}{\partial \xi} + k'_I \frac{\partial^2 \Theta_I^j}{\partial \xi^2} \quad (\text{A.33})$$

By equation (A.33):

$$\frac{\partial \Theta_I^j}{\partial \tau} = (\alpha'_I / k'_I) \frac{\partial k'_I}{\partial \xi} \frac{\partial \Theta_I^j}{\partial \xi} + \alpha'_I \frac{\partial^2 \Theta_I^j}{\partial \xi^2} \quad (\text{A.34})$$

By equation (A.30) and (A.31), and assuming $\left(\frac{k'_{I+1}-k'_I}{\Delta\xi}\right) = \left(\frac{k'_I-k'_{I-1}}{\Delta\xi}\right)$ (This is an important assumption to solve the B.C. 2 problem. In finite difference, this assumption might be established.), equation (A.34) becomes:

$$\frac{\partial\Theta_I^j}{\partial\tau} = (\alpha'_I/k'_I) \left(\frac{k'_I-k'_{I-1}}{\Delta\xi}\right) \frac{-H_{gab}}{k_0k'} \Theta_I^j + \alpha'_I \left[\frac{2}{(\Delta\xi)^2} \Theta_{I-1}^j - \frac{2}{(\Delta\xi)^2} \left(1 + \frac{H_{gab}}{k_0k'} (\Delta\xi)\right) \Theta_I^j \right]$$

That is:

$$\frac{\partial\Theta_I^j}{\partial\tau} = \alpha'_I \frac{2}{(\Delta\xi)^2} \Theta_{I-1}^j - \frac{\alpha'_I}{(\Delta\xi)^2} \left[2 + \frac{H_{gab}}{k_0k'} (\Delta\xi) \left(\frac{k'_I-k'_{I-1}}{k'_I} + 2 \right) \right] \Theta_I^j \quad (A.35)$$

Similarly, one may obtain:

$$\frac{\partial\Theta_I^{j+1}}{\partial\tau} = \alpha'_I \frac{2}{(\Delta\xi)^2} \Theta_{I-1}^{j+1} - \frac{\alpha'_I}{(\Delta\xi)^2} \left[2 + \frac{H_{gab}}{k_0k'} (\Delta\xi) \left(\frac{k'_I-k'_{I-1}}{k'_I} + 2 \right) \right] \Theta_I^{j+1} \quad (A.36)$$

Apply equation. (A.26) at $i = I$,

$$\Theta_I^{j+1} - \frac{\Delta\tau}{2} \frac{\partial\Theta_I^{j+1}}{\partial\tau} = \Theta_I^j + \frac{\Delta\tau}{2} \frac{\partial\Theta_I^j}{\partial\tau} \quad (A.37)$$

The right side of equation (A.37) is equal to:

$$\begin{aligned} \Theta_I^j + \frac{\Delta\tau}{2} \frac{\partial\Theta_I^j}{\partial\tau} &= \Theta_I^j + \frac{\Delta\tau}{2} \left\{ \alpha'_I \frac{2}{(\Delta\xi)^2} \Theta_{I-1}^j - \frac{\alpha'_I}{(\Delta\xi)^2} \left[2 + \frac{H_{gab}}{k_0k'} (\Delta\xi) \left(\frac{k'_I-k'_{I-1}}{k'_I} + 2 \right) \right] \Theta_I^j \right\} \\ &= \alpha'_I \frac{\Delta\tau}{(\Delta\xi)^2} \Theta_{I-1}^j + \left\{ 1 - \frac{\Delta\tau}{2} \frac{\alpha'_I}{(\Delta\xi)^2} \left[2 + \frac{H_{gab}}{k_0k'} (\Delta\xi) \left(\frac{3k'_I-k'_{I-1}}{k'_I} \right) \right] \right\} \Theta_I^j \end{aligned} \quad (A.38)$$

Similarly, the left side of equation (A.37) is equal to:

$$\Theta_I^{j+1} - \frac{\Delta\tau}{2} \frac{\partial\Theta_I^{j+1}}{\partial\tau} = -\alpha'_I \frac{\Delta\tau}{(\Delta\xi)^2} \Theta_{I-1}^{j+1} + \left\{ 1 + \frac{\Delta\tau}{2} \frac{\alpha'_I}{(\Delta\xi)^2} \left[2 + \frac{H_{gab}}{k_0k'} (\Delta\xi) \left(\frac{3k'_I-k'_{I-1}}{k'_I} \right) \right] \right\} \Theta_I^{j+1} \quad (A.39)$$

Combining equation (A.38) and (A.39), one has,

$$\begin{aligned} & \alpha'_I p \Theta_{I-1}^j + \left\{ 1 - \frac{1}{2} \alpha'_I p \left[2 + \frac{H_{ga}^b}{k_0 k'} (\Delta \xi) \left(\frac{3k'_I \Gamma^{k'}_{I-1}}{k'_I} \right) \right] \right\} \Theta_I^j \\ & = -\alpha'_I p \Theta_{I-1}^{j+1} + \left\{ 1 + \frac{1}{2} \alpha'_I p \left[2 + \frac{H_{ga}^b}{k_0 k'} (\Delta \xi) \left(\frac{3k'_I \Gamma^{k'}_{I-1}}{k'_I} \right) \right] \right\} \Theta_I^{j+1} \end{aligned}$$

Finally, for $\xi_i = \xi_I$, the temperatures are calculated by,

$$\begin{aligned} & p \Theta_{I-1}^j + \left\{ \frac{1}{\alpha'_I} - \frac{1}{2} p \left[2 + \frac{H_{ga}^b}{k_0 k'} (\Delta \xi) \left(\frac{3k'_I \Gamma^{k'}_{I-1}}{k'_I} \right) \right] \right\} \Theta_I^j \\ & = -p \Theta_{I-1}^{j+1} + \left\{ \frac{1}{\alpha'_I} + \frac{1}{2} p \left[2 + \frac{H_{ga}^b}{k_0 k'} (\Delta \xi) \left(\frac{3k'_I \Gamma^{k'}_{I-1}}{k'_I} \right) \right] \right\} \Theta_I^{j+1} \end{aligned} \quad (A.40)$$

Equation (A.22), (A.29) and (A.40) compose the numerical solution for the present heat transfer problem. They can be divided into the following matrixes:

B' =

$$\begin{vmatrix} \left(\frac{1}{\alpha'_1} - P \right) p & 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & \frac{p}{2} & \left[\frac{1}{\alpha'_2} - \frac{p}{2} \left(\frac{k'_3 - k'_2}{k'_2} \right) - P \right] & \frac{p}{2} \left(\frac{k'_3 - k'_2}{k'_2} + 1 \right) & 0 & \dots & 0 \\ & & \dots & & & & \\ 0 & 0 & \dots & \frac{p}{2} & \left[\frac{1}{\alpha'_i} - \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} \right) - P \right] & \frac{p}{2} \left(\frac{k'_{i+1} - k'_i}{k'_i} + 1 \right) & \dots & 0 \\ & & & & \dots & & \\ 0 & 0 & \dots & 0 & \frac{p}{2} & \left[\frac{1}{\alpha'_{I-1}} - \frac{p}{2} \left(\frac{k'_I - k'_{I-1}}{k'_{I-1}} \right) - P \right] & \frac{p}{2} \left(\frac{k'_I - k'_{I-1}}{k'_{I-1}} + 1 \right) & 0 \\ 0 & 0 & \dots & 0 & 0 & 0 & p & \left\{ \frac{1}{\alpha'_I} - \frac{1}{2} p \left[\left(\frac{3k'_I \Gamma^{k'}_{I-1}}{k'_I} \right) \frac{H_{ga}^b}{k_0 k'} \Delta \xi + 2 \right] \right\} \end{vmatrix}$$

$C' =$

$$\begin{vmatrix}
 (\frac{1}{\alpha'_1} + P) & -p & 0 & 0 & \dots & 0 & 0 \\
 0 & -\frac{p}{2} & [\frac{1}{\alpha'_2} + \frac{p}{2}(\frac{k'_3 - k'_2}{k'_2}) + P] & -\frac{p}{2}(\frac{k'_3 - k'_2}{k'_2} + 1) & \dots & 0 & 0 \\
 & & \dots & & & & \\
 0 & 0 & -\frac{p}{2} & [\frac{1}{\alpha'_i} + \frac{p}{2}(\frac{k'_{i+1} - k'_i}{k'_i}) + P] & -\frac{p}{2}(\frac{k'_{i+1} - k'_i}{k'_i} + 1) & \dots & 0 \\
 & & & \dots & & & \\
 0 & 0 & \dots & -\frac{p}{2} & [\frac{1}{\alpha'_{I-1}} + \frac{p}{2}(\frac{k'_I - k'_{I-1}}{k'_{I-1}}) + P] & -\frac{p}{2}(\frac{k'_I - k'_{I-1}}{k'_{I-1}} + 1) & 0 \\
 0 & 0 & \dots & 0 & 0 & -p & (\frac{1}{\alpha'_I} + \frac{1}{2}) p [(\frac{3k'_I - k'_{I-1}}{k'_I}) \frac{H_{ga}^b}{k'_I} \Delta\xi + 2]
 \end{vmatrix}$$

and,

$$\Theta^j = \begin{pmatrix} \Theta_1^j \\ \Theta_2^j \\ \vdots \\ \Theta_i^j \\ \vdots \\ \Theta_{I-1}^j \\ \Theta_I^j \end{pmatrix} \quad \Theta^{j+1} = \begin{pmatrix} \Theta_1^{j+1} \\ \Theta_2^{j+1} \\ \vdots \\ \Theta_i^{j+1} \\ \vdots \\ \Theta_{I-1}^{j+1} \\ \Theta_I^{j+1} \end{pmatrix}$$

That is, equation (A.22), (A.29) and (A.40) can be written as:

$$B' \Theta^j = C' \Theta^{j+1} \quad (A.41)$$

Starting from Θ^0 which is the initial condition, for every ξ , $i = 1 \dots I$, $\Theta(\xi_i, 0) = 1$ That is,

$\Theta^0 = (1, 1, 1, \dots, 1)'$, Θ^{j+1} can be calculated from the previous point Θ^j according to equation (A.41). For $j = 1, 2, 3, \dots$, equation (A.41) gives I simultaneous equations,

Figure A.2.

The calculation of the numerical solution was made for LDPE because of the availability of the necessary thermodynamic parameters. The specific heat C_p , specific volume v , and thermal conductivity k [EPSE (1986)] of LDPE applied in the calculation are given in Figures A.3, A.4, and A.5. Other necessary parameters used in the calculation were: $h_a = 20$ [W/(M² K)] [Coulson and Richardson (1977)], $k_g = 0.8$ [W/(M K)] [EPSE(1986)], and $k_a = 0.024$ [W/(MK)] at 0 °C. $T_0 = 150$ °C, $T_1 = 0$ °C, and $p = 0.9$. Sample thickness, $2b = 200$ μ m (sample thickness used in real experiments will be around 150 μ m) was used in the calculation. The cooling conditions were given by heat transfer coefficient h_a .

Figure 3.5 was obtained at heat transfer coefficient of air $h_a = 70$ [W/(M²•K)]. Figure 3.5 shows that the temperature distribution in the sample along the direction, x , perpendicular to the sample plane can be neglected. The temperature gradient mainly exists in the air boundary layer. Therefore, for sample thickness being less than 200 μ m and the cooling intensity, represented by h_a , less than 70 [W/(M²•K)], the sample will evenly be cooled according this calculation.

The temperatures as a function of time during cooling at center and surface of the sample, $x = 0$ and $x = 0.1$ mm, for $h_a = 70$ [W/(M²•K)] are given in Figure A.6. As shown in Figure A.6, the two cooling curves almost superimposed with each other. It also shows a plateau which indicates the occurrence of the crystallization. It took less than 5 sec for temperature to drop from 150 to 50 °C (average cooling rate is 1200 °C/min).

As an examination of the capability of the model to reflect large temperature distribution in the sample, the sample was supposed to be quenched in the ice-water. Figure 3.6 gives the result for such calculation (assuming $h = 500$ [W/(M²•K)]). Figure 3.6 shows that there is still a large temperature distribution in the boundary layer, but the

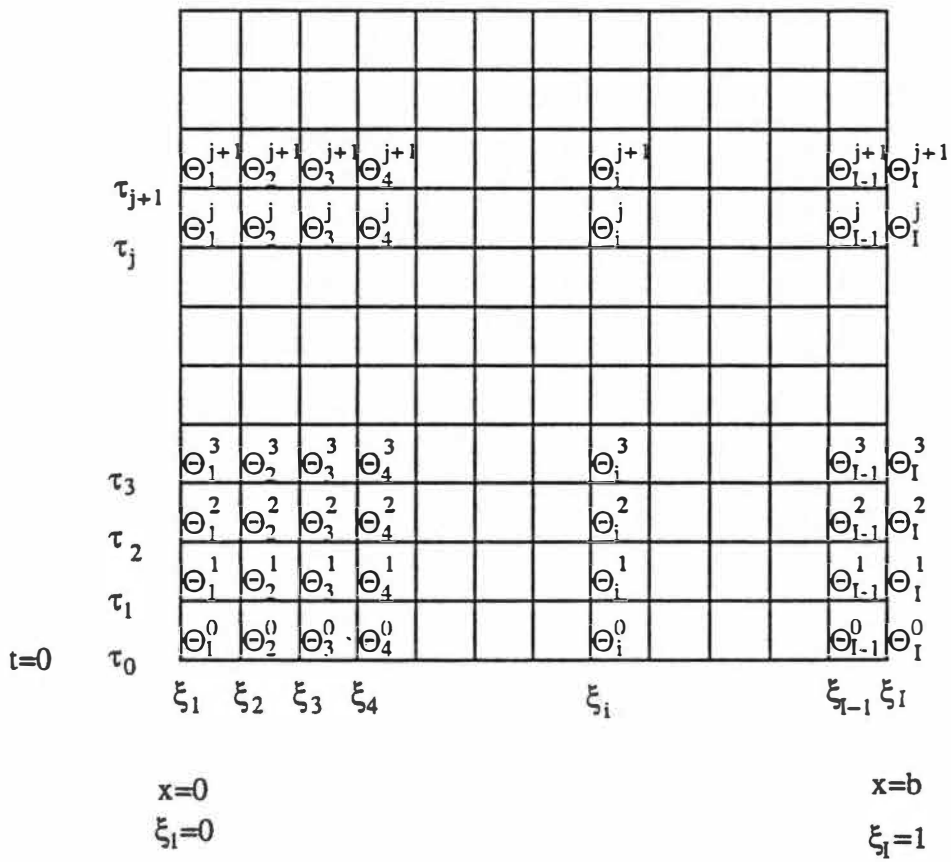


Figure A.2. Variables used in the numerical solution of non-isothermal heat transfer problem for a slab.

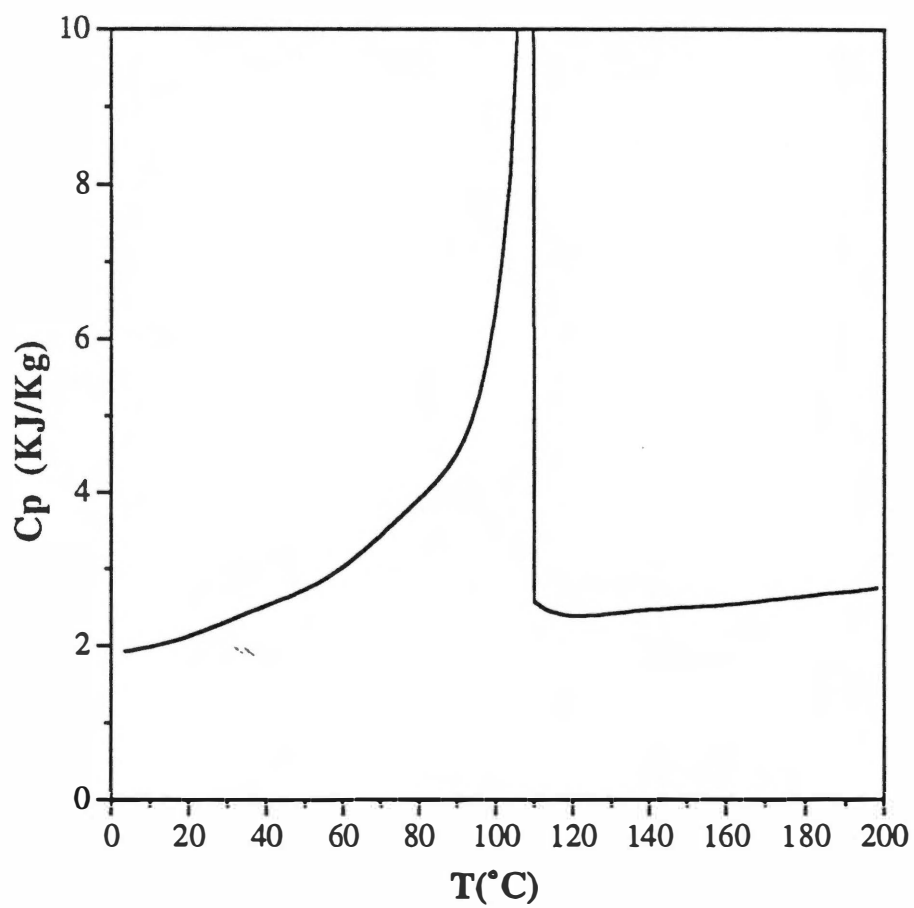


Figure A.3. Specific heat of LDPE (From [EPSE]).

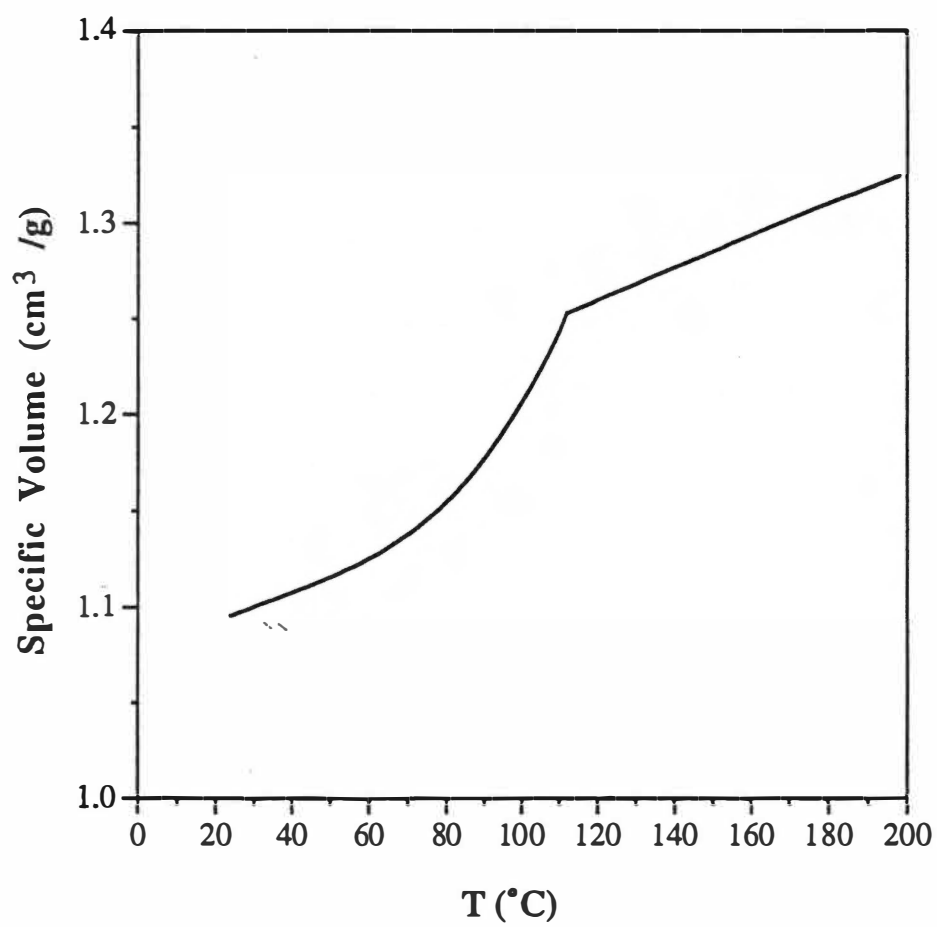


Figure A.4. Specific volume of LDPE.

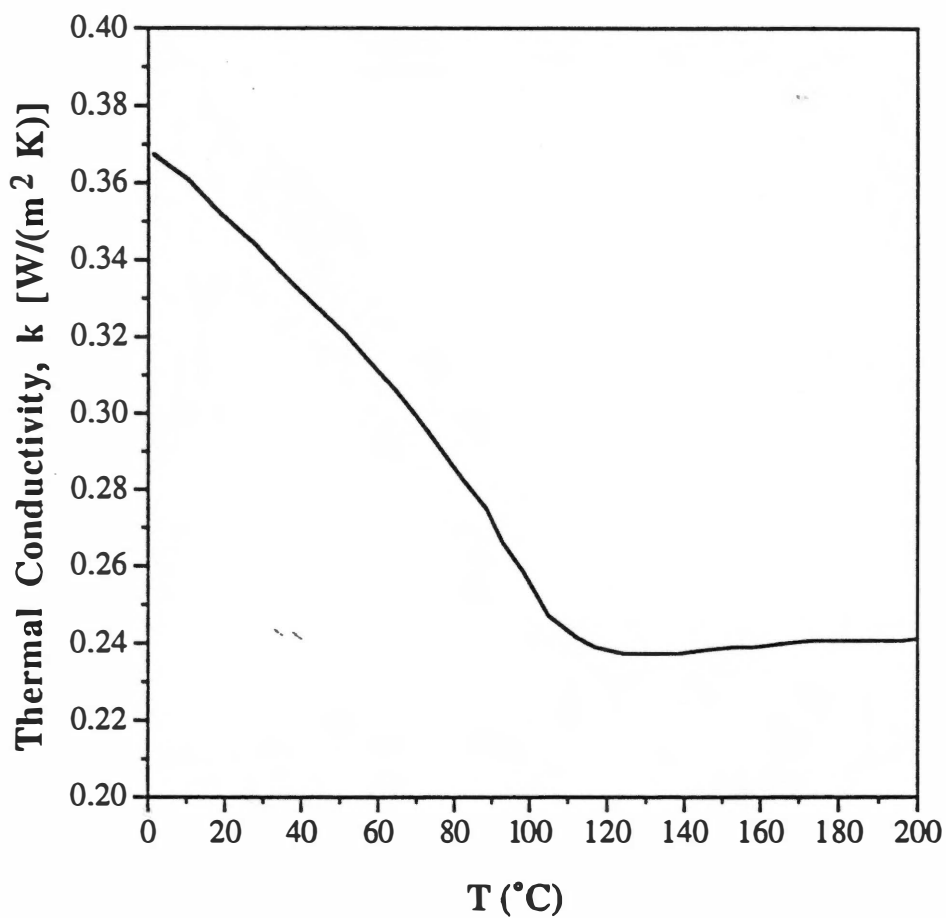


Figure A.5. Thermal conductivity of LDPE.

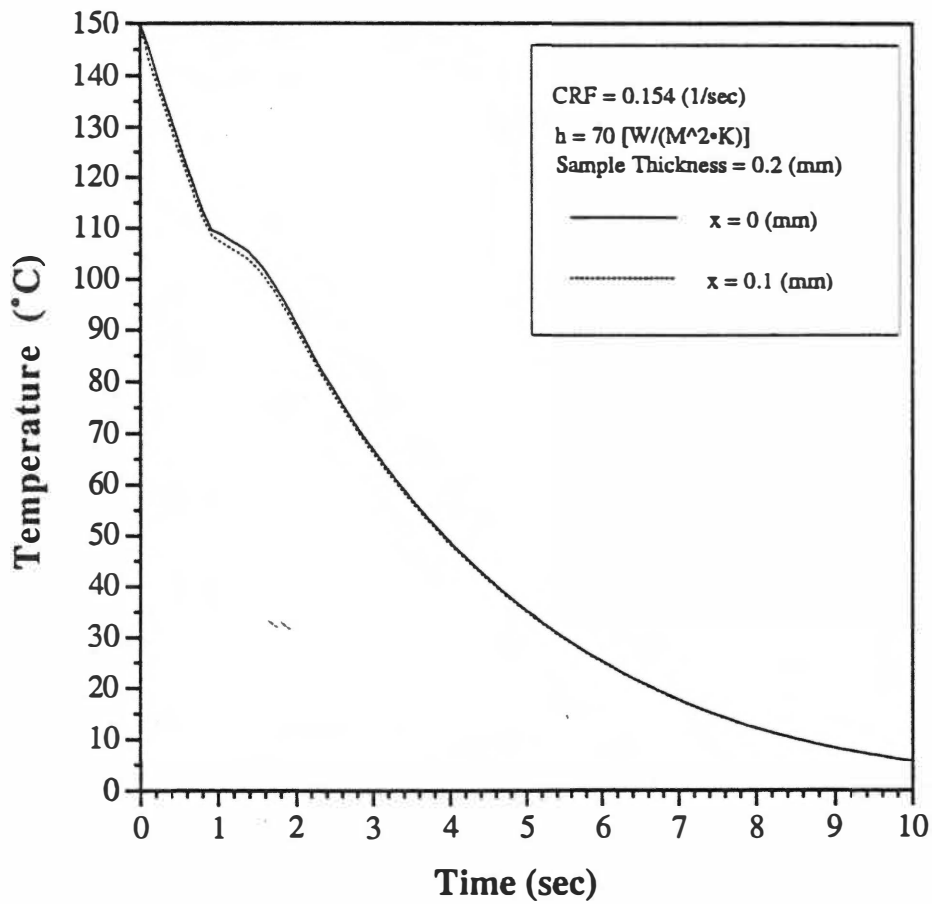


Figure A.6. Cooling curve for a sample cooled down in air.

temperature distributions in the sample at various time can not be neglected at this time. This result also tells us that the even-cooled situation is limited by cooling intensity (and sample thickness). The temperature distribution in sample can be neglected only under not extremely high cooling intensity. Figure A.7 gives the cooling curves at $x=0$ and $x=0.2$ mm for sample quenched in ice-water. As shown in Figure A.7, the temperature on the sample surface cooled down faster than that in the center of the sample in this case. The plateau in the curve for the sample surface is also lower than that in the center. This is because transferring of heat from sample center is resisted by the polymer, while on the polymer surface there is no such resistance and the heat is more quickly carried away by the cooling medium. The average cooling rate for this condition is about 16,000 °C/min.

Figure 3.7 gives the cooling cures at the sample center at various cooling condition. From Figure 3.7 we can see that though the plateaus change somewhat with change in cooling intensity, the crystallization onset positions are fixed. This is because the crystallization in the model is only determined heat capacity, shown in Figure A.3, no matter what a cooling rate is.

On the other hand, one is also able to calculate the Biot number, Bi , to determine if the temperature distribution in the sample is even. The Biot number is defined as,

$$Bi = h (V/A)/k = h (bA/A)/k = h b / k$$

where b is the half thickness of the sample. $h = H_{ga} = 1/(l_g/k_g + 1/h_{air}) = 1/(0.15 \times 10^{-3} / 0.8 + 1/70) = 69.093$ [W/m² K]. From Figure A.5 one can see that for LDPE there always exist $k > 0.24$ W/(mK). Therefore, the dimensionless Biot Number,

$$Bi = h b / k < 69.093 \times 0.1 \times 10^{-3} / 0.24 = 0.029 < 0.1$$

Since the Bi is less than 0.1, the temperature distribution in considered film with thickness = 0.2mm will be even according to the criterion of Biot number.

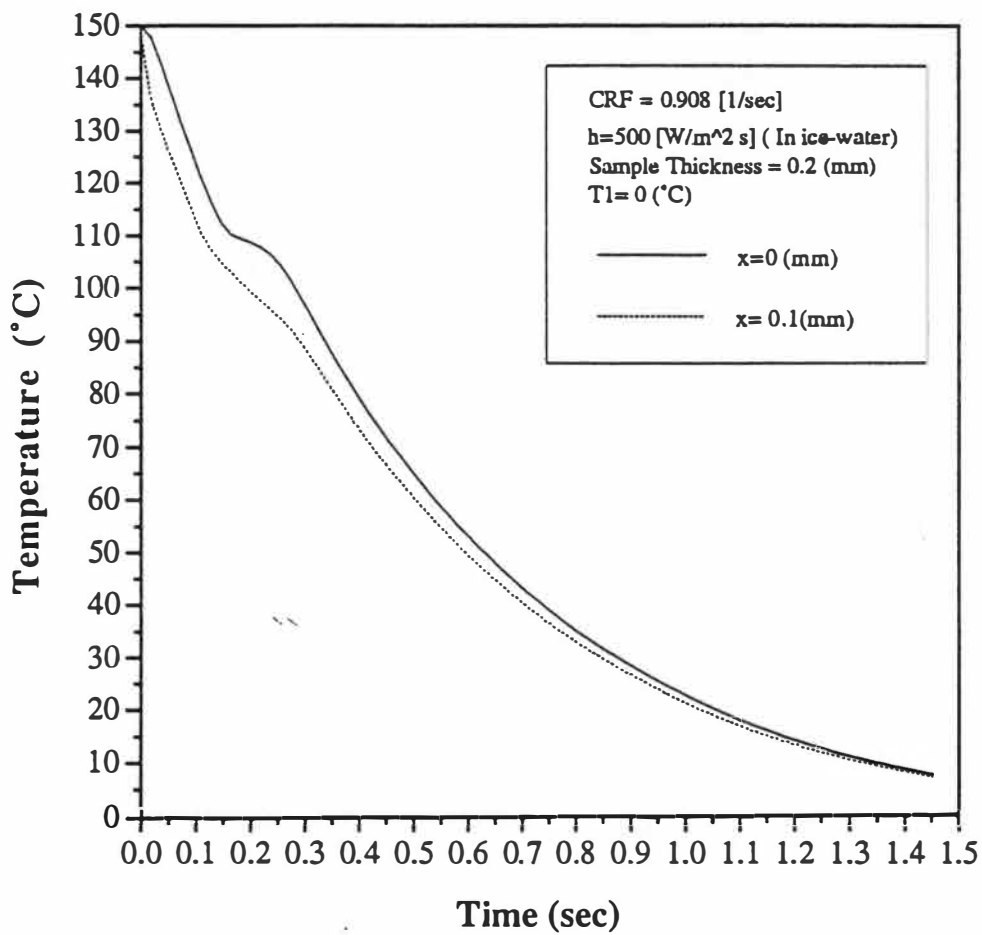


Figure A.7. Cooling curve for a sample quenched in ice-water.

Appendix B

ANALYSIS OF THE LIGHT INTENSITY AS A FUNCTION OF CRYSTALLINITY AND MOLECULAR ORIENTATION IN THE LIGHT DEPOLARIZING MICROSCOPY

B.1. Introduction

This appendix describes a theoretical base for the developed LDM technique. Because of the consideration of molecular orientation, which has not been experimentally verified, the theory was written as an appendix. The main reason to keep this appendix in the present dissertation is that equations which are important to the LDM technique are derived in this appendix which include equations (3.13) and (3.14) used in Chapter 3.

Crystallization under molecular orientation is recommended for future study by light depolarizing microscopy. A ribbon spinning technique might be a suitable method to introduce orientation in such a case.

B.2. Light Intensity From An Oriented Single Crystal

The light intensity transmitted through an oriented crystalline sample is produced by both crystalline and amorphous phases. The light intensity from the crystalline phase depends on crystal birefringence which is a material constant and the orientation of that crystal. This section develops equations to describe the transmitted light from a single crystal which is oriented arbitrarily in space. Oriented amorphous phases also depolarize light and contribute to the measured intensity. Since the amorphous phase is uniform in an optical sense, it may act as one part affecting light traveling. The light intensity produced by the amorphous phase depends on the orientation of the molecules in the amorphous phase. If there is no orientation in the amorphous phase, it will contribute nothing to the total light intensity measured. Since the amorphous part functions as one

part in depolarizing light, it is most possible that it affects the light intensity according to Stein's single crystal equation. This may cause problems to determine the crystallinity by LDM when the sample is oriented. It is helpful to check an oriented non-crystalline sample to see how the sample thickness affects the light intensity. The existence of the oriented amorphous phase introduces difficulties to distinguish the intensities from the amorphous or crystalline phase. One possible approach to this problem is to place the sample with its stretch direction parallel to the direction of the polarizer. Discussions of the relationship between light intensity, crystallinity and sample thickness will be based on crystalline phase.

Assumptions made for the derivation of light intensity equation are: (a) The basic polarizing or birefractive unit is a lamella. (b) The lamella is an uniaxial and optically positive crystal. (c) The molecular chain direction in the lamella is parallel to the optical axis (The optical axis is vertical to lamellar plane). This is motivated by type IV spherulites which have alternately arranged dark and yellow stripes. These stripes are caused by twisting of the lamellae around the a-axis. In the dark stripes, the birefringence is zero, while in the yellow ones, the birefringence reaches a maximum. This indicates that the depolarization is related to the lamellar orientation in space, so that the most basic depolarizing unit was chosen as lamella.

The light intensity equation is derived in a rectangular coordinate system "xyz", Figure B.1. In Figure B.1, the "xz" plane is the plane of the stage, OF, of the microscope, the z-axis is the drawing direction of film; OC, with an angle 45° to the z-axis and in the "xz" plane, is the direction of the polarizer, and the y-direction is the propagation direction of incident light. A lamella with its optical axis being OB is placed into the coordinate system. The angle between OB and z-axis is ϕ , which is the molecular orientation angle with respect to the z-axis. The OBA plane, which includes the optical

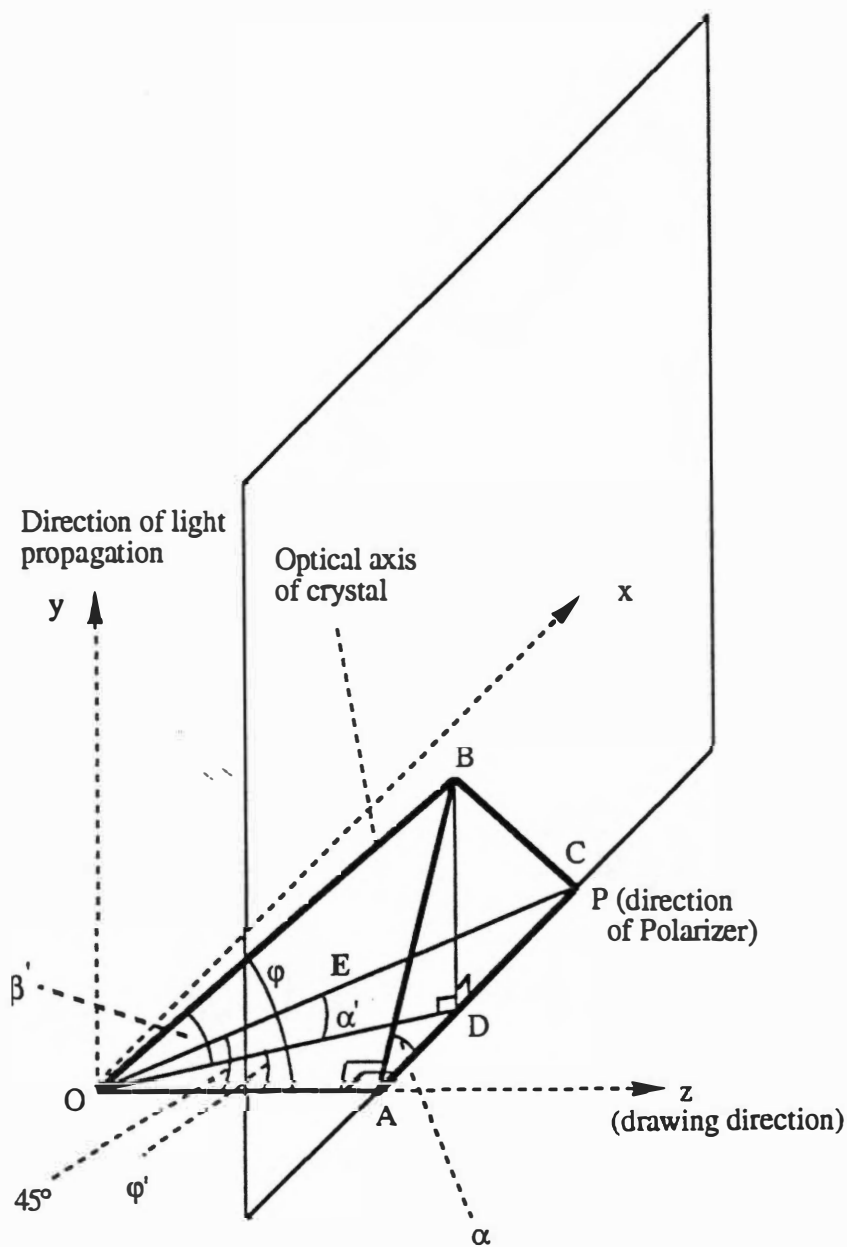


Figure B.1. Coordinate system adopted for the optical analysis of light depolarization by a single crystal. The stage plane of LDM is parallel to xy-plane.

axis, has an angle α to the xz -plane. By angle φ and α the direction of the optical axis is determined. From Figure B.2 and B.1 one can see that the angle between the optical axis and the xz -plane, β' , is equal to the one between incident light and refraction plane (the xz -plane) of the crystal.

B.2.1. Generalized Retardation Equation

Let n be the refractive index; c , the speed of light in vacuum; and v , the speed of light in a medium. These parameters are related by,

$$n = \frac{c}{v} \quad (\text{B.1})$$

The velocity of ordinary ray may be calculated by,

$$v_o = \frac{c}{n_o} \quad (\text{B.2})$$

where n_o is the refractive index of ordinary ray. Similarly, there exists an equation for the extraordinary ray:

$$v_e = \frac{c}{n_e} \quad (\text{B.2b})$$

The time spent by the ordinary ray while traveling through a crystal is:

$$t_o = d_o/v_o \quad (\text{B.3})$$

where d_o is the distance traveled by the ordinary light. By equation (B.1), equation (B.3) may be changed to,

$$t_o = d_o n_o / c \quad \text{or,} \quad c t_o = d_o n_o \quad (\text{B.4})$$

In the same way, there exists:

$$c t_e = d_e n_e \quad (\text{B.5})$$

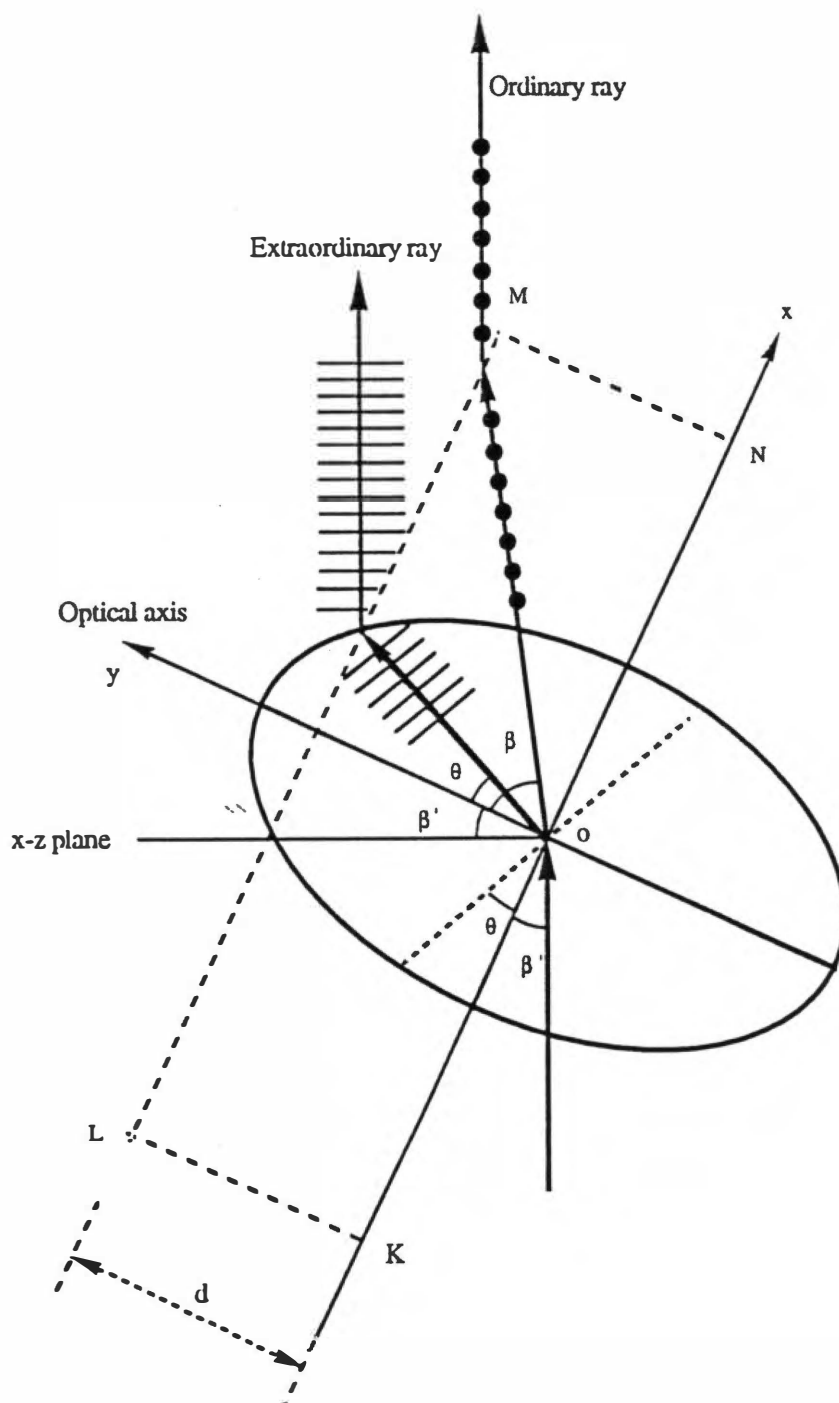


Figure B.2. A polarized light ray, thick with arrow is birefracted by a lamella, KLMN.

Therefore, the path difference between extraordinary and ordinary lights is,

$$\delta\lambda = ct_e - ct_o = d_e n_e - d_o n_o \quad (\text{B.6})$$

where δ is the frequency difference ($2\pi\delta$ is the phase difference) and λ is wave length.

Equation (B.6) can also be written as:

$$\delta = \frac{d_e n_e - d_o n_o}{\lambda} \quad (\text{B.7})$$

The distances which the extraordinary and ordinary ray go through the crystal, d_e and d_o , are related to the lamellar thickness, d , by $d_e = d/\cos(\theta)$, $d_o = d/\cos(\beta)$, see Figure B.2.

Therefore,

$$\delta = \frac{d}{\lambda} [n_e/\cos(\theta) - n_o/\cos(\beta)] \quad (\text{B.7b})$$

By equation (B.11b) and proper manipulating (Let $a=(1-(n_b/n_a)^2)$ and $x = \sin^2(\theta)$, and then $(1-ax)(1-x)=1-x-ax-ax^2 = 1-(1+a)x-ax^2$),

$$\delta = \frac{dn_b}{\lambda} \{ [1 + [2 + (n_b/n_a)^2] \sin^2(\theta) + [1 + (n_b/n_a)^2] \sin^4(\theta)]^{-1/2} - 1/\cos(\beta) \}$$

By equation (B.30) which will be derived below,

$$\begin{aligned} \delta = \frac{dn_b}{\lambda} \{ & [1 + \frac{[2 + (n_b/n_a)^2]}{(n_a/n_b)^2 \{ \frac{n_a^2}{[\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi)]} - 1 \} + 1} + \\ & + \frac{[1 + (n_b/n_a)^2]}{(n_a/n_b)^2 \{ \frac{n_a^2}{[\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi)]} - 1 \} + 1}]^{-1/2} - 1/\cos(\beta) \} \end{aligned}$$

By equation (B.13b) which will be derived below,

$$\delta = \frac{dn_b}{\lambda} \left\{ \left[1 + \frac{[2+(n_b/n_a)^2]}{n_a^2} + \frac{(n_a/n_b)^2 \left\{ \frac{n_a^2}{[\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi)]} - 1 \right\} + 1}{[1+(n_b/n_a)^2]} \right]^{-1/2} + \frac{[1+(n_b/n_a)^2]}{[(n_a/n_b)^2 \left\{ \frac{n_a^2}{[\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi)]} - 1 \right\} + 1]^2} - \frac{1}{[1-(\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi))/n_b^2]^{1/2}} \right\} \quad (B.8)$$

where λ is wave length in the crystal, d is lamellar thickness, n_a refractive index in the direction of the optical axis of the lamella, and n_b is the refractive index perpendicular to the direction of the optical axis of the lamella.

B.2.2. Refraction Index On The Equivalent Optical Axis

The incident light is separated into ordinary and extraordinary rays on a separation plane. This plane needs to be determined first. A concept should be remembered that the oscillating direction of an electrical field of light is perpendicular to the direction of light propagating. Another concept is that the oscillating directions of the two rays, ordinary and extraordinary, are perpendicular to each other. Therefore, at the separating point, where the incident light is separated into two rays, the two electrical field vectors should be in the same plane. This plane will cut the indicatrix and form an ellipse on which the extraordinary ray oscillates along the long axis and the ordinary along the short axis. Figure B.3 shows such a possible cut, FG, on an indicatrix. Figure B.4 displays the cut-section in the C-C direction. In Figure B.4 the amplitude of incident light, E_i , is separated

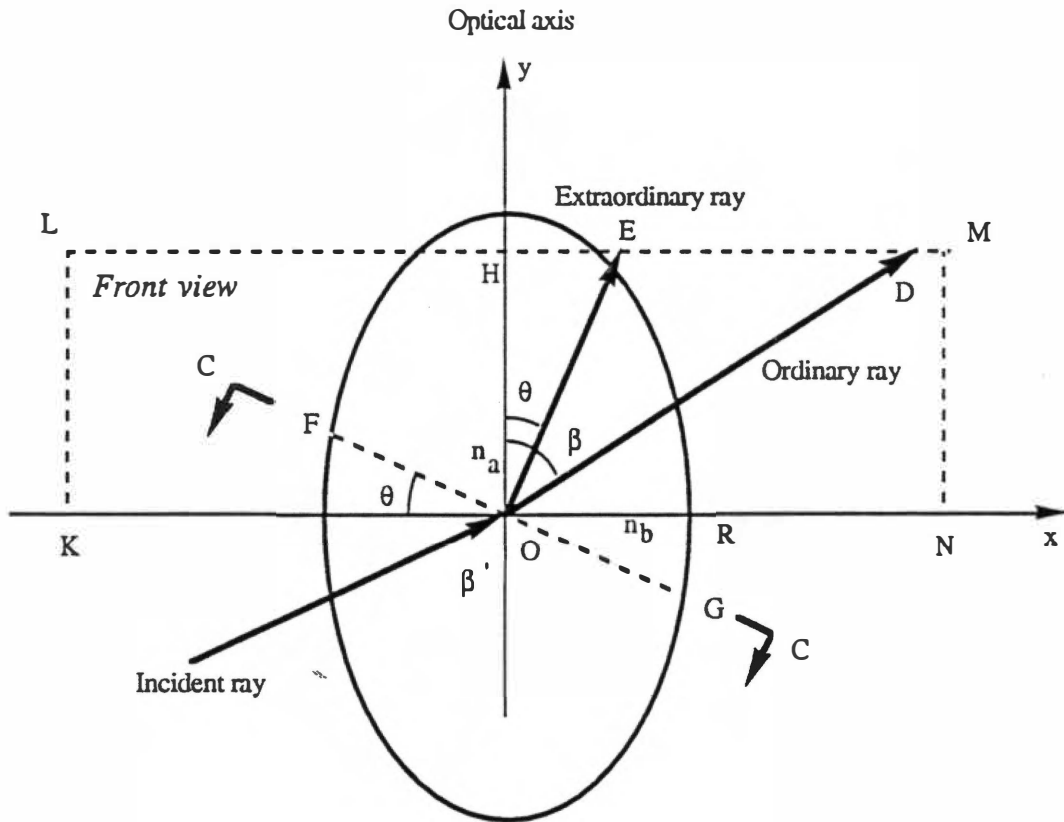


Figure B.3. Separating of incident ray into ordinary and extraordinary rays by a lamella KLMN.

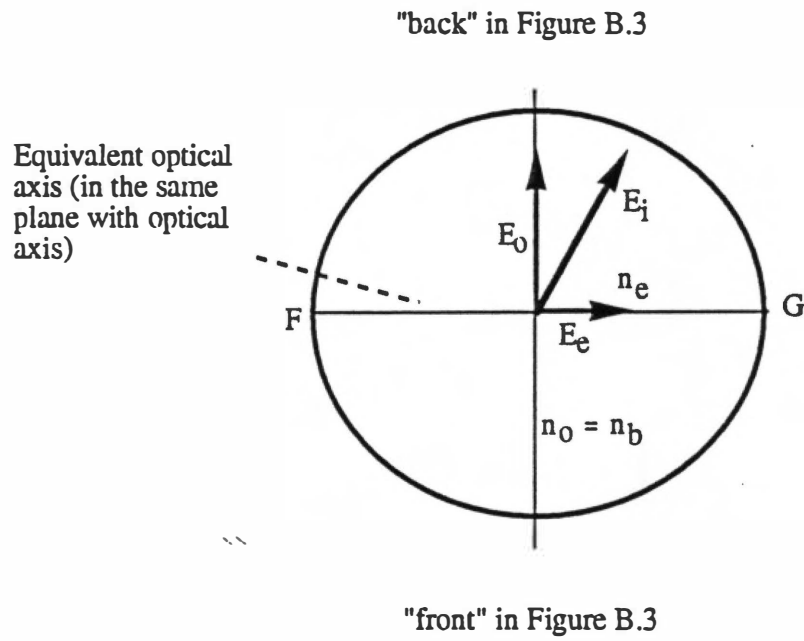


Figure B.4. C - C section view of Figure B.3.

into the one of ordinary ray, E_o , and the one of extraordinary ray, E_e . The propagation directions of ordinary and extraordinary rays are OD and OE in Figure B.3. The location of C-C section can be determined one Figure B.5. in which the directions of propagation and electrical field were shown together. In Figure B.5, FGG'F' plane is the one that C-C section stays. The electrical field vector of extraordinary light is also in this plane. Hence this plane is vertical to the propagation direction of the extraordinary ray, OE. Since the FGG'F' plane includes the z-axis, the short axis of the ellipsoid is also in this plane. The electrical field vector of the ordinary ray is also in that plane because it oscillates along this short axis. Therefore the two electrical field vectors should be vertical to each other. Figure B.6 gives an enlarged picture for the these relations. From these relations one can see that the location of C-C cross section is determined by the propagating direction of extraordinary light.

The propagation direction of the extraordinary ray is determined according to Savelyev (1980). His method is basically the application of Huygens principle. Since the ordinary light observes the reflection law, its direction can be determined first. The wavelet of the ordinary ray with respect to point O at certain time is a circle, Figure B.7, the propagation direction OD will cross the circle at C. Draw a tangent line CF at point C on the circle. Line CF crosses the reflect plane, line KN in Figure B.7, at point F. At the same time, the wave front of extraordinary wavelet from point O, reaches the position shown in Figure B.7 and it is an ellipse. The location of this ellipse can be determined as follows. The oscillation direction of the wave traveling along y-direction is vertical to y-axis. From Figure B.3 one can see that the refractive index in this direction is equal to the one of ordinary ray. Therefore, the wave speed of the extraordinary ray along y-axis is equal to the ordinary ray. Whereas, the oscillation direction of the extraordinary ray which travels along x-direction is in y-axis. The refractive index reaches maximum in y-

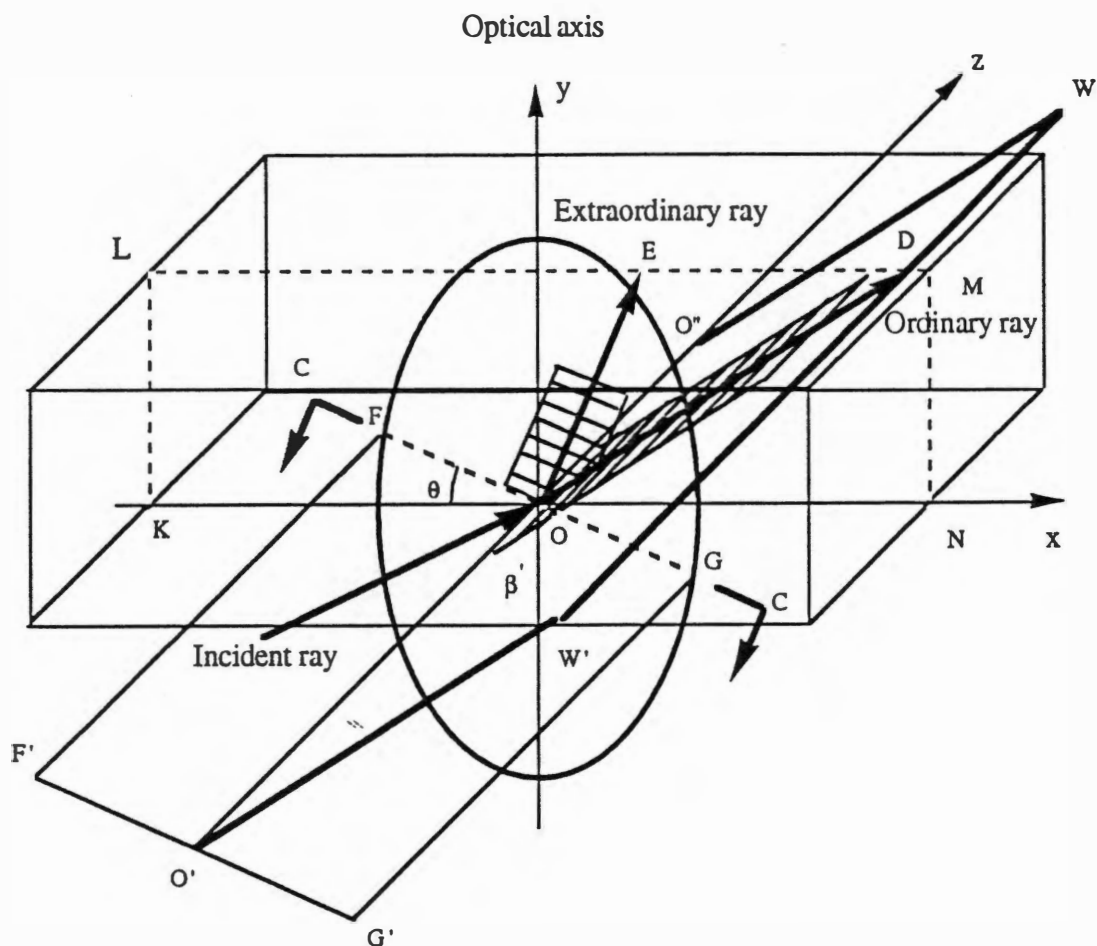


Figure B.5. A incident ray (polarized) in $F'G'FG$ plane is birefracted by a lamella (KLMN is a plane in the lamella). The ordinary ray is vibrating in $O'O''W'W''$ plane and the extraordinary ray is vibrating in KLMN plane.

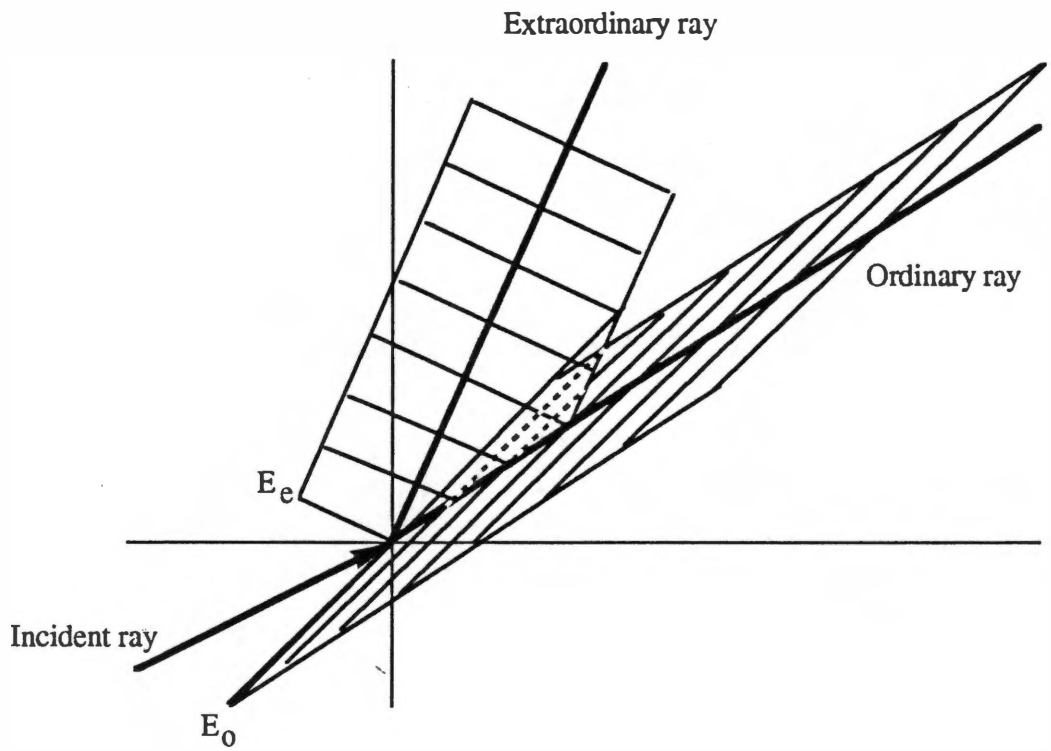


Figure B.6. Relations between the directions of electrical field vectors and propagation of the extraordinary and ordinary rays.

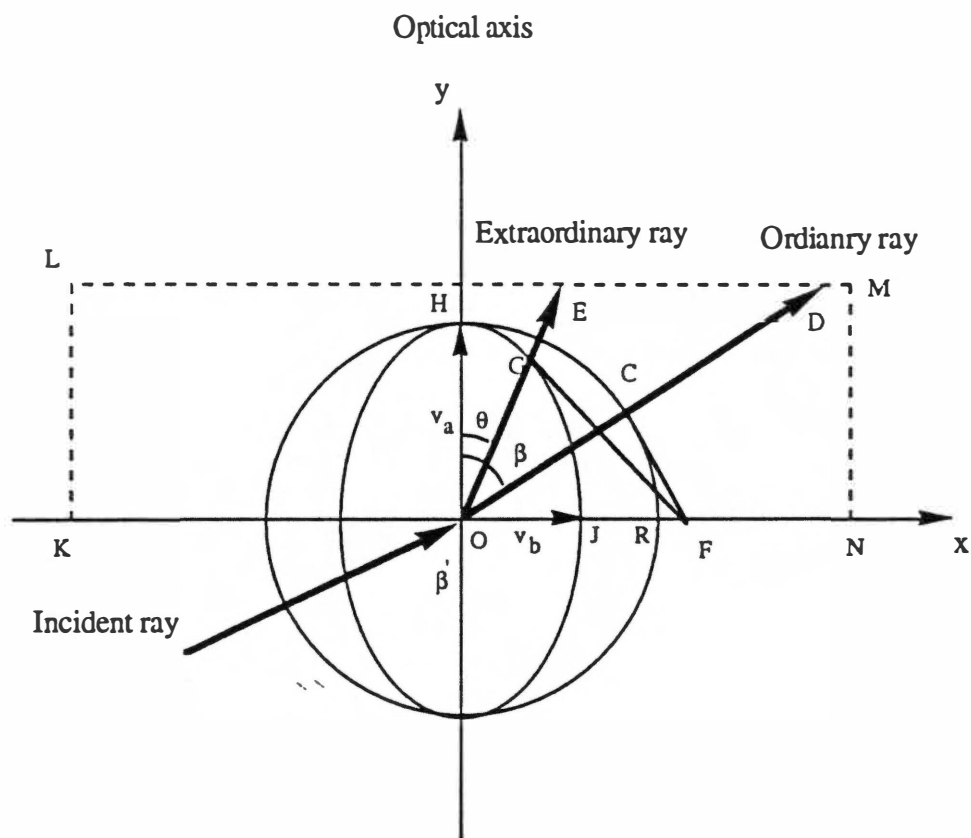


Figure B.7. Determine the direction of extraordinary ray by Huygens principle.

axis for the positive crystal, so that the wave velocity along the x-direction is slower than that of the ordinary ray. To determine the traveling direction of the extraordinary light, one needs to draw a tangent line, FG (Figure B.7), of the ellipse and let it go through point F. The tangent point is G. Now, the angle θ which is between OG and y-axis gives the propagating direction of the extraordinary light. Figure B.8 relates Figure B.7 to three dimension space and it helps to understand these complicated relations. The mathematical analysis for the above descriptions is given in B.3 for ordinary ray and B.4 for extraordinary ray.

The concept of “equivalent optical axis” is introduced here for the convenience of discussion. The equivalent optical axis is referred to the long axis of the ellipse which is the cross section obtained by any plane cutting the indicatrix at an arbitrary angle to the optical axis. Line FG in cross section C-C, Figure B.3, is such an example.

From Figure B.3 and B.2 the following relations may be obtained,

$$\begin{cases} y = \tan(\theta)x \\ (x/n_b)^2 + (y/n_a)^2 = 1 \end{cases} \quad (\text{B.9})$$

where θ is the angle between the extraordinary ray and the optical axis. Solve equation (B.9) for x^2 and y^2 ,

$$x^2 = \frac{1}{[(1/n_b)^2 + (\tan(\theta)/n_a)^2]}, \quad y^2 = \tan^2(\theta) \frac{1}{[(1/n_b)^2 + (\tan(\theta)/n_a)^2]}$$

Therefore, the equation to calculate the refractive index on the equivalent optical axis is,

$$n_e^2 = x^2 + y^2 = \frac{(n_b)^2}{1 - \sin^2(\theta)(1 - (n_b)^2/(n_a)^2)} \quad (\text{B.10})$$

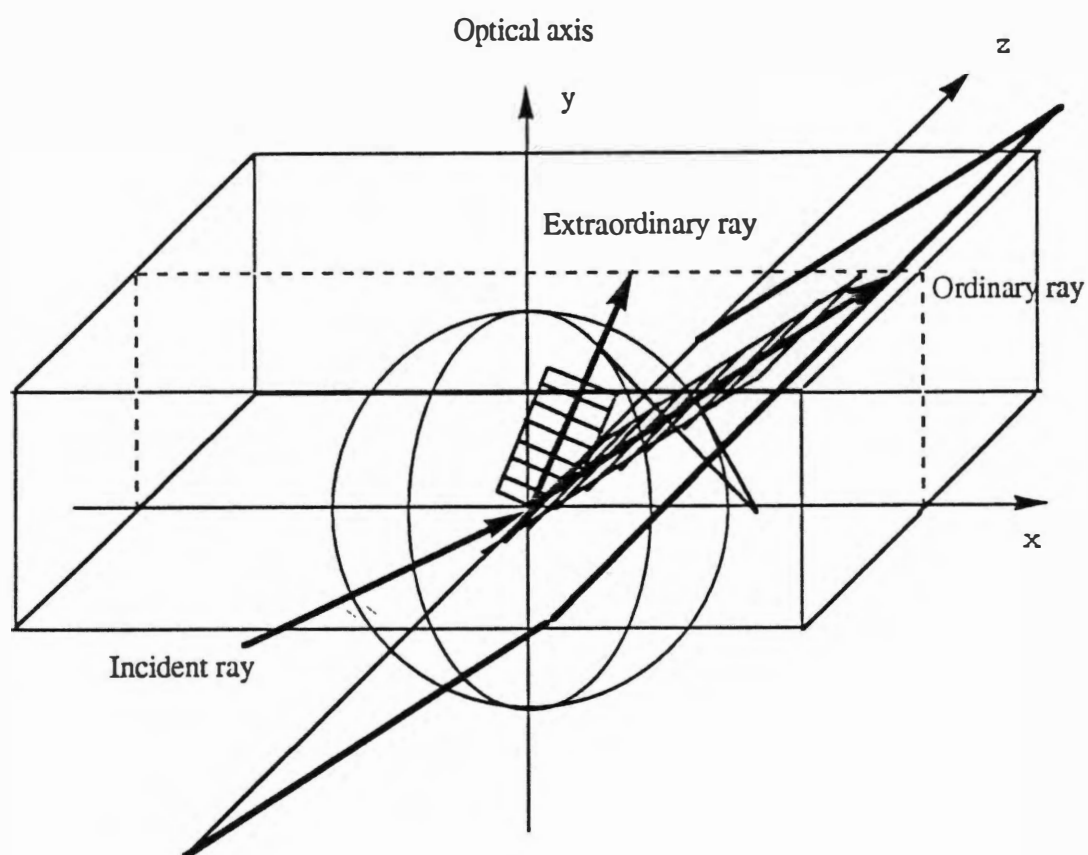


Figure B.8. Relations between directions of lamellar optical axis, vibration of electrical field of extraordinary and ordinary, and the propagation direction of incident, extraordinary and ordinary rays.

or,

$$n_e = \left[\frac{n_b^2}{1 - \sin^2(\theta)(1 - (n_b/n_a)^2)} \right]^{1/2} \quad (\text{B.11})$$

B.2.3. The Propagation Direction Of Ordinary Ray

The propagating direction of the ordinary ray is determined by the refraction law, see Figure B.2,

$$\frac{\sin(\pi/2 - \beta')}{\sin(\beta)} = \frac{\cos(\beta')}{\sin(\beta)} = n_o = n_b$$

This gives,

$$\sin(\beta) = \cos(\beta')/n_b \quad (\text{B.12})$$

or,

$$\sin^2(\beta) = \cos^2(\beta')/n_b^2$$

(B.12b)

or,

$$\cos^2(\beta) = 1 - \cos^2(\beta')/n_b^2$$

By equation (B.33b),

$$\cos^2(\beta) = 1 - [\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi)]/n_b^2 \quad (\text{B.13})$$

or,

$$1/\cos(\beta) = \frac{1}{[1 - (\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi))/n_b^2]^{1/2}} \quad (\text{B.13b})$$

or,

$$\sin^2(\beta) = [\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi)]/n_b^2 \quad (\text{B.13c})$$

B.2.4. Propagation Direction Of Extraordinary Ray

The wave surface of extraordinary ray can be described by an equation of an ellipse, see Figure B.6,

$$(x/b)^2 + (y/a)^2 = 1 \quad (\text{B.14})$$

where

$$a = v_a = v_h = \frac{c}{n_b} \quad (\text{B.15})$$

$$b = v_b = v_v = \frac{c}{n_a} \quad (\text{B.16})$$

Substitute equation (B.15) and (B.16) into (B.14), one has,

$$\left(\frac{x}{c/n_a}\right)^2 + \left(\frac{y}{c/n_b}\right)^2 = 1 \quad (\text{B.17})$$

For ordinary ray, the wave surface is a circle, see also Figure B.7,

$$(x/v_a)^2 + (y/v_a)^2 = 1$$

or,

$$x^2 + y^2 = v_a^2 \quad (\text{B.18})$$

The coordinates for point C in Figure B.7 are found as $y = \tan(90^\circ - \beta)x = \cotan(\beta)x$.

Substitute it into equation (B.17) and solve for x and y,

$$x = v_a \sin(\beta) \quad (\text{B.19})$$

$$y = \cotan(\beta)x = \cotan(\beta) v_a \sin(\beta) = v_a \cos(\beta) \quad (\text{B.20})$$

Finally, the coordinates for point C are,

$$\begin{cases} x = v_a \sin(\beta) \\ y = v_a \cos(\beta) \end{cases} \quad (\text{B.21})$$

Therefore, the equation for line CF is,

$$\sin(\beta)x + \cos(\beta)y = v_a \quad (\text{B.22})$$

Solve for y,

$$y = -\tan(\beta)x + v_a/\cos(\beta) \quad (\text{B.23})$$

The coordinate of point F is:

$$\begin{cases} x = v_a/\sin(\beta) \\ y = 0 \end{cases} \quad (\text{B.24})$$

Substitute $y = 0$ into equation (B.24) and x can be obtained,

$$x = v_a/[\cos(\beta)\tan(\beta)] = v_a/\sin(\beta) \quad (\text{B.25})$$

Thus, the FG equation can be obtained as follows. Assuming the coordinate of G is (x_1, y_1) , then, the FG equation will be,

$$\frac{x_1^2}{(c/n_a)^2} + \frac{y_1^2}{(c/n_b)^2} = 1 \quad (\text{B.26})$$

Point F is on this line. Therefore,

$$x_1 = (c/n_a)^2 \sin(\beta)/v_a \quad (\text{B.27})$$

Point G is also on the ellipse, $\left(\frac{x}{c/n_a}\right)^2 + \left(\frac{y}{c/n_b}\right)^2 = 1$. Substitute equation (B.26) into it and y_1

is obtained,

$$y_1 = (c/n_b) \{ 1 - [(c/n_a) \sin(\beta)/v_a]^2 \}^{1/2} \quad (\text{B.28})$$

According to point G, the slope of line OE is,

$$\tan(90^\circ - \theta) = \cot(\theta) = y_1/x_1 = \left((n_a/n_b)^2 \{ 1/\sin^2(\beta) - (n_b/n_a)^2 \}^{1/2} \right)$$

This leads to,

$$\sin^2(\theta) = \frac{1}{(n_a/n_b)^2 \left\{ \frac{(n_a/n_b)^2}{\sin^2(\beta)} - 1 \right\} + 1} \quad (\text{B.29})$$

Substitute equation (B.13c) into it,

$$\sin^2(\theta) = \frac{1}{(n_a/n_b)^2 \left\{ \frac{n_a^2}{[\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi)]} - 1 \right\} + 1} \quad (\text{B.30})$$

This gives,

$$1/\cos(\theta) = \left\{ 1 - \frac{1}{(n_a/n_b)^2 \left\{ \frac{n_a^2}{[\cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi)]} - 1 \right\} + 1} \right\}^{-1/2} \quad (\text{B.30b})$$

B.2.5. Some Relations

According to Figure B.1, we have the following relations,

$$\begin{cases} \cos(\beta') = DO/BO \\ \cos(\varphi') = AO/DO \\ \cos(\varphi) = AO/BO \end{cases}$$

Therefore,

$$\cos(\varphi')\cos(\beta') = \cos(\varphi) \quad (\text{B.31})$$

There also exist,

$$\begin{cases} \sin(\beta') = BD/BO \\ \sin(\alpha) = BD/AB \\ \sin(\varphi) = AB/BO \end{cases}$$

These lead to,

$$\sin(\alpha)\sin(\varphi) = \sin(\beta') \quad (\text{B.32})$$

or,

$$\sin^2(\beta') = \sin^2(\alpha)(1 - \cos^2(\varphi)) \quad (\text{B.33})$$

or,

$$\cos^2(\beta') = \cos^2(\alpha) + \sin^2(\alpha)\cos^2(\varphi) \quad (\text{B.33b})$$

From equation (B.31) and (B.32), $\cos(\varphi')^2$ can be solved as,

$$\cos(\varphi')^2 = \frac{\cos(\varphi)^2}{\cos(\beta')^2}$$

Substitute equation (B.33b) into it, one obtains,

$$\cos(\varphi')^2 = \frac{1}{\frac{\cos^2(\alpha)}{\cos^2(\varphi)} + \sin^2(\alpha)} \quad (\text{B.34})$$

B.2.6. Generalized Light Transmission Equation

α' in Figure B.1 is used to separate ordinary and extraordinary light rays. Though after refraction the propagating directions of the two light rays are changed, the separation of the two light rays is still according to α' . This can be illustrated as: if the incident light is separated into rays parallel to equivalent optical axis (which will be discussed later) and vertical to that axis before it goes into the crystal, the oscillating directions of the two rays will not be changed after the incident beam. Therefore, $\alpha' = \frac{\pi}{4} - \varphi'$ can be used to separate the two rays. Figure B.9 and B.8 illustrates such separation.

From Figure B.9, The amplitudes of extraordinary and ordinary rays, E_e and E_o , are separated from the one of incident light ray, E_i , as,

$$E_e = E_i \cos(\pi/4 - \varphi') \quad (\text{B.35})$$

$$E_o = E_i \sin(\pi/4 - \varphi') \quad (\text{B.36})$$

From Figure B.10 the amplitudes of the electrical field of extraordinary and ordinary rays in polarizer and analyzer directions, E_{ep} , E_{ea} , E_{op} and E_{oa} are,

$$E_{ep} = E_e \cos(\pi/4 - \varphi') = E_i \cos(\pi/4 - \varphi') \cos(\pi/4 - \varphi') \quad (\text{B.37})$$

$$E_{ea} = E_e \sin(\pi/4 - \varphi') = \frac{E_i}{2} \sin(\pi/2 - 2\varphi') \quad (\text{B.38})$$

$$E_{op} = E_o \sin(\pi/4 - \varphi') = E_i \sin(\pi/4 - \varphi') \sin(\pi/4 - \varphi') \quad (\text{B.39})$$

$$E_{oa} = E_o \cos(\pi/4 - \varphi') = \frac{E_i}{2} \sin(\pi/2 - 2\varphi') \quad (\text{B.40})$$

The amplitude of the electric field which can pass through the analyzer, E_a , is,

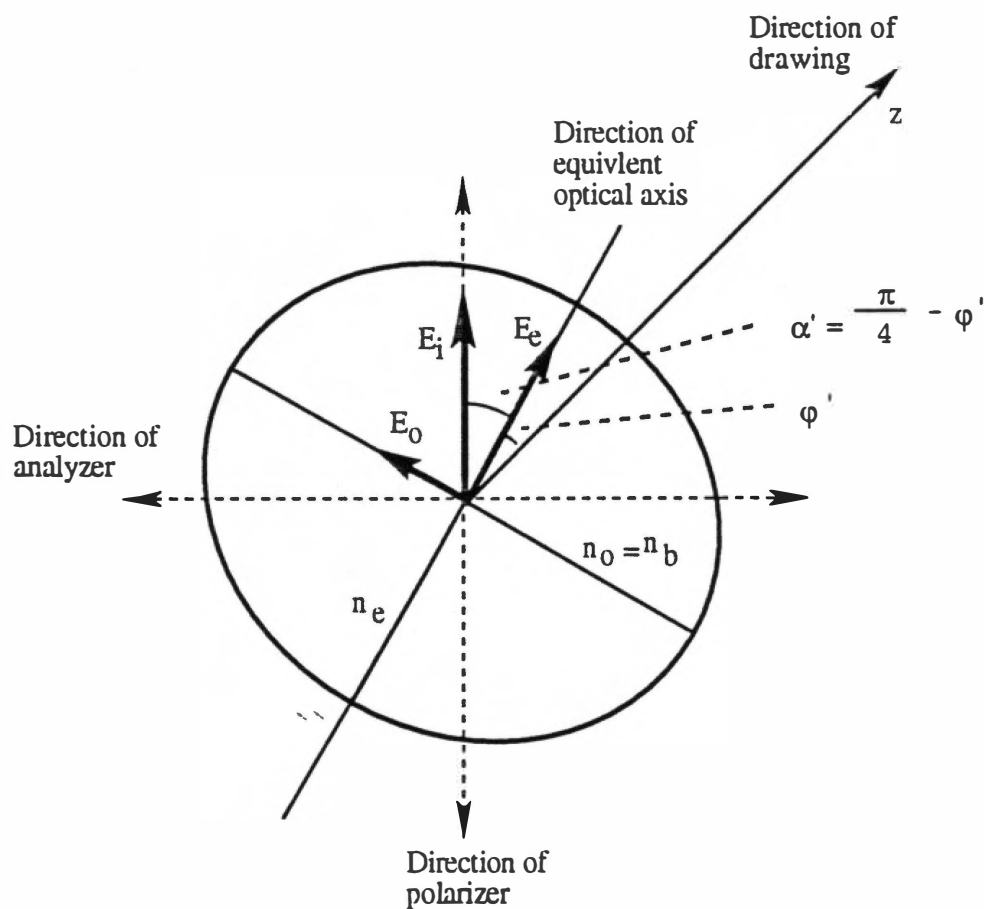


Figure B.9. Separating the amplitude of electrical field of incident ray into the ones of extraordinary and ordinary rays.

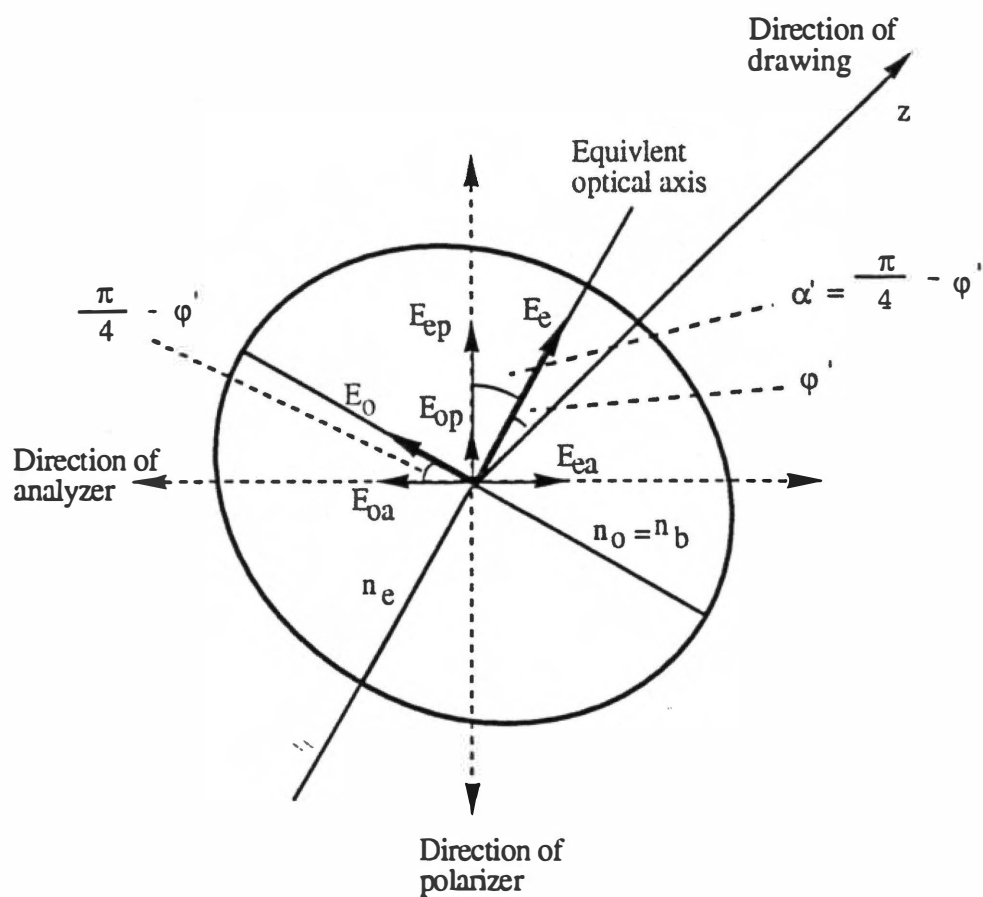


Figure B.10. The amplitudes of electrical field of extraordinary and ordinary rays are separated into components on the directions of polarizer and analyzer.

$$E_a^2 = E_{ea}^2 + E_{oa}^2 + 2E_{ea}E_{oa}\cos(2\pi\delta + \pi) = E_i^2 \cos^2(2\varphi')\sin^2(\pi\delta) \quad (\text{B.41})$$

The transmitted light intensity, I , is,

$$I = I_0 (2\cos^2(\varphi') - 1)^2 \sin^2(\pi\delta)$$

where I_0 is the intensity of incident light. Finally, by using equation (B.34),

$$I = I_0 \left[\frac{2}{\frac{\cos^2(\alpha)}{\cos^2(\varphi)} + \sin^2(\alpha)} - 1 \right]^2 \sin^2(\pi\delta) \quad (\text{B.42})$$

where I is the transmitted light intensity, I_0 is the incident light intensity on the sample, and δ is the frequency difference ($2\pi\delta$ is phase difference) between the extraordinary and ordinary rays and is given by equation (B.8).

When $\alpha = 0$, that is, the optical axis is in x - z plane, the equation changes to,

$$I = I_0 [2\cos^2(\varphi) - 1]^2 \sin^2(\pi\delta)$$

If $\varphi = 0$, i.e. the optical axis is parallel to the draw direction, the equation changes to,

$$I = I_0 \sin^2(\pi\delta)$$

This is the single crystal equation obtained by Stein. This equation can only apply to a single crystal (or lamella) with its optical axis parallel to z -axis in Figure B.1. Whereas equation (B.42) describes a lamella with its optical axis oriented in any direction in space (described by φ and α).

B.3. Light Intensity Equation For A Crystalline Sample

The transmitted light intensity through a lamella (or single crystal) which is oriented in space with angle (α, φ) and is placed between cross polars is given by

equations (B.42) and (B.8). The measured light intensity is a function of crystallinity and orientation in a sample. Equations (B.42) and (B.8), which are for a single crystal, is already rather complicated. Construction of an equation for the light intensity from a polycrystalline sample is much more difficult. To derive such an equation, further assumptions must be made: (1) The interference between rays produced by different lamellae can be neglected. (2) The projection of lamella, which orients in the space, to the plane perpendicular to the incident light beam is equal to the product of the area of lamellar fold surface and the cosine of angle between that surface and a plane vertical to the light beam. (4) The polarized light intensity from individual crystals are independent of each other. There are two problems for light beam to pass through a crystalline sample (film). The first is that it is possible for the polarized rays to go through other crystals down stream. Second is that crystals near the upper surface of the sample may receive light intensity less than I_0 . Both problems are more apparent when the crystallization is nearly finished. Experiments have shown us that more than 90% of the transmitted light intensity measured without analyzer, I_0' , is not affected by the crystal (that is the oscillation direction is intact and still parallel to the polarizer direction.) after the light transmits a sample with thickness of 150 μm . This includes light scattering effect, which is not a small part, to the reduction of I_0 . This tells us that even the crystals near top surface of the sample can receive incident light intensity about the same as the remaining crystals. Therefore, The incident light intensity may be considered constant throughout the sample. Similarly, the depolarized light from the crystal near lower surface of the sample will not be depolarized more than the one near the upper surface (That is to say, they are almost not influenced by other crystals; at most, they might be further depolarized by 10%). Further work needs to be done to distinguish the scattering and polarizing effect on the I_0 in order to obtain more direct evidence for this assumption.

The illuminance (referring to depolarized component which is vibrating in the direction of analyzer) which is contributed by the i th crystal to the total illuminance of sample (under the field of the microscope) is equal to $I_i A_i$, where I_i is the light intensity produced by i th crystal and, A_i is the projection area of i th crystal on a plane perpendicular to the light beam. The total illuminance of the sample is equal to $I A_{\text{micro}}$ which is a summation of the illuminance produced by all crystals,

$$I A_{\text{micro}} = \sum I_i A_i \quad (\text{B.43})$$

where I is the measured light intensity, A_{micro} is the area in the field of the microscope, and I_i is given by equation (B.42). I in equation (B.42) is written as I_i , since I will represent the total or measured light intensity. The equation (B.42) can then be written as:

$$I_i = I_0 \left[\frac{2}{\frac{\cos^2(\alpha_i)}{\cos^2(\varphi_i)} + \sin^2(\alpha_i)} - 1 \right]^2 \sin^2(\pi \delta_i) \quad (\text{B.44})$$

For convenience to derivation, let,

$$f[\cos^2(\alpha_i), \cos^2(\varphi_i)] = \left[\frac{2}{\frac{\cos^2(\alpha_i)}{\cos^2(\varphi_i)} + \sin^2(\alpha_i)} - 1 \right]^2 \quad (\text{B.45})$$

Then, one has,

$$I_i = I_0 f[\cos^2(\alpha_i), \cos^2(\varphi_i)] \sin^2(\pi \delta_i) \quad (\text{B.46})$$

Since lamella is very thin, one can approximately take:

$$\sin^2(\pi \delta_i) \approx \pi \delta_i \quad (\text{B.47})$$

Therefore, equation (B.46) changes to,

$$I_i \approx I_0 f[\cos^2(\alpha_i), \cos^2(\varphi_i)] \pi \delta_i \quad (\text{B.48})$$

Let ,

$$f''[\cos^2(\alpha_i), \cos^2(\varphi_i)] = \frac{n_b}{\lambda} \left\{ \left[1 + \frac{[2 + (n_b/n_a)^2]}{n_a^2} \frac{(n_a/n_b)^2 \left\{ \frac{n_a^2}{[\cos^2(\alpha_i) + \sin^2(\alpha_i) \cos^2(\varphi_i)]} - 1 \right\} + 1}{[2 + (n_b/n_a)^2]} \right]^{-1/2} \right. \\ \left. + \frac{[1 + (n_b/n_a)^2]}{[(n_a/n_b)^2 \left\{ \frac{n_a^2}{[\cos^2(\alpha_i) + \sin^2(\alpha_i) \cos^2(\varphi_i)]} - 1 \right\} + 1]^2} \right. \\ \left. - \frac{1}{[1 - (\cos^2(\alpha_i) + \sin^2(\alpha_i) \cos^2(\varphi_i))/n_b^2]^{1/2}} \right\} \quad (\text{B.49})$$

then, equation (B.8) can be written as,

$$\delta_i = d f''[\cos^2(\alpha_i), \cos^2(\varphi_i)] \quad (\text{B.50})$$

Let,

$$f[\cos^2(\alpha_i), \cos^2(\varphi_i)] = \pi^2 f'[\cos^2(\alpha_i), \cos^2(\varphi_i)] f''^2[\cos^2(\alpha_i), \cos^2(\varphi_i)] \quad (\text{B.51})$$

Using equation (B.50) and (B.51), equation (B.48) can be written as,

$$I_i = I_0 f[\cos^2(\alpha_i), \cos^2(\varphi_i)] d_i^2 \quad (\text{B.52})$$

Substitute this into equation (B.43) and after a few manipulations one obtains,

$$I = I_0 (1/A_{\text{micro}}) \sum f[\cos^2(\alpha_i), \cos^2(\varphi_i)] d_i^2 A_i \quad (\text{B.53})$$

From Figure B.1 and equation (B.33),

$$A_i = A'_i \cos(90^\circ - \beta') = A'_i \sin(\beta') = A'_i [\sin^2(\alpha_i)(1 - \cos^2(\varphi_i))]^{1/2}$$

where A'_i is the area of the i th crystal. Substituting this into equation (B.53), one has,

$$I = I_0(1/A_{\text{micro}}) \sum f^*[\cos^2(\alpha_i), \cos^2(\varphi_i)] d_i^2 A'_i \quad (\text{B.54})$$

where,

$$f^*[\cos^2(\alpha_i), \cos^2(\varphi_i)] = f[\cos^2(\alpha_i), \cos^2(\varphi_i)] [\sin^2(\alpha_i)(1 - \cos^2(\varphi_i))]^{1/2}$$

Now replacing $\cos^2(\alpha_i)$ and $\cos^2(\varphi_i)$ in above equation with $\overline{\cos^2(\alpha)}$ and $\overline{\cos^2\varphi}$ which are the average orientation functions, substitute it into equation (B.54),

$$\begin{aligned} I &= I_0(1/A_{\text{micro}}) \sum f^*[\overline{\cos^2(\alpha)}, \overline{\cos^2(\varphi)}] d_i^2 A'_i \\ &= I_0 f^*[\overline{\cos^2(\alpha)}, \overline{\cos^2(\varphi)}] (1/A_{\text{micro}}) \sum d_i^2 A'_i \end{aligned} \quad (\text{B.55})$$

Similarly, replace d_i by $\bar{d}$, and let $d_i A'_i = v_i$, which is the volume of i th crystal, then equation (B.55) changes to

$$I = I_0 \bar{d} f^*[\overline{\cos^2(\alpha)}, \overline{\cos^2(\varphi)}] (1/A_{\text{micro}}) \sum v_i \quad (\text{B.56})$$

Since the total volume of all crystals $V_c = \sum v_i$, we obtain

$$I = I_0 \bar{d} f^*[\overline{\cos^2(\alpha)}, \overline{\cos^2(\varphi)}] (1/A_{\text{micro}}) V_c \quad (\text{B.57})$$

One notices that during the derivation, there is no limitation to the summation, so that $V_c = \sum v_i$ is true for any kind of nucleation. This means that the equation allows the number of crystals to change during the crystallization. If the sample thickness is l , the sample volume in the light path is V , then, $V = l A_{\text{micro}}$. By this and $X_c = V_c/V$, equation (B.57) changes to:

$$I = I_0 \left(1 - \frac{f^*}{\cos^2(\alpha)} \right) X_c \quad (B.58)$$

Because the optical instrument is not perfect, there is always a zero reading I_z (with polymer melt and cover glasses in the light path). I_z was experimentally found to be a linear function of I_0 :

$$I_z = R_0 I_0 + C$$

where C and R_0 are constants. Therefore, for a real instrument, equation (B.58) should be written as:

$$I = I_0 \left(1 - \frac{f^*}{\cos^2(\alpha)} \right) X_c + I_z = I_0 \left(1 - \frac{f^*}{\cos^2(\alpha)} \right) X_c + R_0 I_0 + C \quad (B.59)$$

By equation (B.56), equation (B.59) can be written as (with assumption made in Chapter 3 to replace I_0 with I_0'):

$$R = \left(1 - \frac{f^*}{\cos^2(\alpha)} \right) X_c + R_0 \quad (B.60)$$

From this equation one can see that when $X_c = 0$, $R = R_0$. The physical meaning of R_0 turns out to be the relative intensity at crystallinity equals zero.

When $t = \infty$, $R = R_\infty$ in equation (B.60). R_∞ is the relative light intensity at the end of the cooling or corresponding to crystallinity $(X_c)_\infty$. Substitute these into equation (B.60), we have,

$$\begin{aligned} \text{at } t = \infty, \quad R_\infty &= \left(1 - \frac{f^*}{\cos^2(\alpha)} \right) (X_c)_\infty + R_0 \\ \text{or} \quad R_\infty - R_0 &= \left(1 - \frac{f^*}{\cos^2(\alpha)} \right) (X_c)_\infty \end{aligned} \quad (B.61)$$

Equation. (B.60) can also be written as:

$$R - R_0 = l \bar{d} f^* X_c$$

Dividing it by equation (B.61), assuming f^* and $\bar{d}$ do not change during crystallization (this needs experimental evidence), one finally gets:

$$\frac{R - R_0}{R_\infty - R_0} = \frac{X_c}{(X_c)_\infty} \quad (\text{B.62})$$

This is the equation which will be used to calculate relative crystallinity.

Equation (B.59) or (B.60) is a basic and most important equation for this research, and it tells us that the light intensity is a linear function of crystallinity, sample thickness, crystal thickness and the molecular orientation. That the light intensity is affected by crystal thickness is what we expected. Since most of the crystallization occurs at a certain temperature and that temperature varies with cooling rate in nonisothermal crystallization, the lamellar thickness could be a function of cooling rate. Before this problem is clarified, we assume that the dimension change by the cooling rate will not affect the measured intensity much, because the magnitude of the lamellar thickness change is usually very small. However, if it is true that the intensity is a function of the lamellar thickness, it will help us to handle lamellar thickening problem in the kinetic equation. This relationship may be easier to check in isothermal condition since different crystallizing temperature gives different crystal size. $f^*[\overline{\cos^2(\alpha)}, \overline{\cos^2(\varphi)}]$ is the function of orientation and it is very complex. The validation of this expression needs to be checked experimentally. A lot of work needs to be done to verify the relationship between relative crystallinity and molecular orientation.

VITA

Zhuomin Ding was born in Shanghai, China on May 1, 1955. He graduated from the Department of Textile and Chemical engineering in Shanghai Textile College, Shanghai, China in April 1981. After working for two years in Shanghai, he entered the China Textile University in Shanghai and received a Master degree in Textile and Chemical Engineering in January 1986. After working for another five years, he joined the program in polymer engineering in Materials Science and Engineering at the University of Tennessee Knoxville in August 1991. He completed all requirements for the Doctor of Philosophy degree in Polymer Engineering in December 1995.

He has been happily married to Hong Zhang for eight years and they have a lovely four-year-old daughter, Chen Ding.