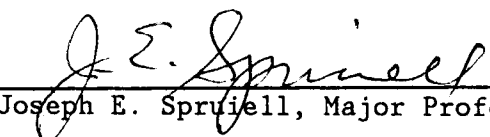
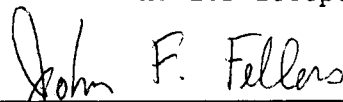
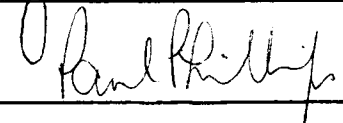


To the Graduate Council:

I am submitting herewith a thesis written by Margaret O. Westbrook entitled "The Effect of Additives and Melt Orientation on the Crystallization and Form II-Form I Crystal-Crystal Transformation Kinetics of Isotactic Polybutene-1." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


Joseph E. Spruiell, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:


Vice Provost
and Dean of The Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at The University of Tennessee, Knoxville, I agree that the Library shall make it available to borrowers under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature Margaret O. Westbrook

Date 8/2/85

THE EFFECT OF ADDITIVES AND MELT ORIENTATION ON THE CRYSTALLIZATION
AND FORM II-FORM I CRYSTAL-CRYSTAL TRANSFORMATION KINETICS
OF ISOTACTIC POLYBUTENE-1

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Margaret O. Westbrook

August 1985

ACKNOWLEDGMENTS

The author wishes to thank her advisor, Professor J.E. Spruiell, for his guidance during this research project. She is also thankful to the Materials Science and Engineering Department along with the Polymer and Textiles Research Association for financial support. Also, she wishes to acknowledge the Shell Development Company for providing the polymer resin used in this study. She appreciates the support and advice throughout her master's work of Paul Westbrook. Dr. J.S. Lin was also very helpful in allowing her to use the ORNL NCSASR scattering center and offering advice on the interpretation. She also appreciates her fellow students for all the help so willingly provided.

ABSTRACT

This work encompasses the effect of additives and melt orientation on the crystallization from the melt and subsequent Form II-Form I crystal-crystal transformation of polybutene-1. Key components in this work are: structural development during secondary crystallization and transformation, and enhancement of the crystallization and transformation rates by compounding of additives as well as melt induced orientation.

To study these effects several experiments were performed. Blends of polybutene-1 (Shell BR200S) and selected additives were mixed in a Brabender screw extruder. The additives studied were polypropylene, diphenyl ether, α -chloronaphthalene, 1-naphthalene acetamide, carbon black, sodium benzoate, and stearic acid. The transformation kinetics in compression molded sheets were followed at 0, 23, 45, and 60 °C by WAXS techniques. The crystallization behavior was studied by differential scanning calorimetry. Structural development was examined by small-angle x-ray (SAXS) and small-angle laser light scattering (SALS) techniques in the BR200S resin.

Fibers were melt spun to various spin draw ratios to study the influence of orientation on the kinetics of the Form II-Form I phase transformation. These results were compared to previous studies on the effect of cold rolling by Hong and Lee of this university. The transformation was followed by wide-angle x-ray diffraction (WAXS) using a Rigaku diffractometer with a fiber attachment. Crystalline

orientation factors were determined from wide-angle x-ray diffraction azimuthal scans.

Important conclusions from this work can be summarized as follows. From the quiescent melt state, an initial crystalline structure develops which undergoes secondary crystallization and transformation to create a well developed ordered structure. The possibility of a very small fraction ($10^{-2}\%$) of voids is shown through invariant analysis of the small-angle x-ray scattering results for the fresh and fully aged samples. This small amount of voids detected does not appreciably affect the crystallinities calculated from density measurements.

The crystallization rate was most affected by crystalline additives. Therefore, it seems by the nature of the effective additives, that the crystallization is nucleation rate controlled. The relative effectiveness of the crystalline additives may be attributed to crystallization temperatures as well as the possible epitaxial nucleation abilities.

Dependent on the nature of the material added, both the enhancement of nucleation and molecular mobility are important factors involved in the acceleration of crystal transformation by blending.

Sample dimension is also shown to affect both secondary crystallization and transformation rates. Samples with higher surface to volume ratios undergo these processes faster. The rate constants of the transformation can be related to the surface to volume ratio of the sample by a relationship developed using an Avrami analysis. The

assumptions involved are that the nuclei are instantaneously present at the surface of the sample and that the crystals grow through the lamellar ribbon with a one-dimensional constant growth rate.

Lastly, increasing the melt orientation also increases the rate of secondary crystallization and transformation; however, solid state deformation, specifically cold rolling, seems to be a more effective method of increasing the rate of crystal-crystal phase transformation.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
II. BACKGROUND	3
2.1. Structure	3
2.2. Properties	4
2.3. Phase Transformation Theory	10
2.4. Crystallization Kinetics of Polybutene-1	19
2.5. Form II - Form I Crystal-Crystal Transformation Kinetics of Polybutene-1	22
III. MATERIALS AND EXPERIMENTAL PROCEDURE	32
3.1. Materials	32
3.2. Sample Preparation	32
3.3. Wide-angle X-ray Diffraction Analysis	36
3.4. Differential Scanning Calorimetry Analysis	44
3.5. Small-angle X-ray and Light Scattering Analysis ...	45
3.6. Mechanical Property Measurement	48
IV. RESULTS AND DISCUSSION	49
4.1. Structure Development During Crystallization and Transformation in BR200S	50
4.1.1. Initial Development of Crystallinity	50
4.1.2. Secondary Crystallization and Transformation	52
4.2. Effect of Additives on the Crystallization and Transformation Kinetics	62
4.2.1. Initial Crystallization Kinetics as Affected by Additives	62
4.2.2. Transformation and Secondary Crystallization Kinetics as Affected by Additives	67
4.2.3. Effect of Temperature on the Transformation Rate of Blends	84
4.2.4. Tensile Mechanical Properties of the BR200S Blends	100

CHAPTER	PAGE
4.3. Effect of Sample Dimensions and Orientation on the Secondary Crystallization and Transformation Kinetics	103
4.3.1. Secondary Crystallization and Transformation Kinetics as Affected by Sample Dimensions	103
4.3.2. Secondary Crystallization and Transformation Kinetics as Affected by Orientation	114
V. CONCLUSIONS	132
BIBLIOGRAPHY	137
APPENDIX	143
VITA	240

LIST OF TABLES

TABLE	PAGE
2-1. Various Properties of the Crystalline Phases of Polybutene-1 (B-12,H-10,N-1 through N-6)	6
2-2. Avrami Exponent Significance (S-7,W-1).....	18
3-1. Sample Name and Identification	33
4-1. Invariant Analysis Based on a Two Phase Scattering Model	61
4-2. Crystallization Temperatures for BR200S Blends	65
4-3. Transformation Half-time Values for Compression Molded Films of the BR200S Blends	83
4-4. Avrami Rate Constants, K, for the BR200S Blends with the Exponent, n, Forced to Equal 1.0	96
4-5. Tensile Mechanical Properties of the BR200S Blends (Fresh and Aged)	101
4-6. Transformation Half-time Values for Spin Drawn Fibers of BR200S, SB05, and PP5	128

LIST OF FIGURES

FIGURE	PAGE
2-1. Flow Chart Showing Formation, Structure, and Transformation of the Different Morphological and Crystalline Forms of Isotactic Polybutene-1 (H-3)	5
2-2. Typical Stress-Strain Curve for Fresh and Aged Polybutene-1 (G-1)	9
3-1. Typical Wide-angle X-ray Diffraction Scan of Fresh and Aged Polybutene-1	37
3-2. Geometry of the PB-1 (110) Plane for the Wilchinsky Analysis of Orientation	42
3-3. Schematic Small-angle Laser Light Scattering Experimental Apparatus, A) Laser B) Polarizer C) First Pinhole Collimator D) Second Pinhole Collimator E) Sample F) Analyzer G) Film	46
3-4. Schematic Small-angle X-ray Scattering Experimental Apparatus (H-12)	47
4-1. Differential Scanning Calorimetry Cooling Curve for BR200S Resin	51
4-2. Volume Fraction of the Crystal Transformed Over Time for BR200S at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C	53
4-3. Crystal Fraction Present as a Function of Time for BR200S at 23 °C	55
4-4. Small-angle Laser Light Scattering Film Patterns of BR200S Water Quenched Film Over a Period of Days: (A) 0.5 hours (B) 6.0 hours (C) 24.0 hours (D) 48 hours	56
4-5. Small-angle X-ray Scattering Patterns of BR200S (A) 0.5 hours, (B) 72.5 hours, (C) months	58
4-6. Small-angle X-ray Scattering Intensity as a Function of Scattering Vector for BR200S Water Quenched Films Over Several Months (A) 0.5 hours (B) 72.5 hours (C) months (D) Kratky Summary Plot	59

FIGURE	PAGE
4-7. Differential Scanning Calorimetry Cooling Curve for the PP10 Blend	63
4-8. Differential Scanning Calorimetry Cooling Curve for the DPE5 Blend	64
4-9. Volume Fraction of the Crystal Transformed Over Time for PP5, PP10, and PP25 Blends	69
4-10. Crystal Fraction Present as a Function of Time for PP5 at 23 °C	70
4-11. Volume Fraction of the Crystal Transformed Over Time for DPE05, DPE2, and DPE5 Blends	71
4-12. Crystal Fraction Present as a Function of Time for DPE5 at 23 °C	72
4-13. Volume Fraction of the Crystal Transformed Over Time for CN05, CN2, and CN5 Blends	74
4-14. Crystal Fraction Present as a Function of Time for CN5 at 23 °C	75
4-15. Volume Fraction of the Crystal Transformed Over Time for CB05 and CB2 Blends	76
4-16. Crystal Fraction Present as a Function of Time for CB2 at 23 °C	77
4-17. Volume Fraction of the Crystal Transformed Over Time for NA05, NA2, and NA5 Blends	78
4-18. Crystal Fraction Present as a Function of Time for NA5 at 23 °C	79
4-19. Volume Fraction of the Crystal Transformed Over Time for SB05 and SB2 Blends	81
4-20. Volume Fraction of the Crystal Transformed Over Time for SA05, SA2, and SA5 Blends	82
4-21. Volume Fraction of the Crystal Transformed Over Time for SB2 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C	86

FIGURE	PAGE
4-22. Volume Fraction of the Crystal Transformed Over Time for NA5 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C	87
4-23. Volume Fraction of the Crystal Transformed Over Time for CB2 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C	88
4-24. Volume Fraction of the Crystal Transformed Over Time for DPE5 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C	89
4-25. Volume Fraction of the Crystal Transformed Over Time for CN5 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C	90
4-26. Determination of the Avrami Exponent Graphically for BR200S Compression Molded Films	92
4-27. Determination of the Avrami Exponent Graphically for the CN2 Blend	93
4-28. Experimental and Calculated Transformation Data for BR200S at 0 °C, 23 °C, 45 °C, and 60 °C by the Avrami Model	94
4-29. Avrami Transformation Rate Constant as a Function of Temperature for the BR200S Blends	99
4-30. Crystal Fraction Present as a Function of Time for the SDR = 1 BR200S Fiber of Diameter 0.736 mm	105
4-31. Crystal Fraction Present as a Function of Time for the SDR = 1 BR200S Fiber of Diameter 1.472 mm	106
4-32. Effect of Sample Thickness on an SDR = 1 Fiber of BR200S	107
4-33. Crystal Fraction Present as a Function of Time for the SDR = 70 BR200S Fiber of Diameter 0.0736 mm (initial)	108
4-34. Crystal Fraction Present as a Function of Time for the SDR = 70 BR200S Fiber of Diameter 1.472 mm (initial)	109

FIGURE	PAGE
4-35. Effect of Sample Thickness on an SDR = 70 Fiber of BR200S	110
4-36. Crystal Fraction Present as a Function of Time for the SDR = 35 BR200S Fiber	116
4-37. Crystal Fraction Present as a Function of Time for the SDR = 105 BR200S Fiber	117
4-38. Herman's Orientation Factor as a Function of Spin Draw Ratio for the BR200S, SB05, and PP5 Fibers	119
4-39. Volume Fraction of the Crystal Transformed Over Time for the BR200S Resin Fibers Formed at 1, 35, 70, and 105 Spin Draw Ratios	120
4-40. Volume Fraction of the Crystal Transformed Over Time for the SB05 Blend Fibers Formed at 1, 35, 70, and 105 Spin Draw Ratios	121
4-41. Volume Fraction of the Crystal Transformed Over Time for the PP5 Blend Fibers Formed at 1, 35, 70, and 105 Spin Draw Ratios	122
4-42. Volume Fraction of the Crystal Transformed Over Time at the Spin Draw Ratio of 1 for BR200S, SB05, and PP5	123
4-43. Volume Fraction of the Crystal Transformed Over Time at the Spin Draw Ratio of 35 for BR200S, SB05, and PP5	124
4-44. Volume Fraction of the Crystal Transformed Over Time at the Spin Draw Ratio of 105 for BR200S, SB05, and PP5	126
4-45. Transformation Half-time as a Function of Spin Draw Ratio for BR200S, SB05, and PP5 Fibers	127
4-46. Effect of Cold Rolling on the Form II - Form I Transformation in BR200S Compression Molded Films (H-10)	129
4-47. Schematic Wide-angle X-ray Film Patterns of BR200S Fiber of SDR = 105 and Cold Rolled Film of Roll Reduction 30%	130

FIGURE	PAGE
A-1. Differential Scanning Calorimetry Cooling Curve for the CN5 Blend	144
A-2. Differential Scanning Calorimetry Cooling Curve for the NA5 Blend	145
A-3. Differential Scanning Calorimetry Cooling Curve for the CB2 Blend	146
A-4. Differential Scanning Calorimetry Cooling Curve for the SB2 Blend	147
A-5. Differential Scanning Calorimetry Cooling Curve for the SA5 Blend	148
A-6. Crystal Fraction Present as a Function of Time for PP10 at 23 °C	149
A-7. Crystal Fraction Present as a Function of Time for PP25 at 23 °C	150
A-8. Crystal Fraction Present as a Function of Time for DPE05 at 23 °C	151
A-9. Crystal Fraction Present as a Function of Time for DPE2 at 23 °C	152
A-10. Crystal Fraction Present as a Function of Time for CN05 at 23 °C	153
A-11. Crystal Fraction Present as a Function of Time for CN2 at 23 °C	154
A-12. Crystal Fraction Present as a Function of Time for CB05 at 23 °C	155
A-13. Crystal Fraction Present as a Function of Time for NA05 at 23 °C	156
A-14. Crystal Fraction Present as a Function of Time for NA2 at 23 °C	157
A-15. Crystal Fraction Present as a Function of Time for SB05 at 23 °C	158
A-16. Crystal Fraction Present as a Function of Time for SB2 at 23 °C	159

FIGURE	PAGE
A-17. Crystal Fraction Present as a Function of Time for SA05 at 23 °C	160
A-18. Crystal Fraction Present as a Function of Time for SA2 at 23 °C	161
A-19. Crystal Fraction Present as a Function of Time for SA5 at 23 °C	162
A-20. Volume Fraction of the Crystal Transformed Over Time for PP5 at Temperatures of 23 °C, 45 °C, and 60 °C	163
A-21. Volume Fraction of the Crystal Transformed Over Time for PP10 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C	164
A-22. Volume Fraction of the Crystal Transformed Over Time for PP25 at Temperatures of 23 °C, 45 °C, and 60 °C	165
A-23. Volume Fraction of the Crystal Transformed Over Time for DPE05 at Temperatures of 23 °C, 45 °C, and 60 °C	166
A-24. Volume Fraction of the Crystal Transformed Over Time for DPE2 at Temperatures of 23 °C, 45 °C, and 60 °C	167
A-25. Volume Fraction of the Crystal Transformed Over Time for CN05 at Temperatures of 23 °C, 45 °C, and 60 °C	168
A-26. Volume Fraction of the Crystal Transformed Over Time for CN2 at Temperatures of 23 °C, 45 °C and 60 °C	169
A-27. Volume Fraction of the Crystal Transformed Over Time for CB05 at Temperatures of 23 °C, 45 °C and 60 °C	170
A-28. Volume Fraction of the Crystal Transformed Over Time for NA05 at Temperatures of 23 °C, 45 °C, and 60 °C	171
A-29. Volume Fraction of the Crystal Transformed Over Time for NA2 at Temperatures of 23 °C, 45 °C, and 60 °C	172

FIGURE	PAGE
A-30. Volume Fraction of the Crystal Transformed Over Time for SB05 at Temperatures of 23 °C, 45 °C, and 60 °C	173
A-31. Volume Fraction of the Crystal Transformed Over Time for SA05 at Temperatures of 23 °C, 45 °C, and 60 °C	174
A-32. Volume Fraction of the Crystal Transformed Over Time for SA2 at Temperatures of 23 °C, 45 °C, and 60 °C	175
A-33. Volume Fraction of the Crystal Transformed Over Time for SA5 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C	176
A-34. Crystal Fraction Present as a Function of Time for BR200S at 0 °C	177
A-35. Crystal Fraction Present as a Function of Time for BR200S at 45 °C	178
A-36. Crystal Fraction Present as a Function of Time for BR200S at 60 °C	179
A-37. Crystal Fraction Present as a Function of Time for PP5 at 45 °C	180
A-38. Crystal Fraction Present as a Function of Time for PP5 at 60 °C	181
A-39. Crystal Fraction Present as a Function of Time for PP10 at 0 °C	182
A-40. Crystal Fraction Present as a Function of Time for PP10 at 45 °C	183
A-41. Crystal Fraction Present as a Function of Time for PP10 at 60 °C	184
A-42. Crystal Fraction Present as a Function of Time for PP25 at 45 °C	185
A-43. Crystal Fraction Present as a Function of Time for PP25 at 60 °C	186
A-44. Crystal Fraction Present as a Function of Time for DPE05 at 45 °C	187

FIGURE	PAGE
A-45. Crystal Fraction Present as a Function of Time for DPE05 at 60 °C	188
A-46. Crystal Fraction Present as a Function of Time for DPE2 at 45 °C	189
A-47. Crystal Fraction Present as a Function of Time for DPE2 at 60 °C	190
A-48. Crystal Fraction Present as a Function of Time for DPE5 at 0 °C	191
A-49. Crystal Fraction Present as a Function of Time for DPE5 at 45 °C	192
A-50. Crystal Fraction Present as a Function of Time for DPE5 at 60 °C	193
A-51. Crystal Fraction Present as a Function of Time for CN05 at 45 °C	194
A-52. Crystal Fraction Present as a Function of Time for CN05 at 60 °C	195
A-53. Crystal Fraction Present as a Function of Time for CN2 at 45 °C	196
A-54. Crystal Fraction Present as a Function of Time for CN2 at 60 °C	197
A-55. Crystal Fraction Present as a Function of Time for CN5 at 0 °C	198
A-56. Crystal Fraction Present as a Function of Time for CN5 at 45 °C	199
A-57. Crystal Fraction Present as a Function of Time for CN5 at 60 °C	200
A-58. Crystal Fraction Present as a Function of Time for CB05 at 45 °C	201
A-59. Crystal Fraction Present as a Function of Time for CB05 at 60 °C	202
A-60. Crystal Fraction Present as a Function of Time for CB2 at 0 °C	203

FIGURE	PAGE
A-61. Crystal Fraction Present as a Function of Time for CB2 at 45 °C	204
A-62. Crystal Fraction Present as a Function of Time for CB2 at 60 °C	205
A-63. Crystal Fraction Present as a Function of Time for NA05 at 45 °C	206
A-64. Crystal Fraction Present as a Function of Time for NA05 at 60 °C	207
A-65. Crystal Fraction Present as a Function of Time for NA2 at 45 °C	208
A-66. Crystal Fraction Present as a Function of Time for NA2 at 60 °C	209
A-67. Crystal Fraction Present as a Function of Time for NA5 at 0 °C	210
A-68. Crystal Fraction Present as a Function of Time for NA5 at 45 °C	211
A-69. Crystal Fraction Present as a Function of Time for NA5 at 60 °C	212
A-70. Crystal Fraction Present as a Function of Time for SB05 at 45 °C	213
A-71. Crystal Fraction Present as a Function of Time for SB05 at 60 °C	214
A-72. Crystal Fraction Present as a Function of Time for SB2 at 0 °C	215
A-73. Crystal Fraction Present as a Function of Time for SB2 at 45 °C	216
A-74. Crystal Fraction Present as a Function of Time for SB2 at 60 °C	217
A-75. Crystal Fraction Present as a Function of Time for SA05 at 45 °C	218
A-76. Crystal Fraction Present as a Function of Time for SA05 at 60 °C	219

FIGURE	PAGE
A-77. Crystal Fraction Present as a Function of Time for SA2 at 45 °C	220
A-78. Crystal Fraction Present as a Function of Time for SA2 at 60 °C	221
A-79. Crystal Fraction Present as a Function of Time for SA5 at 0 °C	222
A-80. Crystal Fraction Present as a Function of Time for SA5 at 45 °C	223
A-81. Crystal Fraction Present as a Function of Time for SA5 at 60 °C	224
A-82. Determination of the Avrami Exponent Graphically for the PP5 Blend	225
A-83. Determination of the Avrami Exponent Graphically for the NA5 Blend	226
A-84. Determination of the Avrami Exponent Graphically for the DPE5 Blend	227
A-85. Determination of the Avrami Exponent Graphically for the SB2 Blend	228
A-86. Determination of the Avrami Exponent Graphically for the SA5 Blend	229
A-87. Determination of the Avrami Exponent Graphically for the CB2 Blend	230
A-88. Volume Fraction of the Crystal Transformed Over Time at the Spin Draw Ratio of 70 for BR200S, SB05, and PP5	231
A-89. Crystal Fraction Present as a Function of Time for the SDR = 1 SB05 Fiber	232
A-90. Crystal Fraction Present as a Function of Time for the SDR = 35 SB05 Fiber	233
A-91. Crystal Fraction Present as a Function of Time for the SDR = 70 SB05 Fiber	234
A-92. Crystal Fraction Present as a Function of Time for the SDR = 105 SB05 Fiber	235

FIGURE	PAGE
A-93. Crystal Fraction Present as a Function of Time for the SDR = 1 PP5 Fiber	236
A-94. Crystal Fraction Present as a Function of Time for the SDR = 35 PP5 Fiber	237
A-95. Crystal Fraction Present as a Function of Time for the SDR = 70 PP5 Fiber	238
A-96. Crystal Fraction Present as a Function of Time for the SDR = 105 PP5 Fiber	239

LIST OF SYMBOLS

English

- A - Surface area
- f_c - Herman's chain orientation factor
- F_I - Form I structure factor
- F_{II} - Form II structure factor
- $\dot{G}$ - Growth rate
- ΔG - Gibb's free energy
- G_{bulk} - Gibb's free energy of the bulk
- ΔG_c - Gibb's free energy of the crystallization
- G_1 - Gibb's free energy of phase one
- G_2 - Gibb's free energy of phase two
- ΔH - Enthalpy
- I_I - Integrated intensity of Form I diffraction peak
- I_I^s - Integrated intensity of Form I standard peak
- I_{II} - Integrated intensity of Form II diffraction peak
- I_{II}^s - Integrated intensity of Form II standard peak
- K - Avrami rate constant
- $l(t)$ - Nucleus length as a function of time
- L/D - Length to diameter ratio
- L.P. - Lorentz polarization factor
- $\dot{N}$ - Nucleation rate
- n - Avrami coefficient
- N_o - Number of instantaneous nuclei present

- P_I - multiplicity of Form I
 P_{II} - multiplicity of Form II
 Q - Small-angle x-ray scattering invariant
 R_I - Correction factor for Form I integrated intensity
 R_{II} - Correction factor for Form II integrated intensity
 S - Entropy
 S/V - Surface to volume ratio
 SDR - Spin draw ratio
 T - Temperature
 T_c - Crystallization onset temperature
 t - time
 $t_{1/2}$ - Half-time of transformation
 $u(t)$ - linear growth rate of crystal
 V_t - Volume of nuclei at time, t
 W, T - Nominal dimensions of nucleus
 X_T - Total crystal fraction
 X_o - Initial crystal fraction
 X_I - Form I crystal fraction
 X_I^s - Standard Form I crystal fraction
 X_{II} - Form II crystal fraction
 X_{II}^s - Standard Form II crystal fraction

Greek

- γ - Surface free energy
 ρ - Density

ρ_a - Density of amorphous fraction

ρ_c - Density of crystalline fraction

ϕ - Volume fraction of crystal transformed

CHAPTER I

INTRODUCTION

Polybutene-1 is a polyolefin which exhibits unusual polymorphism. It exists in at least four different crystalline phases. These phases are identified as the following: Form I; twinned hexagonal, Form I'; untwinned hexagonal, Form II; tetragonal, and Form III; orthorhombic. Of interest in this study is the crystallization of the metastable Form II from the melt and the subsequent crystal-crystal transformation over time to the stable Form I. During this transformation, the helical conformation of the molecule changes from $11/3$ to $3/1$. The hexagonal structure is also more dense than the tetragonal one.

Isotactic polybutene-1 exhibits many desirable properties such as good environmental stress cracking resistance, creep resistance under load, high moisture barrier properties, good electrical insulation characteristics, abrasion resistance, and toughness. However, its slow crystallization and crystal-crystal transformation lead to difficulties in processing and fabrication. Some practical considerations in the material processing are that the product may cold flow due to slow crystallization and that the dimensions change due to the transformation to the denser Form I structure. It is therefore important to understand these processes in order to assure product applicability and practicality of production.

At present the only United States manufacturer of polybutene-1, Shell Development Company, uses the polymer in both hot and cold water piping. The advantages over other olefins are the creep resistance under stress and the retention of mechanical properties up to about 113°C (softening point).

This study includes an examination of the effect of additives, transformation temperature, and melt orientation on the crystallization and crystal-crystal transformation kinetics of polybutene-1. In the present study differential scanning calorimetry was used to determine the effect of selected additives on the crystallization rate. The crystal-crystal transformation was followed using wide-angle x-ray diffraction calibrated with mass density. Also, the transformation was studied with small-angle x-ray and light scattering to evaluate the structural development during this period.

CHAPTER II

BACKGROUND

2.1. Structure

Polybutene-1 was first synthesized by Natta in 1955 by Ziegler-Natta stereospecific polymerization (N-1,N-2,N-3,N-4,N-5). The classic Ziegler system is a TiCl_4 - AlR_3 catalyst (M-1). This catalyst is a typical transition metal halide with an organometallic compound (aluminum alkyl). Natta expanded this work to the Ziegler-Natta catalyst of many combinations of transition metal chlorides with aluminum alkyls. Many works dealing with the details of stereospecific polymerization are available in the literature (B-1,B-3,C-1,H-1,H-2,N-6).

Polybutene-1 is a linear α -olefin with ethyl side groups on every other carbon in the backbone. This fairly substantial side group may account for the slow crystallization from the melt.

Since the first synthesis of polybutene-1, there have been at least four crystalline phases confirmed. Natta et al. determined that polybutene-1 was dimorphic and exhibits both a Form II tetragonal structure with an $11/3$ helix conformation and a melting point of 100 to 120 °C as well as a Form I twinned hexagonal structure with a $3/1$ helix conformation and melting point of 105 to 130 °C (N-1,N-2,N-3,N-4,N-5,N-6). The metastable Form II crystallizes from the melt and then, over a period of days to weeks, transforms to the

stable Form I (N-1,N-2,N-3,N-4,N-5,N-6). The crystalline density of polybutene-1 increases from 0.88 g/cm³ to 0.95 g/cm³. Form II is metastable with respect to Form I at temperatures ranging up to the Form II melting point. Upon heating of Form I the polymer crystal does not revert to Form II before melting (B-2). Later, Holland and Miller discovered Form III orthorhombic and Form I' untwinned hexagonal structures in single crystals grown from solution (H-3). The conditions under which these crystal types form are illustrated in Figure 2-1. Details of these structures and their properties can be found in Table 2-1.

Of major interest to the present research is the relatively slow crystallization of Form II from the melt, and its transformation over time to Form I. These factors have major significance in the practical and economic aspects of the melt processing of polybutene-1.

2.2. Properties

Isotactic polybutene-1 exhibits numerous favorable properties for use as piping, plastic liners, refuse bags, hot fill containers, industrial chemical containers, etc. (C-2,D-1,K-1,L-1). Among the attributes of polybutene-1 are the following: environmental stress cracking resistance, creep resistance under load, high temperature strength (up to about 113 °C), good moisture barrier properties, good electrical insulation characteristics, flexibility, no macroscopic necking, impact resistance, abrasion resistance, and chemical resistance (C-2,D-1,K-1,L-1). The advantages of polybutene-1 over

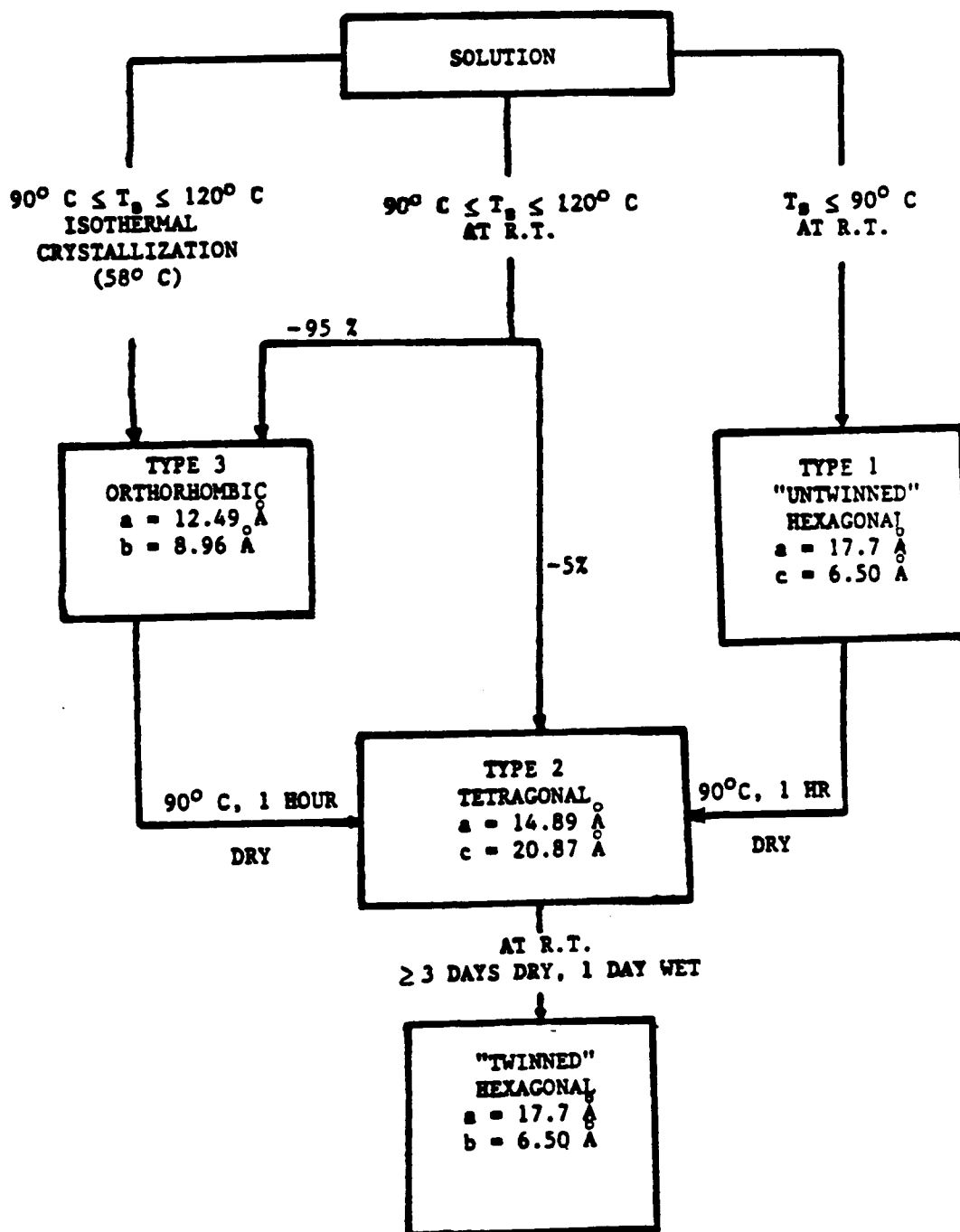


Figure 2-1. Flow Chart Showing Formation, Structure, and Transformation of the Different Morphological and Crystalline Forms of Isotactic Polybutene-1 (H-3)

Table 2-1. Various Properties of the Crystalline Phases of Polybutene-1 (B-12,H-10,N-1 through N-6).

Form	I	I'	II	III
1. Crystal Phase	Twinned Hexagonal	Untwinned Hexagonal	Tetragonal	Orthorhombic
2. Crystal Parameters (Å)	A=17.7 B=17.7 C=6.5	A=17.7 B=17.7 C=6.5	A=14.9 B=14.9 C=20.6-20.8	A=12.4 B=8.9 C=7.6
3. Helix	3/1	3/1	11/3	4/1
4. Density (g/cm ³) (theoretical)	0.95	0.95	0.88-0.90	0.88
5. Monomers per unit cell	18	18	44	8
6. T _m (°C)	135-142	90-100	120-126	90-103
7. H _f , (cal/mole)	1675		800-974	1550
8. X-ray Maxima (θ)	5.1,8.7 10.3	5.1,8.7 10.3	5.9,8.4 9.1	6.1,7.1 8.6,9.3
9. Space Group	R3C or $\overline{R}3C$	$\overline{R}3C$ or R3C		P2 ₁ ² ₁ ² ₁

other olefins, such as polypropylene and polyethylene, are its high creep resistance under load, flexibility, toughness, and abrasion resistance.

Many of the enhanced properties can be attributed to its relatively high molecular weight (10^5). Polybutene-1 does not crystallize as rapidly or at as high a temperature as polyethylene or polypropylene. Since the crystallization occurs in a more viscous melt at lower temperatures, Lindengren suggested that nucleation occurs in numerous locations throughout the substance such that there are crystals with interconnecting molecules (L-1). This morphology would allow for the observed toughness, impact strength, no macroscopic necking, etc.

Of considerable interest is the mechanical behavior of polybutene-1 (L-1). Since it is less crystalline than high density polyethylene or polypropylene, polybutene-1 is more flexible and elastic. In comparison to other olefins it exhibits a somewhat unique behavior under tensile stress. Polypropylene and high density polyethylene show the typical polyolefin behavior of a rapid increase in stress up to a well defined yield point followed by necking and further cold drawing at a slightly lower stress. The necked portion then continues to orient and ultimately fails. In contrast, polybutene-1 exhibits a distinctly different behavior (G-1,L-1). The entire gauge section responds to the stress up to yield followed by no macroscopic necking. The material continues to deform homogeneously up to failure. Fresh samples, consisting of mostly Form II, exhibit

two different stages during the strain hardening period. Initially, the crystal transformation occurs and is then followed by continued molecular orientation up to the failure of the sample. Typical stress-strain curves which provide a physical representation of the aforementioned behavior appear in Figure 2-2. A typical fresh tensile modulus is about 70 MPa; upon secondary crystallization and transformation, the modulus increases to 175 or 200 MPa. Yield strength also increases upon transformation (1 to 10 MPa), Asada et al. noted that as transformation of the sample is increased, the stress required to reach the yield point is also increased. Beyond yield the rate of increase in stress is higher for more highly transformed samples. The ultimate strength increases to a lesser extent with crystal transformation (a 1 MPa increase).

It is observed that polybutene-1 retracts upon fracture. This retraction phenomenon is uncharacteristic of most highly crystalline polymers. One expects this behavior only in elastomers which are characteristically amorphous in the unstretched condition (Q-1,S-1). It has been reported, however, that high elastic recovery is obtained, after certain processing conditions, from polypropylene, poly-3-methylbutene-1, and polyoxymethylene (Q-1,S-1). The elasticity is developed by processing at high stress followed by annealing. This behavior has been termed "hard elastic." Typically there will be 50 to 90% recovery from large strains. Also these materials exhibit the ability to generate large amounts of surface area and volume upon stretching. The polymer is thought to become microvoided and

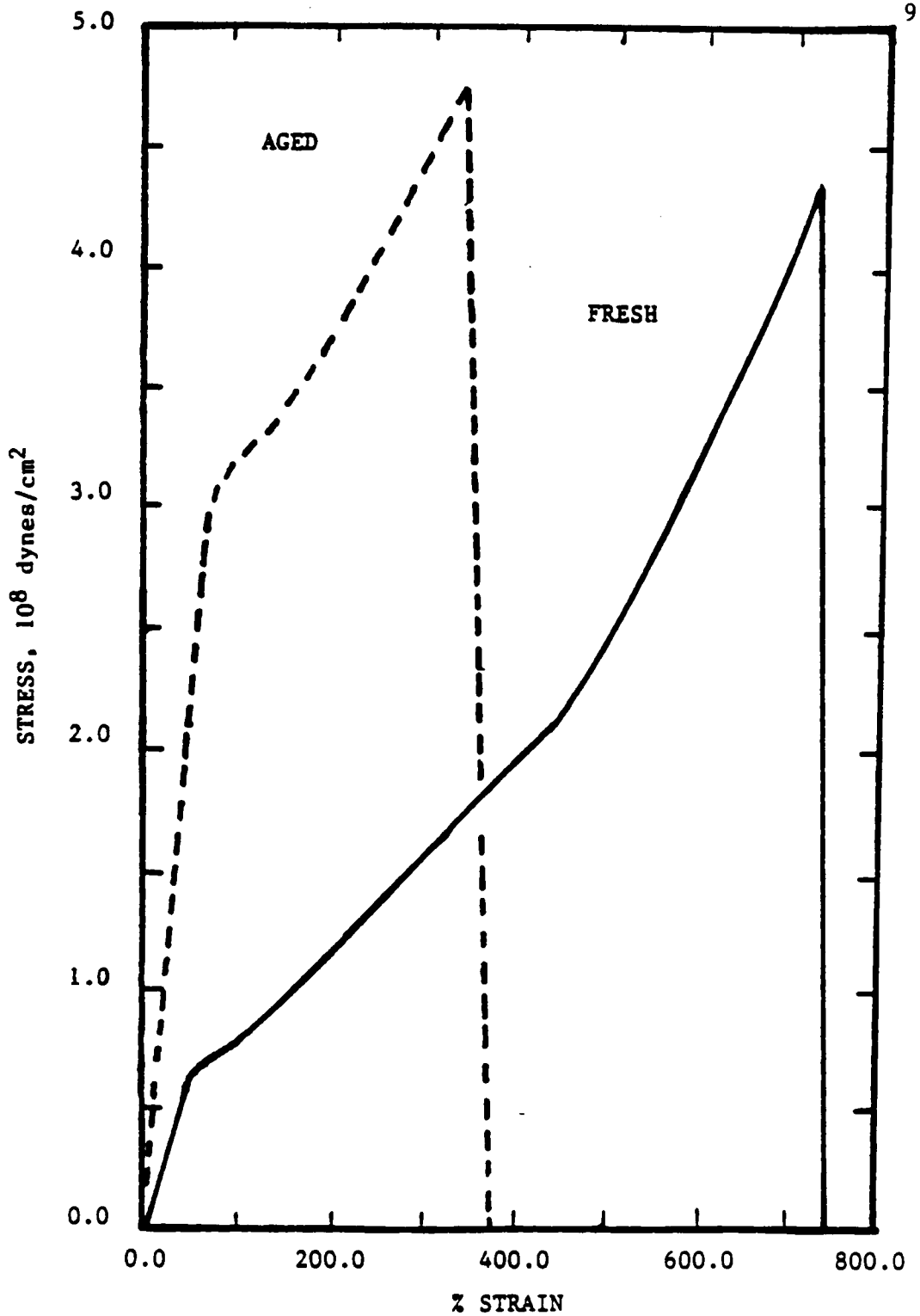


Figure 2-2. Typical Stress-Strain Curve for Fresh and Aged Polybutene-1 (G-1)

therefore porous. Optical observation of immersion oil migrating into the polymer support this postulate (Q-1). Sprague proposed a structural model to explain this behavior (S-1). Stacks of lamellae are bent during the deformation and thus provide the restoring driving force for retraction. It is suggested that interlamellar fibrils provide the continuity of the structure.

Polybutene-1, in contrast, exhibits a similar retractive force without special processing under high stress. The polybutene-1 behavior is attributed both to tie molecules which connect the crystals and to relatively low crystallinity (L-1). Lindengren likens this behavior to that of rubber crosslinked to filler particles. Polybutene-1 also stress whitens which is thought to be due to voiding of the structure because of lateral contraction upon transformation. Two other possible explanations for the whitening are stress induced crystallinity and fibrillation. This again is characteristic of the hard elastic material.

2.3. Phase Transformation Theory

The relatively slow crystallization and crystal-crystal transformation of isotactic polybutene-1 are of considerable interest in polymer processing. Thermodynamically, crystallization or any other transformation from one phase to another may be described as follows.

$$\Delta G = G_2 - G_1 \quad (2-1)$$

The Gibbs' free energy may be represented in terms of the enthalpy and entropy contributions.

$$\Delta G = \Delta H - T\Delta S \quad (2-2)$$

The ΔG is the Gibbs' free energy change for the phase transformation, ΔH is the enthalpy of the transformation, and ΔS is the entropy change of the transformation. The change in Gibbs' free energy must be a negative quantity in order for the transformation to proceed.

Although there is a driving force for crystallization at any temperature below the equilibrium melting temperature (i.e. ΔG is negative), crystallization generally requires a significant supercooling in polymers. This is necessary to provide sufficient driving force to overcome the positive free energy required to create the interface between the crystal nuclei and the melt. Therefore, included in this analysis of nucleation must be a term for the critical surface energy of the incipient nucleus or embryo (W-1). There is a critical size for a stable nucleus such that the surface energy term does not force the free energy to be positive and thus prevent the nucleation. The bulk energy must dominate the system for the nucleation to occur.

$$G_{\text{crystal}} = G_{\text{bulk}} + \Sigma\gamma A \quad (2-3)$$

γ = the surface free energy

A = the surface area

G_{crystal} = free energy of a crystal

Therefore, in the case of crystallization, the free energy of the transformation becomes (W-1)

$$\Delta G = \Delta G_c + \Sigma \gamma A \quad (2-4)$$

Nucleation in polymers may be due to a large supercooling of the melt (sporadic or homogeneous nucleation), stress and orientation induced nucleation, and instantaneous or heterogeneous nucleation by foreign substances (B-7,B-9,K-2,W-1). Classical homogeneous nucleation theory, developed by Gibbs (1906), Volmer (1939), and Kossel (1927), is based on fluctuations in the supercooled phase which overcome the barrier to nucleation (W-1). Foreign surfaces often reduce the required nucleus size since the polymer-particle interface may provide energy to promote the crystal growth. Heterogeneous nucleation was studied by Binsbergen in which he surmised that the important factors are that the additive 1) is not soluble in the melt or that it crystallizes out first, 2) has high polarity in groups resembling good solvents for the polymer, 3) has comparatively low energy surfaces, and 4) is always crystalline (B-7,B-9). Chatterjee and Price also examined the nucleating abilities of certain substances by looking at substrate induced crystallization of polymers (C-4,C-5,C-6). They determined that similarity of chemical structure,

similarity of unit cell type, close match of crystal lattice parameters, and high surface energy are not necessary for a strong nucleating agent. They further determined that crystallinity is not a sufficient condition for a strong nucleating agent for polymers crystallizing from the melt.

Wittmann and Lotz have determined that epitaxial crystallization is an important factor when determining the relative abilities of nucleating agents (W-4). Polyethylene has been found to epitaxially crystallize on polypropylene. In general, carboxylic salts were found to be good nucleating agents for polyolefins. The polar group is thought to enhance the cohesion of the salt and thus prevent the salt from dissolving in the polymer. Matching of lattice parameters was determined to enhance the ability of certain additives to nucleate the crystallization of many polymers. Apparently, the polymer crystal nucleates on the face of a plane and thus its orientation is controlled by the nucleating crystal.

Both the crystallization and crystal-crystal phase transformations can be described using the Avrami analysis. Both processes occur in the condensed phase. Although the phase transformations nucleate from different phases (crystallization nucleates from a liquid and transformation from a solid), the resulting observations are very similar and have been found to follow the Avrami analysis with good agreement. The Avrami analysis has previously been applied to the crystal-crystal phase transformation in polybutene-1 by numerous researchers (A-5,D-2,G-1,O-1,P-1). In the

crystal-crystal transformation, nucleation is thought to be heterogeneous (instantaneous) and interface controlled with linear growth in one dimension. The crystallization was determined to occur by a combination of instantaneous and sporadic nucleation with linear growth in three dimensions.

The Avrami analysis is based upon statistical probabilities of nucleation. For a detailed understanding of its basis and use many works are available (A-1,A-2,A-3,H-4,H-5,W-1). However, a brief explanation of the Avrami analysis follows. The initial efforts to quantitatively characterize the development of crystallinity considering nucleation and crystal growth began around the 1930's. The early researchers were Kolmogoroff, Johnson and Mehl, and Avrami between 1937 and 1941 (W-1). Evans, in 1945, based similar analyses on the problem of expanding waves created by raindrops on the surface of a pool of water (E-1). Flory and Mandelkern (M-1) and Morgan (M-2) applied these principles to polymer crystallization around 1954. The Avrami equation is used to analyze the time dependent transformation of phases. Typically these data are obtained by differential scanning calorimetry or dilatometry in polymer transformations. From theoretical analysis of nucleation and growth, the following equation was evolved for isothermal crystallization.

$$1 - \phi = \exp(-Kt^n) \quad (2-5)$$

K = composite rate constant including
nucleation and growth rates of
crystallites

n = Avrami exponent connoting the
dimensionality of growth and type of
nucleation

t = time elapsed

Φ = volume fraction of material
that has undergone the phase change

$$1 - (X_{\infty} - X_t)/X_{\infty}$$

Several assumptions are inherent in the Avrami analysis (B-4).

1. Nucleation occurs randomly throughout the crystallizing mass.
2. The nucleation may be either sporadic or instantaneous.
Sporadic means that nucleation occurs as a linear function of time. Instantaneous means that all nuclei are present initially.
3. Nuclei grow linearly in one, two, or three dimensions to form rods, discs, sheaves, or spheres respectively
4. The density of the transformed phase remains constant.

A summary of the objections to these simplifications are provided by Wunderlich (W-1).

1. The volume does not remain constant.
2. The linear growth rate is not always linear with time.

3. The number of nuclei may reach a limiting value after consuming all instantaneous nuclei.
4. The crystal does not exactly fit the spherical or or disc-like model.
5. Branching may occur in the crystal substructure.
6. Secondary crystallization may occur.
7. Crystal rearrangement for enhancing perfection may occur after crystallization.

As well as the above objections, the fact that a polymer does not completely crystallize is the basic problem with the assumptions inherent in the Avrami analysis. Due to these complications the Avrami analysis requires support from morphological investigations in order to determine the exact microscopic mechanism. Even so, the Avrami analysis can provide important information and facilitates handling of the data. The rate constant, K , theoretically can be independently determined by microscopic determinations of the nucleation ($\dot{N}$) and growth ($\dot{G}$) rate constants (L-4,P-4). The following equation requires that one assume linear growth in three dimensions and sporadic nucleation. Similar equations can be developed for other special cases.

$$K = \pi \dot{N} \dot{G}^3 (\rho_c / \rho_a) \quad (2-6)$$

ρ_c = crystalline density

ρ_a = amorphous density

$\dot{N}$ = nucleation rate

$\dot{G}$ = linear growth rate

The transformation half-time is defined as the time required for the transformation to occur to an extent corresponding to one half its ultimate level. From the Avrami equation 2-5, it is easily shown that

$$t_{1/2} = (\ln 2 / K)^{1/n} \quad (2-7)$$

n = Avrami coefficient

The value of n may vary over time due to many causes; this variation invalidates the above equation for $t_{1/2}$. Variations may be caused by the following (B-2,H-6,M-1,W-1):

1. Growth of two types of spherulites.
2. The presence of sporadic and instantaneous nuclei.
3. Molecular weight distribution effects.
4. Secondary crystallization.
5. Delayed propagation of crystallization.
6. A combination of initially instantaneous nucleation followed by sporadic nucleation.

The significance of the Avrami exponents are summarized in Table 2-2 (S-7). The nonintegral values are due to diffusion control, which is modelled as the square root of time, and thus the $1/2$ power appears.

Table 2-2. Avrami Exponent Significance (S-7,W-1).

Coefficient, n	Nucleation	Growth Geometry	Growth Control
1/2	Instantaneous	Rod	Diffusion
1	Instantaneous	Rod	Interface
1	Instantaneous	Disc	Diffusion
1-1/2	Instantaneous	Sphere	Diffusion
1-1/2	Homogeneous	Rod	Diffusion
2	Instantaneous	Disc	Interface
2	Homogeneous	Disc	Diffusion
2-1/2	Homogeneous	Sphere	Diffusion
3	Instantaneous	Sphere	Interface
3	Homogeneous	Disc	Interface
4	Homogeneous	Sphere	Interface
≥ 5	Instantaneous	Sheaf	Interface
≥ 6	Homogeneous	Sheaf	Interface

Transformation may be graphically analyzed by plotting the following equation. The Φ is the reduced volume fraction of the material transformed.

$$\log \log(1/(1 - \Phi)) = C + n \log t \quad (2-8)$$

The Avrami exponent, n , is the slope of the straight portion of the line and the rate constant K can be determined from the $t_{1/2}$ and n .

2.4. Crystallization Kinetics of Polybutene-1

The relatively slow crystallization of isotactic polybutene-1 has elicited much interest in its kinetics and mechanism (B-2,C-3, C-4,C-5,C-6,D-2,D-3,E-2,G-2,P-1,S-2). This delayed crystallization has been attributed to the ethyl side groups on every other carbon which create steric hindrance (C-3). Other important factors which may contribute to the slow crystallization are the high molecular weight and the degree of isotacticity. Highly isotactic polybutene-1 requires several days to reach its equilibrium crystallinity. Initial crystallinity after melt processing is approximately 30 to 40% and, after secondary crystallization, rises to about 50 to 60%.

The mechanism of isothermal crystallization of Form II from the melt has been studied by several groups. The experimental observations of Boor and Mitchell were by the appearance of spherulites, formation of peaks in differential thermograms, formation of infrared bands, and dilatometric observation of contraction (B-2).

From experiment they determined an Avrami coefficient of 4.0. This indicates apparently ideal crystallization in which nuclei form at a constant rate throughout crystallization with equal 3-dimensional linear growth. Through dilatometry, Powers, Hoffman, Weeks, and Quinn obtained Avrami exponent values of around 3.2 to 3.8 (P-1). Also by dilatometry, Gordon and Hillier found Avrami exponents close to 3.0 for eight experiments from 97 to 107 °C (G-2). Danusso and Gianotti determined by dilatometry an Avrami exponent of 3.1 (D-2,D-3). These three sets of results indicate equal 3-dimensional growth from instantaneously formed nuclei. The value of n was continually observed to be slightly greater than 3.0 which indicates some degree of sporadic nucleation. By differential scanning calorimetry, Era and Jauhainen determined an Avrami exponent of $n = 2.3$ for the melt to Form II crystallization, which they indicate as heterogeneous nucleation (E-2). This value seems to agree with the values they obtained by x-ray diffraction. However, the preponderance of the experimental evidence indicates three dimensional growth with a combination of instantaneous and sporadic nucleation.

The crystallization temperature dramatically affects the crystallization rate. Gordon and Hillier noted no change in the mechanism when the crystallization temperature was varied (G-2). Boor and Mitchell observed rapid formation of Form II at 95 °C (B-2). The crystallization half-times decreased with decreasing crystallization temperature. The half-times ranged from 380 minutes at 110 °C to less than 0.8 minutes at 62 °C. The rate became very rapid below 100 °C.

Powers, Hoffman, Weeks, and Quinn observed half-times ranging from 2200 minutes at 110 °C to 3.5 minutes at 90 °C. Again there was a marked decrease in half-time around 105 °C. Danusso and Gianotti indicate transformation half-times of crystallization ranging from 3350 minutes at 111 °C to 12 minutes at 98 °C (D-2,D-3).

Several researchers have studied how nucleating agents enhance the crystallization of polybutene-1 (C-4,C-5,C-6,C-7,S-3). Chatterjee found that several moderately active nucleating agents for polybutene-1 were isotactic polystyrene, atactic polystyrene, isotactic polypropylene, polyethylene terephthalate, and aluminum (C-4,C-5,C-6). Chatterjee patented the process of nucleating the crystallization of polybutene-1 using amides and fatty acid amides (C-7). Cortazar studied nucleating agents chosen on the basis of Binsbergen's characteristics of effective nucleating agents (C-8). He chose adipic acid, salicylic acid, p-aminobenzoic acid, sodium benzoate, and sorbic acid. Cortazar suggests, from observation of x-ray diffraction relative peak heights, that the additives do not change the lattice parameters but do influence the crystal growth orientations. All additives enhanced the ultimate crystallinity. Siegmann looked at polypropylene and polybutene-1 blends and the effect on the crystallization temperature (S-3). Polypropylene crystallizes from the melt first and then nucleates the polybutene-1. Hong noted enhancement of the crystallization rate by measuring the temperature of the onset of crystallization (H-10,H-11). He found that 1-naphthalene acetamide and polypropylene significantly enhanced

the onset temperature, while stearic acid and sodium benzoate had little effect.

Stress applied to polymer melts has been noted to affect the rate of crystallization. Haas and Maxwell noted that in polybutene-1 under low shear stress, that the crystallization rate decreases with increasing temperature, while at high shear stress, the crystallization rate increases with increasing temperature (H-7). Wereta and Gogos also noted that the crystallization rate is increased with applied shear stress (W-2).

A few authors have noted that applied pressure enhances the crystallization rate of polybutene-1. Armeniades and Baer report direct crystallization of Form I' above 1000 atm pressure (A-6). Nakafuku and Miyaki determined that pressure accelerated the rate of crystallization (N-7). In fact, they report direct formation of Form I at approximately 910 atm.

2.5. Form II - Form I Crystal-Crystal Transformation Kinetics of Polybutene-1

The Form II - Form I transformation in polybutene-1 is of considerable interest in the processing and ultimate product properties. Studies of the transformation and ways to increase the rate are quite numerous (A-5,A-6,B-2,B-10,B-11,B-12,C-9,C-10,D-2,G-3,G-4,G-5,G-6,G-7,G-8,H-3,H-10,H-11,J-1,J-2,L-2,M-3,N-1,N-7,P-1,P-2,P-3,O-1,R-1,R-2,S-4,S-5,T-1,T-2,W-3). It is well known that the transformation requires from several days to weeks for completion.

Yee and Stein reported that the majority of the transformation occurs within the first 40 hours for unstressed room temperature transformation (Y-2). It is also known that applied stress, additives, and temperature may affect this rate of transformation.

Several researchers have determined an Avrami coefficient for the crystal-crystal transformation. Danusso and Gianotti calculated from dilatometric data a value of around 3.0 which differs from those of other researchers (D-2). They indicate that the transformation occurs in a manner similar to the crystallization. Powers, Hoffman, Weeks, and Quinn determined an Avrami coefficient of around 1.5 to 2.0 for transformation by dilatometry which indicates instantaneous nucleation of discs (P-1). Geil et al. determined an Avrami exponent value of 0.9 indicating instantaneous nucleation followed by linear growth in 1-dimension (G-1). They supported this mechanism with dark field electron microscopy. Their results suggest that several nuclei of Form I develop simultaneously within a tetragonal lamellar ribbon such that several hexagonal crystals arise from one tetragonal crystal. Oda et al. (O-1), Asada et al. (A-5), and Hong and Spruiell (H-10,H-11) also determined Avrami exponents of 1.0, and therefore support the mechanism proposed by Geil (G-1).

The deformation mechanism is of interest when discussing the effect of stress on the transformation. Geil proposes, from a three dimensional x-ray technique, that in fresh samples the molecules perpendicular to the draw direction transform and orient toward the draw direction. Form I crystals are oriented with the c-axis in a

cone of angle 37° around the draw direction. Until transformation was complete the angle remained constant and then decreased dramatically (G-1). Fujita also studied in detail the deformation of polybutene-1 (F-1). He observed preferential orientation of the c-axes by rotation about the b-axes which causes the c-axes to orient toward the draw direction. The mechanism involves intra-lamellar shearing by tilting, detwisting, and micronecking. Lee proposed a model for the cold rolling of polybutene-1 (L-3). For slightly rolled samples, the crystals rotate to bring the c-axes parallel to the roll direction. Further rolling begins to break up the lamellar structure by compression in the normal direction and extension in the roll direction. Ultimately the c-axes are aligned along the roll direction with the a^* -axes aligned with the normal direction. This led to the single crystal texture where the (300) planes became parallel to the rolling plane and the chain axes were parallel to the roll direction. Rolling either fresh or aged samples affects the morphological features equally, however the Form I was less processable than the softer more flexible Form II.

Deformation effects are known to enhance the crystal transformation in polybutene-1. Oda et al. noted a change in the mechanism of transformation, with increased tensile stress or strain, as indicated by a decrease in the Avrami exponent (O-1). Gohil, Miles, and Petermann (G-8) observed that tensile strain seemed to nucleate the transformation. Both these works, along with Geil (G-1) suggest that the tie molecules are strained and thus form several

nuclei along the ribbon. Oda, Maeda, Hibi, and Watanabe also examined the effect of tensile strain on the crystal-crystal transformation (O-1). They observed an increase in transformation rate with increasing tensile strain. Reportedly, at 10 - 20% elongation, polybutene-1 transforms 70% almost immediately. Past 150% elongation the transformation is more rapid than the measurement time. Orientation factors were shown to remain constant when measured at 2 and 20 hours after drawing. Oda et al. indicate that the enhancement is due to stress and not strain. Asada, Sasada, and Onogi report that from 0 to 30% strain orientation and transformation occur. From 30 to 105% strain, crystal transformation predominates while orientation is essentially constant. At greater than 105% strain, the transformation is complete and orientation increases.

Armeniades and Baer suggest that strain energy enhances the transformation mechanism (A-6). They observed that uniaxial stretching increases the rate of transformation. Since the transformation involves a reorganization of the helix to a more extended and dense lattice, they suggest that this creates tensile strains at the interface between the Form II and the Form I matrices. These microscopic strains hinder the continuation of the transformation and densification in undeformed samples by slowing down nucleation and growth. Therefore they suggest that external tensile strain would overcome the internal tensile strains and thus enhance the nucleation and transformation.

Goldbach studied the effect of mechanical stress on the Form II-Form I transformation from -196 to 115 °C (G-3,G-5). Below the temperature for the γ transition (-150 °C) no transformation was observed and brittle fracture occurred. Between -150 and -70 °C brittle-like fracture occurred with transformation occurring on the fracture surface. Between -70 and -20 °C necking occurred and transformation occurred in the necked portion. From -20 up to 70 °C homogeneous deformation and transformation occurred. Since above the yield point shear deformation begins, he believes that shear is the inducing force for the transformation.

Nakafuku and Miyaki studied the effect of pressure on the transformation of Form II to Form I by differential thermal analysis (N-7). They report immediate formation of Form I around 910 atm and Form I' between 1600 atm and 2000 atm. Armeniades and Baer also studied the effect of pressure on the transformation by dilatometry and x-ray diffraction and noted a marked increase in the transformation rate with increased pressure (A-6).

Lee, in his master's thesis at The University of Tennessee, studied the effect of rolling on the transformation rate and the mechanism of deformation (L-3). He found that little orientation was evidenced by wide-angle x-ray film patterns in samples rolled up to 30% reduction; however, the transformation rate was dramatically increased. Hong also examined the effect of cold rolling on the transformation rate (H-10,H-11). He found that even 10% roll reduction significantly increased the crystal transformation rate.

Hong further studied the effect of melt orientation on the transformation rate by film blowing (H-10,H-11). He noted a decrease in the Avrami exponent with increased melt orientation. Increasing the blow up and draw down ratios also increased the biaxial orientation and the transformation rate. This study is the only other known melt orientation research other than the present work. However, for the present work a simple uniaxial melt orientation study was performed such that the effects were more easily quantified.

Researchers have determined that copolymerization, catalyst ash residue, certain additives, etc. may increase the Form II-Form I transformation rate. Siegmann reports that random copolymers of butene-1 and propylene crystallize directly as Form I while block copolymers undergo the Form II-Form I transformation in the polybutene-1 blocks (S-3,S-6). Jones investigated the effect of random copolymers of pentene, propylene, and ethylene with butene-1 monomers (J-1,J-2). These monomers greatly enhanced the crystal transformation rate and in certain cases crystallized Form I directly from the melt. Monomers greater than C_5 and branched comonomers retard the transformation and can even stabilize Form II. This effect is attributed to steric hindrance.

Burns and Turnbull report direct nucleation of Form I from the melt (B-13). In a Phillips resin, the Form II crystallized from large droplets ($> 10 \mu$) at $80^\circ C$ and Form I from small droplets at $71^\circ C$. Another resin (Petro-Tex), from a different manufacturer, exhibited only Form II crystallizing from the melt. They initially attributed

this to lower tacticity of the Petro-Tex sample, but later proved that there were fewer heterogeneities present in that sample to initiate the nucleation of Form I. Clampitt and Hughes report that the degree of catalyst residue in the polymer enhances the transformation rate (C-9). The larger the amounts of ash present in the resin the greater the rate of transformation. They do not, however, attribute this to enhancing the nucleation due to the fact that addition of more such material did not affect the rate.

Boor and Mitchell suggest that the transformation is nucleated by the addition of substances such as isotactic polypropylene, high density polyethylene, stearic acid, and biphenyl (B-13). The atactic noncrystalline polypropylene did not enhance the rate. Apparently the additives act as foreign crystalline surfaces for nucleation of the crystals. Rubin studied the effect of noncrystalline additives on the transformation rate (R-1,R-2). He observed that the α -chloronaphthalene and the diphenyl ether greatly increase the crystal-crystal transformation rate in polybutene-1. This effect is attributed to the ability of the additive to create defects in the structure to aid nucleation and/or to accelerate growth of the stable phase. Hong showed that polypropylene enhanced the transformation rate significantly, while stearic acid and sodium benzoate had only slight effects. The 1-naphthalene acetamide provided no enhancement of the transformation.

The transformation rate is a function of the temperature at which it is carried out. Many researchers have found that the rate for pure polybutene-1 is at a maximum around room temperature, but that maximum is affected by some additives.

Boor and Mitchell followed the transformation by dilatometric contraction over the range of -20 to almost 60 °C (B-12,B-13). For the pure polybutene-1 the maximum rate occurred about 15 °C. Rubin followed the transformation in the range of 20 to 45 °C (R-1). He noted a decrease in the rate with increasing temperature above room temperature. There appears to be a lag in the initiation of the transformation at 45 °C.

Oda et al. studied the phase transformation between -20 °C and 95 °C (O-1). They report a maximum rate up to 60% transformation at 60 °C. Above 60% transformation the rate proceeds fastest about 30 °C. The 100% completion occurs most rapidly at room temperature. They identify two opposing forces to be the reason why room temperature is the ideal transformation temperature. One of these forces is the *Gauche-Gauche* to *Gauche-Trans* transition which causes the intermolecular rotation to be small at low temperature. The other force is the ethyl group's ability to rotate around the helix, which is increased at high temperature.

Gohil et al. suggest that thermal stresses created by the differences in thermal expansion coefficients between phases may enhance the transformation (G-8). Since the stresses may relax more quickly at elevated temperatures, the rate decreases at elevated

temperatures. The rate decreases at low temperatures due to the fact that the differences between thermal expansion coefficients become negligible.

Powers et al. studied dilatometrically the effect of temperature between 10 and 40 °C (P-1). The rate went through a maximum around room temperature. The half-times ranged from 1475 minutes at 10 °C to 1400 minutes at 20 °C and back up to 3900 minutes at 40 °C. Danusso and Gianotti report that half-times ranged from 3850 minutes at 0 °C to 1800 minutes at 20 °C and then increased to 8700 minutes at 50 °C (D-2,D-3).

Boor and Mitchell noted that when 5% polypropylene or 5% stearic acid was added the maximum rate of transformation shifted to about 30 °C (B-12,B-13). Polypropylene and stearic acid both increase the rate above 15 °C but behaved like the parent polymer below 15 °C and above 50 °C.

Boor and Mitchell, Clampitt and Hughes, and Luongo and Hughes all noted an effect of thickness on the rate of transformation (B-13,C-9,L-2). Thinner samples transform more rapidly. This result seems to indicate some effect of the relative amount of surface area per unit volume of material (possibly a surface nucleation effect).

Boor and Youngman report direct formation of Form I' during polymerization by Ziegler type catalysis at -20 °C. These were high molecular weight isotactic polymers (B-11).

Obviously there are numerous variables which may affect the transformation in polybutene-1. Here, it is attempted to resolve the issue of the effect of stress or strain versus orientation, and to determine the mechanisms controlling the effect of crystalline and amorphous additives on the transformation rate.

CHAPTER III

MATERIALS AND EXPERIMENTAL PROCEDURE

3.1. Materials

Shell BR200S isotactic polybutene-1 was utilized in this study of the crystallization and polymorphic transformation. The weight averaged molecular weight is approximately 700,000 with a melt index of 0.4. The degree of isotacticity is between 98.9 and 99.9% and the disordered fraction is randomly distributed. Therefore, this particular resin is highly viscous and retains substantial melt strength. Several additives were blended with the basic resin to determine their effects on the crystallization and transformation. The additives utilized were polypropylene pellets (MI=0.3), 1-naphthalene acetamide powder, carbon black powder, sodium benzoate powder, diphenyl ether liquid, and α -chloronaphthalene liquid. A summary of the blends and their identifying abbreviation appears in Table 3-1.

3.2. Sample Preparation

Blending of the basic resin with the additives was carried out in a Brabender 1/2 inch screw extruder equipped with a mixing screw. This screw provides substantial backflow to enhance the mixing characteristics. First, the additive and BR200S were mixed thoroughly in a glass jar. A master batch with a weight percentage of additive

Table 3-1. Sample Name and Identification

Sample Name	Identification
BR200S	Basic Pure PB-1 Resin MW = 700,000: MI = 0.4
PP5	5.0% (wt.) Polypropylene
PP10	10.0% (wt.) Polypropylene
PP25	25.0% (wt.) Polypropylene
CB05	0.5% (wt.) Carbon Black
CB2	2.0% (wt.) Carbon Black
DPE05	0.5% (wt.) Diphenyl Ether
DPE2	2.0% (wt.) Diphenyl Ether
DPE5	5.0% (wt.) Diphenyl Ether
CN05	0.5% (wt.) α -chloronaphthalene
CN2	2.0% (wt.) α -chloronaphthalene
CN5	5.0% (wt.) α -chloronaphthalene
NA05	0.5% (wt.) Naphthalene Acetamide
NA2	2.0% (wt.) Naphthalene Acetamide
NA5	5.0% (wt.) Naphthalene Acetamide
SB05	0.5% (wt.) Sodium Benzoate
SB2	2.0% (wt.) Sodium Benzoate
SA05	0.5% (wt.) Stearic Acid
SA2	2.0% (wt.) Stearic Acid
SA5	5.0% (wt.) Stearic Acid

greater than that required for the transformation study was made for each blend. This mixture was then extruded at 60 rpm and 175 °C and pelletized. The master batch was then diluted with BR200S to the desired weight percentage and extruded at 20 rpm and 175 °C and chopped into pellets.

Unoriented sheet samples were compression molded on a hot press at 80,000 N force. The mold consisted of an aluminum spacer placed between two ferrotype plates. For each sample, a measured weight (54 g) of polymer was molded to provide a relatively constant sheet thickness (1.02 +/- 0.072 mm). Thus the effect of sample dimension on the crystal transformation was normalized. The hot press platens were heated to 175 °C. A five minute preheat followed by a 15 minute press was the standardized procedure. These samples were used to help understand the effect of additive concentrations on the crystallization and transformation kinetics.

The additive effect on crystallization was examined using differential scanning calorimetry (USDA Perkin Elmer DSC-II). The additive effect on transformation from Form II to Form I and secondary crystallization was followed with wide-angle x-ray diffraction (Rigaku Diffractometer). Compression molded samples were held at 0, 23, 45, and 60 °C to determine the effect of temperature on the transformation rate and enable one to discern the factors controlling the transformation. The samples transformed at 0 °C were aged in a refrigerator, while the samples transformed at 45 and 60 °C were aged in an oven. A new x-ray sample was cut from a large sample held in

the oven or refrigerator for each wide-angle x-ray diffraction measurement. The room temperature sample was simply reused. The samples transformed at 0, 45, and 60 °C were air quenched to their respective aging temperatures, while the 23 °C samples were cooled to room temperature in a water bath at approximately 23 °C.

To determine the effect of melt stress or strain and orientation on the transformation, the Floor Model Instron Capillary Rheometer (TT-C) was used for the spinning of fibers. The barrel temperature was 175 °C. The capillary diameter was 0.736 mm and the L/D ratio was ten. Polymer was packed into the Instron barrel and allowed to preheat for approximately five minutes. The mass flow rate through the die, at 0.508 mm/minute crosshead speed, was measured three times and averaged. This rate was then converted to the extrudate velocity through the use of the polymer density and the cross-sectional area of the die. The take-up motor and controller were calibrated using a strobe light. The take-up velocity is then easily determined with the circumference of the take-up roller. Spin draw ratios (SDR), defined as the ratio of the take-up velocity to the extrudate velocity, were 1, 35, 70, and 105. Fibers were spun through an ice-water bath until a steady spin-line was established, then the sample was collected for one minute. Samples were cut off the roller and clamped into an x-ray sample holder devised to hold the fibers parallel between two metal plates. The transformation was followed with wide-angle x-ray diffraction and when fully transformed the Hermans' chain orientation factor, f_c , was determined utilizing the

fiber orientation program of the Rigaku Geigerflex D/Max-IA diffractometer.

3.3. Wide-angle X-ray Diffraction Analysis

Wide-angle x-ray diffraction was used to follow the Form II-Form I crystal-crystal transformation for films and fibers as well as to determine the chain orientation of the fibers. The methods of data reduction follow.

To track the transformation, the relative integrated intensity of one peak associated with each form was measured over time. In this way the appearance of Form I and disappearance of Form II was recorded. One peak of each form was used to simplify and shorten the analysis to make it a more tractable experimental measurement. The peaks used were the 200 reflection for the Form II and the 110 reflection for the Form I. Figure 3-1 is a typical diffraction pattern which shows the characteristic peaks of Form I and Form II.

The proportional relationship between the integrated intensity and the relative crystal fraction was the basis for calculation of the relative crystallinities. The time dependent relative crystallinities obtained from x-ray diffraction were calibrated using mass density. An isopropanol/water density gradient column was used to measure the density and thus the crystallinity of the fresh samples containing mostly Form II crystallites and aged samples containing Form I crystallites. The crystal fractions were calculated using the following equation derived from rules of mixing.

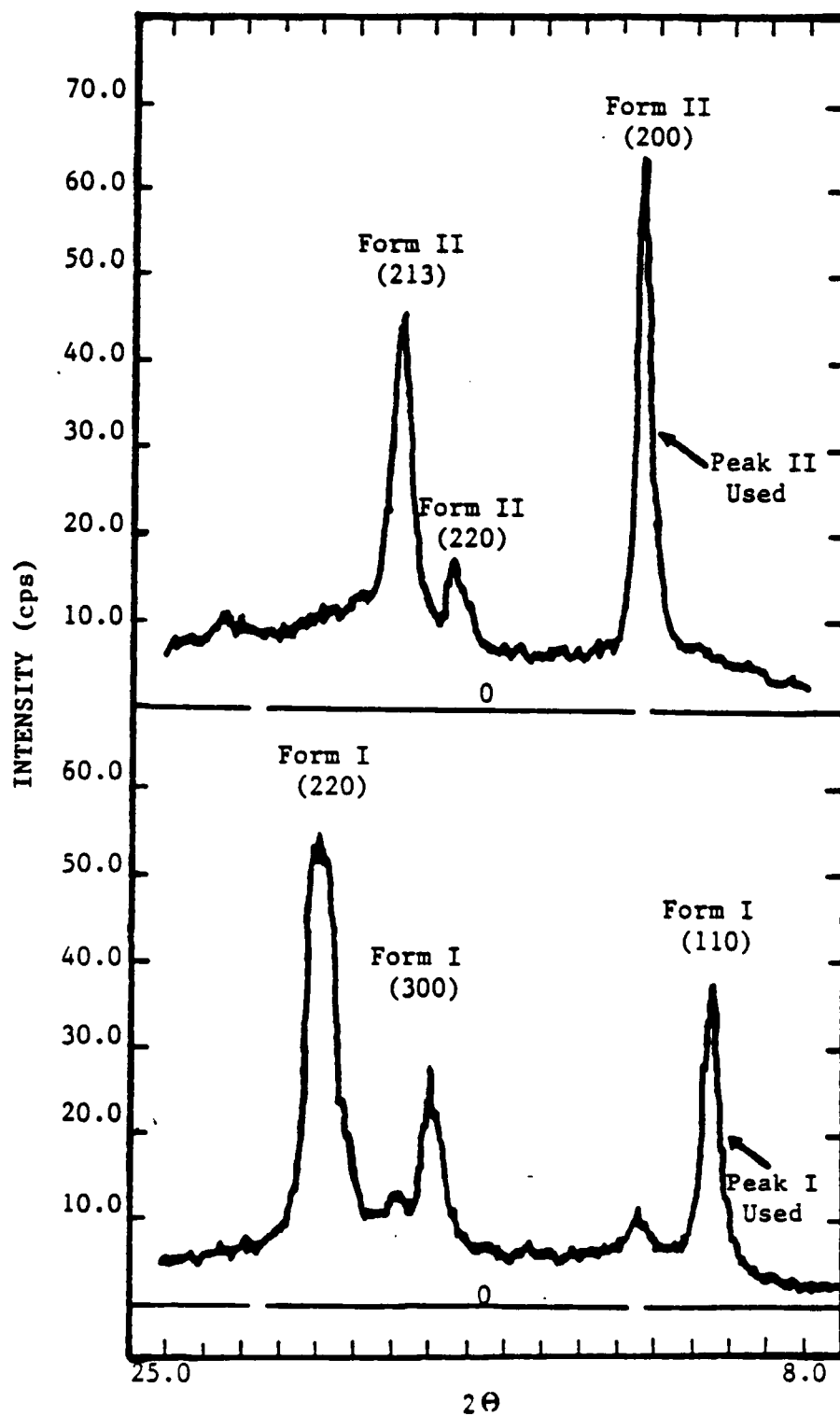


Figure 3-1. Typical Wide-angle X-ray Diffraction Scan of Fresh and Aged Polybutene-1

$$\frac{X_I}{X_I^S} = \frac{I_I}{I_I^S} \quad (3-1)$$

X_I = Relative fraction of Form I

at some time, t

X_I^S = Relative fraction of Form I

in a completely transformed sample

I_I = Integrated intensity of Form I

peak at some time, t

I_I^S = Integrated intensity of completely

transformed sample peak I

X-ray scattering corrections for Lorentz polarization, multiplicity, unit cell volume, and structure factor were made.

$$\frac{X_I}{X_{II}} = \frac{R_{II} I_I}{R_I I_{II}} \quad (3-2)$$

X_{II} = Relative fraction of Form II at some time, t

I_{II} = Integrated intensity of peak II at some time, t

$$R_{II} = \frac{P_{II}}{V_{II}^2} F_{II}^2 \text{ (L.P. II)} \quad (3-3)$$

$$R_I = \frac{P_I}{V_I} F_I^2 \text{ (L.P.I)} \quad (3-4)$$

$$X_c = \frac{\rho_c}{\rho} \left[\frac{\rho - \rho_a}{\rho_c - \rho_a} \right] \quad (3-5)$$

To analyze the data, standard samples of Form II and Form I were used to determine the X_I^s and X_{II}^s (from density) and I_I^s and I_{II}^s (from x-ray). Due to the uncertainty of the atomic positions in the unit cell of Form II and thus F_{II} , these standardized values were used to provide a relative value of R_{II}/R_I . The initial and final values of the relative crystal fractions and diffraction intensities were used as standards, in order to normalize for the mass in the beam and orientation effects on the diffraction pattern. First, the relative fraction of Form I is calculated using Equation 3-1 and then used to determine the relative fraction of Form II from Equation 3-2. These relative phase fractions were also used to express degree of transformation, Φ .

$$\phi = \frac{X_I}{(X_I + X_{II})} \quad (3-6)$$

The volume fraction transformed as a function of time was then analyzed on the Avrami basis as described in Section 2.3. The Avrami equation was analyzed graphically and the values of $t_{1/2}$, K , and n determined per the traditional analysis. Since the Avrami exponent remains approximately equal to one for all the blends and temperatures studied, this value was used consistently such that rate constants could be easily compared on the same basis. Also, the secondary crystallization rate constants were determined per the analysis of Hong and Spruiell (H-10,H-11). The following equation was used to determine the rate constant K from the x-ray diffraction results for the crystal fractions.

$$X_T = X_0 + k \log(t - t_0) \quad (3-7)$$

Wide-angle x-ray diffraction was also used to determine the Hermans' orientation factor, f_c , of the spin drawn fibers after the transformation was complete. A Wilchinsky analysis on the 110 reflection of Form I yields a very simple equation for f_c . The Wilchinsky analysis begins with the following equation (A-1):

$$\begin{aligned} \langle \cos^2 \phi_{110,z} \rangle &= e^2 \langle \cos^2 \phi_{u,z} \rangle + f^2 \langle \cos^2 \phi_{v,z} \rangle + g^2 \langle \cos^2 \phi_{c,z} \rangle \\ &+ 2ef \langle \cos \phi_{u,z} \cos \phi_{v,z} \rangle + 2fg \langle \cos \phi_{v,z} \cos \phi_{c,z} \rangle \\ &+ 2eg \langle \cos \phi_{c,z} \cos \phi_{u,z} \rangle \end{aligned} \quad (3-8)$$

Selected terms can be cancelled by simplifications due to unit cell geometry and the diffraction planes used. Since the Form I unit cell is hexagonal and the diffraction plane is the (110), the following terms are cancelled (A-1).

1) All cross product averages are zero

$$2ef\langle\cos\phi_{u,z}\cos\phi_{v,z}\rangle = 0$$

$$2fg\langle\cos\phi_{v,z}\cos\phi_{c,z}\rangle = 0$$

$$2eg\langle\cos\phi_{c,z}\cos\phi_{u,z}\rangle = 0$$

2) $g = 0$

Equation 3-8 then simplifies to:

$$\langle\cos^2\phi_{110,z}\rangle = e^2\langle\cos^2\phi_{u,z}\rangle + f^2\langle\cos^2\phi_{v,z}\rangle \quad (3-9)$$

From the geometry shown in Figure 3-2, the values of e and f may be obtained.

$$e = \cos\phi_{u,n} = \cos(30^\circ) = \sqrt{3}/2 \quad (3-10)$$

$$f = \cos\phi_{v,n} = \cos(60^\circ) = 1/2 \quad (3-11)$$

From these values of e and f , $\langle\cos^2\phi_{110,z}\rangle$ is calculated. Finally Equation 3-9 reduces to the following:

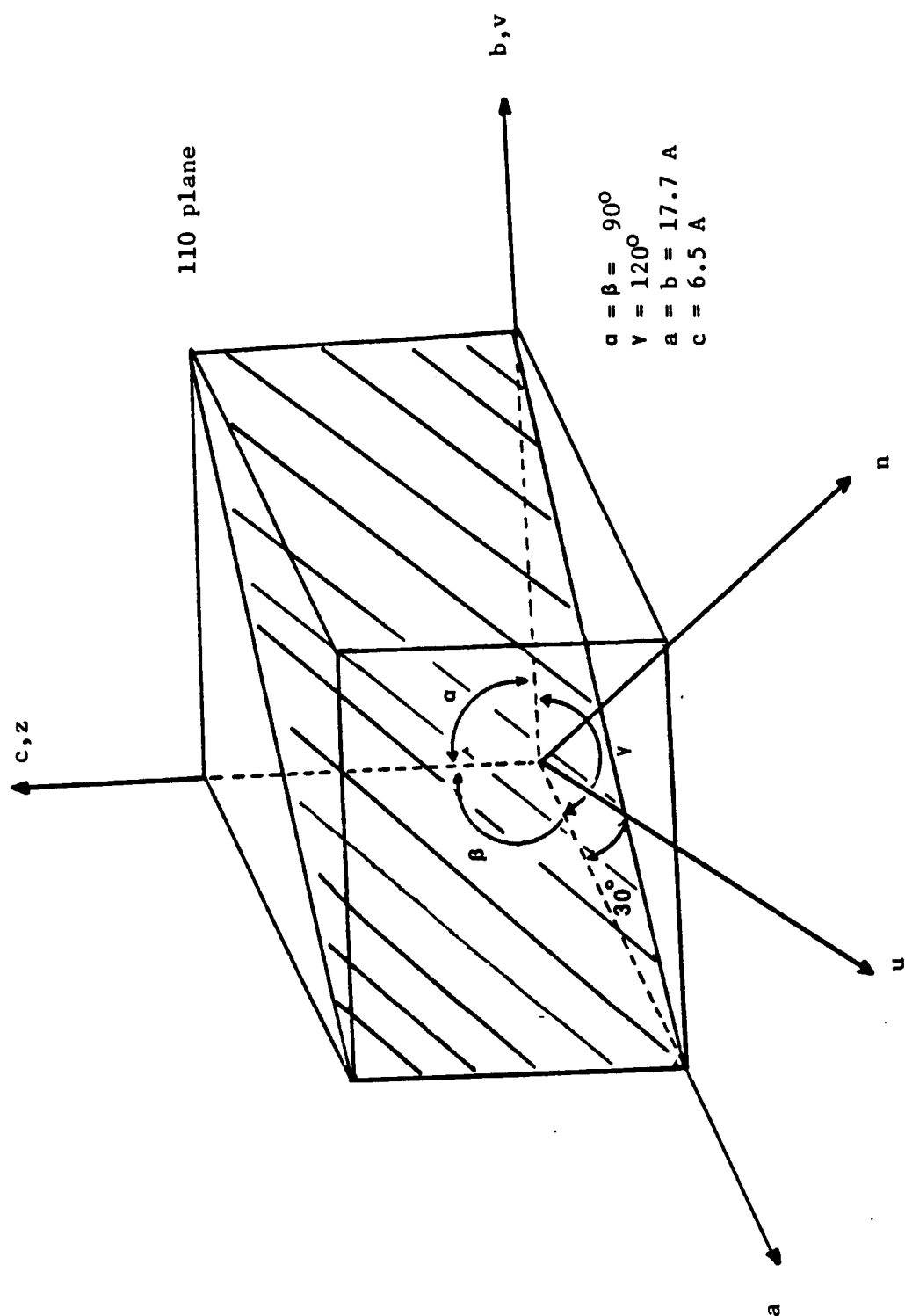


Figure 3-2: Geometry of the PB-1 (110) Plane for the Wilchinsky Analysis of Orientation

$$\langle \cos^2 \phi_{c,z} \rangle = 1 - 2 \langle \cos^2 \phi_{110,z} \rangle \quad (3-12)$$

The Hermans' chain orientation factor is defined as follows.

$$f_c = \frac{3 \langle \cos^2 \phi_{c,z} \rangle - 1}{2} \quad (3-13)$$

Substituting Equation 3-12 into 3-13 f_c now becomes the following:

$$f_c = \frac{3(1 - 2 \langle \cos^2 \phi_{110,z} \rangle) - 1}{2} \quad (3-14)$$

Equation 3-14 can be further simplified to obtain:

$$f_c = 1 - 3 \langle \cos^2 \phi_{110,z} \rangle \quad (3-15)$$

Therefore, with only one diffraction plane (110) the Hermans' orientation factor can be determined from Equation 3-15. The $\langle \cos^2 \phi_{110,z} \rangle$ values are obtained from experimental diffracted intensity data for the (110) plane ($2\theta = 10.8^\circ$) as a function of the azimuthal direction from 0° to 90° . The expression for calculation of $\langle \cos^2 \phi_{110,z} \rangle$ from this intensity data is the following:

$$\cos^2 \phi_{110,z} = \frac{\int I \sin \phi_{110,z} \cos^2 \phi_{110,z} d\phi}{\int I \sin \phi_{110,z} d\phi} \quad (3-16)$$

This equation may be approximated by replacing the integrals with the following summations.

$$\langle \cos^2 \phi_{110,z} \rangle = \frac{\sum_{\phi=0}^{90} I \langle \sin \phi_{110,z} \rangle \langle \cos^2 \phi_{110,z} \rangle}{\sum_{\phi=0}^{90} \langle I \sin \phi_{110,z} \rangle} \quad (3-17)$$

3.4. Differential Scanning Calorimetry Analysis

One simple, widely used measurement of the crystallization rate is that of measuring the onset temperature of crystallization. This technique was used to determine the effect of additives on the crystallization rate of polybutene-1. If the crystallization temperature, T_c , is increased by the presence of additives, the crystallization rate is also assumed to be increased since crystallization begins at an elevated temperature in the cooling cycle. Utilizing the Perkin-Elmer DSC-II the sample weight, heating rate, cooling rate, and annealing time were held constant. Sample weights were approximately 7.0 milligrams. The thermal cycle was from 27 to 160 °C with heating and cooling rates of 20 degrees per minute.

Samples were held for five minutes at 160 °C before the cooling cycle began. The DSC-II data station software was used to determine the crystallization temperature and heat of transformation in an unbiased manner.

3.5. Small-angle X-ray and Light Scattering Analysis

It is known that about 36 hours after molding and approximately 75 percent transformation, isotactic polybutene-1 becomes hazy and less translucent. Some researchers have suggested that the reduced light transmission is due to microvoid formation (G-1). In an attempt to study this phenomenon, the transformation was followed over time using small-angle x-ray and small angle light scattering.

For the laser light scattering experiment a 0.25 mm thick sample of water quenched compression molded film was mounted on a glass slide and covered with immersion oil to prevent surface scattering. A schematic of the light scattering set-up appears as Figure 3-3. The apparatus consists of laser light source, polarizer, two pin hole collimators, sample holder, analyzer, and film holder. Polaroid film patterns were taken over a period of several days.

The small-angle x-ray scattering experiment was performed on water quenched compression molded polybutene-1 sheet. The NCSASR 10 m SAXS facility at Oak Ridge National Laboratory was used in this study. A schematic of the apparatus appears as Figure 3-4. A Rigaku rotating anode x-ray source at 20 kV and 20 mA collimated by one millimeter square pinholes provided the radiation for the experiment. The

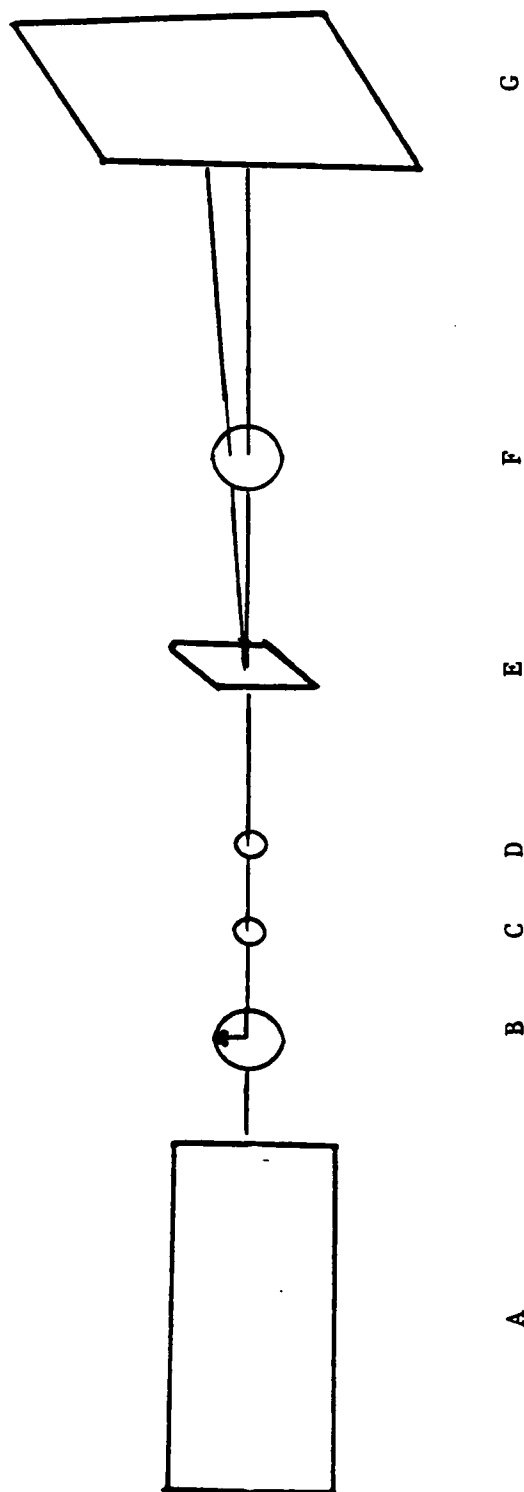


Figure 3-3. Schematic Small-angle Laser Light Scattering Experimental Apparatus, A) Laser B) Polarizer C) First Pinhole Collimator D) Second Pinhole Collimator E) Sample F) Analyzer G) Film

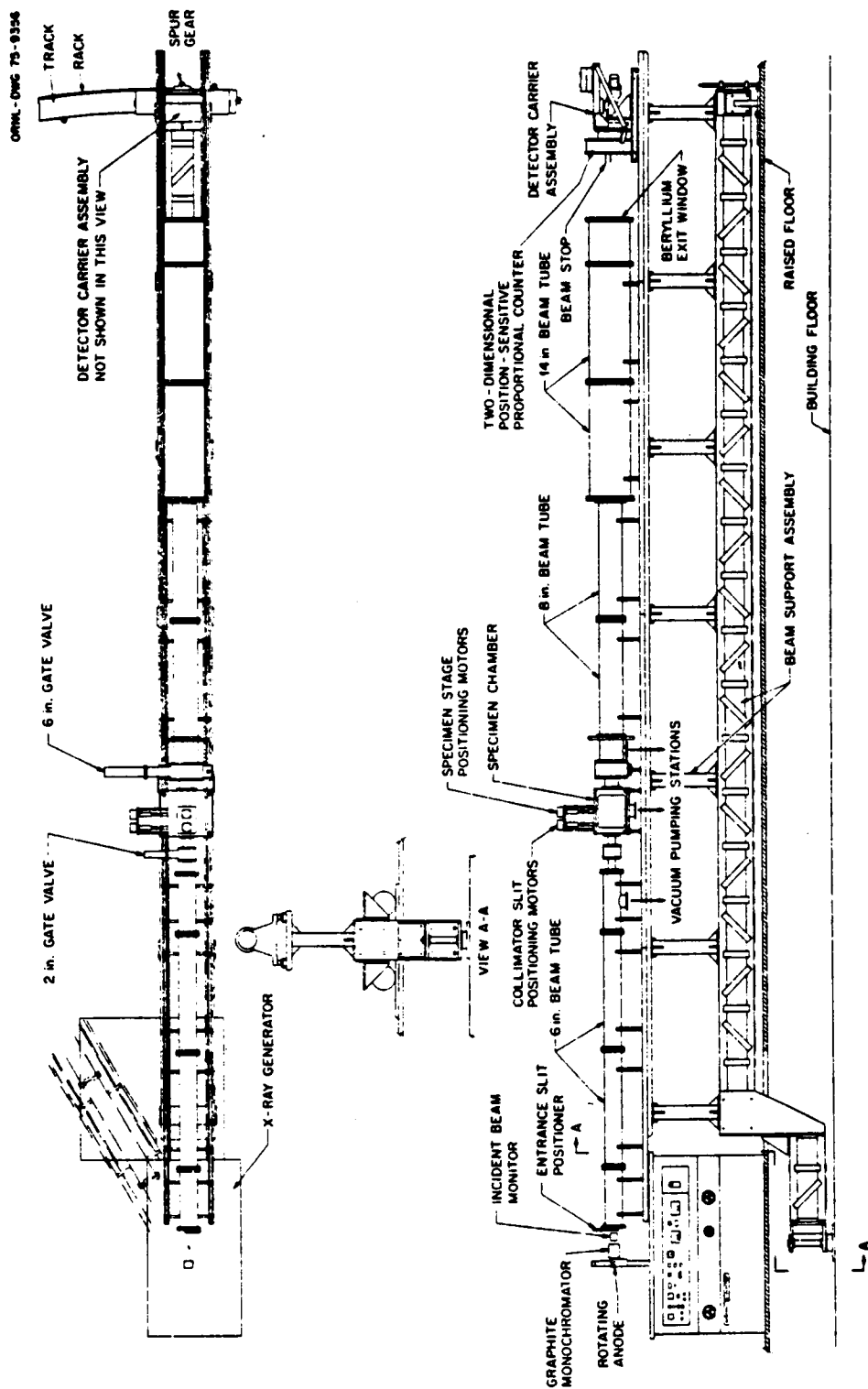


Figure 3-4. Schematic Small-angle X-ray Scattering Experimental Apparatus (H-12)

two-dimensional position sensitive detector provides quantitative scattering data. The sample to detector distance was 5.126 meters. A scattering pattern was taken in increments of three hours for several days. These data were corrected for cosmic radiation, parasitic scattering and detector sensitivity. Guinier analysis was used to determine the average radius of gyration of the scattering centers.

3.6. Mechanical Property Measurement

The tensile mechanical properties were measured via the Table Model 1122 Instron Tensile Tester. The cross head speed was 20 mm/min. Tensile bar samples were cut with an ASTM standard dog bone punch of 25.4 mm gauge length, 6.35 mm width, and sample thickness of about 1.0 mm. Young's modulus, 2% offset yield strength, percent strain at break, and ultimate tensile strength were calculated according to the standard procedures which utilize the original value of cross-sectional area in the calculations (engineering stress).

CHAPTER IV

RESULTS AND DISCUSSION

At The University of Tennessee, there have been prior research projects by Hong, Lee, and Spruiell on the effects of cold rolling, film blowing, and additives on the crystallization and transformation kinetics of isotactic polybutene-1. Both Hong and Lee noted that very small amounts of cold rolling increased the rate of transformation. Lee found little orientation evidenced at even 30% roll reduction. Also noted by Hong was that increasing the blow-up ratio and draw-down ratio in blown films enhanced the transformation rate. Presumably these effects are a result of stress or strain and orientation. Hong also studied the effect of blending polypropylene, sodium benzoate, stearic acid, and 1-naphthalene acetamide with polybutene-1 on the crystallization and transformation rate at room temperature.

The present study extends the work of Hong to uniaxial melt orientation by melt spinning. Blending additives other than the crystalline substances used by Hong, and studies of the transformation rate over an expanded temperature range are other topics of interest in this work. The ultimate purpose of this research was to provide insight into the relative effects of stress or strain, molecular orientation, and selected additives on the crystallization and the Form II-Form I transformation in isotactic polybutene-1.

4.1. Structure Development During Crystallization and Transformation in BR200S

4.1.1. Initial Development of Crystallinity

Polybutene-1 crystallizes relatively slowly in comparison to other olefins such as polypropylene and polyethylene. Substantial supercooling occurs prior to the onset of crystallization. Figure 4-1 shows a typical crystallization curve for the BR200S resin. The onset of crystallization, for a 20 °K per minute cooling rate, occurred at 67 °C which is about 60 degrees below the melting temperature of Form II. Based on the amount of heat dissipated during the crystallization, there is about ten percent crystallinity present immediately after cooling to room temperature. The crystallinity subsequently increases rather rapidly to about 30 to 40 percent. Values in the latter range are generally found by the earliest measurements made on solidified samples using techniques such as density or WAXS. A slow secondary crystallization stage follows and the crystallinity attains an asymptotic value of about 60% over an extended period of time at room temperature. This slow secondary crystallization has been noted by numerous researchers. In fact these same ranges of values have been noted by Hong, Lee, Choi, and Chatterjee (H-10,H-11,L-3,C-2,C-3).

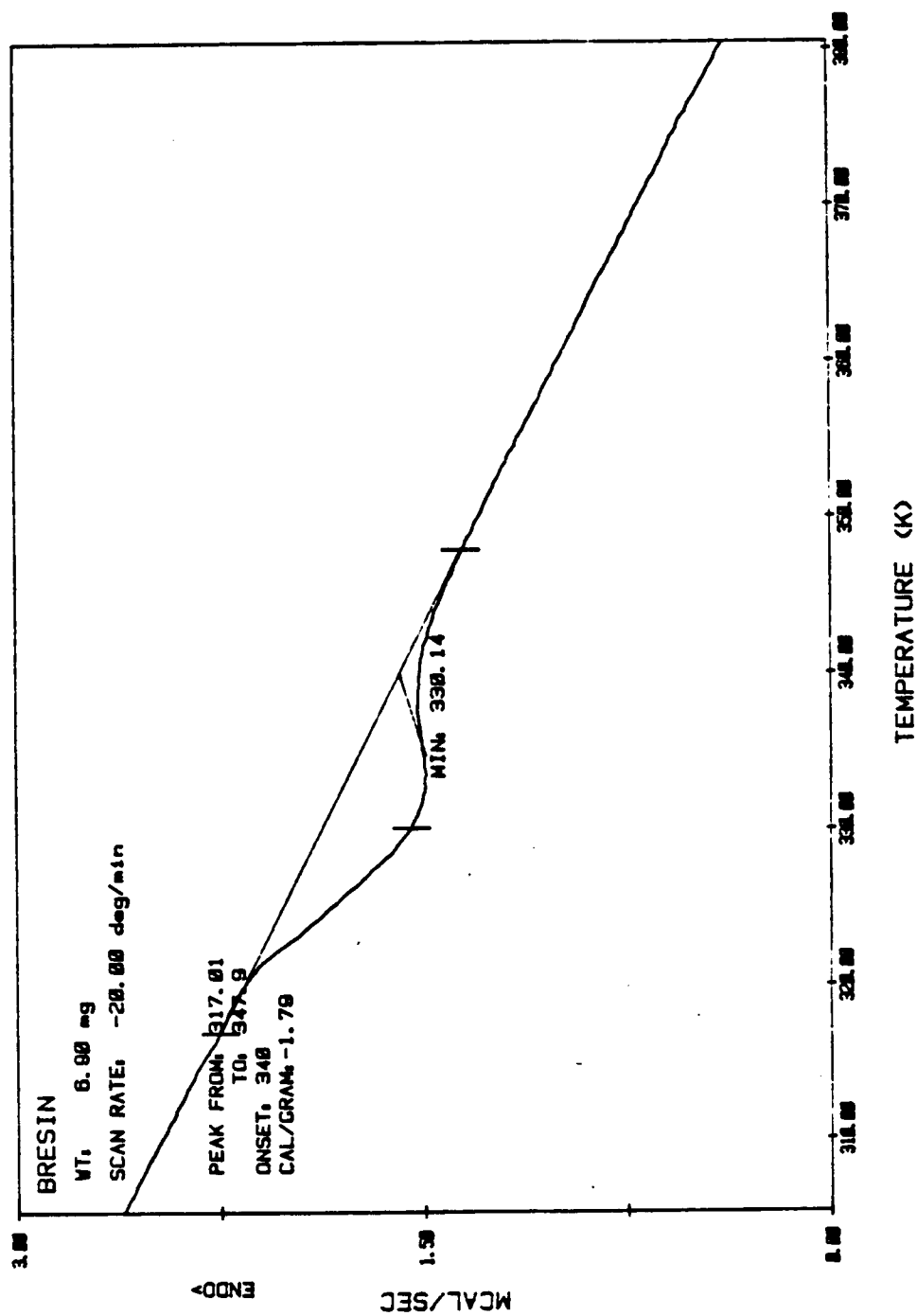


Figure 4-1. Differential Scanning Calorimetry Cooling Curve for BR200S Resin.

4.1.2. Secondary Crystallization and Transformation

The crystal-crystal phase transformation and secondary crystallization occur simultaneously. There are many mechanisms and combinations of mechanisms by which this might occur. Form II may continue to crystallize from the amorphous phase and subsequently transform to Form I or, just as thermodynamically possible, the Form I may crystallize directly from the amorphous phase. There also may be a mechanism by which the Form II and Form I crystals undergo a rearrangement to more perfect crystals. Hong and Spruiell modelled the first two possibilities and determined that their experimental data best fit the case of Form I crystallizing directly from the amorphous phase, but do not rule out the formation of Form II from the amorphous phase (H-10,H-11).

Since transformation and secondary crystallization occur simultaneously, consideration must be given to how these effects are distinguished. Typically the transformation has been followed by measuring the volume fraction of the crystal that has transformed to Form I as seen in Figure 4-2. The volume fraction of the crystal transformed over time shows qualitatively that there is a global transformation occurring and a relative rate, but not that there are several contributions to this transformation occurring simultaneously. For the BR200S samples, the maximum rate of transformation occurred in the range of room temperature. When the temperature was varied above and below room temperature a marked decrease in transformation rate was noted. A more complete way to follow the transformation,

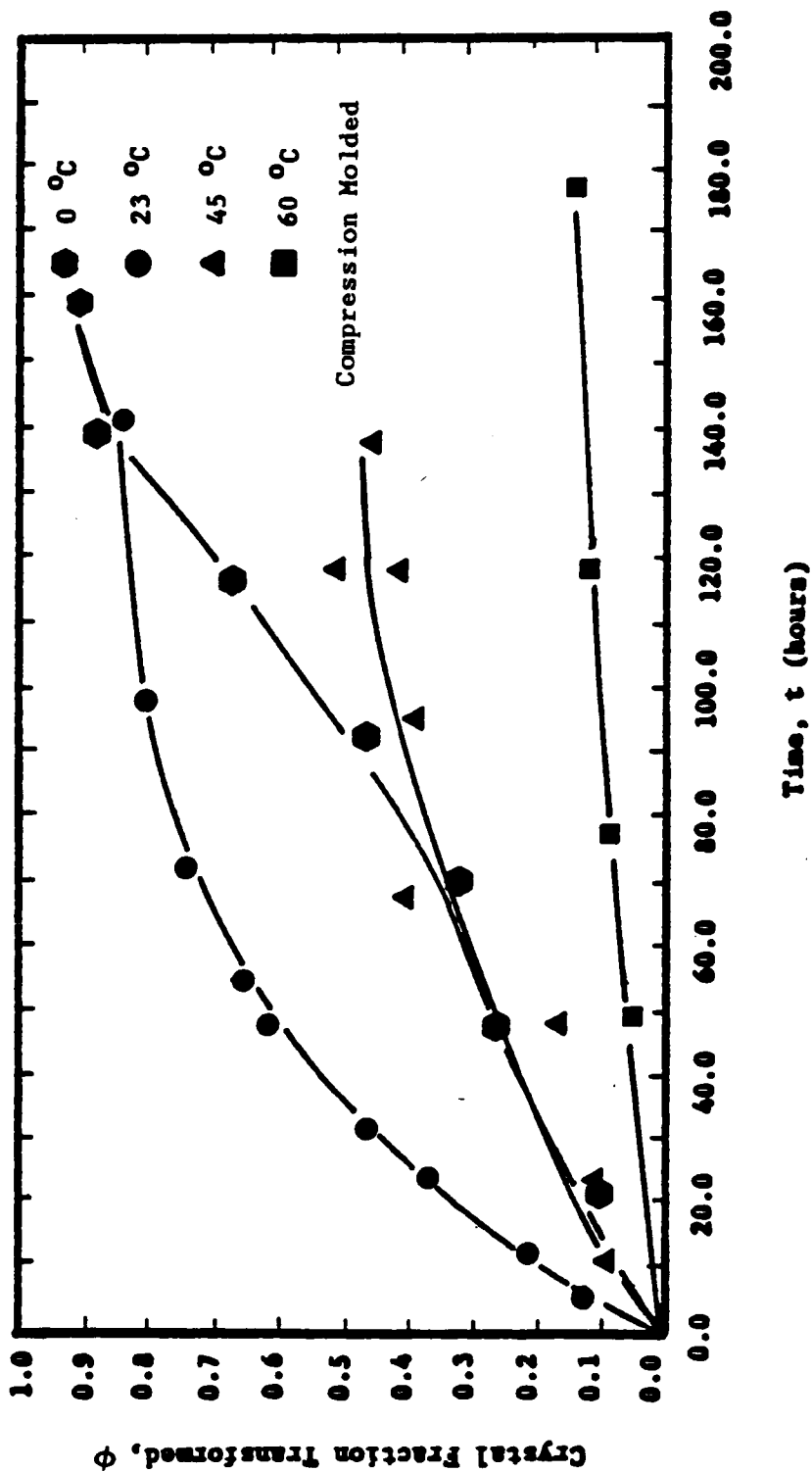


Figure 4-2. Volume Fraction of the Crystal Transformed Over Time for BR200S at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C

developed and used by Hong and Spruiell (H-10,H-11), measures the total crystal fraction as well as the individual contributions of the Form I and Form II fractions. A typical plot of these crystal fractions for BR200S at 23 °C appears as Figure 4-3. In this way one sees both the amorphous-crystal and crystal-crystal phase transformations simultaneously. Although this method is more informative for most situations, to show the relative rates of transformation at each temperature the former method will be utilized.

Small-angle light scattering (SALS) was used to examine the development of structure and possible microvoids upon transformation. During secondary crystallization and transformation, an interesting change in the H_V small-angle scattering pattern was noted. Small-angle light scattering film patterns of the initially formed and quenched BR200S film revealed a four lobed H_V pattern very typical of spherulitic structures. After about 24 hours the pattern became less distinguishable. Still there was a four lobed structure, but less defined. After 48 hours the four lobe pattern was completely indistinguishable. Figure 4-4 illustrates the change in the film pattern over a period of 48 hours. Apparently, the spherulites formed initially as separate, distinguishable entities. This eventual obstruction of the four lobe pattern may be due to the addition of scattering from new sources. Several researchers believe that microvoids may develop upon lateral contraction during transformation (G-1,P-1). These voids may be on the order of the wavelength of light and thus account for the new scattering and the haze developed in the

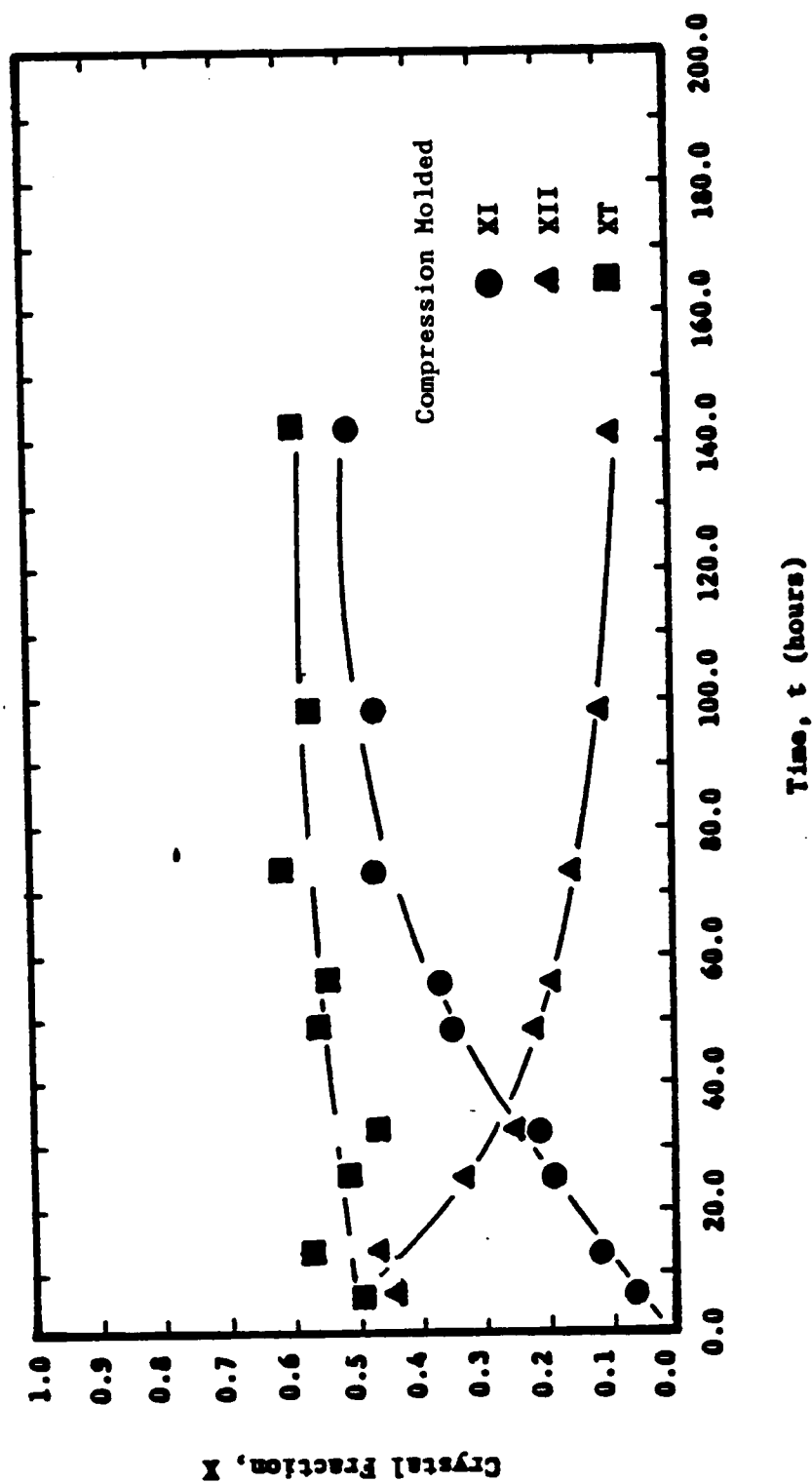
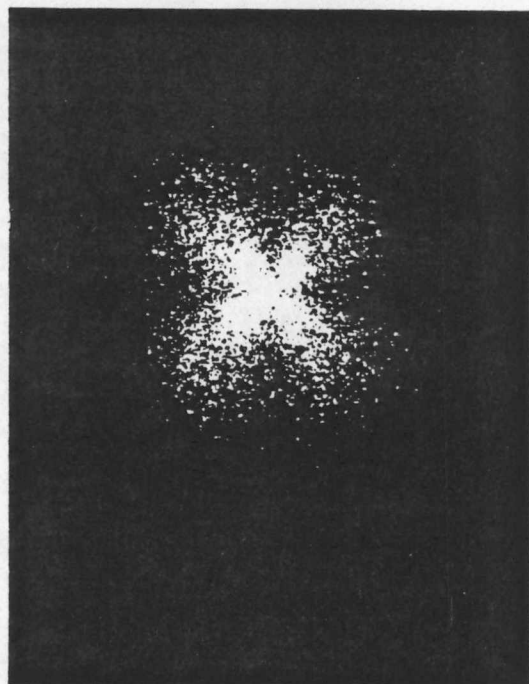
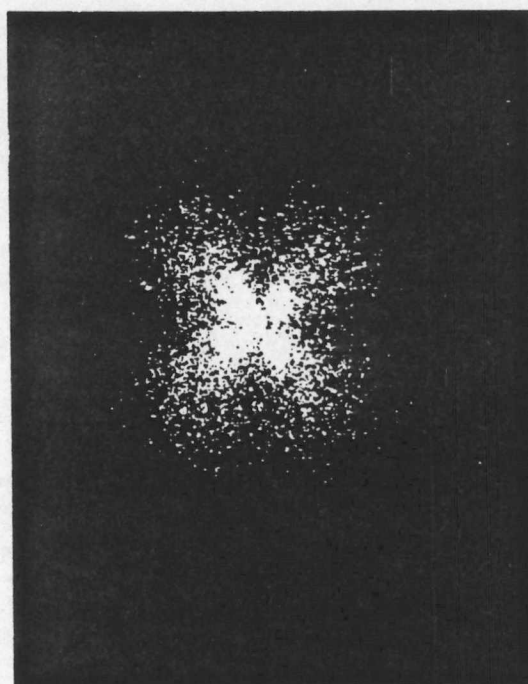


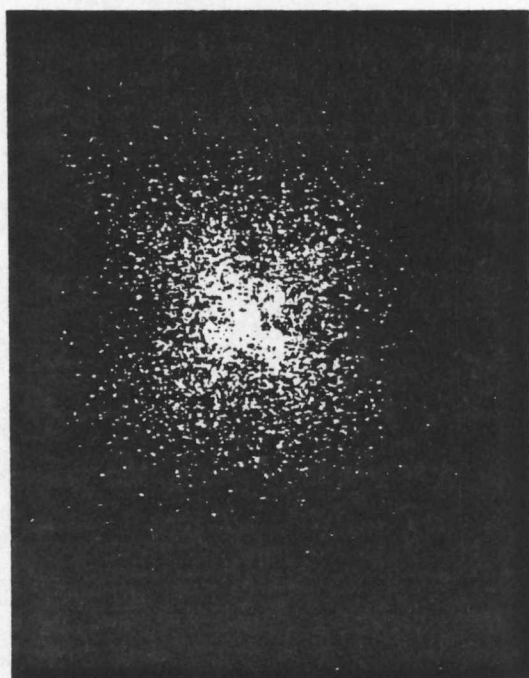
Figure 4-3. Crystal Fraction Present as a Function of Time for BR200S at 23 °C



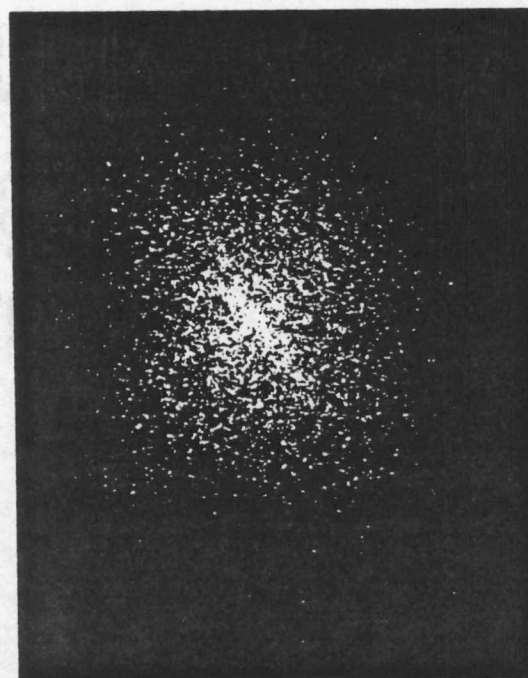
(A)



(B)



(C)



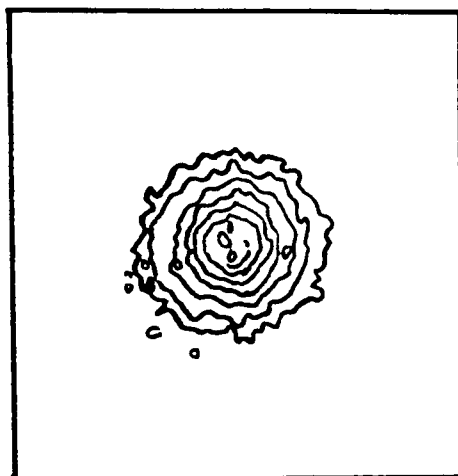
(D)

Figure 4-4. Small-angle Laser Light Scattering Film Patterns of BR200S Water Quenched Film Over a Period of Days: (A) 0.5 hours (B) 6.0 hours (C) 24.0 hours (D) 48 hours

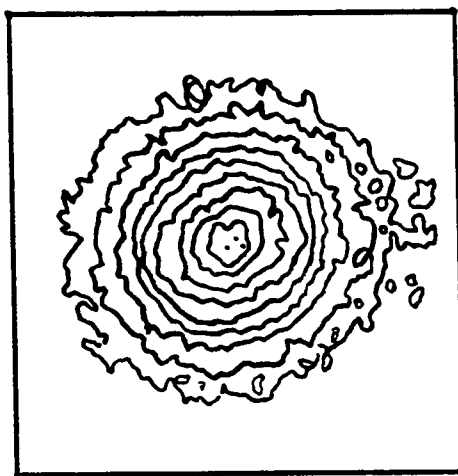
sample. Also to be considered here is the possible contribution by interference of overlapping spherulites and multiple scattering due to film thickness and increased crystallinity.

Small-angle x-ray scattering (SAXS) patterns of the compression molded samples showed that the diffuse isotropic scattering occurred from entities with sizes distributed around an average radius of gyration of 163 Å as calculated using Guinier analysis. Over time the radius of gyration decreased to 144 Å at 72.5 hours. The diffuse scattering intensity also increased due both to the increased crystalline-amorphous density difference, increased crystallinity, and possible void formation during the transformation. Scattering patterns from a fully aged sample contained a large well developed interference peak in the scattered intensity function. Figure 4-5 shows the two-dimensional contour plots for fresh, aged 72.5 hours and fully aged samples of polybutene-1. Figure 4-6 contains the radially averaged intensity plots with a summary Kratky plot which shows more graphically the long period development. From this Kratky plot the long period spacing may be calculated. It is observed that during the time between three days and several months, the long period spacing of approximately 230 angstroms becomes well developed.

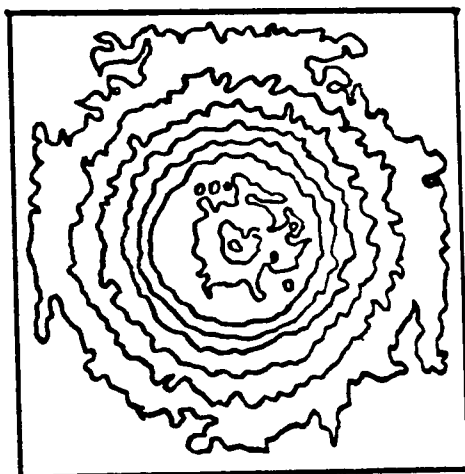
The possibility of microvoid formation upon crystal transformation in polybutene-1 can be investigated by a SAXS invariant analysis. Kratky and Milholic (K-2) show that the scattering power, Q/V , of a two phase system is proportional to the relative volume fraction of phases and their electron density difference.



(A)



(B)



(C)

Figure 4-5. Small-angle X-ray Scattering Patterns of BR200S
(A) 0.5 hours, (B) 72.5 hours, (C) months

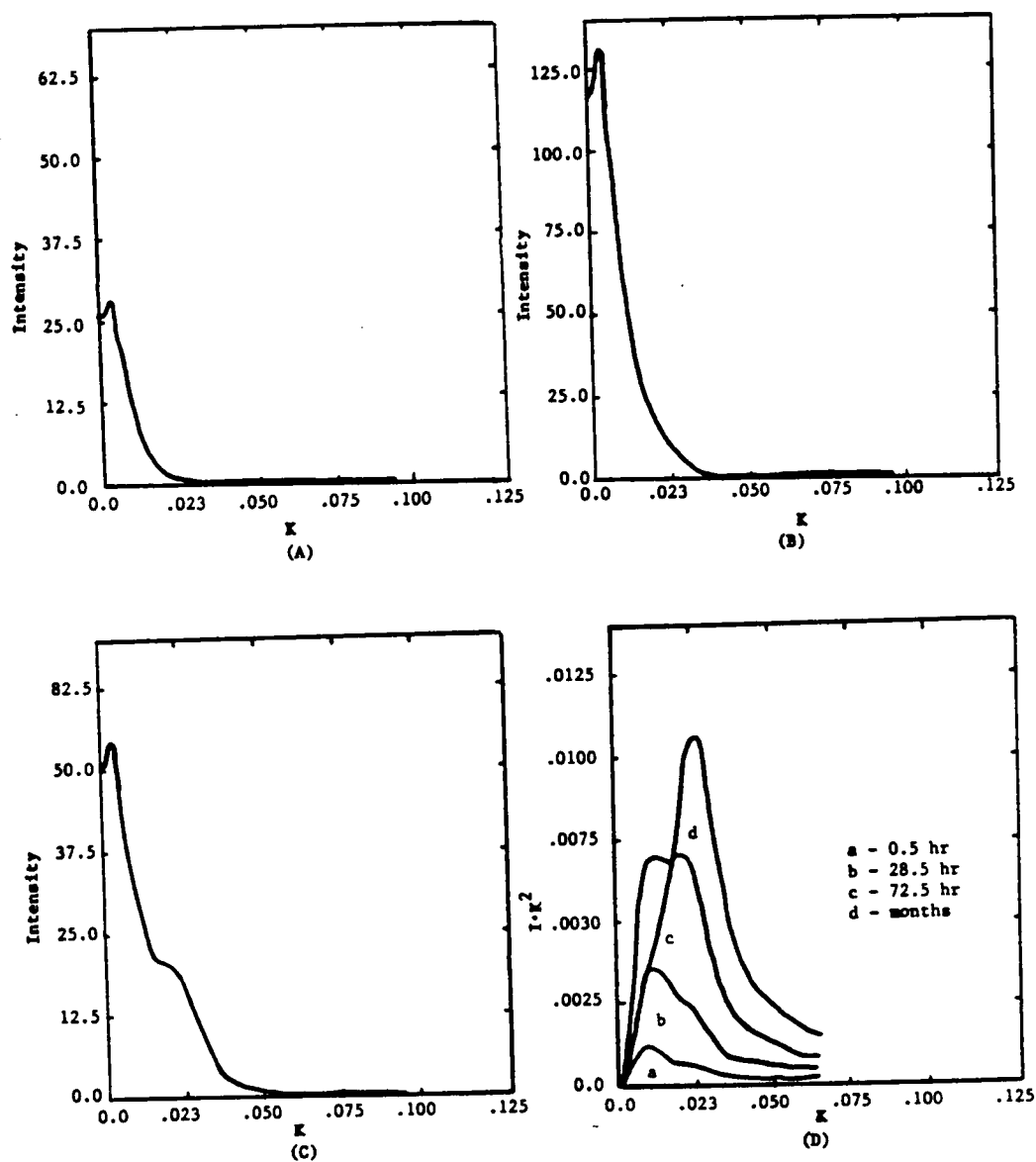


Figure 4-6. Small-angle X-ray Scattering Intensity as a Function of Scattering Vector for BR200S Water Quenched Films Over Several Months (A) 0.5 hours (B) 72.5 hours (C) months (D) Kratky Summary Plot .

$$Q = (\Delta\rho)^2 \phi_1 (1 - \phi_1) V \quad (4-1)$$

$\Delta\rho$ = electron density difference between phases

ϕ_1 = Volume fraction of phase 1 (eg. crystallinity)

$1 - \phi_1$ = Volume fraction of phase 2

Table 4-1 summarizes the calculated and observed invariants for fresh, aged 72.5 hours and fully aged samples. It can be shown, from a theoretical basis, that the crystal densification from Form II to Form I combined with secondary crystallization from 50 to 60 percent (see Section 4.2.2) will cause the scattering invariant to increase by a factor of 6.4. The observed scattering invariant increase between Figures 4-5 A and C is equal to 7.9

Thus the observed scattering power increase is not strictly accountable on the basis of crystal transformation alone, and therefore the formation of a third phase is likely. This third phase is interpreted as microvoid formation due to reorganization of the crystalline structure.

Depending on the void fraction, the crystal fractions obtained through mass density techniques may be altered. Therefore, the void fraction was estimated based on the excess scattering invariant and the density difference between the bulk polymer and the voids. A void fraction of no greater than 0.04% was determined. The error in density from voids present in this percentage would be 0.5%.

Table 4-1. Invariant Analysis Based on a Two Phase Scattering Model

Aging Time	$(\Delta\rho)^2 \phi_1 (1 - \phi_1)$ Calculated (Eu/cm ³) ²	Theoretical Invariant Increase (%)	Q Observed (Eu/cm ³) ²	Observed Invariant Increase (%)
0.5 hr	8.25×10^{-5}	0	8.06×10^{-5}	0
72.5 hr	-	-	46.7×10^{-5}	570
months	52.8×10^{-5}	640	63.3×10^{-5}	790

Therefore, as determined by small-angle x-ray scattering, the void fraction determined has little effect on the crystallinity determined using mass density techniques.

4.2. Effect of Additives on the Crystallization and Transformation Kinetics

4.2.1. Initial Crystallization Kinetics as Affected by Additives

Certain additives have been found to increase the rate of crystallization as well as the total crystallinity. As measured using differential scanning calorimetry, the crystallization onset temperature was correlated to the crystallization rate. The cooling curves obtained showed exotherms of different natures. Figures 4-7 and 4-8 represent two typical types. Further data for other additives appear in Figures A-1 through A-5 on pages 144 through 148. Compared to the basic resin, the PP10 blend exhibits a sharper and larger peak which indicates that crystallization occurred over a smaller temperature range and that the crystal fraction was increased over the BR200S. In contrast, the DPE5 blend shows a broader and smaller peak indicating less enhancement of the crystallization. Table 4-2 contains all of the crystallization onset temperatures of the different blends. At a 20 °K per minute cooling rate, the 1-naphthalene acetamide, carbon black, and polypropylene blends were the most effective at enhancing the crystallization rate. However, the diphenyl ether, α -chloronaphthalene, sodium benzoate, and stearic acid blends were somewhat less effective.

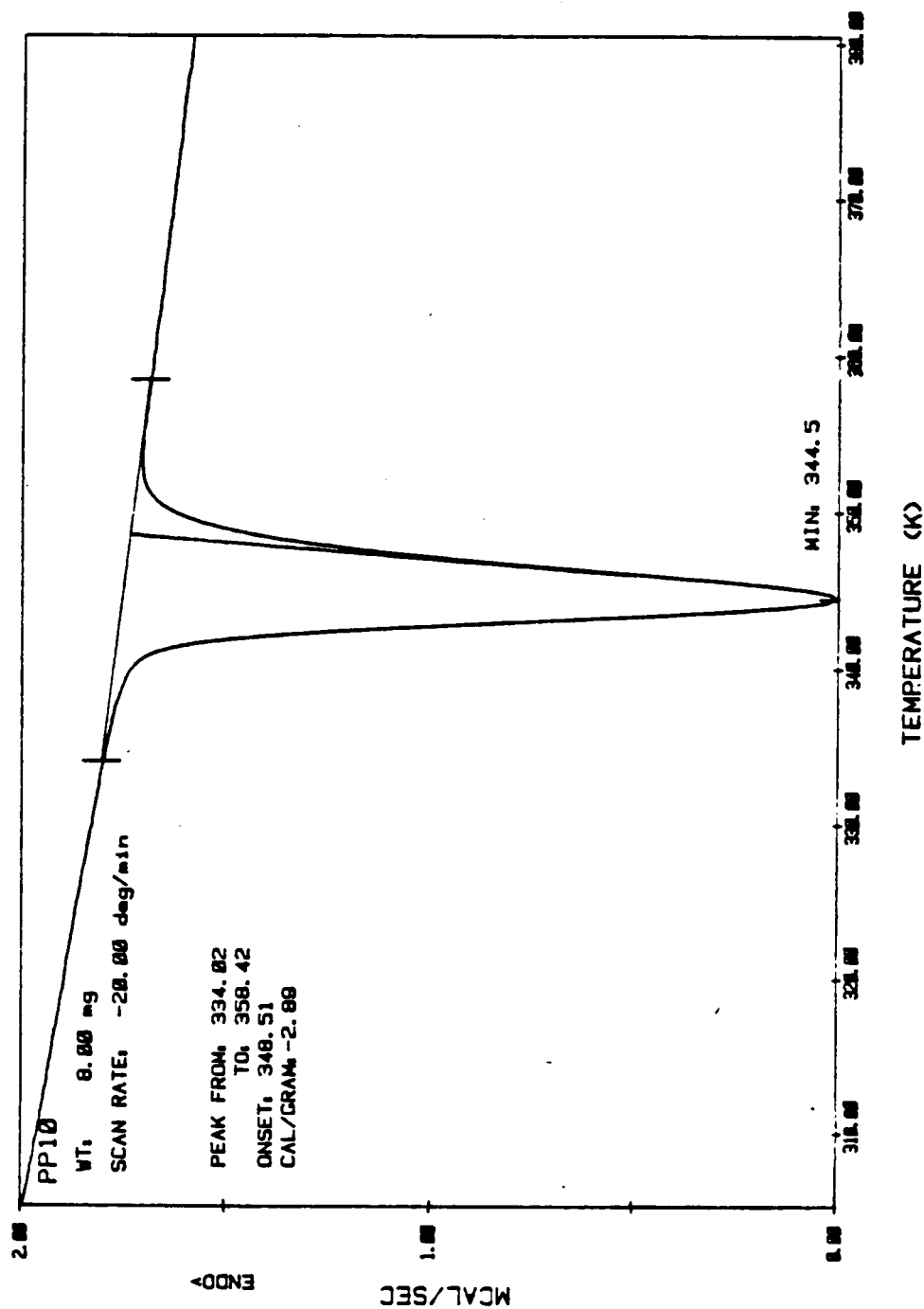


Figure 4-7. Differential Scanning Calorimetry Cooling Curve for the PP10 Blend

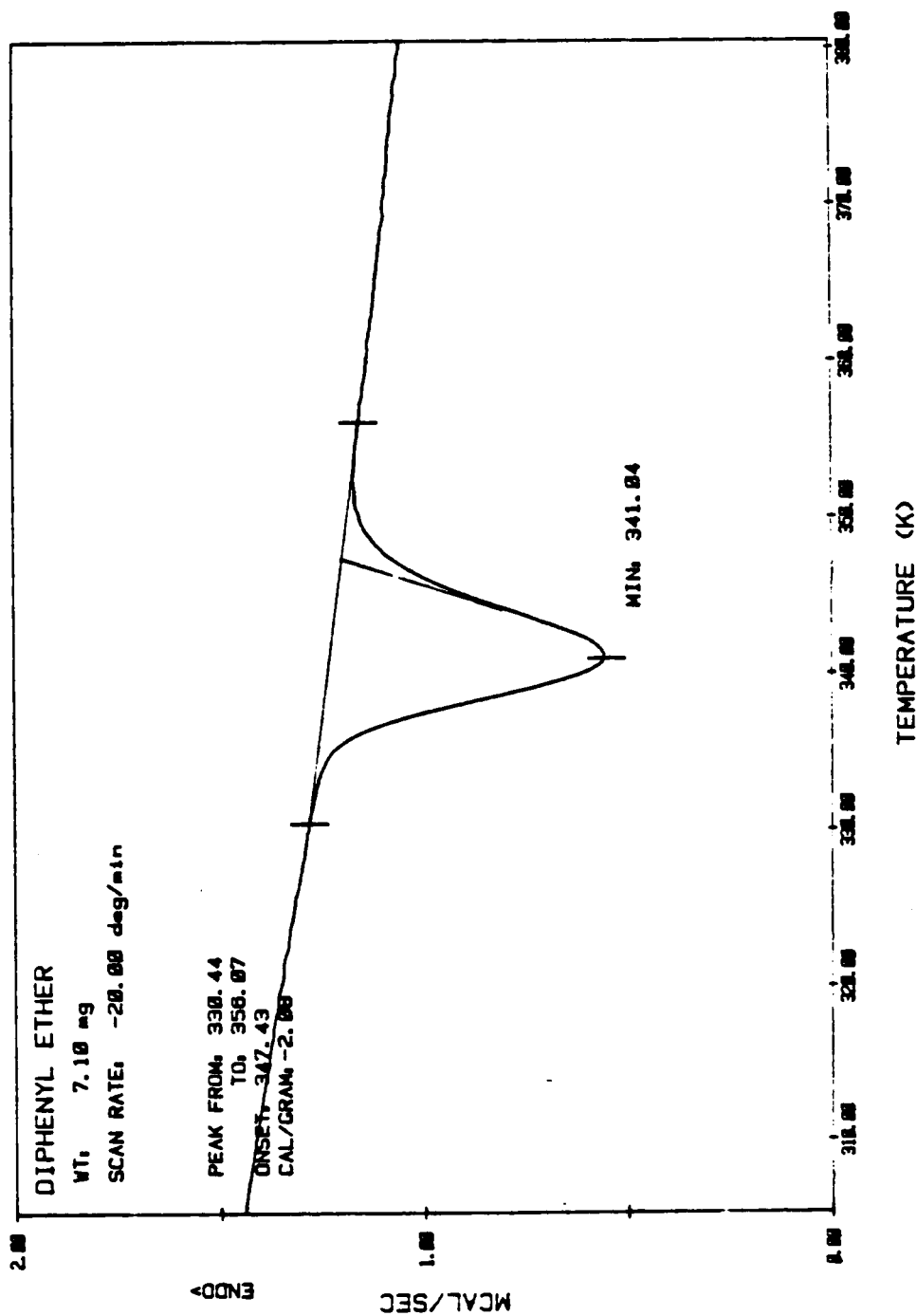


Figure 4-8. Differential Scanning Calorimetry Cooling Curve for the DPE5 Blend

Table 4-2. Crystallization Temperatures for BR200S Blends

Sample	$T_c, ^\circ\text{C}$	$T_{mI}, ^\circ\text{C}$	$T_{mII}, ^\circ\text{C}$
BR200S	67	111	108
PP5	74	114	108
PP10	76	115	108
PP25	78	115	109
CB05	79	114	109
CB2	81	116	109
DPE05	75	111	108
DPE2	74	110	108
DPE5	74	111	108
CN05	73	113	108
CN2	76	113	108
CN5	72	111	108
NA05	85	112	109
NA2	85	111	109
NA5	81	115	109
SB05	74	116	108
SB2	76	115	108
SA05	72	115	108
SA2	71	110	107
SA5	69	110	105

In general all the additives studied enhanced the crystallization rate to some extent. Since the melting temperature of 1-naphthalene acetamide is 184 °C, the foreign crystalline nuclei were present instantaneously until the ultimate depletion of the available nucleation centers. Chatterjee noted the excellent ability of 1-naphthalene acetamide to nucleate the crystallization in his patent series (C-7). Carbon black, another highly effective crystallization rate enhancer, also provides finely dispersed foreign surfaces for immediate nucleation of the crystallization. Polypropylene, slightly less effective at crystallization enhancement, begins to crystallize below 160 °C. This separate polypropylene crystallization exotherm was observed in the 25% (wt.) polypropylene sample when crystallized in the differential scanning calorimeter. Therefore, as noted by several research groups (B-13,C-4,C-5,C-6,S-3), the polypropylene crystallized at a somewhat higher temperature than the BR200S and provided a foreign nucleation site. The possibility of epitaxial nucleation must also be considered in this case. Even though sodium benzoate is an excellent nucleating agent for polypropylene crystallization, its effect in polybutene-1 was minimal. Stearic acid, another crystalline additive which was not as effective as the others, crystallizes at a temperature close to the onset of crystallization of polybutene-1 and provided no solid phase interface to nucleate the polymer. The liquid additives, diphenyl ether and α -chloronaphthalene, provided slight enhancement of crystallization. Since these liquids are relatively poor solvents for polybutene-1,

they provide phase separation within the structure. They may also act to lower the viscosity of the melt to some extent. The melting temperatures of the fully aged samples were enhanced by the same additives which enhanced the crystallization most effectively. The melting temperatures of the fresh samples were not affected by the additives. These melting temperatures appear in Table 4-2 on page . Indicated by these melting temperatures is that little, if any, of the additives dissolve in the polybutene-1.

Most of these additives tended to enhance the initial crystallinity as well as the initial crystallization rate. The area under the peak in the DSC-II cooling curve indicated that at a cooling rate of 20 °K per minute there were comparatively high initial crystallinities present in the blends of polypropylene (16%), carbon black (13%), sodium benzoate (18%), and α -chloronaphthalenes (13%). A slightly lower crystal fraction was present in the 1-naphthalene acetamide (10%), stearic acid (6%), and diphenyl ether blends (11%). Except for the stearic acid, all the blends had initial crystal fractions equal to or higher than the BR200S (10%).

4.2.2. Transformation and Secondary Crystallization Kinetics as Affected by Additives

Many additives are known to enhance the transformation rate of polybutene-1. Some authors suggest that crystalline additives are the only effective crystal transformation enhancers (B-9,B-10,B-11,C-9, S-3,S-6). To the contrary, Rubin suggested that crystallinity is not

a necessary or sufficient quality for a successful transformation enhancing additive in polybutene-1 (R-1). He studied diphenyl ether, α -chloronaphthalene, glycerin, and carbon black. Diphenyl ether and α -chloronaphthalene are both liquids near room temperature and he observed that both enhance the crystal transformation. Glycerin and carbon black, however, did not enhance the transformation rate. In the present work, both crystalline and amorphous additives in various concentrations were studied.

Figure 4-9 shows the volume fraction of crystal transformation with time for the polypropylene blends. One can see a marked transformation rate increase in PP5 over the basic resin with a slightly higher rate in the PP10 and PP25 blends. There seemed to be a saturating effect past which the concentration did not increase the rate dramatically. Figure 4-10 shows the total crystallinity of the 5% (wt.) polypropylene blends over the transformation time. The PP5 blend crystallized rapidly to 50% and increased to 70% over about 50 hours. The secondary crystallization rate constant was increased, by the polypropylene, from the BR200S value of 0.055 hr^{-1} to 0.156 hr^{-1} .

Diphenyl ether, a liquid additive, seemed to increase the transformation rate significantly. Figure 4-11 exhibits the volume fraction transformed over time for the these blends. The DPE2 and DPE5 blends markedly increased the transformation rate. In fact the DPE5 blend had a much higher rate of transformation than even the PP25 blend. As in the case of polypropylene, Figure 4-12 shows that diphenyl ether increased the rate of secondary crystallization. In

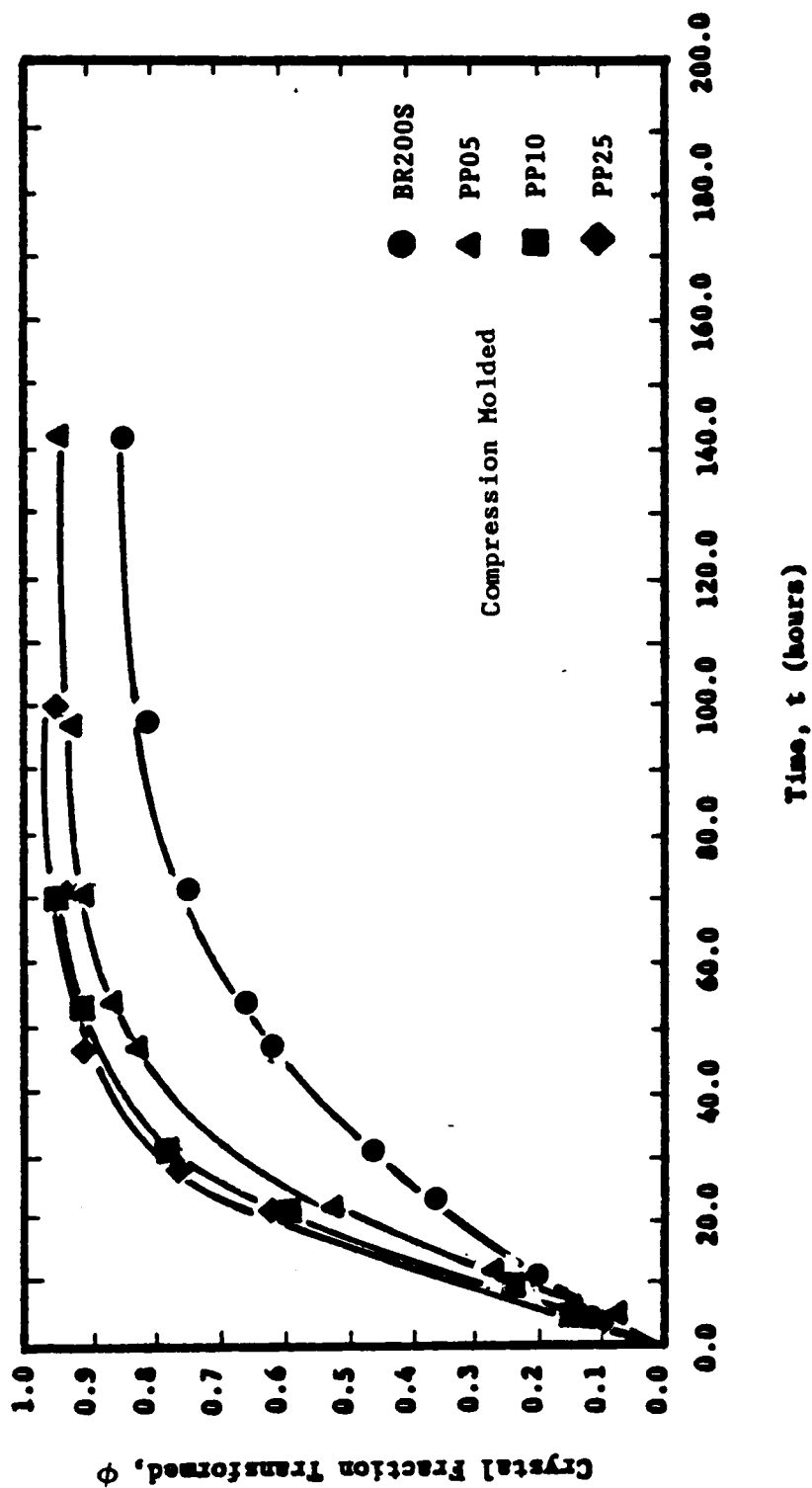


Figure 4-9. Volume Fraction of the Crystal Transformed Over Time for PP5, PP10, and PP25 Blends.

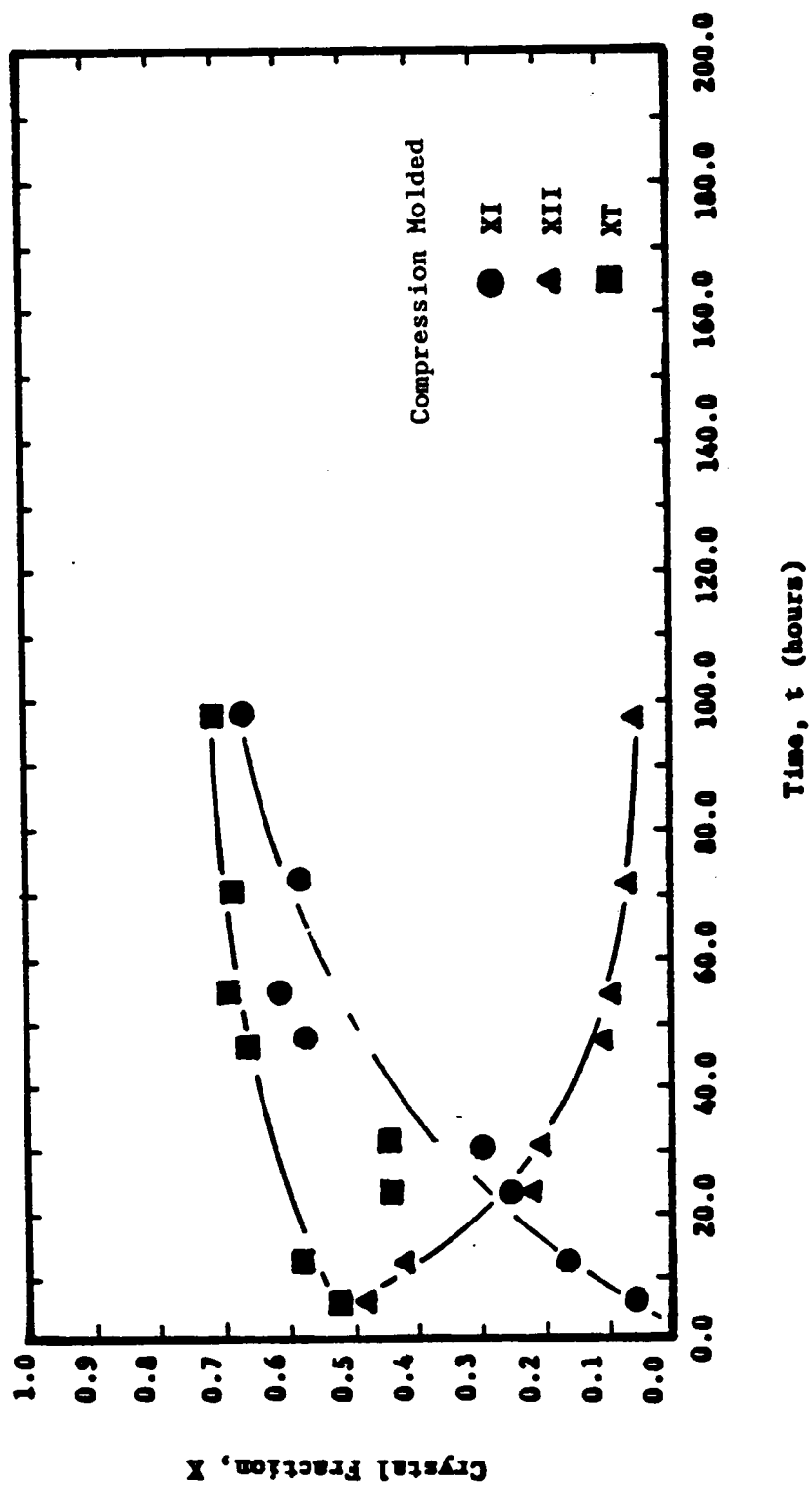


Figure 4-10. Crystal Fraction Present as a Function of Time for PP5 at 23 °C

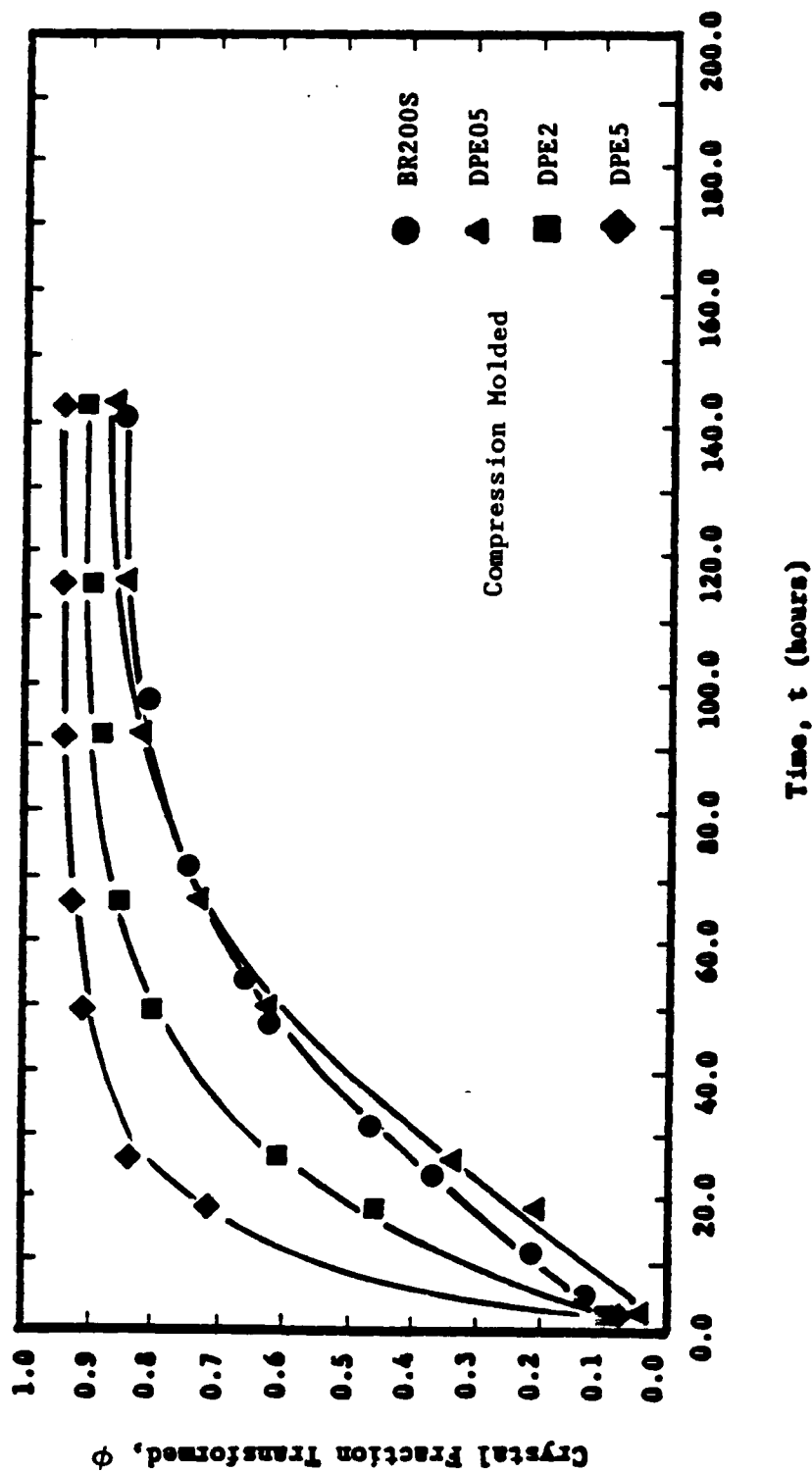


Figure 4-11. Volume Fraction of the Crystal Transformed Over Time for DPE05, DPE2, and DPE5 Blends

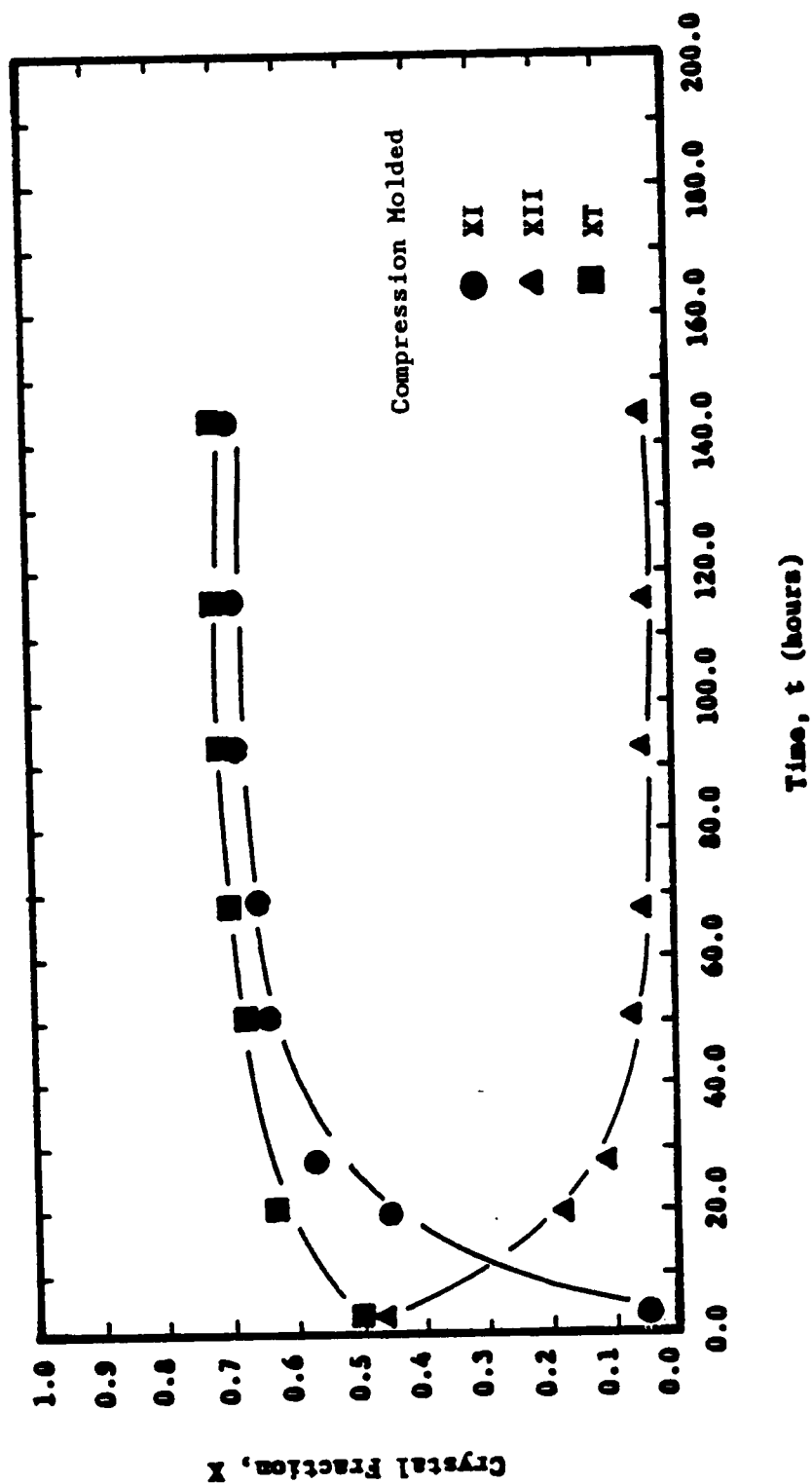


Figure 4-12. Crystal Fraction Present as a Function of Time for DPE5 at 23 °C

fact, the secondary crystallization rate constant increased to 0.123 hr^{-1} .

Another liquid additive, α -chloronaphthalene, also increased the rate of crystal transformation as illustrated in Figure 4-13. Interestingly, the CN5 blend surpassed both the PP25 and DPE5 blends for increasing the transformation rate. As before, Figure 4-14 shows that the secondary crystallization rate is increased by the presence of the α -chloronaphthalene fraction. The secondary crystallization rate constant increased to 0.129 hr^{-1} .

Carbon black yielded unusual results in that it may actually have inhibited the transformation rate at room temperature. Figure 4-15 shows the reduction in the transformation rate by carbon black. As the concentration of carbon black increased, the initial delay in the transformation also increased. In the CB2 blend the crystallinity increased from 50% to 70% over about 140 hours, as seen in Figure 4-16. The secondary crystallization rate constant increased to 0.125 hr^{-1} .

The 1-naphthalene acetamide did not significantly effect the crystal transformation for all blends. As noted by Hong, in small quantities the 1-naphthalene acetamide had little effect. Figure 4-17 shows the rates as a function of time for the 1-naphthalene acetamide blends. As indicated in Figure 4-18, the initial and final crystallinities for the NA5 blend were 70%. Interestingly, the 1-naphthalene acetamide was the only additive observed which exhibited no secondary crystallization period during the experimental time

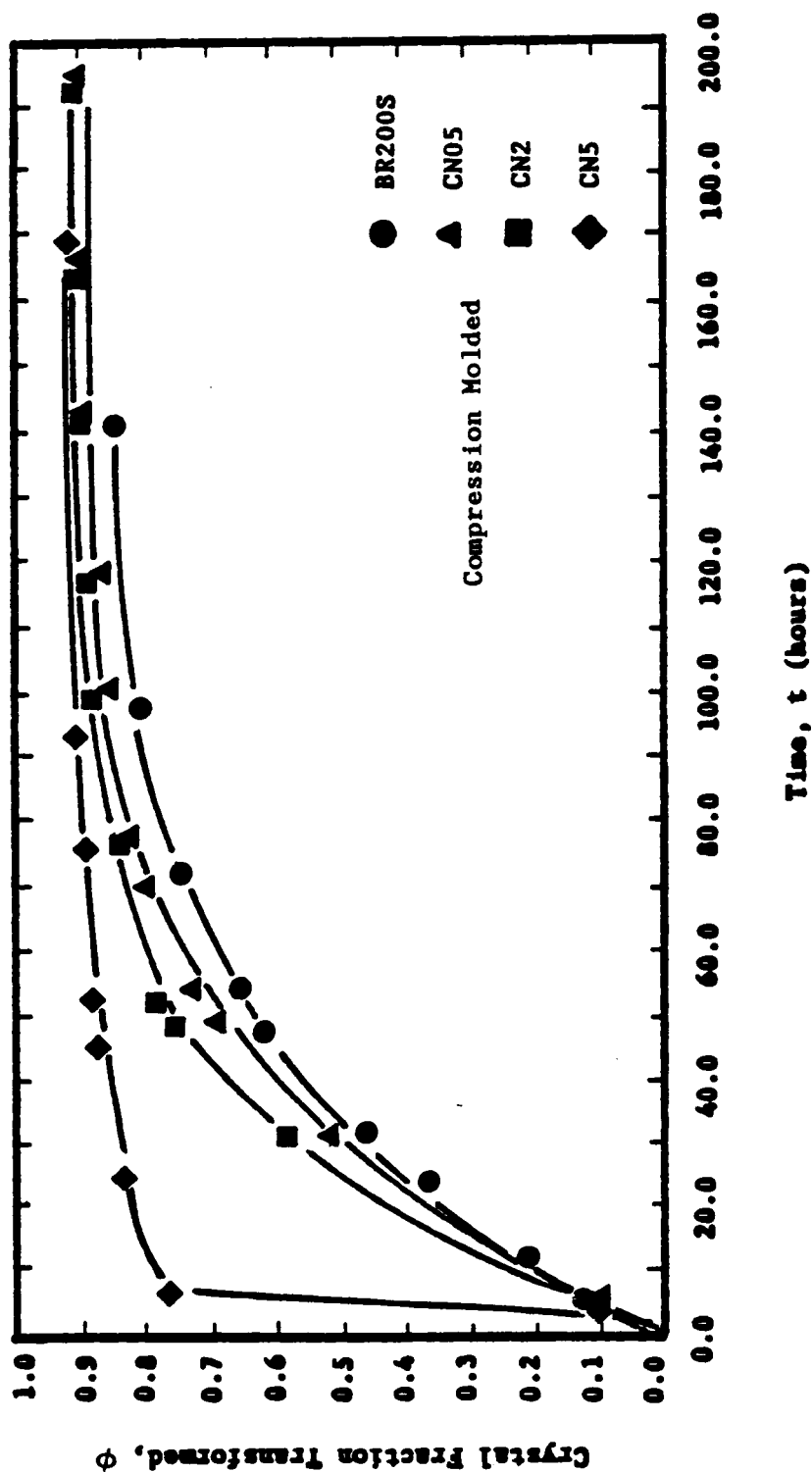


Figure 4-13. Volume Fraction of the Crystal Transformed Over Time for CN05, CN2, and CN5 Blends

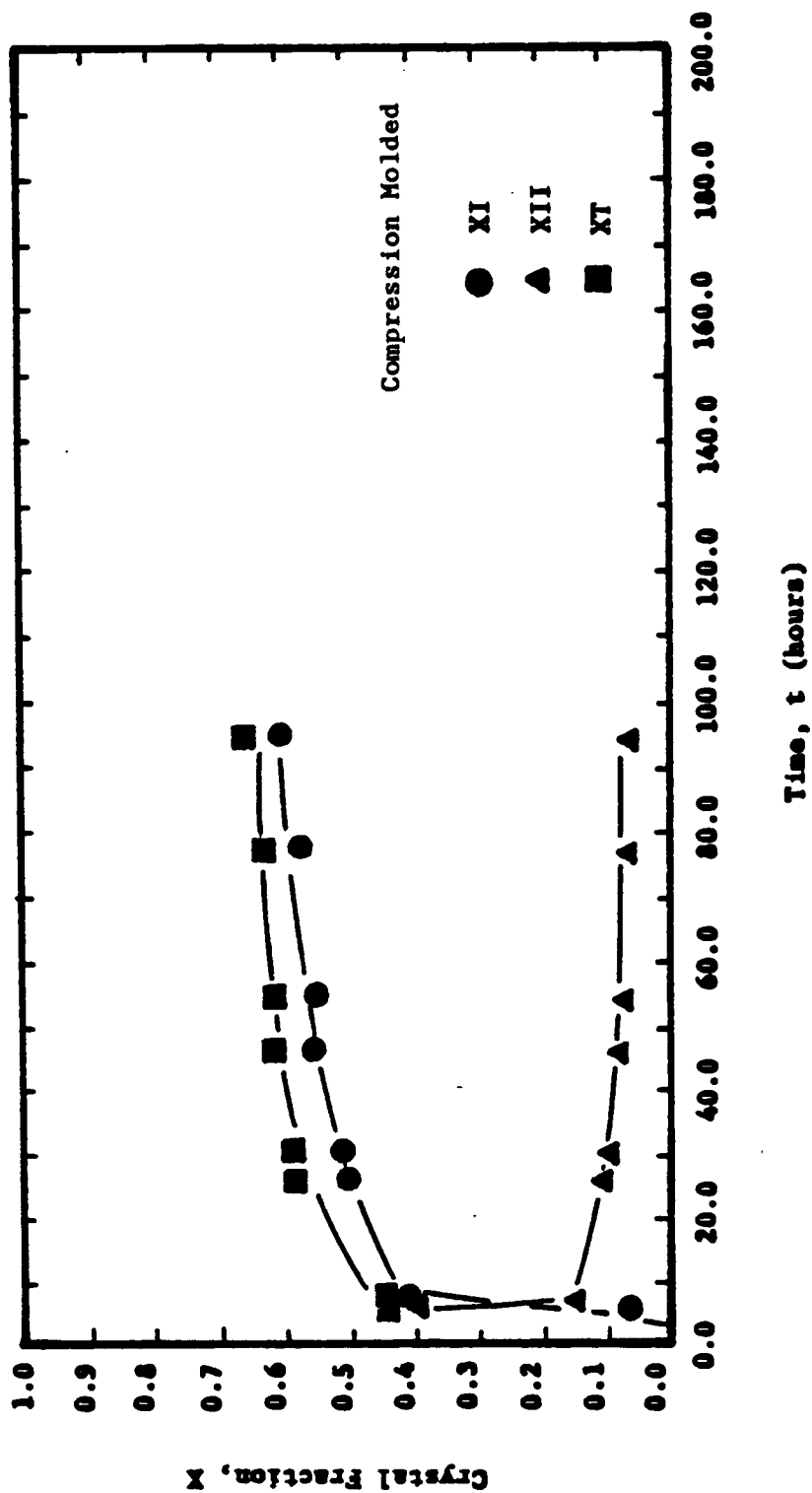


Figure 4-14. Crystal Fraction Present as a Function of Time for CN5 at 23 °C

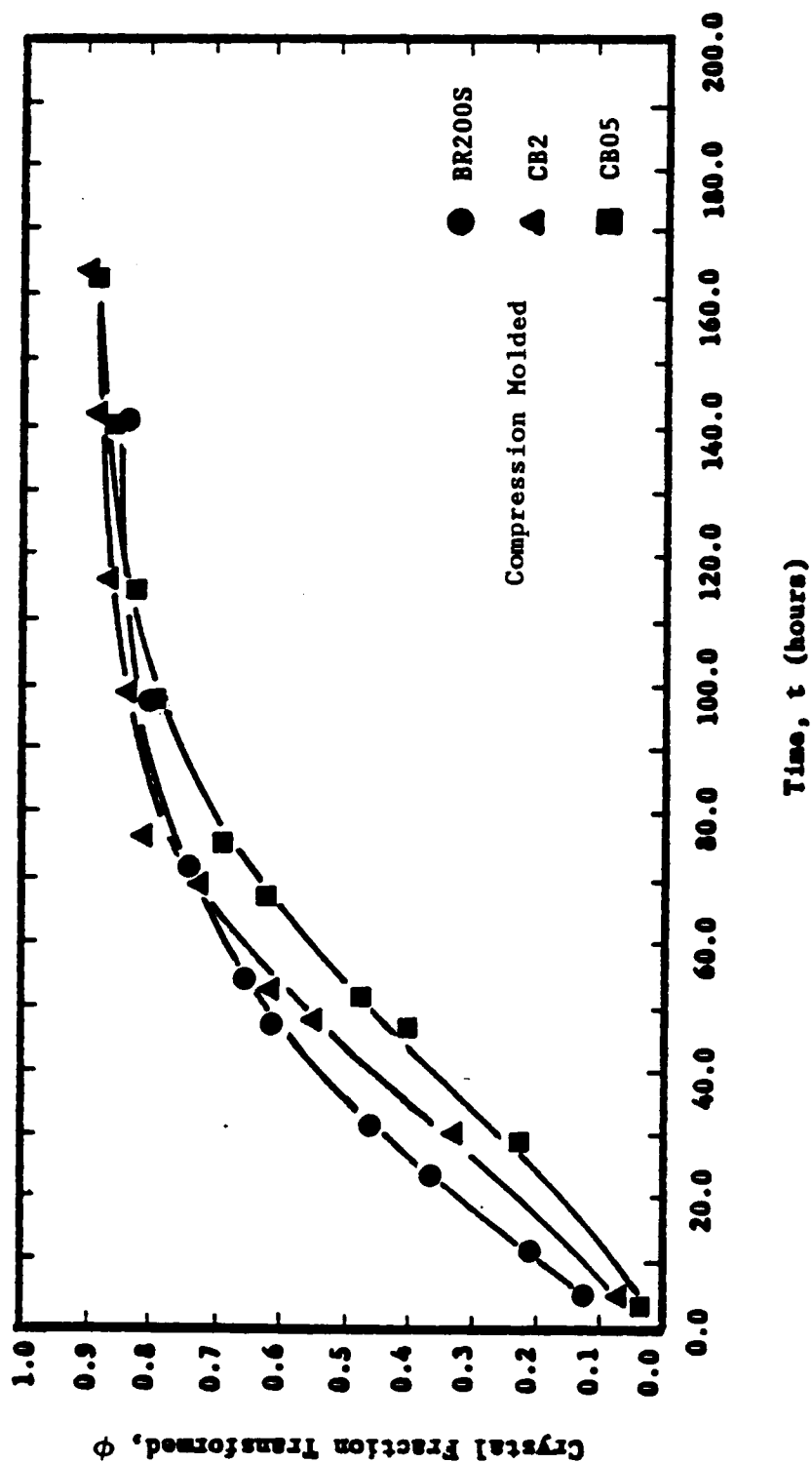


Figure 4-15. Volume Fraction of the Crystal Transformed Over Time for CB05 and CB2 Blends

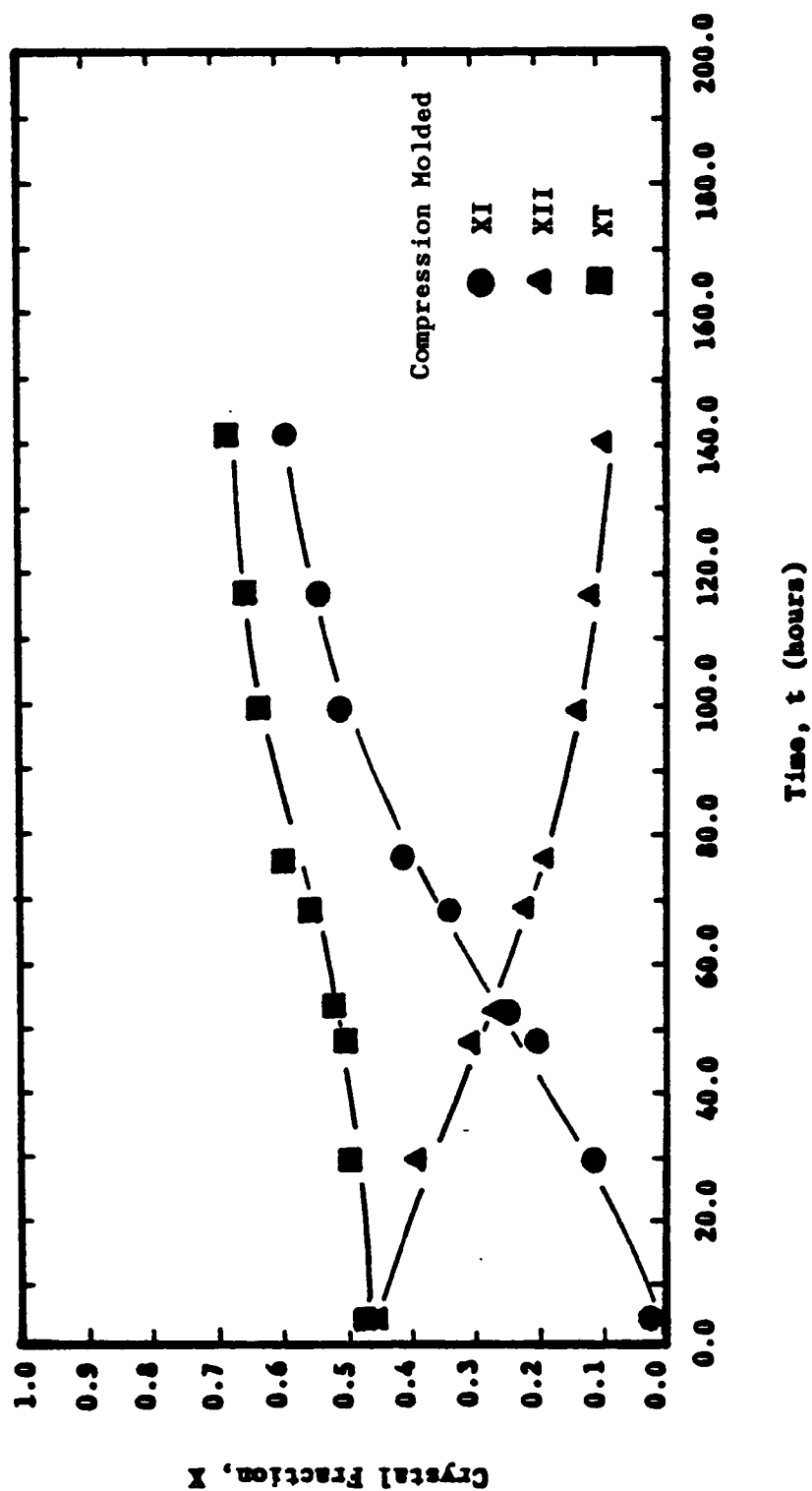


Figure 4-16. Crystal Fraction Present as a Function of Time for CB2 at 23 °C

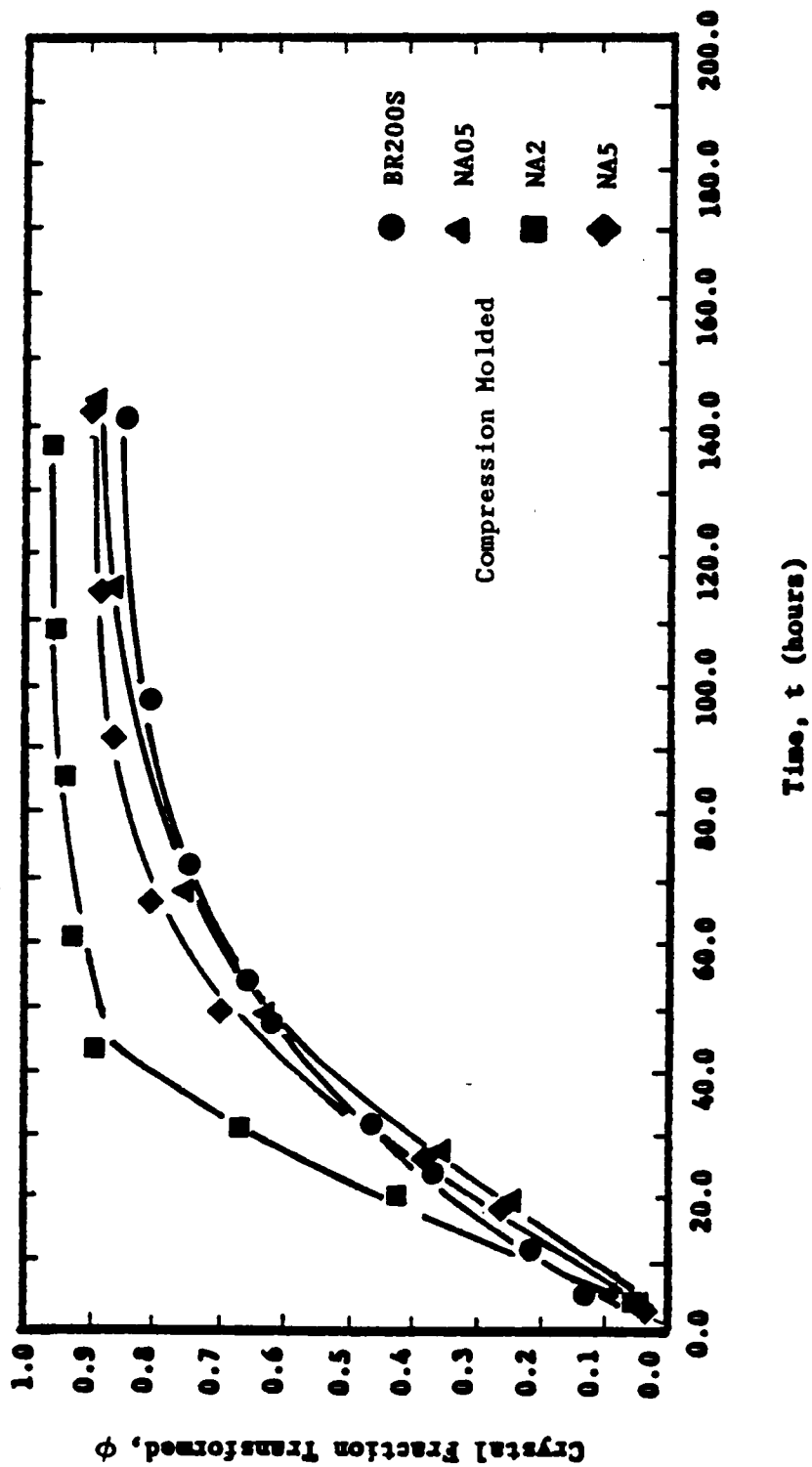


Figure 4-17. Volume Fraction of the Crystal Transformed Over Time for NA05, NA2, and NA5 Blends

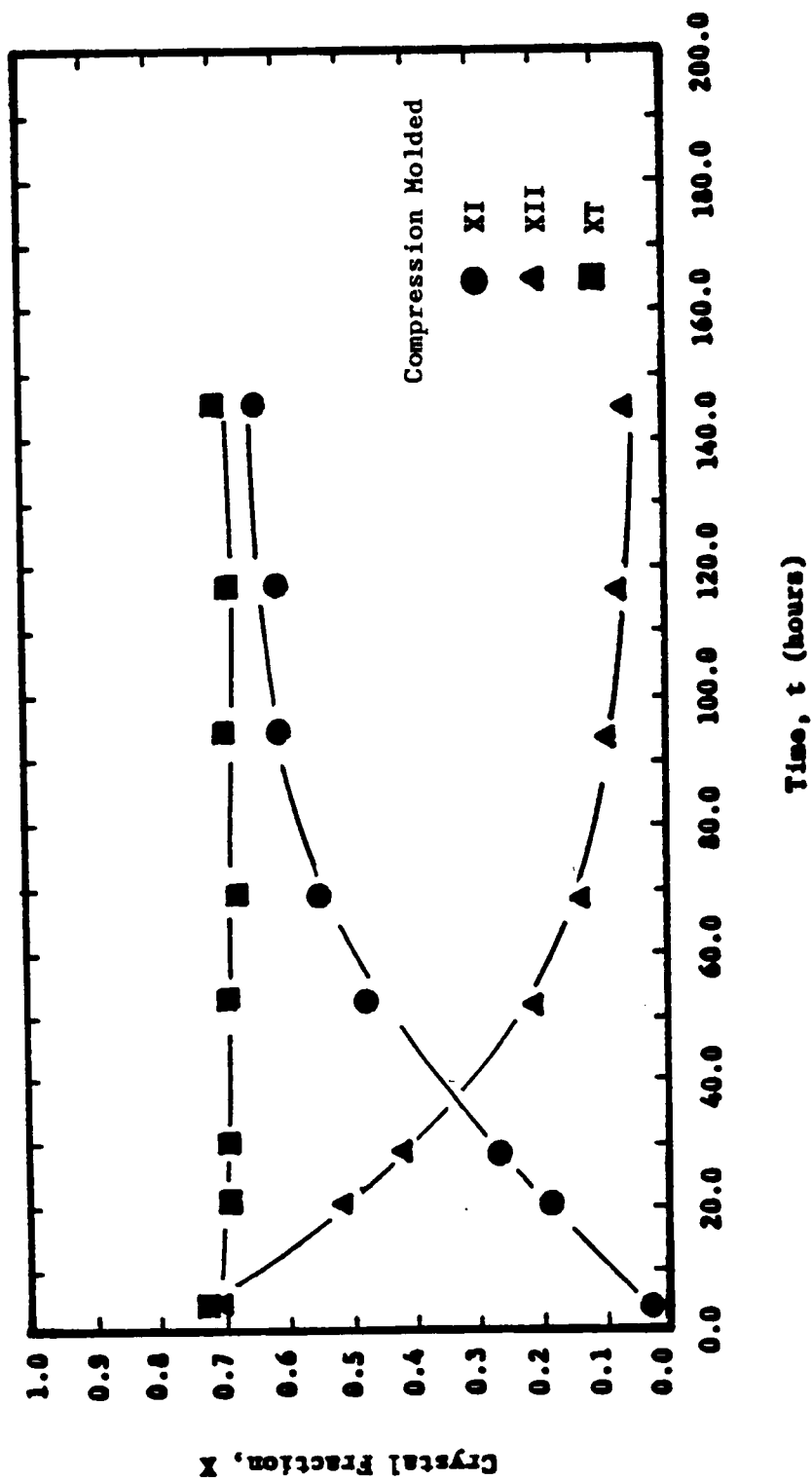


Figure 4-18. Crystal Fraction Present as a Function of Time for NA5 at 23°C

frame. This additive may have enhanced the nucleation to such an extent that the secondary crystallization was not evident in this study.

The sodium benzoate blend exhibits no significant effect on the transformation rate of the BR200S. Figure 4-19 shows no significant differences between this blend and the parent polymer. However, the secondary crystallization rate constant was increased to 0.146 hr^{-1} .

The stearic acid blends enhanced the transformation rate to a significant extent. Figure 4-20 shows the behavior of these blends. Also the stearic acid enhanced the secondary crystallization rate quite significantly. The rate constant increased to 0.20 hr^{-1} .

To summarize the rate effects, half-times of transformation at room temperature are provided in Table 4-3. The two liquid additives, α -chloronaphthalene and diphenyl ether, were most effective at increasing the transformation rate at 23°C . Polypropylene exhibited a less significant effect on the transformation. The 1-naphthalene acetamide, sodium benzoate, and stearic acid had much less significant effects. Carbon black appears to have slightly inhibited the transformation rate. The only additive for which polybutene-1 exhibited no secondary crystallization during the experimental time frame was 1-naphthalene acetamide. However, all of the additives studied did enhance the secondary crystallization rate to some extent. For information about other additive concentrations, Figures A-6 through A-19 on pages 149 through 162 should be consulted.

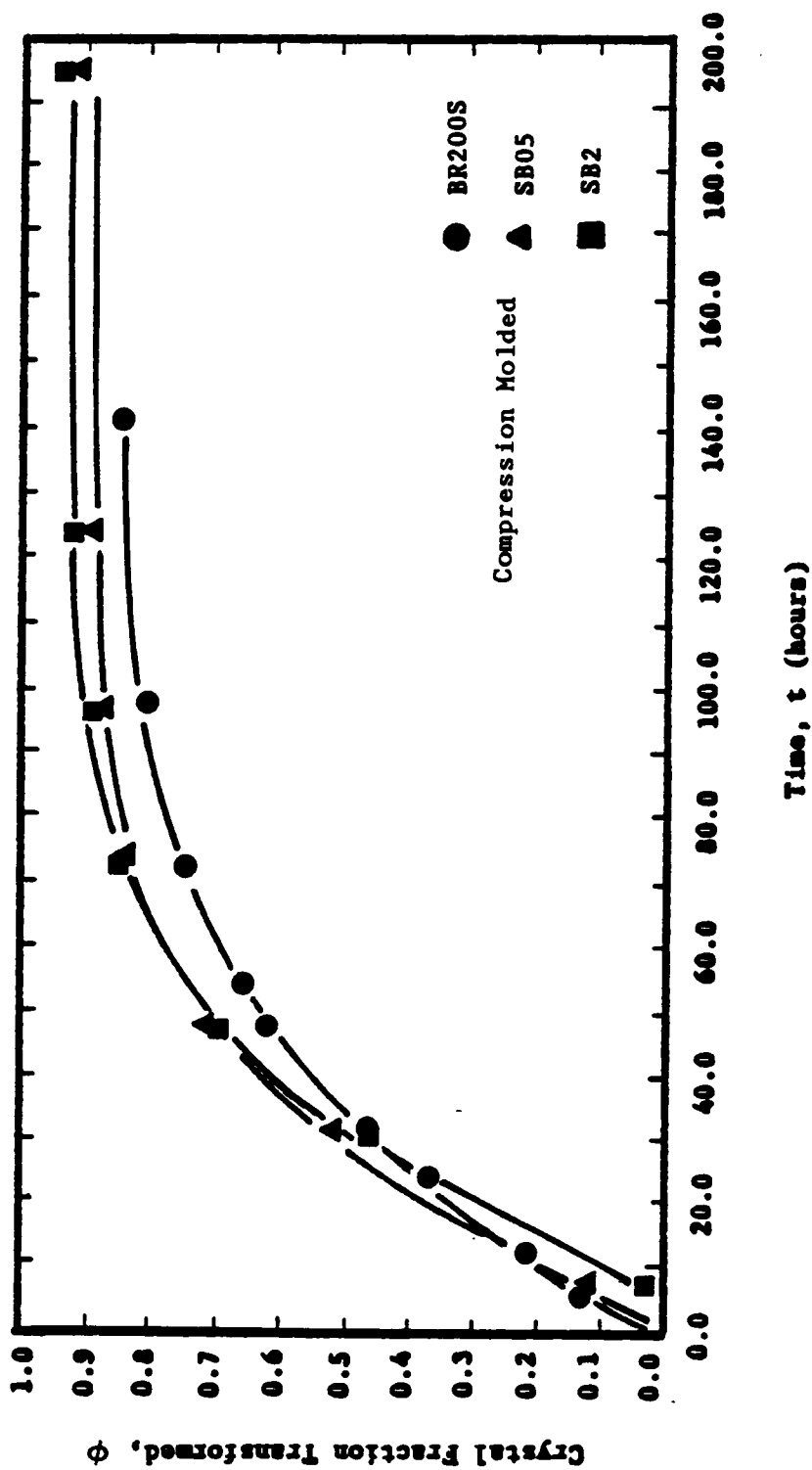


Figure 4-19. Volume Fraction of the Crystal Transformed Over Time for SB05 and SB2 Blends

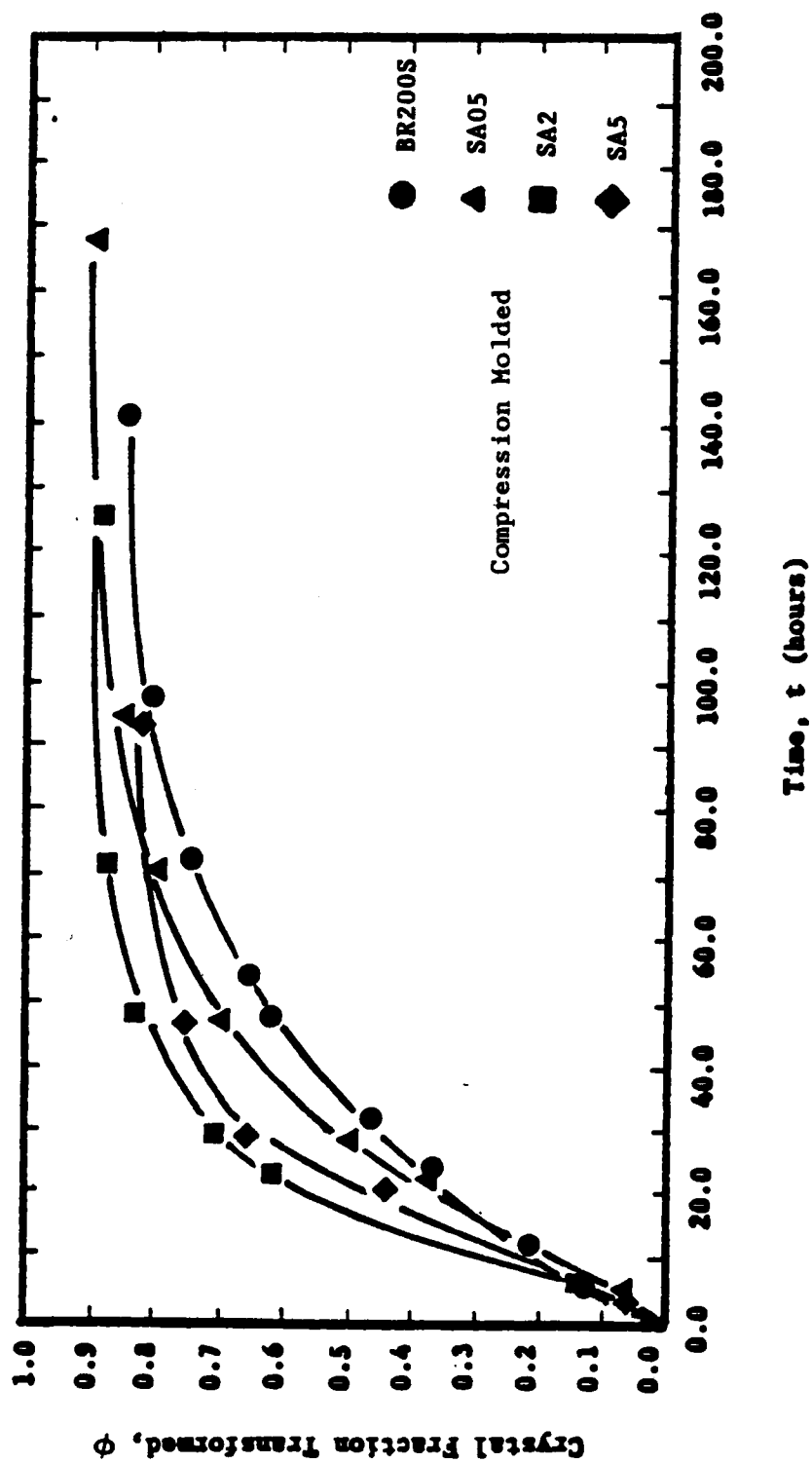


Figure 4-20. Volume Fraction of the Crystal Transformed Over Time for SA05, SA2, and SA5 Blends

Table 4-3. Transformation Half-time Values for Compression Molded Films of the BR200S Blends

Sample	Half-time, (hours)
BR200S	34.5
PP5	22.0
PP10	16.5
PP25	16.0
CB05	40.5
CB2	53.5
DPE05	39.0
DPE2	18.5
DPE5	10.0
CN05	30.0
CN2	24.0
CN5	3.5
NA05	36.0
NA2	23.0
NA5	34.5
SB05	30.0
SB2	31.5
SA05	30.0
SA2	17.0
SA5	23.0

In agreement with Rubin (R-1), these results show that a crystalline additive was not necessary to enhance the transformation rate. In fact, the two liquid additives were more effective at increasing the transformation rate than the polypropylene and other crystalline additives. It seemed that the perfection of the structure (amount of impurities or irregularities) as well as the increased mobility of the molecules may indeed have had significant contributions to the transformation. The liquid additives may have acted as plasticizers for the polybutene-1. To further examine these contributions of mobility and nucleation, studies were carried out at temperatures both above and below room temperature.

4.2.3. Effect of Temperature on the Transformation Rate of Blends

At temperatures above the maximum rate, crystal transformation is nucleation rate controlled due to the decreased ability to form stable nuclei. Transformation below that temperature is considered to be growth rate controlled due to the decreased mobility of the polymer chains. Transformation studies for each blend mentioned above were performed at 0, 23, 45, and 60 °C. These results will help determine the mechanism by which the above additives enhance the crystal transformation rate in polybutene-1.

Little difference in the overall temperature dependence is visible between the transformation rates for the SB2, SA5, and PP10 blends and the BR200S found in Figure 4-1 on page 51.

Figure 4-21 shows the crystal transformation over time as a function of temperature for the SB2 blend. The maximum rate appears to remain around room temperature. Both the 0 and 45 °C data appear to have similar rates and the 60 °C data seems to be extremely slow in all cases. The NA5 blend shows a markedly different behavior. In this case there is no discernible difference between the 45 and the 23 °C rates with the 0 and 60 °C rates being much lower. Figure 4-22 illustrates these effects. In the case of the CB2 blend, there seems to be little difference between the 0 and the 23 °C rates while the 45 and 60 °C rates are significantly lower. Figure 4-23 exhibits these transformation data.

In the case of the DPE5 liquid blend, seen in Figure 4-24, both the 45 and the 60 °C rates are much slower than the 23 °C, but the 0 °C rate seems to be the fastest. Figure 4-25 shows that the other liquid additive, α -chloronaphthalene, produces a blend which at 5% (wt.) exhibits a slower rate for the 0, 45, and 60 °C temperatures than at 23 °C. But, the 0 °C rate is much higher than the 45 °C rate. The transformation results of all additive concentrations at each temperature are found in Figures A-20 through A-81 on pages 163 through 224.

Hong showed in his work that the addition of polypropylene, stearic acid, sodium benzoate, and 1-naphthalene acetamide did not change the Avrami coefficient values from the accepted value of 1.0 (H-10,H-11). This observation indicates that the additives do not significantly alter the basic mechanism by which polybutene-1

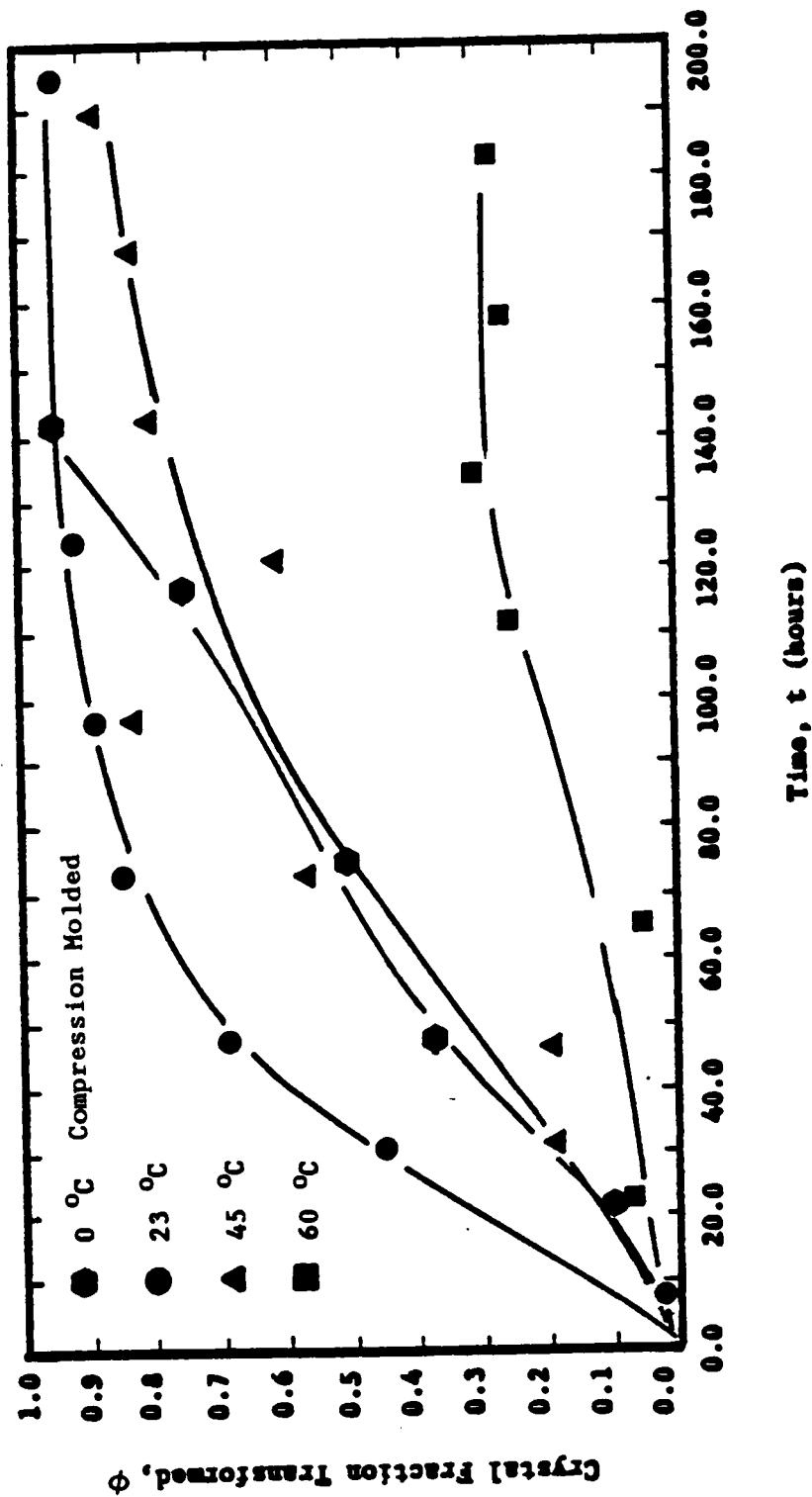


Figure 4-21. Volume Fraction of the Crystal Transformed Over Time for SB2 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C

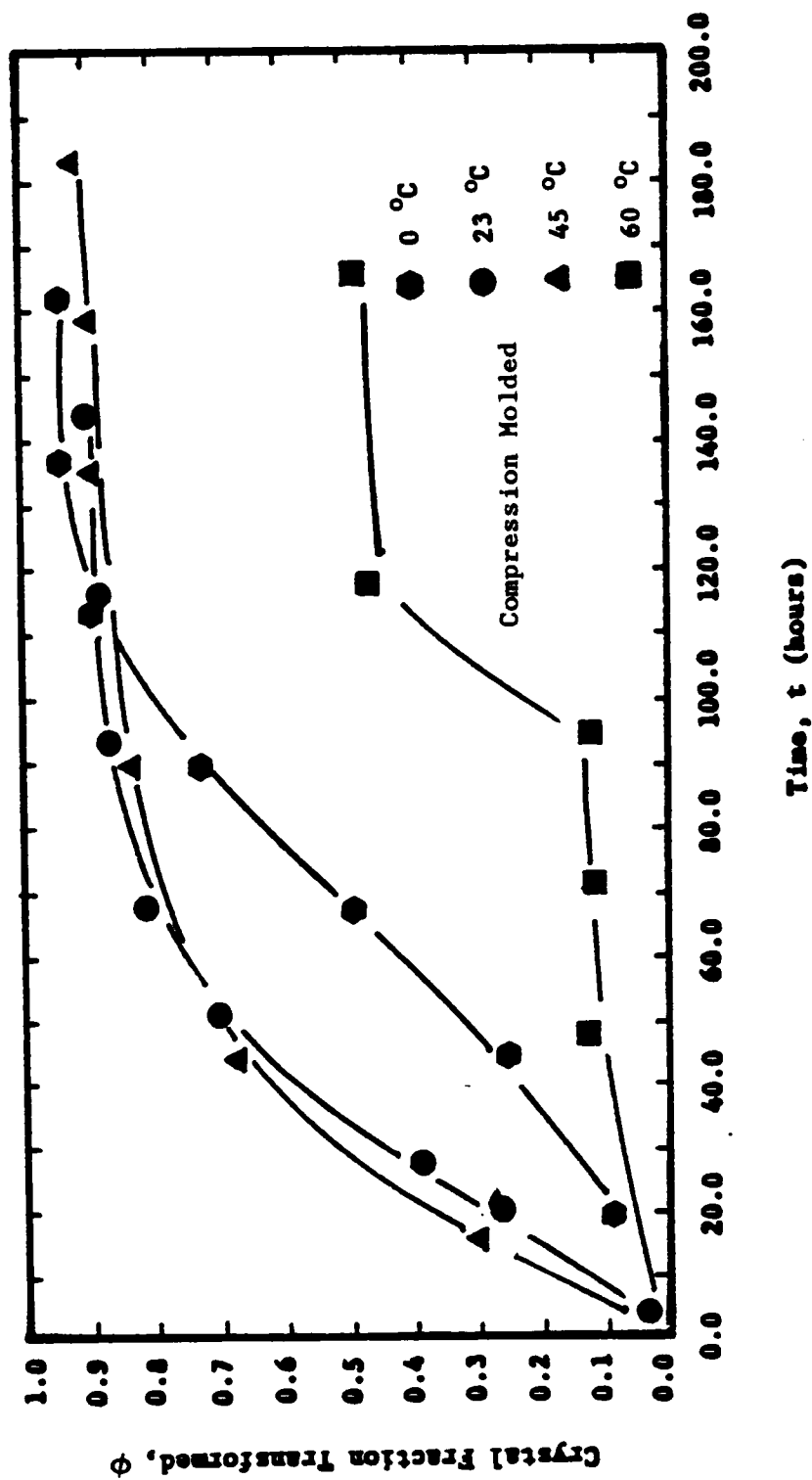


Figure 4-22. Volume Fraction of the Crystal Transformed Over Time for NA5 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C

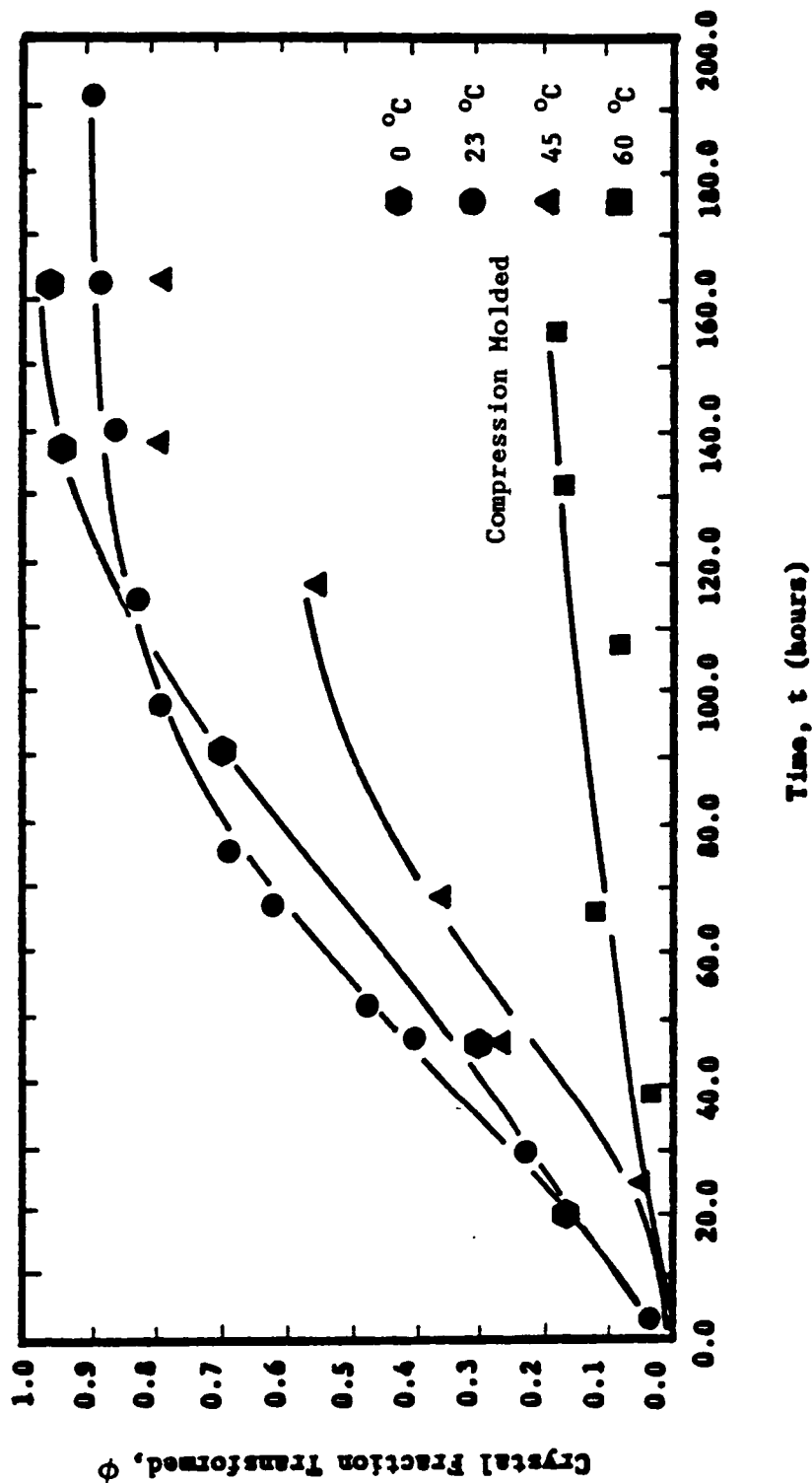


Figure 4-23. Volume Fraction of the Crystal Transformed Over Time for CB2 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C

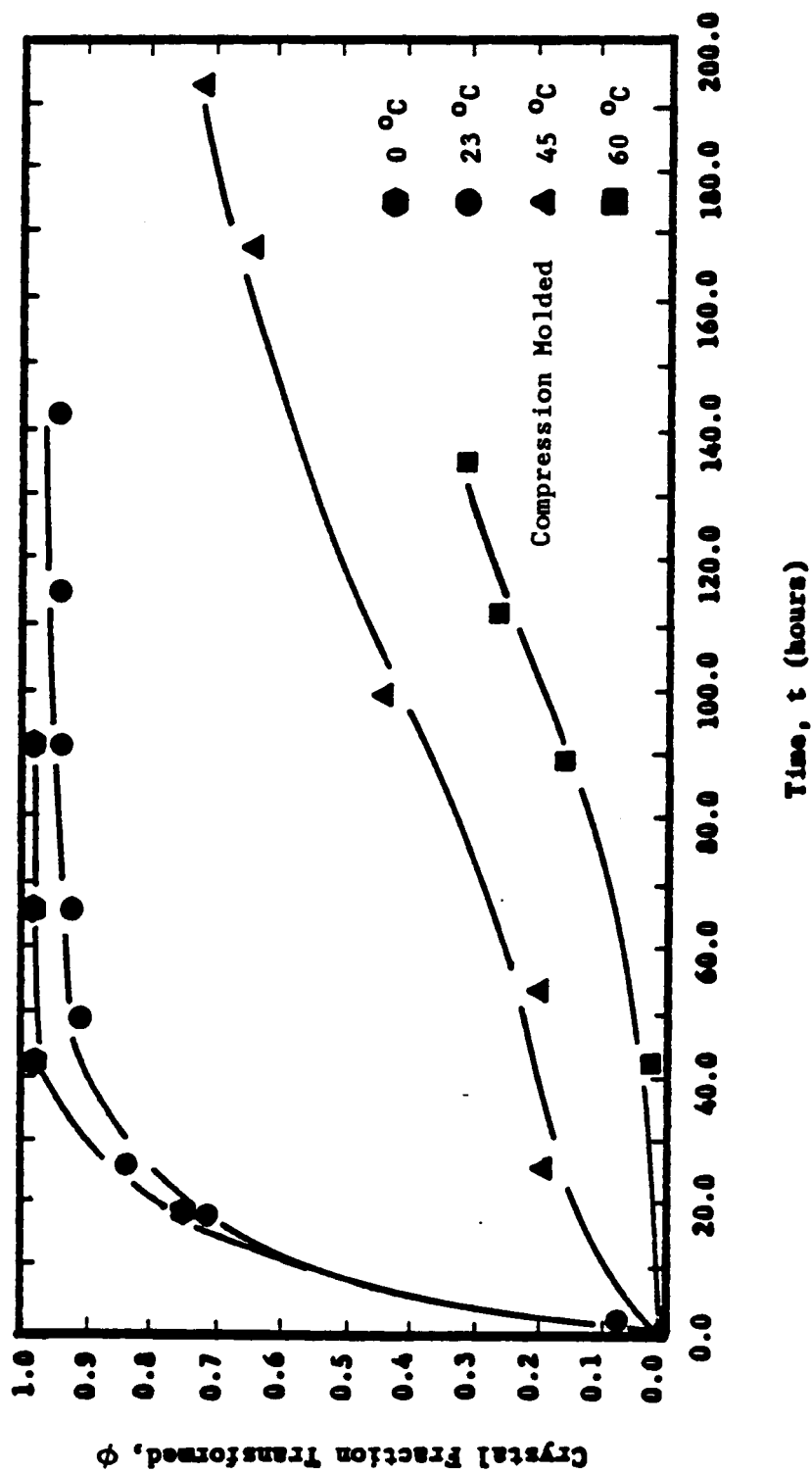


Figure 4-24. Volume Fraction of the Crystal Transformed Over Time for DPE5 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C

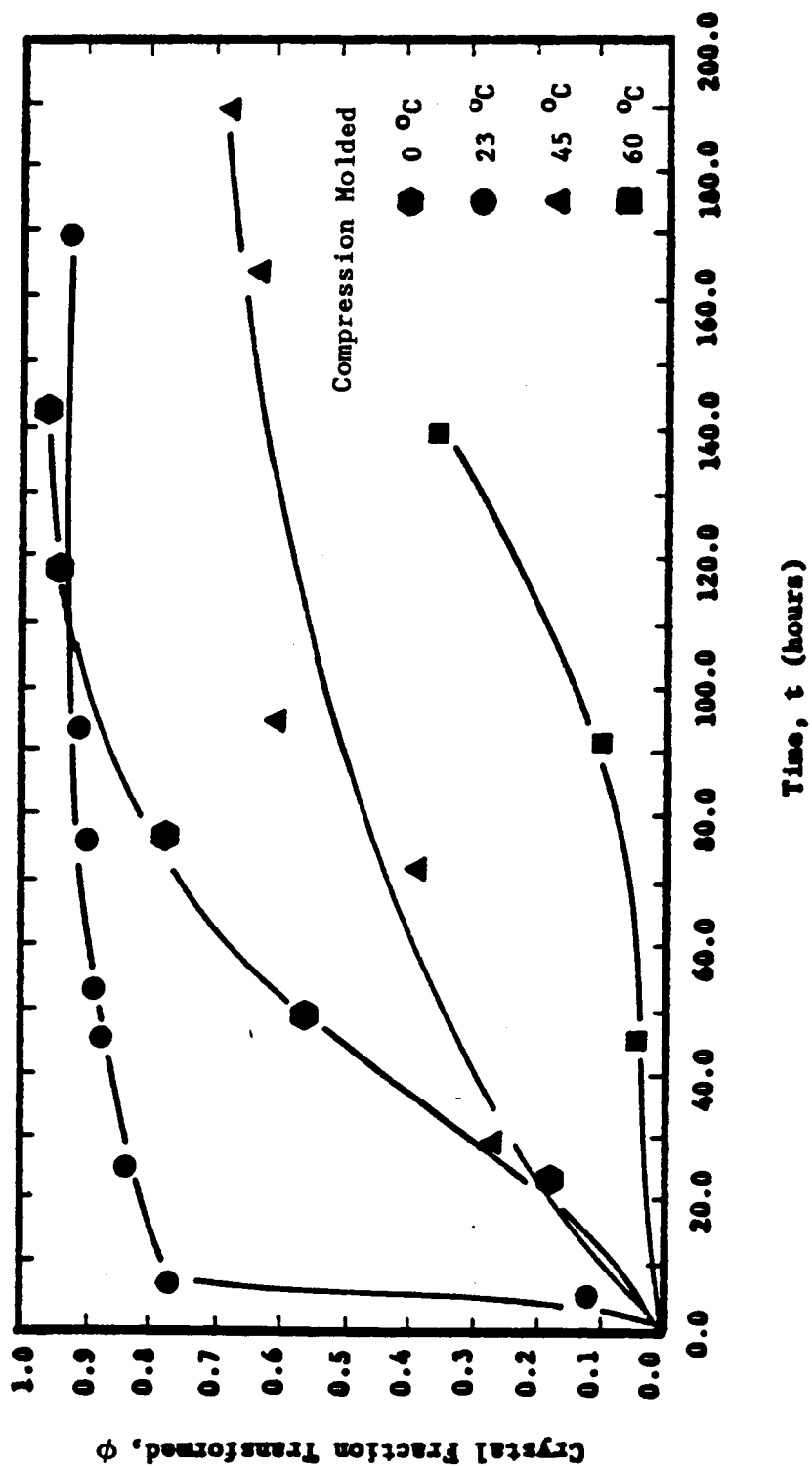


Figure 4-25. Volume Fraction of the Crystal Transformed Over Time for CN5 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C

transforms. From Figure 4-26 one sees that the Avrami exponent for BR200S at 0, 23, 45, and 60 °C remains within experimental error of the 1.0 value. Further, Figure 4-27 shows that a liquid additive, α -chloronaphthalene, does not significantly affect the Avrami exponent. Using the Avrami analysis on each blend provided exponents of approximately 1.0 or slightly greater, as seen in Figures A-82 through A-87 on pages 225 through 230.

In order to compare all additives, concentrations and temperatures on the same basis, the exponent value of 1.0 was fixed for all data such that comparison of the rate constants could be made. There tended to be some erratic variation due to extraneous factors. For example, some additives transformed the sample so rapidly that the portion which fits the Avrami analysis was not well developed. Also, the samples transformed at temperatures above and below room temperature were inherently erratic due to the measurement procedure. When the standard value of $n = 1.0$ was used in the Avrami equation for the phase transformation, a least squares regression routine was used to minimize the error between the calculated and experimental volume fraction data. The experimental transformation data fit the calculated values well at all four temperatures. Variations occurred toward the longer times in the 0 °C data where the experimental values began to approach the 23 °C data. The experimental and fitted values for transformation of the basic resin appear together in Figure 4-28.

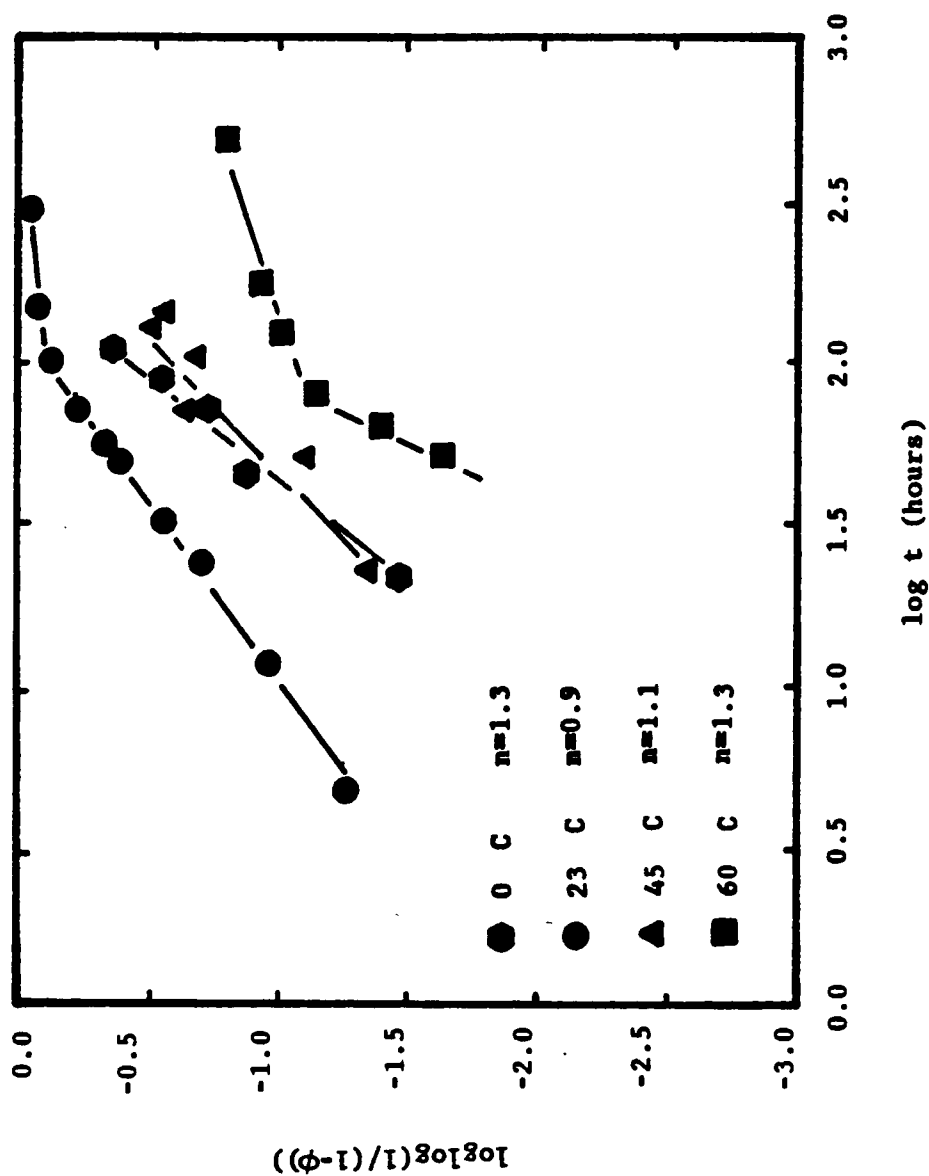


Figure 4-26. Determination of the Avrami Exponent Graphically for BR200S Compression Molded Films

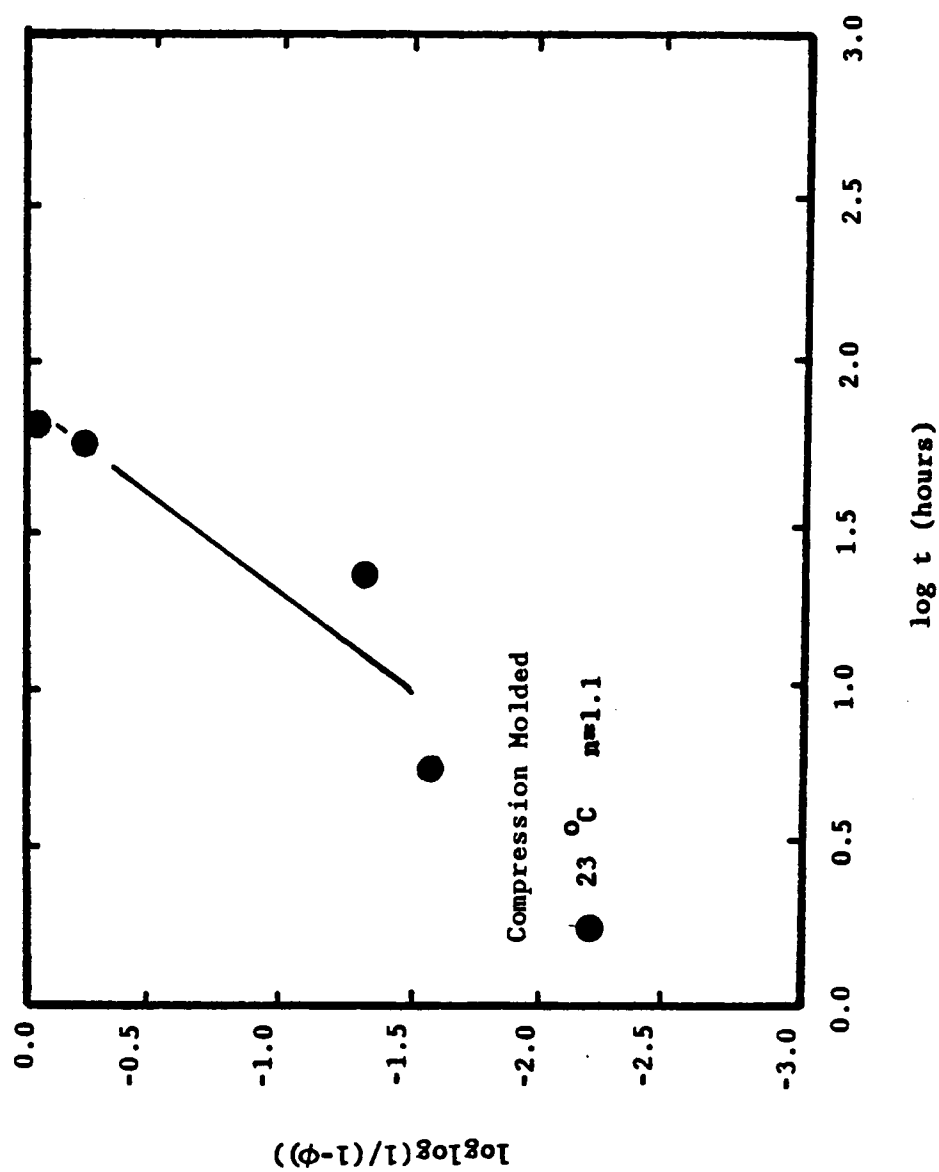


Figure 4-27. Determination of the Avrami Exponent Graphically for the CN2 Blend

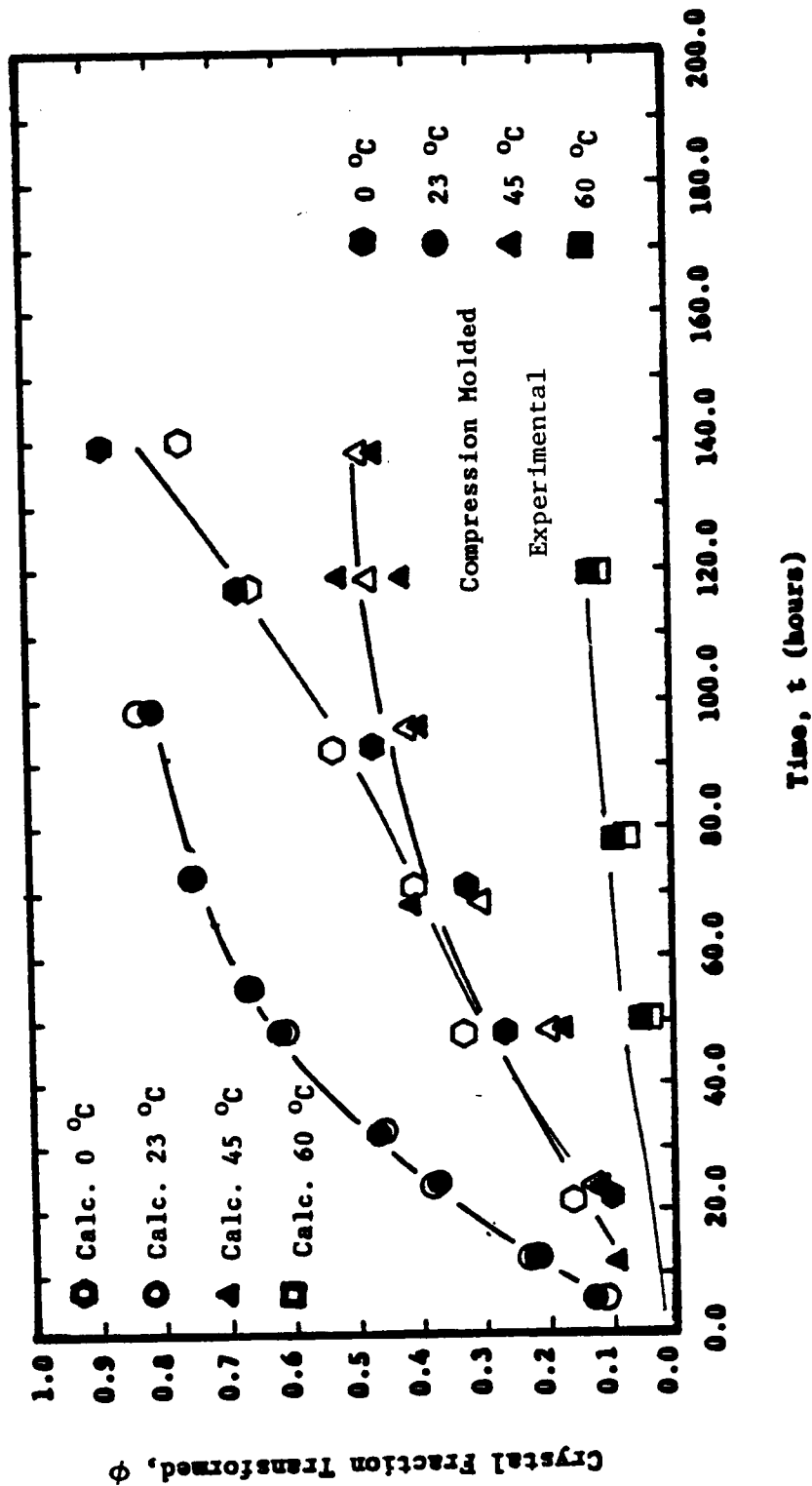


Figure 4-28. Experimental and Calculated Transformation Data for BR200S at 0 °C, 23 °C, 45 °C, and 60 °C by the Avrami Model

Table 4-4 summarizes all of the rate constants for each additive concentration at each temperature. The values provided are the rate constants, K , and the least squares error between the calculated and experimental transformed fraction, Φ . In general there were three types of effects seen for the controlling factors in the transformation. Polypropylene, stearic acid, α -chloronaphthalene, sodium benzoate, and 1-naphthalene acetamide may have slightly affected both the growth and nucleation rate control regions. Diphenyl ether shifted the maximum transformation rate to the growth rate region. Carbon black inhibited the rate.

An example of the first effect is given by polypropylene. At zero and 45 °C, there were only small increases in transformation rate over the basic resin. At 23 °C, the maximum rate increased significantly, while there was no difference in the rate at 60 °C. In the case of polypropylene the maximum rate seemed to remain in the range of 23 °C; while this additive caused the transformation rate to still be increased in the nucleation control region and approached the parent polymer behavior in the growth control region. As discussed by Boor, polypropylene primarily acts to nucleate the transformation. Boor et al. noted that the rate of transformation was increased in the nucleation control region by polypropylene and stearic acid (B-13).

Table 4-4. Avrami Rate Constants, K, for the BR200S Blends with the Exponent, n, Forced to Equal 1.0

Sample	0 °C			23 °C			45 °C			60 °C		
	K, hr	Ave. ϕ	Error	K, hr	Ave. ϕ	Error	K, hr	Ave. ϕ	Error	K, hr	Ave. ϕ	Error
BR200S	.008	.030		.019	.081		.005	.029		.0005	.016	
PP5				.033	.041		.004	.072		.0009	.102	
PP10	.014	.062		.041	.003		.012	.089		.0006	.069	
PP25				.047	.091		.006	.013		.0006	.051	
DPE05				.017	.022		.005	.088		.001	.035	
DPE2				.032	.013		.007	.126		.002	.043	
DPE5	.074	.001		.069	.008		.006	.019		.002	.014	
CN05				.022	.025		.006	.005		.0009	.003	
CN2				.023	.039		.007	.036		.002	.007	
CN5	.017	.036		.093	.190		.007	.028		.001	.040	
CB05				.017	.089		.009	.041		.0009	.068	
CB2	.013	.079		.013	.026		.007	.062		.0008	.009	
NA05				.017	.015		.019	.042		.003	.014	
NA2				.036	.030		.021	.014		.0015	.011	
NA5	.013	.095		.021	.019		.020	.056		.002	.081	
SB05				.024	.011		.006	.069		.001	.019	
SB2	.011	.049		.023	.009		.010	.093		.001	.034	
SA05				.023	.012		.003	.023		.0006	.003	
SA2				.040	.009		.005	.019		.001	.007	
SA5	.011	.055		.028	.021		.008	.028		.002	.004	

An example of the second effect is given by diphenyl ether. At 0 °C the DPE5 blend exhibited an order of magnitude enhancement of the transformation rate over the BR200S pure resin. In fact at 0 °C the transformation of the DPE5 blend proceeded slightly more rapidly than the 23 °C transformation of that same blend. The 45 and 60 °C transformations of the diphenyl ether blends exhibited no significant increase in transformation rate. In the diphenyl ether blends, the temperature at which the maximum transformation rate occurred seemed to have been shifted toward the growth rate control region while the rate approached that of the BR200S homopolymer in the nucleation control region. Indicated in this example was primarily growth rate control. This result is due to the liquid additive acting as a poor solvent (solubility barrier of $4.5 (\text{J/m}^3)^{1/2} \times 10^{-3}$). The resulting mixture increases polymer chain mobility and thus the crystal transformation is enhanced. Apparently the strong ability to enhance the growth rate allows the diphenyl ether to be significantly more effective at enhancing the transformation at low temperatures than polypropylene.

Thirdly, as noted by Rubin, the carbon black blends generally inhibited the transformation behavior of polybutene-1. At 0 °C there was only a slight difference between the BR200S and the CB2 blend. At 23 °C the carbon black inhibited the transformation. At elevated temperatures the rate became only slightly higher than the BR200S indicating that the nucleation was not extremely significant in this case even though a foreign crystalline surface was provided for the

initiating site. The rate peak was broadened toward each direction and there was little effect in either the nucleation or growth control regions.

The characteristic shape of the transformation rate as a function of temperature appears as Figure 4-29. Characteristic of the transformation rate was a smooth curve with a maximum rate near room temperature. The lower temperature side of the maximum was the growth rate control region and the higher temperature side was the nucleation rate control region. This growth rate is not the same concept as the melt-crystal growth rate, but does encompass similar ideas. The helix elongates and the crystal structure reorganizes. Thus on the micro-scale motion must occur. Overall there appeared to be a significant correspondence between the type of additive and how it may have contributed to the total transformation enhancement.

Generally, the two poor solvent additives provided the most significant increase in the rate of transformation at 23 °C. For α -chloronaphthalene the growth control factor was not quite so dominant as in the diphenyl ether case. In this instance the rate of the blend approached the BR200S in the nucleation control region while enhancing the transformation rate in the growth control region. At 23 °C the transformation was near the maximum and in fact was more rapid than all other blends considered here. Being a slightly poorer solvent (miscibility barrier of $5.5 \text{ (J/m}^3)^{1/2} \times 10^{-3}$) for polybutene-1 than diphenyl ether, it seems that the growth rate was not as significantly enhanced. But, since the maximum was shifted to a lower

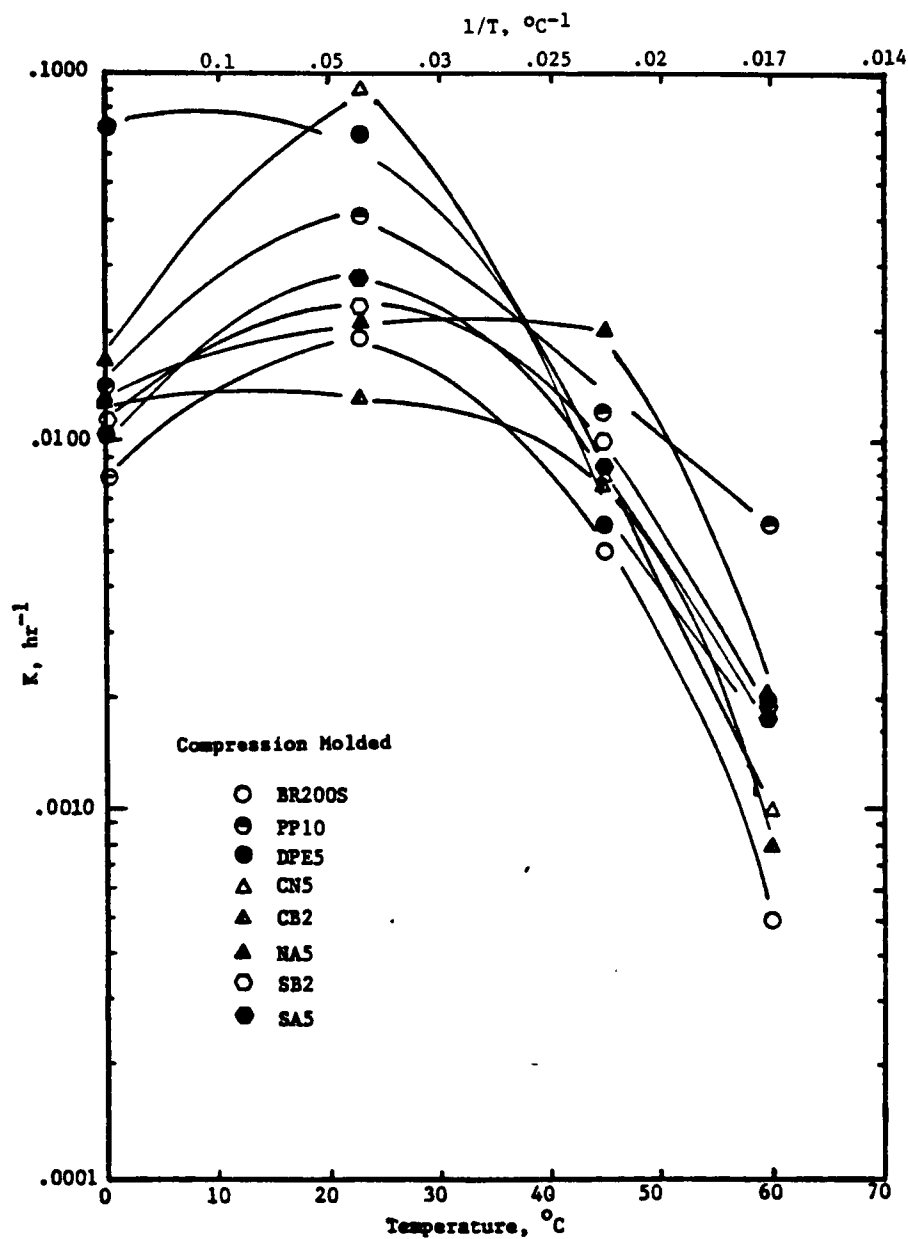


Figure 4-29. Avrami Transformation Rate Constant as a Function of Temperature for the BR200S Blends

temperature for the diphenyl ether, α -chloronaphthalene had a higher rate at 23 °C.

To further examine the mechanisms of enhancement of the transformation rate, one must extend the study of the additives to the micro-scale. To actually observe the transformation through microscopy with the crystalline and liquid additives present would then elucidate the mechanistic effects of each type.

4.2.4. Tensile Mechanical Properties of the BR200S Blends

It is well known that as polybutene-1 transforms and crystallizes the mechanical properties improve. Therefore the effect of certain additives on the tensile properties provides insight into the ultimate product enhancement. The modulus, 2% offset yield strength, percent strain to break, and ultimate tensile strength were measured for the BR200S and PP10, DPE2, DPE5, CB2, NA2, and NA5 blends. Table 4-5 provides a summary of the fresh (mostly Form II) and aged (mostly Form I) tensile properties.

Fresh samples of BR200S exhibited an average modulus of 54 MPa. The fresh modulus was most dramatically increased in the PP10 blend. This relatively high concentration of polypropylene increased the modulus to 76 MPa. It seems that polypropylene's ability to nucleate crystallization, as well as positive interaction between the polymeric materials in the blend may have been responsible for the superior modulus. The next most effective modulus enhancing additive was 1-naphthalene acetamide in concentrations of 2% (wt.) and 5% (wt.).

**Table 4-5. Tensile Mechanical Properties of the BR200S Blends
(Fresh and Aged)**

Sample	E (MPa)	UTS (MPa)	% Elongation	2% Yield Strength (MPa)
PB-1 Fresh	54	43	490	3.3
PB-1 Aged	160	44	500	12.0
PP10 Fresh	76	39	410	4.3
PP10 Aged	230	43	490	13.0
DPE2 Fresh	54	43	460	3.3
DPE2 Aged	150	43	480	12.0
DPE5 Fresh	60	38	400	3.4
DPE5 Aged	150	46	500	10.0
CB2 Fresh	59	34	350	3.8
CB2 Aged	140	28	280	12.0
NA2 Fresh	68	41	420	3.7
NA2 Aged	190	31	290	14.0
NA5 Fresh	69	32	360	4.1
NA5 Aged	190	29	290	14.0

They increased the modulus to 68 MPa and 69 MPa respectively. This enhancement was probably due to the excellent ability to nucleate primary crystallization. Carbon black at 2% (wt.) and diphenyl ether at 5% (wt.) enhanced the modulus to 59 MPa and 60 MPa respectively. The carbon black enhancement was also due to the fact that it increased the initial crystallization rate. Carbon black also acts as a filler to stiffen the matrix. The diphenyl ether enhances the transformation rate such that the modulus is increased. Similar effects were seen with the 2% offset yield strength determined for the fresh samples.

Compared to the basic resin, the ultimate tensile strength was slightly less for the majority of fresh blends. The breaking strength may have decreased due to the blends consisting of separate phases thereby weakening the system. Similarly the elongation to break decreased slightly with the addition of additives.

When aged more than 336 hours, the modulus of the BR200S samples increased to 160 MPa. Again, the greatest increase in modulus was observed in the PP10 blend. The increase was up to 230 MPa. A small increase was seen in the 1-naphthalene acetamide blends (190 MPa). As before, these effects were most likely due to crystallinity enhancements. Little effect was seen in the carbon black and diphenyl ether blends. Similar effects were seen in the 2% offset yield strength determined for the aged samples.

As in the fresh samples, the ultimate tensile strengths of aged blends were similar to or lower than those of the aged basic resin. This seems to indicate that the phases are not completely compatible and thus phase separation causes this weakening of the system.

In summary, the most significant effect of the additives was on the modulus and 2% offset yield strength of the fresh samples. It was indicated that polypropylene stiffened the structure most significantly perhaps due to crystallization rate enhancement by nucleation as well as the polymeric nature as an additive. The 1-naphthalene acetamide and carbon black blends followed closely in effect again due to their probable ability to enhance the nucleation of crystallization.

4.3. Effect of Sample Dimensions and Orientation on the Secondary Crystallization and Transformation Kinetics

4.3.1. Secondary Crystallization and Transformation Kinetics as Affected by Sample Dimensions

As suggested by a few researchers, the sample thickness is an important variable in studies of the secondary crystallization and transformation rates in polybutene-1 (B-9,C-9,L-2). It has been seen that the crystallization and transformation occur most rapidly close to the sample surface (C-4,C-5,C-6,L-2). The effect may be related to surface energy, interfacial nucleation, heat transfer, mobility, etc.

To illustrate the effect of sample dimensions on the secondary crystallization and transformation rates, the following results are provided. As seen in Figure 4-30, the BR200S SDR=1 fiber of 0.736 mm diameter had 20% relative crystal fraction at the first measurement (within one hour) and reached an asymptotic value of 45% to 50% in about 45 hours. In the 1.472 mm diameter fiber of SDR = 1 the initial relative crystal fraction was about 20% and reached a value of 45% to 50% in about 70 hours. These results are illustrated in Figure 4-31. Secondary crystallization also seemed to be reduced in rate. The rate constant of the secondary crystallization decreased from 0.096 hr for the 0.736 mm fiber to 0.076 hr for the 1.472 mm fiber. Due to the increase in the sample diameter, Figure 4-32 shows the important effect of sample dimensions at a SDR = 1 for the transformation in the BR200S resin. Doubling the diameter of the fiber with no draw down substantially decreased the rate of transformation. As a result, there may be an effect of relative surface area per unit volume of sample. An interesting note on Figures 4-33, 4-34, and 4-35 was that the spin drawing of the melt overcame the surface area per unit volume effect for both the secondary crystallization and transformation. Both of the SDR = 70 fibers, with initial diameters of 0.176 mm and 0.088 mm, secondarily crystallized and transformed approximately at the same rates. The melt orientation overcomes the energy barrier to transformation by aligning the molecules such that the thickness effect was negligible.

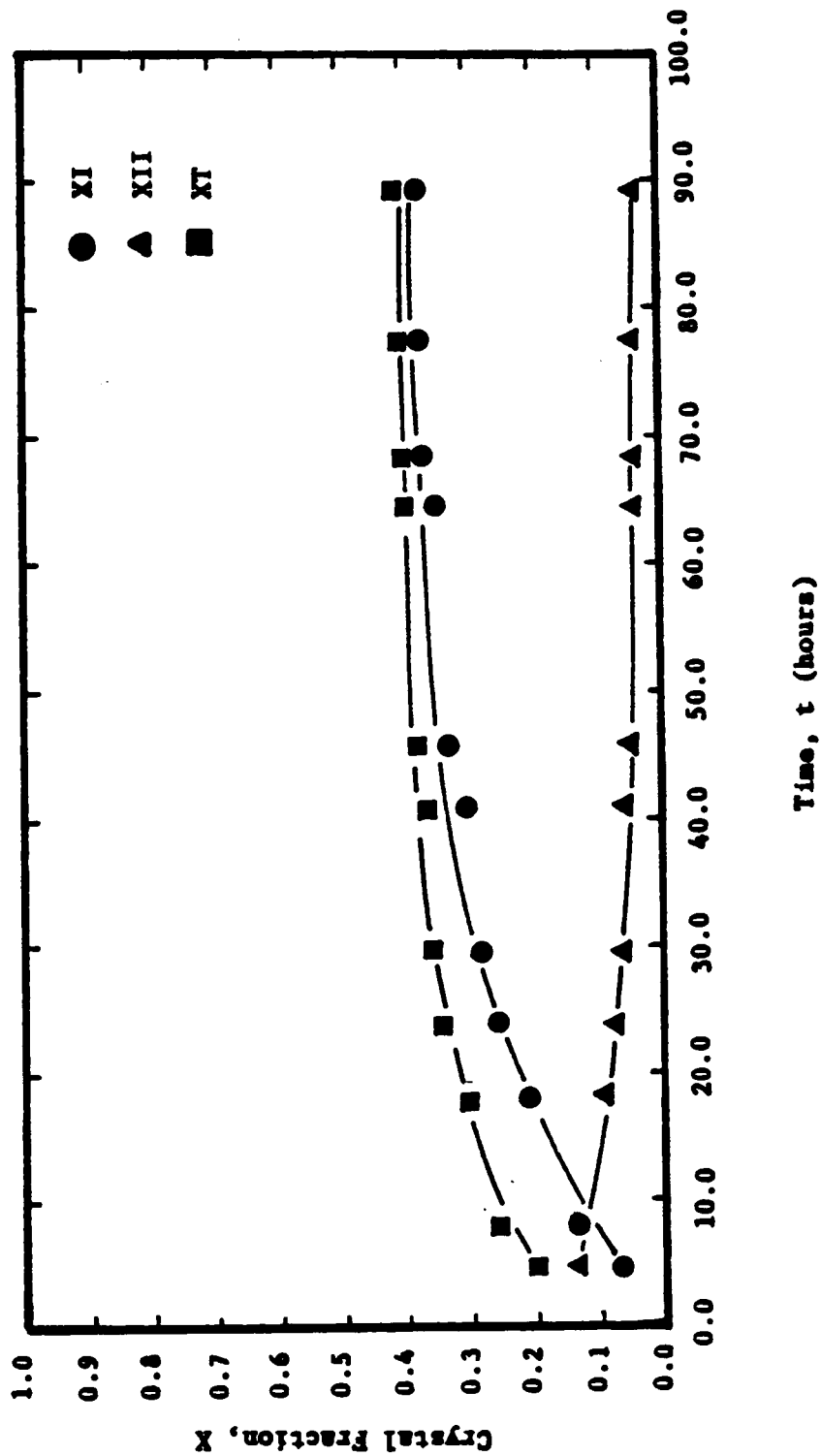


Figure 4-30. Crystal Fraction Present as a Function of Time for the SDR = 1 BR200S Fiber of Diameter 0.736 mm

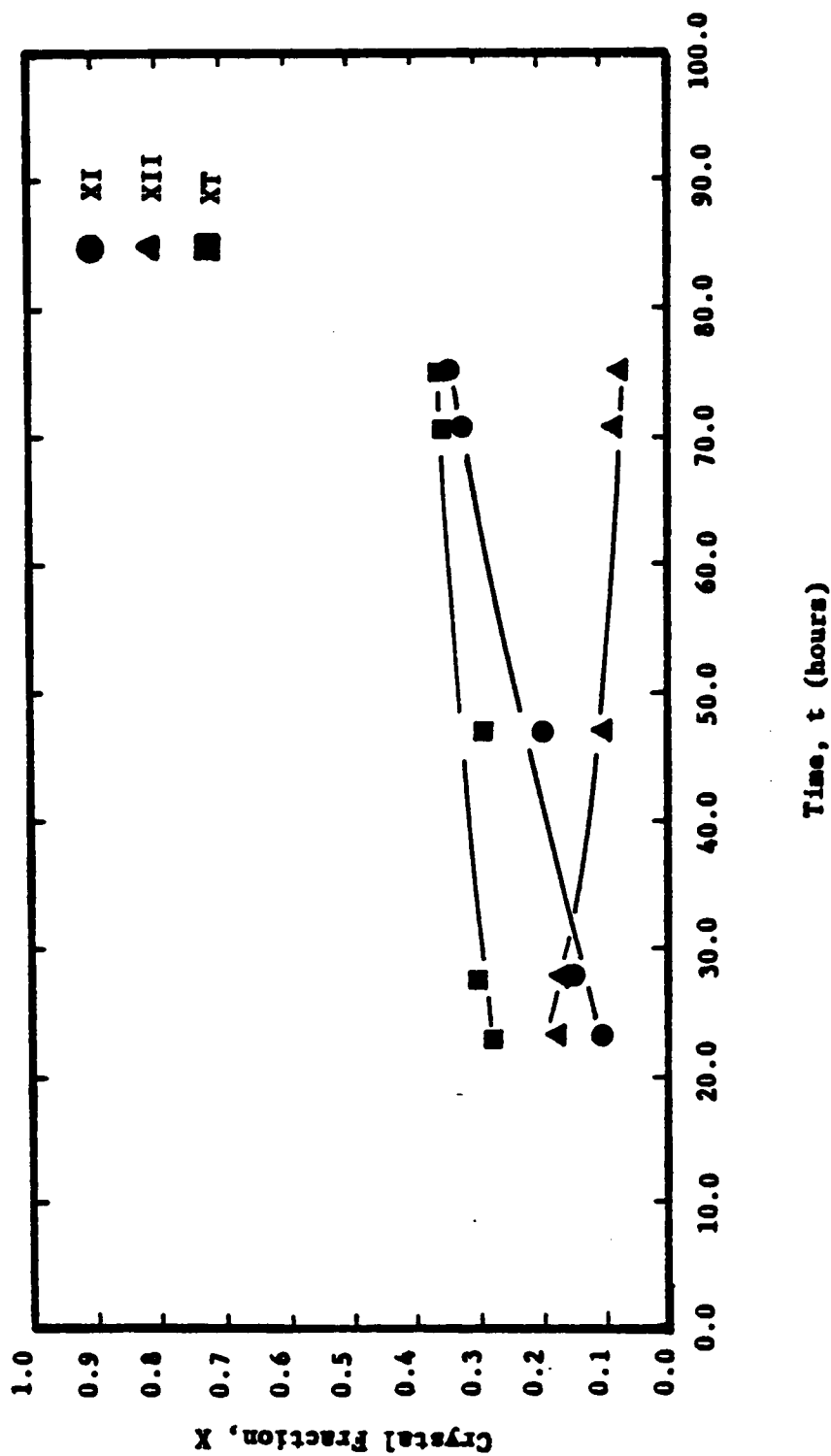


Figure 4-31. Crystal Fraction Present as a Function of Time for the SDR = 1 BR200S Fiber of Diameter 1.472 mm

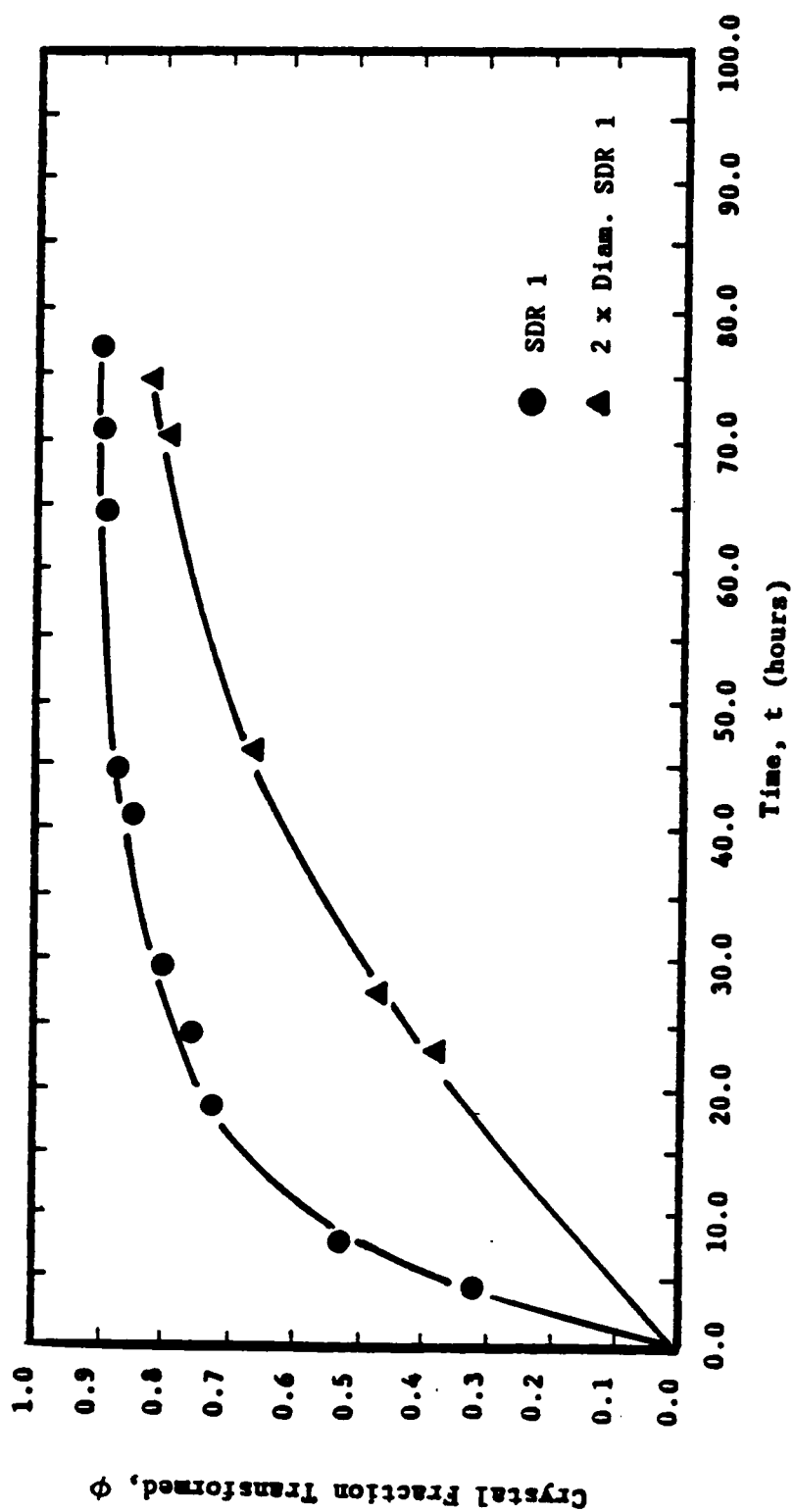


Figure 4-32. Effect of Sample Thickness on an SDR = 1 Fiber of BR200S

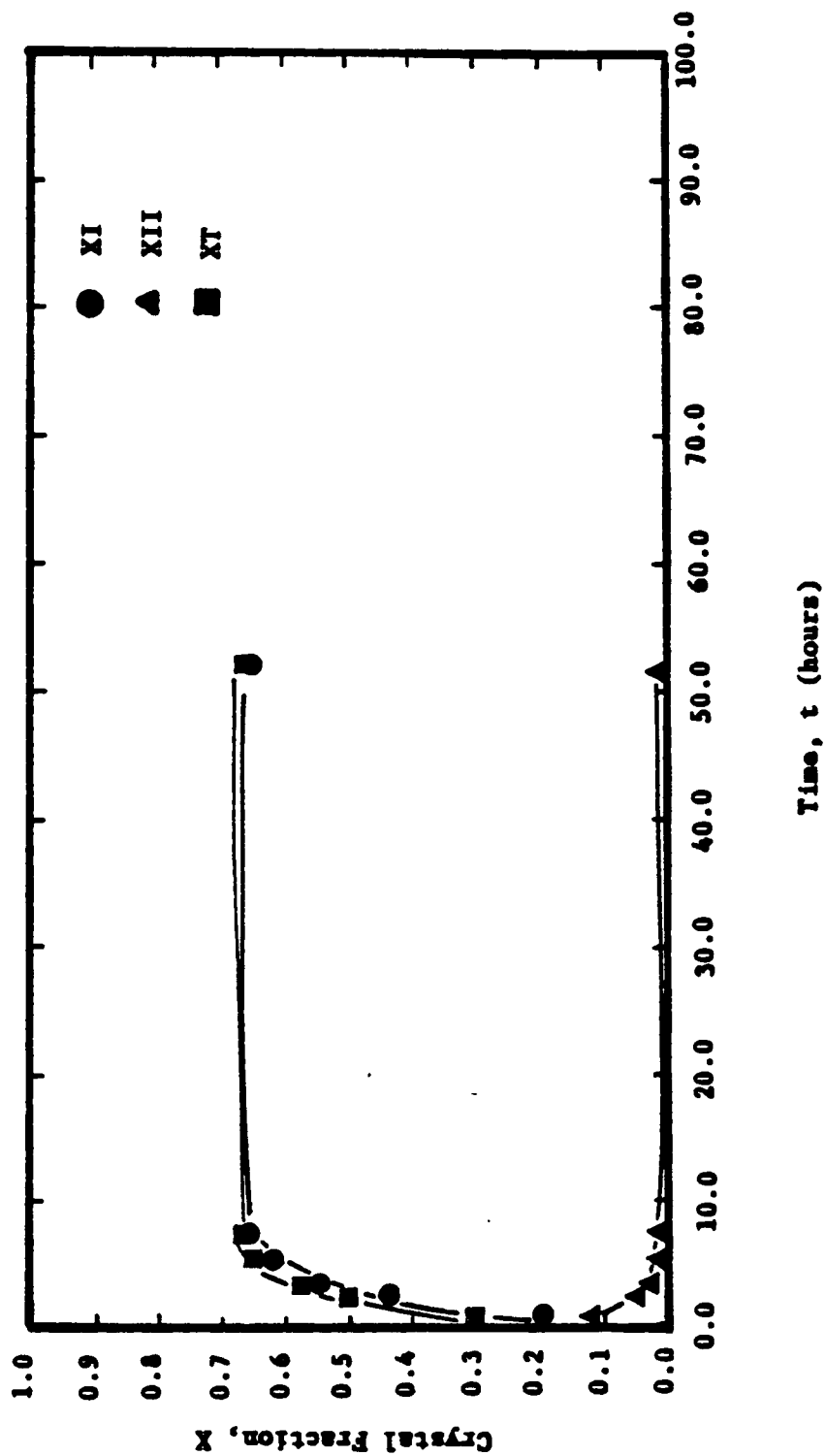


Figure 4-33. Crystal Fraction Present as a Function of Time for the SDR ≈ 70 BR200S Fiber of Diameter 0.0736 mm (initial)

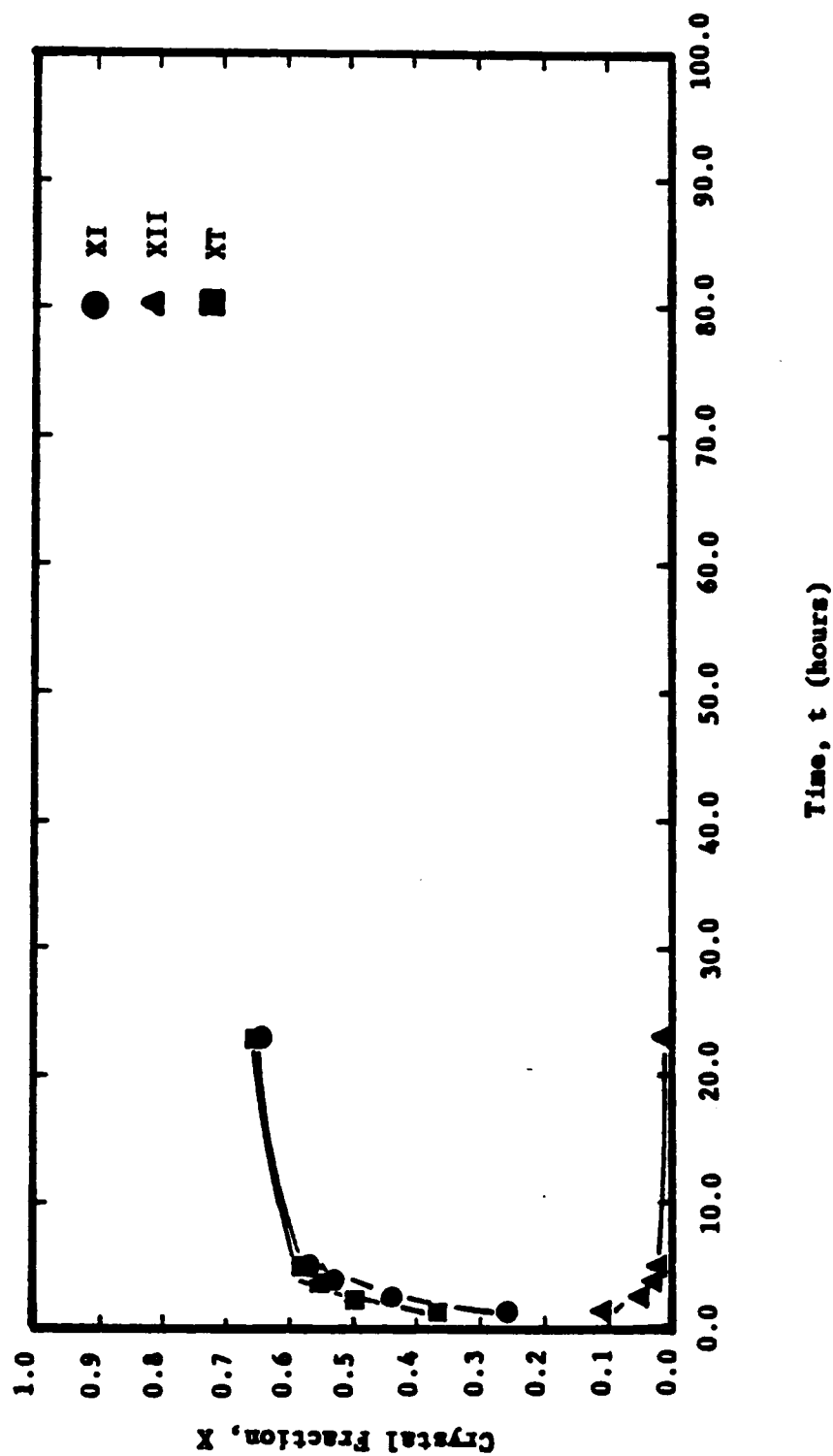


Figure 4-34. Crystal Fraction Present as a Function of Time for the SDR = 70 BR200S Fiber of Diameter 1.472 mm (initial)

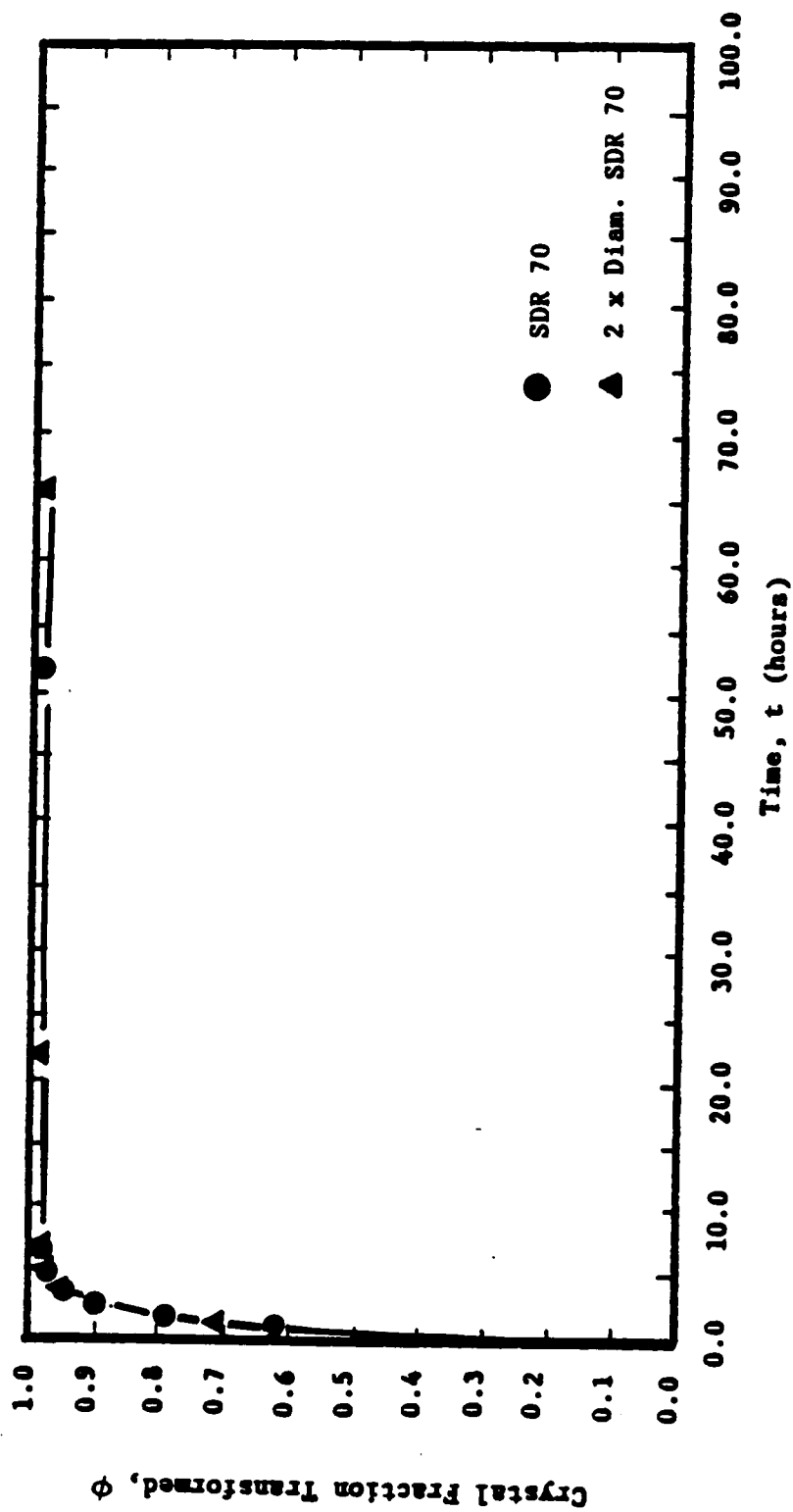


Figure 4-35. Effect of Sample Thickness on an SDR = 70 Fiber of BR200S

Given several assumptions about the nature of the surface nuclei, it is possible to derive a relationship between the Avrami rate constant and sample geometry. In order to try to discern some relationship between dimension and the rate constant, both of the fibers of SDR = 1.0 and the unoriented compression molded sheet of BR200S results were utilized. For fiber-like samples the surface to volume ratio reduces to $2/\text{radius}$ and for the sheet samples to $2/\text{thickness}$ (assuming an infinite sheet).

To quantify this effect and determine the dependence on surface area per unit volume, an equation for the transformation mechanism of one-dimensional growth and instantaneous surface nucleation was developed. This model assumes a constant number of nuclei, N , which are present instantaneously and a linear one-dimensional growth rate, $u(t)$. The dimension of the growth is l and is a function of time.

$$l(t) = \int_0^t u(t) dt \quad (4-2)$$

and the growth rate is

$$u(t) = dl/dt \quad (4-3)$$

The volume of a ribbon-like crystal is

$$V_n = lWT = WT \int_0^t u(t) dt \quad (4-4)$$

Now, the transformed volume for all crystals at time, t , must be considered.

$$V_t = N_o W T \int_0^t u(t) dt \quad (4-5)$$

The rate of transformation of the volume is

$$\frac{dV_t}{dt} = N_o W T \cdot u(t) \quad (4-6)$$

Also crystal impingement must be accounted for by a term for the volume fraction of untransformed material.

$$\frac{dV_t/V}{dt} = \frac{N_o W T u(t)}{V} \cdot (1 - V_t/V) \quad (4-7)$$

Solving the differential equation by utilizing an integrating factor and assuming that the growth rate is constant, the value of the volume transformed becomes

$$V_t/V = 1 - \exp \frac{-N_o W T}{V} \cdot ut \quad (4-8)$$

Where the rate constant can be described in terms of the dimensions of the sample.

$$K = \left(\frac{N_o WT}{V} \right) \cdot u \quad (4-9)$$

$$N_o WT = S \quad (4-10)$$

and

$$K = \frac{S}{V} \cdot u \quad (4-11)$$

The K values calculated from the Avrami analysis for $n = 1.0$ were $.067 \text{ hr}^{-1}$ for the .37 mm radius fiber, $.023 \text{ hr}^{-1}$ for the .74 mm radius fiber, and $.005 \text{ hr}^{-1}$ for the compression molded sheet of thickness 1.4 mm. This linear relationship between K and S/V provides a growth rate from the experimental data of 0.014 mm/hr with a correlation of 0.991 from linear regression. Utilizing the calculated growth rate and the linear relationship in equation 4-8, the K values were 0.065 hr^{-1} , 0.028 hr^{-1} , and 0.016 hr^{-1} for the 0.37 mm radius fiber, the 0.74 mm radius fiber, and the compression molded sheet of thickness 1.4 mm respectively. This prediction seems to be very good in thin samples, but as the thickness increases toward infinity, and thus the surface to volume ratio toward zero, the relationship breaks down. This breakdown, as evidenced by the presence of a negative

intercept, may be due to the existence of other transformation nuclei which are not located on the surface.

Therefore, when comparing data of different dimensions for the pure, unoriented polybutene-1, one could choose a basis of one S/V ratio on which to report normalized values.

4.3.2. Secondary Crystallization and Transformation Kinetics as Affected by Orientation

Unmodified polybutene-1 exhibits slow secondary crystallization and transformation. It has been noted that stress or strain and orientation enhance these rates. The effect of melt orientation, with assumably negligible stress, on the secondary crystallization will be discussed, followed by the effect of melt orientation on the crystal-crystal transformation.

As seen in Figure 4-30 on page 105, the BR200S fiber of spin draw ratio (SDR) of 1.0 and 0.736 mm diameter exhibited an initial crystal fraction of 20% which increased to 45% or 50% in about 45 hours. The secondary crystallization rate constant was 0.096 hr^{-1} . The initial values of crystallinity are lower than the compression molded values due to the use of an ice water bath quench instead of a room temperature water bath quench. It has been noted that rapidly quenched samples initially exhibit a time lag in the crystallization and transformation (B-13,H-10).

Orientation induced crystallization has been a well accepted phenomenon in polymer systems. Figure 4-36 shows the SDR = 35 BR200S fiber which had initial relative crystallinity of about 28% and reached about 65% in around 50 hours. The SDR = 70 BR200S fiber had initial relative crystal fraction of 30% and reached 65% in about 5 hours as seen in Figure 4-33 on page 108. At 105 SDR the BR200S fiber had initial relative crystal fraction of about 50% and increased to 60% in about 3 hours. This behavior is seen in Figure 4-37. The secondary crystallization rate constants increased as follows: 0.27 hr^{-1} for the SDR = 35, 0.39 hr^{-1} for the SDR=70, and 0.55 hr^{-1} for the SDR = 105. Therefore, increasing the spin draw ratio seemed to increase the relative crystal fractions as well as the rate of secondary crystallization. The crystal fraction reached an asymptotic value of about 60% to 65% above a SDR of 35. Similar behavior appeared for the SB05 and PP5 data which appear in Figures A-88 through A-96 on pages 231 through 239.

It is also well known that mechanical stress or strain (i.e. tensile, rolling, pressure) enhances the rate of crystal-crystal transformation in isotactic polybutene-1. In an attempt to clarify the contributions of stress, strain, and orientation to the transformation enhancement the following experimental analysis is provided. As before, the homopolymer resin (BR200S) and blends containing, 0.5% (wt.) sodium benzoate, and 5.0% (wt.) polypropylene were melt spun into fibers. Spinning was carried out with spin draw ratios of 1, 35, 70, and 105.

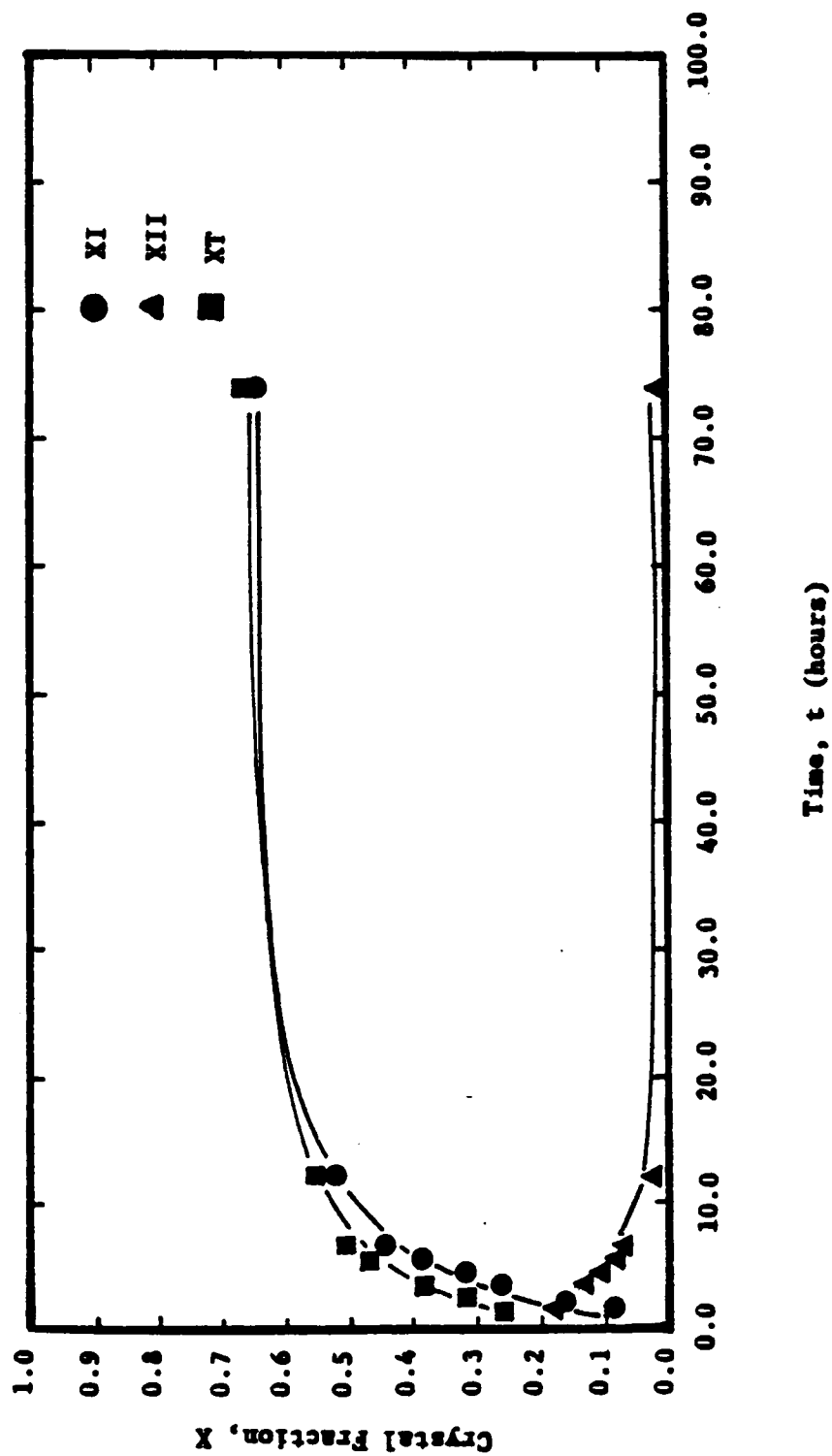


Figure 4-36. Crystal Fraction Present as a Function of Time for the SDR = 35 BR200S Fiber

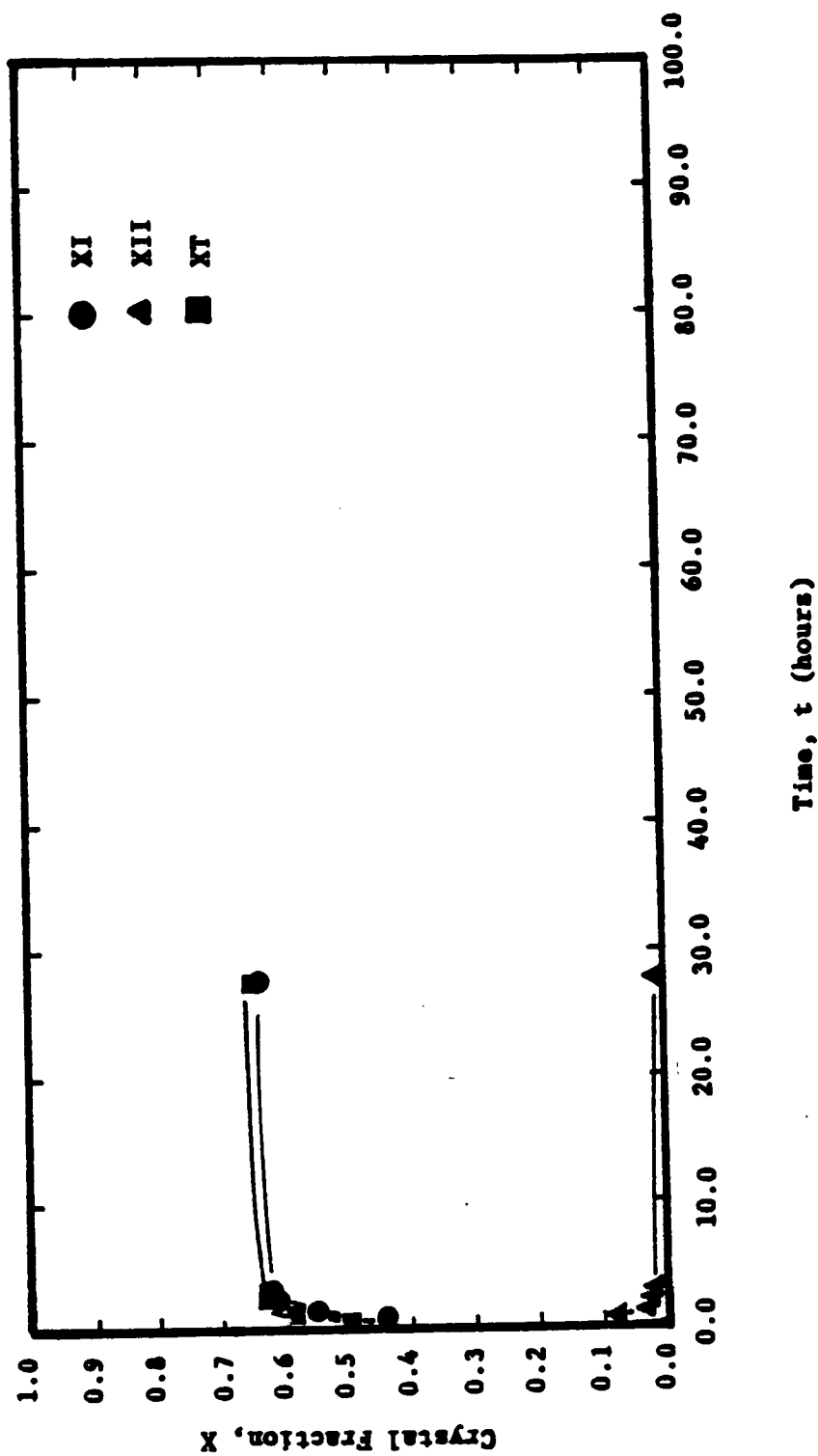


Figure 4-37. Crystal Fraction Present as a Function of Time
for the SDR = 105 BR200S Fiber

Molecular orientation increases with increasing draw ratio as quantified in terms of the Hermans' orientation factor, f_c . As shown in Figure 4-38 the f_c values increased sharply to around 0.85 at SDR = 35 and then gradually up to about 0.90 at SDR = 105 for the basic resin. It is noted that slightly lower values of f_c were observed for the blends. The lesser degree of orientation observed in the blends seems reasonable due to alteration of the polymer melt rheology by the addition of these substances or the degradation of the polybutene-1 due to the blending.

Melt spinning of polybutene-1 has been found to increase the rate of transformation. In all samples, increasing the spin draw ratio increased the transformation rate. However, as the spin draw ratio (SDR) increased, there seemed to be a diminishing rate of enhancement of the transformation. Above 105 SDR the sample was completely transformed within the minimum time of fiber formation and sample measurement (approximately 4 minutes). Figures 4-39 through 4-41 show the volume fraction transformed of the crystal over a period of about 100 hours for BR200S, SB05, and PP5.

The additives seemed to affect the transformation rate at low SDR with a diminishing importance as the SDR increased. As in the case of films, Figure 4-42 shows that at SDR = 1 the sodium benzoate at 0.5% (wt.) only slightly increased the transformation rate while polypropylene at 5% (wt.) provided a greater increase in the transformation rate. Figure 4-43 shows that there is a decreased effect of additives for samples with SDR values of 35. Both the 0.5%

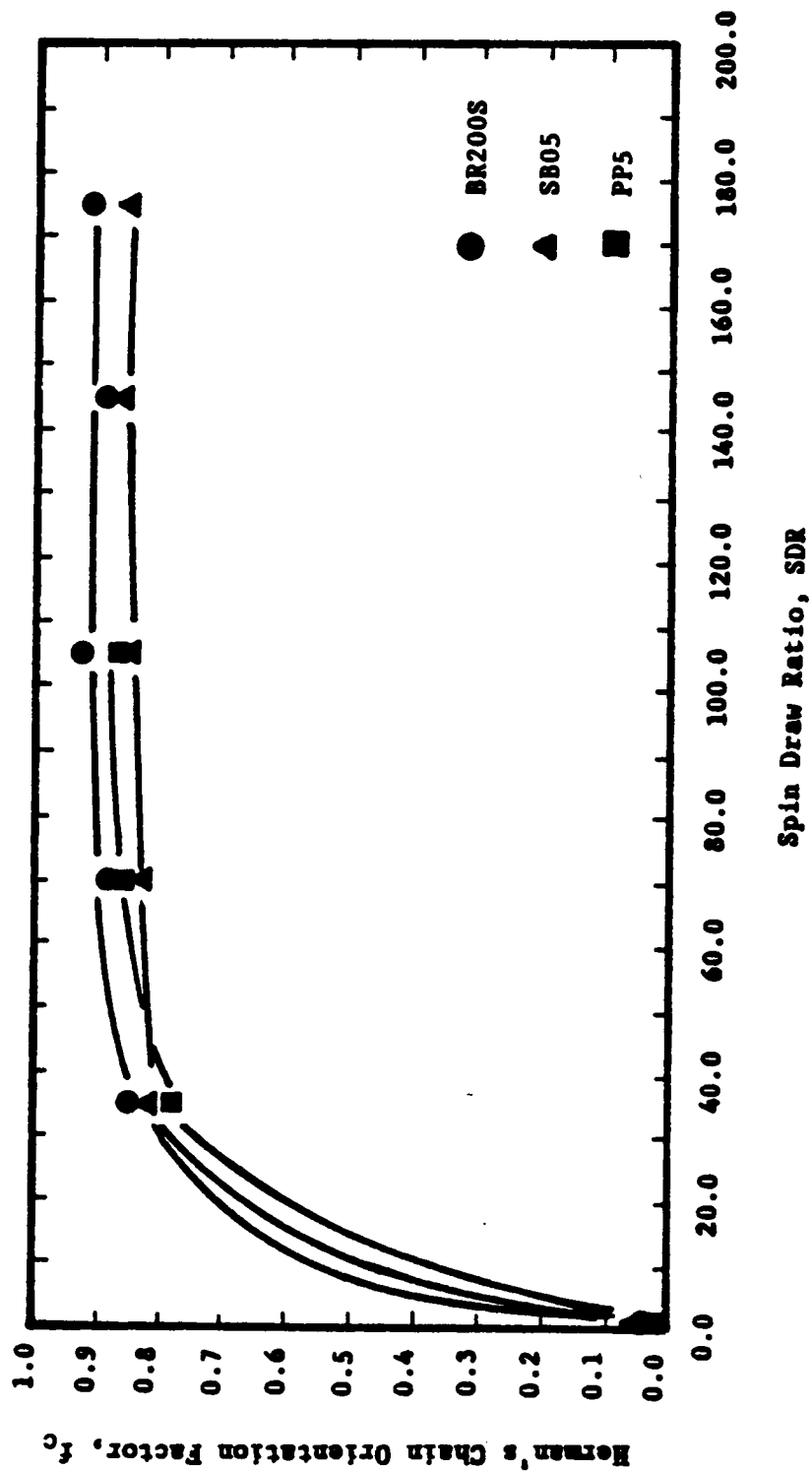


Figure 4-38. Herman's Orientation Factor as a Function of Spin Draw Ratio for the BR200S, SB05, and PP5 Fibers

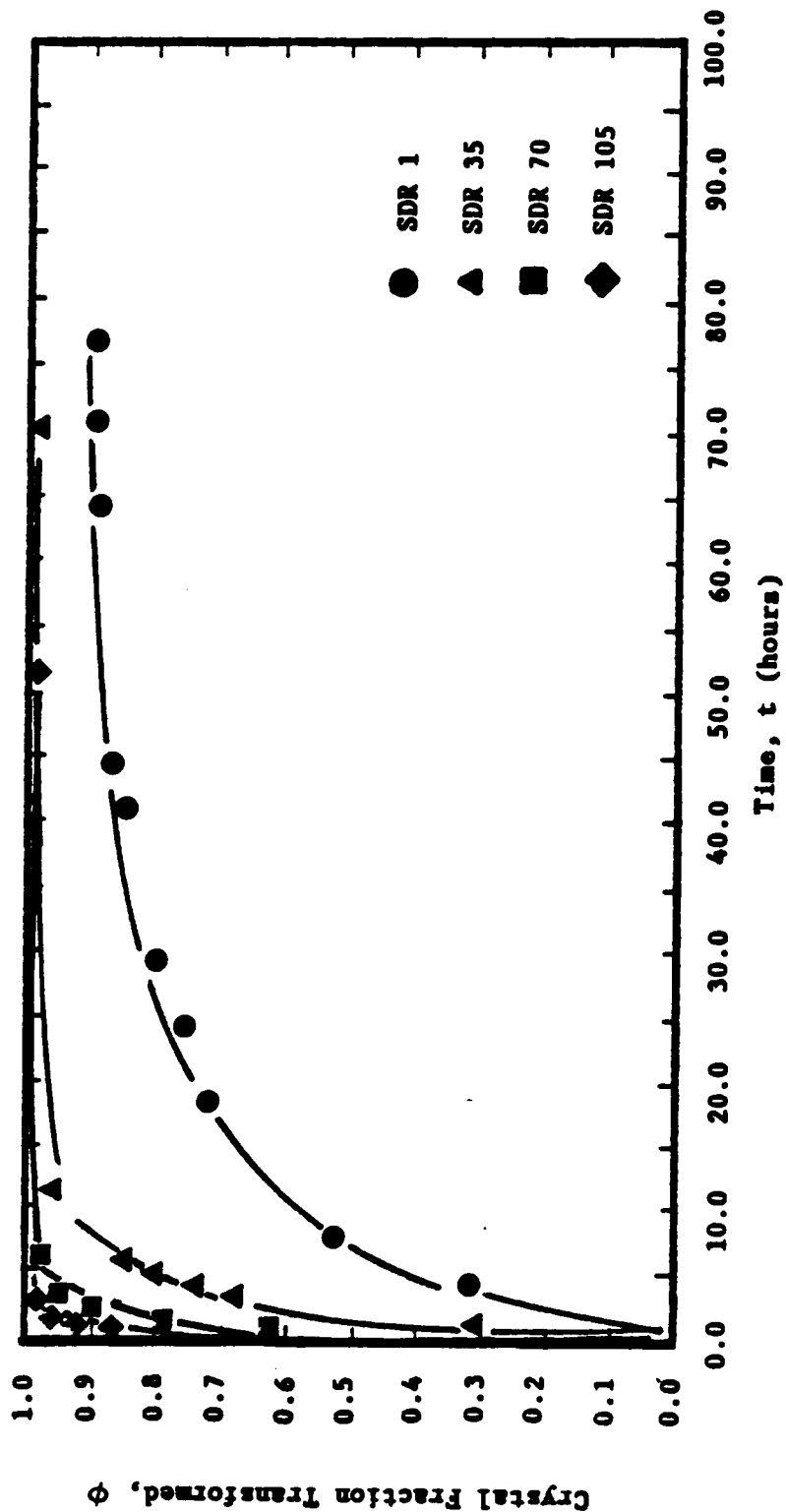


Figure 4-39. Volume Fraction of the Crystal Transformed Over Time for the BR200S Resin Fibers Formed at 1, 35, 70, and 105 Spin Draw Ratios

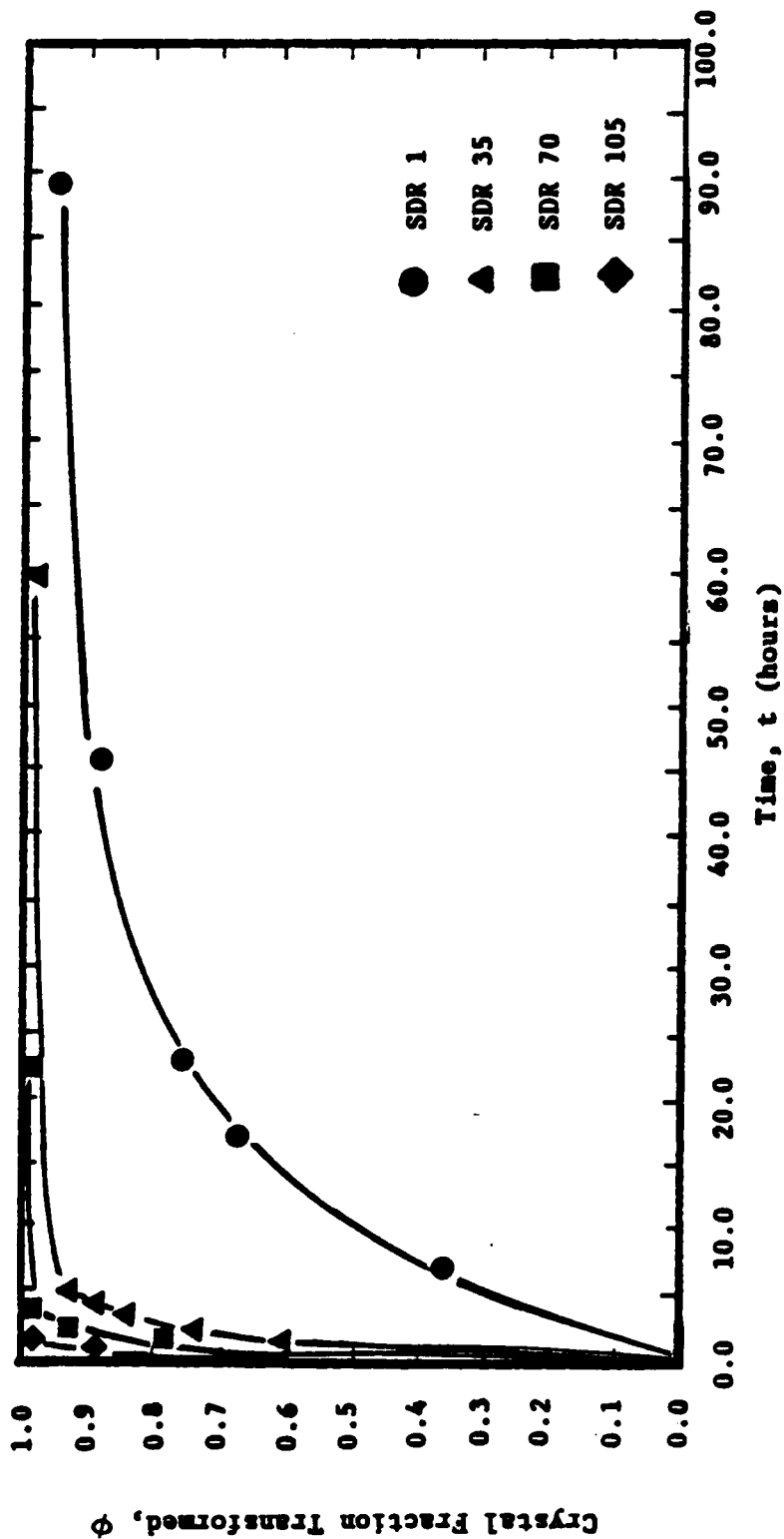


Figure 4-40. Volume Fraction of the Crystal Transformed Over Time for the SB05 Blend Fibers Formed at 1, 35, 70, and 105 Spin Draw Ratios

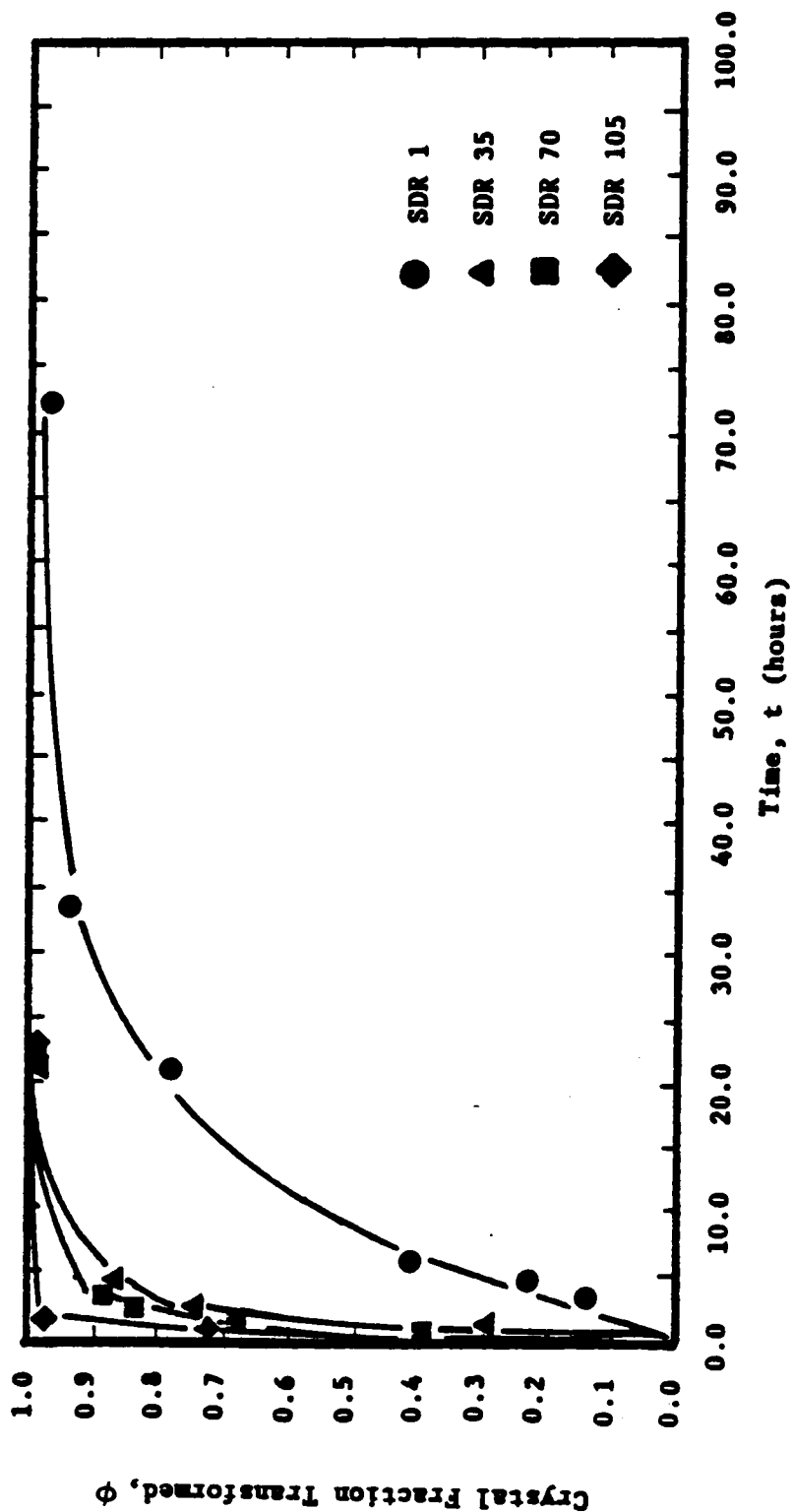


Figure 4-41. Volume Fraction of the Crystal Transformed Over Time for the PP5 Blend Fibers Formed at 1, 35, 70, and 105 Spin Draw Ratios

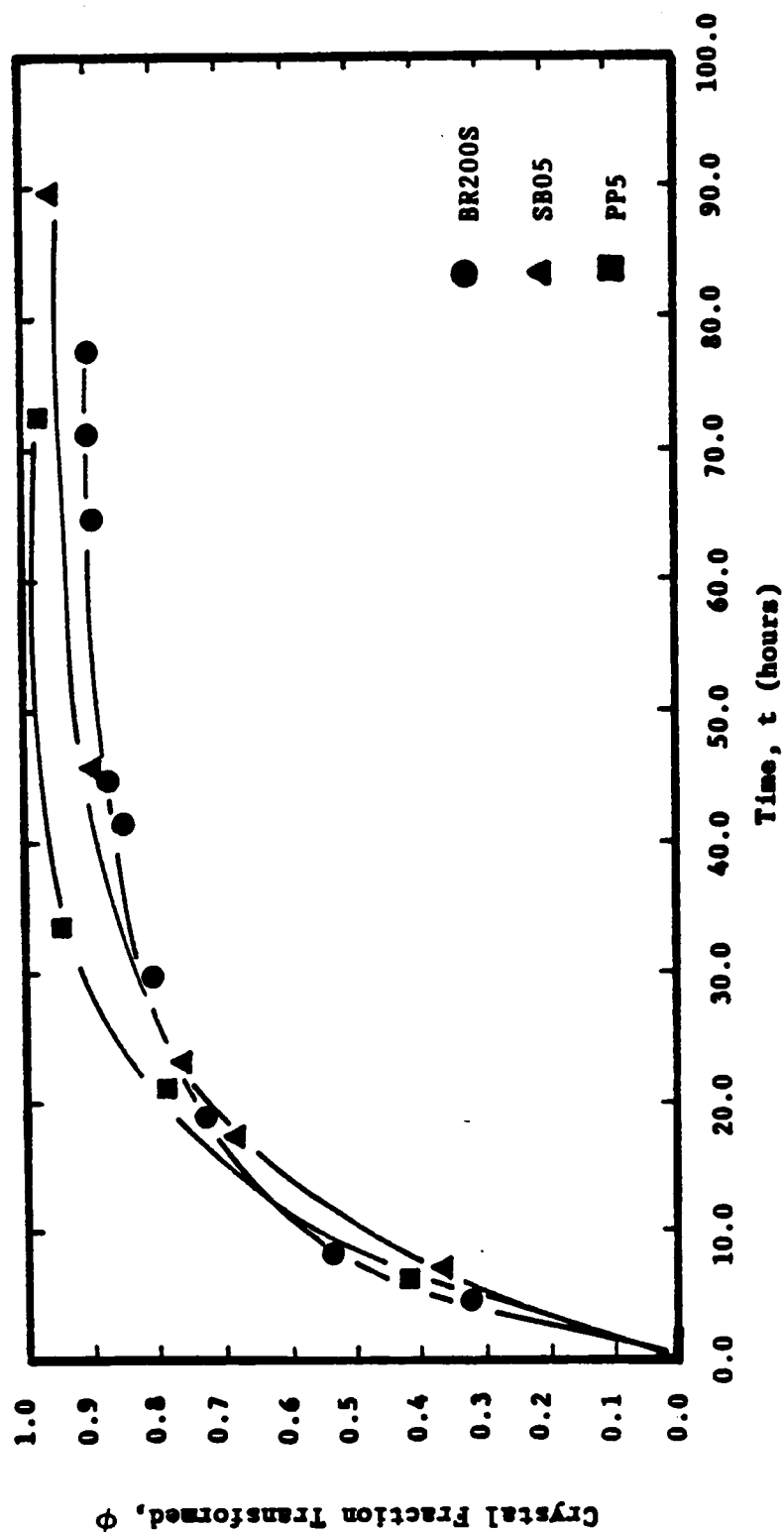


Figure 4-42. Volume Fraction of the Crystal Transformed Over Time at the Spin Draw Ratio of 1 for BR200S, SB05, and PP5

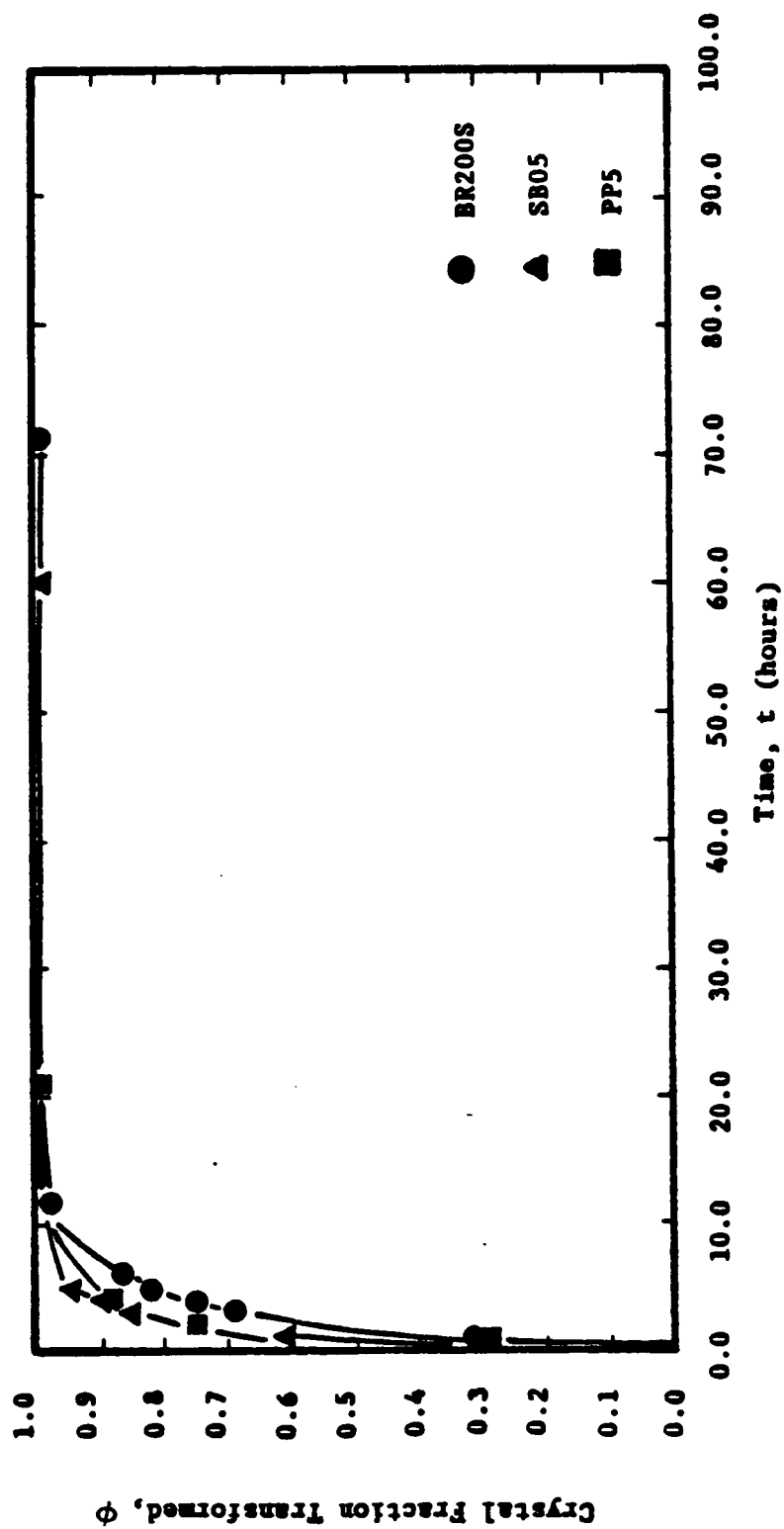


Figure 4-43. Volume Fraction of the Crystal Transformed Over Time at the Spin Draw Ratio of 35 for BR200S, SB05, and PP5

(wt.) sodium benzoate and 5.0% (wt.) polypropylene seemed to enhance the rate only slightly above the basic resin. As shown in Figure 4-44 at a SDR = 105 there was no distinguishable additive enhancement of the transformation rate over the basic resin.

The transformation half-times decreased sharply with increasing SDR. Figure 4-45 shows that the half-times decreased rapidly to about 1 to 2 hours at SDR values of 35 and then gradually decreased to about 0.5 hours at 105 SDR. Past 105 SDR the measurements were not possible due to almost instantaneous transformation. Table 4-6 summarizes the half-time ($t_{1/2}$) values. Although the half-times for the SDR = 1 fibers with additives were lower than the BR200S, the transformations overtake the BR200S after the initial lag time.

K.B. Hong and Y.D. Lee found in their respective master's works on polybutene-1 that very slight amounts of cold rolling (even 10% roll reduction) will enhance the transformation rate as dramatically as found in this research by the 105 SDR in the fibers (H-10,L-3). Figure 4-46 shows Hong's data for the transformation of lightly cold rolled film. Y.D. Lee provided extensive morphological studies on the cold rolled films of polybutene-1. This study shows that even at 30% cold roll reduction there was little evidence of orientation in the BR200S as seen in the schematic wide-angle x-ray film pattern in Figure 4-47. The fiber at SDR = 105 shows a high degree of orientation with an f_c value of about 0.9. Therefore, it seems that stress or strain, and not necessarily orientation, enhances the transformation most effectively. To facilitate transformation it

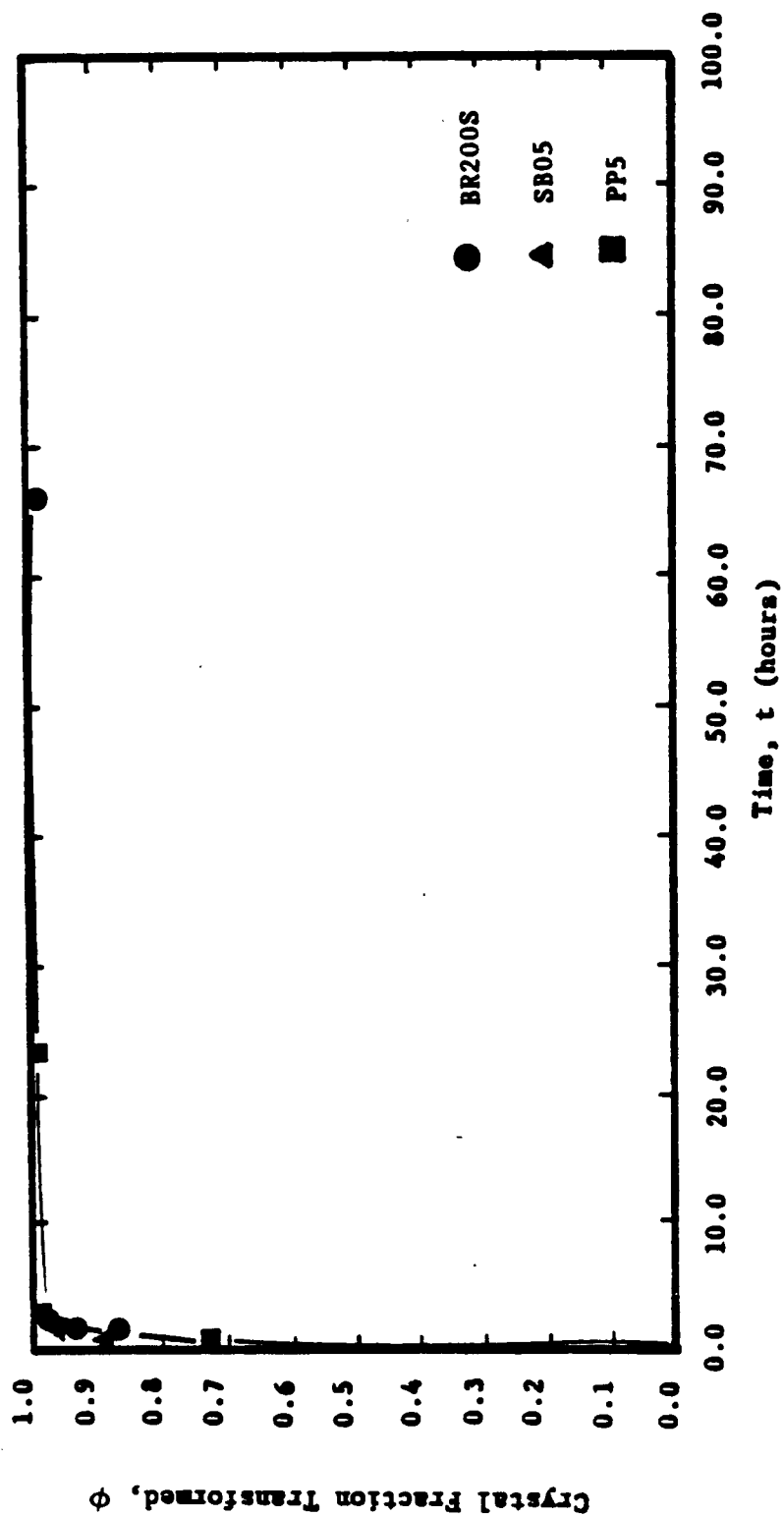


Figure 4-44. Volume Fraction of the Crystal Transformed Over Time at the Spin Draw Ratio of 105 for BR200S, SB05, and PP5

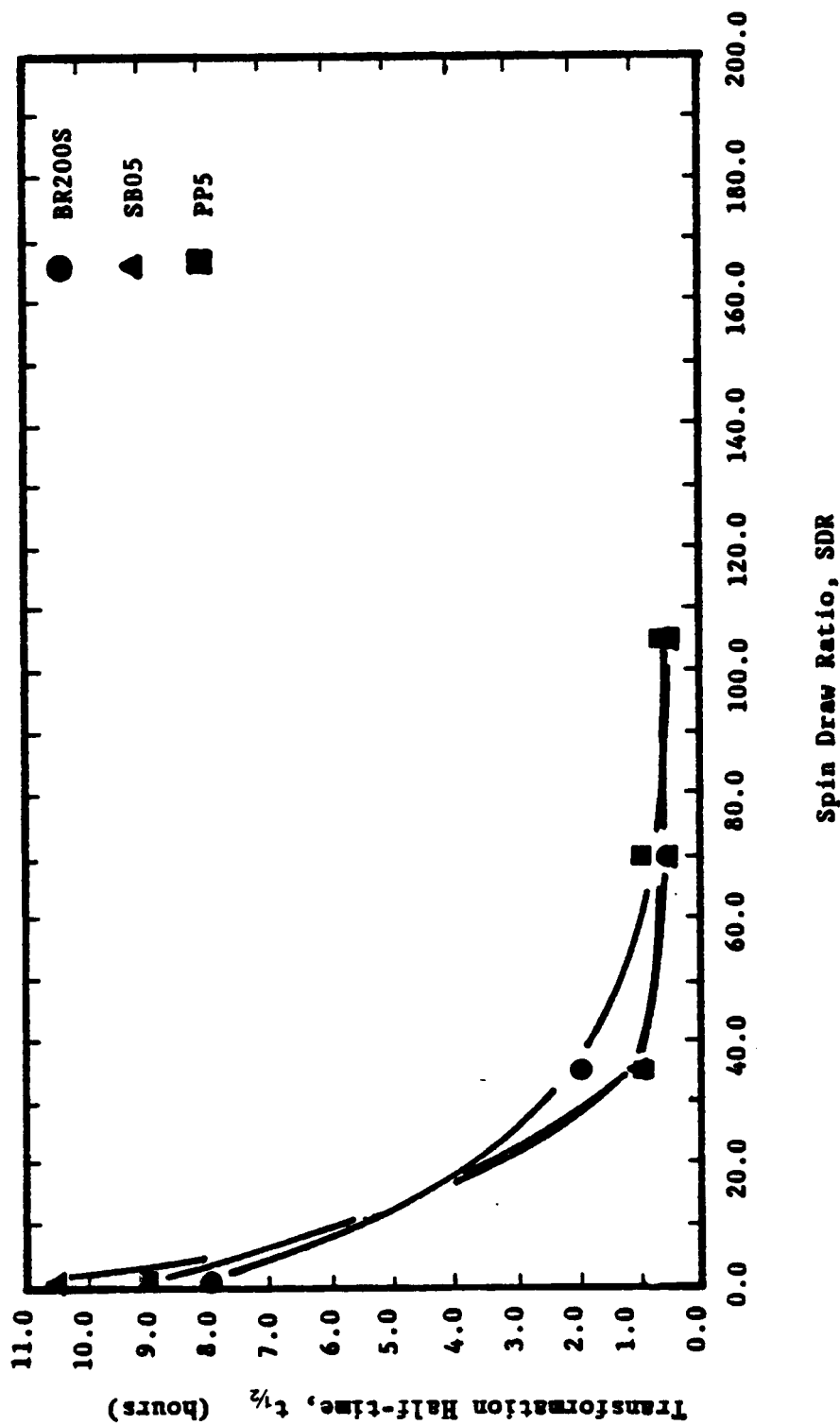


Figure 4-45. Transformation Half-time as a Function of Spin Draw Ratio for BR200S, SB05, and PP5 Fibers

Table 4-6. Transformation Half-time Values for Spin Drawn Fibers of BR200S, SB05, and PP5.

Sample Name	Half-time, (hours)
BR200S	
1 SDR	8.0
35 SDR	2.0
70 SDR	0.5
105 SDR	0.5
SB05	
1 SDR	10.5
35 SDR	1.0
70 SDR	0.5
105 SDR	0.5
PP5	
1 SDR	9.0
35 SDR	1.0
70 SDR	1.0
105 SDR	0.5

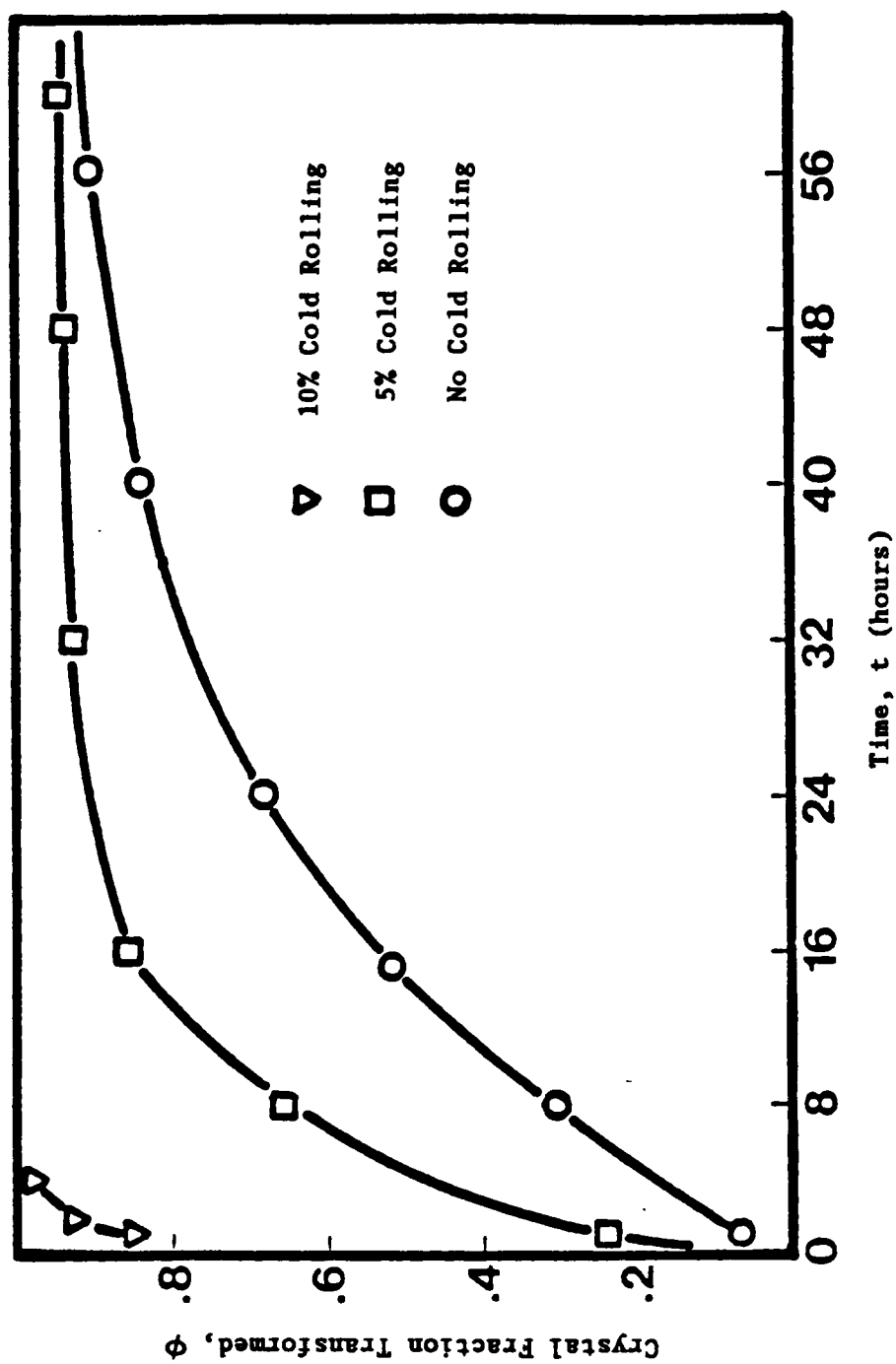


Figure 4-46. Effect of Cold Rolling on the Form II - Form I Transformation in BR200S Compression Molded Films (H-10)

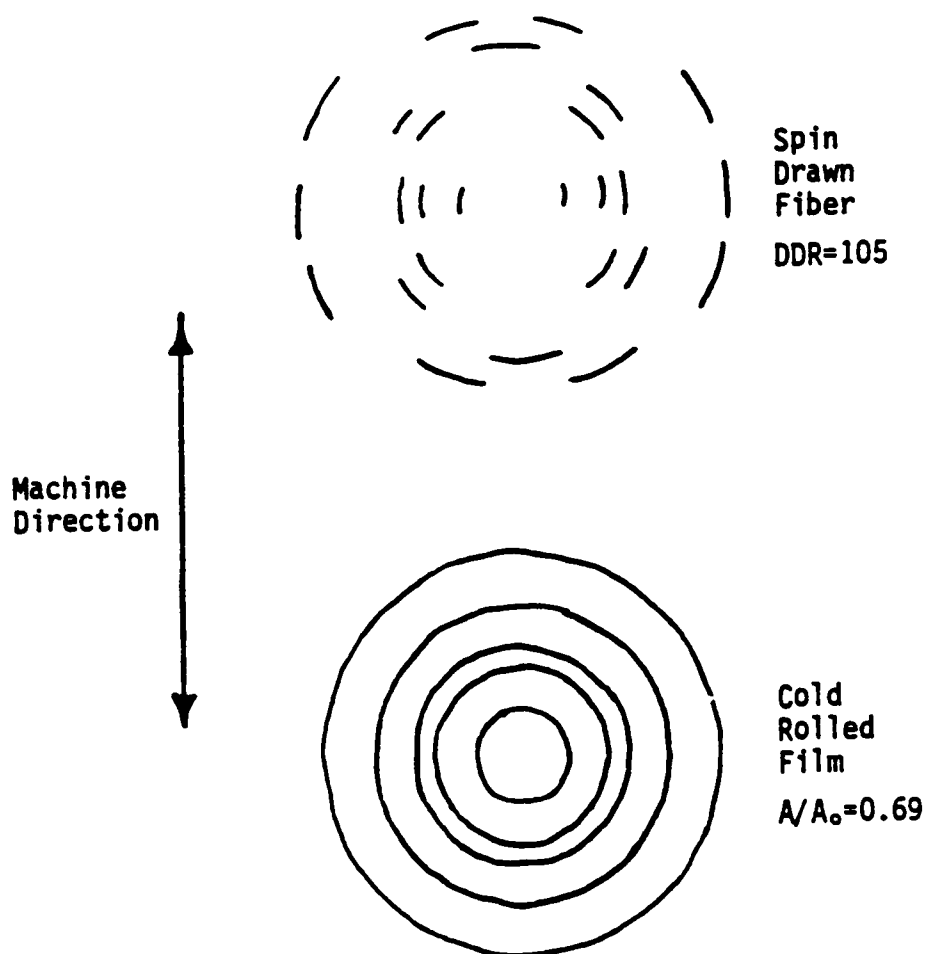


Figure 4-47. Schematic Wide-angle X-ray Film Patterns of BR200S Fiber of SDR = 105 and Cold Rolled Film of Roll Reduction 30%

is more favorable to induce stresses in the solid state rather than to orient the chains by the spin drawing of fibers.

CHAPTER V

CONCLUSIONS

This work provided insight into the structure development during secondary crystallization and transformation of polybutene-1, the effects of selected additives on the crystallization and transformation, and the contributions of stress or strain versus molecular orientation to the above mentioned transformations.

Samples were blended containing various weight fractions of certain additives. To study the effects and controlling factors on the transformation, x-ray diffraction was used. Compression molded samples were transformed at 0, 23, 45, and 60 °C to look at the effect on the transformation rate. The crystallization was studied using differential scanning calorimetry. The change in the crystallization onset temperature was utilized to measure the relative crystallization rates of the blends.

To examine the effect of molecular orientation on the transformation and crystallization, fibers were spun at draw ratios of 1, 35, 70, and 105. The transformation was again followed using x-ray diffraction to determine the relative crystal fractions present. The results of this orientation and transformation study were then compared to the effects of cold rolling observed by Hong and Lee.

Structure development during transformation was examined using small-angle light and small-angle x-ray scattering measurements carried out on compression molded water quenched films.

From these aforementioned experiments numerous conclusions may be generated.

1. In unstressed, unmodified BR200S films the initial crystallization resulted in a spherulitic superstructure which upon secondary crystallization and transformation developed a regularly spaced long period order of $230 \text{ \AA}$.

2. Selected additives increased the crystallization rate in the polybutene-1. The most effective crystallization rate enhancing additives studied were, in order, 1-naphthalene acetamide, followed by carbon black and then polypropylene. The diphenyl ether, α -chloronaphthalene, sodium benzoate, and stearic acid enhanced the crystallization rate slightly. The important characteristic for enhancement of crystallization is the presence of homogeneously distributed foreign matter of relatively high crystallization temperature. Also to be considered in the case of crystalline additives would be the possibility of epitaxial nucleation. This phenomenon might enable the distinction between the relative nucleation abilities of the crystalline additives.

3. Certain additives enhance the transformation rate of the polybutene-1. At 23°C the compression molded films of CN5 and DPE5, the liquid additive blends, were the most effective at increasing the transformation rate. The next most effective additive was

polypropylene at a 10% (wt.) concentration. Stearic acid at 5% (wt.) followed polypropylene in effectiveness. Sodium benzoate at 2% (wt.) and 1-naphthalene acetamide at 5% (wt.) had little effect on the rate while carbon black at 2% (wt.) inhibited the transformation rate. Apparently these additives had synergistic effects on the transformation. The α -chloronaphthalene enhanced both the nucleation rate and even more so the growth rate controlled regions. Contributions by both of these effects made it the most effective transformation enhancer. The diphenyl ether, a slightly better solvent than the α -chloronaphthalene, enhanced primarily the growth rate with no discernible effect on the nucleation rate. Polypropylene enhanced the nucleation rate to a greater extent than the growth rate. The other additives had insignificant enhancements in both nucleation and growth rates. This result seems to indicate a need for heterogeneous nucleation as well as for enhanced chain mobility. The secondary crystallization rate was effectively eliminated, within the experimental time frame, by 5% (wt.) 1-naphthalene acetamide. Other additives enhanced the rate but to a lesser extent.

4. Tensile properties were enhanced most effectively by the same additives which increased the crystallization and transformation rates as well as ultimate crystallinity. Most affected were the moduli and yield strengths of both the fresh and aged samples. Conversely, ultimate strengths were decreased in the blends due the nature of these materials, or interface incompatibility, and thus the phases may readily separate.

5. It was shown that sample dimensions affect the rate of secondary crystallization and transformation in unmodified polybutene-1. Samples with large surface areas per unit volume were observed to transform more rapidly than samples with small surface areas per unit volume. It was also shown that melt orientation diminishes this effect.

6. Molecular orientation developed by fiber spinning produced higher crystal fractions as well as slight enhancements of the secondary crystallization rate. The relative final crystal fractions increased from about 50 to 65% with an increase of SDR from 1 to 35. Above 35 SDR no further significant change was evident.

7. The increase in spin draw ratio in polybutene-1 fibers increases the rate at which the Form II-Form I transformation occurs. The Hermans' chain orientation factors increased with SDR while the transformation half-times decreased. Above a SDR of 105 the transformation occurred so rapidly that the measurement was not possible. However, most of the transformation acceleration occurred below a SDR of 70. When compared to cold rolled transformation and orientation data, the stress induced by cold rolling without orientation development appeared to be more effective than the melt chain orientation by fiber spin drawing. In fact, little orientation was evidenced at even 30% roll reduction while 10% reduction transformed the sample as well as a highly oriented fiber formed at a SDR of 105.

Recommendations in the area of polybutene-1 transformation and crystallization research lie in the realm of additive and sample dimension effects. It is of interest that additives which highly enhance either the crystallization or transformation do not necessarily promote the other to any significant extent. For instance, 5% (wt.) 1-naphthalene acetamide completely eliminates the slow secondary crystallization while having little or no effect on the transformation, while α -chloronaphthalene and diphenyl ether increase the transformation rate with only a slight effect on the crystallization. Further study in this area might be an investigation of the synergistic effects of combinations of additives in promoting crystallization and transformation. Also of interest (as indicated by the effect of carbon black) might be the retardation of this transformation to retain a softer, more flexible material for certain applications or processes such as stamping.

Also, the microscopic examination of the effects of the liquid versus crystalline additives would enable the distinction of the "growth" and "nucleation" enhancement mechanisms.

The relationship between the surface to volume ratio and the Avrami rate constant warrants further study of its applicability to modified polybutene-1.

BIBLIOGRAPHY

BIBLIOGRAPHY

- A-1. Alexander, L.E., "X-ray Diffraction Methods in Polymers Science," New York: Robert E. Krieger Publ. Co., 1979.
- A-2. Avrami, M., J. Chem. Phys., 7, 1103 (1939).
- A-3. Avrami, M., J. Chem. Phys., 8, 212 (1940).
- A-4. Avrami, M., J. Chem. Phys., 9, 177 (1941).
- A-5. Asada, T., J. Sasada and S. Onogi, Polym. J., 3,no. 3, 350 (1972).
- A-6. Armeniades, C.D. and E. Baer, J. Macromol. Sci. (Phys.), B1(2), 309 (1967).
- B-1. Blais, P. and R.J. Manley, J. Polym. Sci., A-1, 6, 291 (1968).
- B-2. Boor, J. and J.C. Mitchell, J. Polym. Sci., Part A, 1, 59 (1963).
- B-3. Billmeyer, F.W., "Textbook of Polymer Science," Third Edition. New York: John Wiley and Sons, 1984.
- B-4. Banks, W. and A. Sharples, Makro. Chem., 59, 233 (1963).
- B-5. Banks, W. and J.N. Hay, J. Polym. Sci., A2, 9, 4059 (1964).
- B-6. Bahadur, S. and A. Henkin, Poly. Eng. Sci., 13, 422 (1973).
- B-7. Binsbergen, F.L., Polymer, 11,253 (1970).
- B-8. Billmeyer, F.W., "Textbook of Polymer Science," Second Edition. New York: Wiley Interscience, 1971.
- B-9. Binsbergen, F.L. and B.G.M. DeLange, Polymer, 11, 309 (1970).
- B-10. Ball, R. and R.S. Porter, J. Polym. Sci., Polym. Letters Ed., 15, 519 (1977).
- B-11. Boor, J. and E.A. Youngman, J. Polym. Sci., Polym. Letters Ed., 2, 903 (1964).
- B-12. Boor, J. and J.C. Mitchell, J. Polym. Sci.: A, 1, 59 (1963).
- B-13. Burns, J.R. and D. Turnbull, J. Polym. Sci. A2, 6, 775 (1968).
- B-14. Boor, J. and J.C. Mitchell, J. Polym. Sci., 62, 570 (1962).

- C-1. Coover, H.W., J. Polym. Sci.: Part C, 4, 1511 (1955).
- C-2. Chatterjee, A.M., "Modern Plastics Encyclopedia," J. Agranoff, Ed., New York: McGraw Hill, 1975.
- C-3. Choi, S.Y., J.P. Rakus and J.L. O'Toole, Poly. Eng. Sci., Oct., 349 (1966).
- C-4. Chatterjee, A.M., F.P. Price and S. Newman, J. Polym. Sci., Polym. Phys., 13, 2369 (1975).
- C-5. Chatterjee, A.M., F.P. Price and S. Newman, J. Polym. Sci., Polym. Phys., 13, 2385 (1975).
- C-6. Chatterjee, A.M., F.P. Price and S. Newman, J. Polym. Sci., Polym. Phys., 13, 2391 (1975).
- C-7. Chatterjee, A.M., United States Patent, No. 4,320,209.
- C-8. Cortazar, M., C. Sarasola and G.M. Guzman, Eur. Polym. J., 18, 439 (1982).
- C-9. Clampitt, B.H. and R.H. Hughes, J. Polym. Sci.: Part C, 6, 43 (1964).
- C-10. Cojazzi, G., V. Malta, G. Celotti, R. Zannetti, Die Makromol. Chem., 177,915 (1976).
- D-1. Deanin, R.D., Soc. Plast. Eng. J., Jan., 43 (1967).
- D-2. Danusso, F. and G. Gianotti, Die Makromol. Chem., 88, 149 (1965).
- D-3. Danusso, F., G. Gianotti and G. Polizzotti, Macromol. Chem., 80,13 (1964).
- E-1. Evans, V.R., Trans. Far. Soc., 41, 365 (1965).
- E-2. Era, V.A. and T. Jauhiainen, Die Angewandte Makromol. Chem., 43, 157 (1975).
- F-1. Fujita, K., M. Diao, R. Okumura, S. Suehiro, S. Nomura, and H. Kawai, Polym. J., 15, 6, 449 (1983).
- G-1. Geil, P.H., Y.C. Yang, K.W. Chau, C.C. Hsu and A. Agarwal, 41st SPE ANTEC, 29, 404 (1983).
- G-2. Gordon, M. and I.H. Hillier, Polymer, 6, 213 (1965).

- G-3. Goldbach, G. and G. Peitscher, J. Polym. Sci., Polym. Letters Ed., 6, 783 (1968).
- G-4. Gohil, R.M. and R.D. Patel, Die Angewandte Makromol. Chem., 64, 43 (1977).
- G-5. Goldbach, V.G., Die Angewandte Makromol. Chem., 29/30, 213 (1973).
- G-6. Goldbach, V.G., Die Angewandte Makromol. Chem., 39, 175 (1974).
- G-7. Geacintov, C., R.B. Miles, H.J.L. Schuurmans, J. Polym. Sci.: Part A-1, 4, 431 (1966).
- G-8. Gohil, R.M., M.J. Miles, and J. Petermann, J. Macromol. Sci., Phys., B21(2), 189 (1982).
- G-9. Geacintov, C., R.S. Schotland and R.B. Miles, J. Polym. Sci.: Part C, 6, 197 (1966).
- H-1. Ham, G.E., J. Polym. Sci., 46, 475 (1960).
- H-2. Hoeg, D.F., "The Stereochemistry of Macromolecules," A.D. Ketley, Ed., Vol. 1, 47, New York: Marcel Dekker, (1968).
- H-3. Holland, V.F. and R.L. Miller, J. Appl. Phys., 35, 3241 (1964).
- H-4. Hay, J.N. and P.J. Mills, Polymer, 23, 1380 (1982).
- H-5. Hay, J.N., Brit. Polym. J., 11,137 (1979).
- H-6. Hillier, I.H., J. Polym. Sci.: Part A, 3, 3067 (1965).
- H-7. Haas, T.W. and B. Maxwell, Polym. Eng. Sci., 9, 225 (1969).
- H-8. Holden, H.W., J. Polym. Sci.: Part C, 6, 209 (1964).
- H-9. Holland, V.F. and R.L. Miller, J. Appl. Phys., 11, 35 (1964).
- H-10. Hong, K.B., University of Tennessee, Knoxville, Master's Degree Thesis.
- H-11. Hong, K.B. and J.E. Spruiell, Preprint, J. Appl. Phys., (1985).
- H-12. Hendricks, R.W., J. Appl. Cryst., 2, 15 (1978).
- J-1. Jones, A.T., J. Polym. Sci., Polym. Letters Ed., 3, 591 (1965).
- J-2. Jones, A.T., Polymer, 7, 23 (1966).
- K-1. Kline, G.M., "Modern Plastics Encyclopedia," March, 78 (1971).

- K-2. Kratky, O., and G. Milholic, J. Polym. Sci., 2, 449 (1963).
- L-1. Lindengren, C.R., Polym. Eng. Sci., 10, 3, 163 (1970).
- L-2. Luongo, J.P. and R. Salovey, J. Polym. Sci.: Part A-2, 4, 997 (1966).
- L-3. Lee, Y.D., University of Tennessee, Knoxville Master's Degree Thesis.
- L-4. Lovinger, A.J., J.O. Chua, and C.C. Gryte, J. Poly. Sci., Phys. Ed., 15, 641 (1977).
- M-1. Mandelkern, F.A. Quinn and P.J. Flory, J. Appl. Phys., 25, 830 (1954).
- M-2. Morgan, L.B., J. Appl. Chem., 4, 160 (1954).
- M-3. Miller, R.L. and V.F. Holland, J. Polym. Sci., Polym. Letters Ed., 2, 519 (1964).
- N-1. Natta, G, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, G. Morajlio and J. Morajlio, J. Amer. Chem. Soc., 77, 1708 (1955).
- N-2. Natta, G, Atti Accad. Nazl. Lincei, Mem. Classe Sci. Fis., Mat. Nat., 4, 61 (1955).
- N-3. Natta, G., J. Polym. Sci., 16, 143 (1955).
- N-4. Natta, G., Macromol. Chem., 16, 213 (1955)
- N-5. Natta, G., P. Corradini and I.W. Bassi, Rend. Accad., Naz. Lincei, 19, 404 (1955).
- N-6. Natta, G., Macromol. Chem., 35, 94 (1960).
- N-7. Nakafuku, C. and T. Miyaki, Polymer, 24, 141 (1983).
- O-1. Oda, T., M. Maeda, S. Hibi and S. Watanabe, Kobunshi Ronbunshu, Eng. Ed., 3, 2, 1249 (1974).
- P-1. Powers, J., J.D. Hoffman, J.J. Weeks and F.A. Quinn, J. of Res., Nat. Bur. of Stds., Phys. and Chem., 69A, 4 (1965).
- P-2. Petermann, J., R.M. Gohil, J.M. Schultz, R.W. Hendricks, and J.S. Lin, J. Mat. Sci., 16, 265 (1981).

- P-3. Petraccone, V., B. Pirozzi, A. Frasci and P. Corradini, Eur. Polym. J., 12, 323 (1975).
- P-4. Padden, F.J. and H.D. Keith, J. Appl. Phys., 30, 1479 (1959).
- Q-1. Quynn, R.G. and H. Brody, J. Macromol. Sci., Phys., B5(4), 721 (1971).
- R-1. Rubin, I.D., J. Polym. Sci., Polym. Letters Ed., 2, 747 (1964).
- R-2. Rubin, I.D., J. Polym. Sci.: Part A, 3, 3803 (1965).
- S-1. Sprague, B.S., J. Macromol. Sci., Phys., B8(1-2), 157 (1973).
- S-2. Sastry, K.S. and R.D. Patel, Eur. Polym. J., 8, 63 (1972).
- S-3. Siegmann, A., J. Appl. Polym. Sci., 27, 1053 (1982).
- S-4. Sastry, K.S. and R.D. Patel, Eur. Polym. J., 9, 177 (1973).
- S-5. Sasaguri, K., M.B. Rhodes, and R.S. Stein, J. Polym. Sci., Polym. Letters Ed., 1, 571 (1963).
- S-6. Siegmann, A., J. Appl. Polym. Sci., 24, 2333 (1979).
- S-7. Schultz, J., "Polymer Materials Science," Englewood Cliffs, N.J.: Prentice Hall, (1974).
- T-1. Tanaka, A., N. Sugimoto, T. Asada and S. Onogi, Polym. J., 7, 529 (1975).
- T-2. Tanaka, A., N. Sugimoto, T. Asada and S. Onogi, Rep. on Prog. in Polym. Phys., Japan, 18, 449 (1975).
- W-1. Wunderlich, B., "Macromolecular Physics," Vol. 2, New York: Academic Press, (1976).
- W-2. Wereta, A. and C.G. Gogos, Polym. Eng. Sci., 11, 19 (1971).
- W-3. Woodward, A.E., J. Polym. Sci.: Part A-2, 6, 1987 (1968).
- W-4. Wittmann, J.C., and B. Lotz, J. Polym. Sci., Phys. Ed., 19, 1837 (1981).
- Y-1. Yang, R. and R.S. Stein, J. Polym. Sci.: Part A-2, 5, 939 (1967).
- Y-2. Yee, R.Y. and R.S. Stein, J. Polym. Sci.: Part A-2, 8, 1661 (1970).
- Z-1. Ziegler, K., E. Holzkamp, H. Breil and H. Martin, Angew. Chem., 67, 426, 541 (1955).

APPENDIX

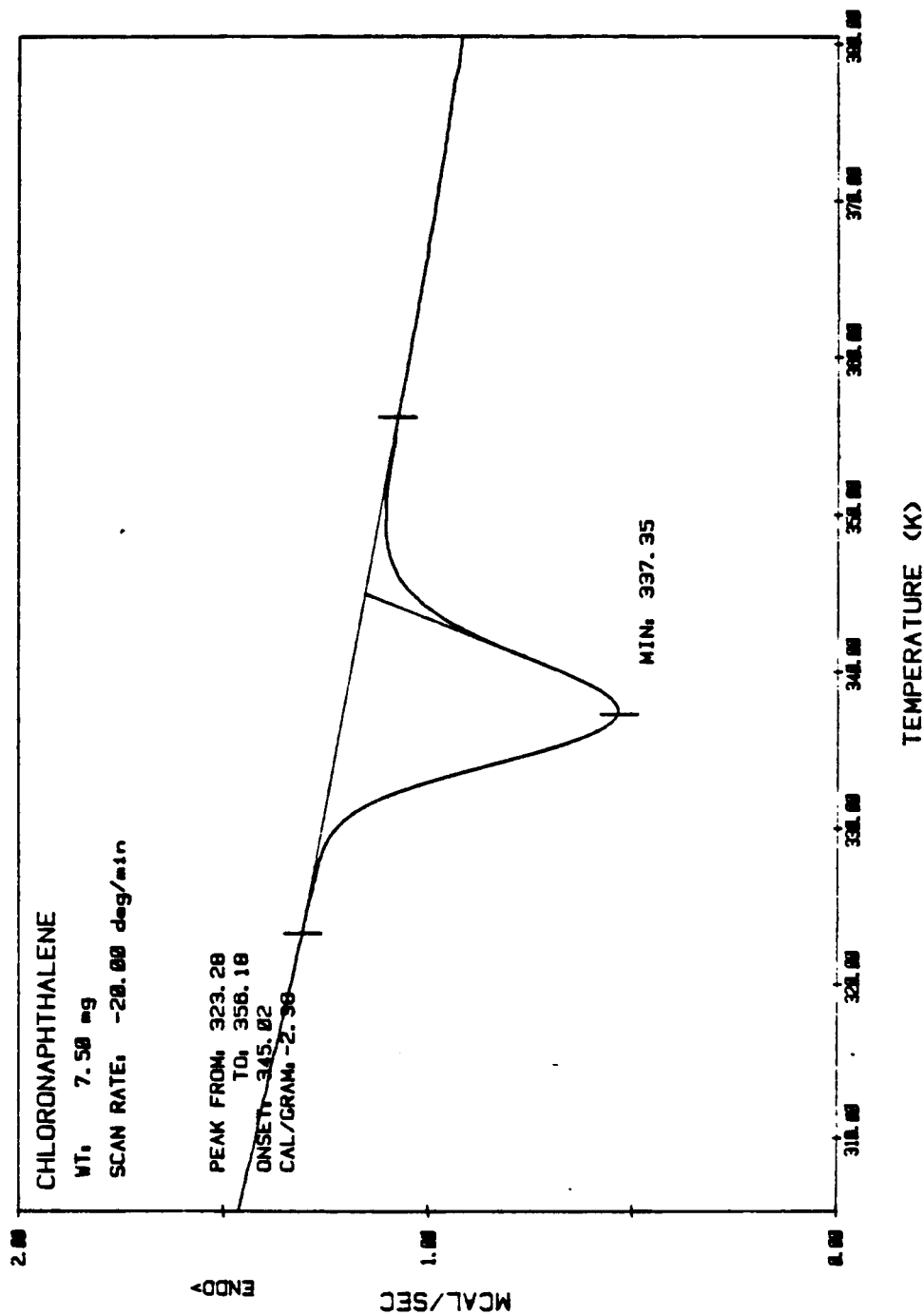


Figure A-1: Differential Scanning Calorimetry Cooling Curve for the CN5 Blend

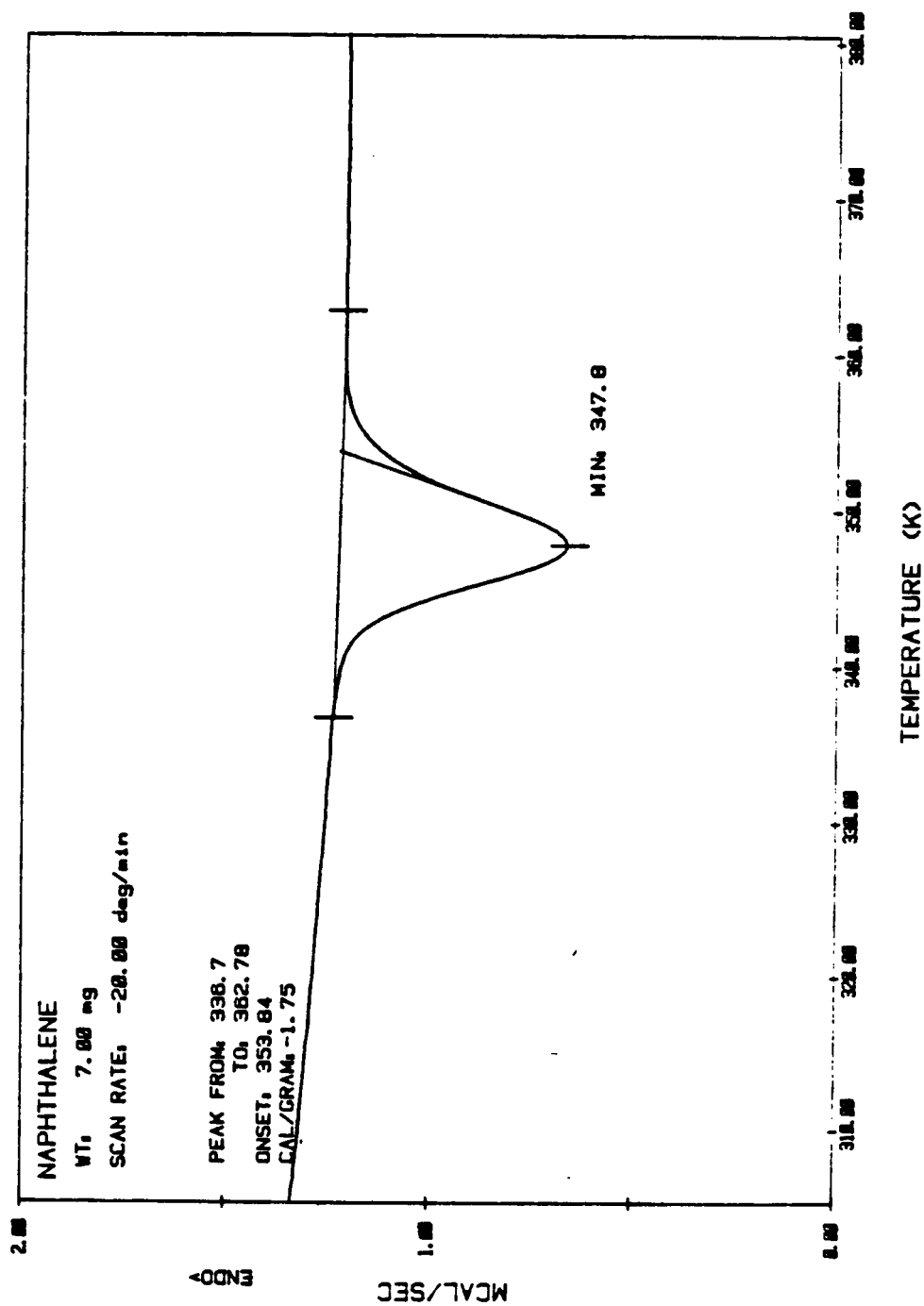


Figure A-2. Differential Scanning Calorimetry Cooling Curve for the NA5 Blend

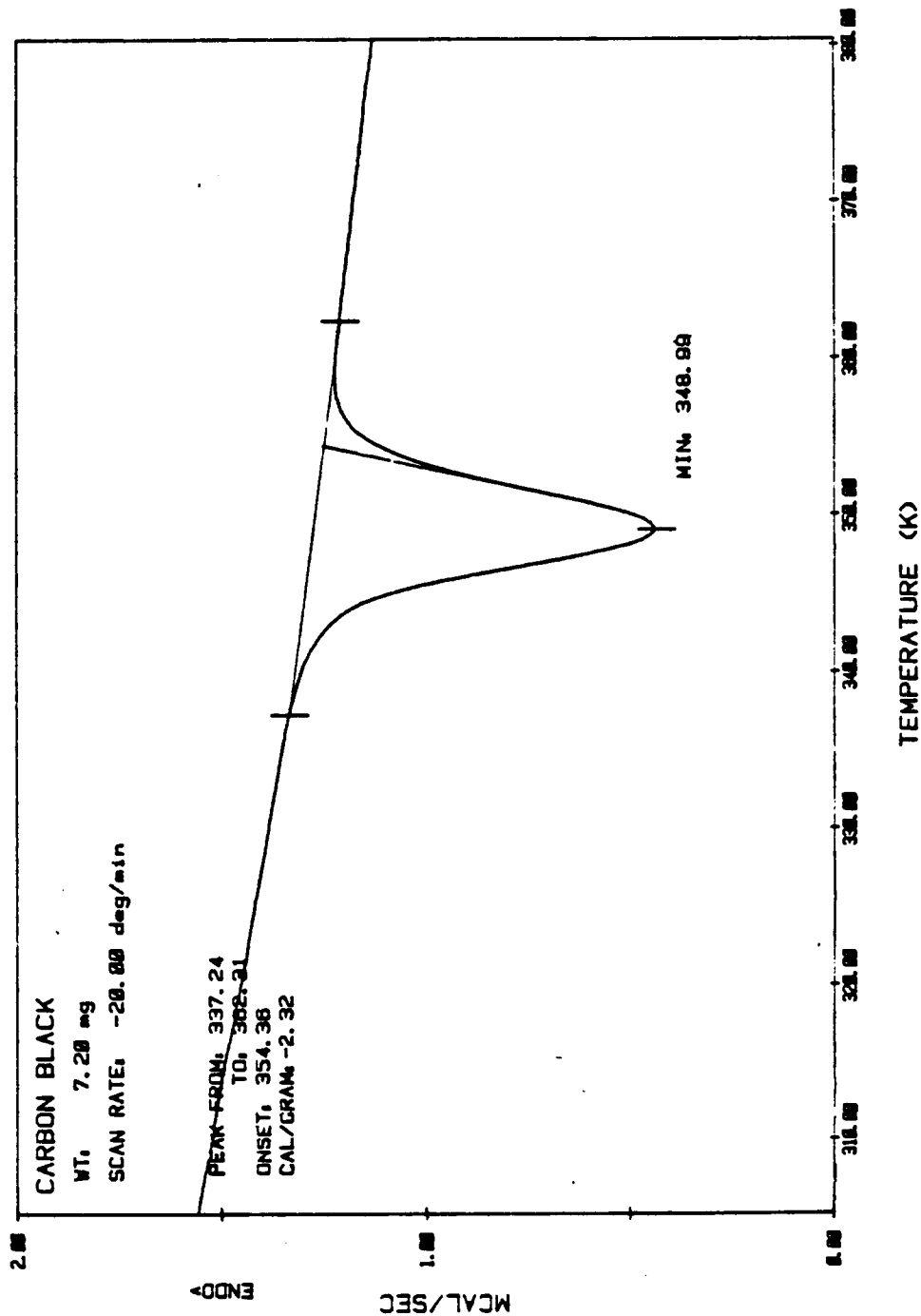


Figure A-3. Differential Scanning Calorimetry Cooling Curve for the CB2 Blend

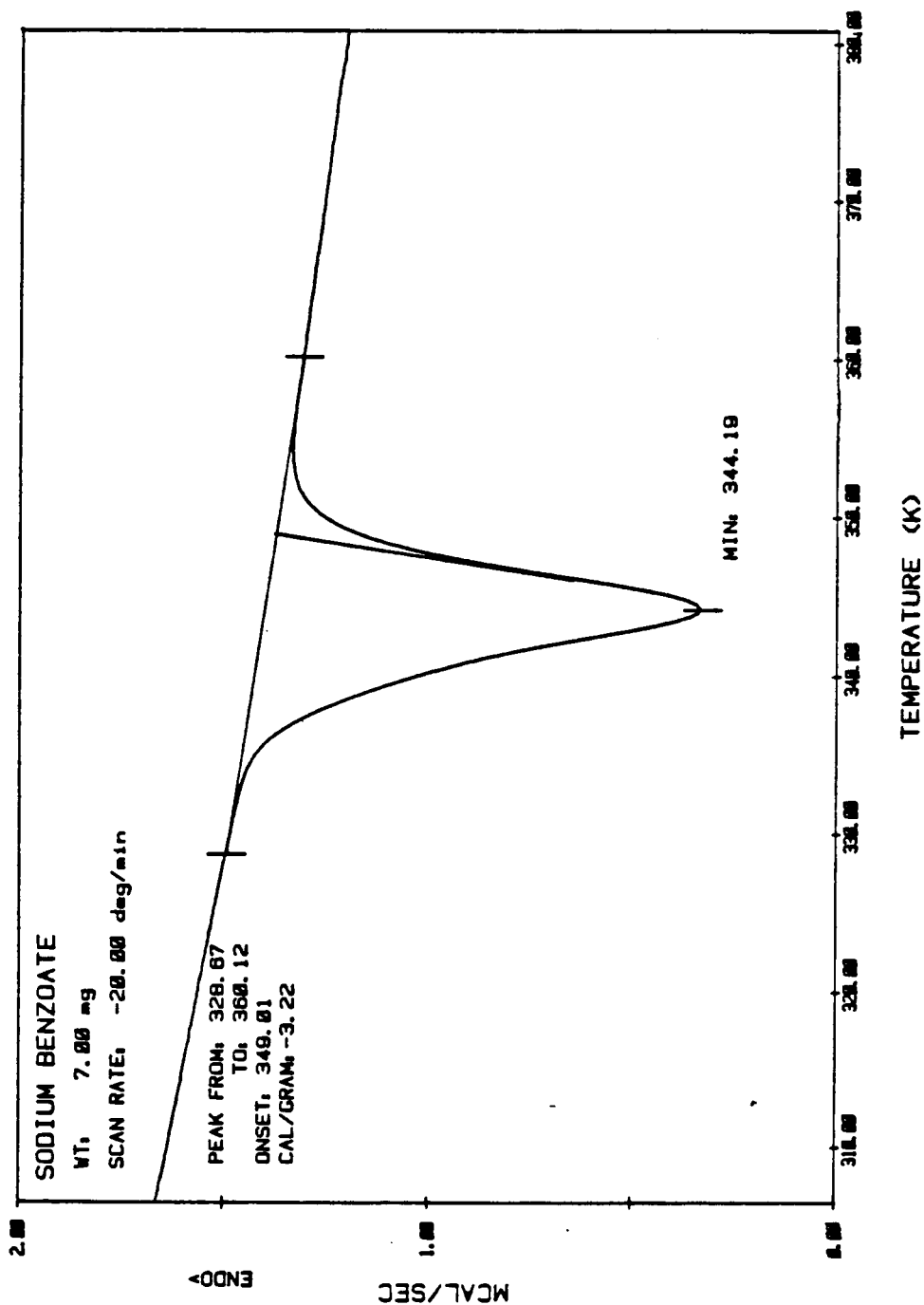


Figure A-4. Differential Scanning Calorimetry Cooling Curve for the SB2 Blend

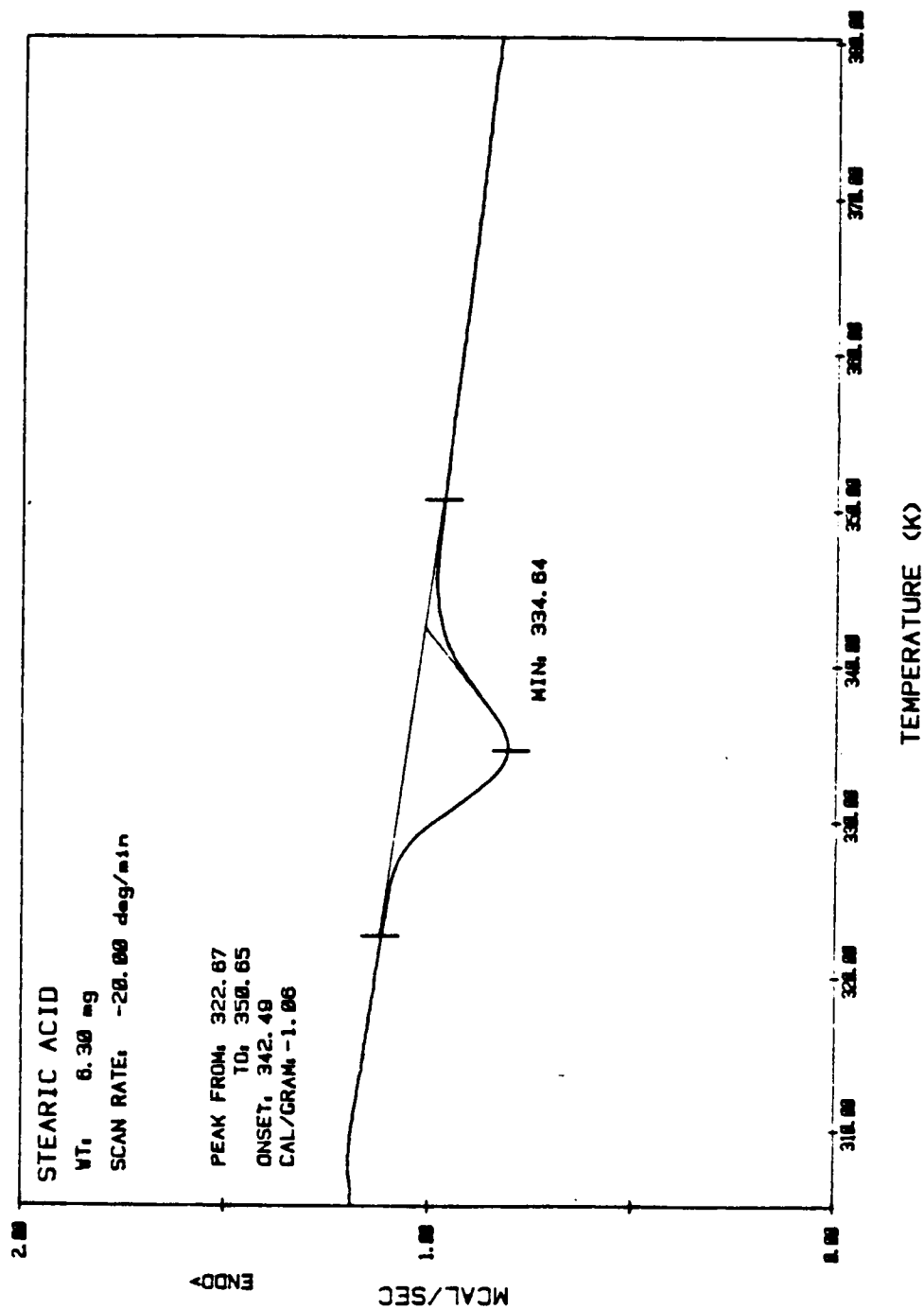


Figure A-5. Differential Scanning Calorimetry Cooling Curve for the SA5 Blend

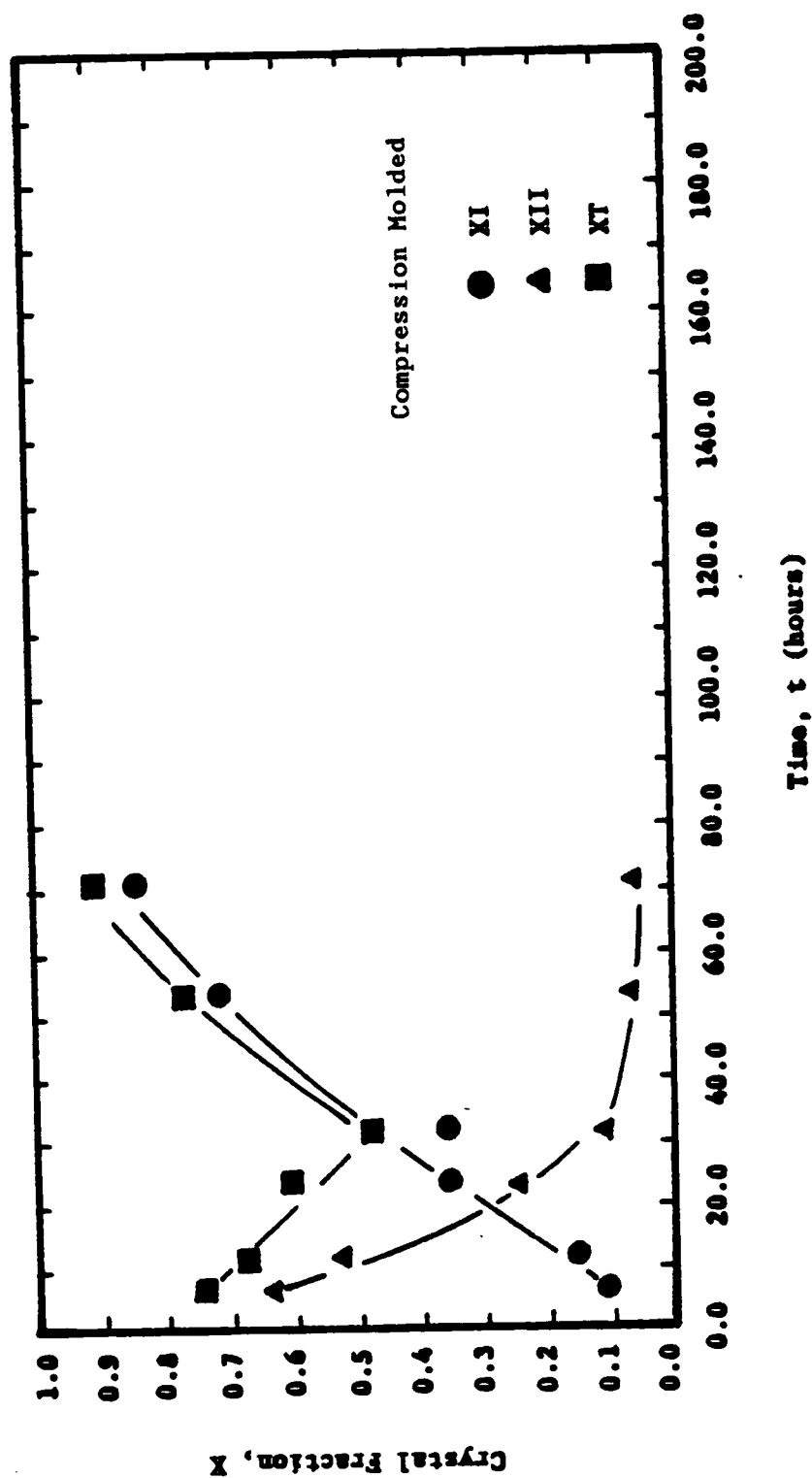


Figure A-6. Crystal Fraction Present as a Function of Time for PP10 at 23 °C

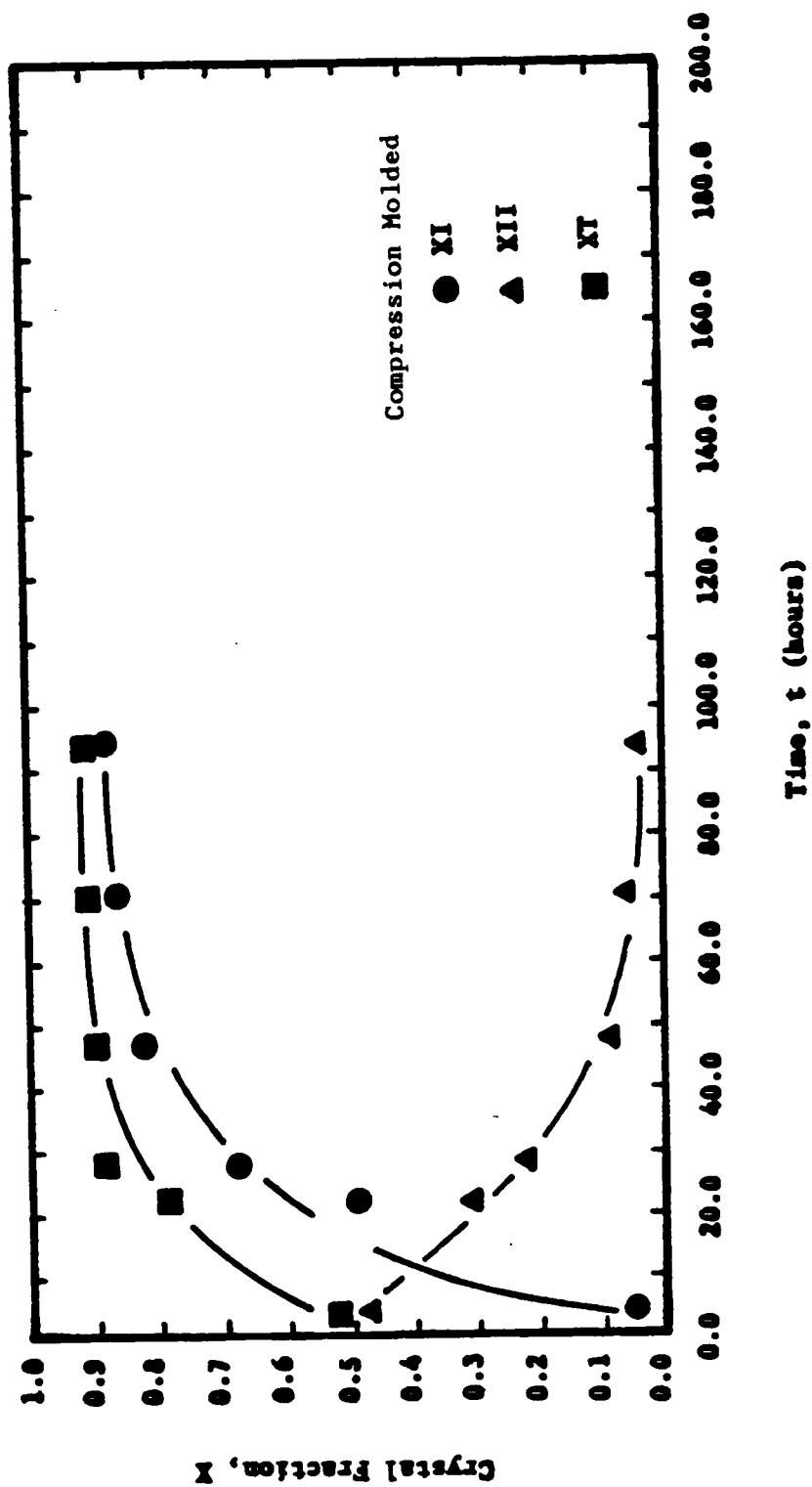


Figure A-7. Crystal Fraction Present as a Function of Time for PP25 at 23 °C

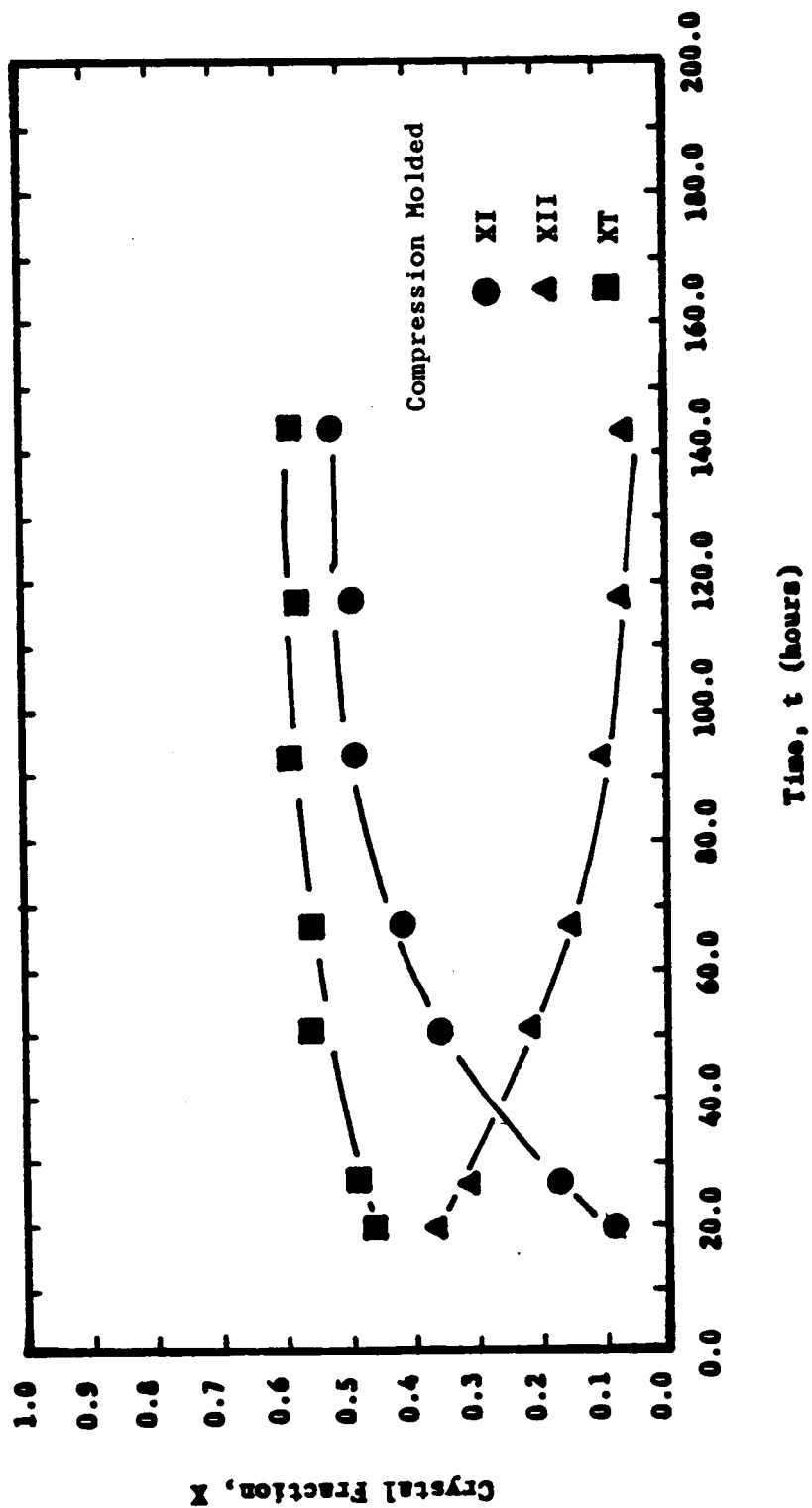


Figure A-8. Crystal Fraction Present as a Function of Time for DPE05 at 23°C

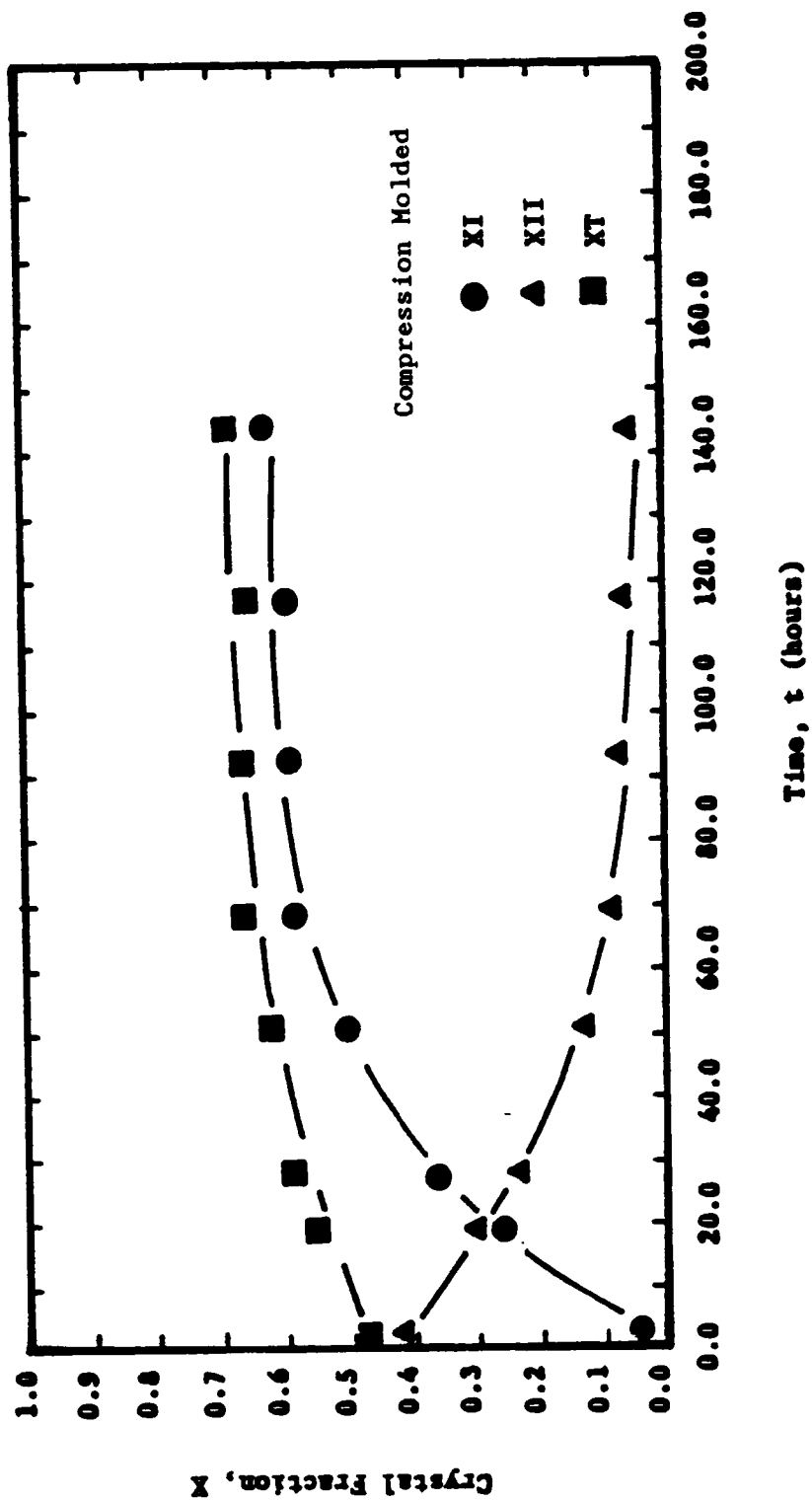


Figure A-9: Crystal Fraction Present as a Function of Time
for DPE2 at 23 °C

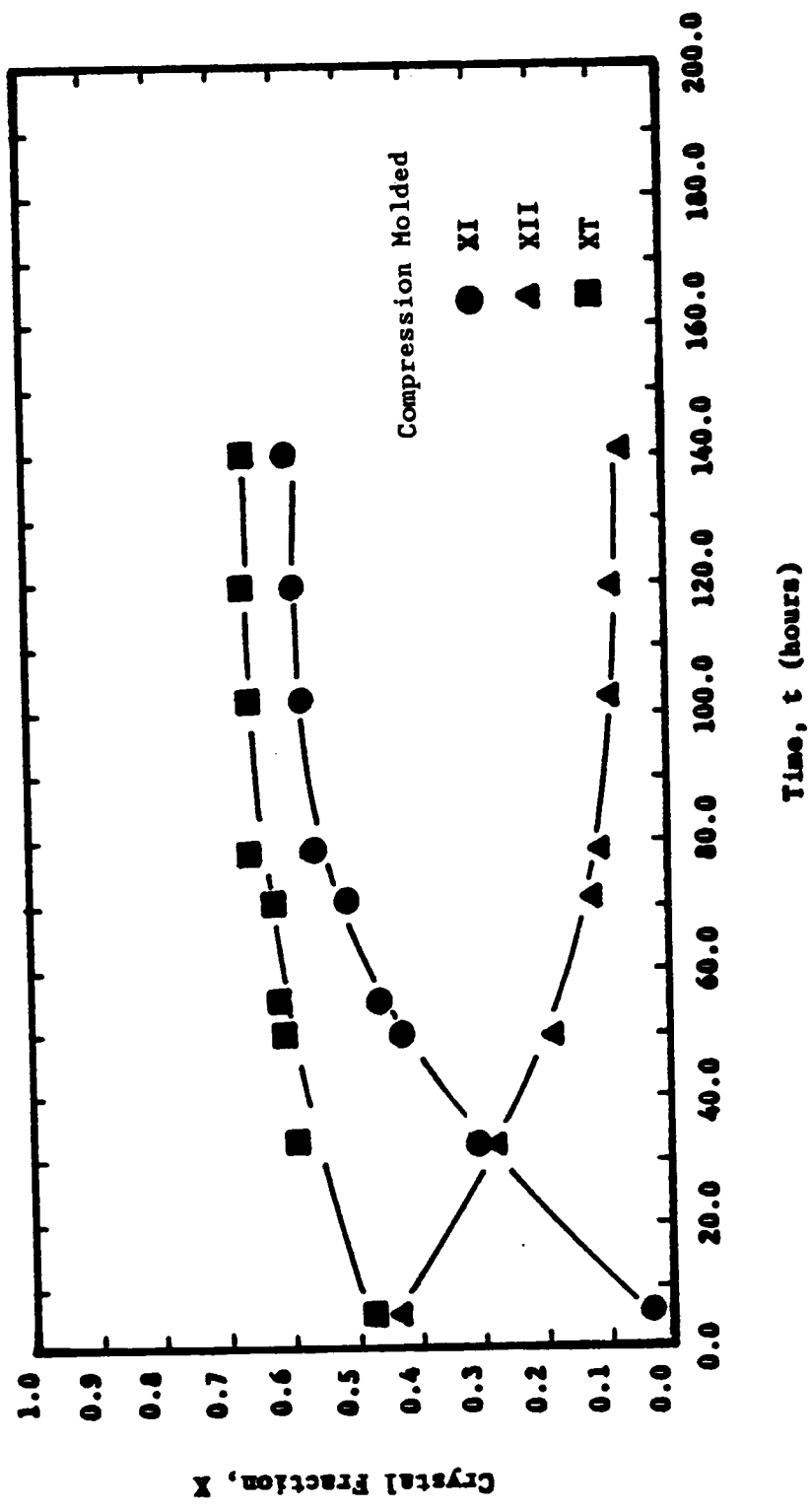


Figure A-10. Crystal Fraction Present as a Function of Time for CN05 at 23 °C

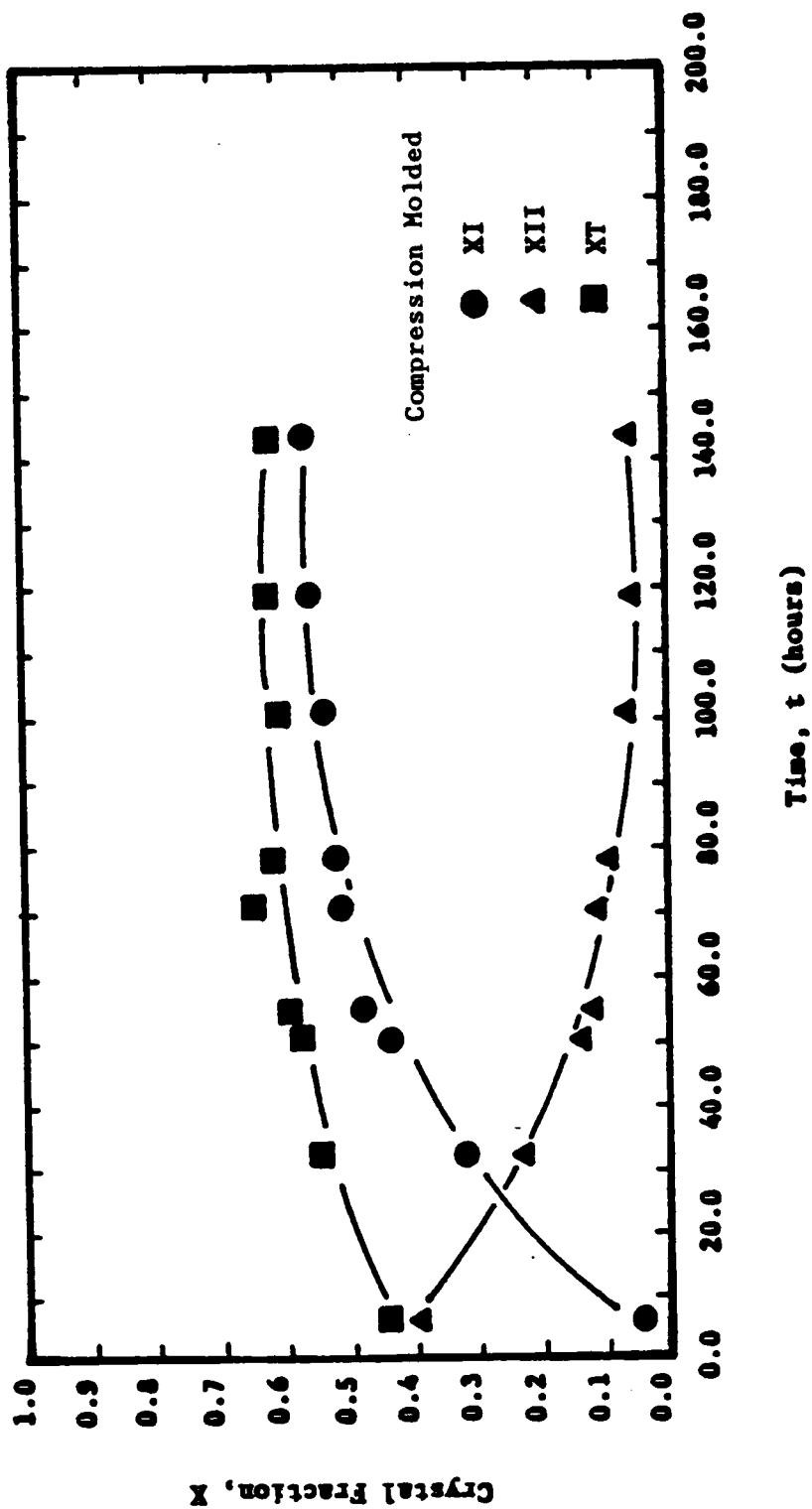


Figure A-11. Crystal Fraction Present as a Function of Time for CN2 at 23 °C

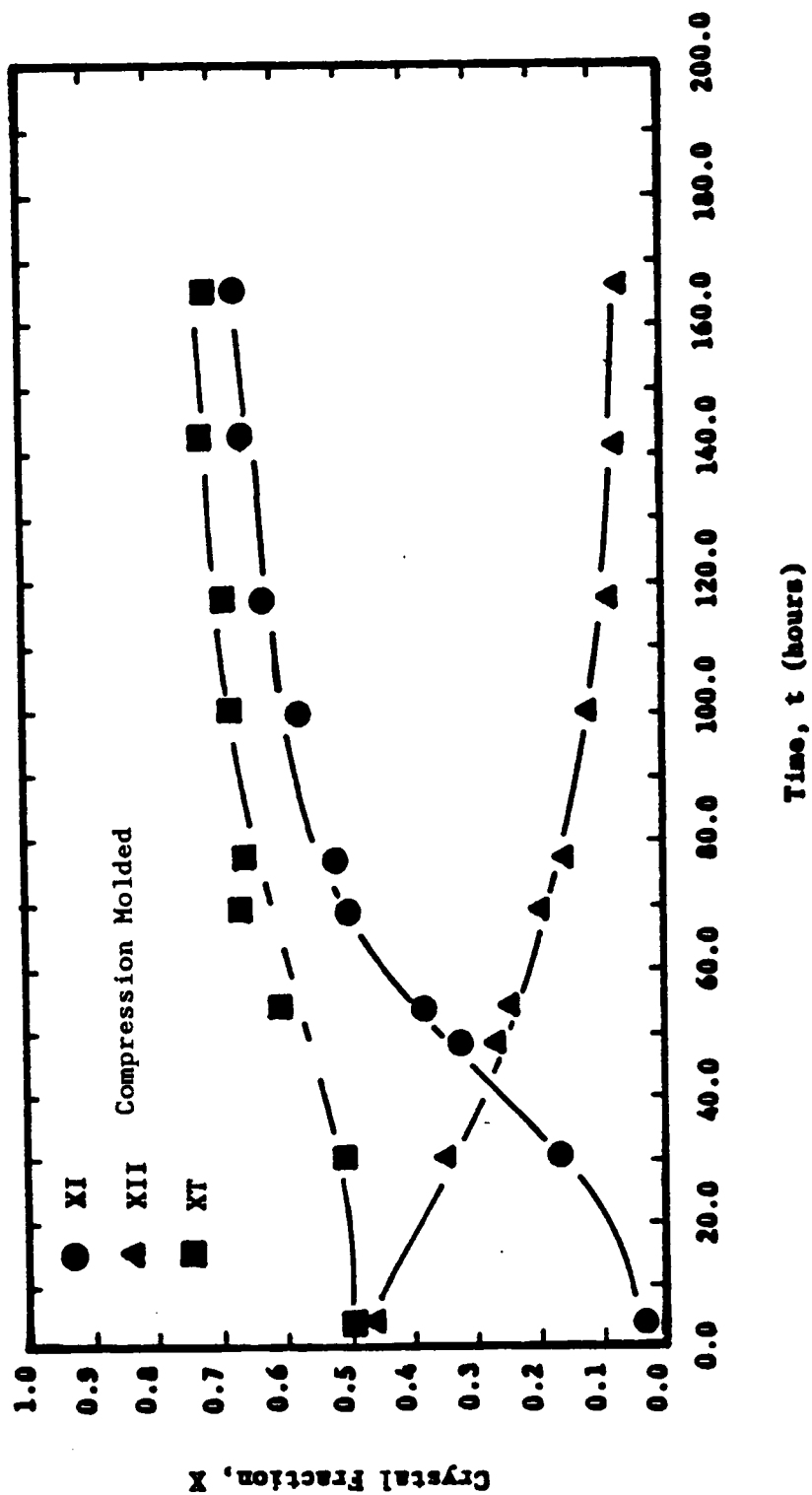


Figure A-12. Crystal Fraction Present as a Function of Time for CB05 at 23 °C

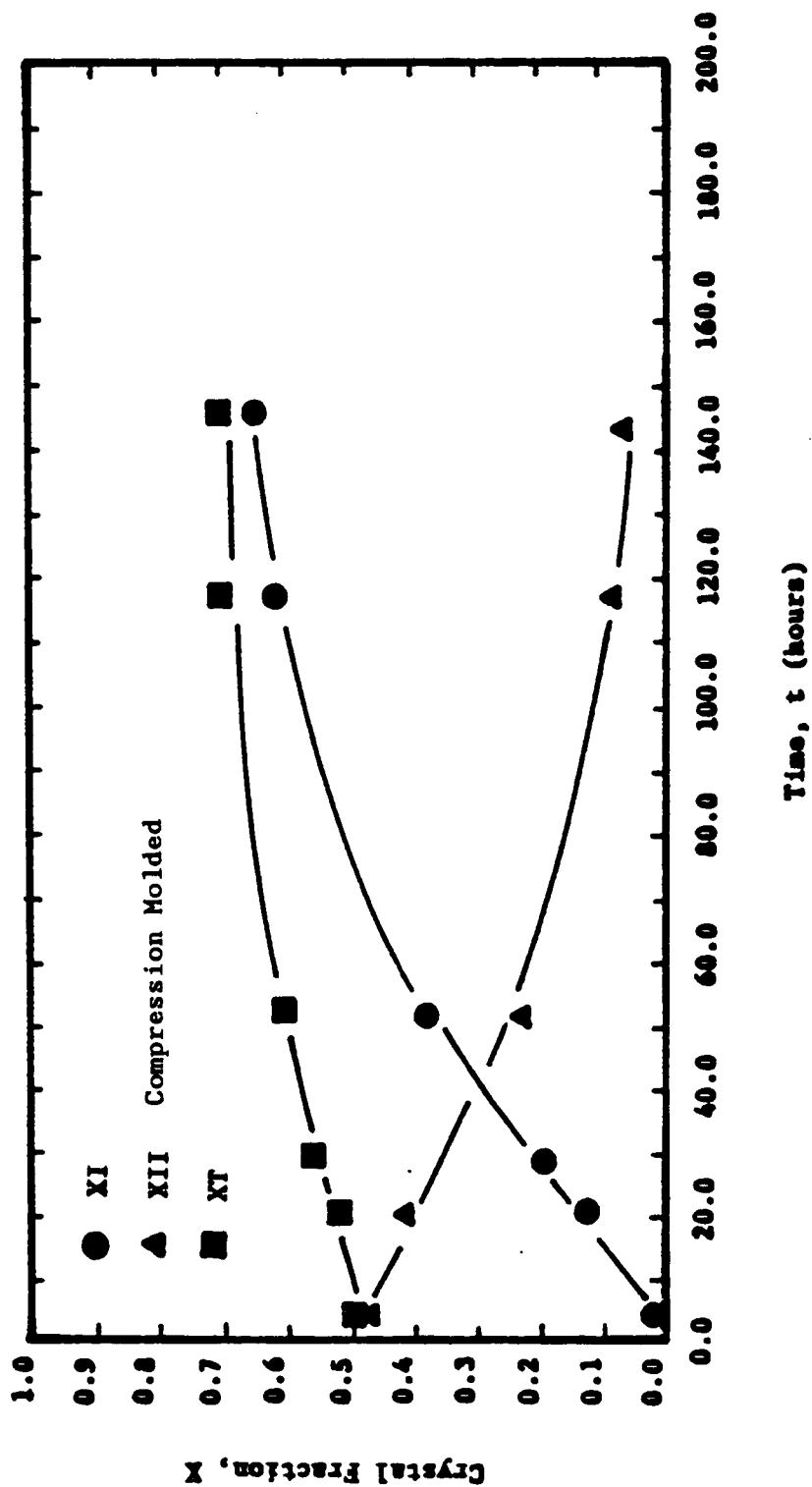


Figure A-13. Crystal Fraction Present as a Function of Time for NA05 at 23 °C

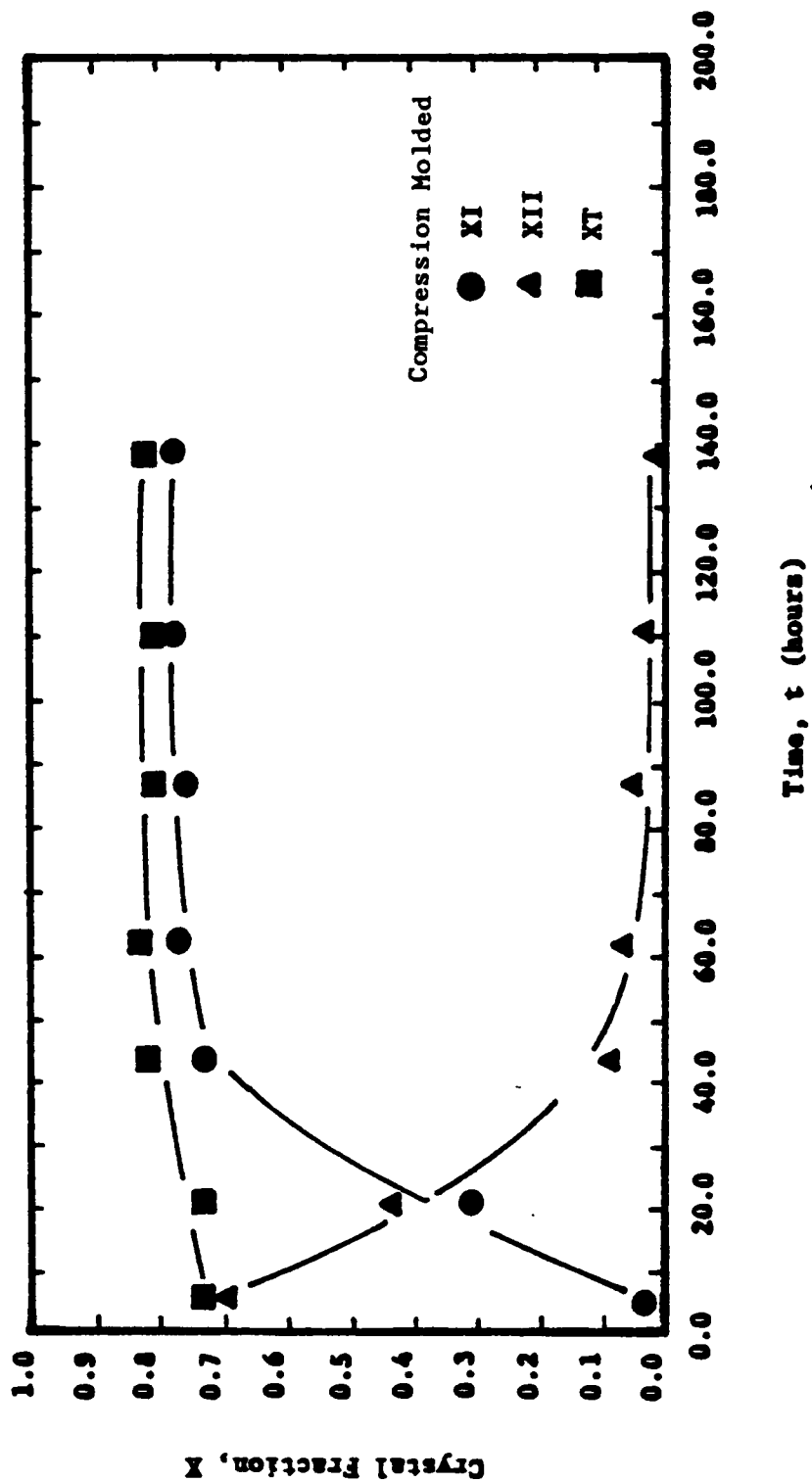


Figure A-14. Crystal Fraction Present as a Function of Time for NA2 at 23 °C

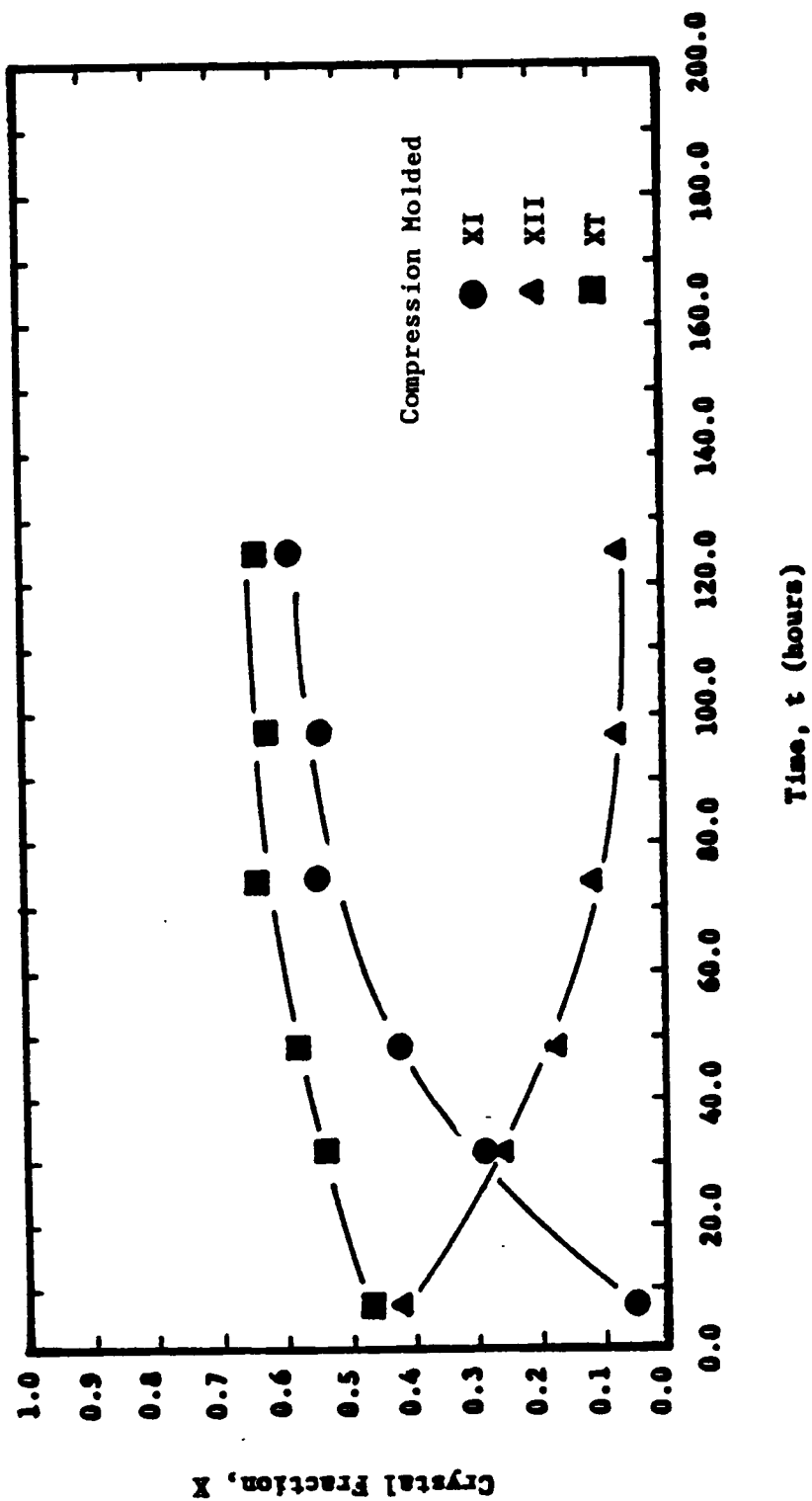


Figure A-15. Crystal Fraction Present as a Function of Time for SB05 at 23 °C

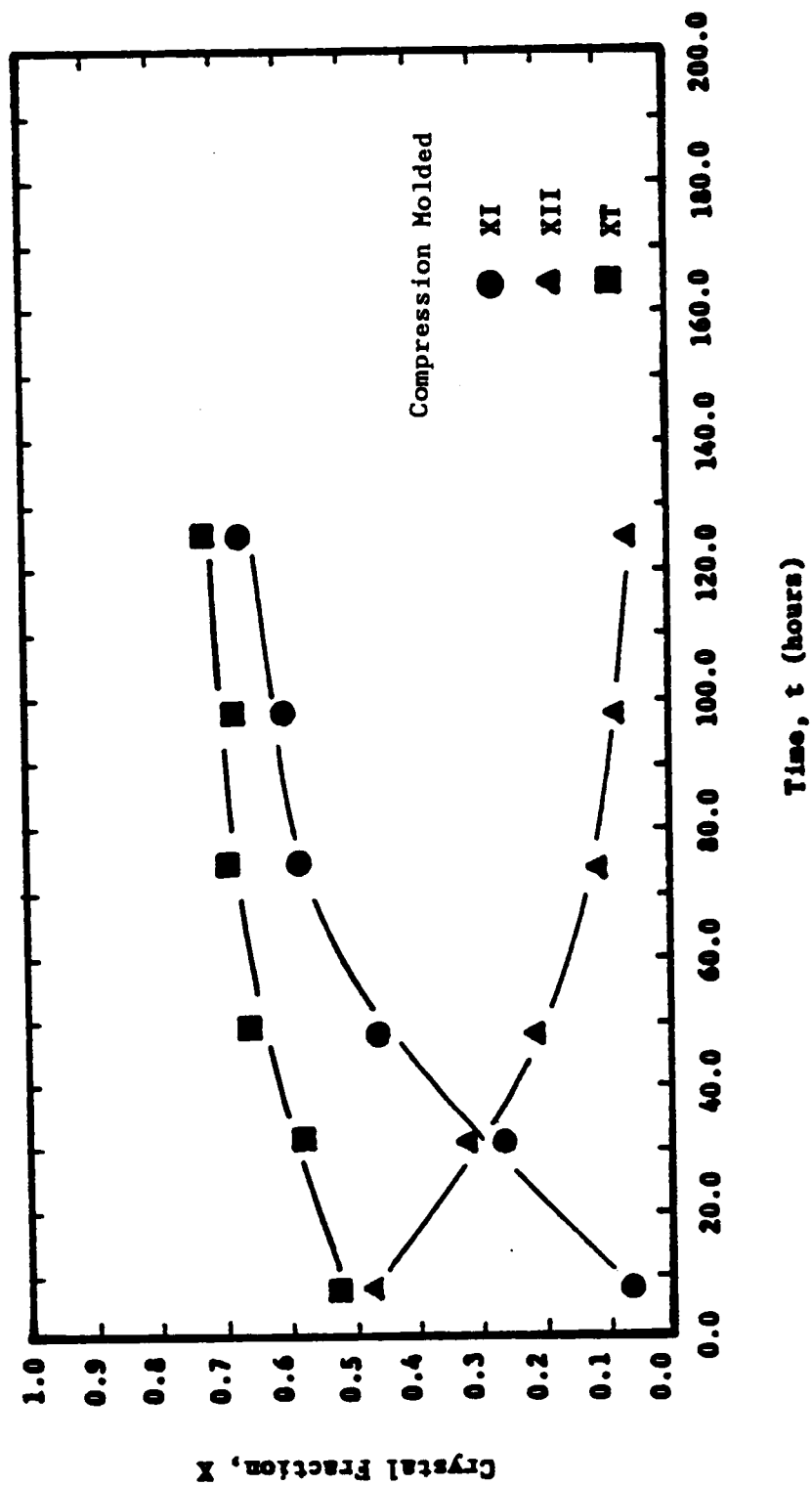


Figure A-16. Crystal Fraction Present as a Function of Time for SB2 at 23 °C

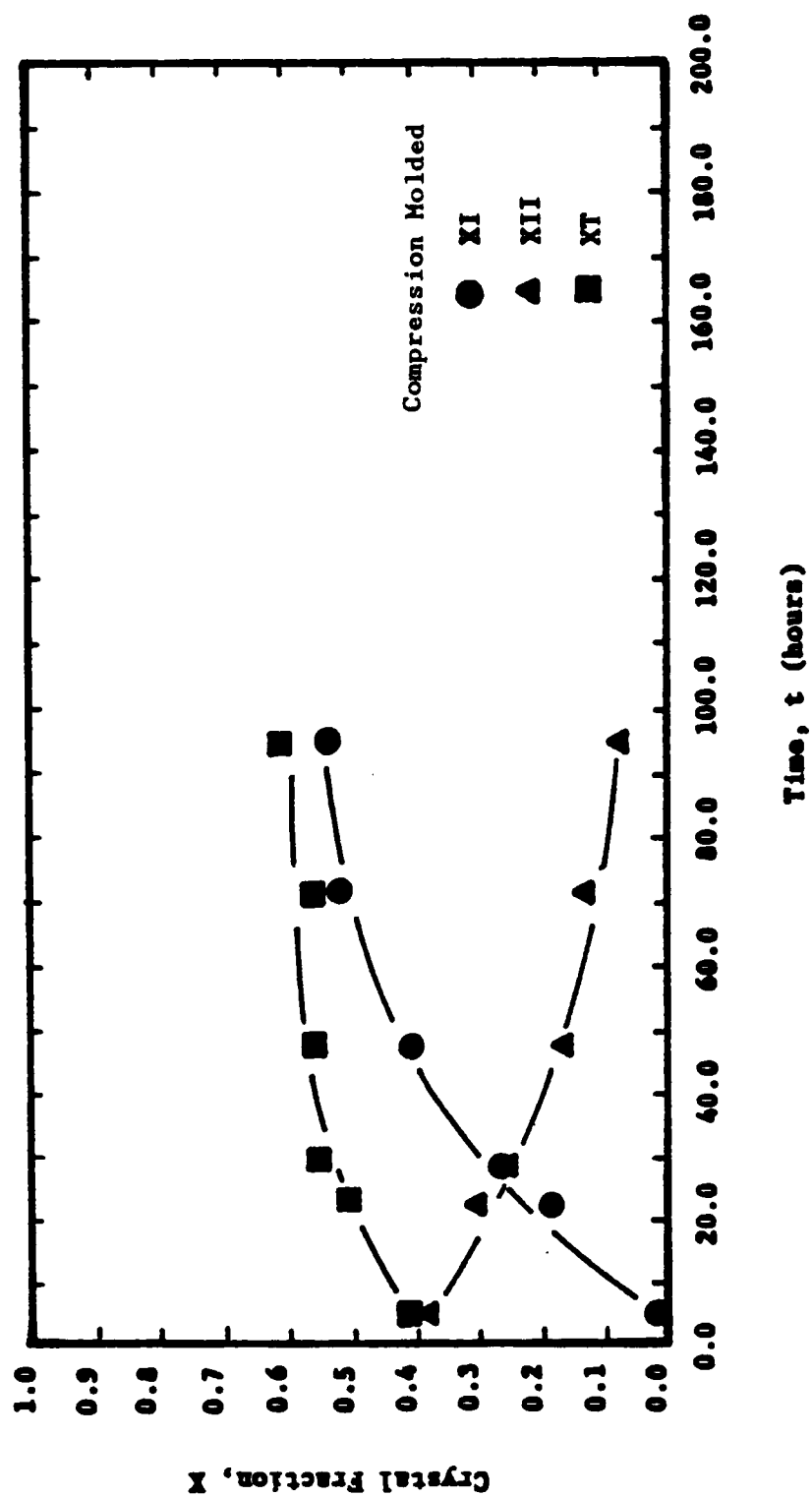


Figure A-17. Crystal Fraction Present as a Function of Time for SA05 at 23°C.

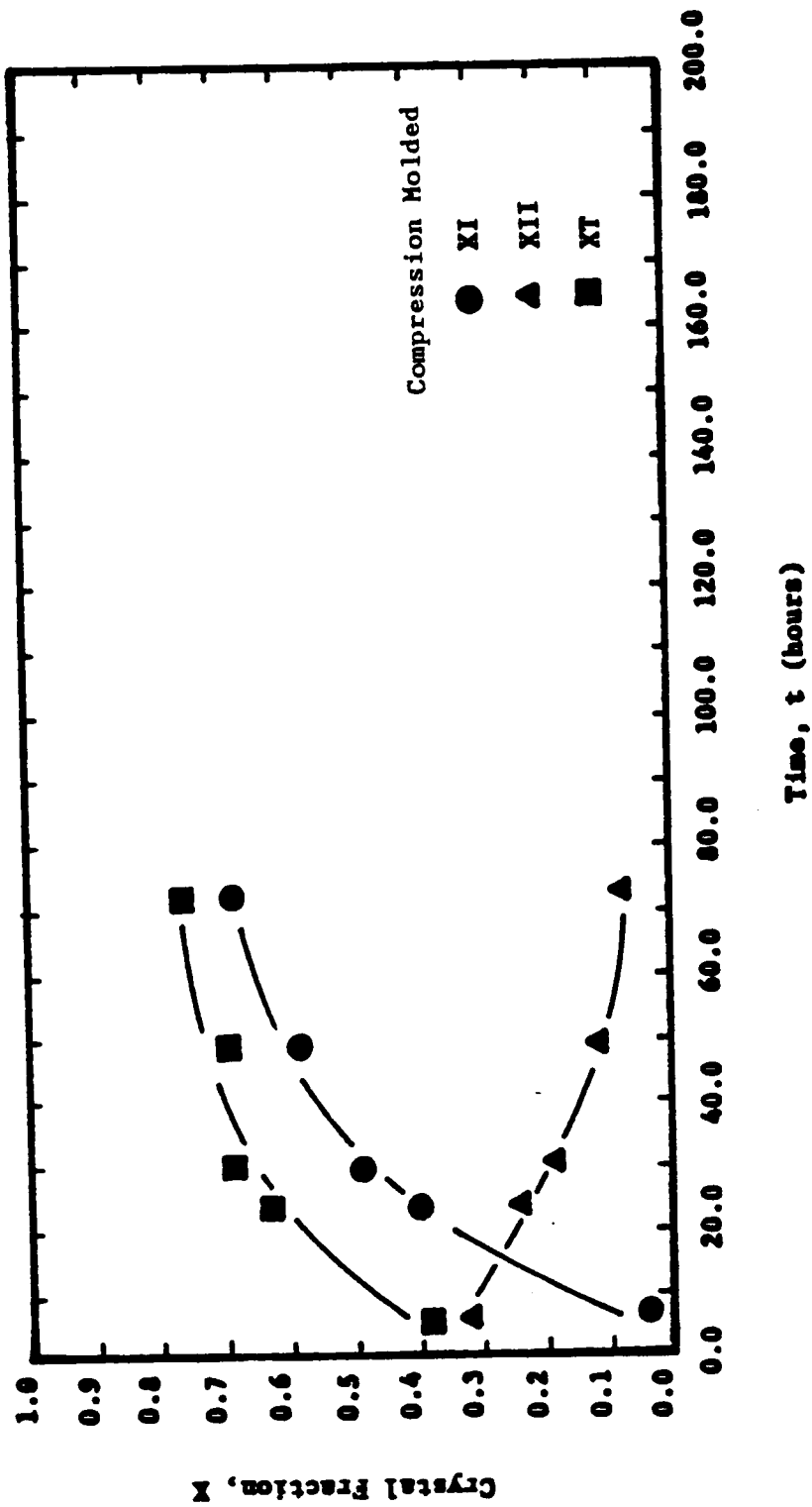


Figure A-18. Crystal Fraction Present as a Function of Time for SA2 at 23 °C

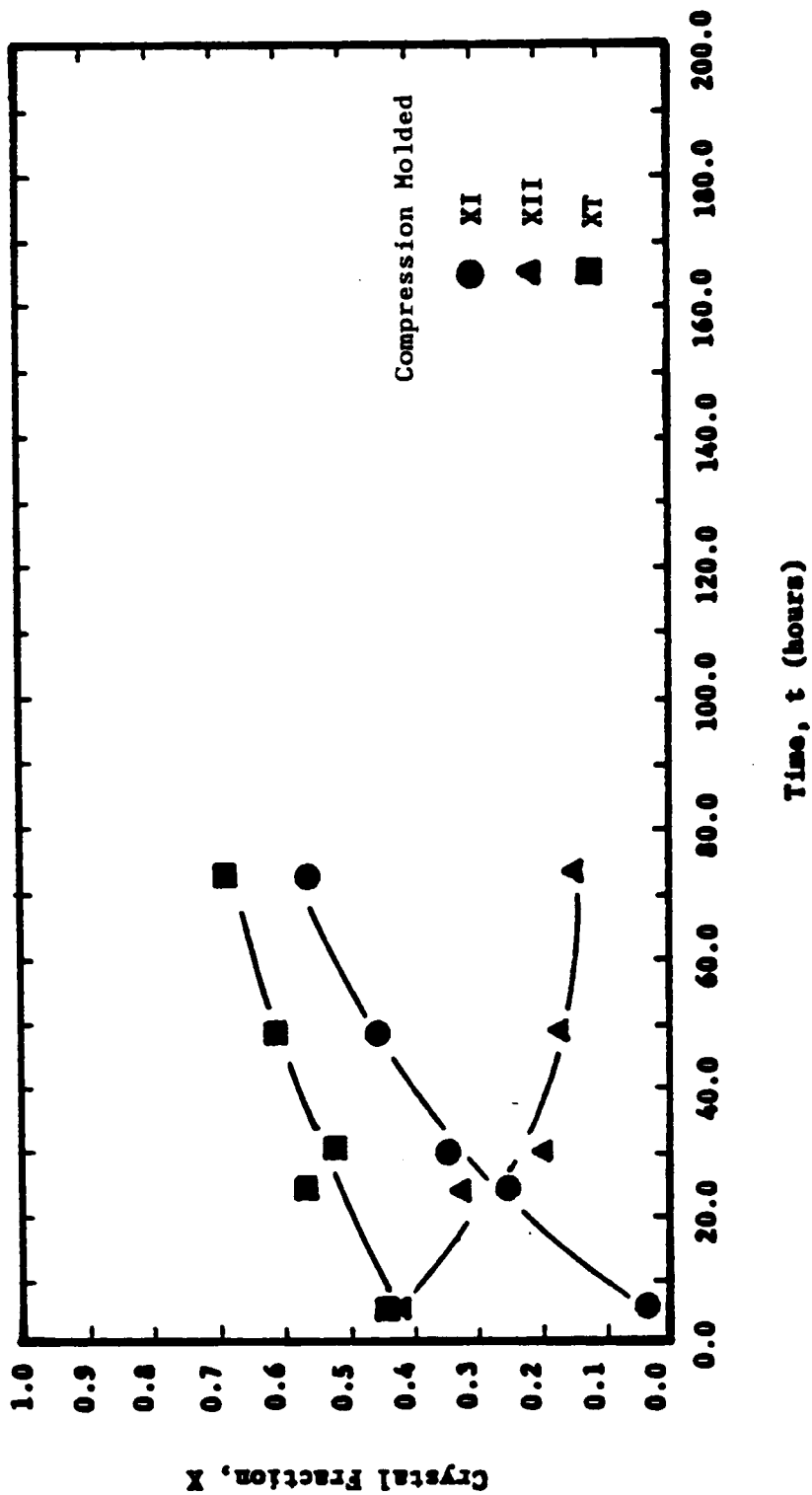


Figure A-19. Crystal Fraction Present as a Function of Time for SA5 at 23 °C

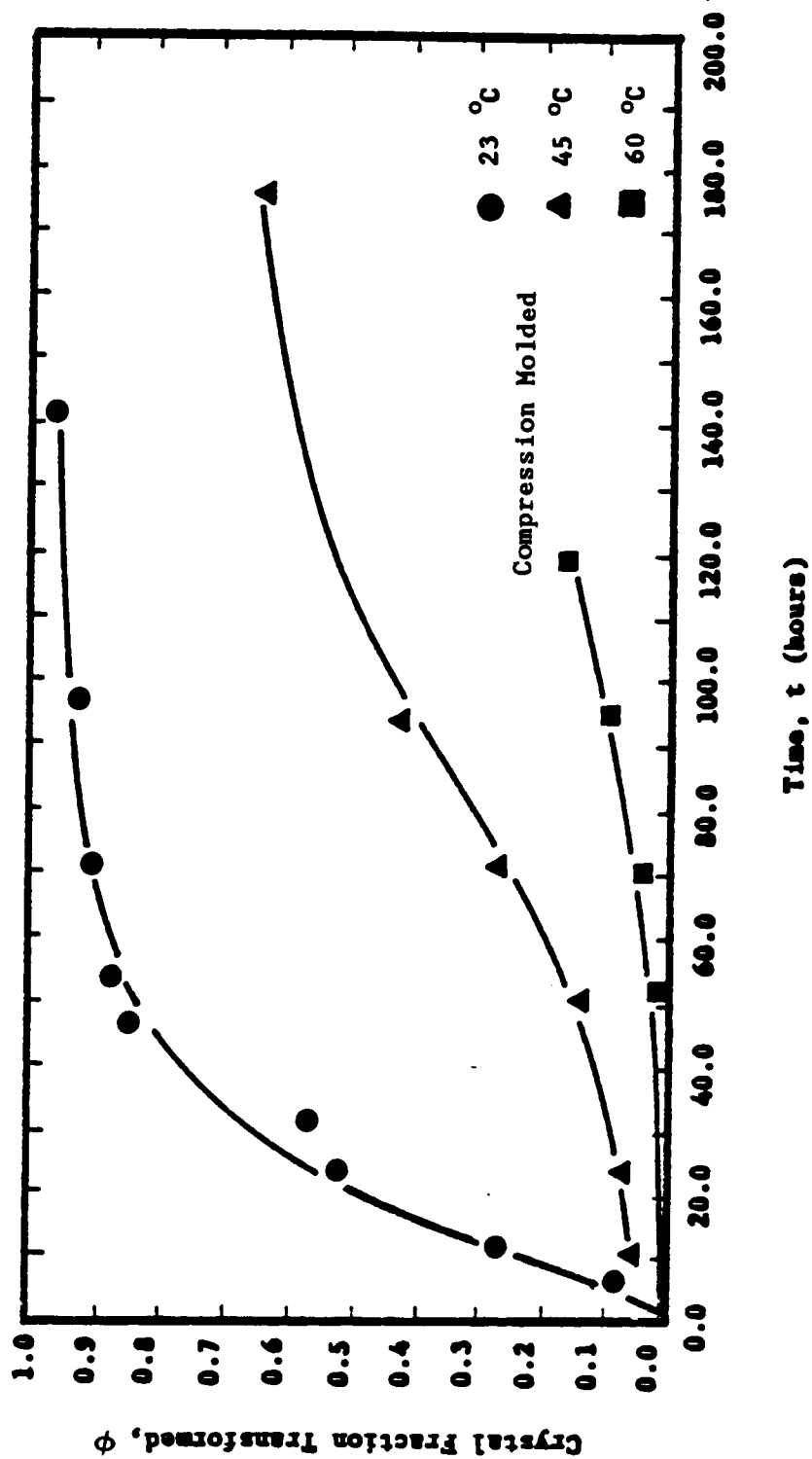


Figure A-20. Volume Fraction of the Crystal Transformed Over Time for PP5 at Temperatures of 23 °C, 45 °C, and 60 °C

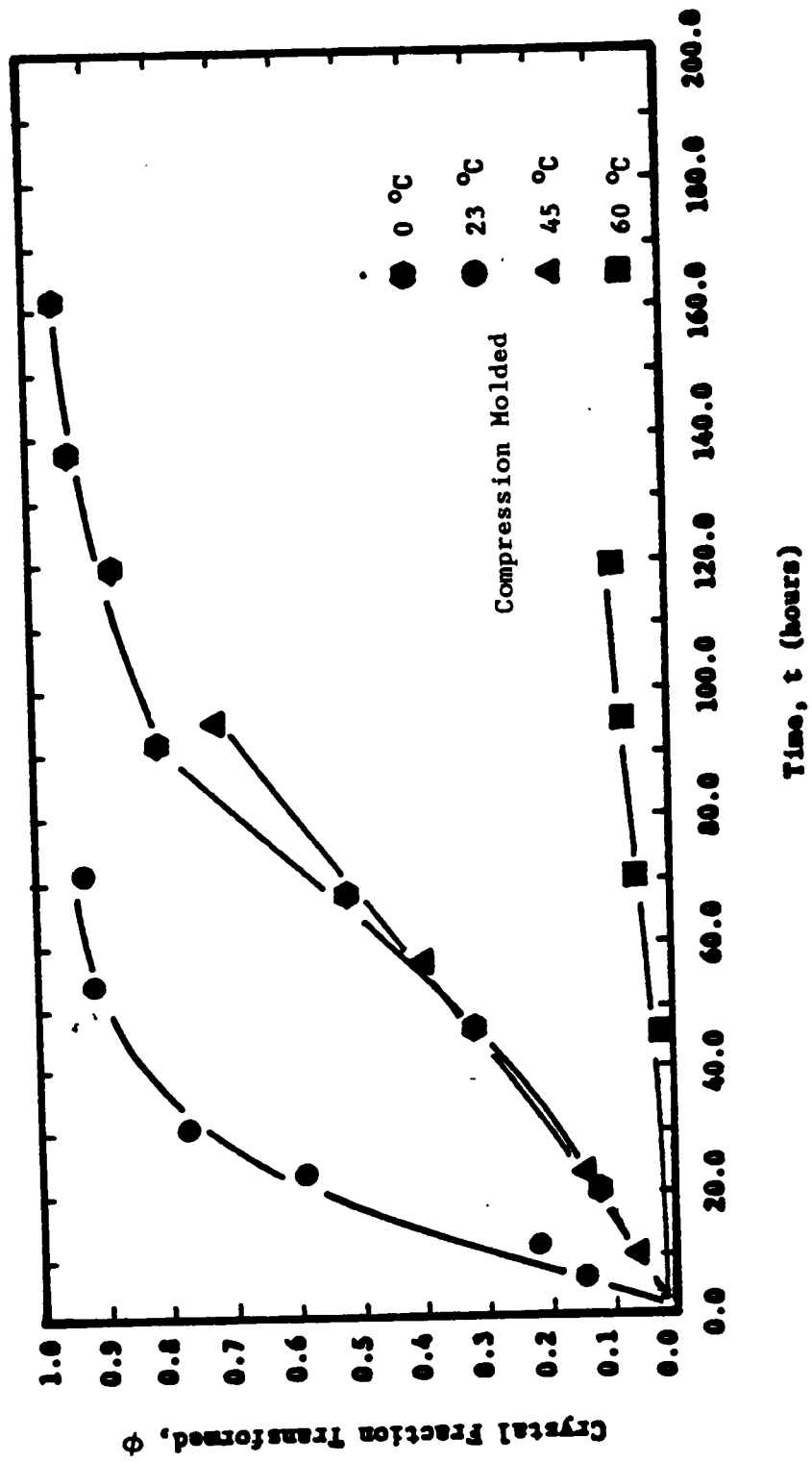


Figure A-21. Volume Fraction of the Crystal Transformed Over Time for PP10 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C

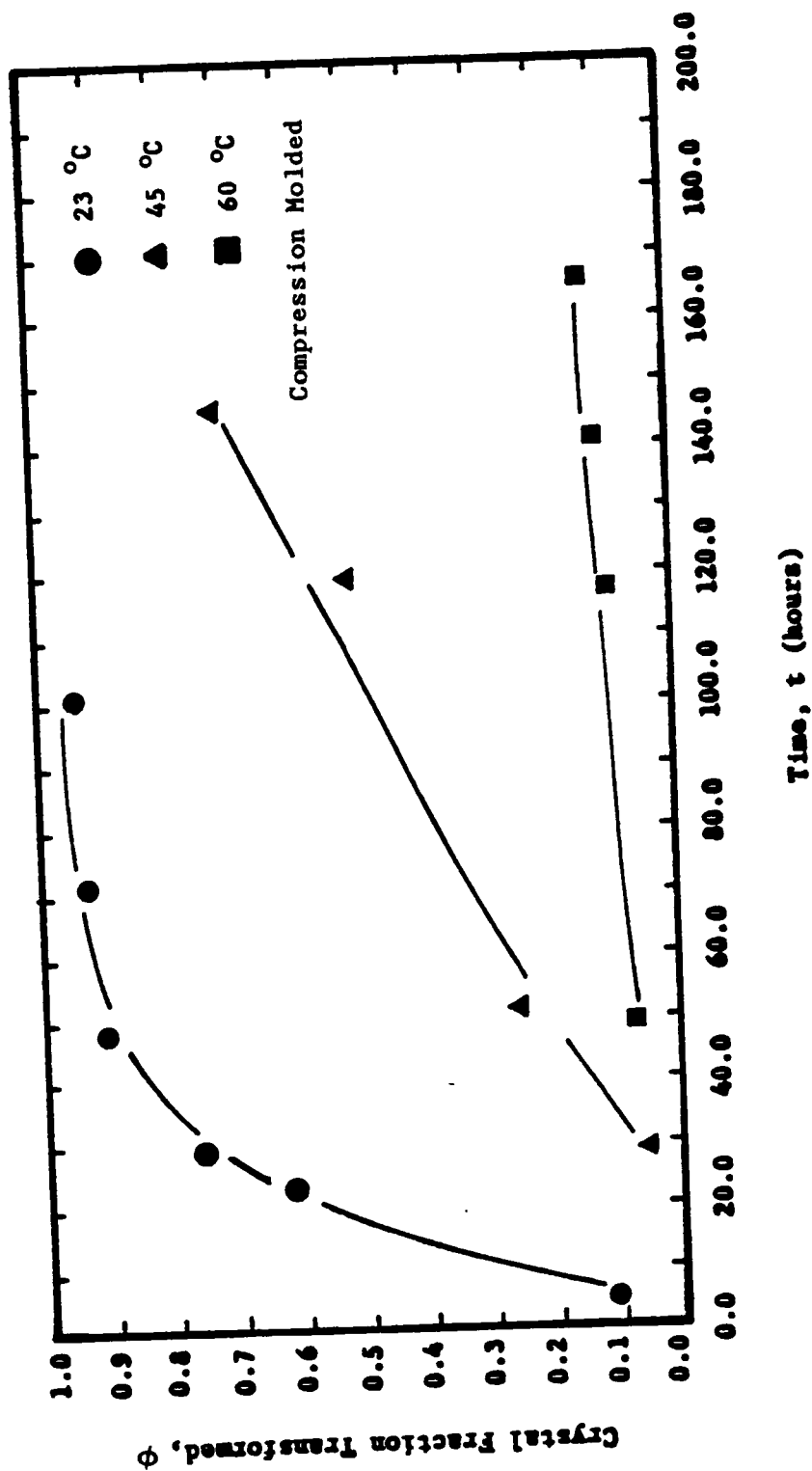


Figure A-22. Volume Fraction of the Crystal Transformed Over Time for PP25 at Temperatures of 23 °C, 45 °C, and 60 °C

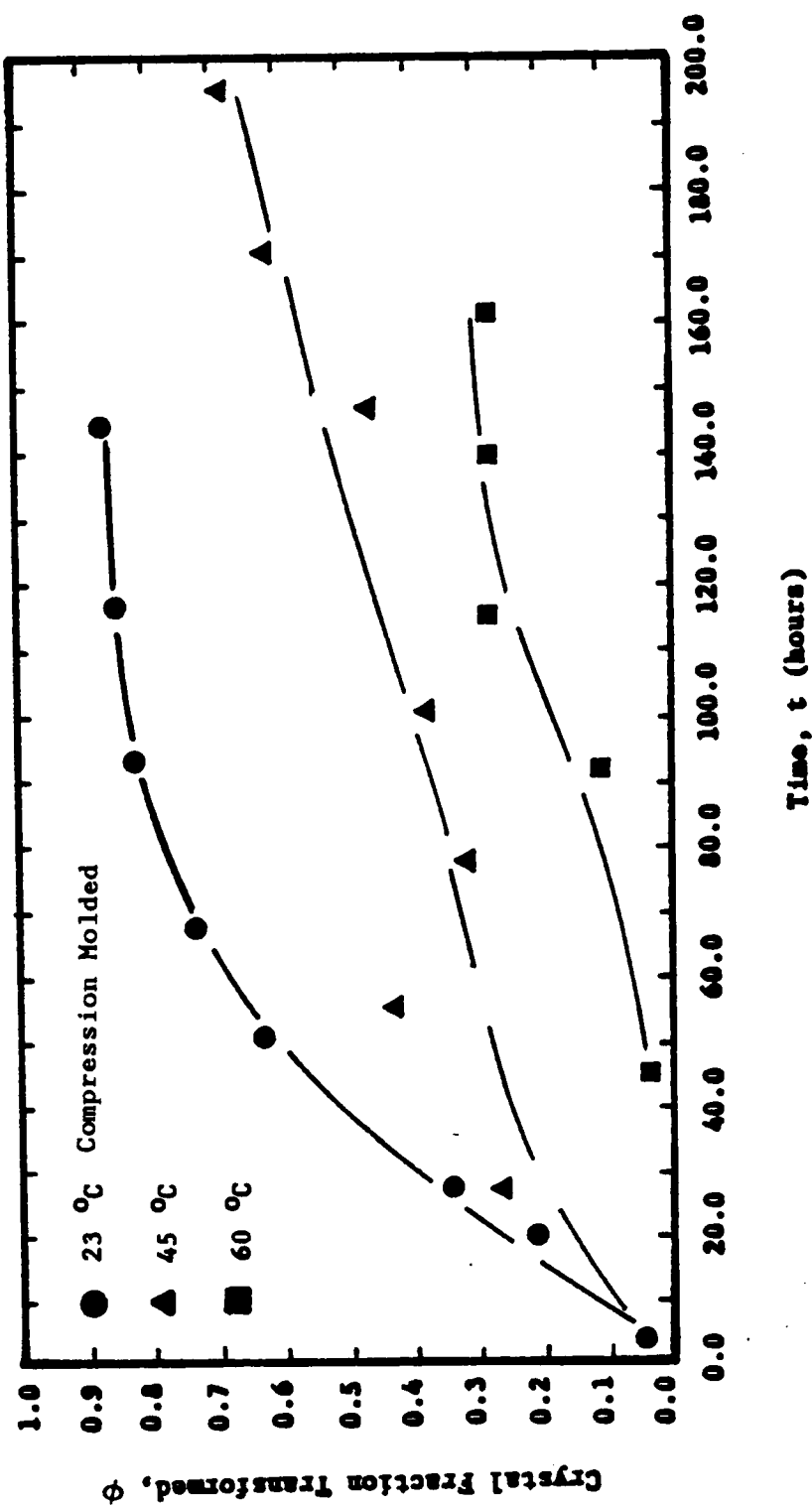


Figure A-23: Volume Fraction of the Crystal Transformed Over Time for DPE05 at Temperatures of 23 °C, 45 °C, and 60 °C

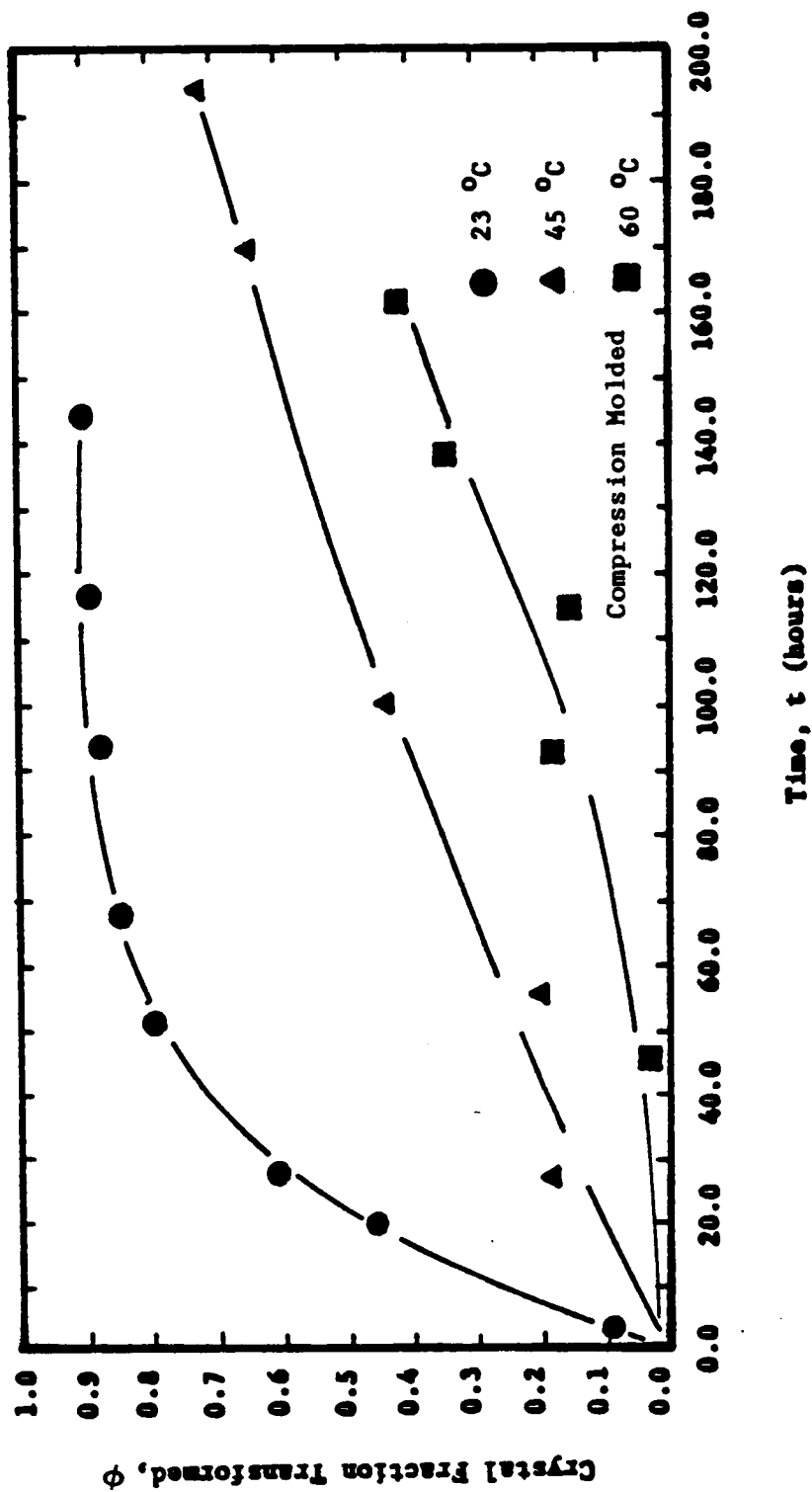


Figure A-24. Volume Fraction of the Crystal Transformed Over Time for DPE2 at Temperatures of 23 °C, 45 °C, and 60 °C

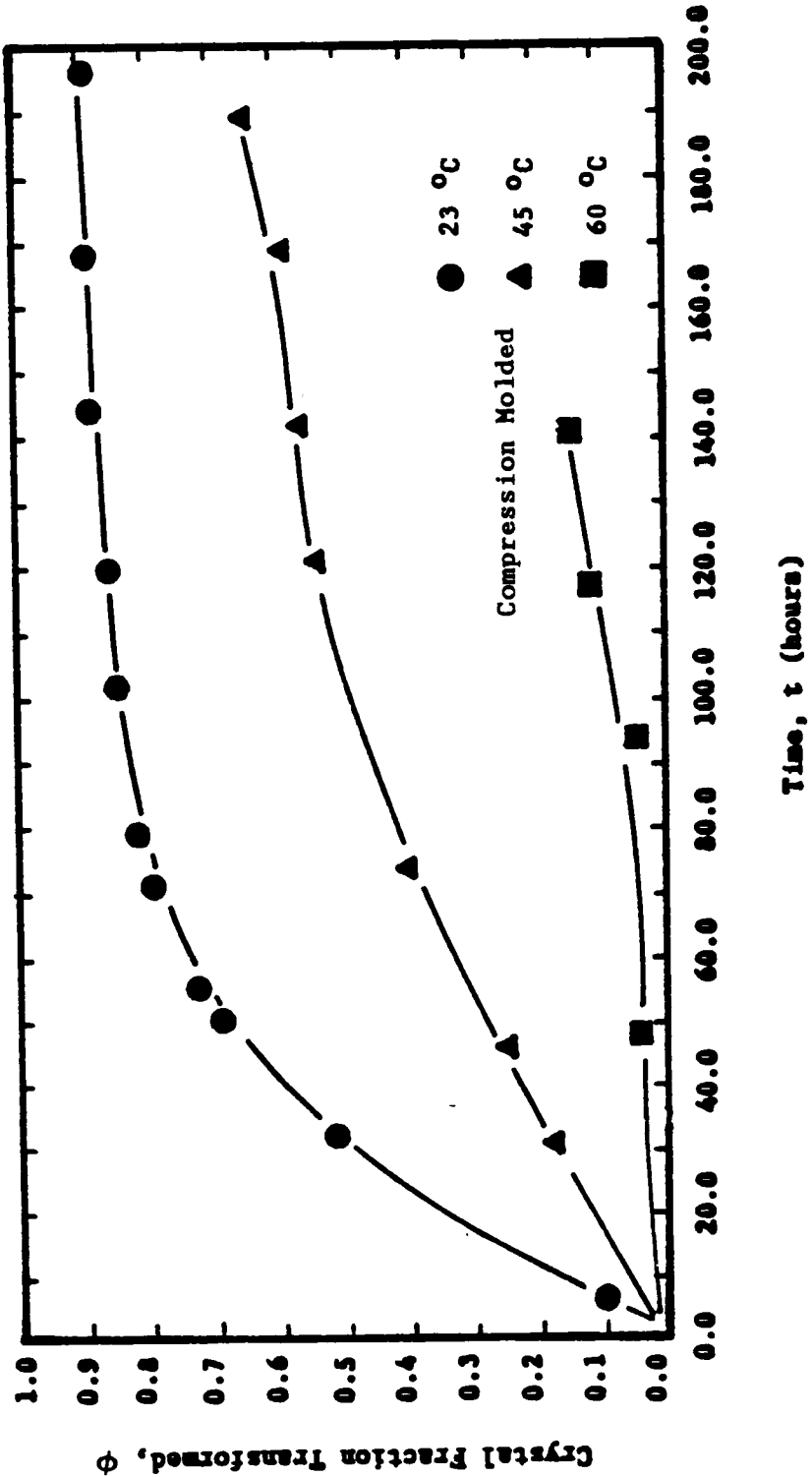


Figure A-25. Volume Fraction of the Crystal Transformed Over Time for CN05 at Temperatures of 23 °C, 45 °C, and 60 °C

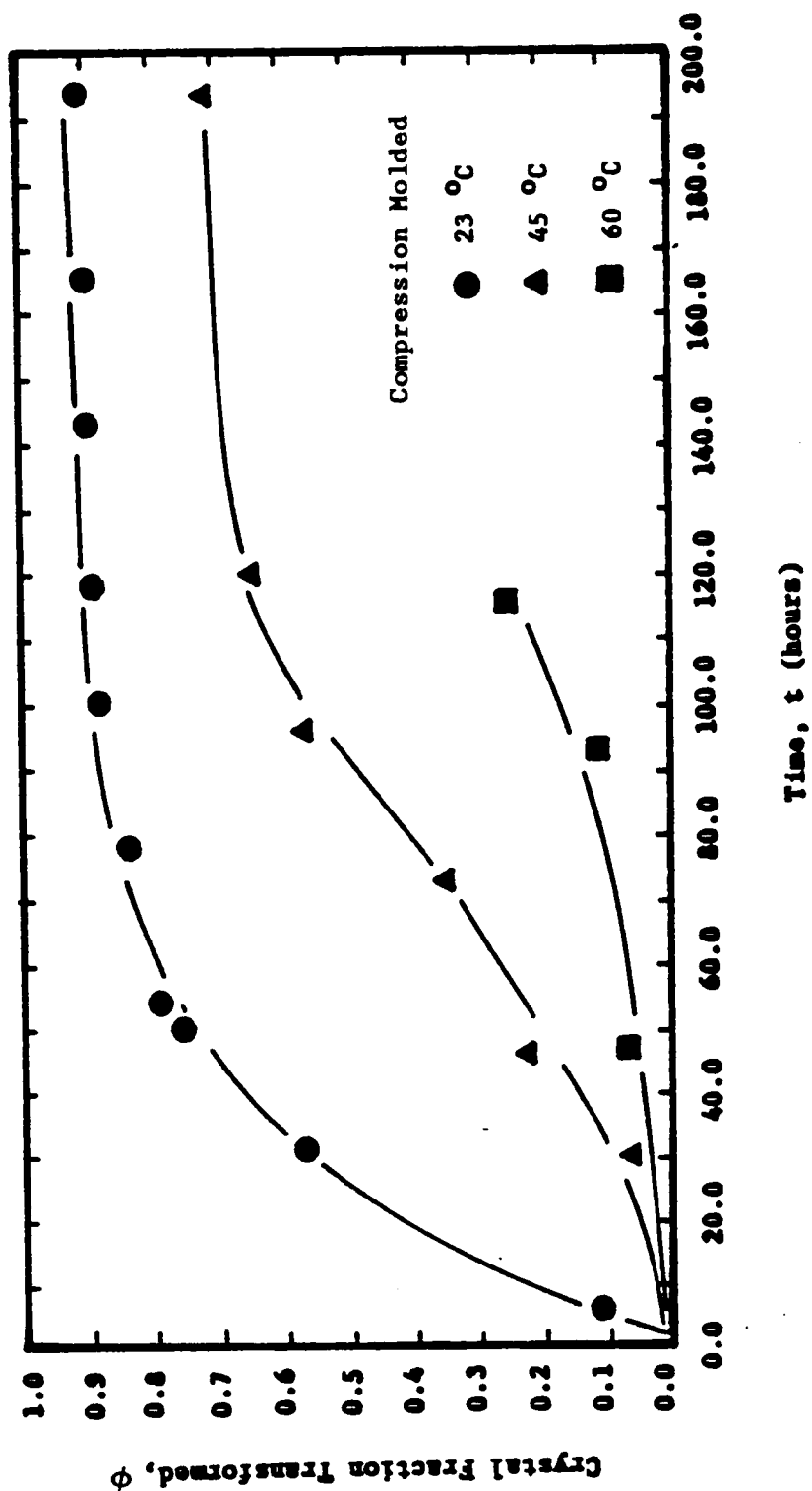


Figure A-26: Volume Fraction of the Crystal Transformed Over Time for CN2 at Temperatures of 23 °C, 45 °C and 60 °C

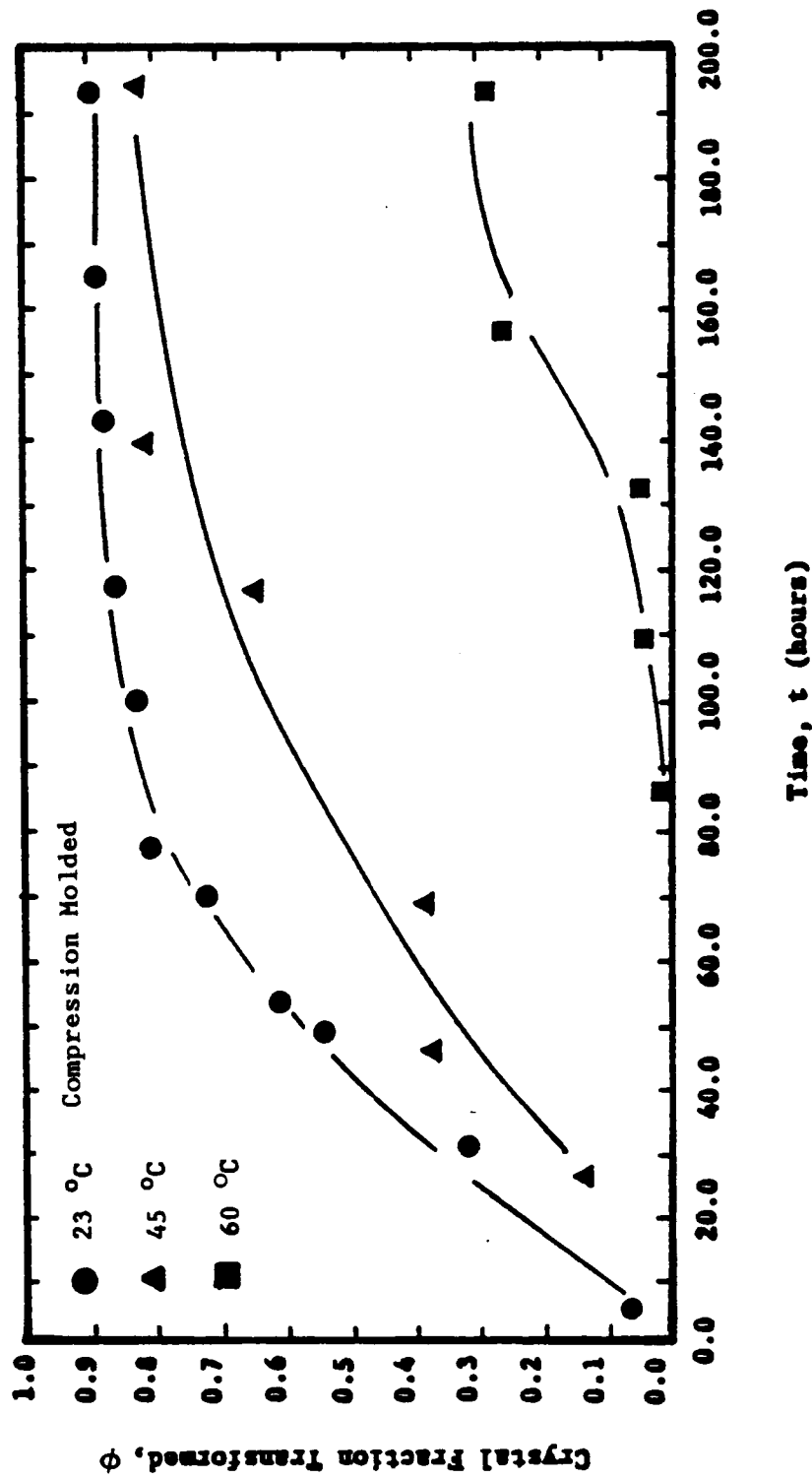


Figure A-27. Volume Fraction of the Crystal Transformed Over Time for CB05 at Temperatures of 23 °C, 45 °C and 60 °C

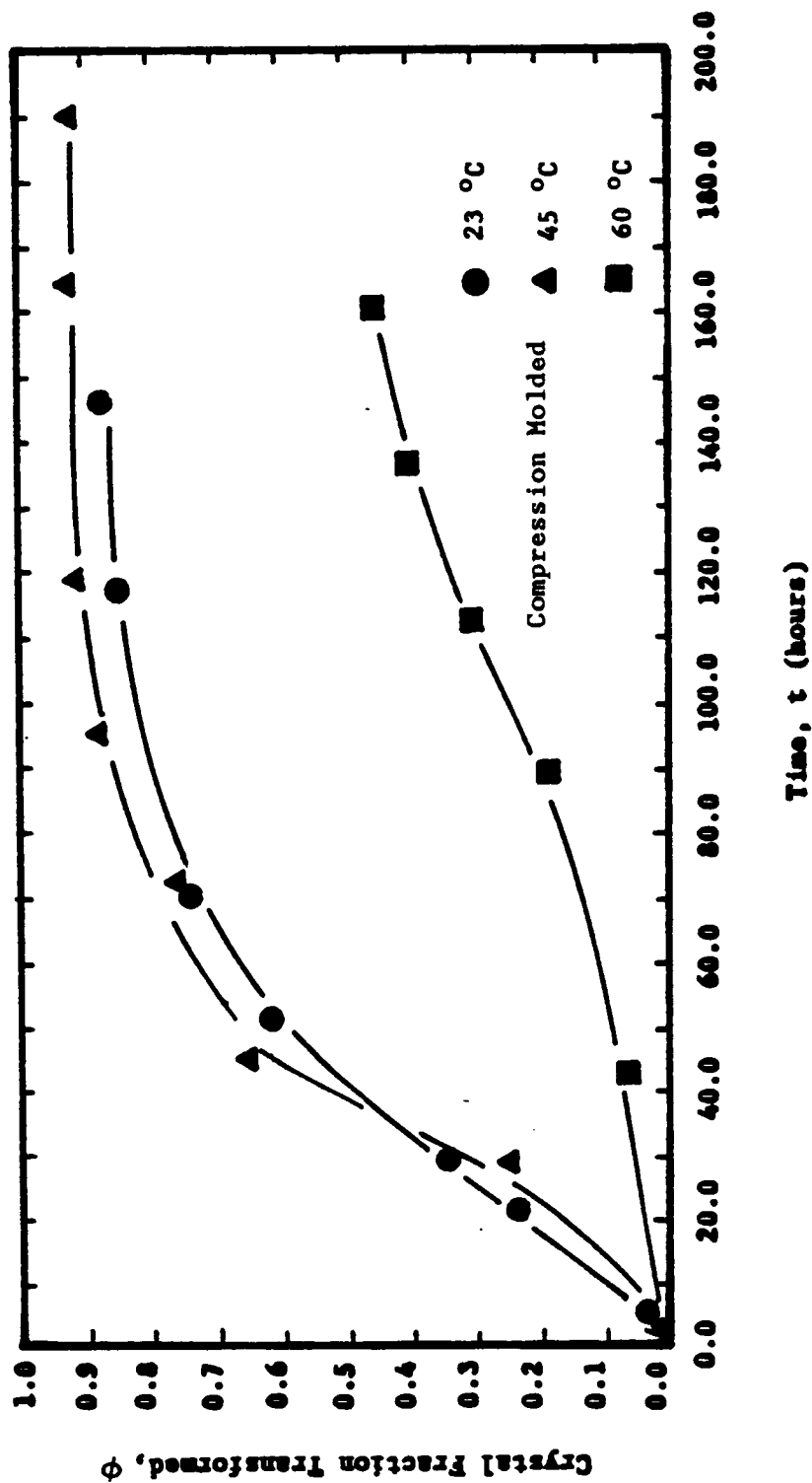


Figure A-28. Volume Fraction of the Crystal Transformed Over Time for NAO5 at Temperatures of 23 °C, 45 °C, and 60 °C

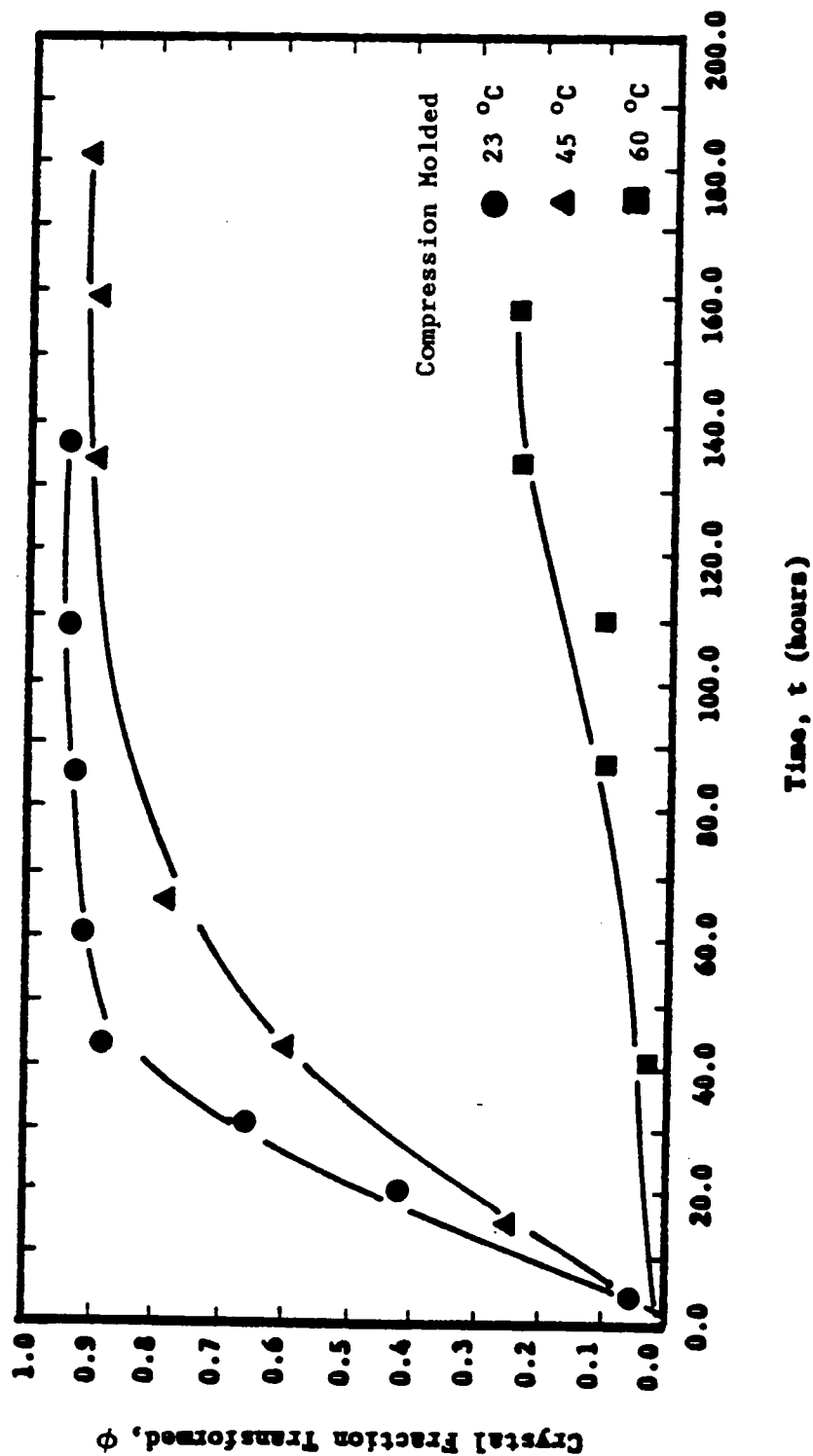


Figure A-29. Volume Fraction of the Crystal Transformed Over Time for NA2 at Temperatures of 23 °C, 45 °C, and 60 °C

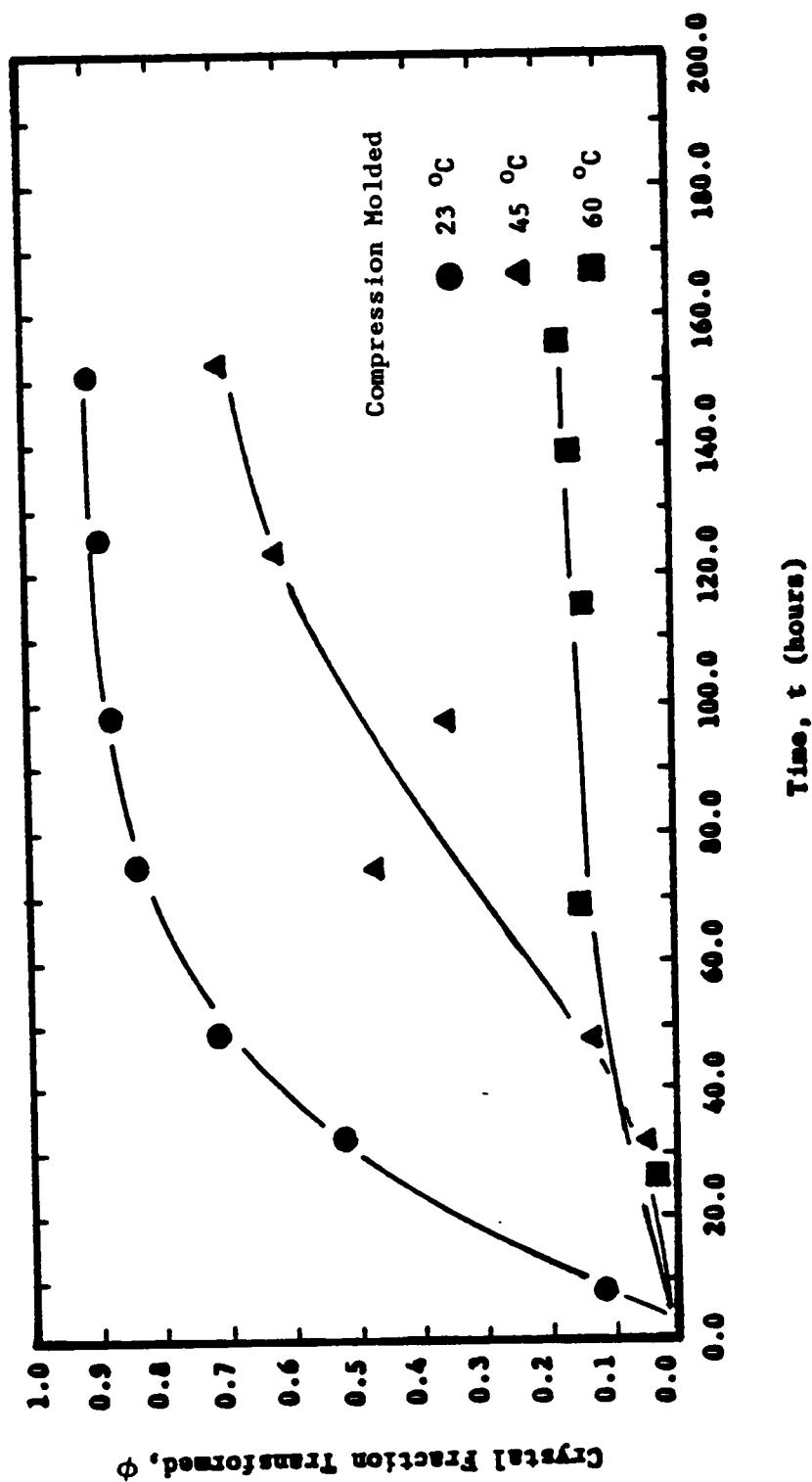


Figure A-30: Volume Fraction of the Crystal Transformed Over Time for SB05 at Temperatures of 23 °C, 45 °C, and 60 °C

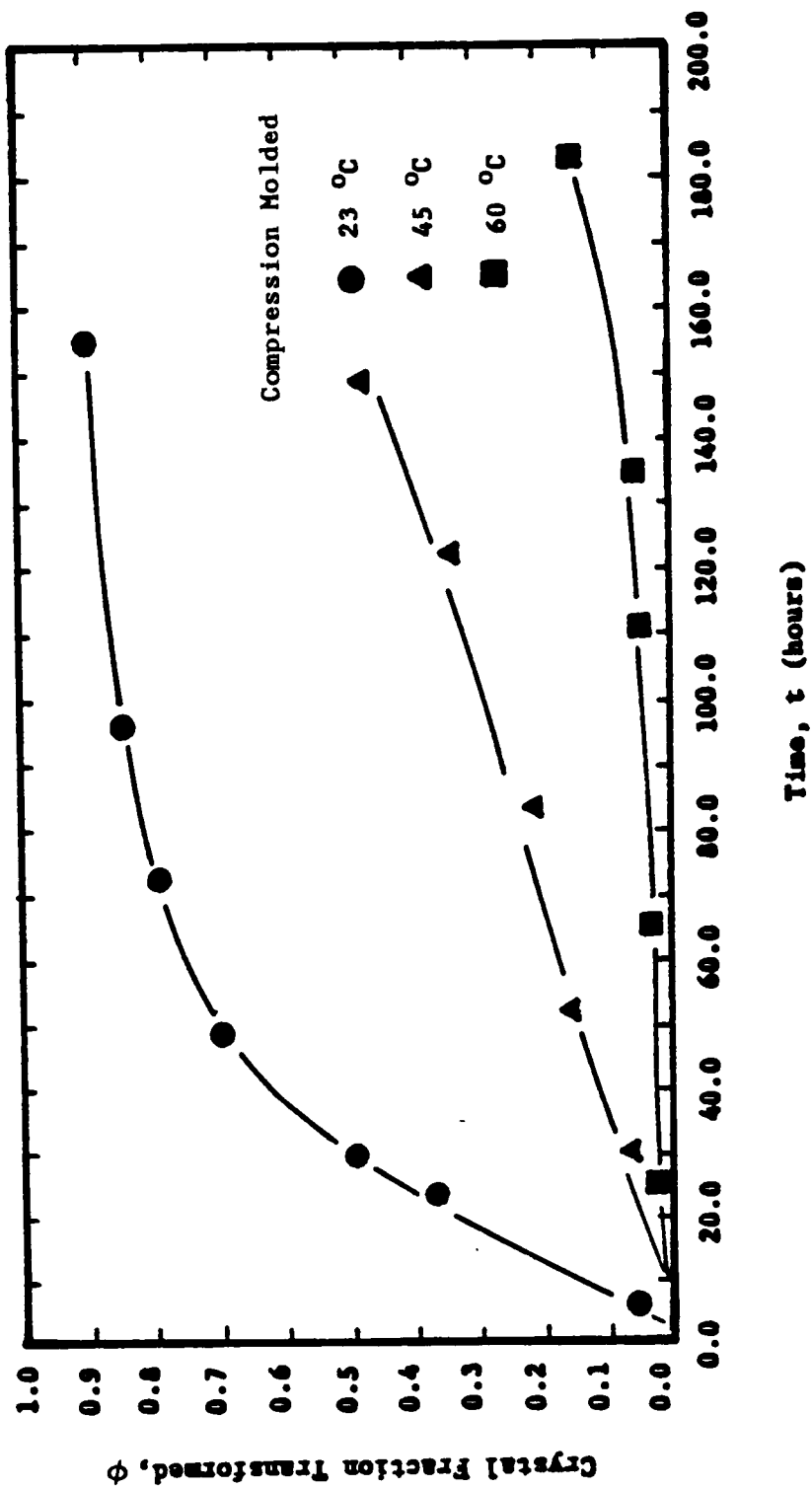


Figure A-31. Volume Fraction of the Crystal Transformed Over Time for SA05 at Temperatures of 23 °C, 45 °C, and 60 °C

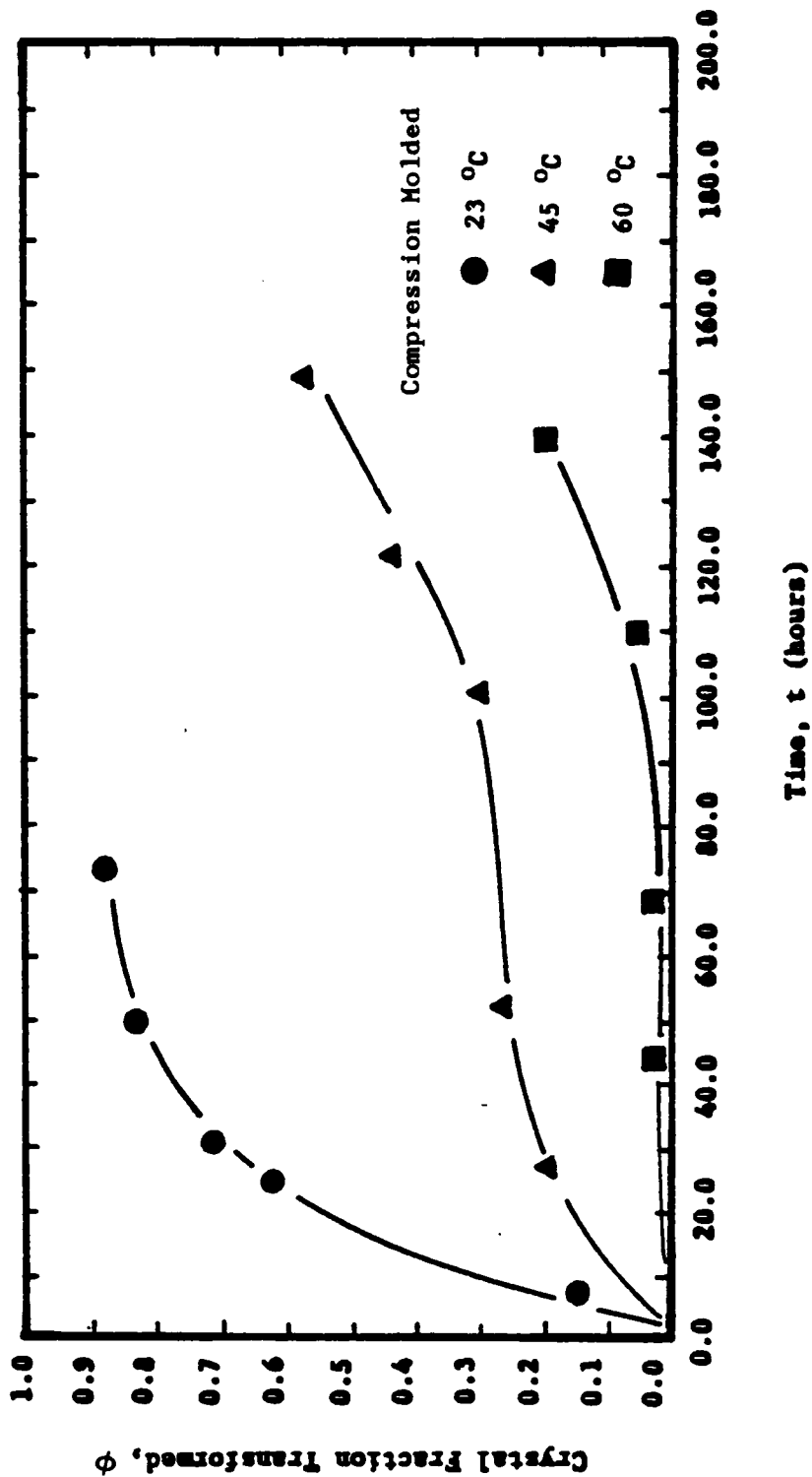


Figure A-32. Volume Fraction of the Crystal Transformed Over Time for SA2 at Temperatures of 23 °C, 45 °C, and 60 °C

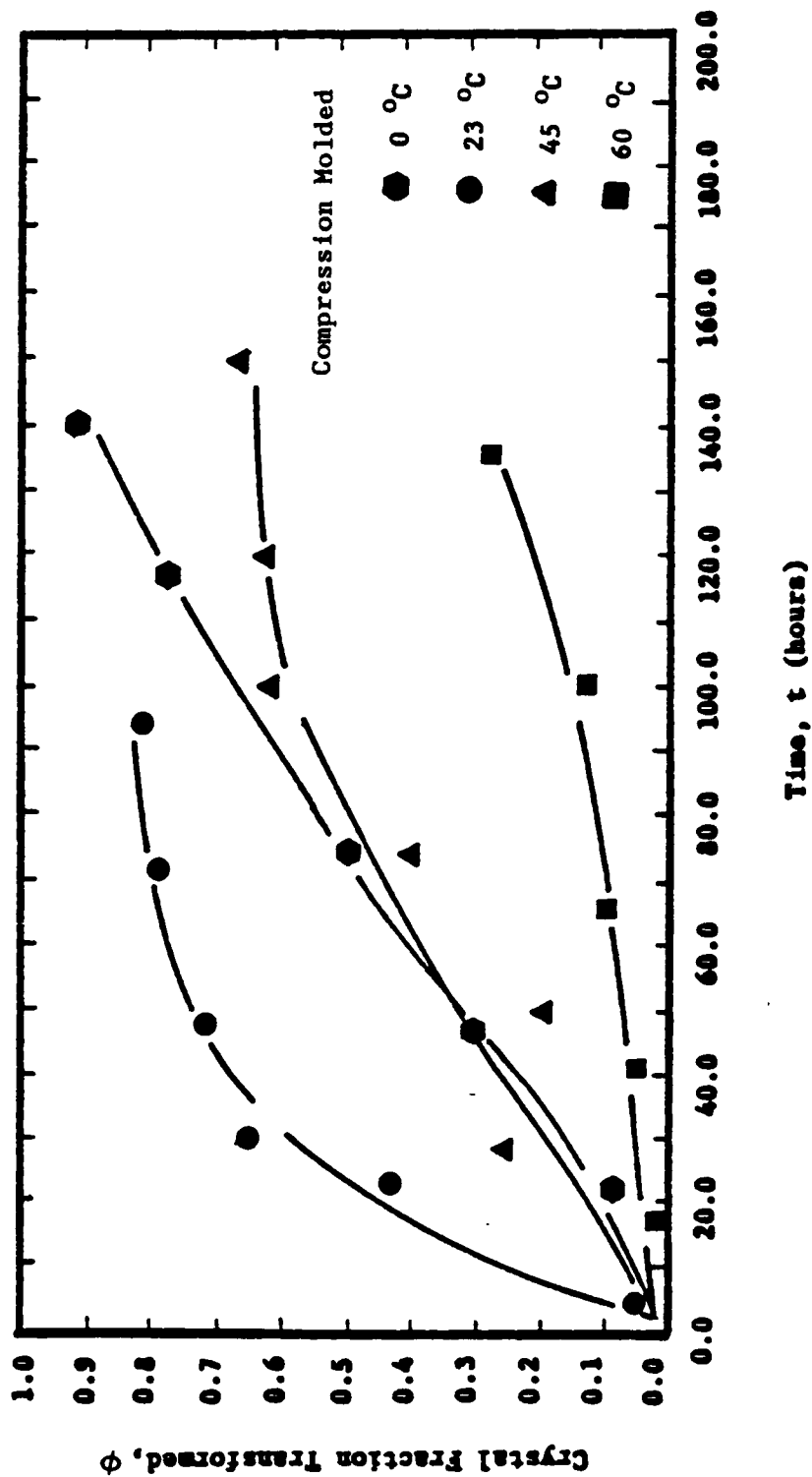


Figure A-33. Volume Fraction of the Crystal Transformed Over Time for SA5 at Temperatures of 0 °C, 23 °C, 45 °C, and 60 °C

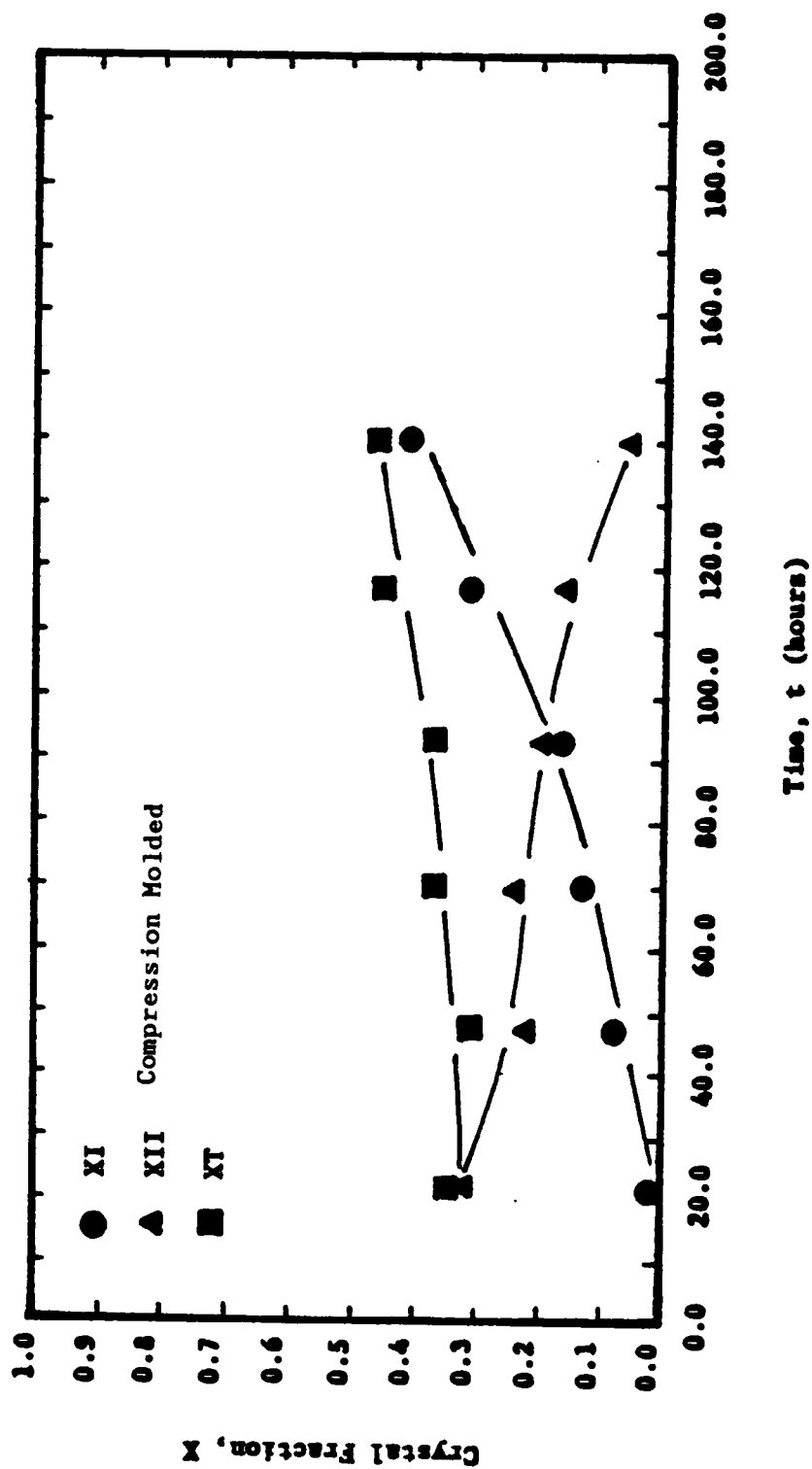


Figure A-34: Crystal Fraction Present as a Function of Time for BR200S at 0 °C

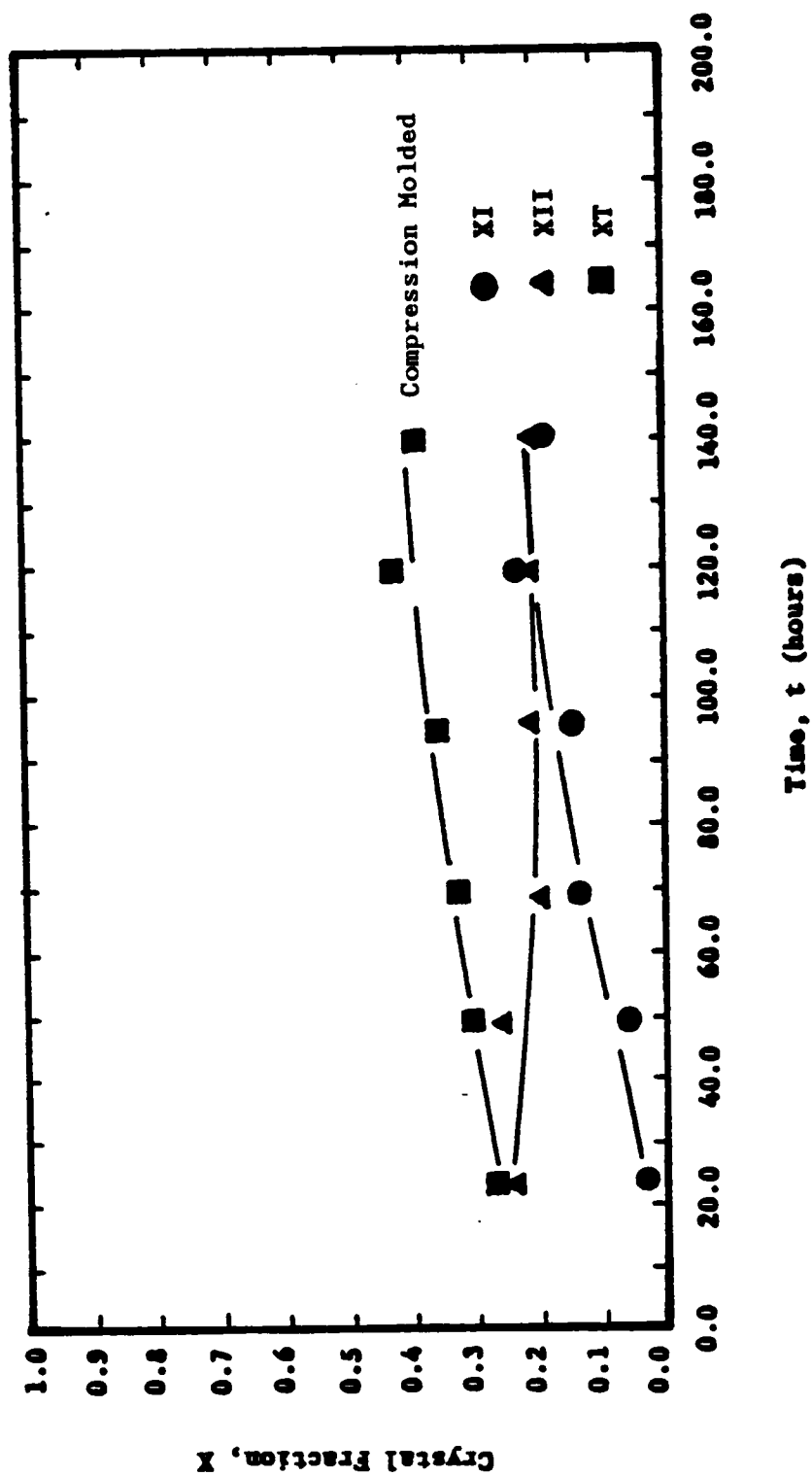


Figure A-35. Crystal Fraction Present as a Function of Time for BR200S at 45 °C

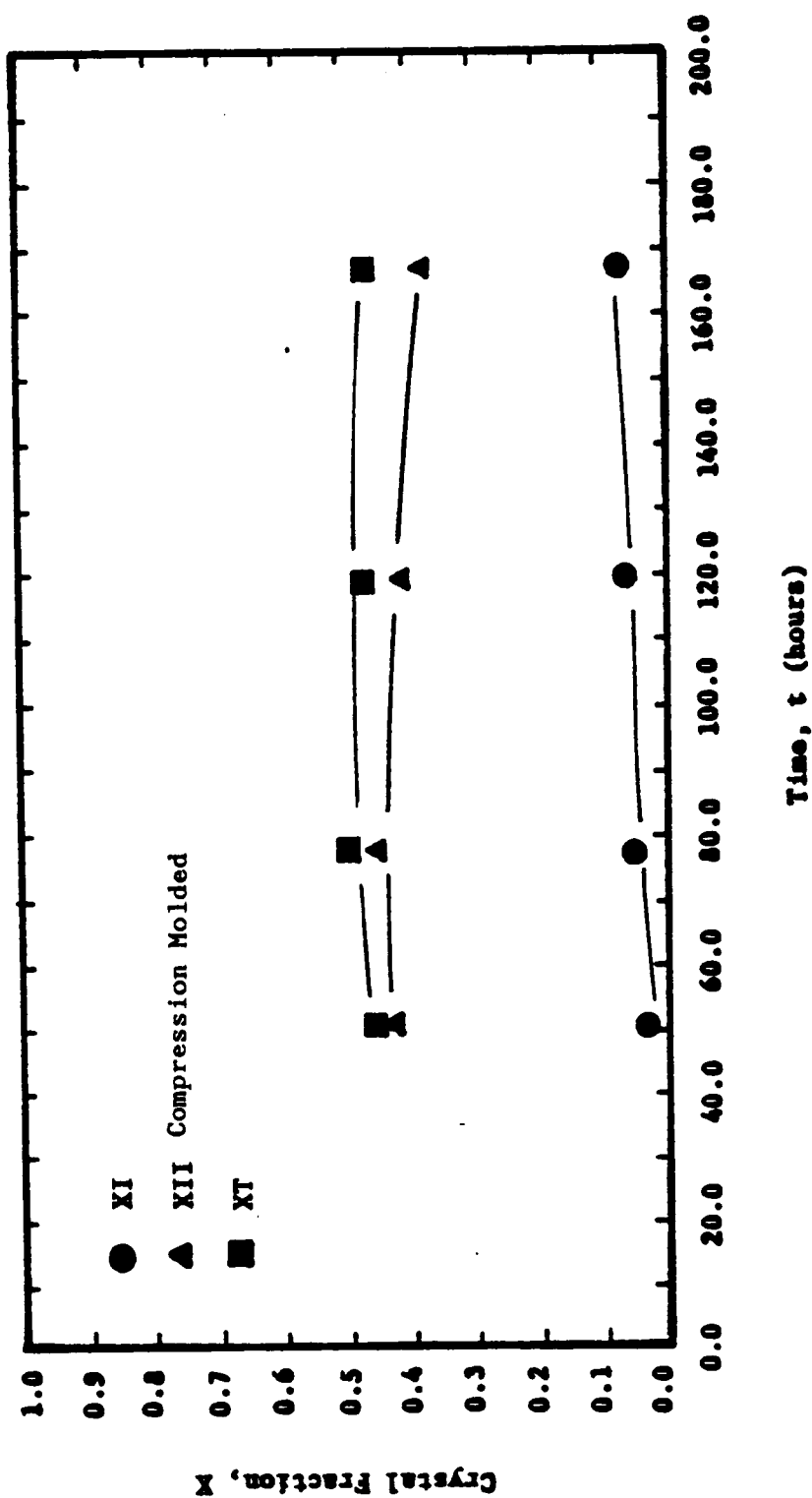


Figure A-36. Crystal Fraction Present as a Function of Time for BR200S at 60 °C

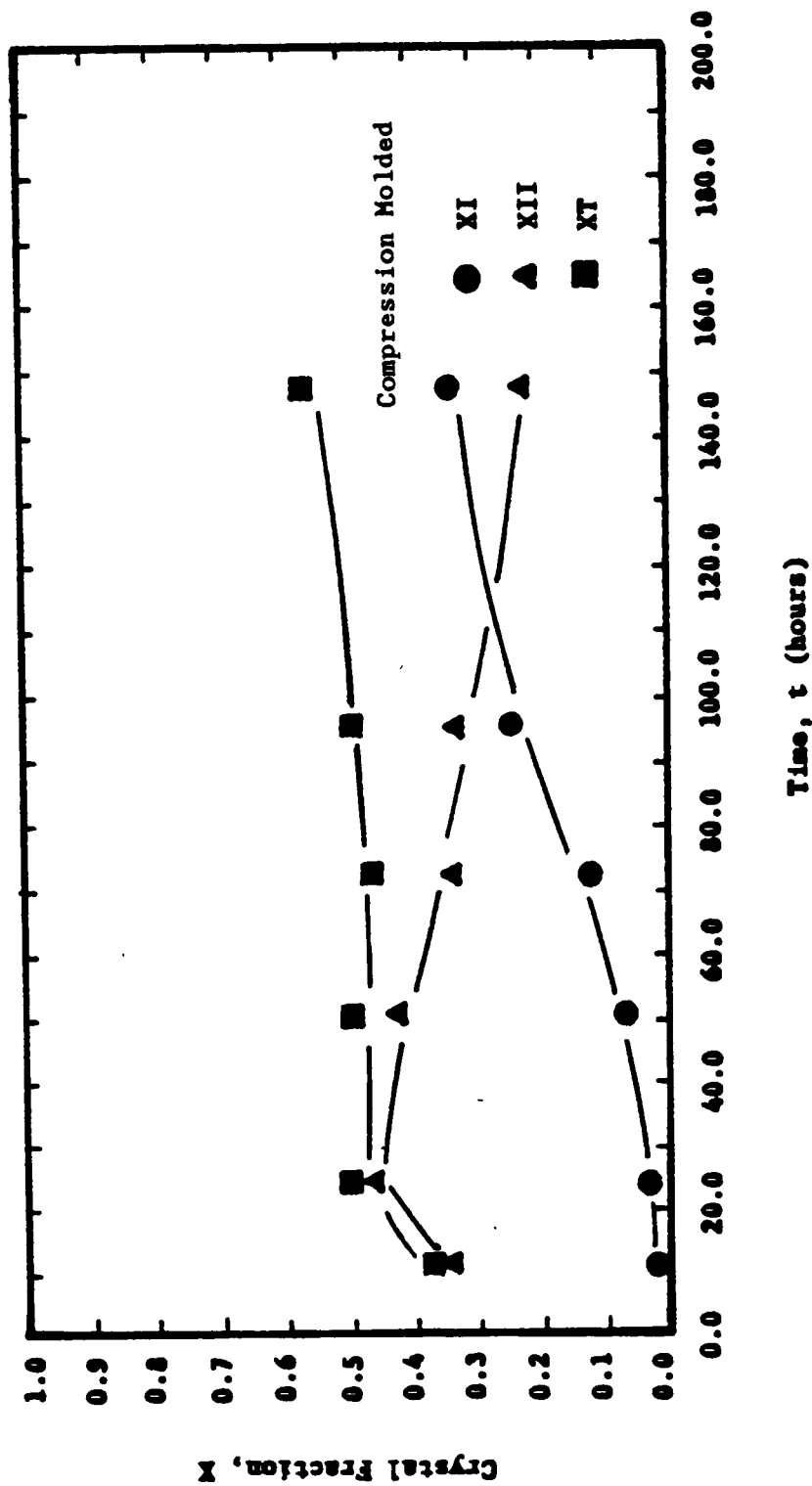


Figure A-37. Crystal Fraction Present as a Function of Time for PP5 at 45 °C

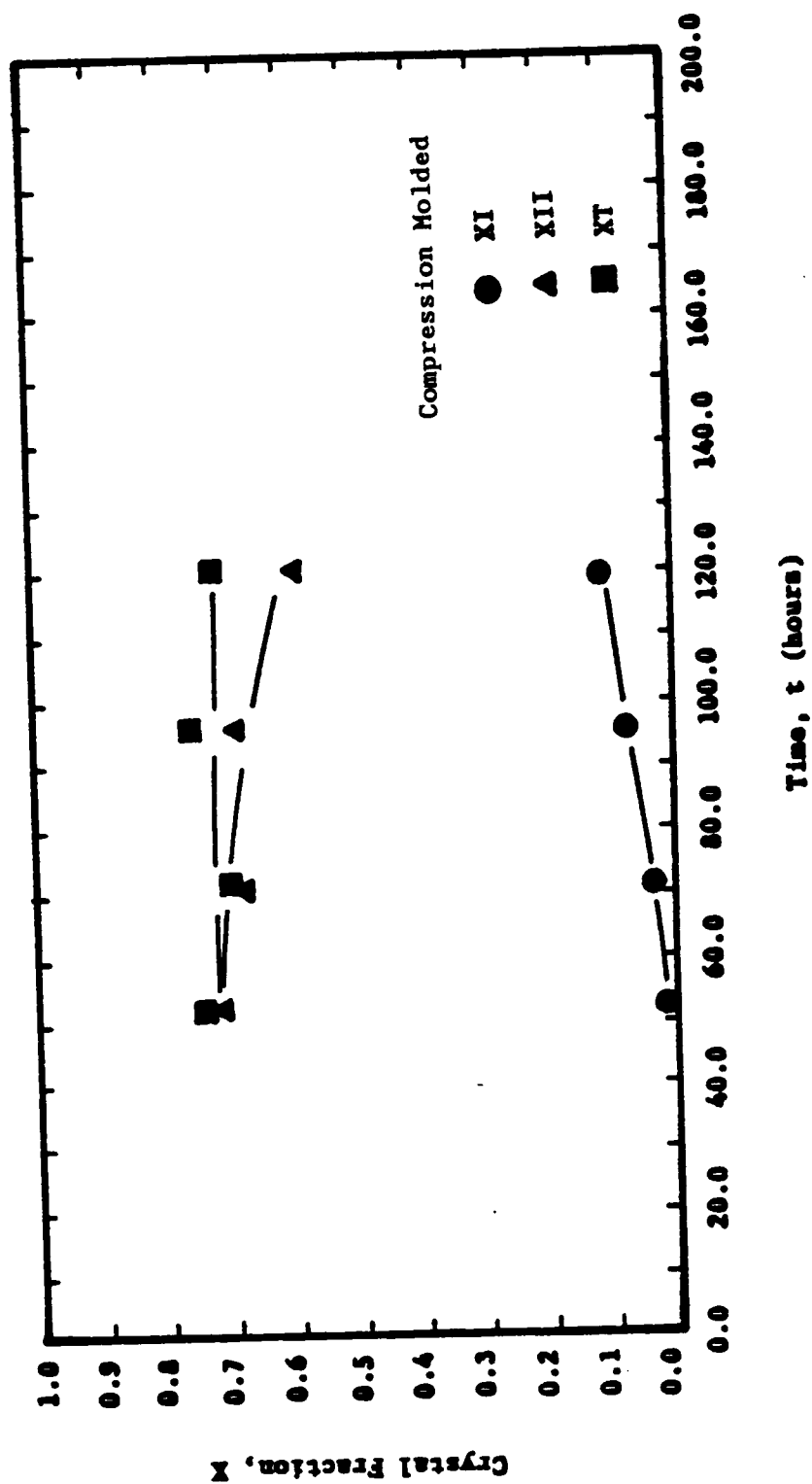


Figure A-38. Crystal Fraction Present as a Function of Time for PP5 at 60 °C

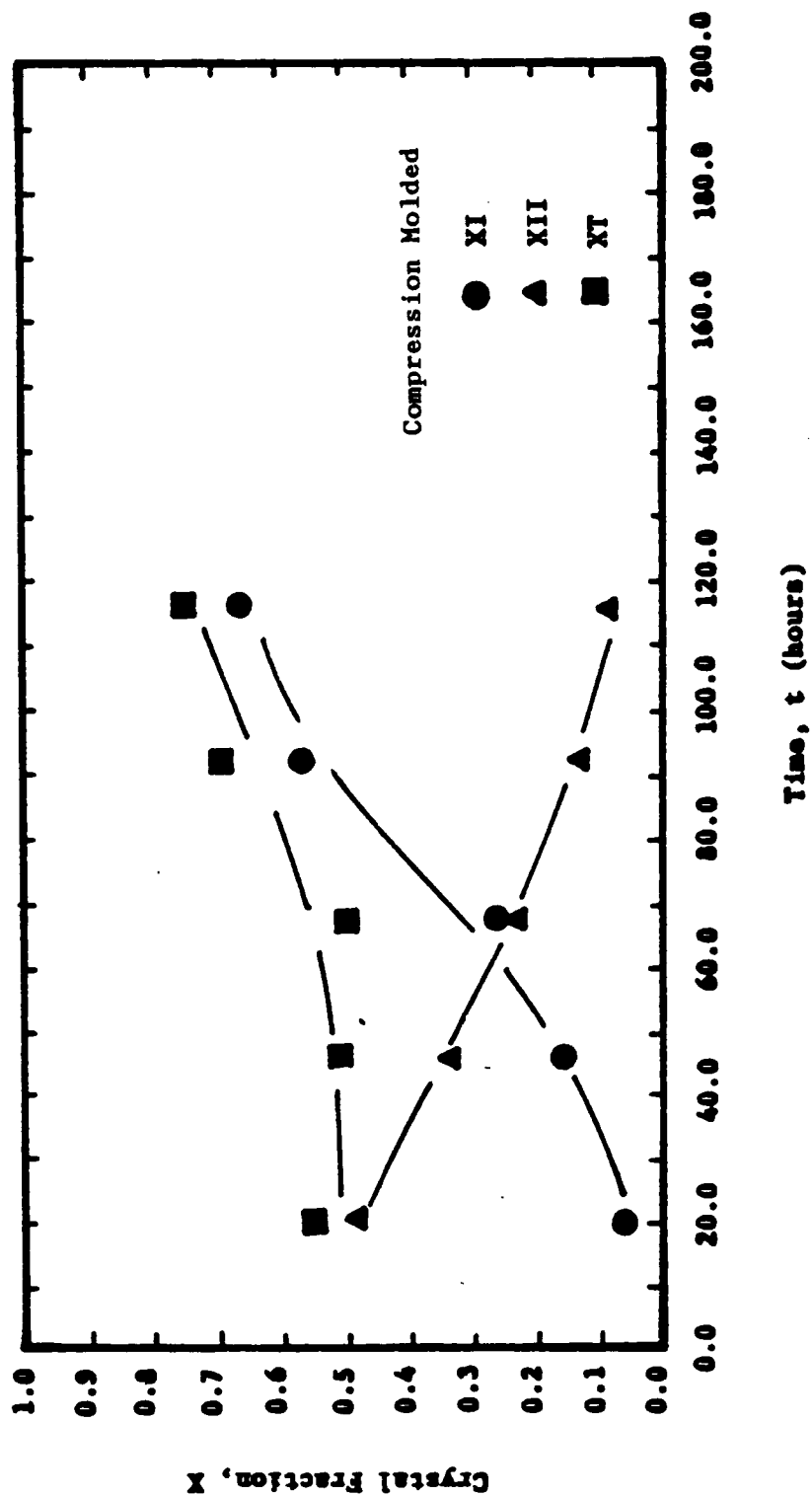


Figure A-39. Crystal Fraction Present as a Function of Time for PP10 at 0°C

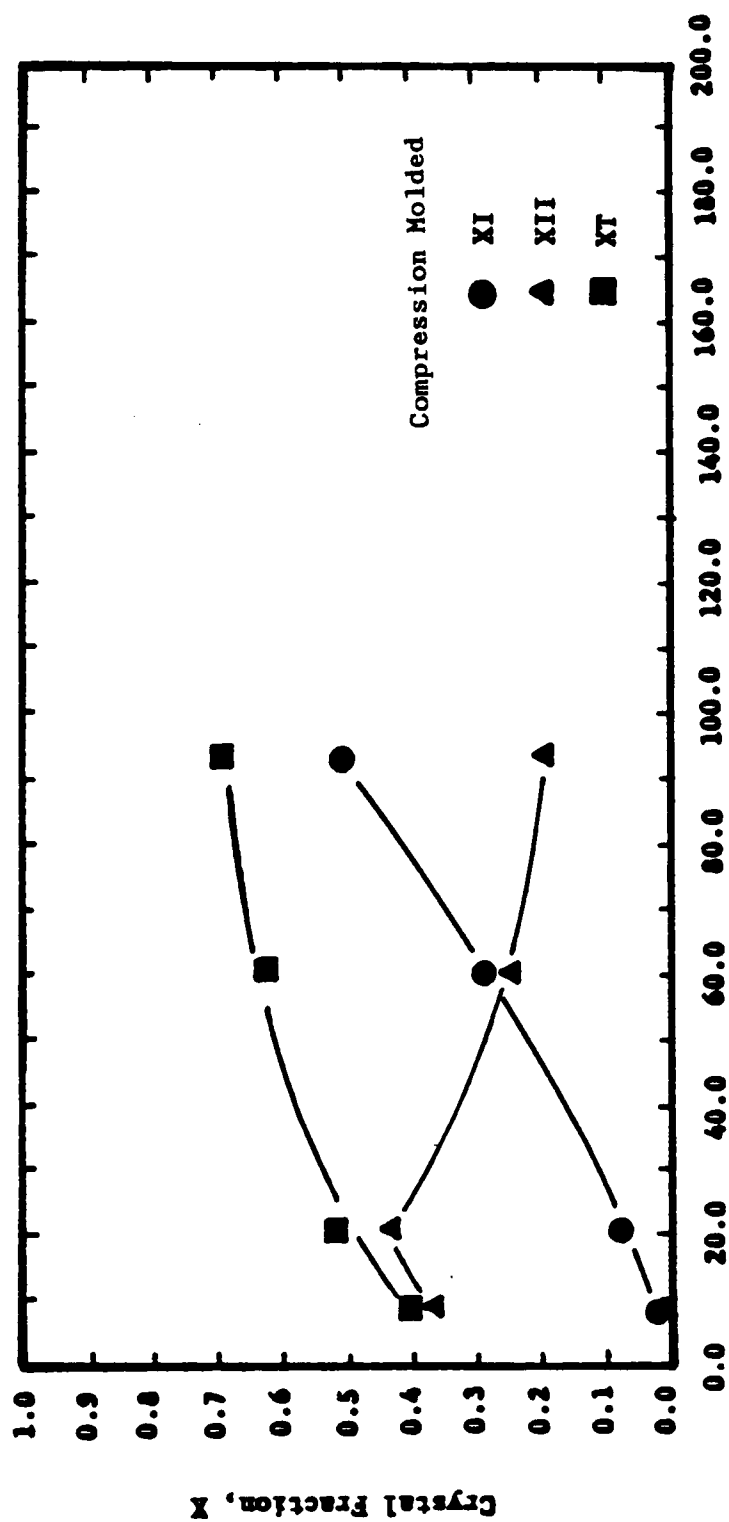


Figure A-40. Crystal Fraction Present as a Function of Time for PP10 at 45 °C

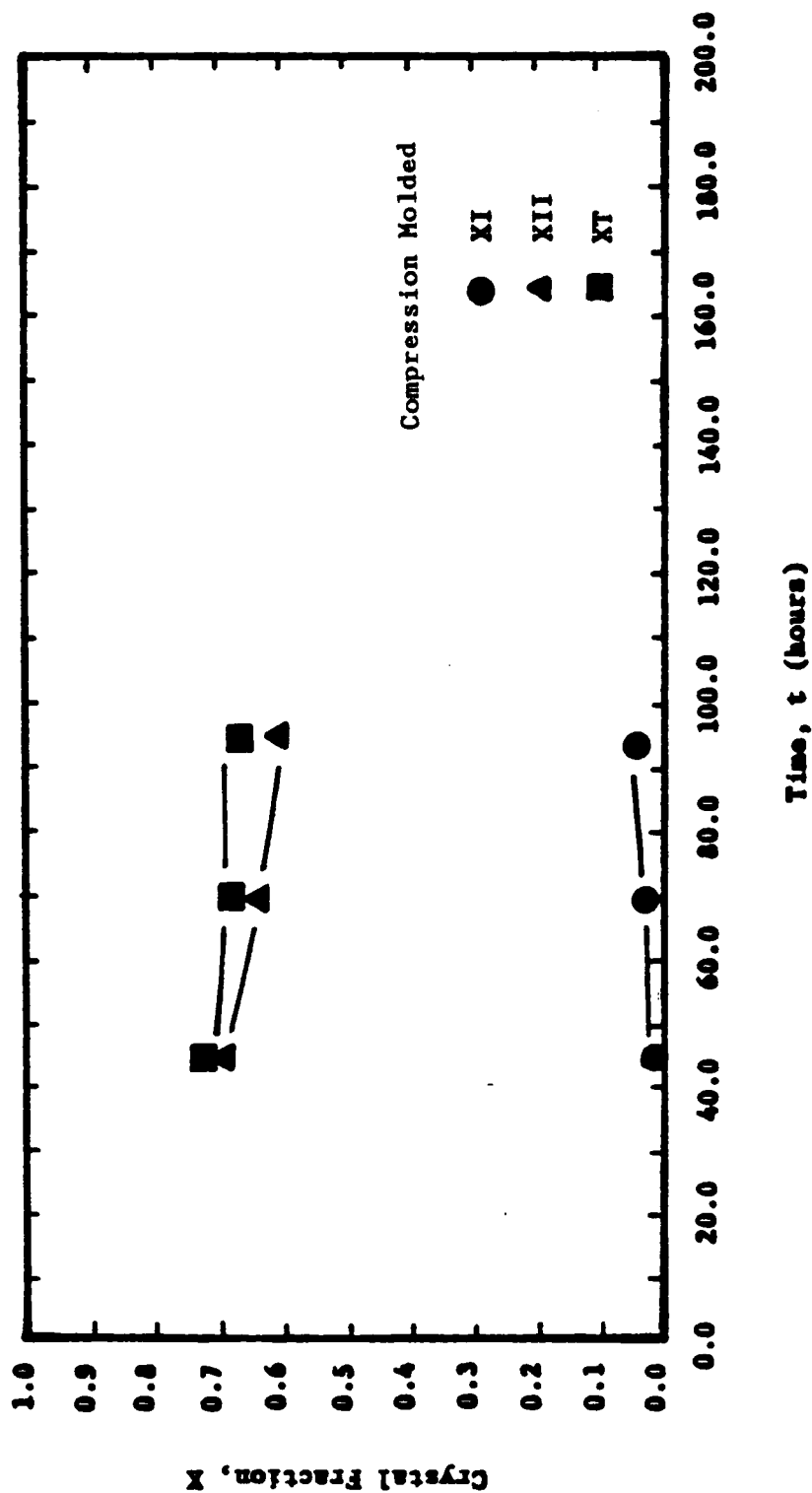


Figure A-41. Crystal Fraction Present as a Function of Time for PP10 at 60 °C

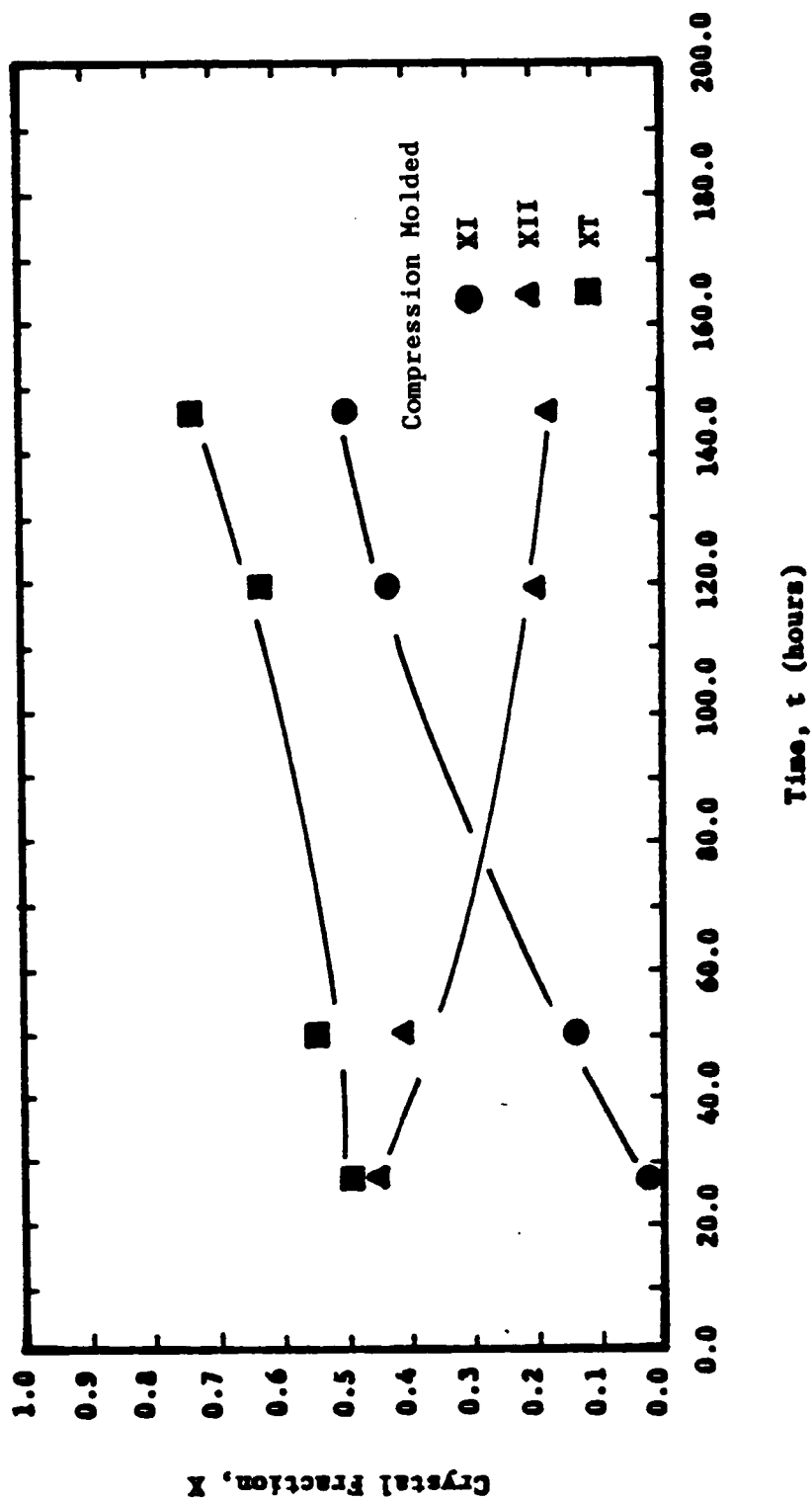


Figure A-42. Crystal Fraction Present as a Function of Time for PP25 at 45 °C

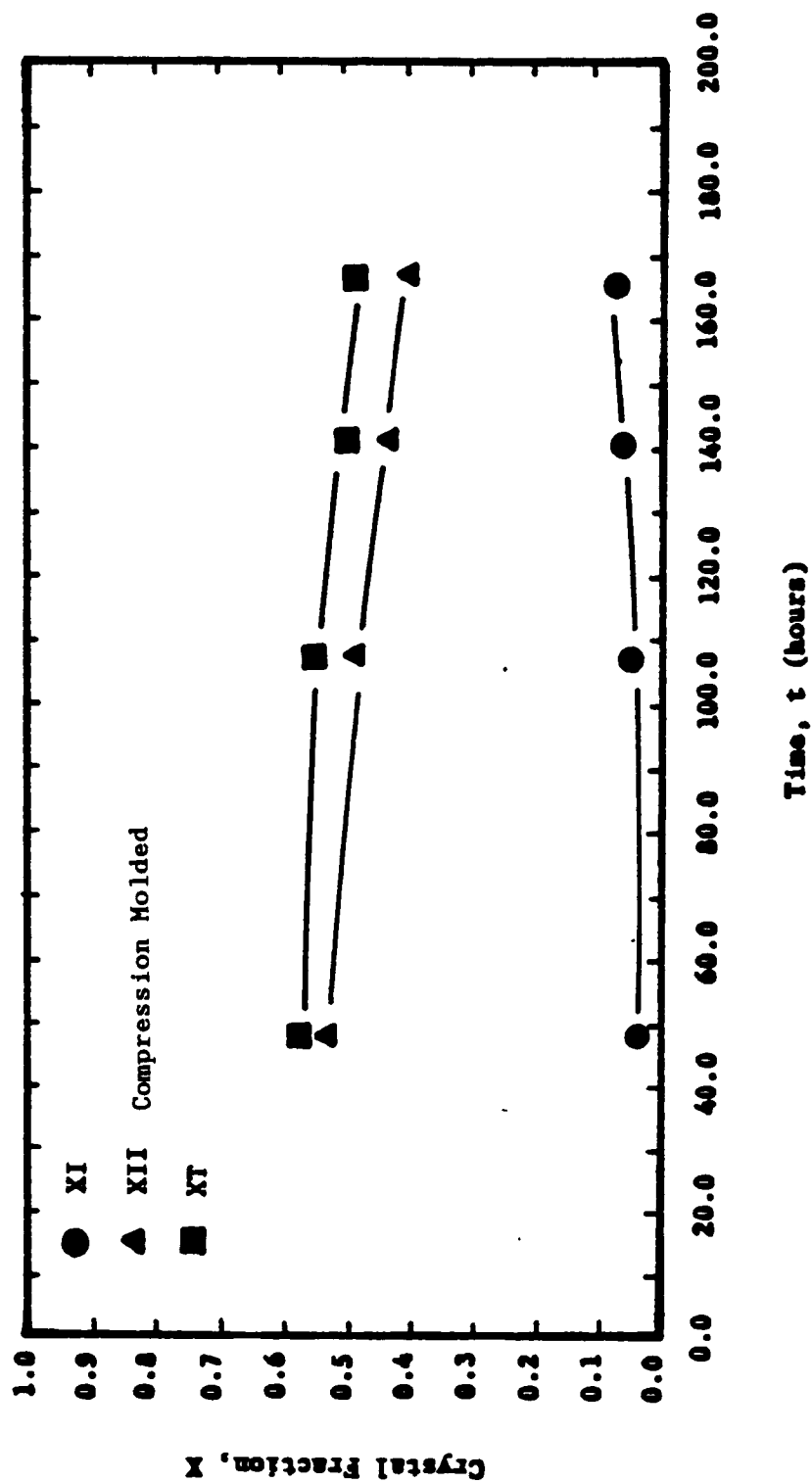


Figure A-43. Crystal Fraction Present as a Function of Time for PP25 at 60 °C

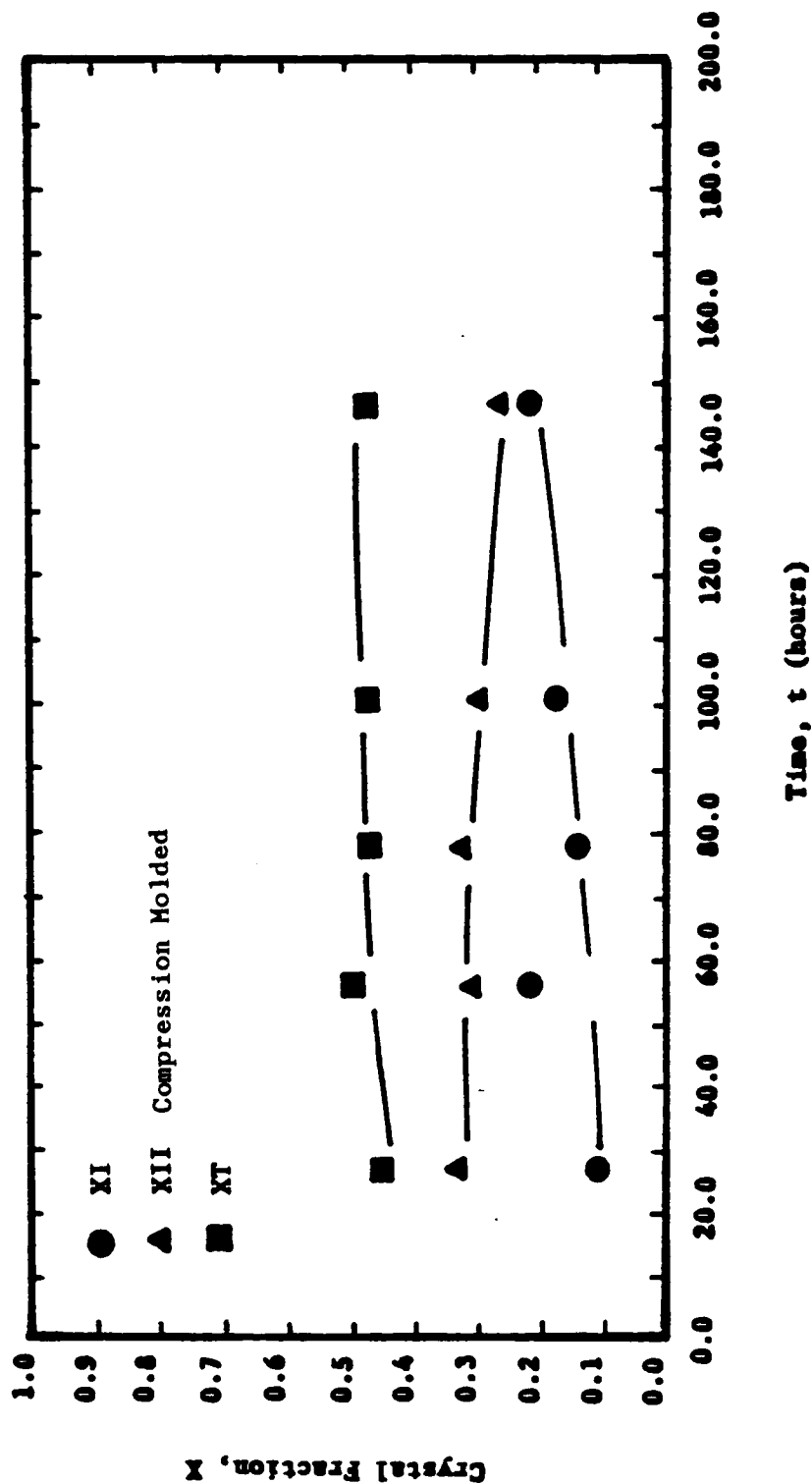


Figure A-44. Crystal Fraction Present as a Function of Time for DPE05 at 45 °C

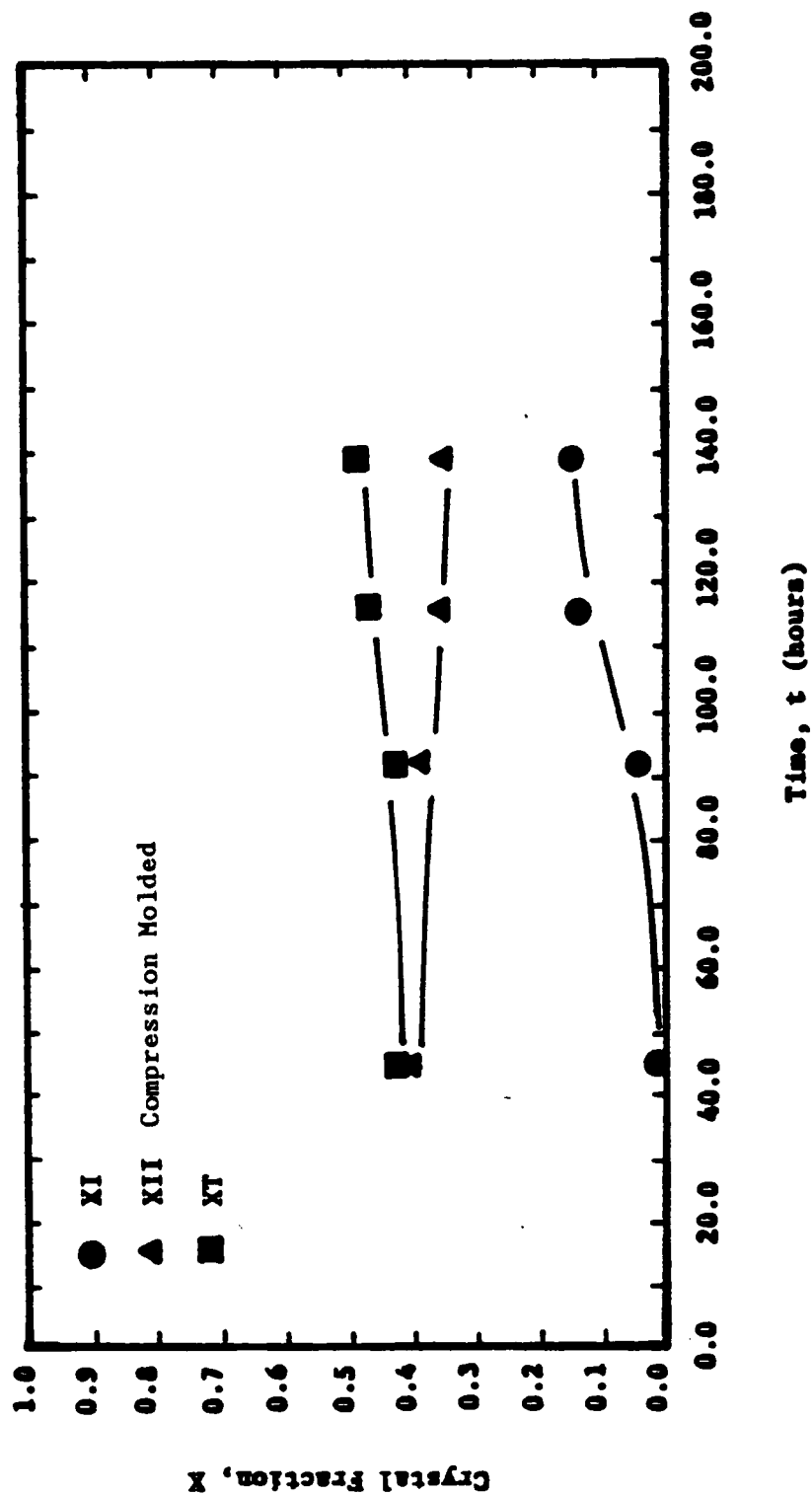


Figure A-45. Crystal Fraction Present as a Function of Time for DPE05 at 60 °C

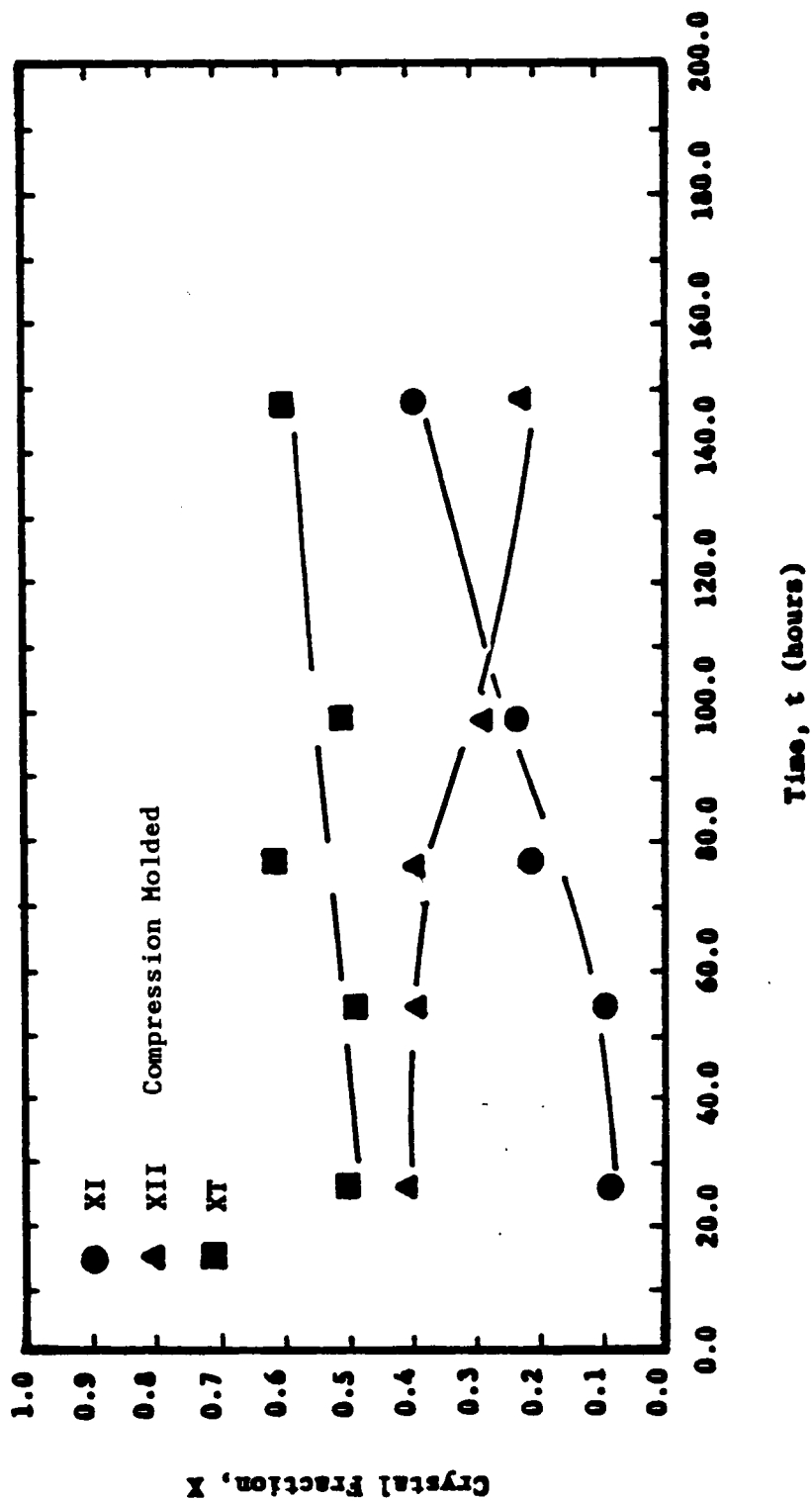


Figure A-46. Crystal Fraction Present as a Function of Time for DPE2 at 45 °C

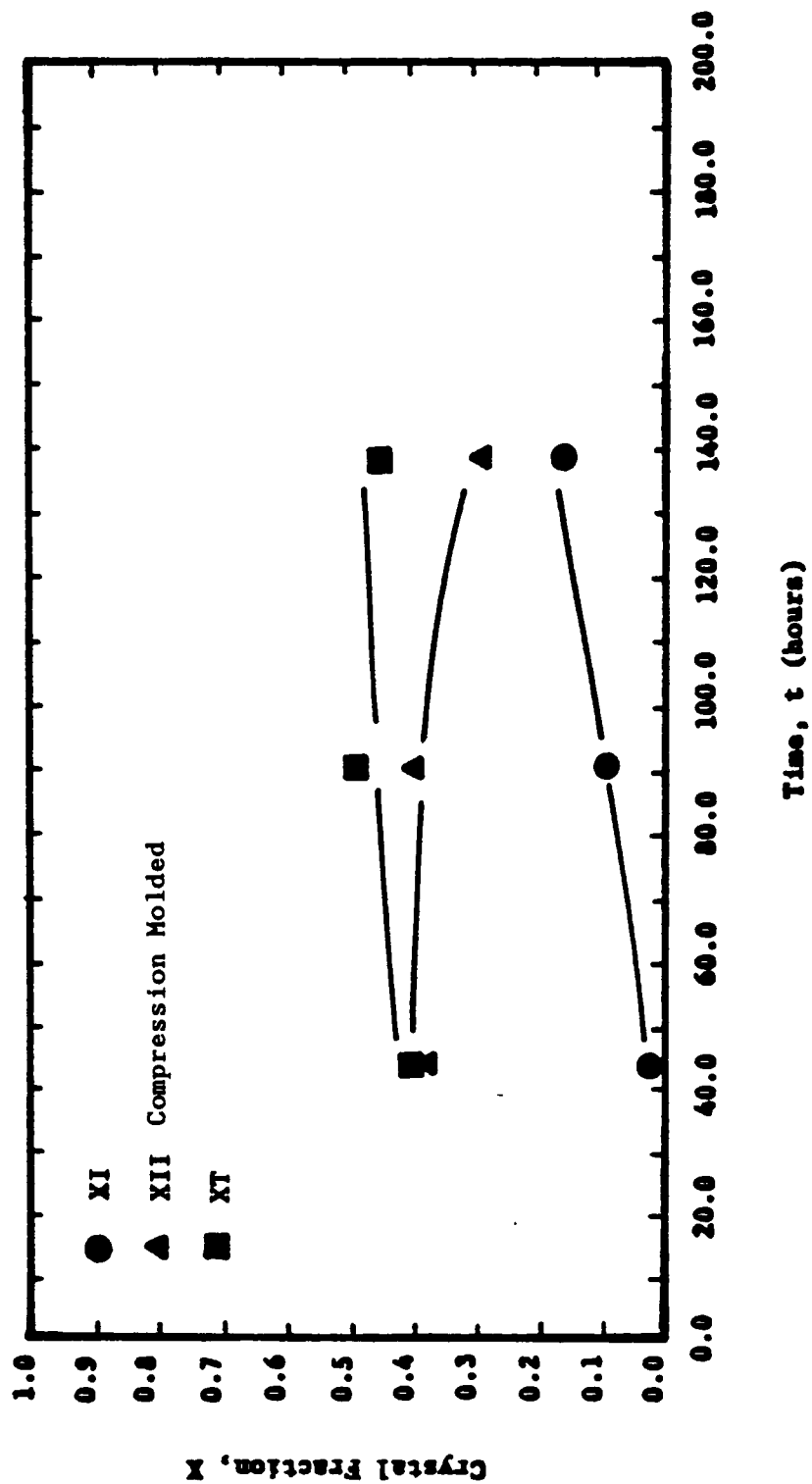


Figure A-47. Crystal Fraction Present as a Function of Time for DPE2 at 60 °C

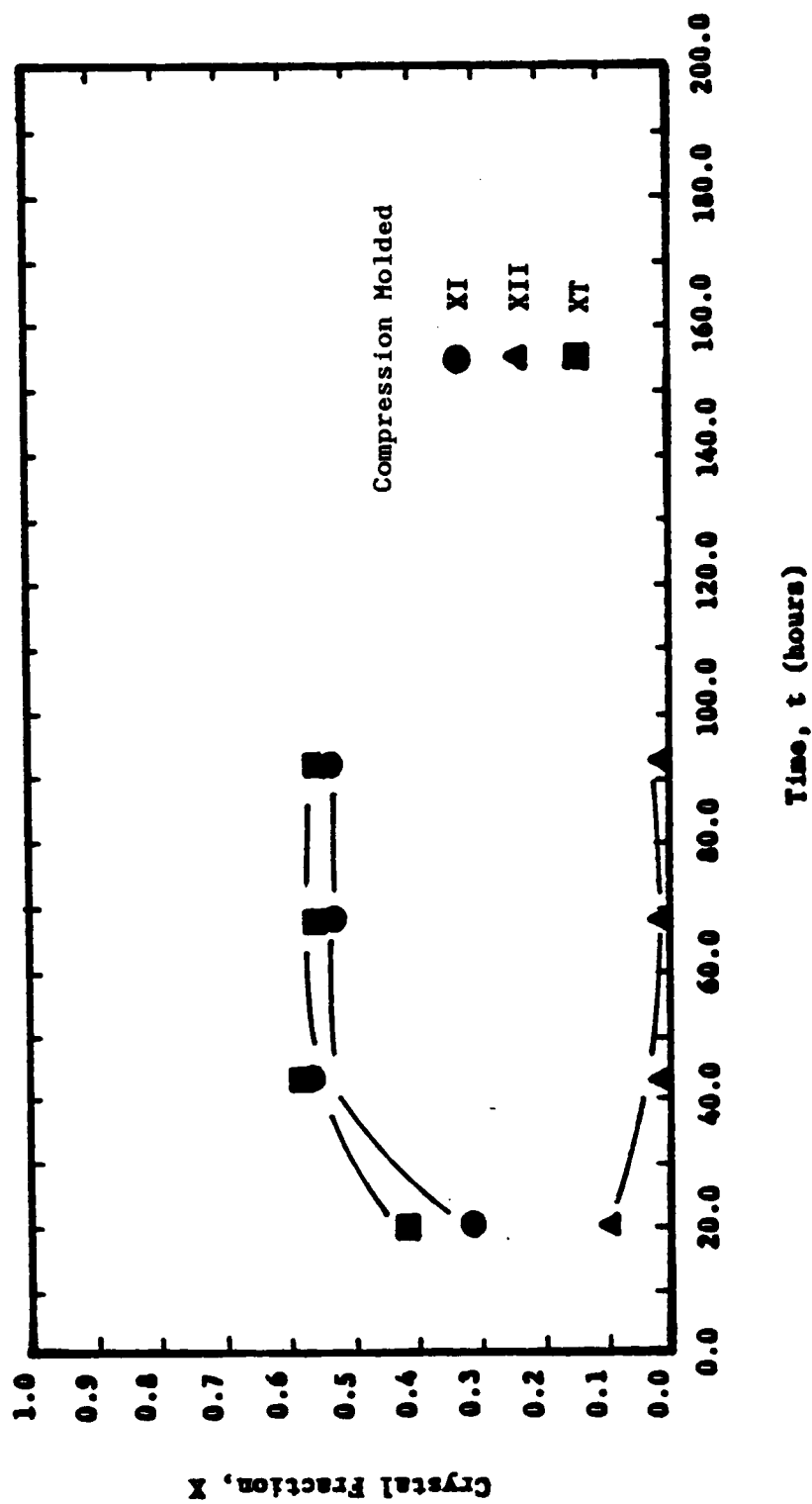


Figure A-48. Crystal Fraction Present as a Function of Time for DPE5 at 0°C

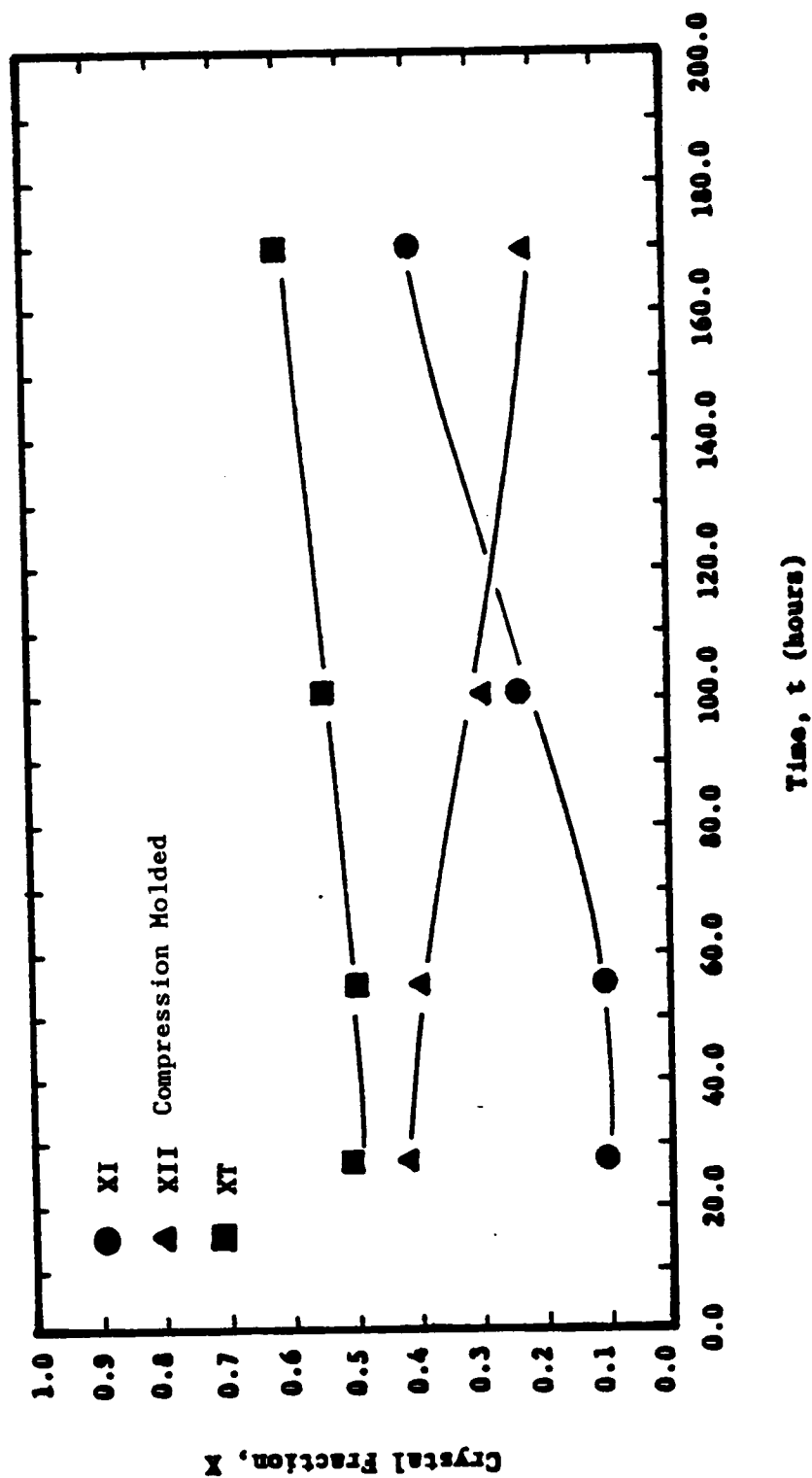


Figure A-49. Crystal Fraction Present as a Function of Time for DPE5 at 45 °C

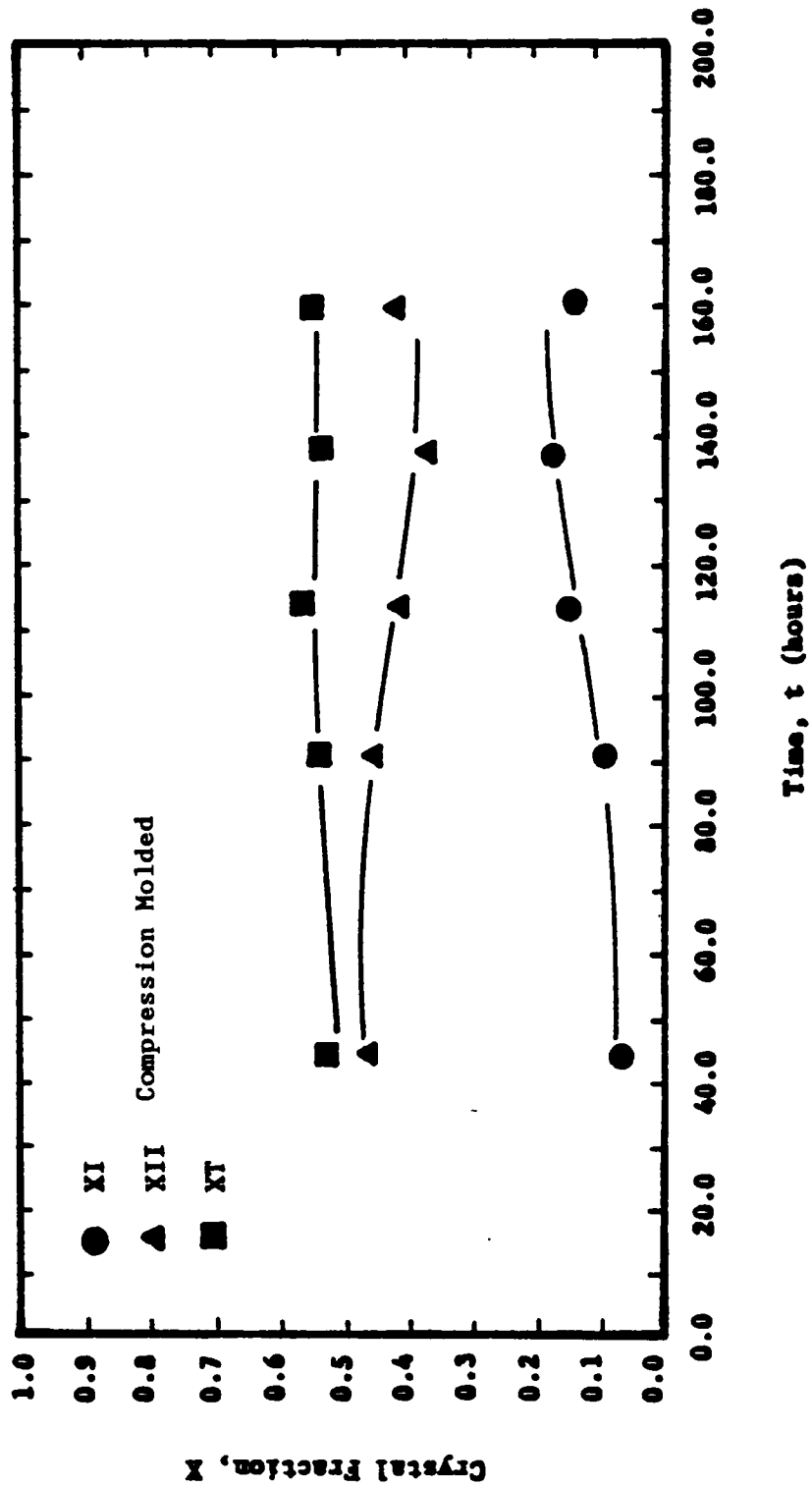


Figure A-50. Crystal Fraction Present as a Function of Time for DPE5 at 60 °C

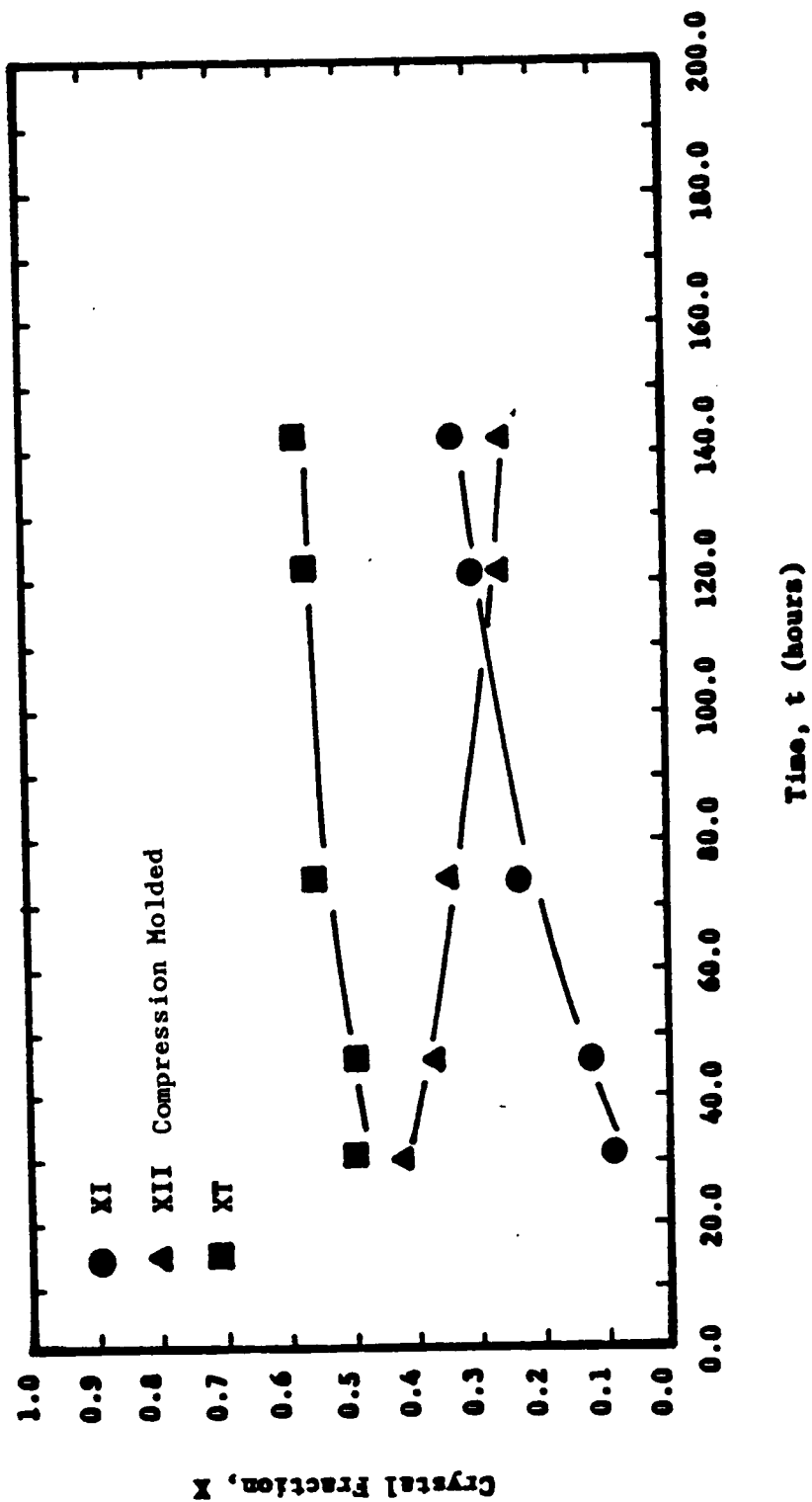


Figure A-51. Crystal Fraction Present as a Function of Time for CN05 at 45 °C.

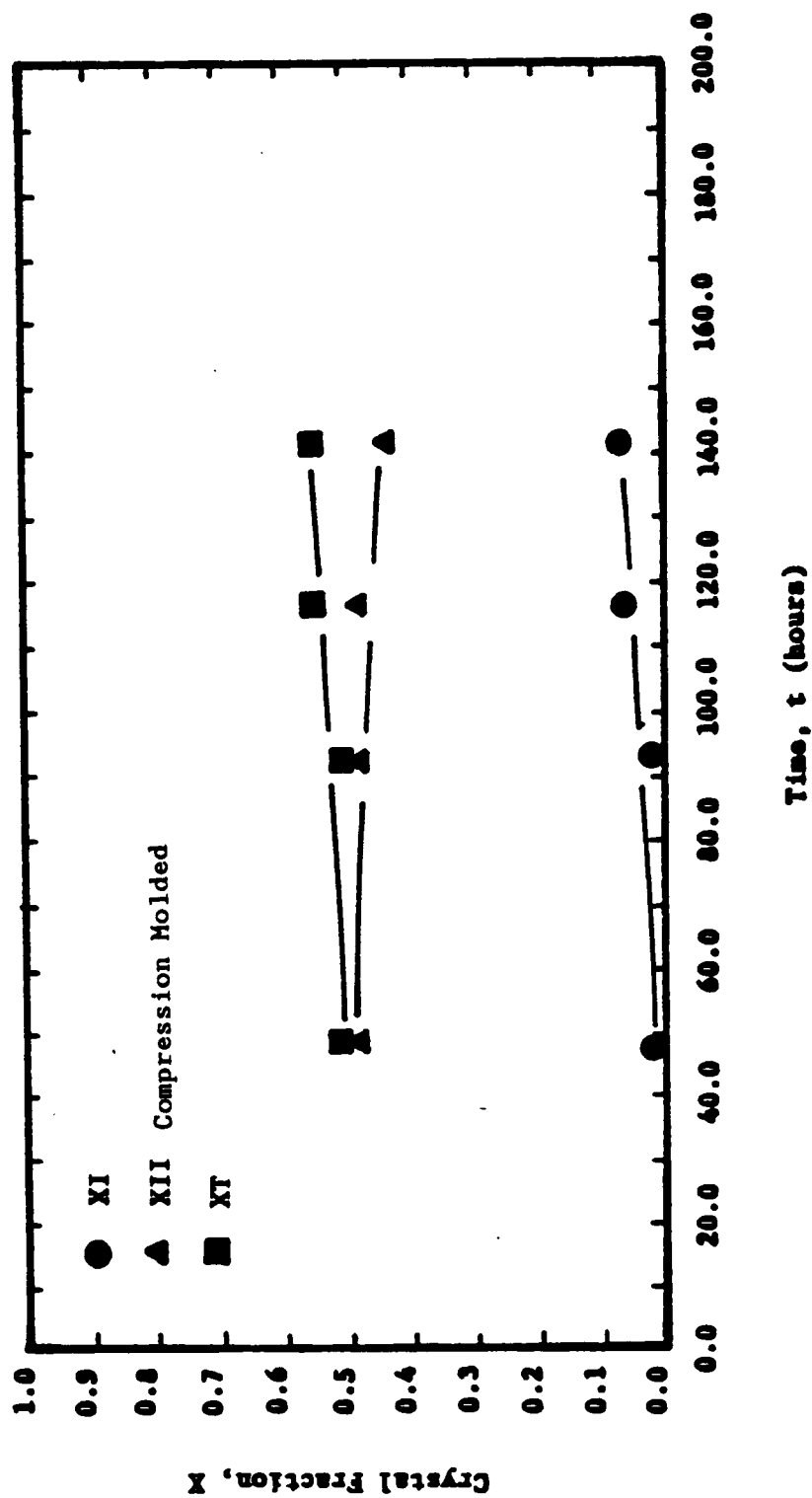


Figure A-52. Crystal Fraction Present as a Function of Time for CN05 at 60 °C

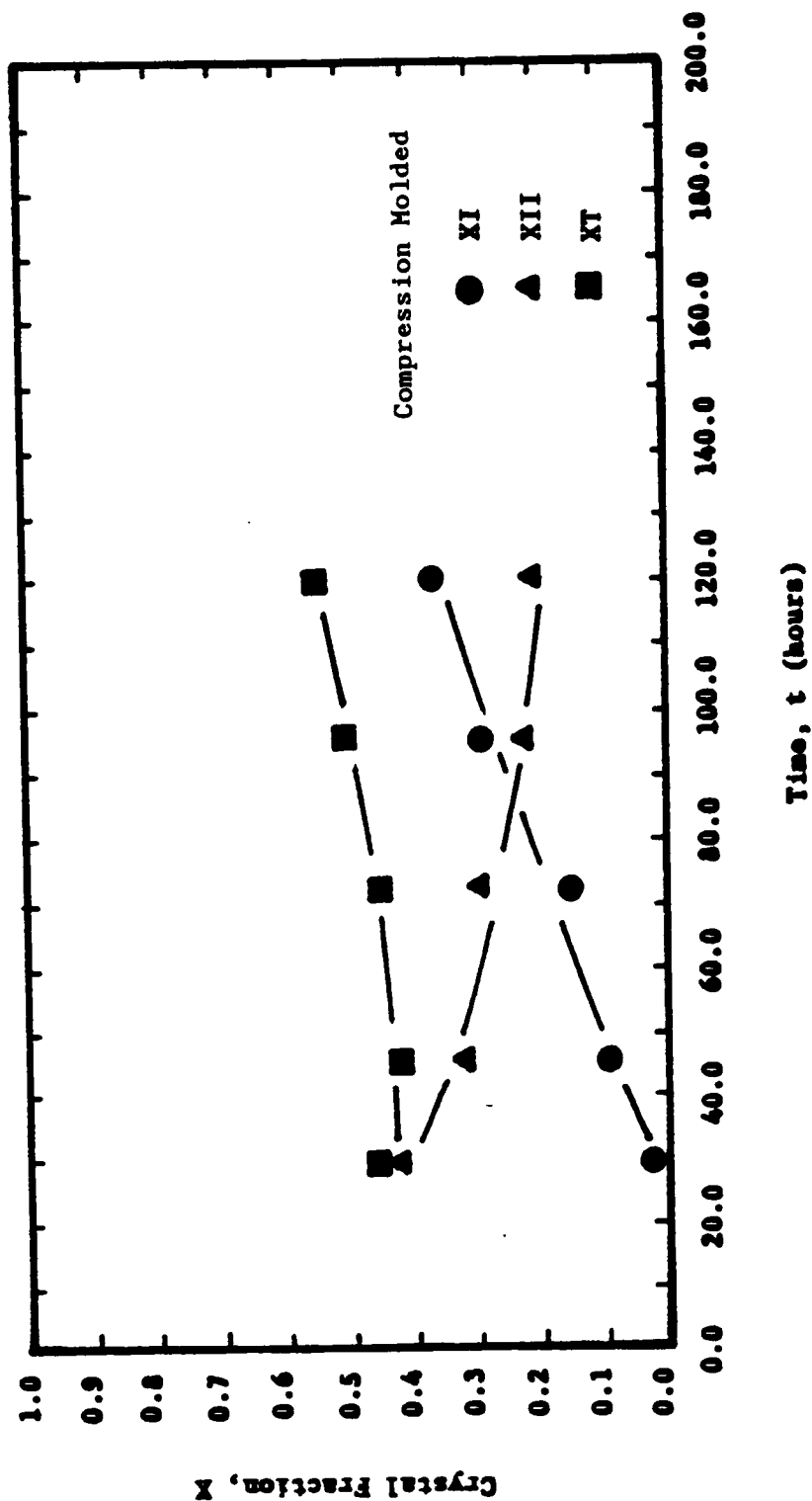


Figure A-53. Crystal Fraction Present as a Function of Time for CN2 at 45 °C

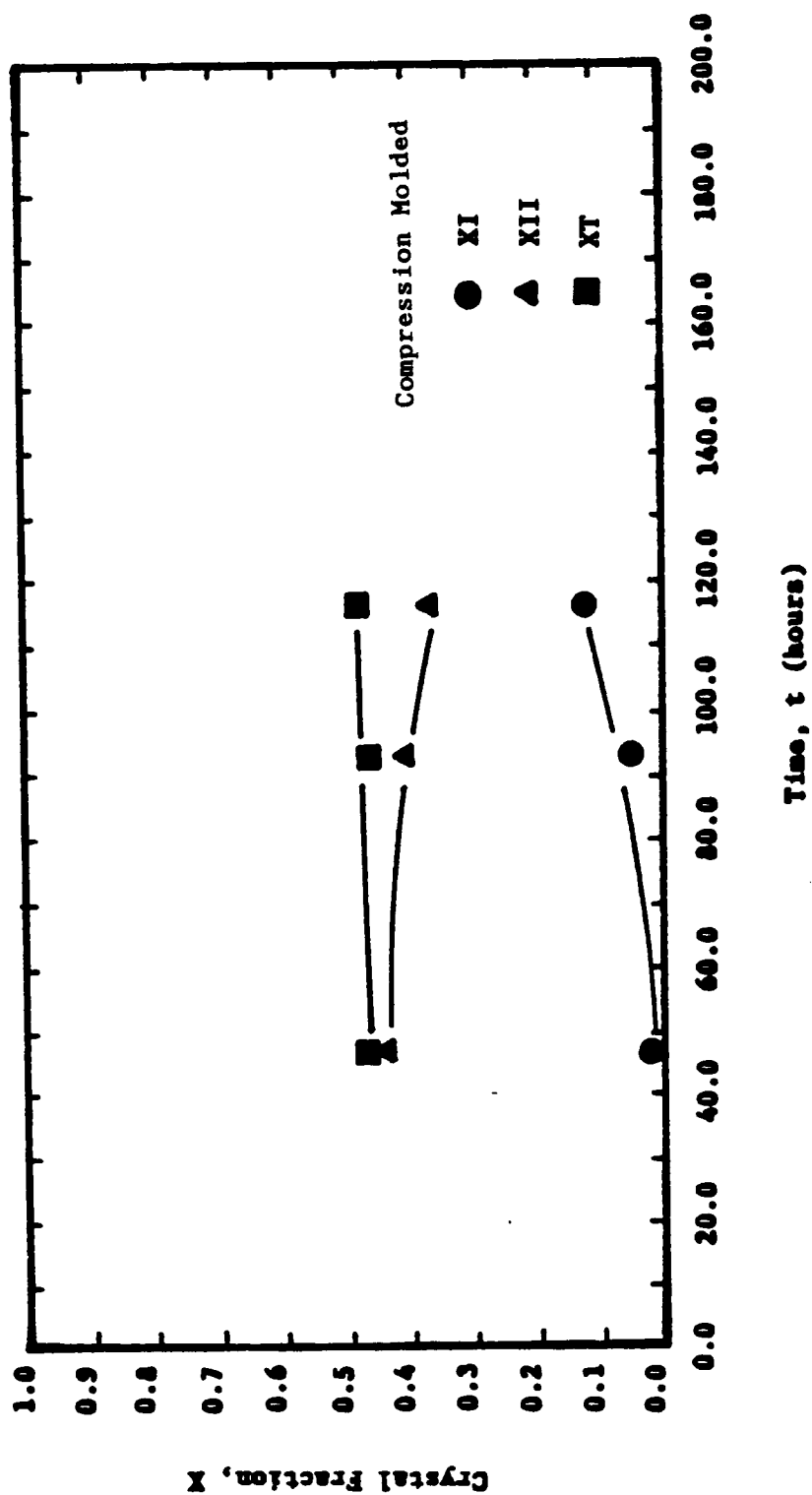


Figure A-54. Crystal Fraction Present as a Function of Time for CN2 at 60 °C

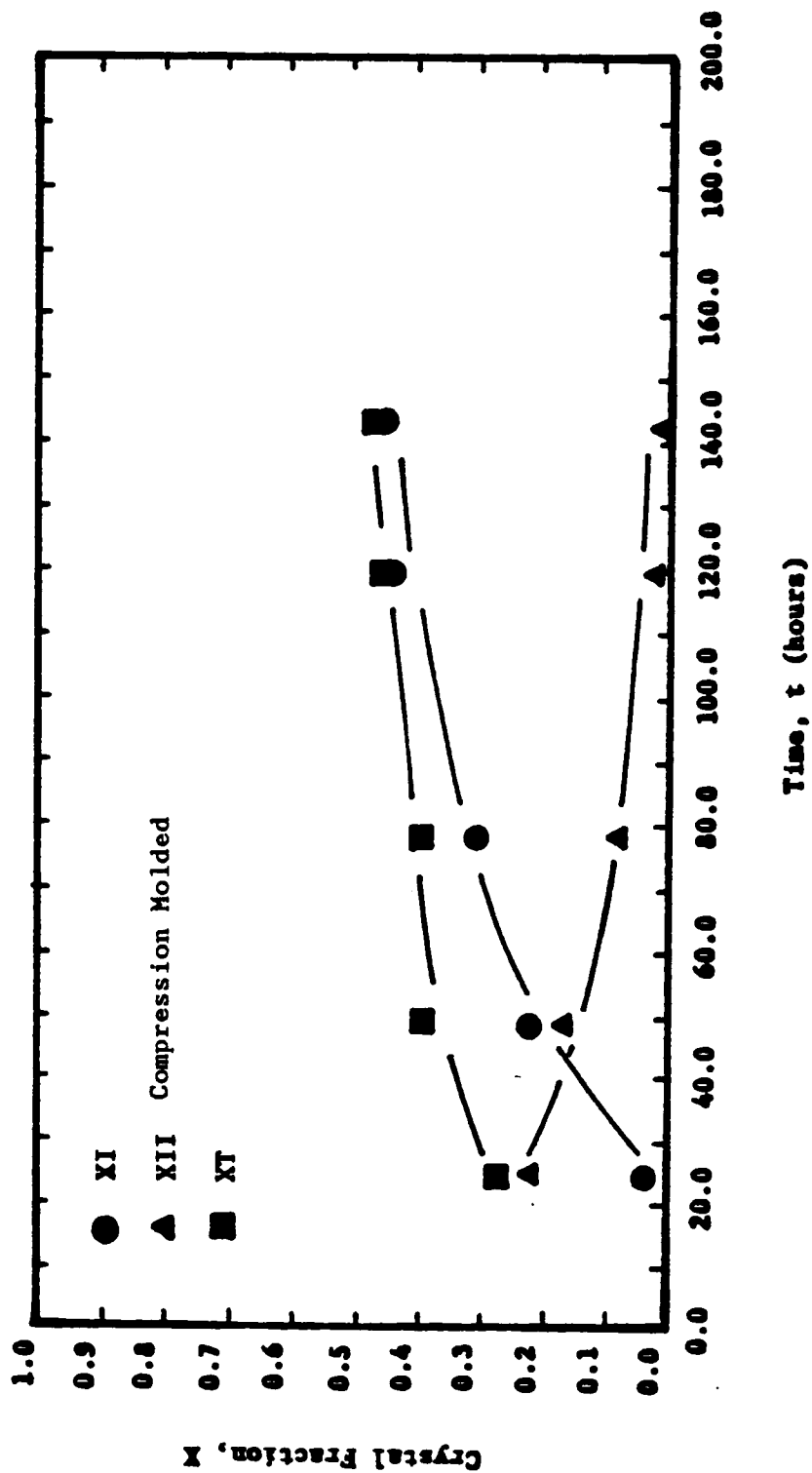


Figure A-55. Crystal Fraction Present as a Function of Time for CN5 at 0 °C

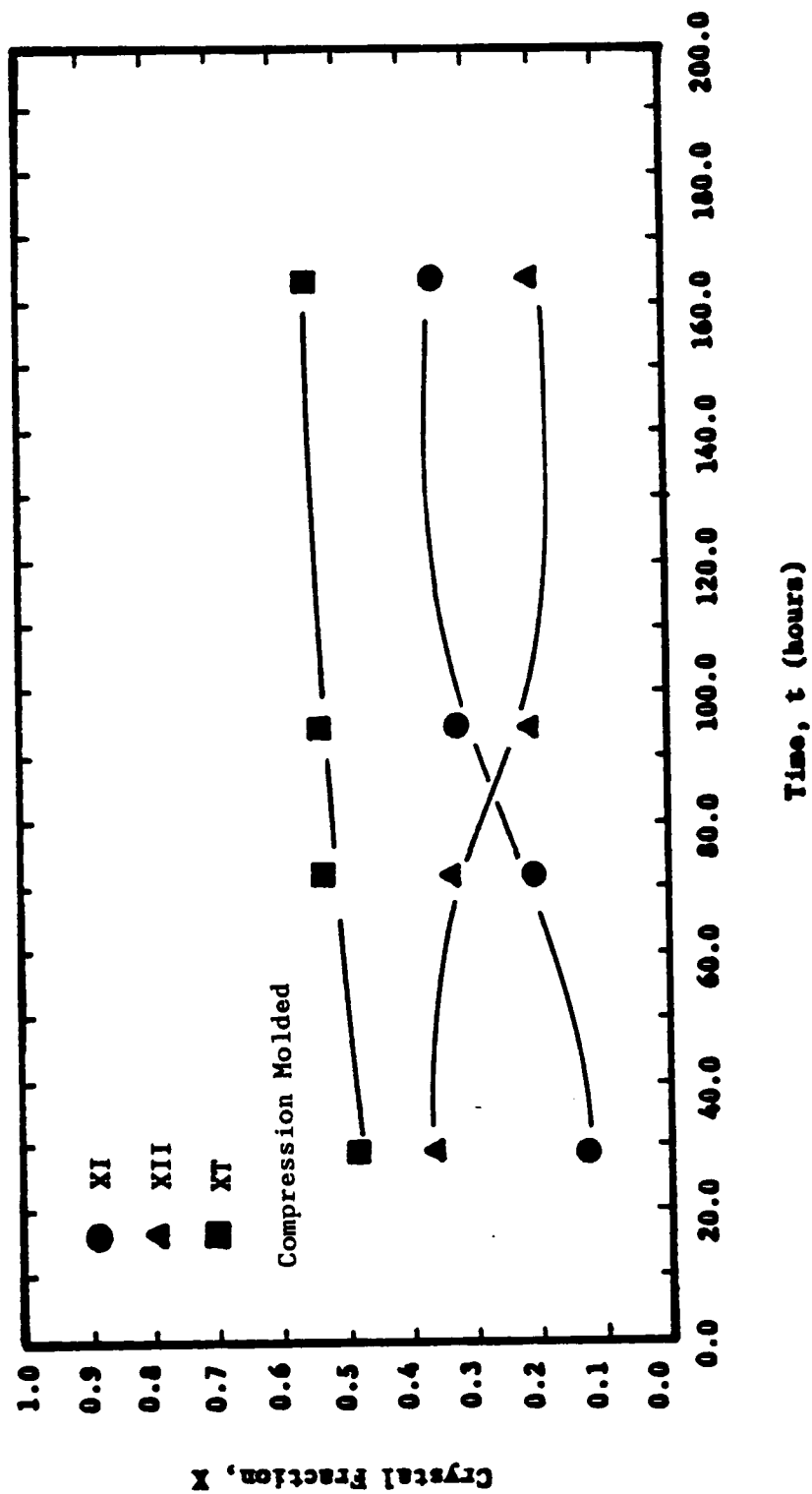


Figure A-56. Crystal Fraction Present as a Function of Time for CN5 at 45 °C

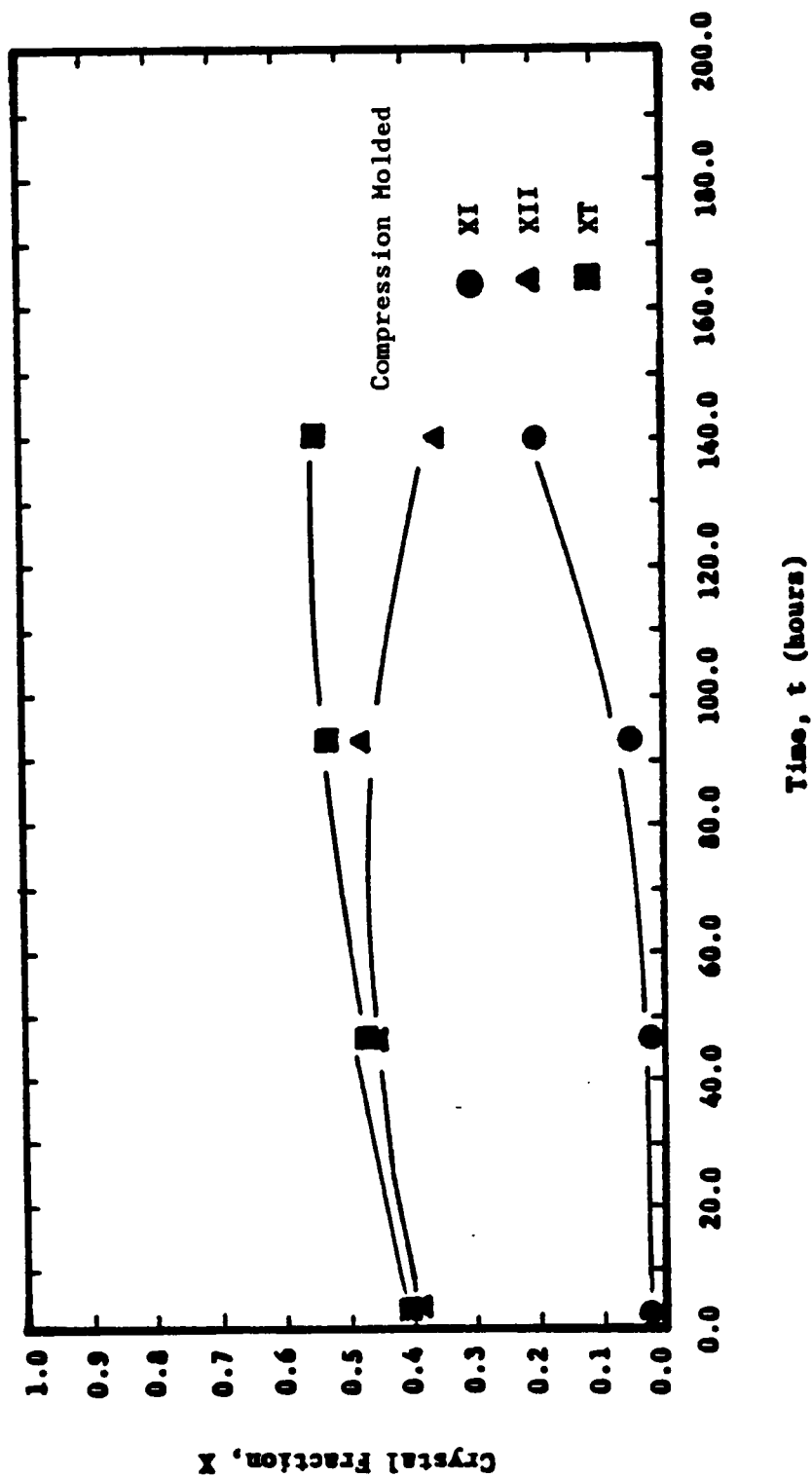


Figure A-57. Crystal Fraction Present as a Function of Time for CN5 at 60 °C

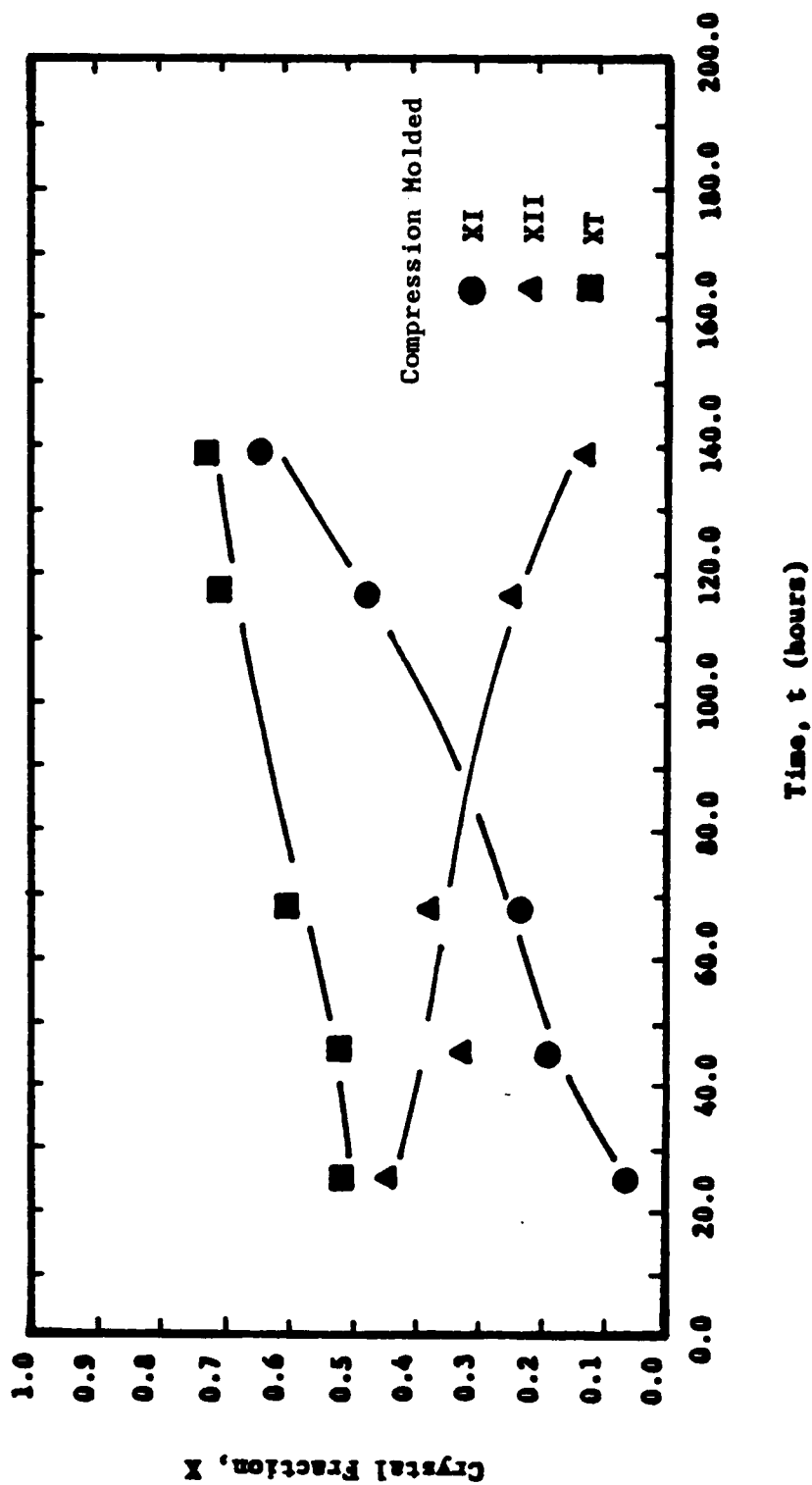


Figure A-58. Crystal Fraction Present as a Function of Time for CB05 at 45 °C

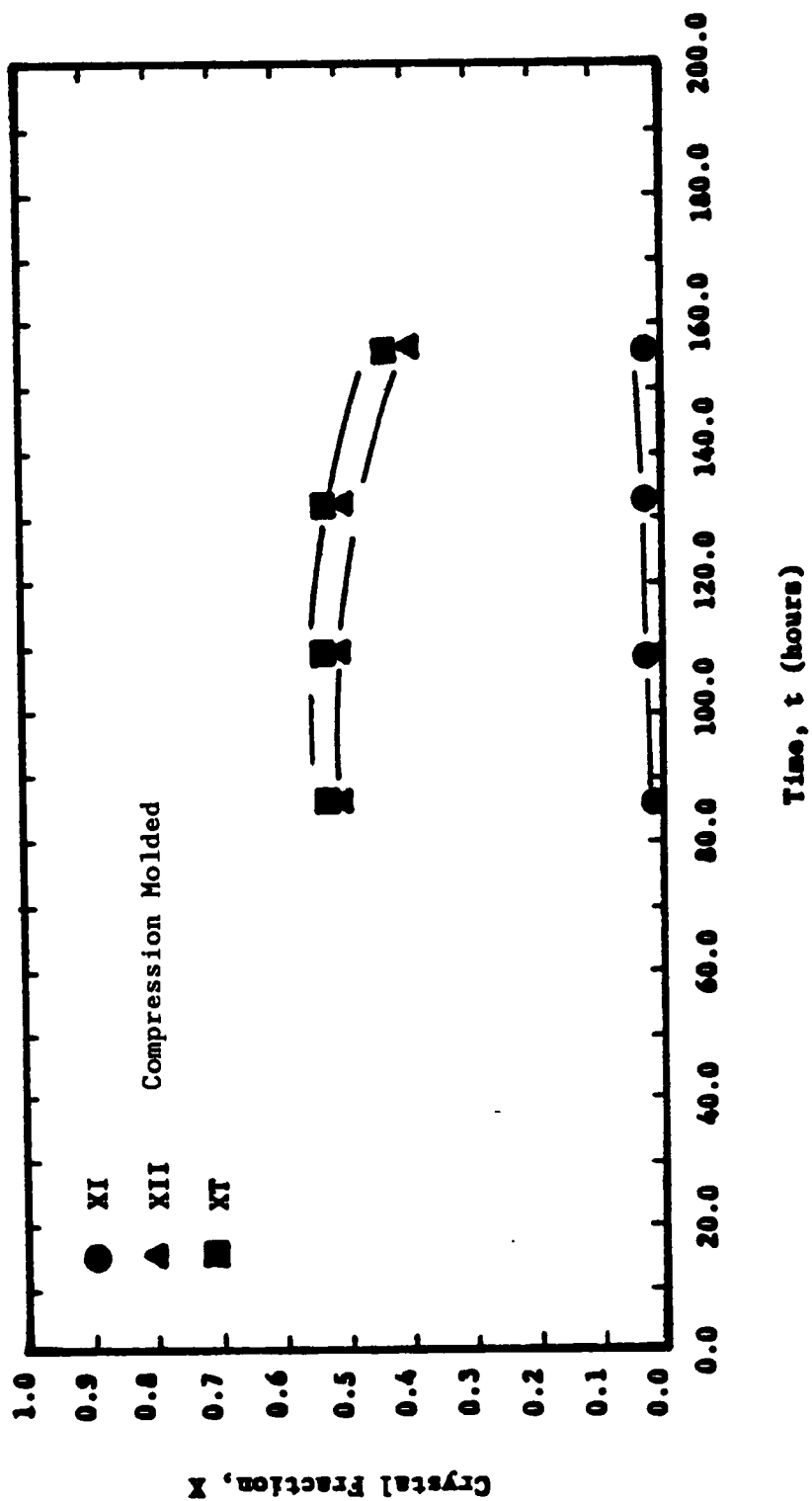


Figure A-59. Crystal Fraction Present as a Function of Time for CB05 at 60 °C

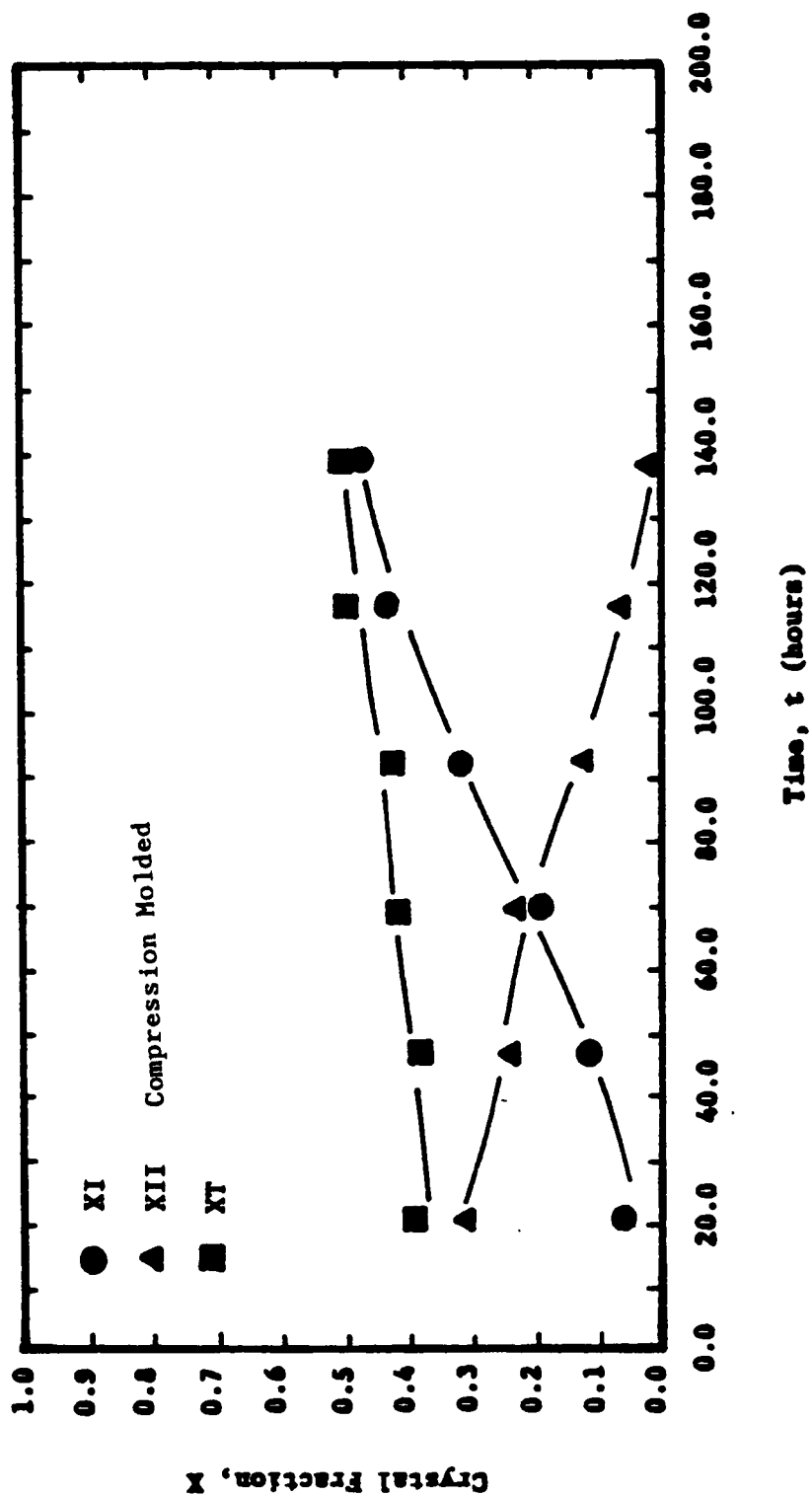


Figure A-60. Crystal Fraction Present as a Function of Time for CB2 at 0 °C

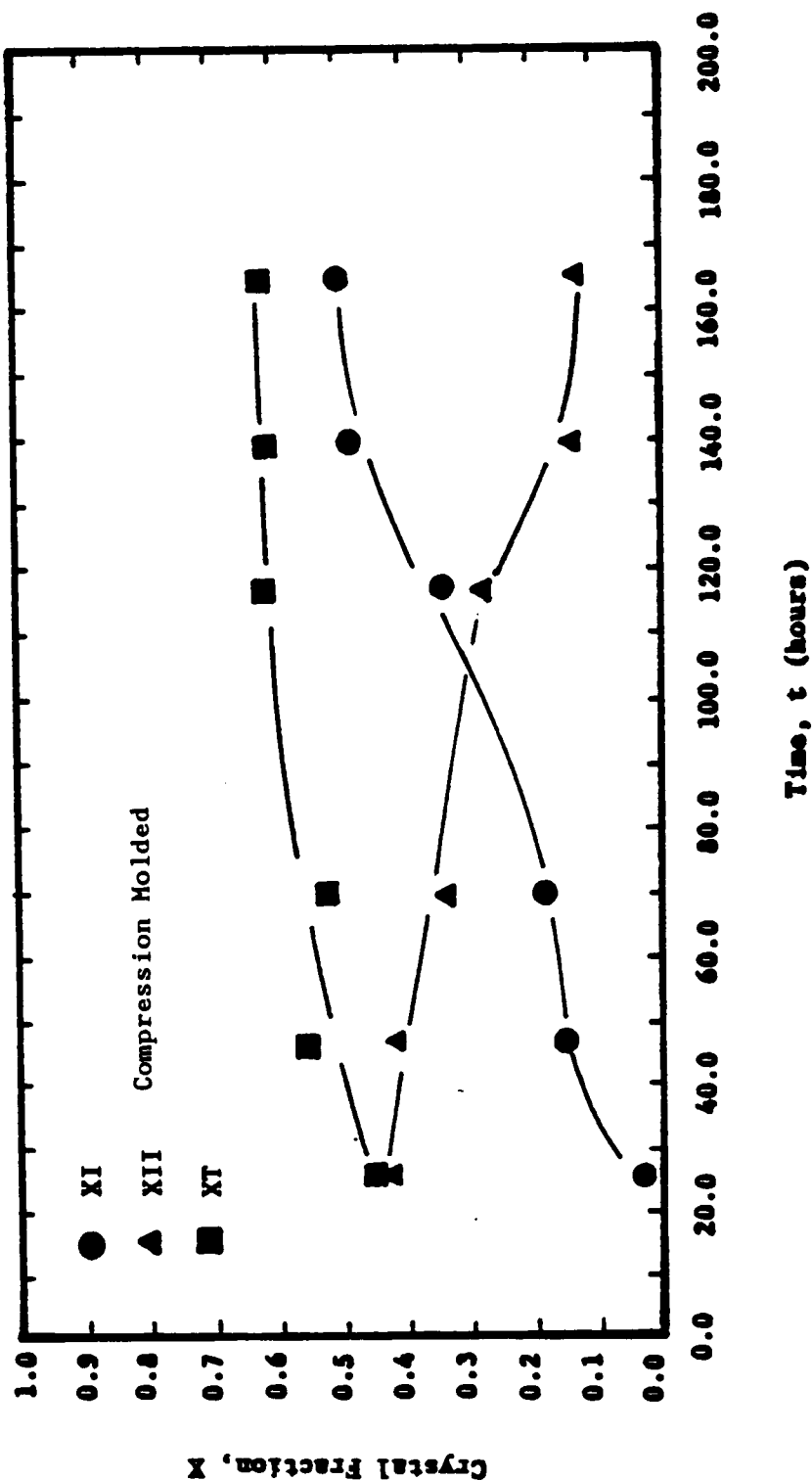


Figure A-61. Crystal Fraction Present as a Function of Time' for CB2 at 45 °C

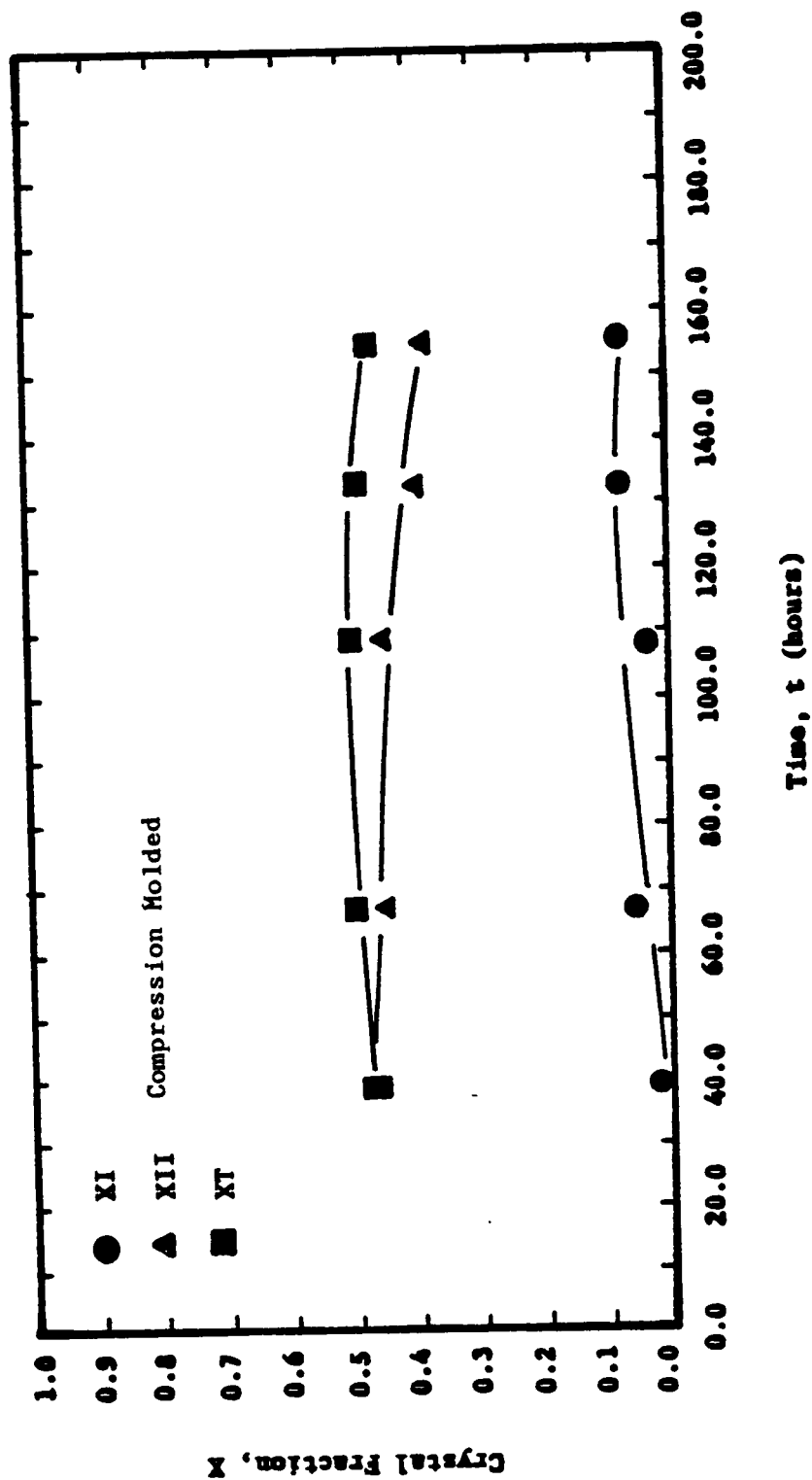


Figure A-62. Crystal Fraction Present as a Function of Time for CB2 at 60 °C

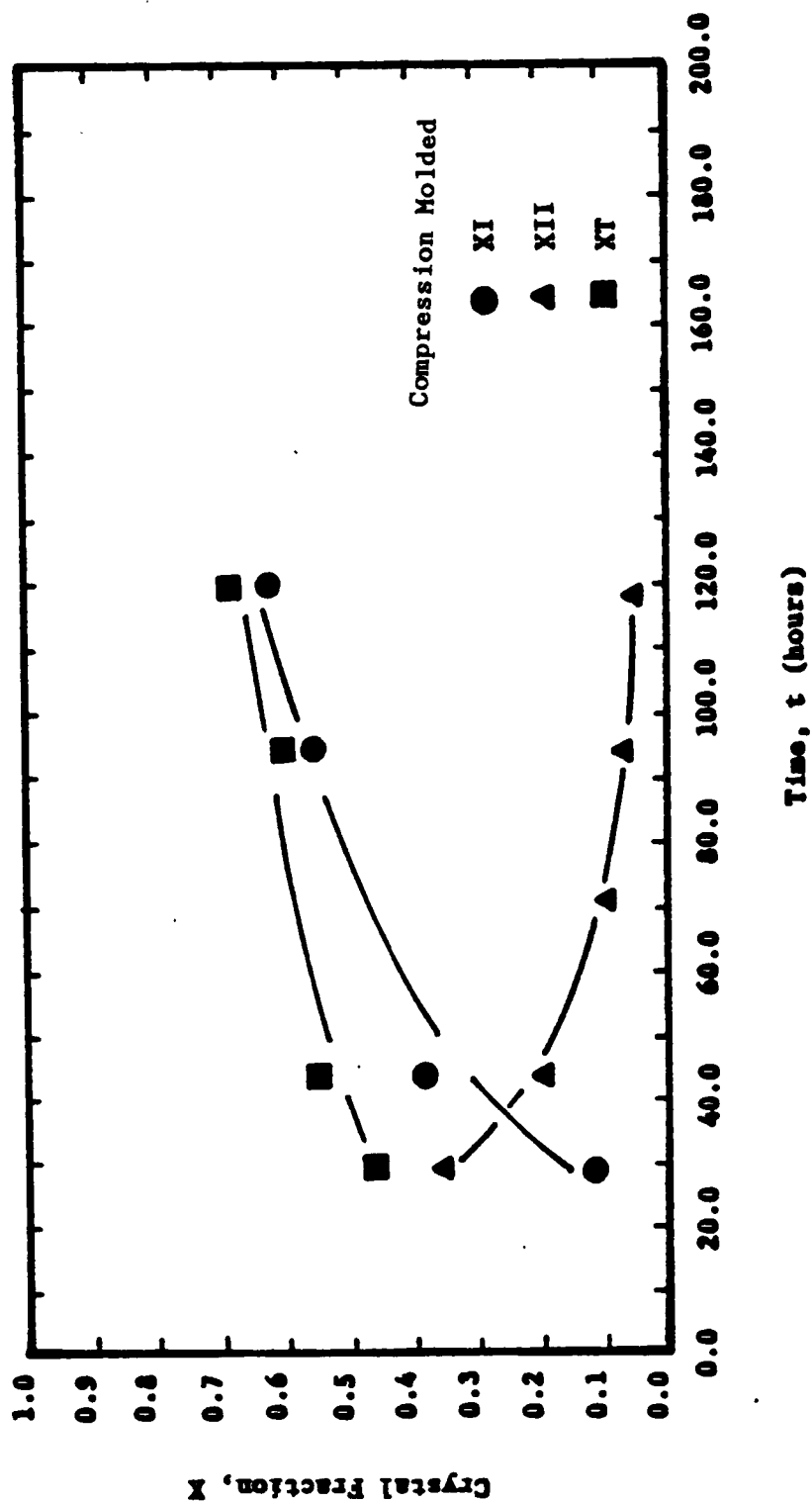


Figure A-63. Crystal Fraction Present as a Function of Time for NA05 at 45 °C

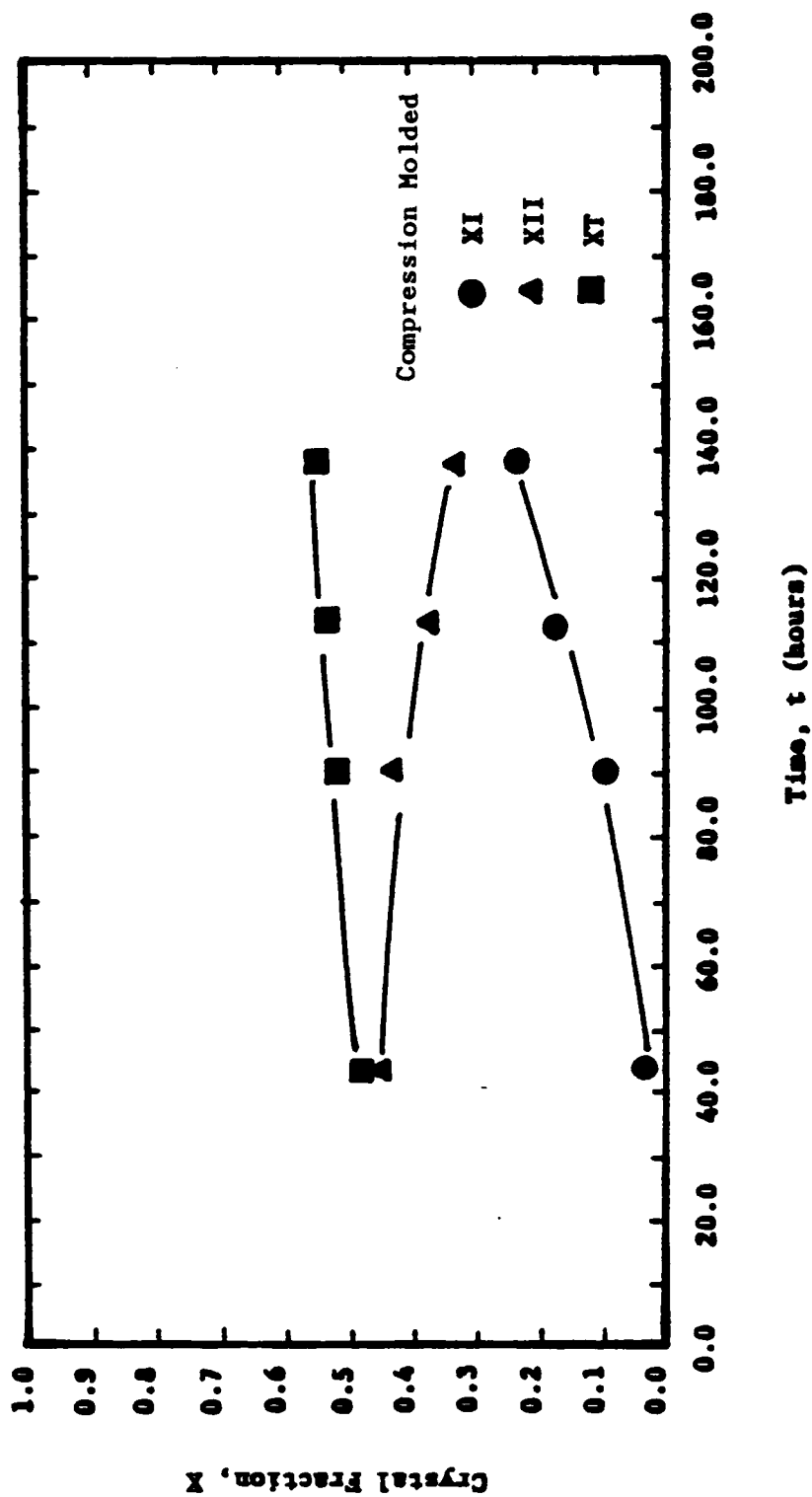


Figure A-64. Crystal Fraction Present as a Function of Time:
for NA05 at 60 °C

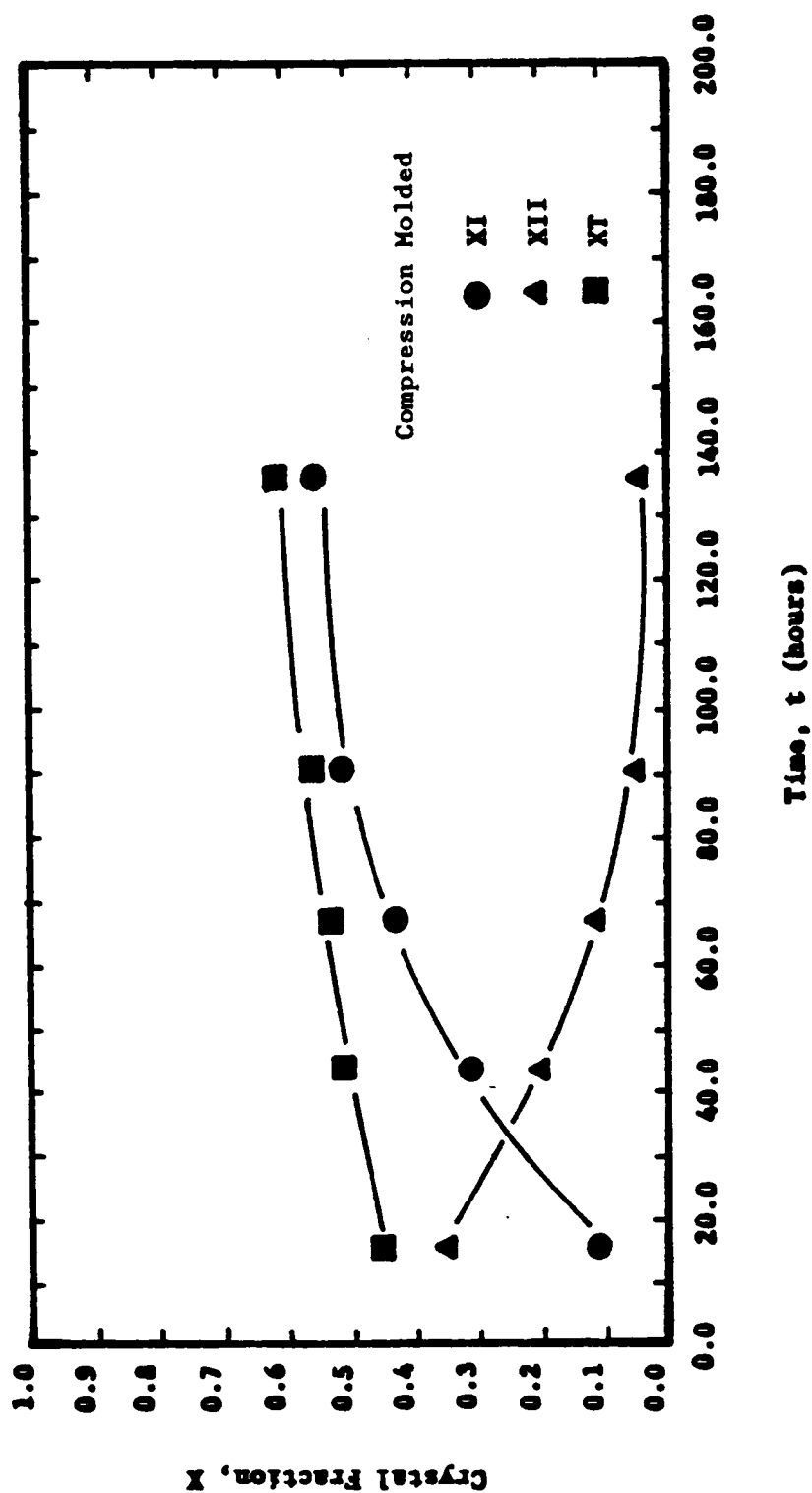


Figure A-65. Crystal Fraction Present as a Function of Time for NA2 at 45 °C

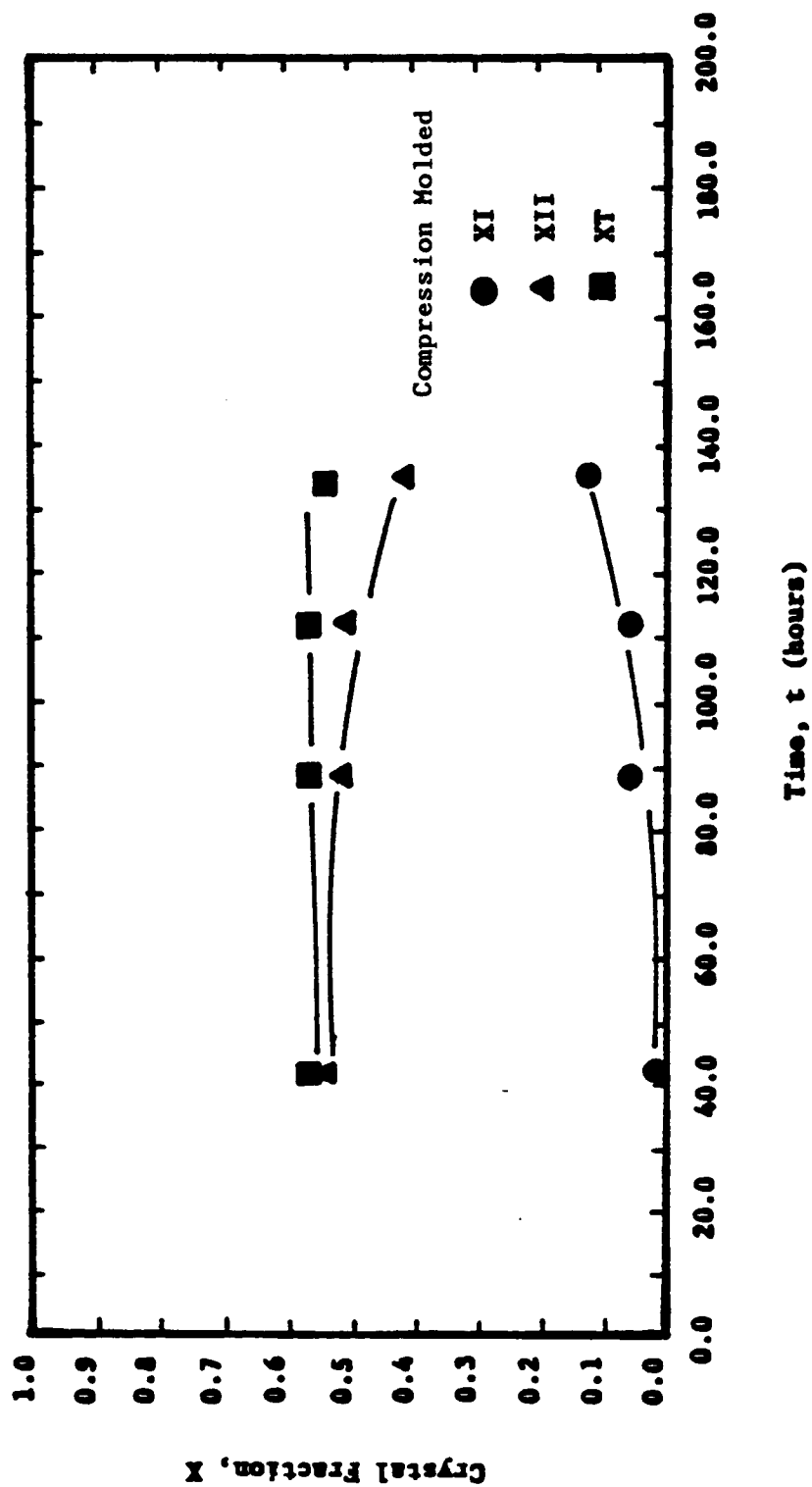


Figure A-66. Crystal Fraction Present as a Function of Time for NA2 at 60 °C

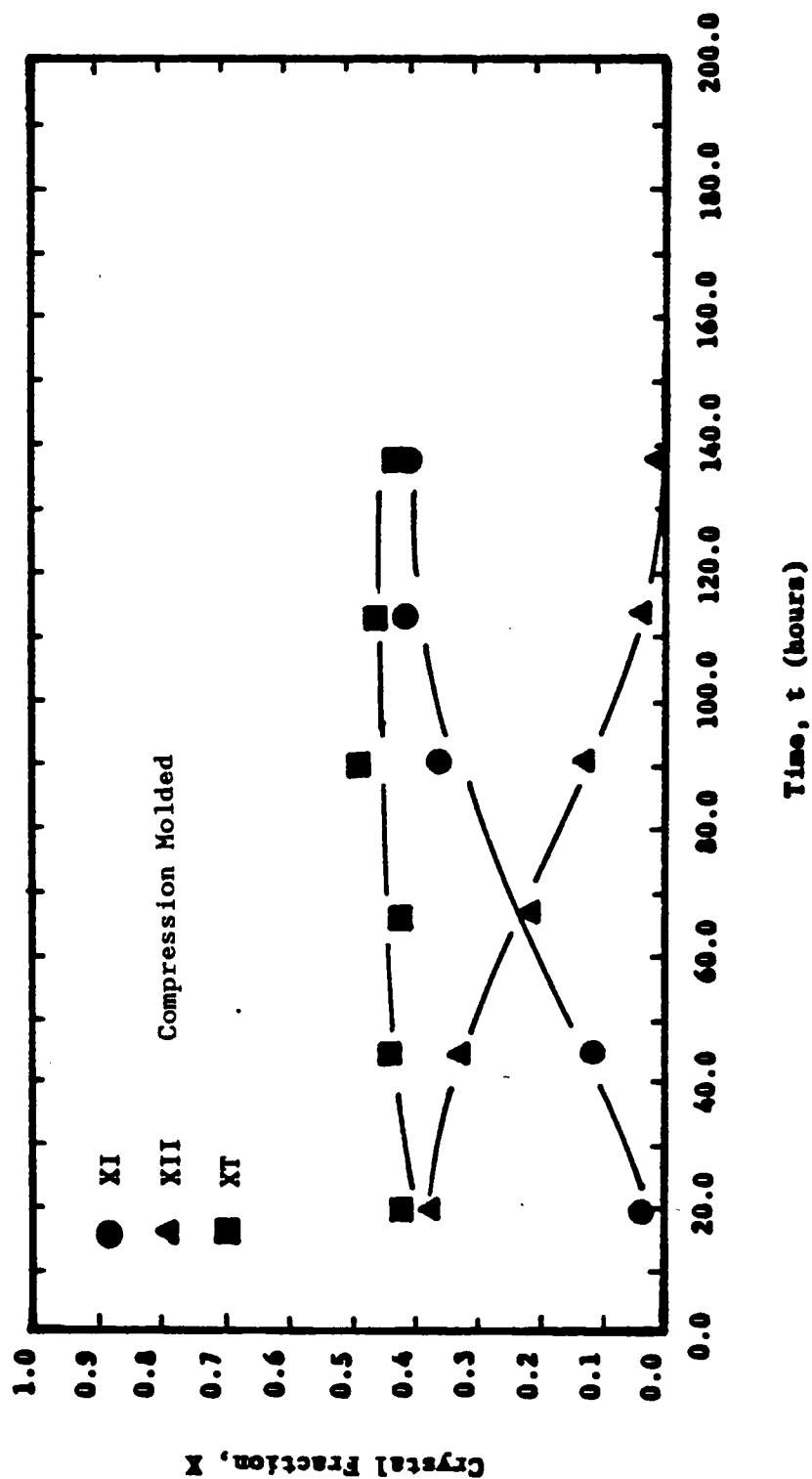


Figure A-67. Crystal Fraction Present as a Function of Time for NA5 at 0 °C

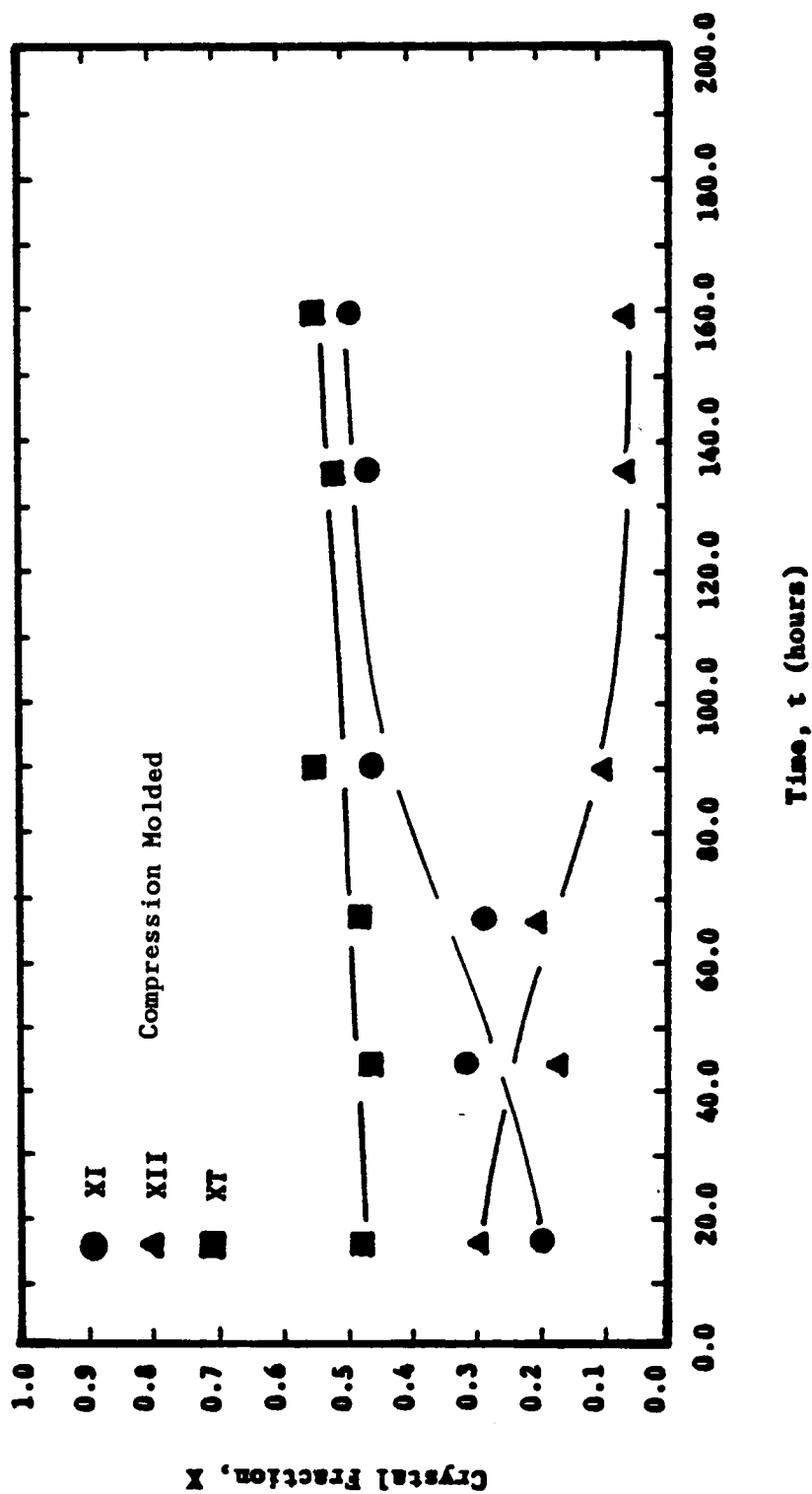


Figure A-68. Crystal Fraction Present as a Function of Time for NA5 at 45 °C

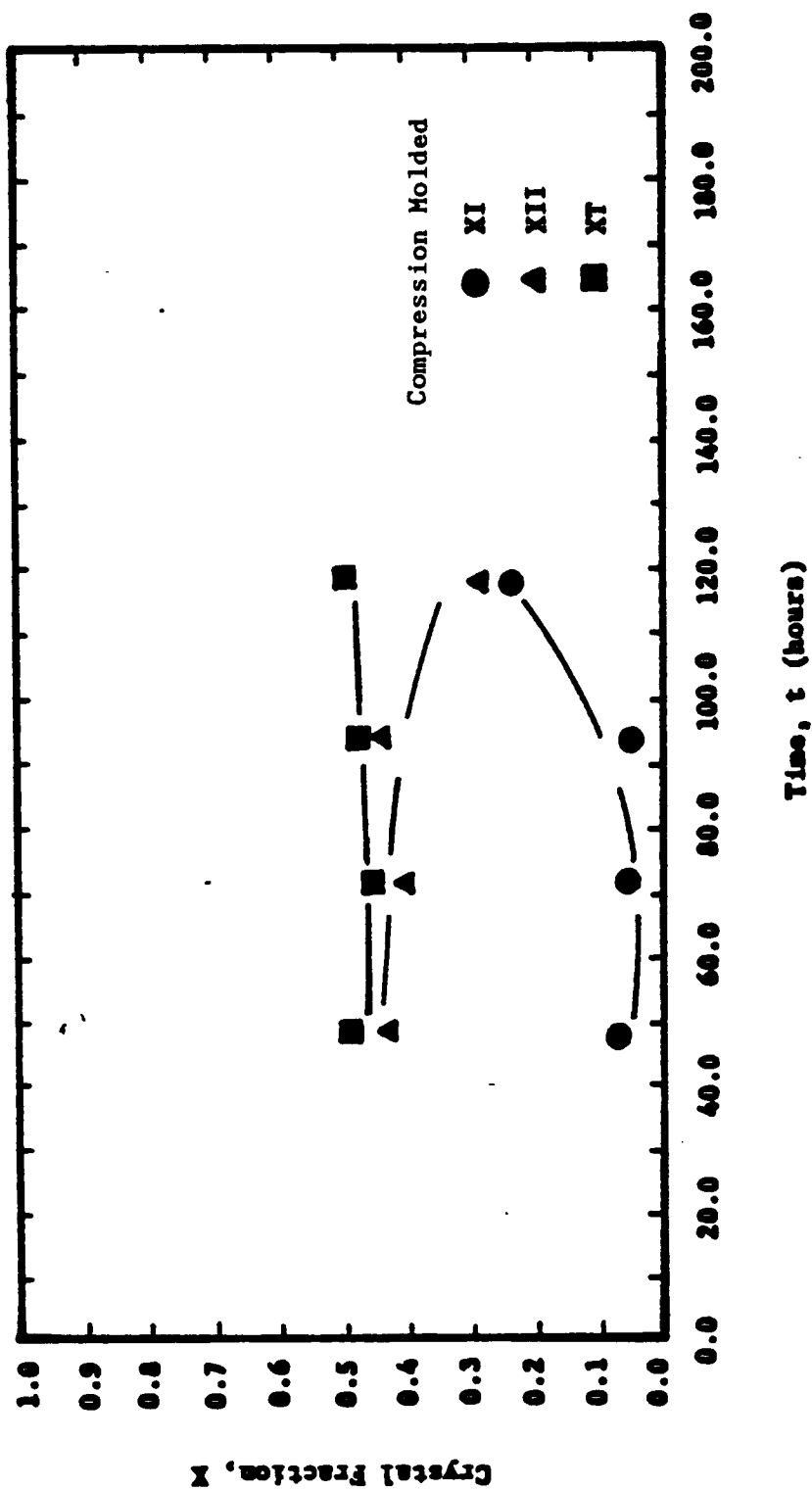


Figure A-69. Crystal Fraction Present as a Function of Time for NA5 at 60 °C

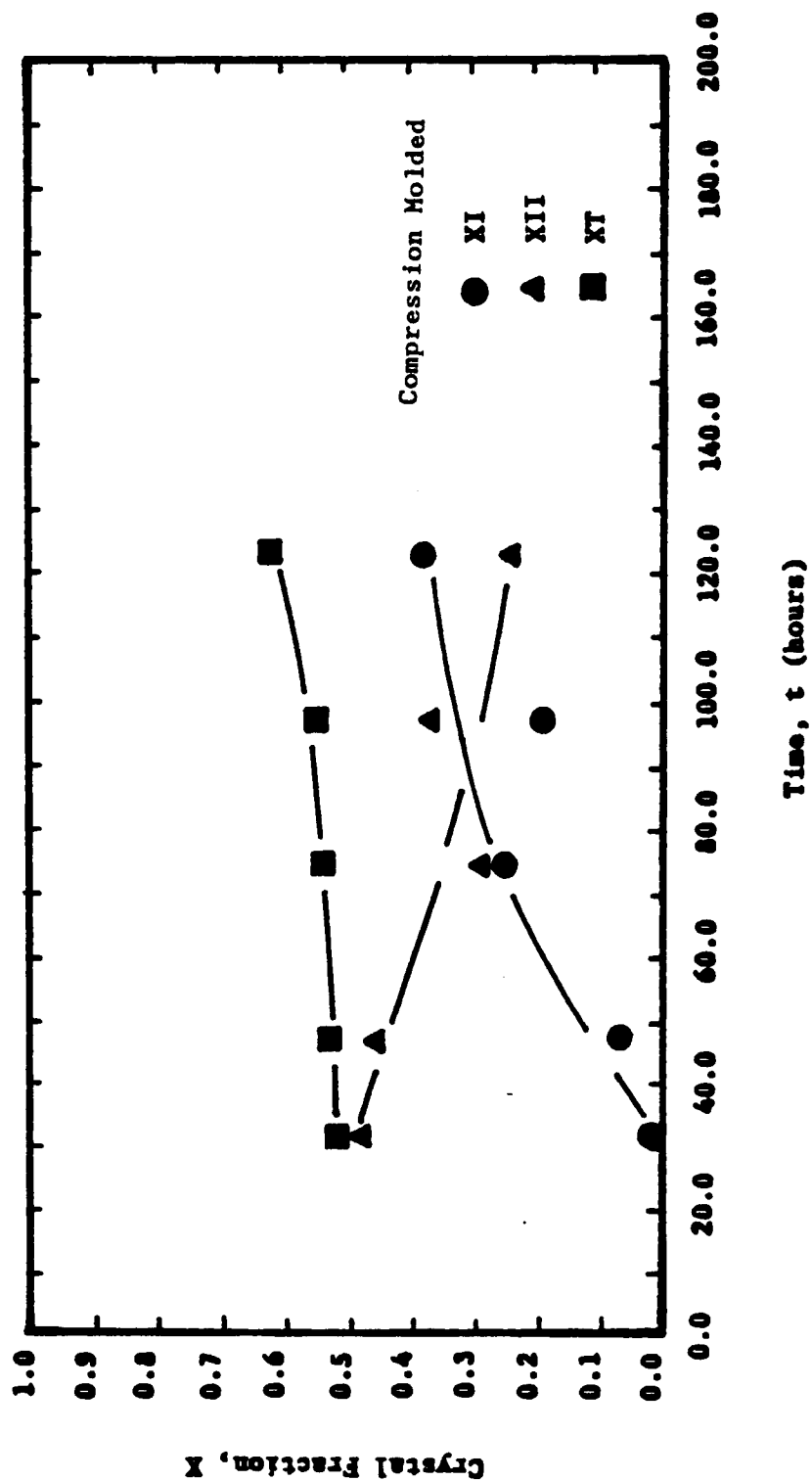


Figure A-70. Crystal Fraction Present as a Function of Time for SB05 at 45 °C

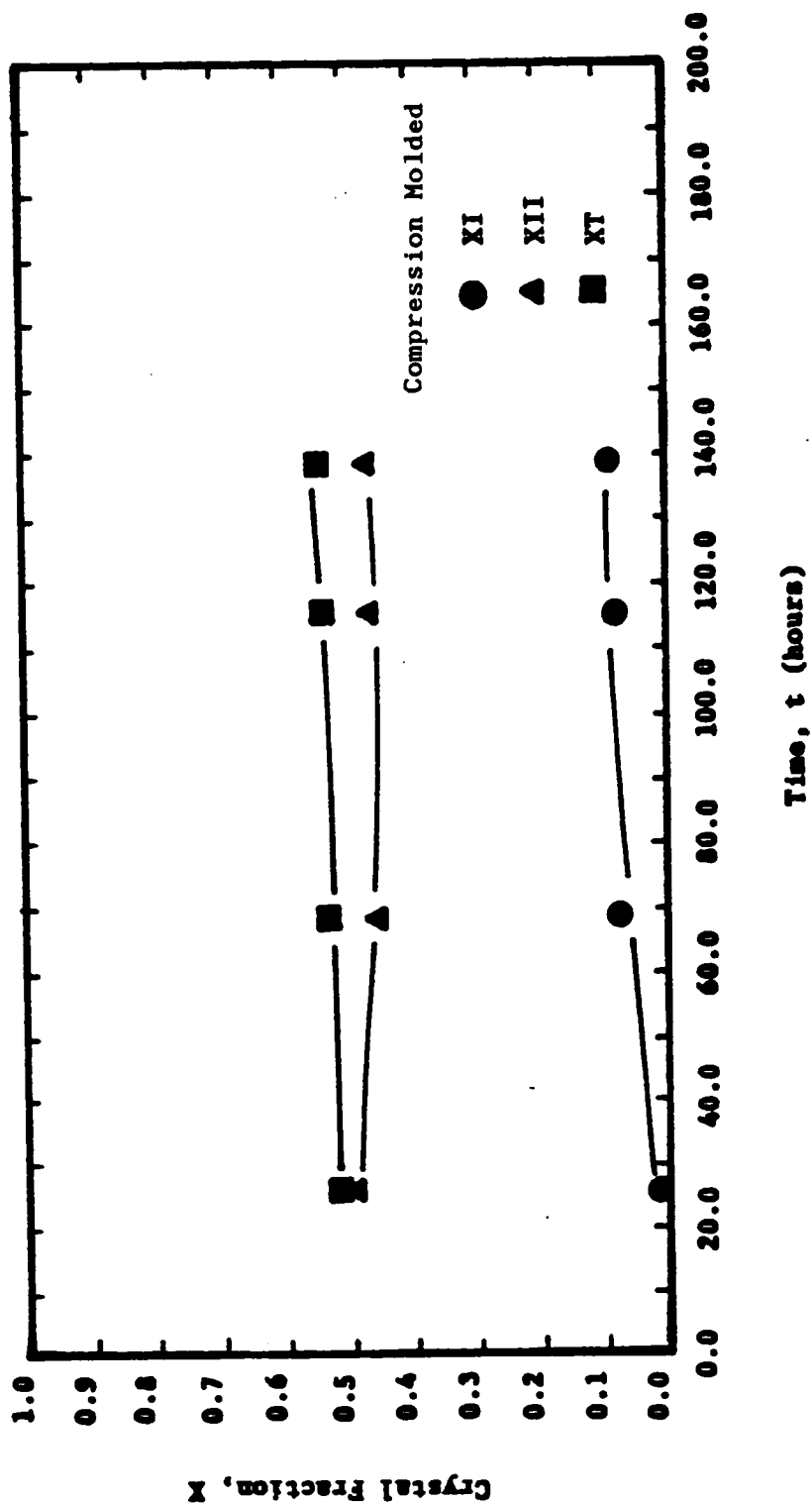


Figure A-71. Crystal Fraction Present as a Function of Time for SB05 at 60 °C

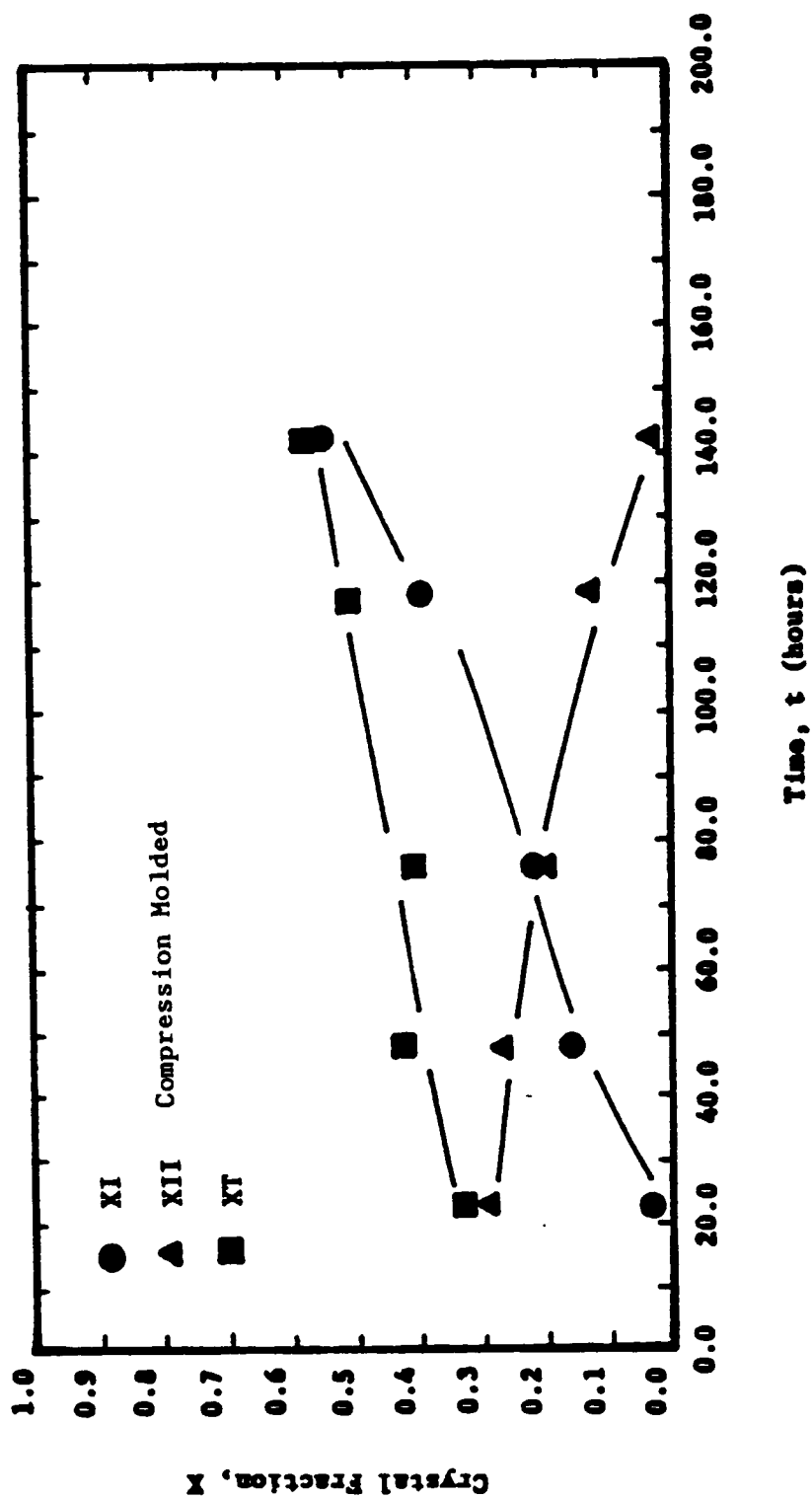


Figure A-72. Crystal Fraction Present as a Function of Time for SB2 at 0 °C

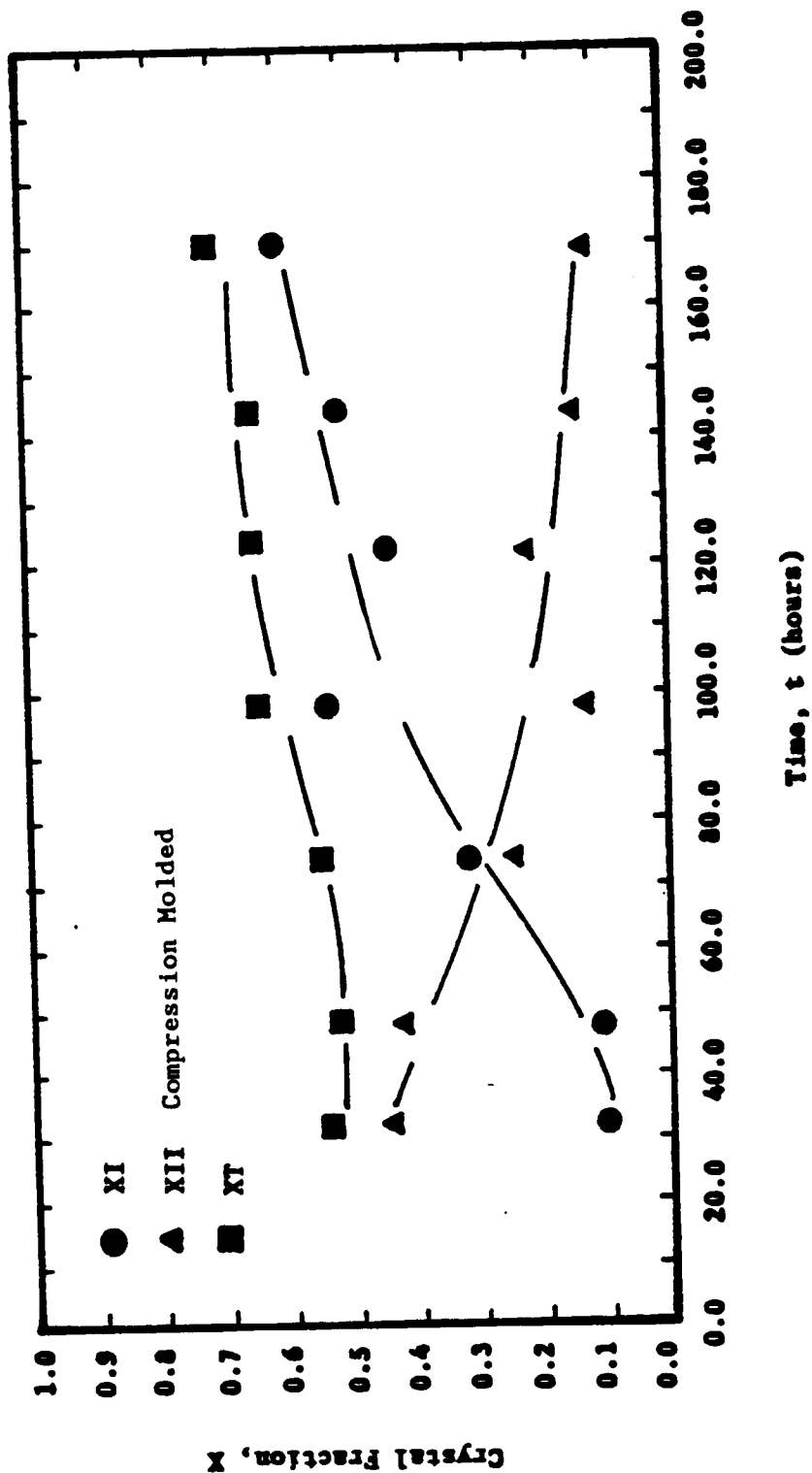


Figure A-73. Crystal Fraction Present as a Function of Time for SB2 at 45 °C

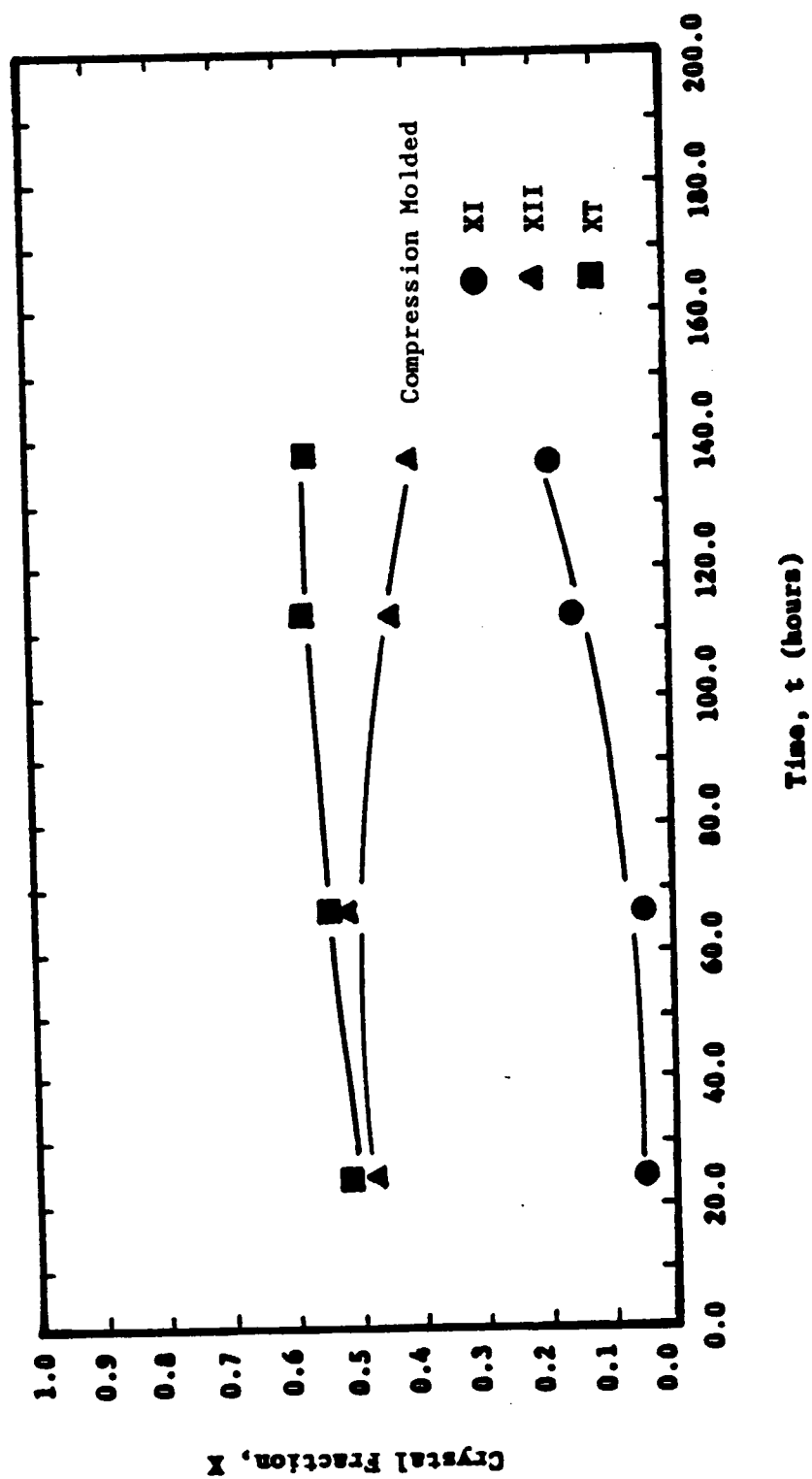


Figure A-74. Crystal Fraction Present as a Function of Time for SB2 at 60 °C

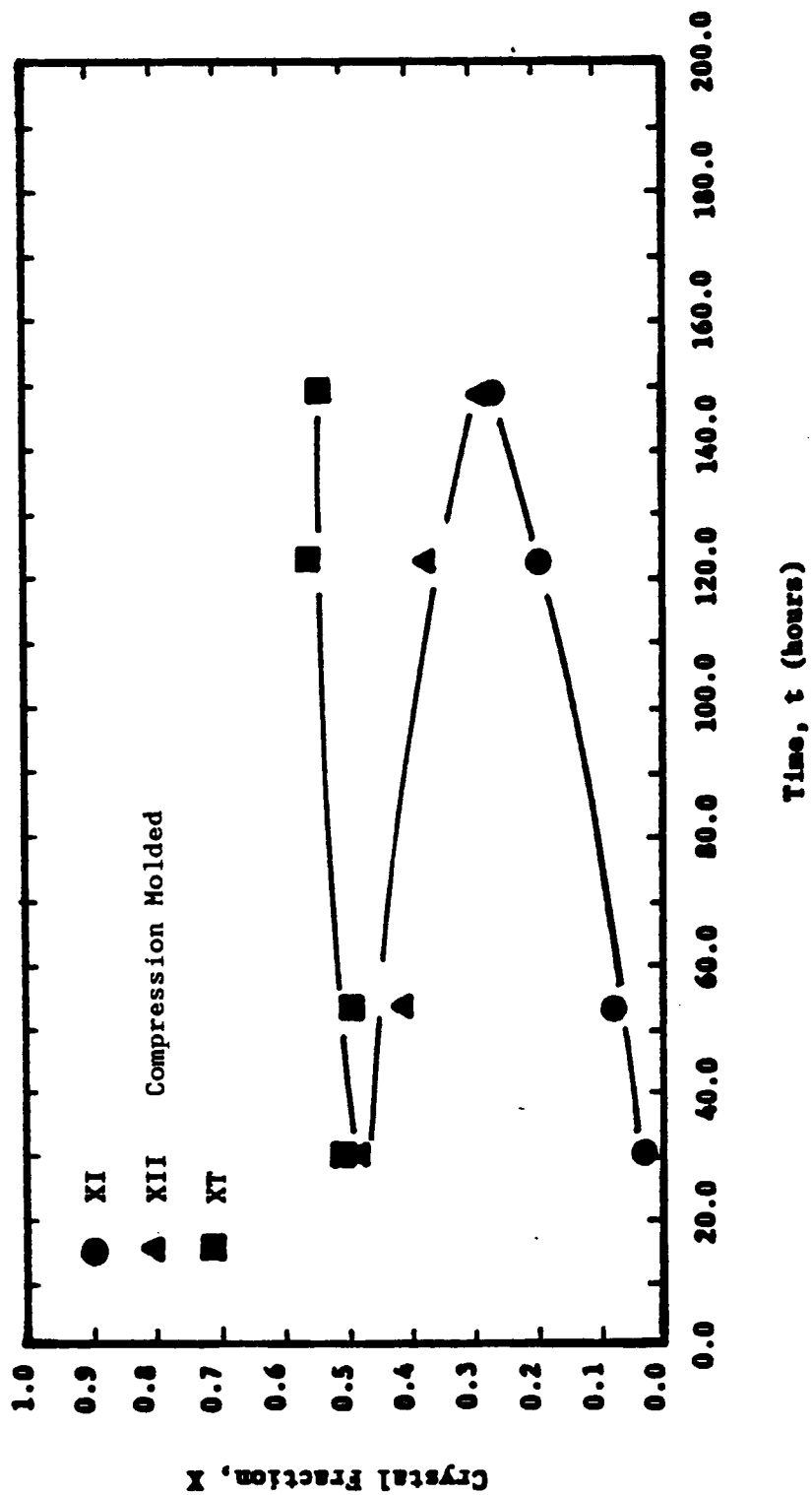


Figure A-75. Crystal Fraction Present as a Function of Time for SA05 at 45 °C

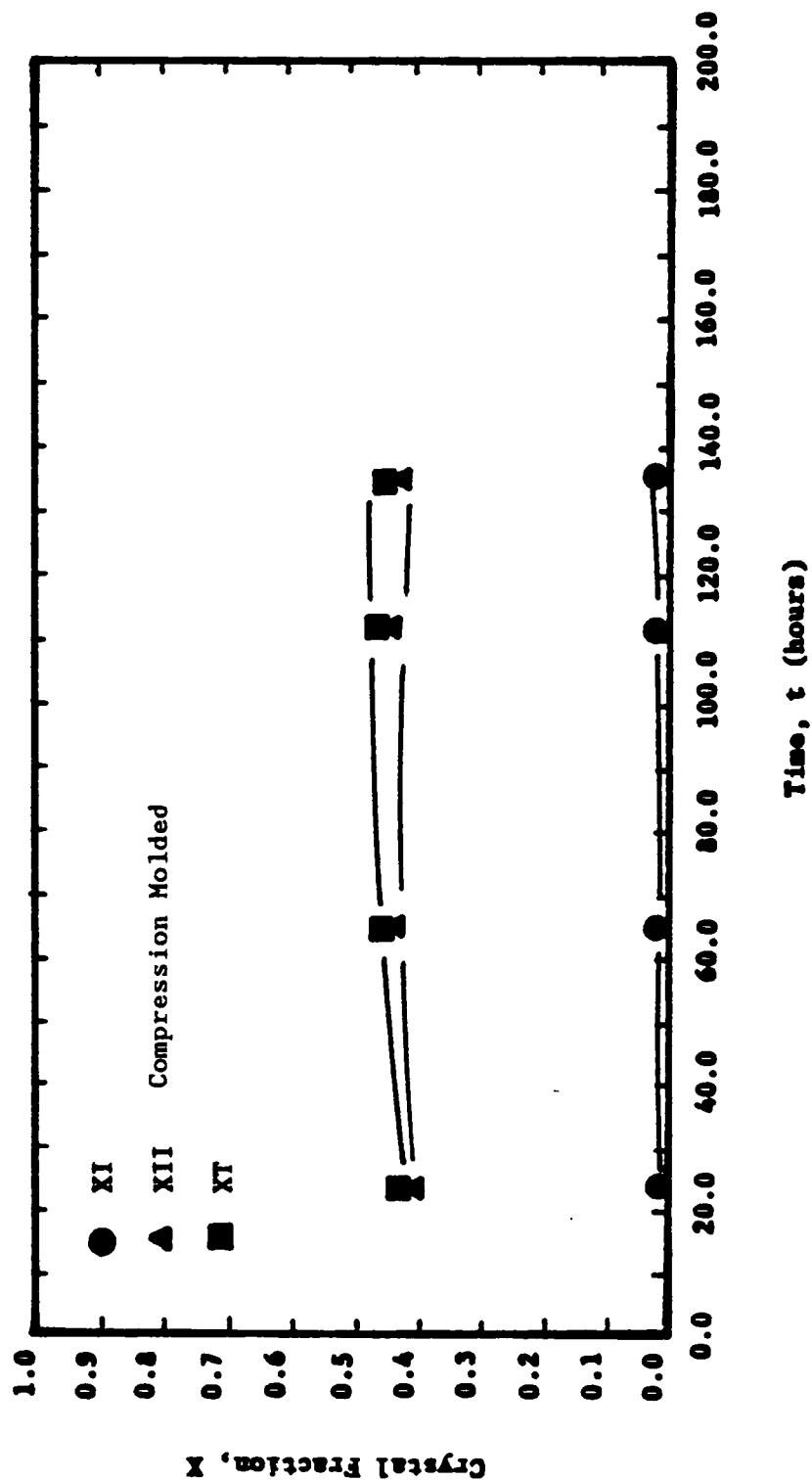


Figure A-76. Crystal Fraction Present as a Function of Time for SA05 at 60 °C

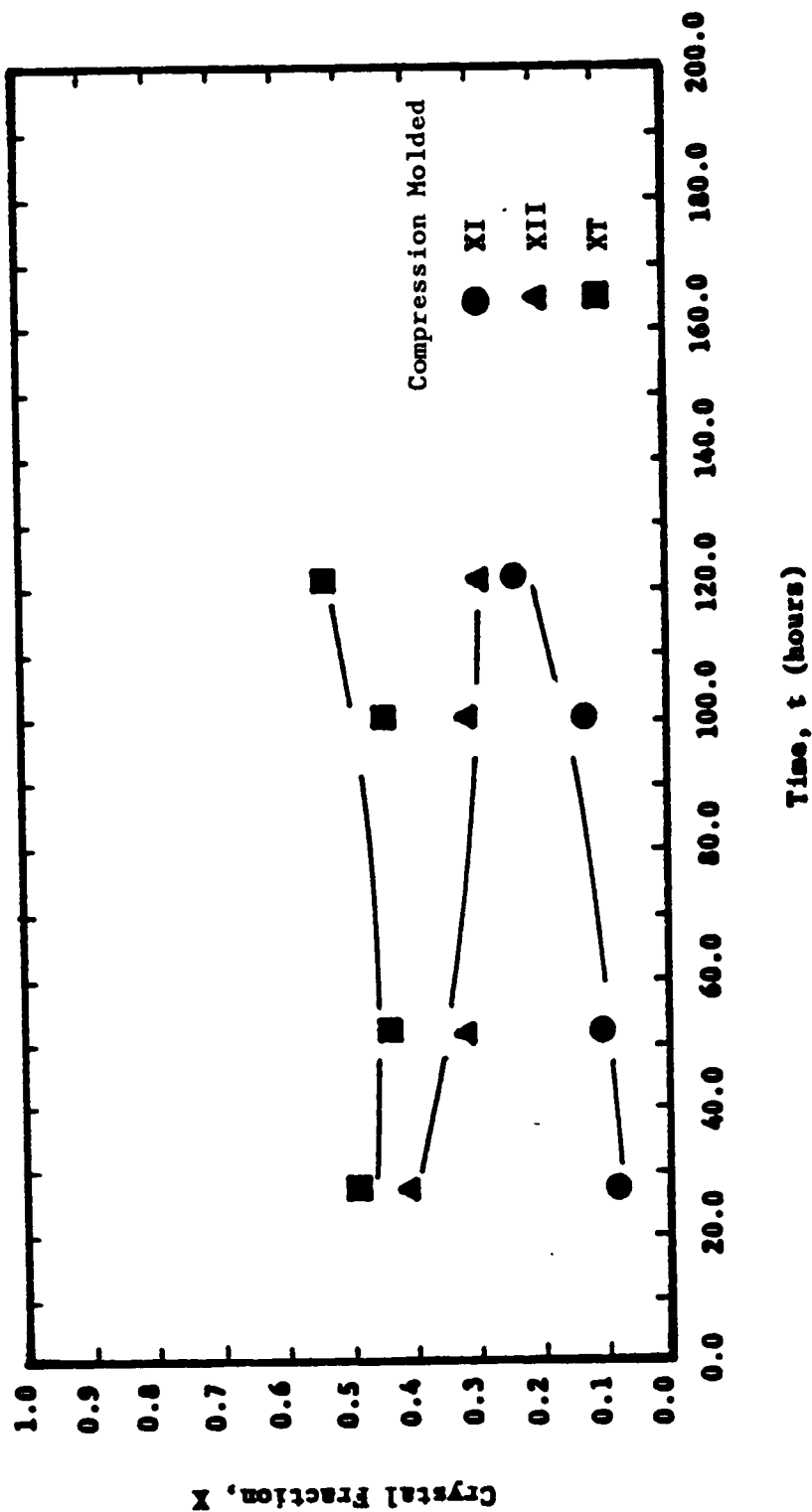


Figure A-77. Crystal Fraction Present as a Function of Time for SA2 at 45 °C

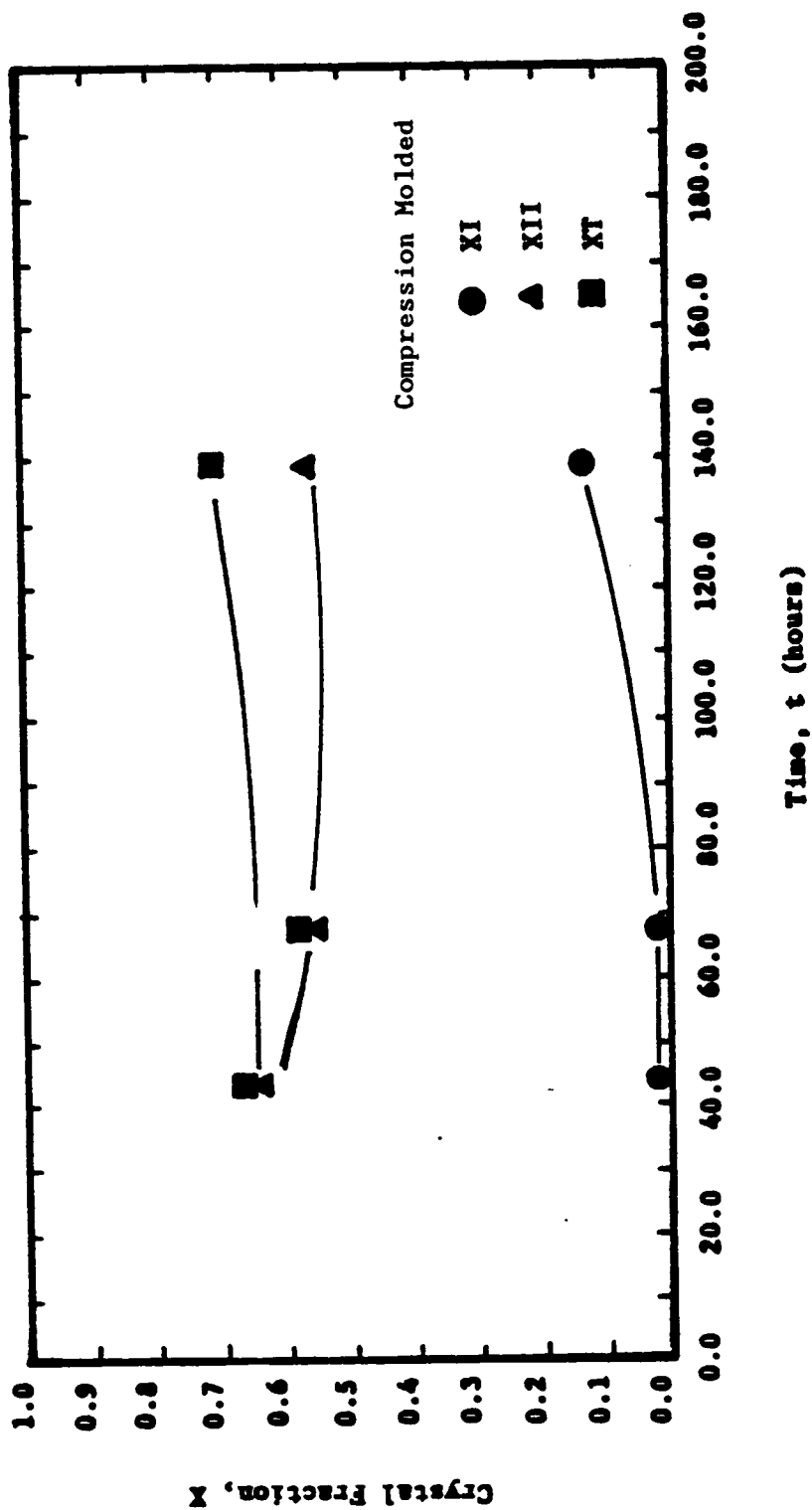


Figure A-78. Crystal Fraction Present as a Function of Time for SA2 at 60 °C

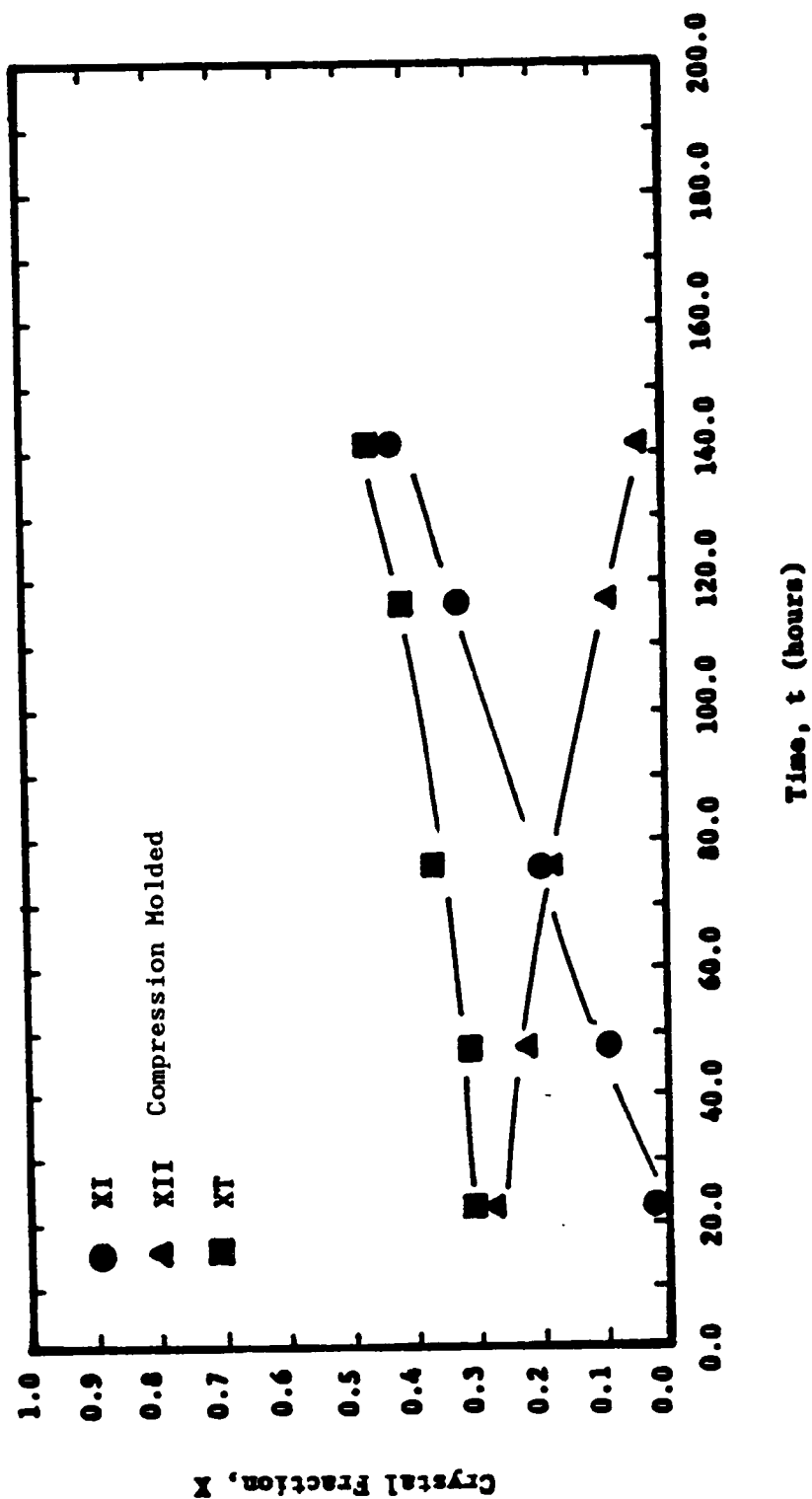


Figure A-79. Crystal Fraction Present as a Function of Time for SA5 at 0 °C

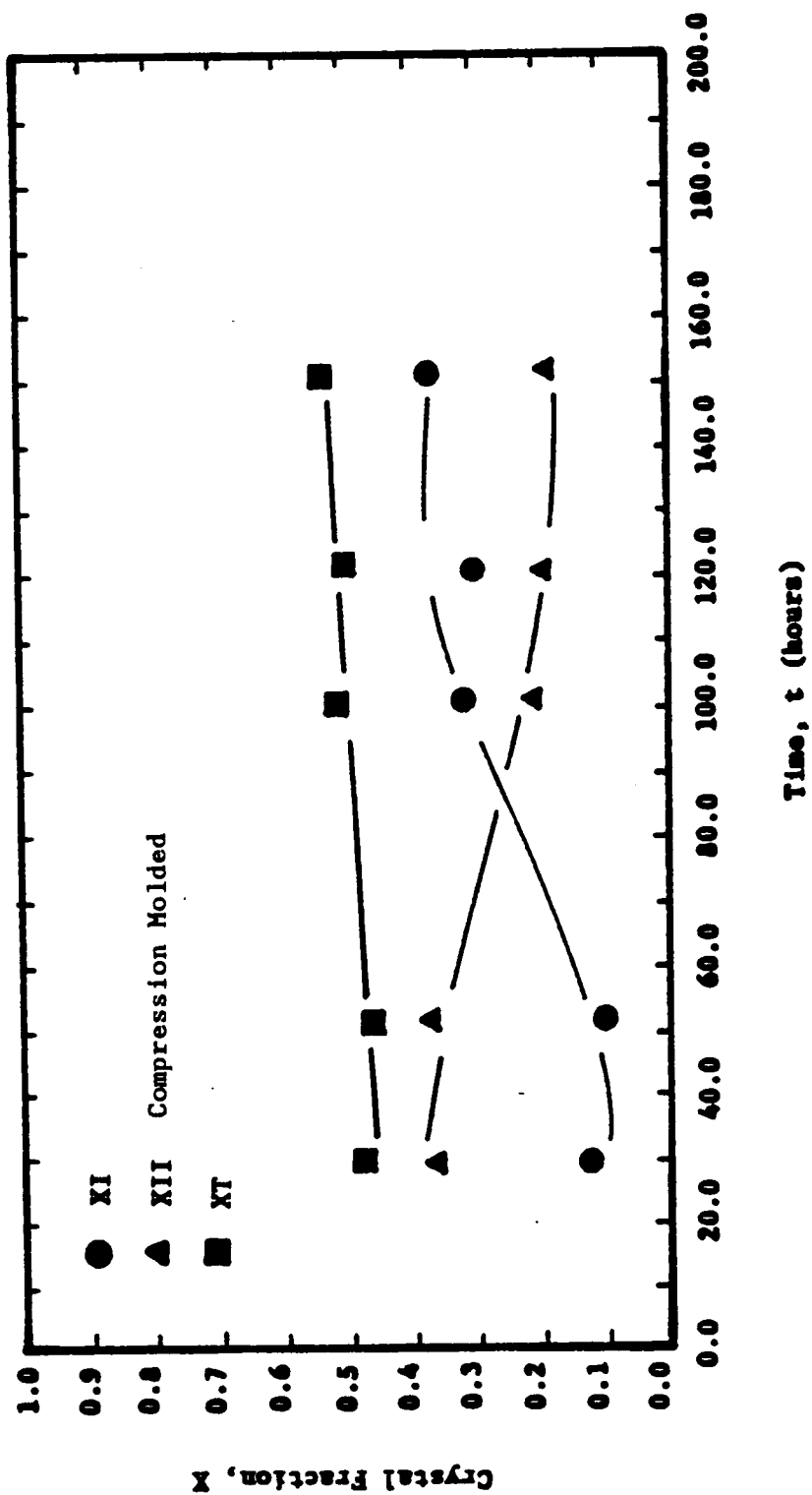


Figure A-80. Crystal Fraction Present as a Function of Time for SA5 at 45 °C

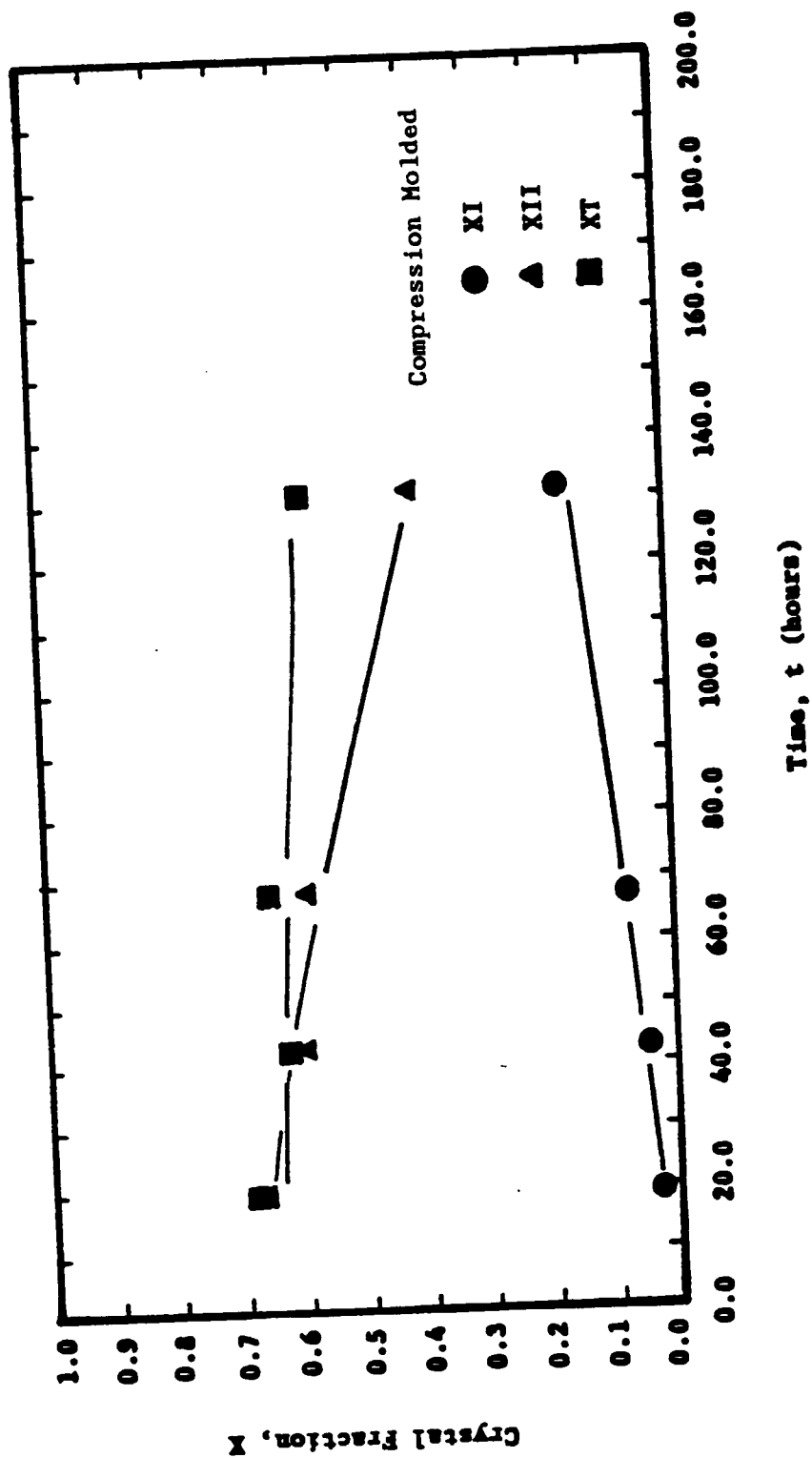


Figure A-81. Crystal Fraction Present as a Function of Time for SA5 at 60 °C

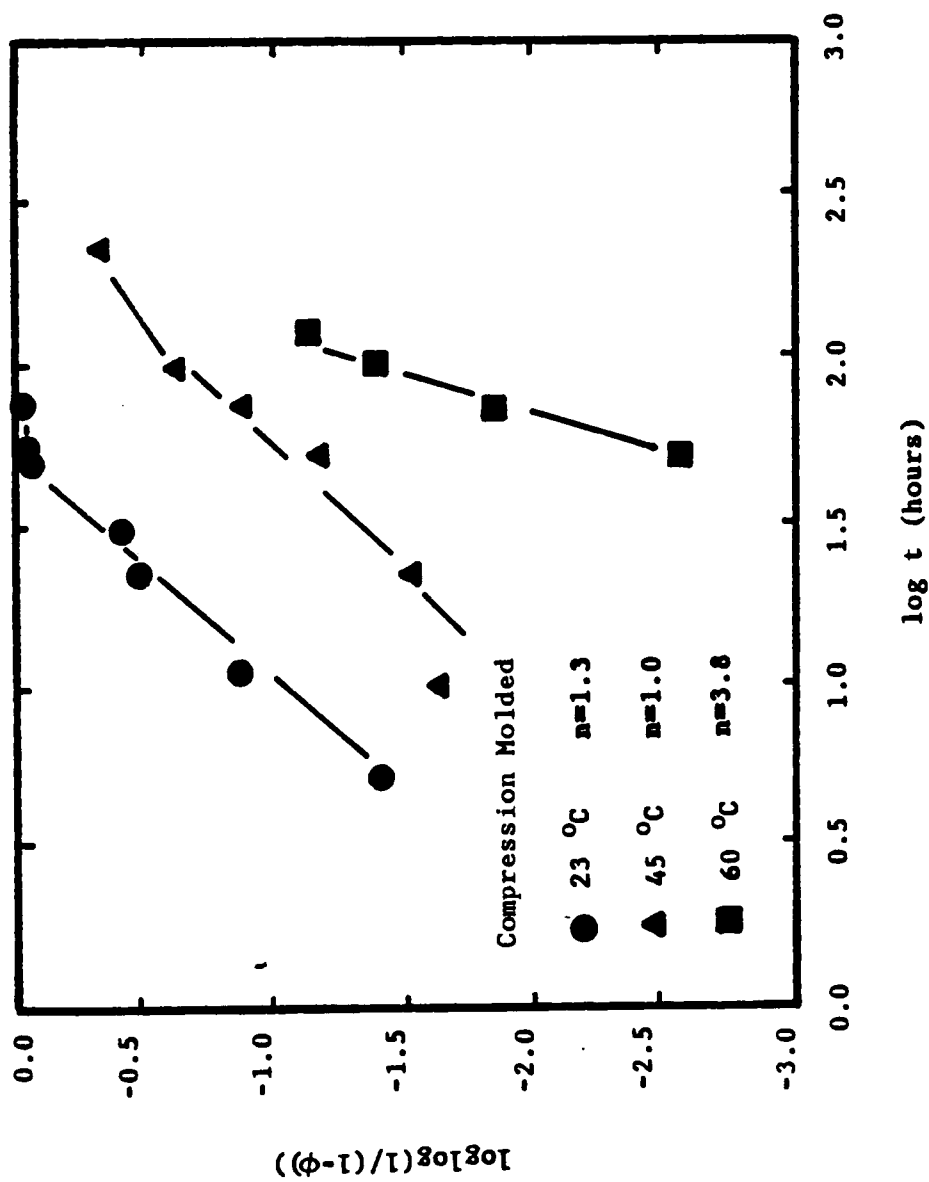


Figure A-82. Determination of the Avrami Exponent Graphically for the PP5 Blend

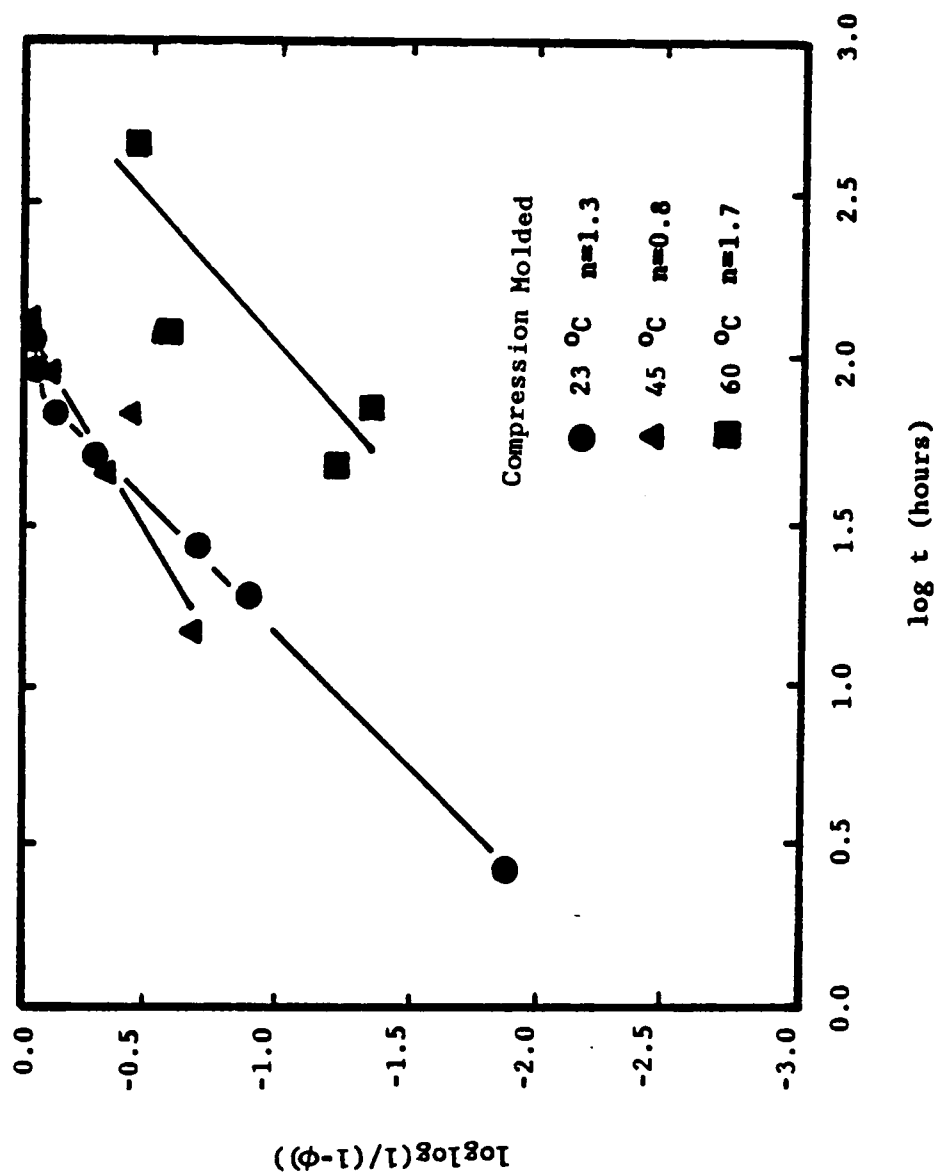


Figure A-83. Determination of the Avrami Exponent Graphically for the NA5 Blend

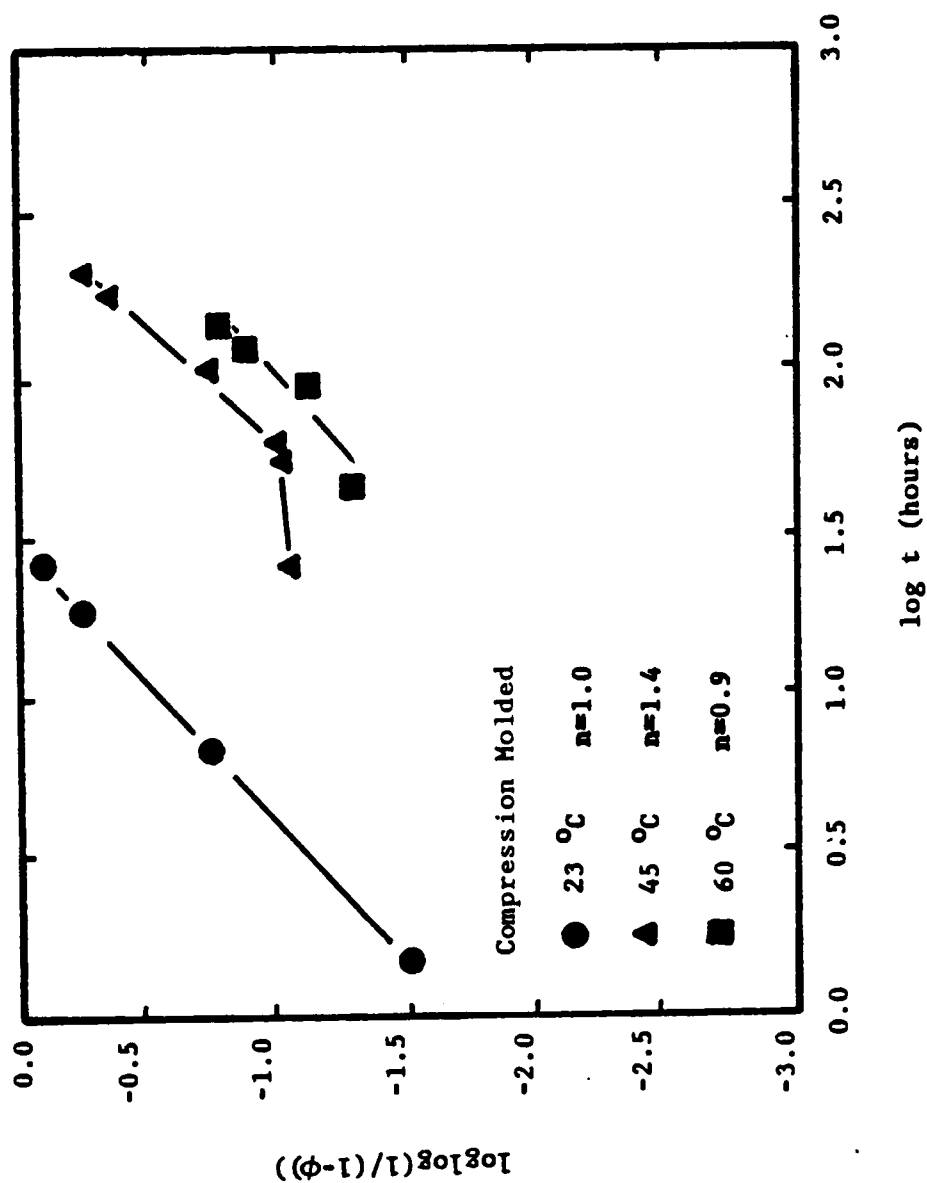


Figure A-84. Determination of the Avrami Exponent Graphically for the DPE5 Blend

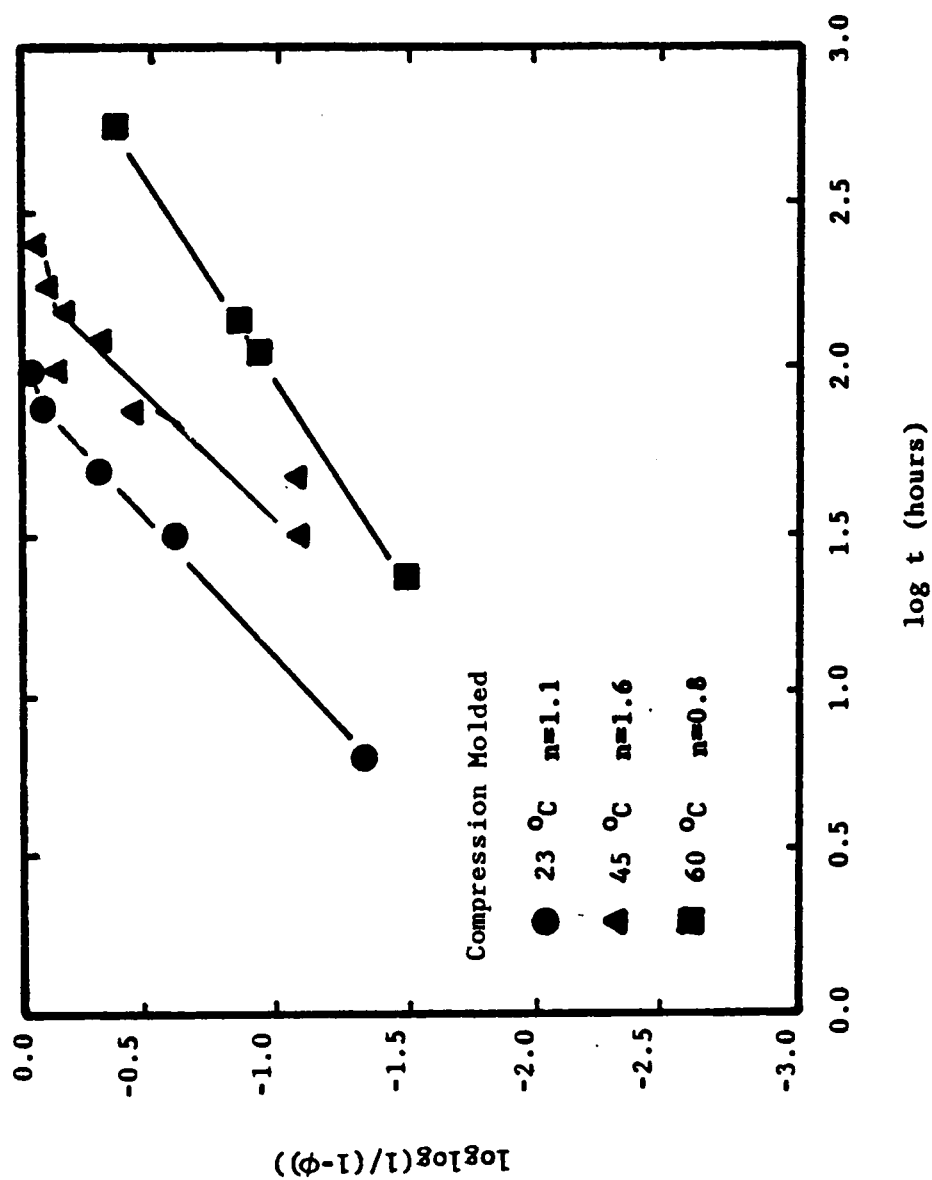


Figure A-85. Determination of the Avrami Exponent Graphically for the SB2 Blend

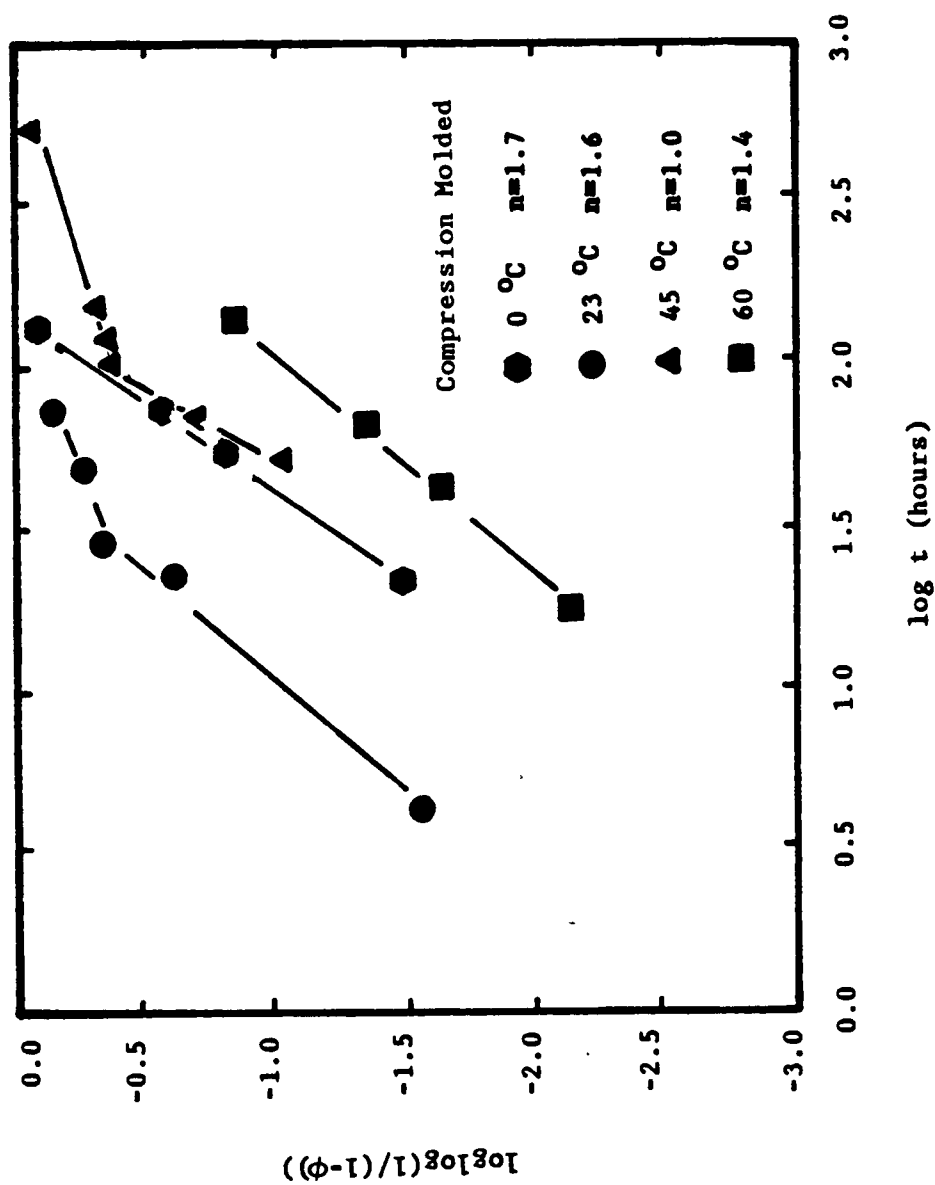


Figure A-86. Determination of the Avrami Exponent Graphically for the SA5 Blend

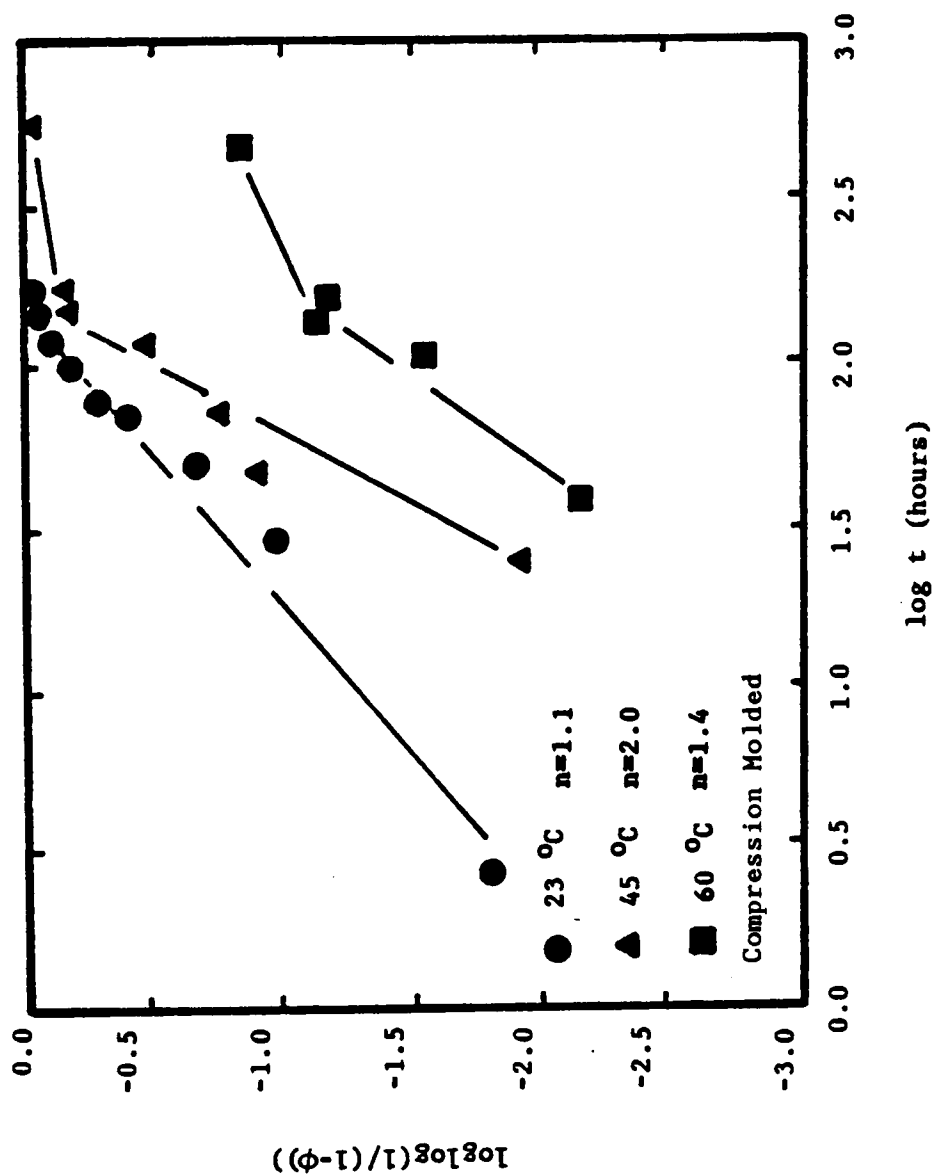


Figure A-87. Determination of the Avrami Exponent Graphically for the CB2 Blend

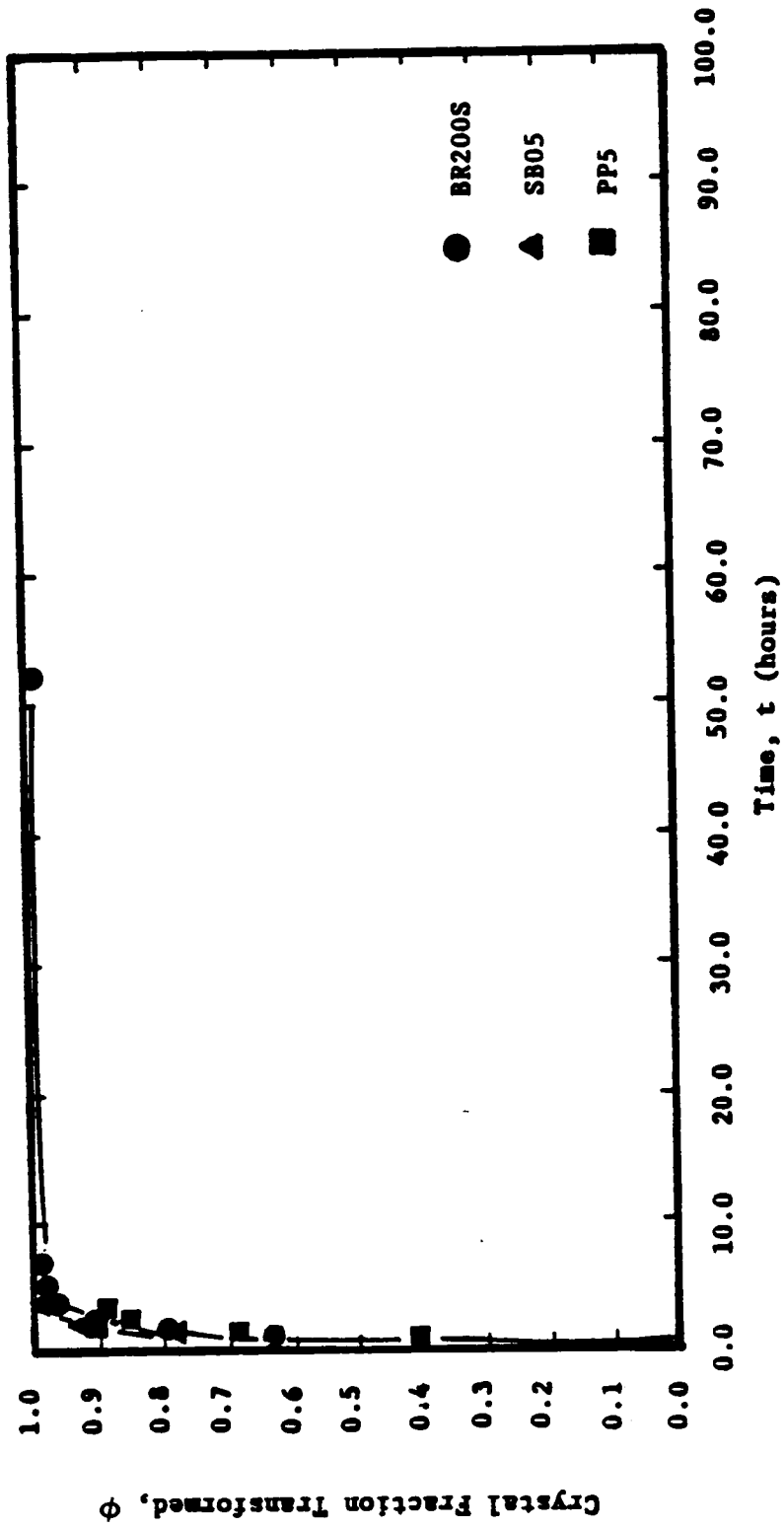


Figure A-88. Volume Fraction of the Crystal Transformed Over Time at the Spin Draw Ratio of 70 for BR200S, SB05, and PP5

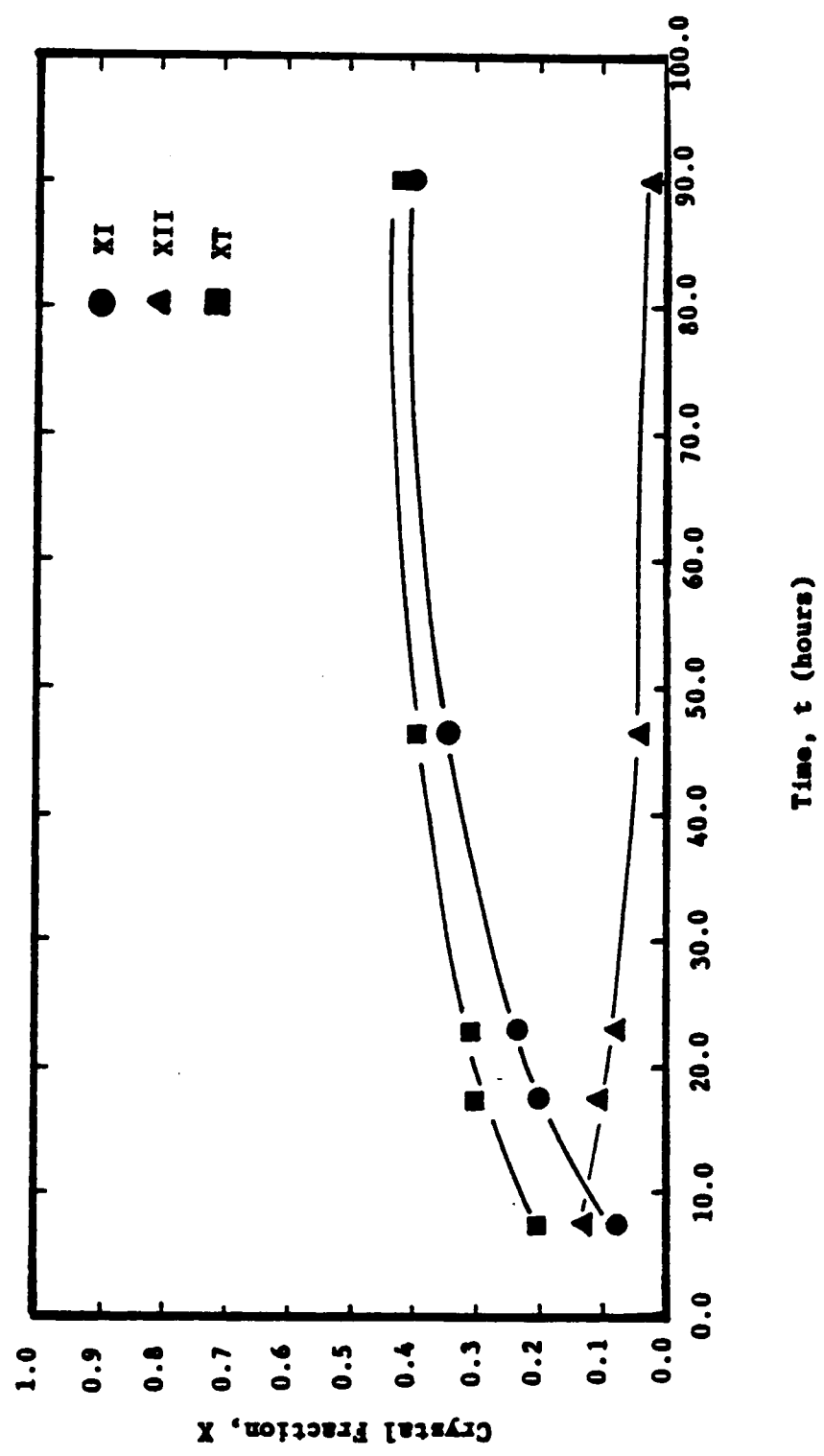


Figure A-89. Crystal Fraction Present as a Function of Time for the SDR = 1 SB05 Fiber

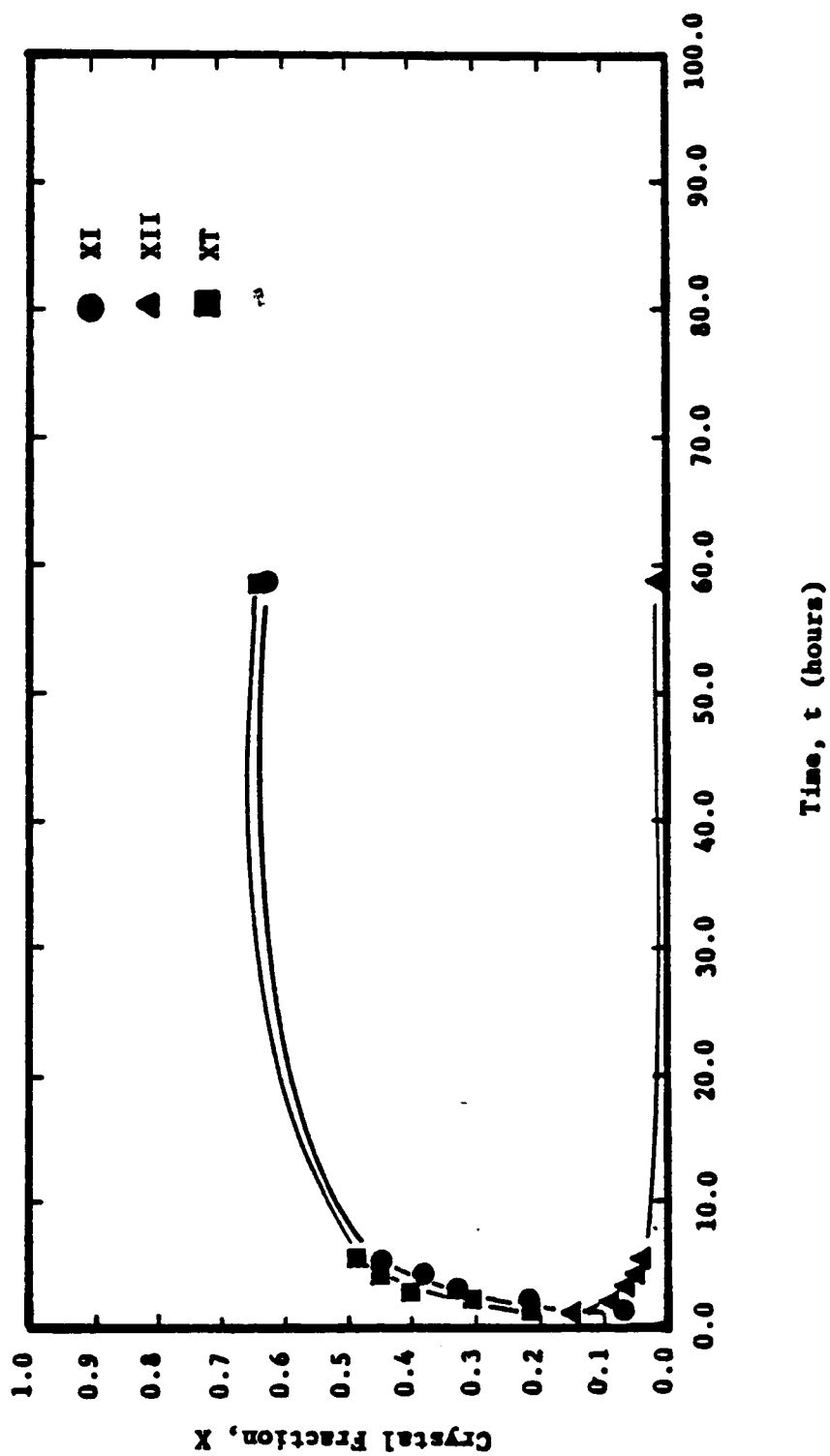


Figure A-90. Crystal Fraction Present as a Function of Time for the SDR = 35 SB05 Fiber

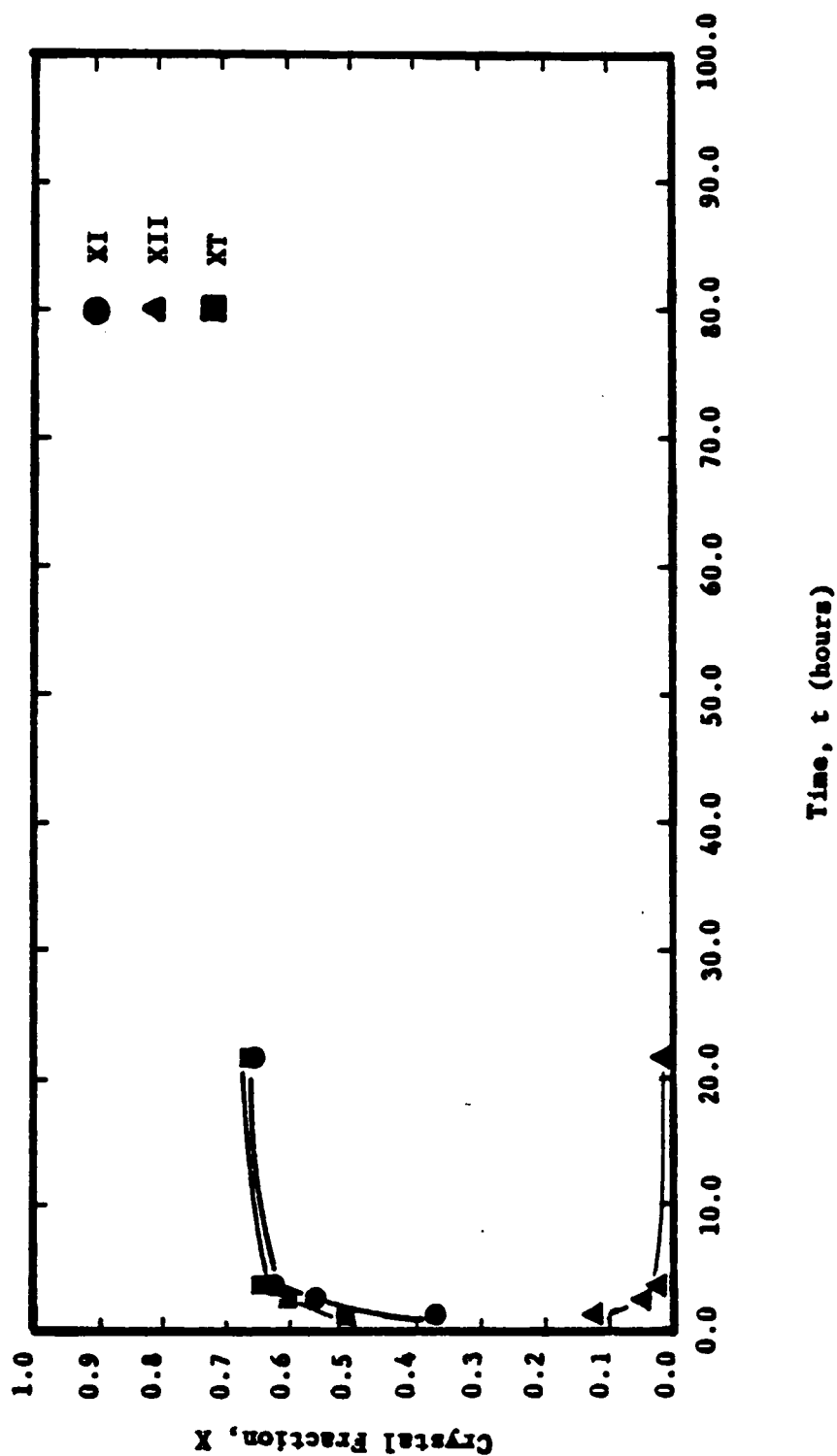


Figure A-91: Crystal Fraction Present as a Function of Time
for the SDR = 70 SB05 Fiber

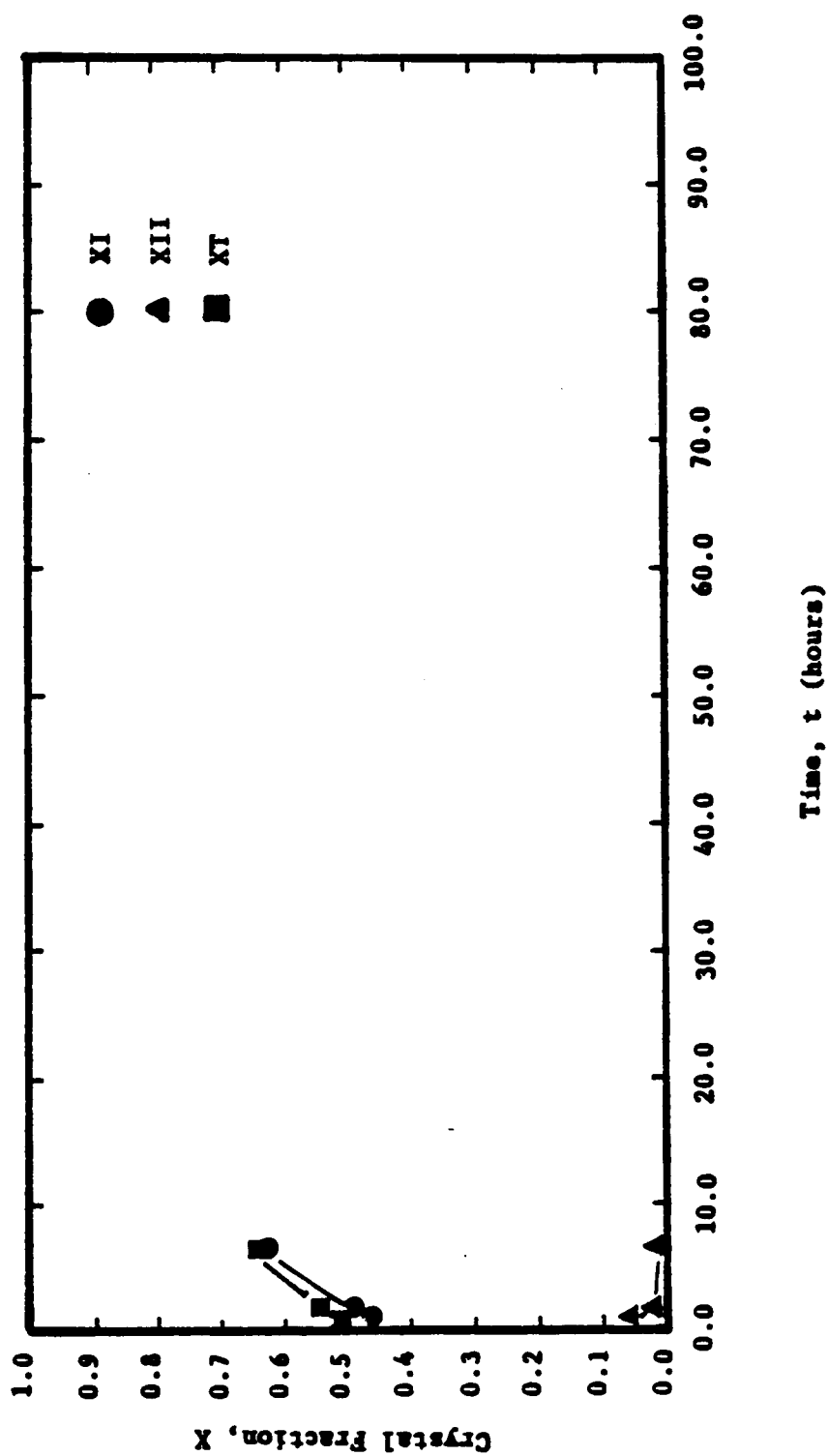


Figure A-92. Crystal Fraction Present as a Function of Time for the SDR = 105 SB05 Fiber

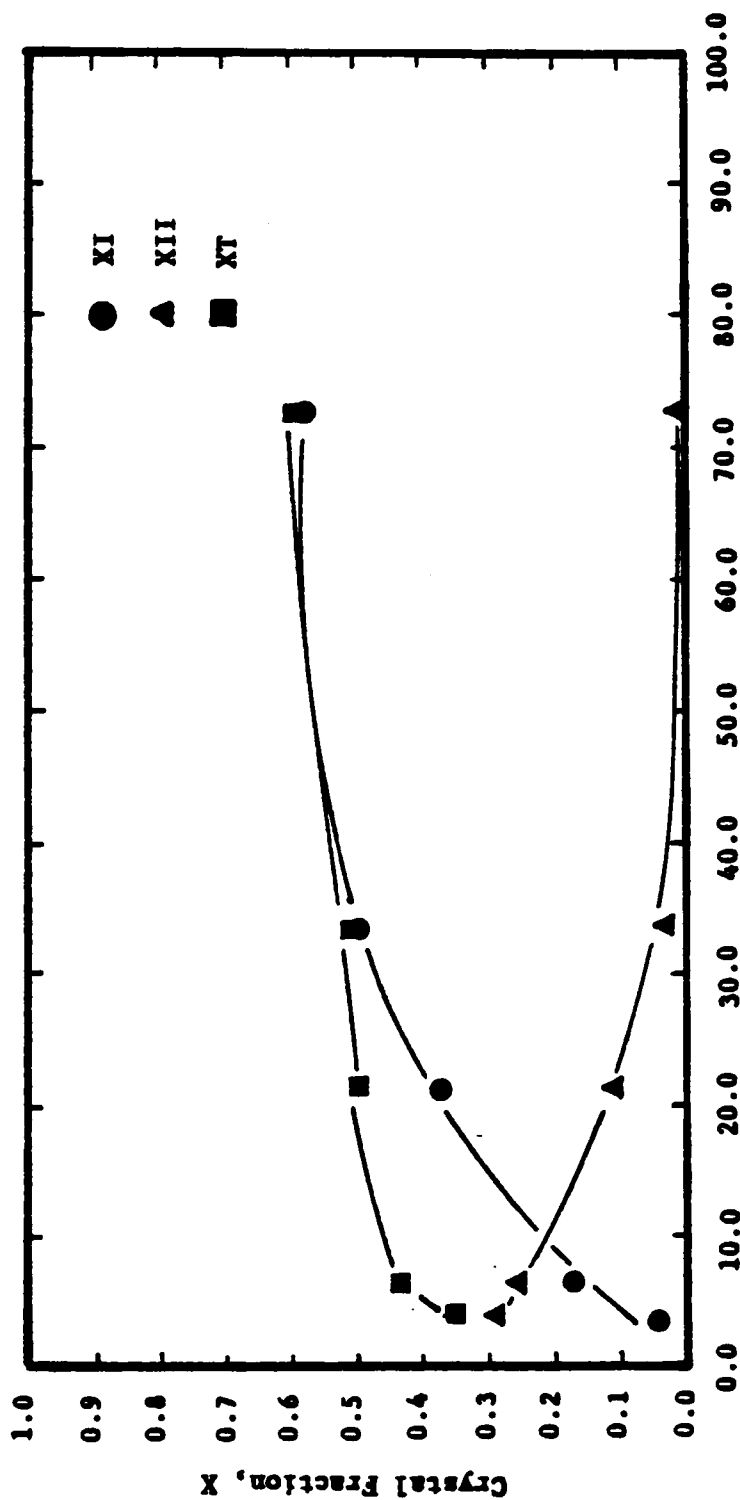


Figure A-93. Crystal Fraction Present as a Function of Time
for the SDR = 1 PP5 Fiber

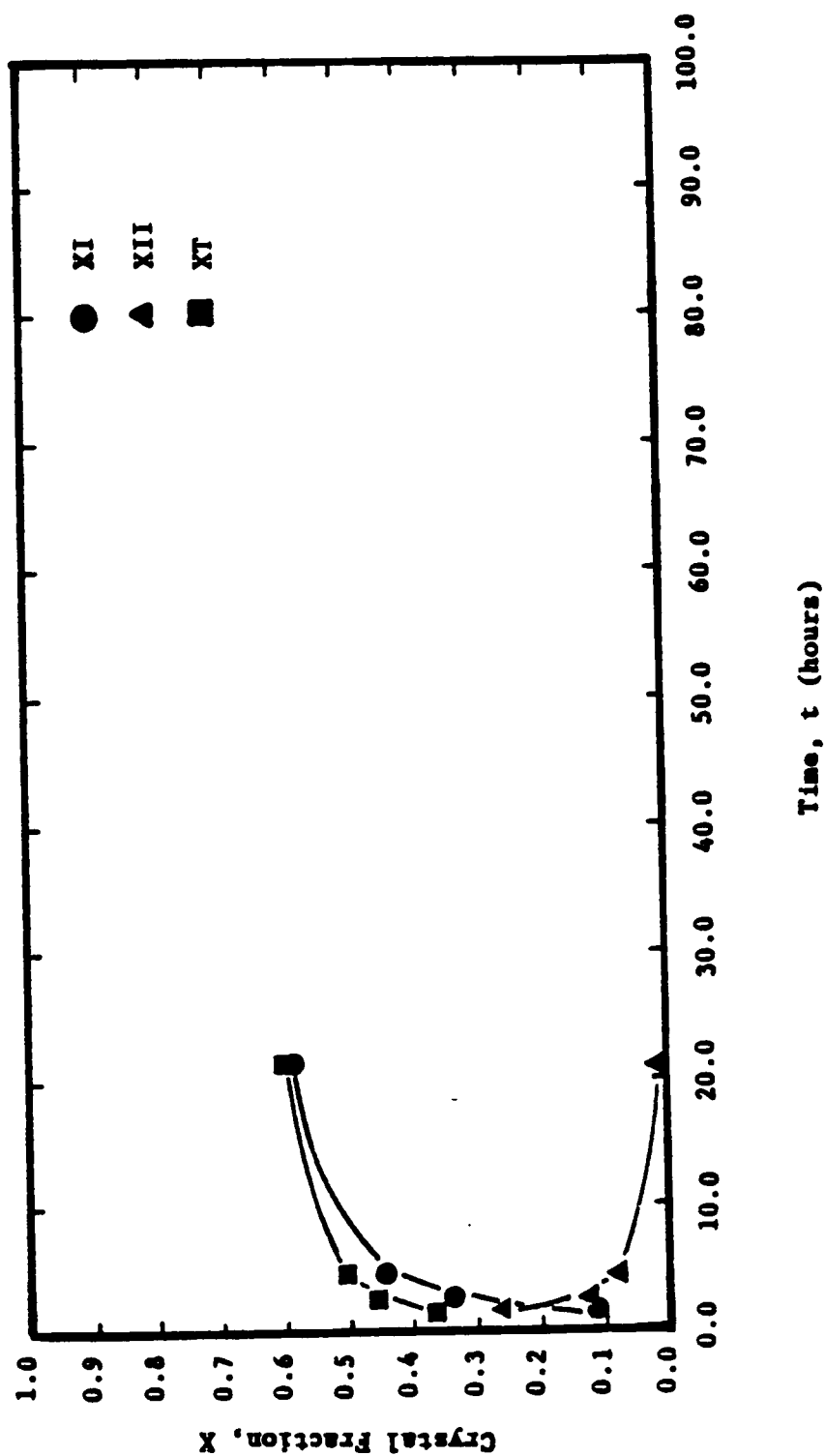


Figure A-94. Crystal Fraction Present as a Function of Time for the SDR = 35 PP5 Fiber

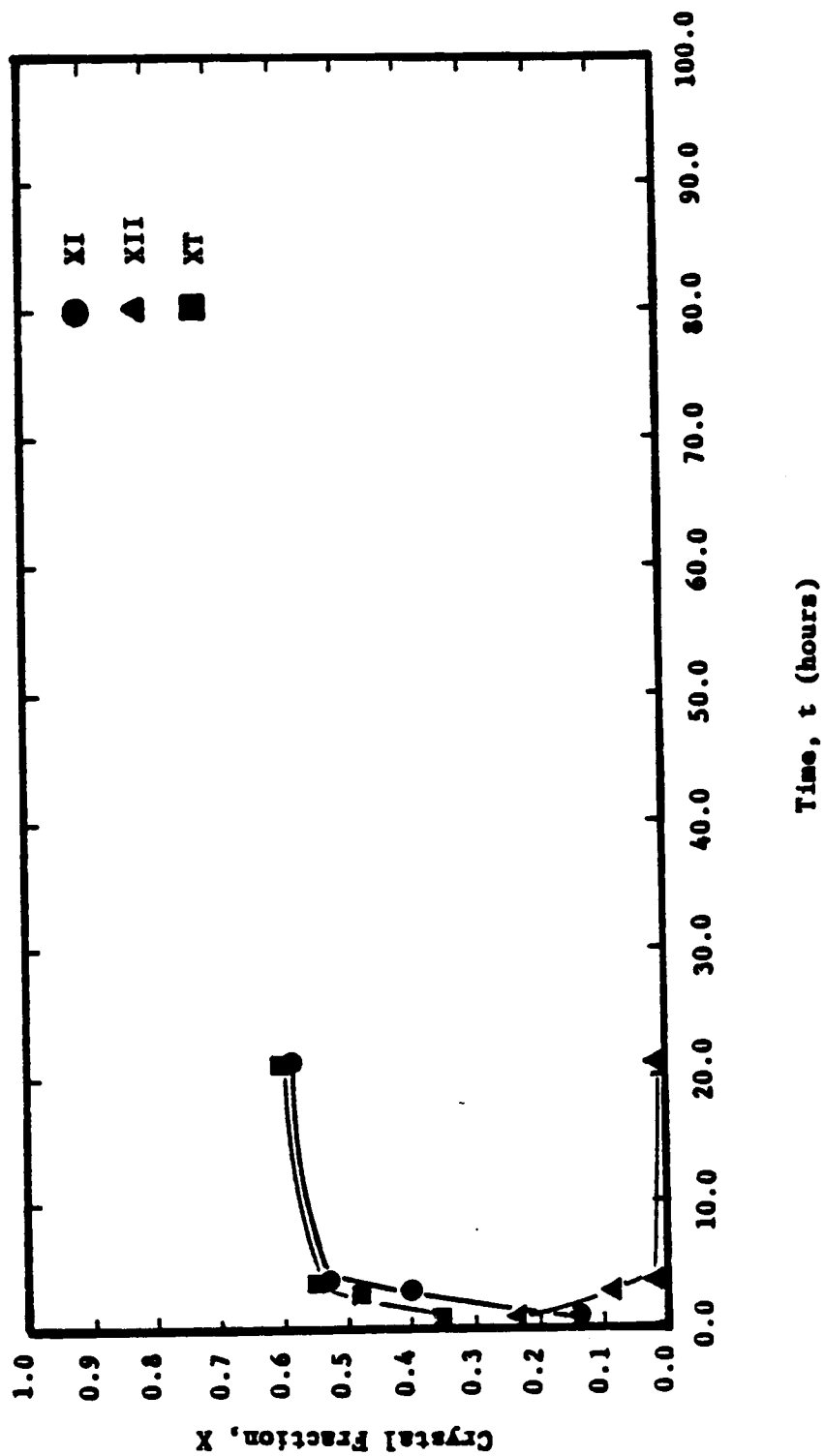


Figure A-95. Crystal Fraction Present as a Function of Time for the SDR = 70 PP5 Fiber

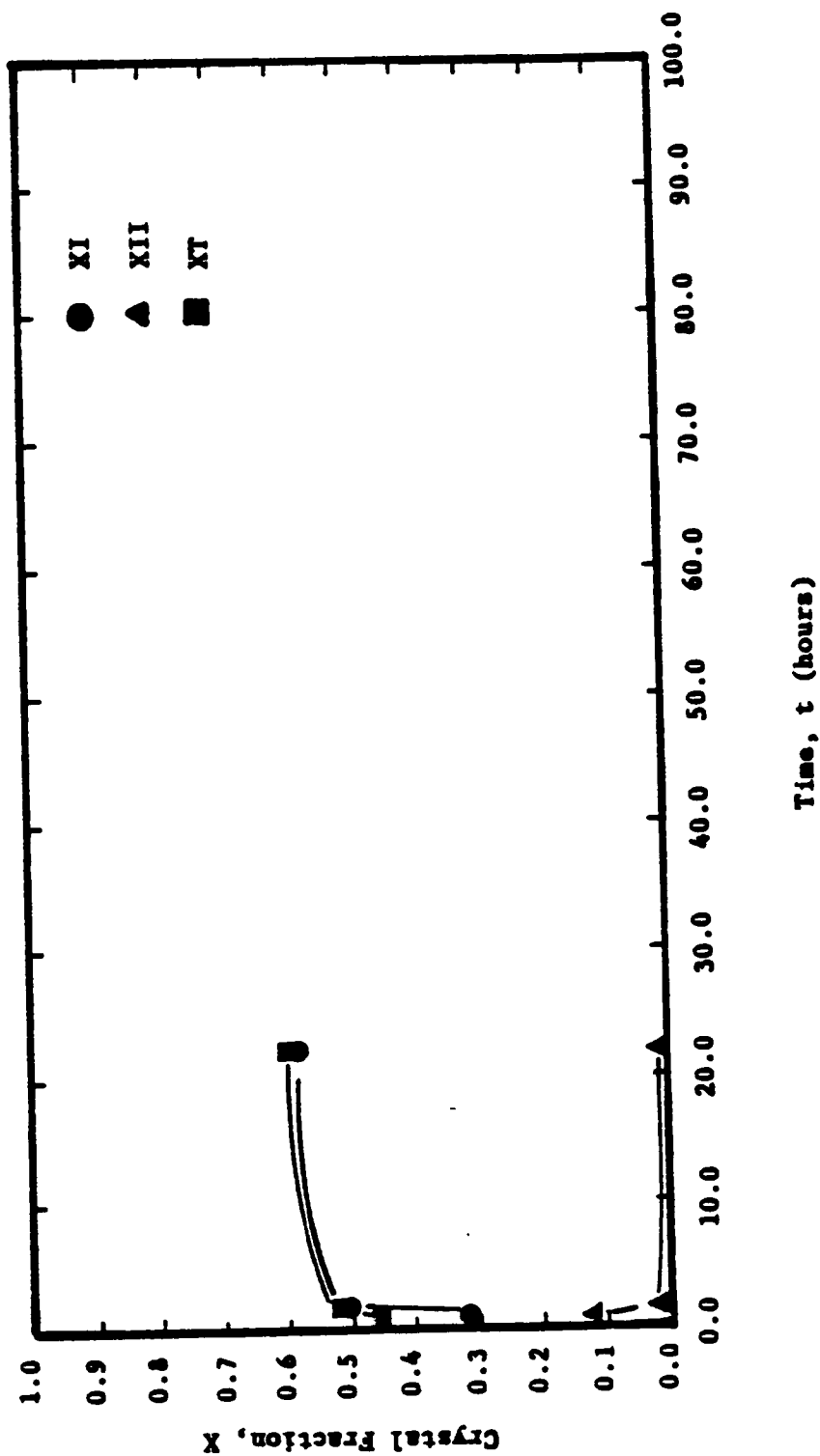


Figure A-96. Crystal Fraction Present as a Function of Time
for the SDR = 105 PP5 Fiber

Vita

Margaret Westbrook was born on October 10, 1961 in Memphis Tennessee. She graduated with high honors from Briarcrest High School in Memphis. She then attended the University of Tennessee and graduated with a Bachelor of Science in Chemical Engineering with honors in 1983. She continued at U.T. in Polymer Engineering and worked with Dr. J.E. Spruiell as her advisor. After receiving her Master of Science in Polymer Engineering in August 1985, she will work for Shell Development Company in Houston, Texas.