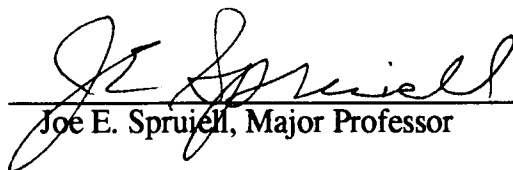


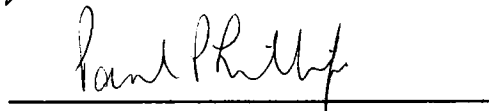
To the Graduate Council:

I am submitting herewith a thesis written by Suzanne M. Williams entitled "The Effects of Comonomer Content and Tacticity on the Nonisothermal Crystallization Kinetics of Polypropylene." 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.


Joe E. Spruiell, Major Professor

We have read this thesis
and recommend its acceptance:





Accepted for the Council:


Associate Vice Chancellor and
Dean of the Graduate School

The Effects of Comonomer Content and Tacticity on the
Nonisothermal Crystallization Kinetics
of Polypropylene

A Thesis

Presented for the

Master of Science Degree

The University of Tennessee, Knoxville

Suzanne M. Williams

December, 1995

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ABSTRACT

The quiescent nonisothermal crystallization kinetics of six polypropylene resins varying in tacticity and ethylene content were investigated by light depolarizing microscopy (LDM) and differential scanning calorimetry (DSC). Crystallization behavior was defined for cooling rates in the range of 5 - 4000°C/min.

The overall transformation kinetics were found to be strongly dependent on three parameters: tacticity, comonomer content, and sample purity. In general, the homopolymers crystallized faster than the copolymers. The homopolymers and copolymers alike showed increased crystallization rates with increasing isotactic content. Furthermore, the effect of ethylene comonomer functioned to decrease the crystallization rate. Nucleating impurities existed in one homopolymer and two copolymer samples, causing significant differences in nucleation densities between these and the other resins. A purification process was introduced to remove these impurities; the resultant nucleation density values of all samples then fell in the same range. This purification procedure affected no changes in the observed crystal growth geometry or growth rates. The growth rate data were analyzed in terms of the established regime theory and were found to follow the Hoffman-Lauritzen equation originally developed for isothermal crystallization. Here, the separation of the growth curves was again attributed to the rather independent influence of tacticity and comonomer content. The effect of these parameters on melting behavior and degree of crystallinity was also analyzed.

Bulk crystallization data were analyzed according to Avrami theory and a comparison between DSC and LDM results was made. The Avrami exponent was

found to be fairly independent of technique. Some discrepancies between the techniques were observed, however, in the form of unexpected crystallization rate trends given by preliminary DSC experiments. These trends were seen to follow those defined by LDM once the nucleating impurities were removed; thus, the initial discrepancies were attributed to a lesser degree of sensitivity of the LDM technique due to the significantly higher cooling rates employed.

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CHAPTER 1

INTRODUCTION

Polypropylene has become one of the world's major commodity plastics today, distinguished by its low density and high crystallinity which yields a high strength-to-weight ratio useful to many applications. The widespread applicability of polypropylene ranges from injection molded parts used in the appliance and automotive fields to filaments used for rope and carpeting. There are three molecular forms of polypropylene: isotactic, syndiotactic, and atactic. Isotactic polypropylene is the most common form and is almost exclusively processed by industry. The isotactic form of polypropylene is essentially a linear polymer which accounts for the high degree of crystallinity it can achieve.

Crystallization studies of polypropylene, along with other semicrystalline polymers, have been conducted for years, in order to understand and optimize the processing of these polymers due to their importance to industry. Most of the theory developed thus far deals with isothermal conditions, however processing typically occurs under dynamic nonisothermal conditions. As a result, there has been a need to facilitate further understanding of the nonisothermal case. Several attempts have been made to develop this theory for the nonisothermal case based on the theory for isothermal conditions, but there remains to be a uniformly accepted argument in this relatively new area of study. Furthermore, the nonisothermal research presented thus far almost exclusively deals with low cooling rates with a need to explore high cooling rate conditions.

This research project involved a systematic study of the nonisothermal crystallization kinetics of six polypropylenes of varying tacticity and comonomer content. Light Depolarizing Microscopy (LDM) and differential scanning calorimetry (DSC) techniques were used to obtain crystallization data. The research objectives were as follows:

- (1) to investigate the effect of tacticity and comonomer content on crystallization rates under nonisothermal conditions;
- (2) to determine the nonisothermal crystallization kinetics for the PP-Et copolymers by applying the CRF approach set forth by Ding and Spruiell (21) for high and low cooling rates;
- (3) to determine if LDM and DSC crystallization data for slow cooling rates is comparable.

The results of this research increased the understanding of nonisothermal crystallization kinetics of polypropylene with specific attention to the effects of tacticity and ethylene content under high cooling rate conditions.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymerization

Isotactic polypropylene was first made by Natta (80), soon after linear polyethylene was produced at low pressure and ambient temperature with a catalyst system of titanium tetrachloride-aluminum triethyl. Ziegler-Natta catalysts were employed as the initiator system in the production of polypropylene. These stereospecific initiators consist of an organometallic compound of a metal (from Group I - III) and a halide or other derivative of a transition metal (Group IV - VIII). The polymerization process can be conducted either as a continuous or batch process and in solution or suspension. For polypropylene, a suspension polymerization is usually carried out in a hydrocarbon solvent with a coordination initiator system of titanium trichloride (TiCl_3) and diethylaluminum chloride $\{(\text{C}_2\text{H}_5)_2\text{AlCl}\}$. A hydrocarbon solvent typically used may be n-heptane or a similar solvent that can dissolve the monomer and atactic polymer only, leaving the isotactic polymer unaffected.

The polymerization process begins once the initiator system is fed into the polymerization reactor as a suspension. The initiator system provides the species which initiates polymerization and coordinates the incoming monomer with the propagating chain end in a manner such that stereospecific addition can occur. It is important to control the purity of the raw material since the purity greatly affects the characteristics of the polymer produced (18). Recent improvements in processes and initiator systems have improved the quality of isotactic polypropylene produced. For example, a higher degree of stereoregularity can be achieved which improves the

properties and eliminates the necessity to remove the atactic portion; also, a much higher yield of polymer can be obtained by using a significantly smaller amount of initiator.

Once the polymerization process is completed, the removal of both the catalyst residues and the atactic polymer has been traditionally employed. The removal of catalyst residues has been achieved by solubilization or decomposition with such agents as acids, bases, or alcohols, while the removal of atactic polymer has been accomplished by methods of filtration or centrifugation in conventional systems. In both cases, the resultant polymer properties are improved due to these elimination steps. Catalyst residues, for example, can both decrease the stability of the polymer in heat or light and diminish the electrical properties if left in the polymer.

2.2 Crystalline Structure and Morphology of Isotactic Polypropylene

Isotactic polypropylene, iPP, crystallizes in a helical conformation in which alternate chain bonds take trans and gauche positions in a three-fold screw axis. Since the methyl side groups are not bulky, the helix has exactly three units per turn.

Four types of crystals have been observed for isotactic polypropylene depending on the thermal history. The monoclinic crystal has the dimensions $a=6.66\text{\AA}$, $b=20.78\text{\AA}$, $c=6.495\text{\AA}$; $\alpha=\gamma=90^\circ$, and $\beta=99.62^\circ$ (100). This is the most common and most stable of the crystal types and tends to dominate under isothermal crystallization conditions for low undercoolings. It is called the α form (81).

The second crystal type is the hexagonal β structure which occurs sporadically at a low isothermal crystallization temperature ($T_c < 130^\circ\text{C}$) or in crystallization in a temperature gradient (54). Generally, the β structure is only a minor component in the bulk sample which largely contains α crystals. The β form is characterized primarily by two reflections at $d=5.53\text{ \AA}$ and $d=4.17\text{ \AA}$, although some fifteen other

reflections have been identified. There have been many attempts (10, 54, 100) to derive the unit cell of the β form of unoriented specimens. The most recent investigations agree on a basic hexagonal lattice model with $a=b=6.36\text{\AA}$ and $c=6.49\text{\AA}$. A model that accounts for additional reflections, however, yields the dimensions of $a=b=11.03\text{\AA}$ and $c=6.49\text{\AA}$. Unidirectional packing of the helical chains in the unit cell has been proposed, along with a calculated density value of 0.92 g/cm^3 .

The third type is the γ form, originally proposed to be a triclinic unit cell (100); the γ form has been most easily produced by bulk crystallization at high pressures, but also observed from crystallization of stereoblock copolymers and low molecular weight fractions ($M_w=15,000$). The dimensions of this triclinic unit cell were reported as $a=6.54\text{\AA}$, $b=21.40\text{\AA}$, $c=6.50\text{\AA}$, $\alpha=89^\circ$, $\beta=99.6^\circ$, and $\gamma=99^\circ$. The γ form has more recently been assigned a face-centered orthorhombic unit cell containing non-parallel chain stems (10), a unique arrangement among polymers, with the unit cell dimensions of $a=8.54\text{\AA}$, $b=9.93\text{\AA}$, and $c=42.41\text{\AA}$. Here, the chains lie parallel to both the diagonals in the a - b plane and form an angle of 81.2° . Recently, Mezghani and Phillips (74) have shown that the amount of γ form present is proportional to the ethylene content in polypropylene-ethylene copolymers and to crystallization temperature. Hence, the lower the supercooling, the higher the amount of γ form present. The γ phase has also been produced at elevated pressures from high molecular weight homopolymers (15); diffraction patterns of samples produced in this manner are the same as those given by the low molecular weight polymers. If the pressure is varied, the α and γ forms are observed. The γ form begins to coexist with the α form as the crystallization pressure is increased and becomes the dominant form existing at a pressure of 2 kbar (15, 52).

The fourth type is the condis phase (conformationally disordered), previously called "smectic mesophase" or "paracrystalline" (35, 100). This type is the least perfect crystal form since it possesses an order intermediate between the amorphous (atactic) and crystalline states; it is obtained by rapid quenching of molten isotactic polypropylene (35). The helices have a parallel orientation and the packing perpendicular to their axes is more disordered than along the axes; this somewhat non-random helical packing led Natta et al (82) to suggest the term "smectic" to indicate a higher degree of order than the molecular parallelism found in a nematic liquid crystalline phase. The reported density for the smectic form is 0.88 g/cm^3 (81), slightly higher than the value of 0.85 g/cm^3 reported for amorphous PP.

The topic of polymer crystallization has been extensively explored and continues to be surrounded by controversy. One widely recognized explanation for the polymer crystallization process, given by Keller (57), introduced the concept of chain folding in solution grown polymer single crystals. This theory states that the chain molecule must fold back and forth on itself as it traverses the lamella since the polymer molecules are at least $1000\text{\AA}$ long and the lamellae are only about $100\text{\AA}$ thick. This model for adjacent reentry folding predicts regular folding with short, uniform folds in which the chain exits the crystal and reenters at an adjacent crystal site. Bulk grown polymer crystals formed from the melt, however, form spherical aggregates known as spherulites.

Spherulites are made of chain folded lamellae which radiate outward from a central nucleus (Figure 2.1). Spherulitic growth in the radial dimension increases linearly with time until impingement occurs on another growing spherulite. During the primary crystallization process, the spherulite develops from the nucleus by growth of sheaf-like structures; the growth continues until impingement occurs,

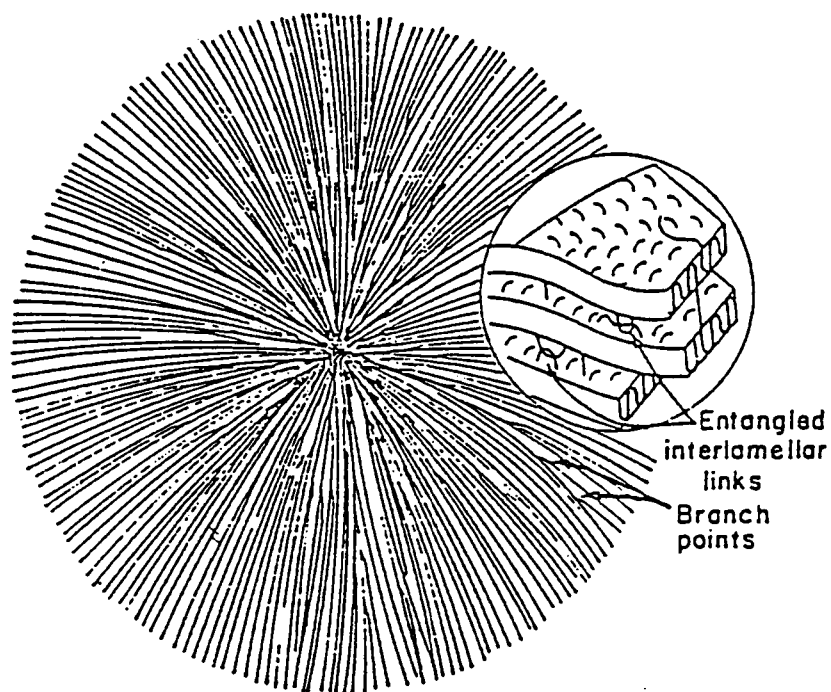


Figure 2.1. Schematic of a polymer spherulite.
Source: Hoffman, J.D. et al, in "Treatise on Solid State Chemistry,"
vol 3, Plenum Press, N.Y. (1976).

resulting in a polyhedron shape. Continued development within the spherulite occurs as the interlamellar material is transformed into crystalline material; this process is termed secondary crystallization. Both the nature of branching occurring by the growing radial lamellae and the crystals formed between the branches affect the fine structure of the spherulite.

Four distinct types of spherulites have been found using light depolarizing microscopy (LDM) (86), each distinguished by its birefringence and the temperature range at which its formation can occur: (1) Spherulites with negative, very high birefringence and very fine textures; formation occurs in the range of 120-128°C when the molten polymer is quenched to this range; (2) Spherulites with negative, high birefringence which form at 130°C; (3) Spherulites with low, positive birefringence, forming in the range of 120-132°C; and (4) Spherulites with weak, negative birefringence, forming in the range of 138-148°C. For a crystallization temperature less than 140°C, however, the largest number of observed spherulites are "mixed"; these fail to exhibit a distinct Maltese cross and appear as radial arrays of mixed areas of positive and negative birefringence. Differences in birefringence exhibited by the various types of spherulites are due to the relative proportions of tangential and radial lamellar components present in each type (37). For example, positive birefringence results from tangential lamellae, while negative birefringence results from radial lamellae.

The lamellae are arranged in a complex manner in isotactic polypropylene. For certain conditions, a three-dimensional array of nearly orthogonal 'cross-hatched' lamellae has been seen. The β crystal form does not show this radial-tangential arrangement, but instead exhibits smooth stacks and sheets.

A second model for chain folding, proposed by Flory (27), describes nonadjacent reentry (switchboard model) in which the chains fold and reenter a crystal site at some random location; thus, the irregular reentry of the folded chains results in random, loose folds.

Since the adjacent reentry model results in a regularly folded surface, the only possible defects could be the ends of the molecules which could form as short, flexible rods above the surface, or fold back into the crystal, thereby creating a gap. While it has been shown by infrared studies that adjacent reentry folding is the predominant folding mechanism in polyethylene (5), nonadjacent reentry is accepted as occurring to some extent as shown by the existence of interlamellar and intercrystalline links.

A third model was proposed by Hermann et al (40): the fringed-micelle model. The model includes regions of order (crystalline) and regions of disorder (amorphous) being traversed by long molecules. The space limitations at the crystal-liquid interface and the density defect nature of single crystals were used as a basis for constructing the switchboard model.

It is reasonable to assume that various types of fold structures may exist in polymer molecules, depending on the conditions at which crystallization occurs, since various macroscopic morphologies have been seen for different crystallization conditions through the use of microscopy techniques. Nevertheless, the assumption that adjacent reentry folding occurs (either solely or predominantly) is used in many kinetic theories to describe polymer crystal growth and has adequately predicted lamellar thickness and growth rates for the cases of crystallization from the melt and from dilute solution.

2.3 Physical and Thermal Properties of PP and PP-PE Copolymers

Equilibrium Melting Temperature, T_m°

Polypropylene is unique in that it is typically observed to melt 10-30°C below the equilibrium melting temperature (108). The literature values of equilibrium melting temperature T_m° of polypropylene range from 160 - 212°C (65, 78). This range is large because the T_m° values are not directly available experimentally, since the polypropylene crystals typically grown are metastable; as a result, a method for estimating T_m° is usually employed. There are several techniques described in the literature (9, 29, 64), and the uncertainty in T_m° as given by these techniques can be as high as 20°C. According to Krigbaum (63), the value of T_m° of monoclinic i-PP is 186±2°C. Samuels (92) reports a value of 185°C, while Wunderlich argues that a T_m° of 187.5°C is most likely since it produces a reasonable prediction of fold surface free energy (around 100 ergs/cm²).

It is necessary to account for lamellar thickening which can occur at the crystallization temperature or even during the heating process required to obtain a melting curve (88). Recently, Phillips and Mezghani (74) have shown by Small Angle X-ray Diffraction that crystal thickening in polypropylene favors thicker lamellae which, in turn, results in the previously reported, erroneously high values of T_m° in the range of 210°C; they have reported a value of 186°C.

Several authors have investigated the effect of molecular weight on equilibrium melting temperature (16, 83, 108). The consensus is that T_m° is slightly depressed with decreasing molecular weight. Wunderlich (108), in particular, postulated little or no significant change in physical properties with increasing molecular weight for macromolecules of at least 1000 atoms; a maximum of 3-5 °C change in T_m° may result in the case of molecular weight above 10,000.

The equilibrium melting temperature has been studied to some degree for polypropylene copolymers with low ethylene content. The equation for equilibrium melting temperature T_m° for copolymers containing large crystallizable monomer sequences has been derived by Flory (26):

$$\frac{1}{T_m'} - \frac{1}{T_m^\circ} = - \left(\frac{R}{\Delta H_f} \right) \ln(n_A) \quad (2.1)$$

T_m' represents the maximum melting temperature of the random copolymer, n_A the mole fraction, and ΔH_f the heat of fusion per mole of repeating A units. Flory employed the eutectic assumption where the main units (A) and co-units (B) of the molecules are completely miscible in the melt, and B is completely excluded from the A crystals. Thus, the resulting equation relates the copolymer melting point dependence on mole fraction n of the crystallizing constituent.

For propylene-ethylene copolymers containing low levels of ethylene (<10%), it has been shown experimentally that the equilibrium melting temperature T_m° decreases with increasing ethylene content (2). This composition dependence of T_m° is accounted for by the assumption that less perfect crystals of the propylene-ethylene copolymer are formed by increasing the ethylene content; likewise, the depression in T_m° is dependent on the type of ethylene distribution along the propylene-based chain. Here, the equilibrium melting temperature was found according to the Hoffman relation (42): $T_m' = T_m \left(\frac{\beta - 1}{\beta} \right) + \frac{T_c}{\beta}$ where T_m' is the maximum melting temperature, T_m the equilibrium temperature (also called T_m°), and T_c the crystallization temperature. For this case, the temperature corresponding to the maxima in the DSC endotherms was assumed to be the maximum melting temperature T_m' of the sample in the α form; this assumption was based on a study by Turner-

Jones (101) which showed that propylene-ethylene random copolymers produced mixed α/γ crystallinity on slow cooling from the melt.

Melting and the Heat of Fusion, ΔH_f^*

The melting temperature of a polymer is governed by factors such as surface free energies, lattice imperfections, lamellar thickness, and others. Specifically, surface free energies and lamellar thickness must be accounted for when deriving an expression for melting point. One such expression has been shown to be:

$$T_m = T_m^\circ (1 - 2\sigma_e / \Delta h_f l) \quad (2.2)$$

where Δh_f is the heat of fusion per unit volume of crystal, σ_e the fold surface free energy, l the thickness of a single lamellar polymer crystal, and T_m° the equilibrium melting temperature (14). This relationship demonstrates that the observed melting point of a thin crystal will be decreased by an amount $2\sigma_e / \Delta h_f l$ below that of an infinite crystal (T_m°).

Another factor influencing polymer melting is copolymerization. According to Flory (125), the melting of a crystalline homopolymer occurs over a range of only a few degrees for a slow heating rate (the observed melting temperature is rate dependent); the melting point is then the point at which the melting process is abruptly completed. This is not the case for copolymers which exhibit a much broader melting range and do not show a well-defined melting point (122-124). This behavior has been attributed to the occurrence of the crystallizable units in sequences bounded along the polymer chain by comonomer units where the comonomer units are excluded from the crystalline regions (exclusion model); thus, the breadth of the melting range is due to the sequence length variations found in the copolymer.

It has been shown experimentally that T_m° decreases with ethylene incorporation, for example, so it follows that the observed maximum melting point would be depressed also. This expected depression has been observed by Davis (20), who reports a 4.4°C drop in maximum melting temperature per percent ethylene incorporated as measured by Differential Scanning Calorimetry (DSC). Here, the maximum melting temperature was defined as the maximum in the DSC endotherm.

Values cited in the literature for heats of fusion have been reported to vary significantly for polypropylene (2, 30, 53). These results have been obtained from methods ranging from diluent melting experiments to direct calorimetry. It has been argued (108) that unusually high values of heat of fusion have been obtained by extrapolation of the diluent melting temperatures to the equilibrium dissolution temperature, a method described by Lauritzen (64). According to data presented by several authors (25, 51, 103, 104), a reasonable value for the heat of fusion of a 100% crystalline sample of isotactic polypropylene is approximately 165 J/g.

Avella et al studied composition-properties relationships for propylene-ethylene copolymers containing a range of 0-9 weight percent ethylene content (2). The heat of fusion, ΔH_f , for each sample studied was determined using DSC; the ΔH_f for a 100% crystalline sample was calculated as the ratio between ΔH_f^* (apparent enthalpy of fusion) and the WAXS crystallinity index X_c , using the assumption that is X_c is independent of thermal history of the sample. The ΔH_f was shown to be composition dependent and to decrease dramatically with increasing ethylene content: $\Delta H_f=184$ J/g for iPP (0% ethylene) and $\Delta H_f=66$ J/g for a copolymer with 9 weight percent ethylene. (Note that the value for ΔH_f^* used here was one previously determined by Avella and coworkers and is erroneously high according to those previously cited authors).

Glass Transition Temperature, T_g

Multiple glass transition temperatures, T_g , are reported for polypropylene. These are not only difficult to distinguish but also to correlate to tacticity (49). Calorimetry and dilatometry have been utilized in identifying the T_g of polypropylene (35). The glass transition has been reported to be 260K (35, 103). The relationship between T_g and molecular weight is reported to follow the equation $T_g = T_g^\infty - \left(\frac{K}{M_n} \right)$ where T_g^∞ is the glass transition temperature at an infinite molecular weight, K a constant that is polymer dependent, and M_n the number average molecular weight (6, 97).

The nature of the chain repeat units (e.g. comonomer units) has effects on T_g closely related to symmetry, chain stiffness, intermolecular forces, and conformational energies. The T_g values for copolymers usually fall between those of the corresponding homopolymers (6). The average polarity and chain stiffness of the individual homopolymers can be used as approximate values for a random copolymer. Hence, T_g can be estimated for copolymers based on weight fractions and the T_g of each homopolymer. There are several equations which can be applied, three of which will be presented.

First, Fox (28) presented the equation

$$T_g = T_g(\infty) - \frac{\left[\frac{(m + m_e) [\Delta\alpha T_g + \Delta v_o]}{\alpha_\infty - B + \frac{(m + m_e) \Delta\alpha}{M}} \right] \frac{1}{M}}{\quad} \quad (2.3)$$

to relate T_g to molecular weight M where m is the weight of a X unit, m_e the combined weight of the two chain ends, α_∞ the volume-time coefficient at ∞ , $\Delta\alpha = \alpha_1 - \alpha_\infty$, $\Delta v = v_o(1) - v(\infty)$ for v =specific volume, and B a constant. Fox has found

that an increase in molecular weight of a given polymer causes an increase in T_g which results from a decrease in v . Second, Wood (106) presented an equation for the T_g calculation of a copolymer:

$$T_g = T_{g1} - M_2 k \frac{T_{g2} - T_{g1}}{1 - (1 - k)M_2} \quad (2.4)$$

where M_1 and M_2 are the mass fractions of each homopolymer, and k a constant characteristic of the polymer. Third, another form of this type of equation was given by Couchman (19):

$$\ln T_g = \frac{\sum X_i \Delta C_{pi} \ln(T_{gi})}{\sum X_i \Delta C_{pi}} \quad (2.5)$$

where X_i is the composition variable, e.g. molecular weight, and ΔC_{pi} the pure component glass transition increments of heat capacity. Couchman's approach is derived for random solutions and is based on a relationship between differential changes of temperature and pressure.

In a related experimental investigation, Davis (20) studied the effects of ethylene incorporation on the crystallization temperature T_c and the glass transition temperature T_g . In both cases, the temperatures were found to decrease with increasing ethylene content: a 3.6°C drop in crystallization temperature per percent ethylene and a 2°C drop in T_g per percent ethylene incorporated (20). The decrease in crystallization temperature was explained as a consequence of the structural irregularity of the copolymer hindering the crystal lattice formation, and the resultant lower degree of crystallinity leading to a lower crystallization temperature.

Density and Degree of Crystallinity

Most polymers, including isotactic polypropylene, are semicrystalline, containing regions of order and disorder. There exists a close relationship between

structural regularity of molecules and crystallizability. Those that can achieve a high degree of crystallinity are those with chemically and geometrically regular structures. Copolymerization introduces some degree of irregularity in a molecular structure, e.g. chain branching; however, this does not prevent crystallization from occurring, but only limits the extent to which it occurs.

The reported densities of amorphous and monoclinic crystalline polypropylene are 0.85 and 0.95 g/cm³, respectively (76). The degree of crystallinity can be calculated using density by assuming molar volume is independent of stereoregularity:

$$\chi_c = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \quad (2.6)$$

Here, ρ is the sample density, while ρ_c and ρ_a are the densities of the crystalline and amorphous regions respectively (96). The percent crystallinity values reported for polypropylene range from 30-65% according to thermal history (108). Other properties can be used to calculate degree of crystallinity; these include specific volume (126), specific heat (127), and specific enthalpy of fusion (128). For example, the specific enthalpy of fusion can be used to define the weight fraction crystallinity by $X_c = \Delta H_s / \Delta H_f$, where ΔH_s represents the observed specific enthalpy of fusion for a polymer sample, and ΔH_f is that for the crystalline phase of that polymer.

Molecular Weight and Tacticity

The molecular weight, molecular weight distribution (MWD), and tacticity all affect the rate of polymer crystallization, degree of crystallinity, and melting temperature. These effects have been studied for a number of polymer systems. In

an attempt to establish a calorimetric index for polypropylene isotacticity by studying thermal properties, Burfield et al (12) found correlations between isotacticity and crystallization, along with an effect of molecular weight on crystallization and melting temperatures; specifically, both temperatures increased with increasing molecular weight. According to Martuscelli et al (71, 72), both tacticity and MWD affected crystallization rate.

More recently, Paukkeri and Lehtinen (87) investigated the influence of both isotacticity and molecular weight on crystallization and melting behavior for highly isotactic (92 - 95%), high molecular weight polypropylenes. In the molecular weight range of $M_w=22,000 - 947,000$, isotacticity was the main parameter determining crystallization temperature, melting temperature, crystallinity, and crystallization rate in isothermal experiments; whereas, molecular weight had almost no effect on crystallinity and only a small influence on crystallization rate. In a related study (1), a noticeable effect of molecular weight (in the range 52,000-520,000) on linear growth rate in isotactic polypropylene was seen. At high supercoolings, a maximum in the growth rate occurs as a function of molecular weight. Janimak et al (114) found the Avrami index (n) to decrease with isotacticity at a constant ΔT for $\Delta T < 48K$ and noted this to be indicative of the influence of isotacticity on the three-dimensional development of crystal texture.

2.4 Isothermal Crystallization Kinetics

The kinetics of polymer crystallization are very complex and only partially understood. Many attempts at describing the phenomena of polymer crystallization have been made (4, 31, 43, 55), yet none fully explain all aspects pertaining to polymer crystallization successfully. Isothermal crystallization was studied initially

and later used as a basis for the development of nonisothermal crystallization theory. It is useful to present the isothermal kinetic theories first in order to properly explain the fundamental differences of the nonisothermal case.

Avrami Theory

The Avrami analysis (4) attempts to describe the kinetics of general phase changes. The original Avrami derivations have since been adapted to the needs of polymer science by Mandelkern (69), Evans (24), Meares (73), and Hay (39). The new derivations follow four basic assumptions. First, the crystals are assumed to be spherical in shape, a geometry which aids in the simplification of the mathematical description. Second, nucleation is assumed to be heterogeneous (the nuclei are predetermined). Third, randomly distributed centers in the melt act as nucleation sites. Fourth, the growth rate is assumed to be radially directed and constant.

Following the derivation for the Avrami equation according to the above assumptions (24, 39, 69, 73, 91), the mechanisms for crystallization can be broken down into two cases: heterogeneous and homogeneous. Both cases yield basically the same result for the crystallinity expression known as the Avrami equation:

$$\chi_t = 1 - \exp(-kt^n) \quad (2.7)$$

where n , called the Avrami index, relates the time dependence, and k is the rate constant dependent on both nucleation and growth. Both n and k are dependent on crystal geometry as well as the nucleation mode. The rate constant k can be evaluated using the half-time of crystallization based on $k = \frac{\ln 2}{(t_{1/2})^n}$, or as the initial slope of the plot of $\ln[-\ln(1 - \chi_t / \chi_\infty)]$ vs t^n . A plot of $\ln[-\ln(1 - \chi_t / \chi_\infty)]$ versus $\ln(t)$ is predicted to be linear theoretically, resulting in a slope of n and intercept of $\ln(k)$.

Some theoretical values of the Avrami index and the rate constant for different morphologies and nucleation modes are listed in Table 2.1.

Avrami theory has been shown to predict properly the increase in crystallinity exhibited in the early stage of phase transformation. This theory is founded on assumptions which are only partially valid for polymers. For example, the cessation of spherulitic growth occurs due to impingement and corresponds to the end of phase change in the case of inorganic materials; this is not the case for polymers. Polymeric spherulites continue to grow after impingement occurs (secondary crystallization). This secondary crystallization process proceeds during the growth of spherulites and continues after the cessation of spherulitic growth. As a result, Avrami theory fails to account for the more complex process of secondary crystallization that occurs for polymers toward the last stages of crystallization. Furthermore, the Avrami index, predicted to be an integer, is frequently a decimal number and is sometimes difficult to determine. The shape of the curves generated from the plot of $\ln[-\ln(1 - \chi_t / \chi_\infty)]$ versus $\ln(t)$ is not always a straight line as predicted. It is generally found that the lengthy crystallization times for polymer systems, along with the presence of a mixture of heterogeneous and homogeneous nucleation, is not accounted for by this theory.

Nucleation and Growth Theories

Several nucleation and growth theories have been developed based on classical nucleation theory to explain the kinetics of spherulitic growth which occurs in crystallizing polymers such as PP and PE. Classical nucleation theory accounts primarily for the formation of the primary nucleus, while the nucleation and growth theories account for both formation of the primary nucleus and its subsequent growth.

Table 2.1 Theoretical values of the Avrami index and the rate constant for different morphologies and nucleation modes .

Source: Elias, H. in Macromolecules, Plenum Press, N.Y. (1977).

Crystal Growth	Nucleation	Avrami index (n)	Rate constant (k)
Fibril	Heterogeneous	1	GAN^a
	Homogeneous	2	$GA/2\dot{N}$
Disc	Heterogeneous	2	$\pi G^2 D \dot{N}^b$
	Homogeneous	3	$\pi/3 G^2 \dot{N}$
Sphere	Heterogeneous	3	$4\pi/3 G^3 \dot{N}$
	Homogeneous	4	$\pi/3 G^3 \dot{N}$
Sheaf	Heterogeneous	5	-
	Homogeneous	6	-

a Constant cross section area A.

b Constant thickness D.

These theories provide useful information concerning the morphological changes of the crystalline phase during the crystallization process and are most beneficial when used in conjunction with crystallization kinetic theories.

Primary Nucleation

Classical nucleation theory (33) is based on one important assumption: there is a nucleation barrier caused by the crystal surface which can be overcome by fluctuations in the undercooled phase. Under isothermal conditions, Boltzmann's law can be applied to show the probability of the presence of a nucleus of critical size (constant volume and energy) is a function of the entropy change, ΔS , and is proportional to $\exp\left(\frac{-\Delta G}{kT}\right)$ for ΔG =free energy of crystallization.

Heterogeneous nucleation is more common than homogeneous nucleation in melt crystallized polymers due to the presence of preexisting foreign surfaces which act to enhance the rate of nucleation; this increase occurs as the free energy barrier of primary nucleation is decreased. For the case of heterogeneous nucleation, the number of nucleation sites is predetermined, causing the number of these nuclei to level off at a certain point as the sites are depleted.

The nucleation rate for the case of homogeneous nucleation has been defined in such a way as to show a rate dependence in terms of competing processes (99):

$$\dot{N} = \frac{IkT}{h} \exp\left(\frac{-E_{act}}{RT}\right) \exp\left(\frac{-\Delta W^*}{kT}\right) \quad (2.8)$$

where $\dot{N}$ = nucleation rate, I = number of nuclei, E_{act} = activation energy for transport the melt to a crystal site, R = the gas constant, K = Boltzmann's constant, and ΔW^* = free energy to form a crystal nucleus of critical size. Here, the driving force for nucleation (ΔW^*) is incorporated with the rate of molecular transport in the

melt (E_{act}); these are opposing forces since the former increases as temperature decreases, while the latter decreases as the temperature decreases. The result is an effective maximum in the nucleation rate at some temperature between the equilibrium melting temperature and the glass transition temperature; hence, the curve can be described to represent the driving force for nucleation to be small at high temperature conditions (resulting in a low nucleation rate), and the molecular mobility to control the nucleation rate at low temperature conditions (Figure 2.2).

Secondary Nucleation and Spherulite Growth Rates

Secondary nucleation theory predicts the growth rate and fold period of lamellae from the melt and single crystals from solution as a function of supercooling (ΔT). The crystallization kinetics of a polymer are influenced by the degree of supercooling. Hoffman (42) has described the growth rate of a polymer during crystallization for the case of an adjacent reentry model:

$$G = G_o \exp \left[\frac{-U^*}{R(T - T_\infty)} \right] \exp \left[\frac{-K_g}{T\Delta Tf} \right] \quad (2.9)$$

Here, G_o is the preexponential factor containing quantities not strongly temperature dependent, U^* the activation energy of chain motion (reptation) in the melt, R the gas constant, T the crystallization temperature, T_∞ the theoretical temperature at which all motion associated with viscous flow or reptation ceases. K_g is the nucleation rate

constant, defined as $K_g = \frac{Yb_o\sigma\sigma_eT_m^o}{k\Delta H_f}$. This equation for K_g will be discussed in

detail shortly. The values of T_∞ and U^* to be employed in equation 2.9 can be obtained by an estimation method given by Suzuki and Kovacs (95). One condition

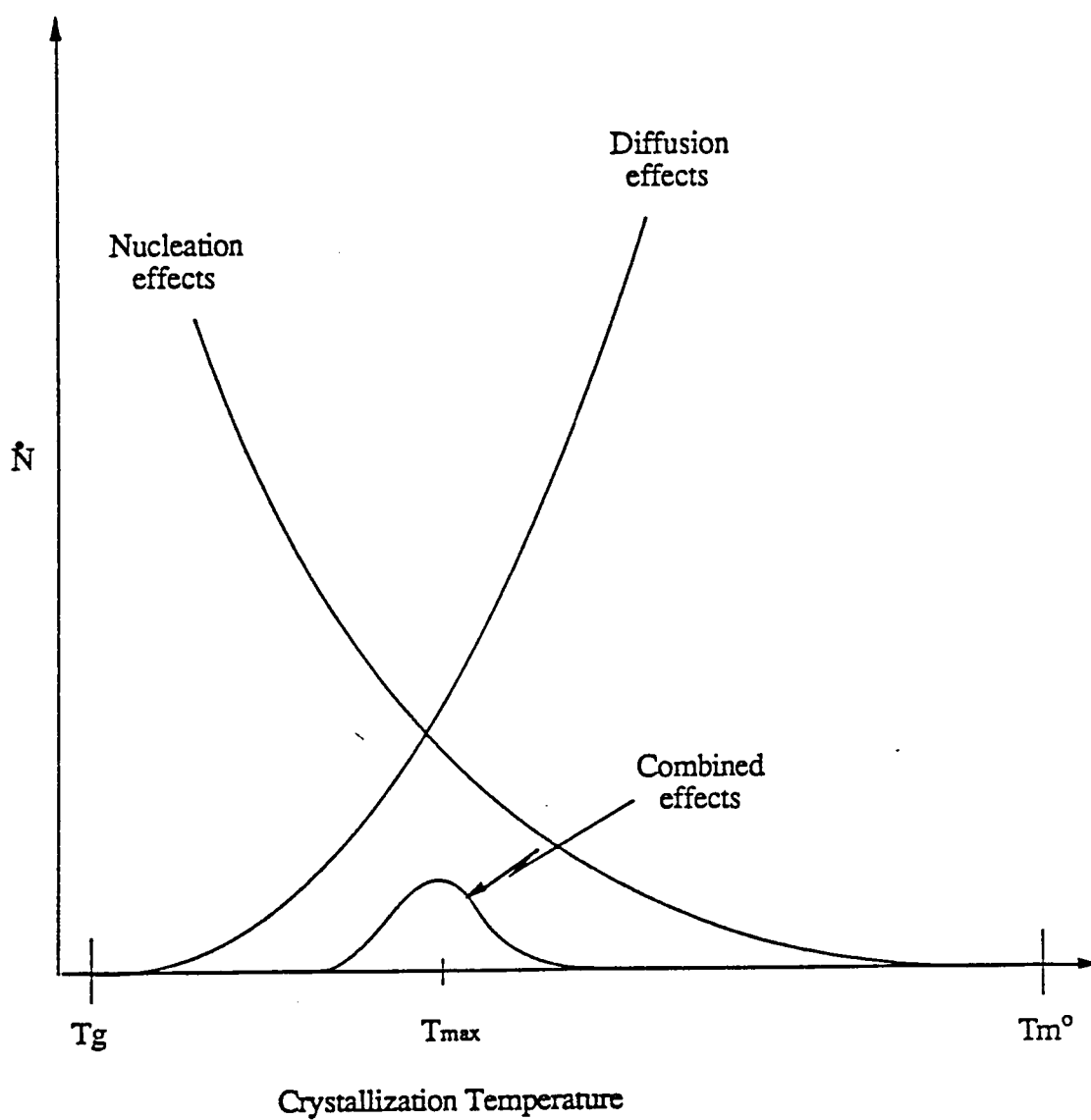


Figure 2.2. Schematic representation of the dependence of the nucleation rate on the crystallization temperature.

necessary to apply this method, however, is that the entire growth curve must already be defined; this condition proves to be a limitation in the case of materials which can crystallize rapidly and achieve a high degree of crystallinity, e.g. polypropylene and polyethylene. In the case of polypropylene, however, recent advances in the area of nonisothermal kinetics studies (21) have allowed further definition of the growth curve (although, it remains to be 100% defined).

Hoffman and Lauritzen (45) have developed a kinetic theory for low to moderate supercoolings. The concept of the sensitivity of the structure of the fold surface brought forth the proposal of Regime Theory. This theory describes the crystallization kinetics under the condition of low supercoolings as Regime I, while the kinetics for moderate supercoolings are described as Regime II. Single nucleation occurs in Regime I, and multiple nucleation occurs in Regime II. The theory was later expanded to include large supercooling behavior, or Regime III (42, 44). More specifically, the three regimes are distinguished by the relative rates of lateral growth of a layer of molecules and the rate at which new layers are formed. The idealized schematic model is shown in Figure 2.3.

The nuclei are deposited sporadically in time on the substrate at a rate i per unit length in Regime I; g is the rate of spread of these nuclei on either side of the surface nucleus and is much larger than i in this case. Hence, the result of further surface nucleation is the formation of a new layer (length L and thickness b_0) at the growth front prior to deposition of yet another new layer. This regime favors the model of regular adjacent reentry folding of lamellae.

Regime II is defined as $g \approx i$, relating similar magnitudes of the nuclei deposition rate and the spreading rate. Here, multiple surface nuclei are formed on the

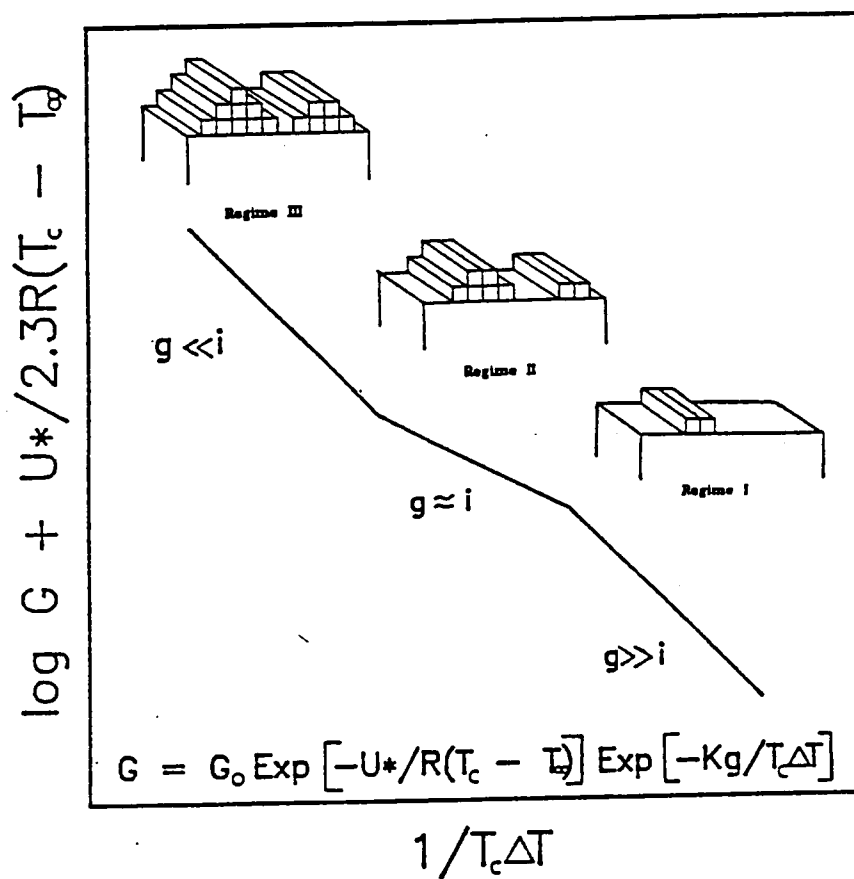


Figure 2.3. Schematic of Hoffman-Lauritzen crystallization regimes.

same surface, causing the surface to be uneven. The amount of disorder at the crystalline-amorphous interface is increased due to the presence of tie molecules which also form. This regime favors the switchboard model for lamellar folding.

Regime III is defined by the condition of $g \ll i$, or the deposition rate is much larger than the spreading rate. This limits the molecular chains to only a few folds prior to entering the amorphous phase. Either a switchboard type model can occur, where the chains reenter the same lamella, or they can reenter the next lamella. These tie molecules occur, similar to Regime II, but with a maximum amount of disorder at the crystalline-amorphous interface.

The previously defined quantity K_g is the nucleation constant and is indicative of the growth regime. The value Y used to determine K_g is typically 4 for the case of Regime I or III, or a value of 2 for Regime II. Two other parameters, σ and σ_e , account for the lateral surface and end surface free energy values, respectively. All other parameters have already been defined for the nucleation and growth equations presented. The utility of these relationships lies in a plot of $\ln G + U^*/R(T - T_\infty)$ vs. $1/T\Delta T f$ which predicts the same slope for Regimes I and III (displaced due to their respective temperature dependencies); the slope of Regime I and III is twice the value of the slope for Regime II, see Figure 2.3.

There has been much investigation into the spherulitic growth of isotactic polypropylene in terms of regime theory. Some conclusions based on experimental results are as follows. Hoffman and Clark (46) have found a transition from Regime II to Regime III near 137°C for an undercooling of $\Delta T \approx 48^\circ\text{C}$. The change in slope was 2.087. Furthermore, a vertical offset of the lines was observed and attributed to

effects of molecular weight and/or tacticity. Magill (67, 68) and Griffith (36) have reported results for polypropylene similar to those given by Hoffman and Clark. They have argued that the lower melt viscosity and fewer chain entanglements in lower molecular weight fraction allows greater chain mobility and a faster rate of crystallization.

Overall, the regime theory developed by Hoffman and Lauritzen has proven useful despite some limitations: it does not describe any fluctuations in crystal stem length or the effects of the crystal substrate, such as the finite size of the crystal face where deposition of the growth strip occurs.

2.5 Nonisothermal Crystallization Kinetics

Dilatometry, calorimetry, and microscopy can be used to obtain isotherms which can then be superimposed for different temperatures by shifting along the $\log(\text{time})$ axis (108). Plots of the change in relative crystallinity versus $\log(t/t^*)$ have been made by Nakamura et al (79). Here, t^* represents the time at which 50% crystallinity has been reached. As a result, it was found that the isotherms are superposable but only to approximately 70% crystallinity. It was concluded based on this information that the portions of the isotherms up to 70% are due to primary crystallization and hence can be described according to the Avrami equation. The part of the curve past 70% crystallinity must be due to secondary crystallization. Therefore, Nakamura et al (79) attempted to modify the Avrami equation accordingly.

They attempted to modify phase transformation theory for isothermal crystallization developed by Avrami (4) and Evans (24) to derive a fundamental expression of the nonisothermal process based on the isokinetic condition. This condition assumes that the characteristic kinetics of phase change remain unchanged

during crystallization. A basic assumption in this analysis is that crystal growth ceases when impingement occurs. The resulting equation given by Nakamura et al is as follows:

$$\chi(t) = 1 - \exp[-E(t)] \quad (2.10)$$

where

$$[E(t)] = \frac{\rho_c}{\rho_l} \left[\int_0^t N(\tau) v(t, \tau) d\tau \right] \quad (2.11)$$

Here, E is the total volume of growing grains if overlap is neglected, ρ_l and ρ_c the densities of the liquid and crystalline phases, respectively, $N(\tau)$ the nucleation rate at time τ , and v the volume at time t of a growing grain formed at time τ . An exact analysis of crystallization comes from the calculation of E regardless of whether the process is isothermal or nonisothermal. E can be easily obtained if the temperature dependence of nucleation rate and that of growth rate are found separately.

Two different approaches can be taken to reach a final equation for the transformed weight fraction:

$$\chi(t) = 1 - \exp \left[- \left(\int_0^t K(T) d\tau \right)^n \right] \quad (2.12)$$

where n is the Avrami index determined from isothermal crystallization data and $K(T)$ is related to the isothermal crystallization rate, $k(T)$, by $K(T) = k(T)^{1/n}$. The first approach follows a series of steps beginning with Avrami's description of nucleation rate for the analysis of equation 2.11: $N'(t) = v(t)N(t)$ where $v(t)$ is the probability of the formation of a growth nucleus per germ nucleus per unit time, and $N(t)$ the number of germ nuclei per unit volume at time t which decreases from the number of germ nuclei $\bar{N}$ per unit volume of the liquid phase prior to crystallization. To simplify the analysis, a characteristic time ξ was introduced after Avrami through the

transformation $\xi(t) = \int_0^t v(\tau) d\tau$. With the use of ξ , equation 2.11 yields a new expression for three-dimensional growth:

$$E(\xi) = \frac{\rho_c}{\rho_l} \left[\bar{N} \int_0^\xi \exp(-\xi') \sigma \left(\int_{\xi'}^\xi \frac{G}{v} du \right) d\xi' \right] \quad (2.13)$$

where $G(t)$ is the growth rate at time t , σ a shape factor equal to $4\pi/3$ for a sphere, and G/v a function of temperature. Next, equation 2.13 can be integrated, knowing that G/v is constant in isothermal crystallization, to obtain:

$$E(\xi) = 6 \left(\frac{\rho_c}{\rho_l} \right) \sigma \bar{N} \left(\frac{G}{v} \right)^3 \left(\exp(\xi) - 1 + \xi - \frac{\xi^2}{2!} + \frac{\xi^3}{3!} \right) \quad (2.14)$$

For the nonisothermal case, the description given by equation 2.13 remains the same, but the unit of measure of ξ in terms of the real time t is variable during the process; hence, this equation is a formal description of nonisothermal crystallization. As a result, the crystallinity-time relation in the nonisothermal crystallization can then be predicted from the isothermal data by calculating $\chi(t)$ in equation 2.12. The assumption of the isokinetic condition is not expected to hold true in all cases since very different factors are involved with the nucleation and growth processes; yet, the Avrami index will be more reliable since it is less sensitive to the change in G/v with temperature (79). Other assumptions used for the isokinetic condition include the following: (1) three-dimensional growth, (2) $\bar{N}$ is constant, (3) G/v is independent of temperature even though v and G change with external conditions (isokinetic), and (4) the final absolute crystallinity is independent of the cooling process.

Using the above assumptions, equations 2.10 and 2.14 can be used to express the characteristic kinetics of phase change in a nonisothermal process in terms of the characteristic time. This result leads to the transformed weight fraction written in a form similar to that given by Avrami for isothermal crystallization, already given as equation 2.12.

The second approach leans toward a better mathematical expression and is based on the following: (1) the existence of predetermined nucleation and sporadic nucleation simplifies the equation for three-dimensional growth, (2) a characteristic time similar to that used in the first approach is introduced, (3) G/μ is independent of time in isothermal crystallization, and (4) G/μ is independent of temperature. These guidelines lead to the same equation for the transformed weight fraction as the first approach, namely equation 2.12.

A different model for nonisothermal crystallization kinetics in which nonisothermal data can be treated directly was presented by Ozawa (85). This model follows two basic assumptions: (1) the heating or cooling rate of the amorphous polymer is constant, and (2) the derivation presented by Evans in 1945 is valid. Hammami (38) has derived an equation that describes nonisothermal crystallization based on the above assumptions:

$$1 - \frac{\chi_t}{\chi_\infty} = \exp \left[\frac{-\chi_c(T)}{|\xi|^n} \right] \quad (2.15)$$

where $\chi_c(T)$ is the cooling function of nonisothermal crystallization at temperature T , n an integer varying between 1 and 4, dependent on nucleation type and dimension of growth, and ξ the cooling rate. Manipulating equation 2.14 yields a new equation which can be used to generate a linear plot of $\ln \left[-\ln \left(1 - \frac{\chi_t}{\chi_\infty} \right) \right]$ versus $\ln(|\xi|)$, yielding a slope of n and an intercept of $\ln(\chi_c(T))$. The limitation of this theory includes the complications introduced by secondary crystallization, since the model only accounts for primary crystallization, i.e. the plots are linear for the early stages of crystallization but non-linear for the later stages. It cannot be applied in its present form to conditions in which the cooling rate changes with time.

Ziabicki (113) has modified the Avrami analysis for the needs of the nonisothermal process of melt-spinning. An equation has been derived based on the isothermal Avrami equation which assumes there is a first order rate of transformation from the amorphous phase to the crystalline one:

$$\frac{\chi_t}{\chi_\infty} = 1 - \exp\left[-\left(\int_0^t k(T)dt\right)\right] \quad (2.16)$$

$k(T)$ represents the isothermal rate constant. A second equation has been derived based on a new "kinetic crystallizability" parameter, defined as $\Gamma = \int_{T_s}^{T_m} k(T)dT$, where the cooling is $\xi = -\left|\frac{dT}{dt}\right|$:

$$\frac{\chi_t}{\chi_\infty} = 1 - \exp\left(-\frac{\Gamma}{\xi}\right) \quad (2.17)$$

A third approach to improving the Avrami analysis was given by Kamal and Chu (50) in which a fundamental nonisothermal equation was derived based on an approach by Hiller (41) in which secondary crystallization is assumed to be a slow first-order process relative to primary crystallization. A two stage model was proposed for the isothermal case:

$$\chi(c, t) = \chi(p, \infty)\{1 - \exp(-Z_p t^n)\} + \chi(s, \infty)\chi_s \int_0^t \{1 - \exp(-Z_p \theta^n)\}\{\exp(-Z_s(t - \theta))\}d\theta \quad (2.18)$$

where the subscripts p and s refer to primary and secondary, respectively, and $\chi(c, t)$ to the fractional crystallinity at time t .

Next, using the assumption that nonisothermal crystallization may be treated as a series of isothermal crystallization steps and that secondary crystallization is negligible, the equation for isothermal theory, $\chi(t) = \chi(\infty)\{1 - \exp(-Zt^n)\}$, can be modified to the following:

$$\chi(t) = \chi(\infty)\left\{1 - \exp\left(-\int_0^t Z(T(t))nt^{n-1}dt\right)\right\} \quad (2.19)$$

where $Z(T(t))$ is a function of temperature T , but not strictly of time t . Isothermal crystallization data may be used here to solve equation 2.19.

A fourth approach to improving the Avrami analysis was given by Khanna and Taylor (59, 60). This approach claims the rate constant k and activation energy E to both be functions of the index n and modifications to the relevant equation are made accordingly:

$$\frac{\chi(t)}{\chi_{\infty}} = 1 - \exp(-kt)^n \quad (2.20)$$

The consequence of this change appears to allow for correct predictions of k and E and comparisons of crystallization rates of systems with different n values while maintaining the original link of the Avrami equation to nucleation and growth mechanisms.

This method is proposed to be easier to apply to nonisothermal crystallization rates of polymers in a practical process. It takes into account the effects of both nucleation and growth in the overall crystallization rate which is reflected by the crystallization temperature T_c for controlled cooling (60). This method also introduces a CRC parameter, known as a crystallization rate coefficient. It represents the change in cooling rate β required to cause a 1°C change in supercooling and is given by:

$$CRC = \frac{\Delta\beta}{\Delta T_c} \quad (2.21)$$

This parameter was introduced to allow for direct comparison of crystallization rates of polymers on a single scale. It has been tested against and found to be in accordance with well-established trends. There is one problem with this parameter, namely its difficulty in distinguishing between two equal crystallization temperatures with different half-height peak widths as given by DSC crystallization curves.

A similar method to Khanna's approach was introduced most recently by Ma et al (112). Using DSC crystallization curves, three temperatures are recorded: T_{in} , T_c , and $T_{1/2}$, representative of the temperature where the graph first departs from the baseline, the temperature where the exotherm shows the peak, and the temperature at 50% under the peak, respectively. The half-crystallization time can be calculated as follows:

$$t_{1/2} = \frac{T_{in} - T_{1/2}}{\beta} \quad (2.22)$$

Here, $T_{1/2}$ may be replaced by T_c when the peak is symmetric and the difference between $T_{1/2}$ and T_c is negligible. Next, the CRP, or crystallization rate parameter, can be found by the slope of the line given by $\frac{1}{t_{1/2}}$ versus cooling rate. It is useful to

note here that the higher the crystallization rate is, the higher the resulting slope.

This method was applied successfully to compare PP-copolymers with PP homopolymers. The results showed decreased values of crystallization rates of the copolymers as opposed to the homopolymers due to (1) the relatively irregular molecular chain of the copolymer increasing the activation energy of homogeneous nucleation, and (2) the slower nucleation rate for copolymers than for homopolymers. These two methods given by Khanna and Ma and co-workers were both introduced to simplify the current methods of analysis, specifically applied to DSC crystallization curves.

The attempts to describe the nonisothermal process based on modified Avrami theory which have been presented thus far account for primary and secondary crystallization processes, either separately, regardless of whether or not the two occur consecutively or simultaneously, or by adding a term into the original crystallization rate equation to account for secondary crystallization. Results vary significantly

according to the approach and no single approach has been accepted as correct at this time.

Yet another approach to nonisothermal theory, given by Choe and Lee (17), stems from Tobin's theory of phase transition kinetics with growth site impingement (97, 98). This approach uses a linear combination of two terms concerning growth processes initiated by heterogeneous and homogeneous nucleation:

$$\begin{aligned} \alpha(t) &= \alpha_1(t) + \alpha_2(t) \quad (2.23) \\ &= \{k_1 * \exp[3E_d/RT] * \exp[-(3\psi_1 T_m^\circ)/T(T_m^\circ - T)] * \\ &\quad [1 - \alpha(t)]^2 * t^2\} + \{k_2 * \exp[-4E_d/RT] * [-(3\psi_1 + \psi_2)T_m^\circ / \\ &\quad T(T_m^\circ - T)] * [1 - \alpha(t)]^2 * \int_0^t \int_0^t (t-\omega)^2 * [1 - \alpha\omega]^2 d\omega\} \end{aligned}$$

where

$\alpha(t)$ - overall crystallization rate at time t

$\alpha_1(t)$ - crystallization rate contributed by growth process due to heterogeneous nucleation

$\alpha_2(t)$ - crystallization rate contributed by growth process due to homogeneous nucleation

E_d - diffusional activation energy of crystallizing segments across a phase boundary

ψ_1 - constant related to free energy of formation of critical nucleus on growing crystal surface

ψ_2 - constant related to free energy of formation of growth embryo in homogeneous nucleation

The constant k_1 is found by:

$$k_1 = 4 p N v_0^3 \quad (2.24)$$

where

k_1 - rate constant for $\alpha_1(t)$

N - number of effective nuclei

v_0 - univ. constant for semi-crystalline polymer = 7.5×10^8 mm/sec

Although a number of attempts have been made to analyze nonisothermal crystallization kinetics, it remains unclear as to which interpretation is most accurate. The majority of research undertaken thus far has dealt with relatively slow cooling rates, primarily related to DSC studies which can only obtain reasonable data for cooling rates less than or equal to $40^\circ\text{C}/\text{min}$ due to thermal gradients produced across the sample thickness and undesirably large deviations between the sample and program temperatures. Similarly, few light depolarizing microscopy (LDM) studies have been conducted for the nonisothermal case in order to follow crystallization during cooling. In some cases, a hot stage has been used for controlled sample cooling, yet the cooling rates failed to be constant for rates greater than $10^\circ\text{C}/\text{min}$ (37).

A newly developed technique for nonisothermal cooling has been introduced by Ding and Spruiell (21). This technique was developed based on LDM for the study of very high cooling rates (up to $2500^\circ\text{C}/\text{min}$). A description of the technique and method of analysis follows.

For typical dynamic nonisothermal conditions of polymer processing, the temperature of the cooling medium is kept constant, yielding a variable sample cooling rate. Such is the case for this technique. Thus, light intensity measurements corresponding to temperature measurements are recorded. A VCR technique may also be used to compare light intensity and temperature measurements to simultaneously recorded images of spherulites. Thus, growth rates can be directly measured.

Initially, the gas being used to heat and cool the polymer could not be accurately controlled and no quantitative measurement of the cooling rate could be obtained. A simplified heat transfer analysis was used to solve this problem:

$$V \frac{\rho C_p dT}{dt} = -AH_{ga}(T - T_s) \quad (2.25)$$

where ρ is the density, C_p the specific heat, V the volume of the polymer sample under the field of the microscope, A the area through which heat transfer occurs, and T_s the temperature of the cooling medium in the sample chamber. The definition of $1/H_{ga}$ is as follows:

$$1/H_{ga} = \frac{1}{\left(\frac{k_g}{l_g}\right) + 1/h_a} \quad (2.26)$$

where k_g is the thermal conductivity of the cover glass, l_g the cover glass thickness, $h_a = \frac{k_a}{l_a}$ the heat transfer coefficient of the air, k_a the thermal conductivity of air, and l_a the thickness of the air layer where the temperature is greater than T_s . This heat transfer equation can be solved based on the following assumptions: (1) k_g and k_a are constant for the cooling process, and (2) ρ and C_p are constant to the temperature before crystallization. The result is

$$T - T_s = (T_o - T_s) \exp\{-(CRF)t\} \quad (2.27)$$

where CRF is the cooling rate factor with units of 1/sec and equals $\frac{AH_{ga}}{V\rho C_p}$. CRF can

be calculated by direct regression of the experimental temperature curve and is used to describe the cooling rate.

Measurements of light intensities using the LDM technique are obtained simultaneously with and without the crossed polar analyzer. This accounts for the variation in light intensity due to a light scattering effect in which transmitted light intensity varies due indirectly to the crystalline fraction in the sample. This can be further explained in that there exists a direct relationship between the light intensity I

transmitted through the sample and analyzer and the sample thickness, l , the absolute crystallinity, X_t , and the incident light intensity I_0' . $I = AI_0'lX_c + I_z$ shows the proportionality of I_0' to the light intensity measured without an analyzer, I_0 , where A is a proportionality constant related to the effect of removing the analyzer, along with the geometric and optical sample quality. I_z accounts for any small amount of light that may leak through the crossed polars when there is no crystallinity in the sample. There also exists a linear relationship between I_z and I_0 :

$$I_z = R_o I_o + C_o \quad (2.28)$$

where C is a constant given by experimentation. The relative light intensity R , given by $R = \frac{(I - C)}{I_o}$, is obtained from $R = A l X_c + R_o$. Based on the relative light

intensity, the relative crystallinity can be obtained if the sample thickness is kept constant:

$$\theta = \frac{X_c}{(X_c)_\infty} = \frac{R - R_o}{R_\infty - R_o} \quad (2.29)$$

R_o is the value of R for $X_c=0$, while R_∞ and $(X_c)_\infty$ are the relative intensity and crystallinity for a sample at $t=\infty$, respectively. Neglecting secondary crystallization, the final crystallinity is theoretically equivalent to the crystallinity of the transformed solid material; thus, the relative crystallinity is equal to the fraction of transformed material.

This technique has been applied to isotactic polypropylene. It has been concluded that the CRF is an acceptable parameter for describing the cooling rate as seen by measured cooling curves for various rates. In each case, a plateau resulting from the heat of crystallization liberated during the crystallization process occurs after the initial temperature drop. The rate of temperature change is lower after the plateau due to smaller temperature differences between the polymer sample and the cooling

medium. A good fit to the measured temperature was obtained for each curve, indicating that CRF is useful in describing the cooling rate according to equation 2.25. The existence of the plateau temperature was explained by the rate of energy release during crystallization being higher than the rate at which energy is carried away by the cooling medium during crystallization.

Reduction in light intensities with and without the analyzer was found to occur due to the light scattering of the spherulites. This scattering is related to the size and number of spherulites present in the sample. It has been found that a small amount of background light leaks through crossed polars when viewing an isotropic melt, despite the fact that, ideally, no light should pass through. This problem is accounted for by I_z , representing the amount of light leaking through and given in equation 2.26.

An induction period was observed in plots of the relative light intensity, R , versus time. The curves showed the induction period to occur after the temperature was below the equilibrium melting point and before the onset of crystallization. This period was found to decrease with increasing cooling rate. Furthermore, the relative light intensity was found to be a function of the absolute crystallinity. Thus, it follows that the crystallinity decreases with increasing cooling rate, while the crystallization rate increases with increasing cooling rate.

From diameter measurements of spherulites plotted versus time, spherulite growth rates were shown to be constant during crystallization for a given cooling rate. The growth rate was found to increase with increasing cooling rate which corresponds to a decreasing plateau temperature. Due to the highly nonisothermal nature of this process, the spherulite growth region was found to be limited to a very short time interval; this interval was found to correspond to the appearance of the plateau in the

cooling curve and the region in which a dramatic increase in bulk crystallinity was seen. One last result was the reduction in light intensity at an early stage of crystallization being indicative of the production of a large number of nuclei during crystallization at high cooling rates.

CHAPTER 3

EXPERIMENTAL

3.1 Resin Identification and Characterization

The materials used for this study were six polypropylene (PP) resins provided by the Exxon Chemical Company. These samples included a high tacticity PP (HT-PP), low tacticity PP (LT-PP), three PP-Et copolymers containing 1.5%, 3%, and 5% Ethylene, respectively, and a median isotactic homopolymer (MT-PP) used for comparisons. Sample characterization data including MFR, ethylene content given by FTIR, number and weight average molecular weights, and polydispersity are listed in Table 3.1.

3.2 Experimental Procedure

Sample Preparation

All samples were studied in their as-received condition; in some cases, xylene-purified polymer was also studied for comparison. This purification process involved dissolution of the polymer in xylene, followed by precipitation in methanol and subsequent washing; the polymer was vacuum-filtered and dried in a vacuum oven at 80°C for a minimum of twenty-four hours. This process yielded polymer in the form of powder.

Each sample was prepared using a Mettler FP 82 hot stage controlled by a Mettler FP 80 programmable controller. A single pellet was melt-pressed into a thin film between two cover glasses (Figure 3.1). The purified polymer was pressed into a thin film directly from its powder form. Film thicknesses of both 150 μm and 50

Table 3.1. As-received polypropylene resin properties**.

UT Code	MFR	FTIR % Ethylene	Mn (by GPC)	Mw (by GPC)	Polydispersity (=Mw/Mn)
LT-PP	37	0	54,867	134,841	2.46
HT-PP	36	0	59,010	131,128	2.22
MT-PP	35	0	60,330	143,825	2.38
1.5% RCP	35	1.4	49,214	158,590	3.22
3% RCP	35.4	3.0*	61,549	142,160	2.31
5% RCP	31	4.9	66,474	150,114	2.26

**This value for percent ethylene was determined at UTK.

* All resin characterizations reported in this table were performed by Exxon Chemical Co. and results released to UTK.

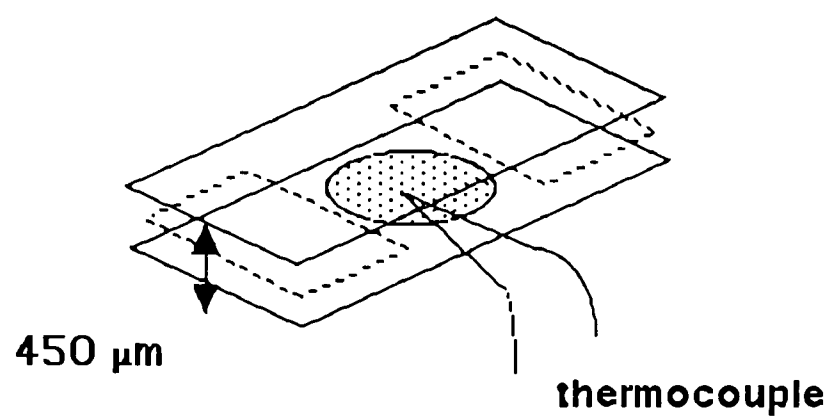


Figure 3.1. Sample configuration for LDM studies.

μm were prepared. An iron-constantan thermocouple was inserted directly into each sample. Thermocouples of diameter=76.2 μm were used in conjunction with the 150 μm thick samples, while thermocouples of diameter=25.4 μm were inserted in each 50 μm film. In all cases, the polymer film was sandwiched between two 150 μm thick cover glasses.

Spacers were also placed between the cover glasses in order to aid in uniform pressing across the sample. The spacers used for pressing the 150 μm thick samples were glass coverslips, also of 150 μm thickness; however, capton film of thickness=30 μm functioned as spacers in the preparation of the 50 μm samples.

Nonisothermal Crystallization

The crystallization kinetics of polypropylene under nonisothermal conditions were investigated by the use of two techniques, namely Light Depolarizing Microscopy (LDM) and Differential Scanning Calorimetry (DSC). LDM was utilized to define a range of very high cooling rates (150-4000°C/min), while DSC served to define the low cooling rate range (5-40°C/min).

Light Depolarizing Microscopy

A schematic of the experimental set-up is shown in Figure 3.2. A special sample chamber was mounted securely on the stage of an Olympus BH2 optical

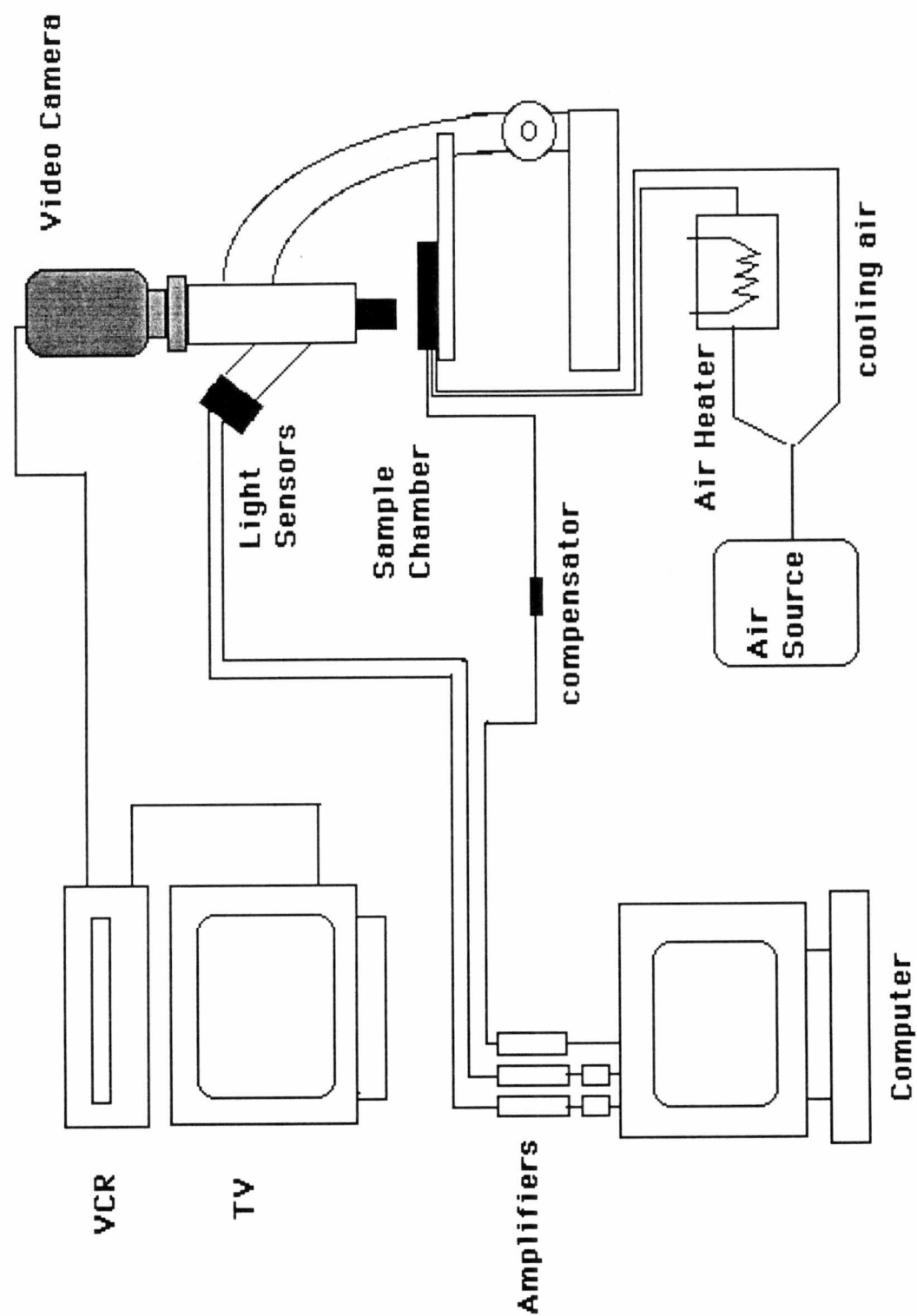


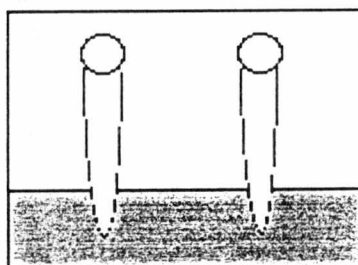
Figure 3.2. Experimental set-up for nonisothermal studies using the LDM technique.

microscope equipped with cross polars. Temperature measurements were obtained from the thermocouple embedded in the sample.

The 25.4 μm thermocouples posed a physical problem: standard thermocouple plugs and sleeving could not be used with these thermocouples due to their extremely delicate nature. This was resolved by locally insulating the 25.4 μm thermocouple at the point where the thermocouple exited the metal sample chamber and setting up a junction point to connect to a thicker (76.2 μm), insulated thermocouple. This junction was achieved through the use of alligator clips and Bakelite, as shown in Figure 3.3, where the two different thermocouple wires (25.4 μm and 76.2 μm) were laid across one another and pinched together. This junction was elevated to a height even with the stage height of the microscope due to constraints given by the thermocouple lengths (12 inches).

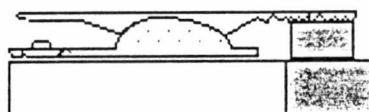
Light sensors replaced the eyepieces and were connected to an IBM personal computer in order to obtain light intensity measurements corresponding to temperature measurements during the crystallization process. Measurements were obtained simultaneously with and without the crossed polar analyzer to account for the variation in light intensity due to a light scattering effect in which transmitted light intensity varies due indirectly to the crystalline fraction in the sample. For each experiment, the intensity of the light source was controlled at a particular level given by a calibration technique. This level corresponded to a power reading of 8.7 Volts on the OPTI QUIP model 2100 DC power source. The DC power source replaced the original Olympus power source in order to minimize noise in the system.

Top View



Side View

Half of
Alligator Clip



Insulation

Figure 3.3. Thermocouple junction set-up for use of 1 mil thermocouples.

Heating and cooling of the sample was controlled by a series of flow meters connecting the air source (Nitrogen gas) to the sample chamber. The sample was heated and cooled by gas (air) flowing into the sample chamber directly from both sides. A three-way solenoid valve controlled the flow of air, directing it to either the cooling line or to the heating line, where a heat exchanger elevated the temperature to the desired point. The heating gas was turned off once the desired temperature was reached (and the sample was fully melted); the temperature used for polypropylene was approximately 205°. At this time, the cooling gas (room temperature) was turned on and data collection began automatically at 190°C.

A VCR technique was used to compare light intensity and temperature measurements to simultaneously recorded images of spherulites. Thus, growth rates could be directly measured. This technique allowed sufficient time resolution for cooling rates up to 2500°C/min since 60 frames of images per second could be obtained.

The iron-constantan thermocouples provided sufficient response time for the temperature range of interest. The 76.2 μm thermocouple had a response time of 0.08 seconds to detect a change from 426.7°C to 37.8°C, while the 25.4 μm thermocouple could detect the same change in only 0.05 seconds. This response time was acceptable since there was only a need to detect a temperature change of 165°C in a minimum of 1-2 seconds depending on cooling rate. Both the 76.2 and 25.4 μm thermocouples were calibrated against a standardized thermocouple. The calibration

curve is shown in Figure 3.4. The thermocouples were found to be accurate within 1.1°C.

Data were obtained for cooling rates of approximately 125°, 800°, 1900°, 2400°, and 4000°C/min, although other rates in this range were also obtained due to limitations of the control of air flow. All data was modified according to the appropriate light scattering coefficient; the necessity of and process for determining these coefficients is outlined next.

It was necessary to determine a correction factor for an observed light scattering effect (21). This scattering was due to the high nucleation density and small crystal size present under high cooling rate conditions. It is necessary to introduce some equations to fully describe the process of determining this light scattering constant. First, $I'_o = I_o - I_s$ defines the relationship between I'_o (the intensity of the light source), I_o (the experimental light intensity measured without the analyzer), and I_s (the light intensity due to scattering). This equation can be rearranged based on the assumption that the reduction of light intensity (due to the scattering) measured under constant I_o is equal to the reduction caused by a variation of I_o without the scattering:

$$I = I'_o(l_d f^* X_c + R_o) + C \quad (3.1)$$

Here, I = light intensity transmitted through the sample and analyzer, l_d = sample thickness, X_c = crystallinity, R_o = relative light intensity for $X_c=0$, and C = constant given by experimentation. This can be simplified to

$$I = (\text{constant})I'_o + C \quad (3.2)$$

if sample thickness, crystallinity, and orientation are fixed. Thus, there exists a linear relationship between I and I'_o which can be used to determine C .

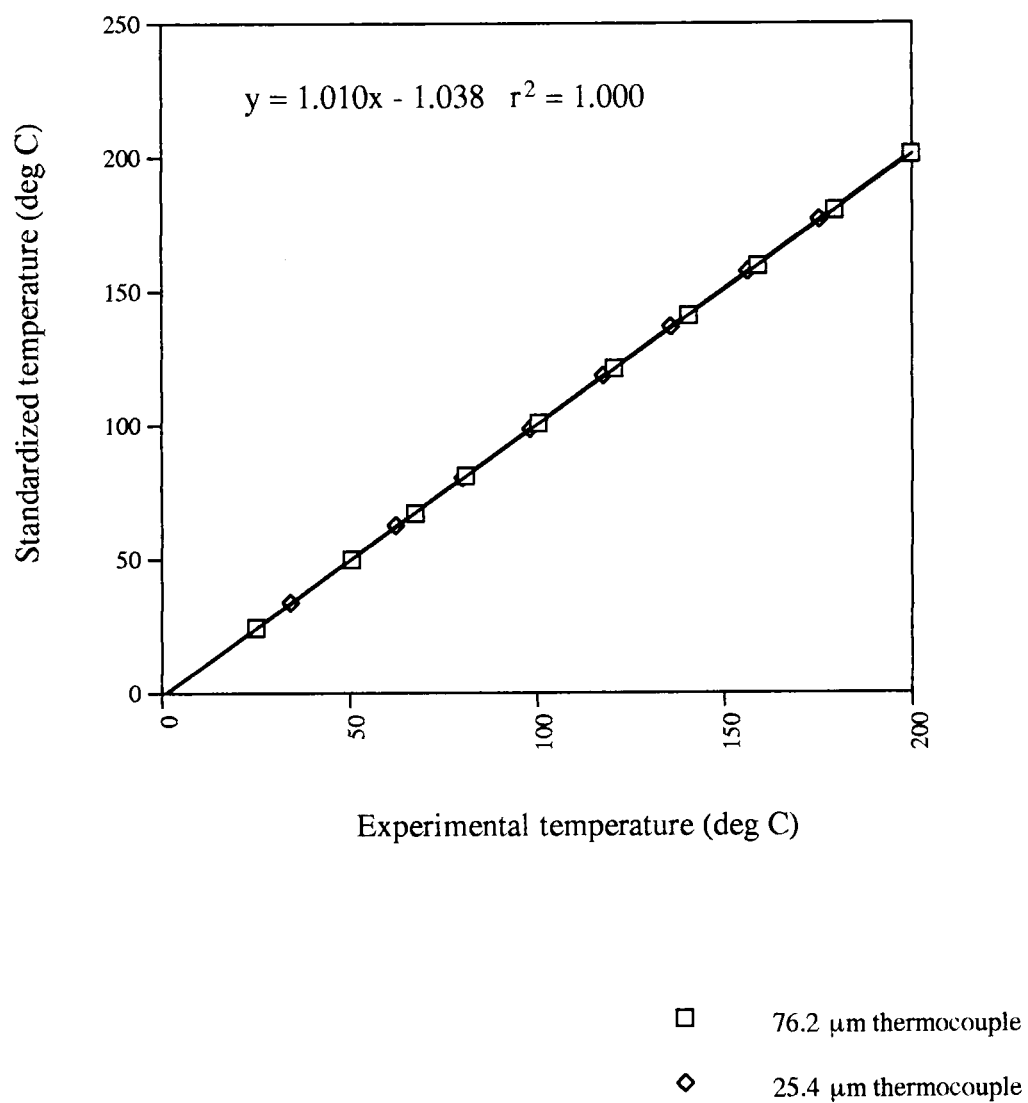


Figure 3.4. Calibration curve for experimental thermocouples against a standardized thermocouple.

The procedure for obtaining C was set forth by Ding and Spruiell (21) when it was applied to polypropylene homopolymers. This process involved measuring I and I_o' values at different levels of intensity of the light source for a series of samples of one polymer type but varied degrees of crystallinity. The data were plotted, regressed, and the intercepts (excluding the glass sample) were averaged (Figure 3.5); this average was the light scattering constant C .

The value determined by Ding for polypropylene homopolymers ($7.8773e^{-2}$) was utilized in this investigation to correct data for MT-PP, HT-PP and LT-PP, and 1.5% RCP (random copolymer) samples. The constant successfully corrected curves for the 1.5% RCP due to the small amount of ethylene incorporated having a similar scattering effect to the homopolymers, but was unsuccessful in the case of the 3% and 5% RCP. Therefore, the same procedure for determining the new scattering coefficient was performed for the 3% RCP (Figure 3.6). This constant, $8.141e^{-3}$, was used to correct data for the 3% and 5% RCP. An example of this correction is shown in Figure 3.7. The effect of scattering was removed from the relationship between R and l_d , f^* , and X_c by rearranging equation 3.1 and defining the left side as R :

$$R = \frac{I - C}{I_o'} = l_d f^* X_c + R_o \quad (3.3)$$

The result of correcting for this effect was a quantity R that is proportional to the crystallinity at any point in the crystallization process. This quantity is desired for further analysis of the crystallization kinetics.

Once the data was modified according to the appropriate light scattering constant, it was formatted for further treatment in Excel 5.0. Avrami theory was applied for data analysis once cooling rates were determined.

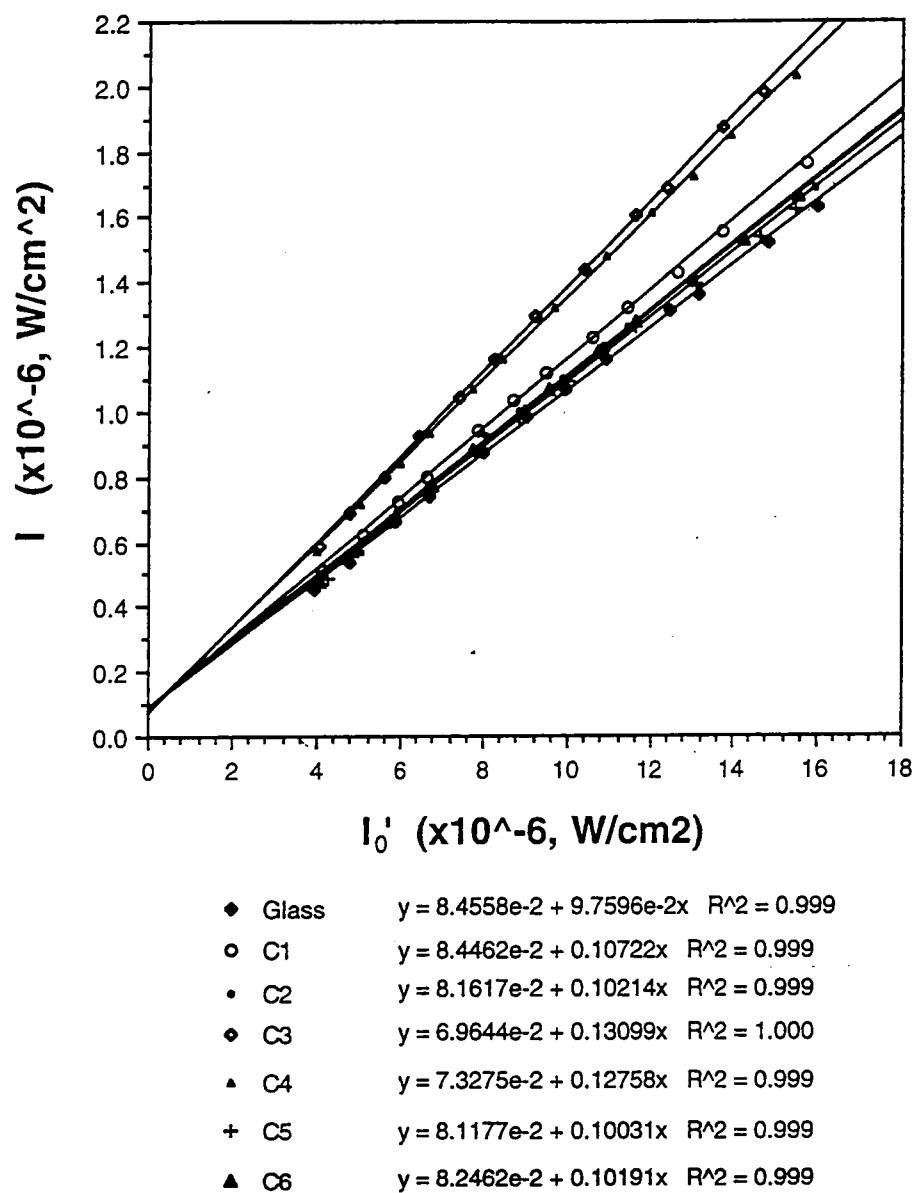
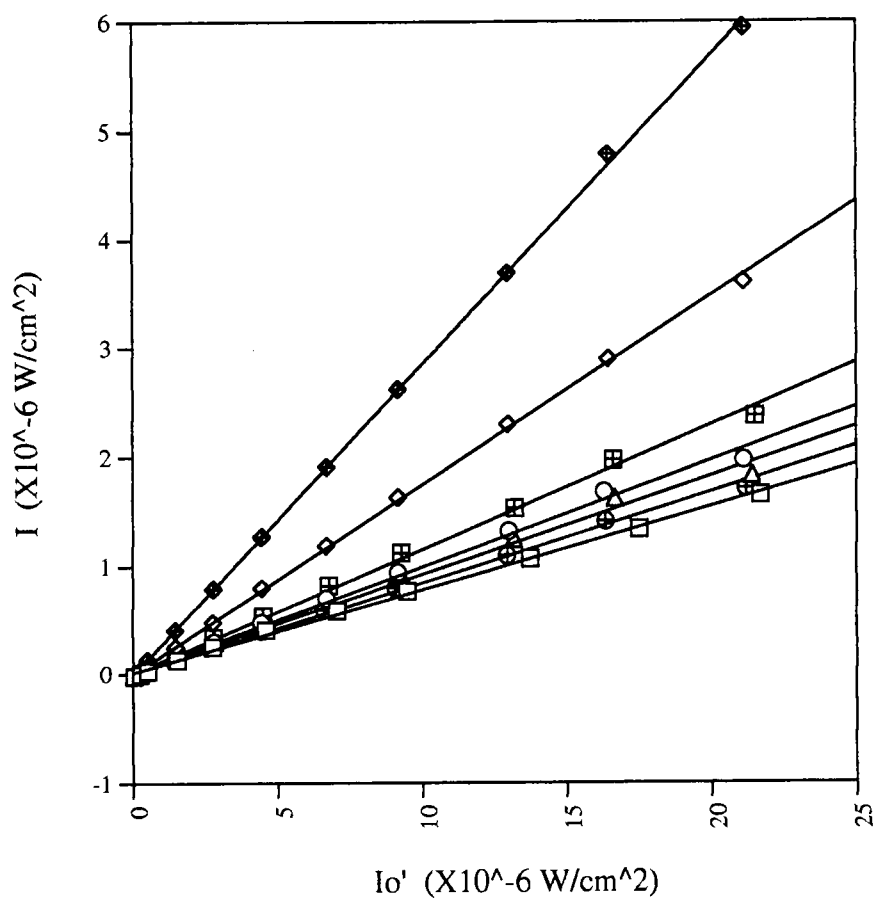


Figure 3.5. Light intensity (I) as a function of light intensity without analyzer (I_0') for PP homopolymers according to Ding (22).



$y = 0.077x + 0.014$	$r^2 = 0.997$	□	Glass
$y = 0.174x + 0.001$	$r^2 = 0.999$	◇	C1
$y = 0.098x + 0.013$	$r^2 = 0.995$	○	C2
$y = 0.090x + 0.018$	$r^2 = 0.992$	△	C3
$y = 0.114x + 0.009$	$r^2 = 0.997$	⊠	C4
$y = 0.286x - 0.009$	$r^2 = 1.000$	◆	C5
$y = 0.083x + 0.011$	$r^2 = 0.997$	⊕	C6

Figure 3.6. Light intensity, I , as a function of light intensity without analyzer, I_o' , for 3% RCP.

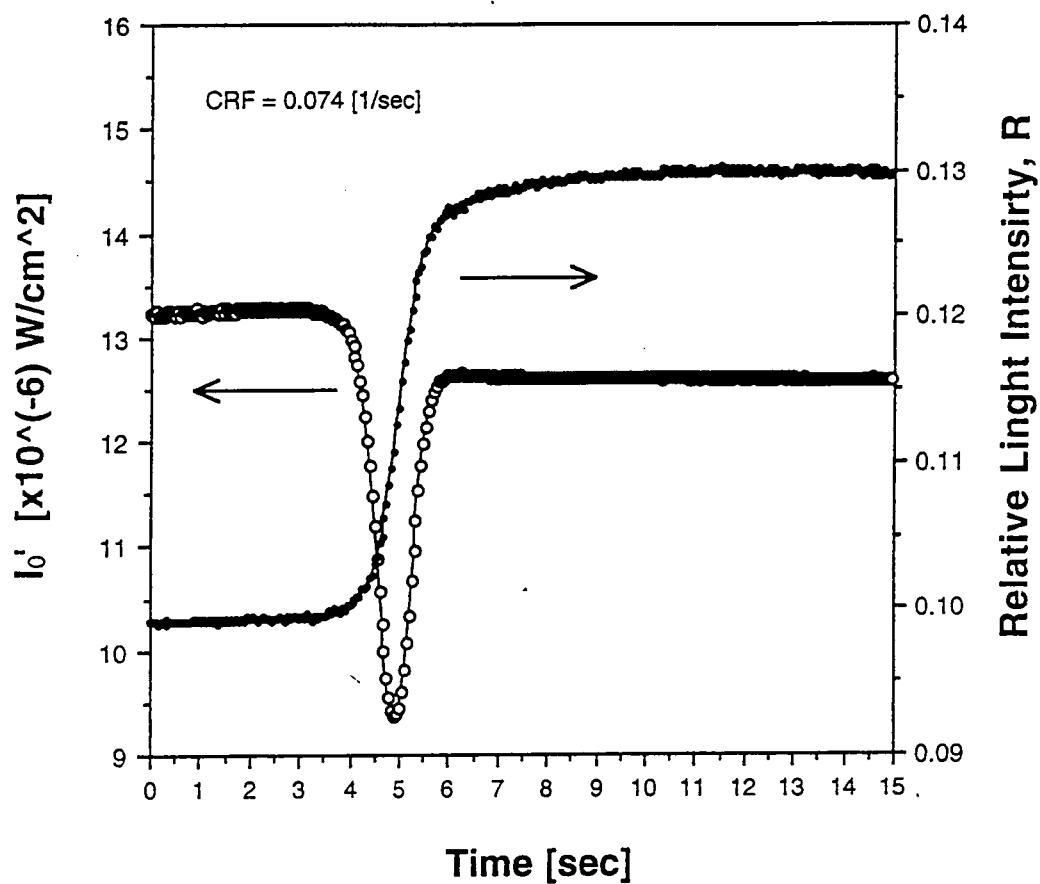


Figure 3.7. Changes in relative light intensity and light intensity (measured without the analyzer) with time as measured during the cooling process by LDM.

Differential Scanning Calorimetry

A Perkin-Elmer Series 7 Thermal Analysis Differential calorimeter was used to study the nonisothermal kinetics of both the as-received and xylene-purified resins. The DSC7 was connected to a Perkin-Elmer 7500 Professional Computer through a TAS7 Instrument Controller. The DSC7 calorimeter was calibrated for temperature using a pure indium standard ($T_m^\circ = 156.60^\circ\text{C}$) according to the procedure described in the user's manual.

Slices of the polymer pellets were cut and weighed for obtaining DSC data for the as-received samples. The xylene-purified polymer was weighed directly in its powder form and subsequently analyzed. This procedure aided in minimizing the introduction of contaminants. Sample weights in the range of 4 - 8 mg were used. Melting temperatures were obtained for each material by heating at a rate of $40^\circ\text{C}/\text{min}$ from 40°C to 200°C in every case. The sample was then held isothermally at 200°C for 3 minutes, and finally cooled back to 40°C at a constant cooling rate under the flow of dry nitrogen. Crystallization data were obtained for cooling rates of 5, 10, 20, and $40^\circ\text{C}/\text{min}$. The crystallization data were converted directly into DOS format and analyzed in Excel 5.0.

Density

A Density Gradient Column (DGC) was prepared using isopropanol and ethylene glycol to produce a density gradient covering a range of $0.85 - 0.95 \text{ g}/\text{cm}^3$. The preparation and procedure was given by Wust (109). The equation defining the

calibration curve for the column yielded an r-squared value of 0.99, indicating a nearly linear fit.

Samples were melt-pressed and cooled at rates of 125°, 800°, 1900°, 2400°, and 4000°C/min. The films were removed from the glass slides, cut into various shapes, and placed in the DGC. A minimum of twenty-four hours was allowed for equilibration of the samples in the column. Sample positions were recorded for density determinations, and hence absolute crystallinity values were obtained.

Infrared Spectroscopy

Melt-pressed films were prepared to do tacticity estimations by Fourier Transform Infrared Spectroscopy (FTIR). Spectra were obtained for all samples, and areas of the 995 and 974 cm^{-1} absorption bands were determined. A ratio of these areas was taken in each case (974/995 cm^{-1}) and tacticity estimations were made according to a calibration curve of peak areas versus known tacticity values of some of the homopolymers.

Purified samples to be studied by FTIR were prepared by the following steps. The purification process previously described was performed for the 1.5% and 5% RCP, the HT-PP, and the MT-PP. After the process was completed, the volume of the residual xylene solution was decreased by approximately seven-fold by evaporation in order to concentrate the solution. The concentrated solutions were analyzed by an FTS-40 Infrared Spectrometer by placing several drops of solution on a KBr plate and evaporating off the solvent. The region of 4000 - 400 cm^{-1} was examined.

Further studies were conducted of the traces of residual solids upon complete evaporation of these solutions. Solids were obtained for the HT-PP and the MT-PP only, since the concentrations of the other solutions were slightly lower and yielded no trace solids. Analysis of these solids was achieved through use of the microscope attachment to the FTS-40 which allows analysis of minute quantities of sample. The region of $4000 - 700 \text{ cm}^{-1}$ was examined in this case.

X-ray Diffraction

X-ray film patterns were generated by a pin-hole technique using $\text{Cu K}\alpha$ radiation. Sample preparation included melt-pressing two films (thickness = $50 \text{ }\mu\text{m}$) of each polypropylene, cooling one at a low cooling rate (approximately $850^\circ\text{C}/\text{min}$) and one at a high cooling rate (approximately $4000^\circ\text{C}/\text{min}$). One sample of MT-PP was also prepared at an even higher cooling rate: about $7000^\circ\text{C}/\text{min}$. Each film was removed from between the glass slides and cut into three rectangular pieces which were stacked together, yielding a sample thickness of $150 \text{ }\mu\text{m}$. The exposure time employed was 4 hours.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Further Sample Characterization

Isotacticity by FTIR

Infrared spectroscopy has been utilized in the characterization of isotactic polypropylene and polypropylene copolymers in terms of crystallinity (105), sequence distributions (11), stereoregularity (62), copolymer composition (93), and additive and impurity content (66). Nuclear Magnetic Resonance (NMR) is the most commonly utilized technique for tacticity determinations, however information from NMR was unavailable for the present study; thus, Fourier Transform Infrared Spectroscopy (FTIR) was used to estimate the percent isotactic content in all resins.

FTIR has been used as a technique for estimating tacticity in polypropylene by Luongo (66). The basic assumption employed in this method is that polypropylene consists of an isotactic phase which is mostly crystalline and an atactic phase which is considered to be primarily amorphous. The areas of the absorption bands occurring at 995 and 974 cm^{-1} , corresponding to 100% isotactic and 100% atactic material, respectively, are taken as a ratio (974/995 cm^{-1}) to estimate the percent isotactic or atactic phase present. Luongo has estimated the accuracy of this method to be $\pm 2\%$.

This method was applied to estimate changes in isotacticity in the polypropylene resins for the present research. A calibration curve was constructed using the experimental ratios for the HT-PP, LT-PP, and a theoretical 100% isotactic sample (Figure 4.1). The values for percent isotacticity for the HT-PP and the LT-PP were given by the Exxon Chemical Company in terms of percent heptane insolubles

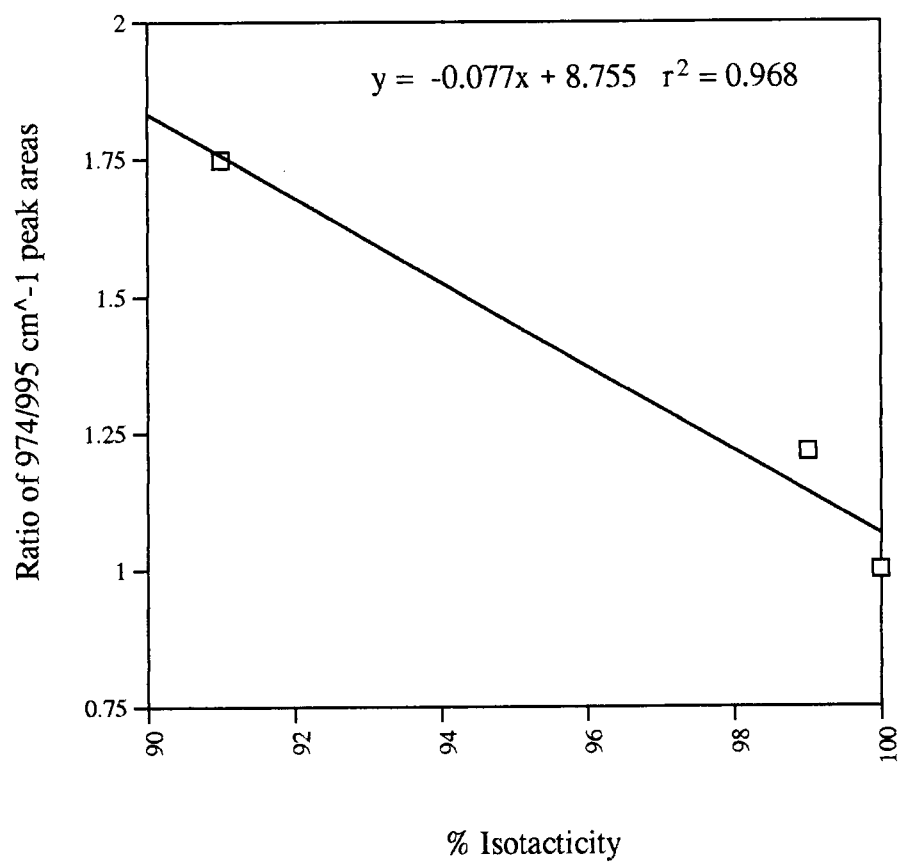


Figure 4.1. Calibration curve for determining isotacticity of homopolymers by FTIR.

and were used to calibrate the remaining results. Table 4.1 gives the experimental ratios of the peak areas for all samples and the corresponding estimated percent isotacticity. The MT-PP had an isotactic content between that of the HT-PP and LT-PP, and the copolymers were found to have relatively high isotactic contents (92-96%). Note that by this method, the isotacticity decreases with copolymer content, but the copolymer tacticity values are in the same range as the homopolymers.

Comonomer Content by FTIR

A method of determining copolymer composition for polypropylene-ethylene copolymers using FTIR has been described by Skaare et al (93). This method was used to quantify the percent ethylene content for the 3% RCP.

A polyethylene doublet occurs at 730 and 720 cm^{-1} , assigned as a CH_2 rock, in a PP-PE copolymer. The area of this doublet is ratioed against the area of the polypropylene band occurring at 900 cm^{-1} . Since the areas of the absorption bands are used, it is not necessary to consider the band splitting occurring for the PE peak as a factor that influences the end result. This is due to the band areas being more significant in representing vibrational intensities than peak heights, since the band areas are fairly independent of spectral resolution, band asymmetry, and band splitting (93).

The PE/PP band ratio is plotted against $1/X_{\text{pp}}$ where X_{pp} is the mole fraction of PP. Thus, the calibration curve was constructed in this manner using known values of ethylene content given by the Exxon Chemical Co. (also by FTIR) for the 1.5% RCP and 5% RCP, along with a 2.6% sample which was also available for the purposes of calibration (Figure 4.2). The resulting value determined for the 3% RCP was found to be 3.0% ethylene.

Table 4.1. Determinations of % isotactic PP given by FTIR.

Sample	Ratio of Peak Areas (974/995 cm ⁻¹)	Calculated % Isotactic PP
HT-PP*	1.215	99
MT-PP	1.581	93
LT-PP*	1.749	91
1.5% RCP	1.386	96
3% RCP	1.510	94
5% RCP	1.698	92

*Values for % Isotactic PP were given by the Exxon Chemical Company in terms of percent heptane insolubles. They were used to calibrate the remaining results.

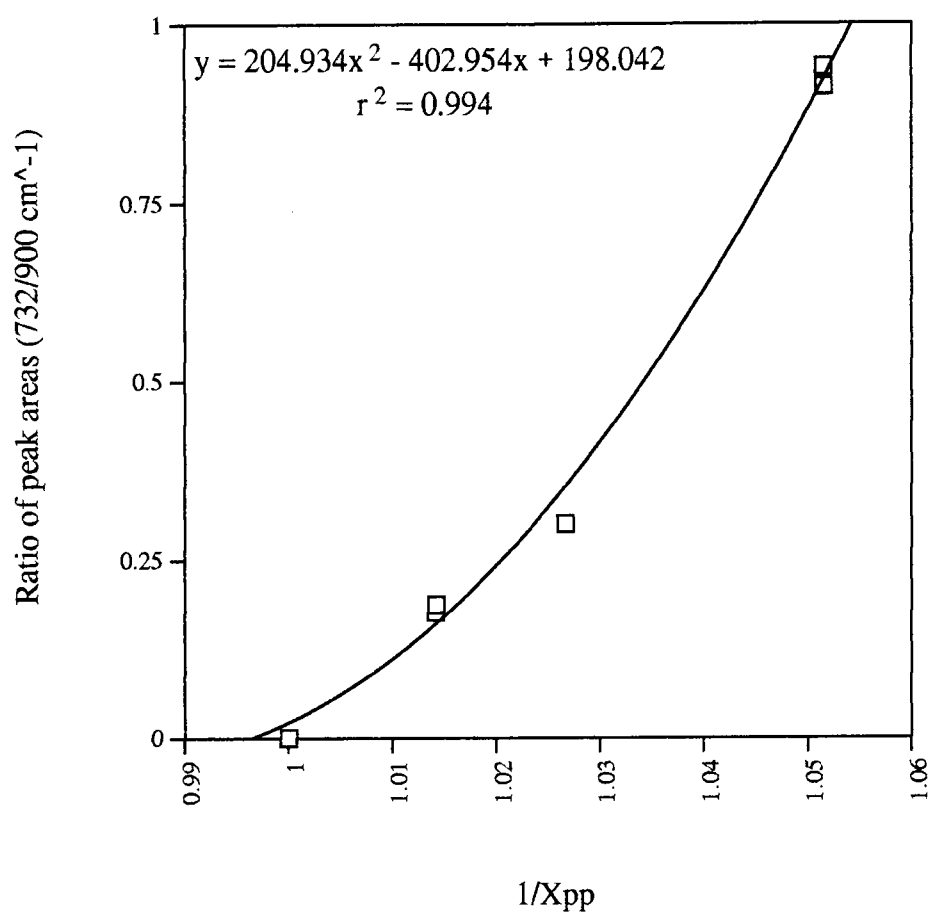


Figure 4.2. Calibration curve for comonomer content given by FTIR.
(X_{pp}=the mole fraction of PP in the copolymers).

Melting

DSC was utilized for the study of melting behavior of the polypropylenes. The melting temperature, T_m , values were acquired at a heating rate of 20°C/min and are listed in Table 4.2. The T_m values increased with increasing isotacticity (from low to high) for both the homopolymers and the copolymers (Figure 4.3). The comonomer content was also a factor affecting the melting trend. The T_m decreased with increasing ethylene content (Figure 4.4); furthermore, all copolymers melted at temperatures below those given by the homopolymers. Thus, the 1.5% RCP melted at a lower temperature than the three homopolymers, followed by the 3% RCP and 5% RCP which melted at increasingly lower temperatures. According to these data, the tacticity and ethylene content both play a fairly independent role in influencing the melting behavior. In the case of the copolymers, these two parameters are complementary: decreasing isotacticity and increasing ethylene content both function to lower the melting temperature.

Crystallization Behavior given by DSC

Crystallization data were acquired by DSC for cooling rates of 5, 10, 20, and 40°C/min. The crystallization temperature, T_c , is plotted versus cooling rate in Figure 4.5. The HT-PP crystallized at the highest temperatures over the range of cooling rates studied. The overall homopolymer trend, however, was seen to be:

$$\text{HT-PP} > \text{LT-PP} > \text{MT-PP}$$

$$T_c \text{ decreasing} \rightarrow$$

Table 4.2. Melting temperature data given by DSC
for a heating rate of 20 degC/min.

Sample	Melting Temperature (deg C)
HT-PP	166.9
LT-PP	160.5
MT-PP	165.0
1.5% RCP	154.3
3% RCP	143.7
5% RCP	132.2

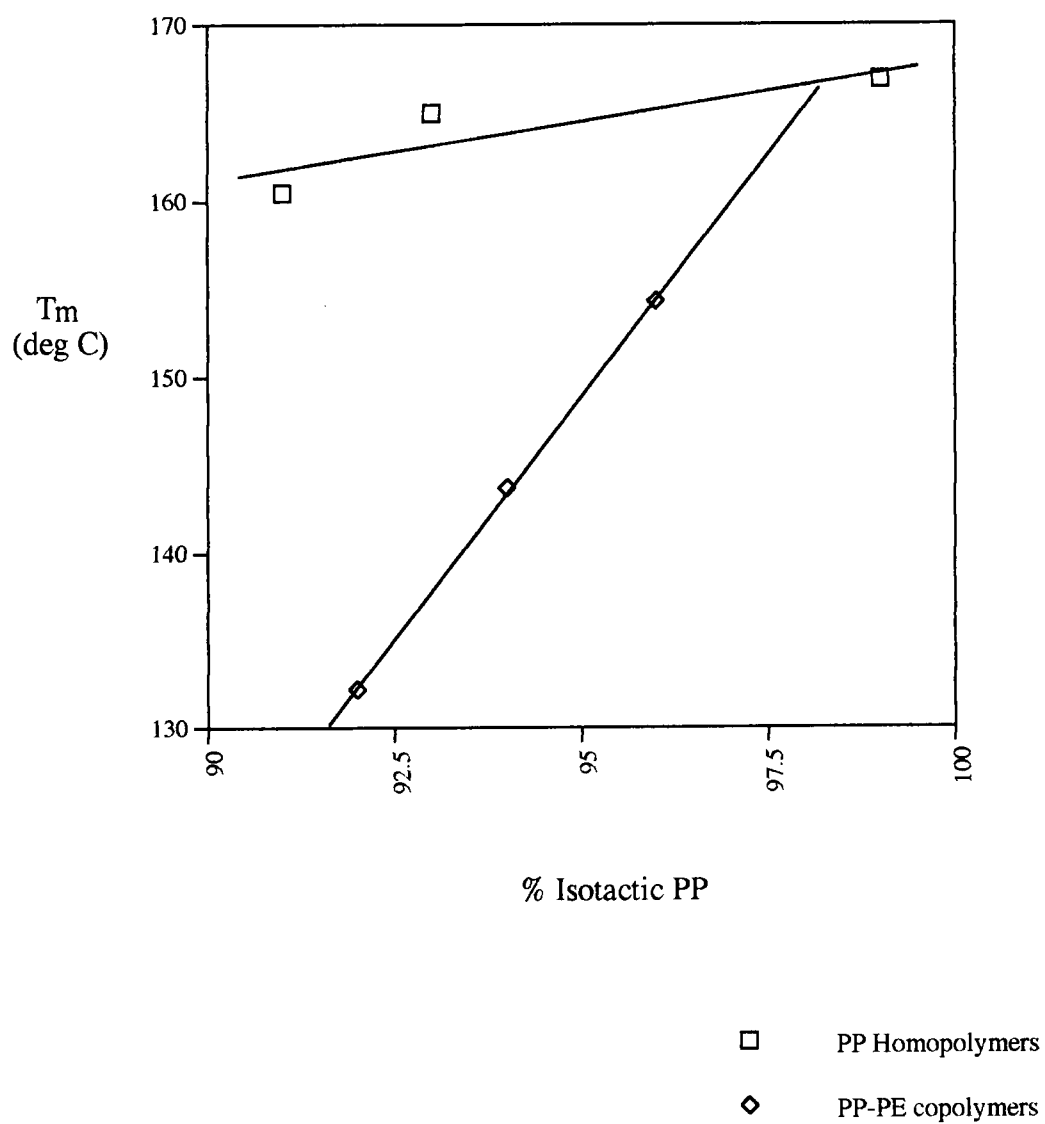


Figure 4.3. Melting temperature vs percent isotactic PP in both homopolymers and ethylene copolymers.

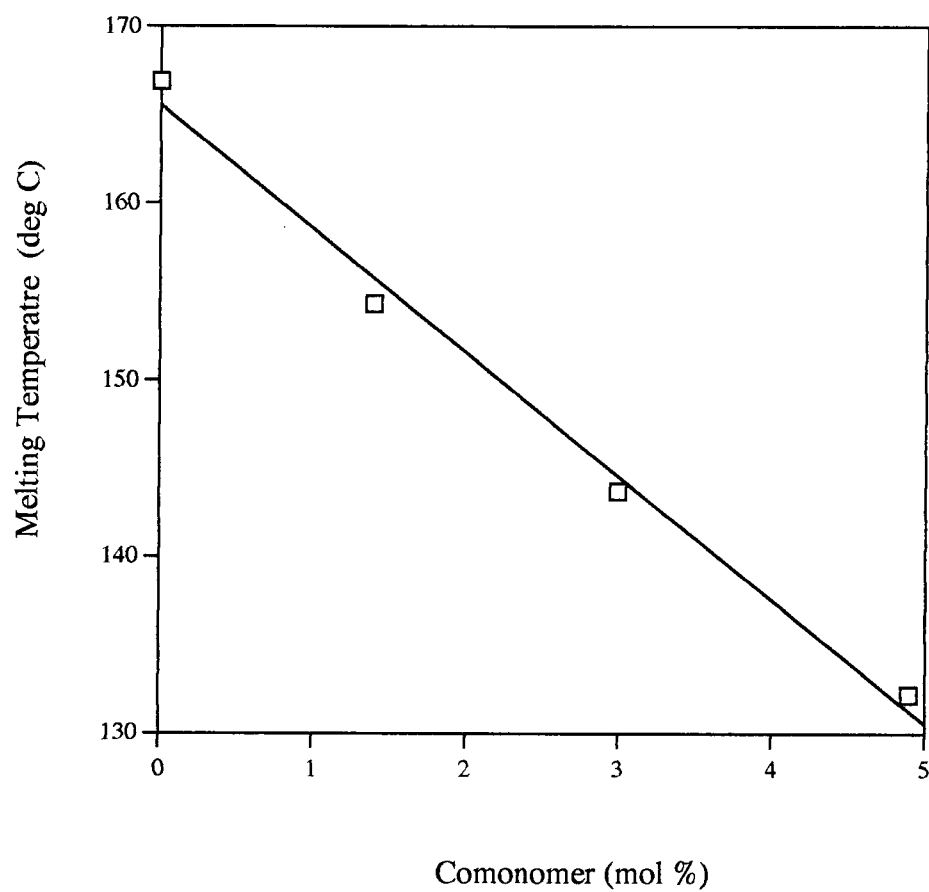


Figure 4.4. Effects of comonomer content on the melting temperature of isotactic polypropylene.

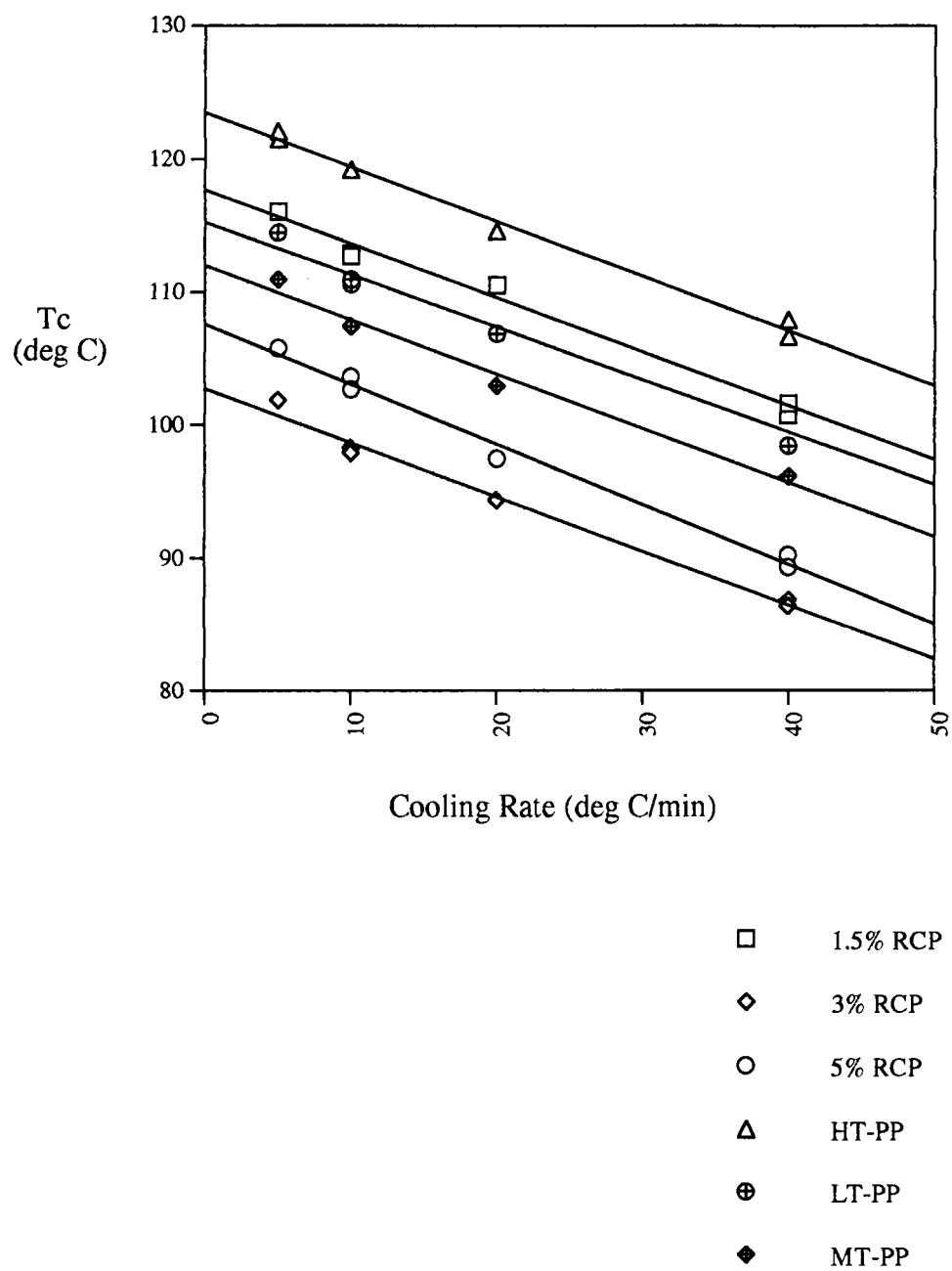


Figure 4.5. Changes in crystallization temperature with cooling rate as given by DSC.

It was unexpected to find the LT-PP crystallizing at a higher temperature than the MT-PP, since the higher degree of isotactic material in the MT-PP should allow for a faster crystallization rate (or higher T_c). The copolymer trend was found to be

$$1.5\% \text{ RCP} > 5\% \text{ RCP} > 3\% \text{ RCP}$$

$$T_c \text{ decreasing} \rightarrow$$

where the 1.5% RCP actually crystallized at a higher temperature than both the MT-PP and LT-PP. Once again, this behavior was unexpected, since the literature reports increasing comonomer content to affect a decrease in the crystallization temperature (101).

The Avrami index values and corresponding rate constants were evaluated for DSC cooling curves obtained at a rate of $20^\circ\text{C}/\text{min}$ (Table 4.3). The range of n was approximately 3.5 to 6.2, and the highest value occurred for the 3% RCP. The value of n seems to increase with isotactic content except for the unusually high value of the 3% RCP. In addition, k decreases as n increases. As was previously noted, Avrami theory does not account for mixed nucleation modes and only predicts the exponents to be integers. Thus, these data indicate three-dimensional growth, but a mixed nucleation mode may be occurring. Furthermore, since variations in the exponent are predicted for various crystal geometries, e.g. $n=3$ or 4 for spheres and $n=5$ or 6 for sheaves, depending on nucleation mode (24), it stands to reason that the variations seen here may also be attributed, in part, to variations in crystal geometry within the sample.

Characterization of Purified Samples

A purification process was introduced in an attempt to remove any impurities in the resins which may have contributed to the unexpected trends in crystallization

Table 4.3. Avrami index values as given by DSC
for a cooling rate of 20 degC/min.

Sample	Avrami index	Rate constant (k)
HT-PP	4.021	5.52E-06
MT-PP	3.782	2.44E-05
LT-PP	3.449	3.97E-05
1.5% RCP	4.774	2.71E-06
3% RCP	6.216	1.46E-06
5% RCP	4.642	6.59E-07

behavior shown by DSC. As a result, the “purified” polymer could be studied. This process was outlined in Chapter 3. Once the purified polymer samples were obtained, studies of thermal properties and crystallization behavior were conducted and the results compared with those of the as-received resins.

Melting

The melting temperatures for the purified polymers are compared to that of the as-received polymers for a heating rate of 40°C/min (see Table 4.4). The “purification” process resulted in a decrease of melting temperature for all samples. In most cases, the change was relatively small, of the order of 1°C. It would be expected that the purification process removes some quantity of atactic (amorphous) polymer which does not precipitate out of solution with the isotactic portion during purification; however, an increasing isotactic content should cause an increase in the melting temperature. Thus, the removal of atactic polymer is not consistent with the decreased melting temperatures seen in Table 4.4. Furthermore, the removal of any nucleating impurities by the purification procedure would be expected to decrease the crystallization temperature. A decrease in crystallization temperature corresponds to a decrease in lamellar thickness; hence, melting data acquired after the samples were crystallized from the melt should exhibit a lower melting temperature due to the decreased lamellar thickness.

DSC Crystallization Behavior

The purification process affected changes in the crystallization temperatures, demonstrated in a plot of relative crystallinity versus temperature (Figure 4.6). The most important effect observed in this plot is that the copolymers now follow the

Table 4.4. Comparison of melting data of as-received and purified samples.

AS-RECEIVED SAMPLES			PURIFIED SAMPLES		
Sample	Heating Rate (deg C/min)	Tm (deg C)	Sample	Heating Rate (deg C/min)	Tm (deg C)
1.5% RCP	40	153.437 153.483 153.466	1.5% RCP	40	152.558 152.158 152.147
3% RCP	40	148.488 148.522 148.542	3% RCP	40	147.008 146.938 146.992
5% RCP	40	137.400 137.529 137.749	5% RCP	40	134.737 136.252 135.237
LT-PP	40	157.972 158.194 158.111	LT-PP	40	157.355 157.343 157.456
HT-PP	40	168.284 168.150 168.287	HT-PP	40	165.712 165.600 165.653
MT-PP	40	166.150 165.744 166.213	MT-PP	40	162.182 162.751 162.072

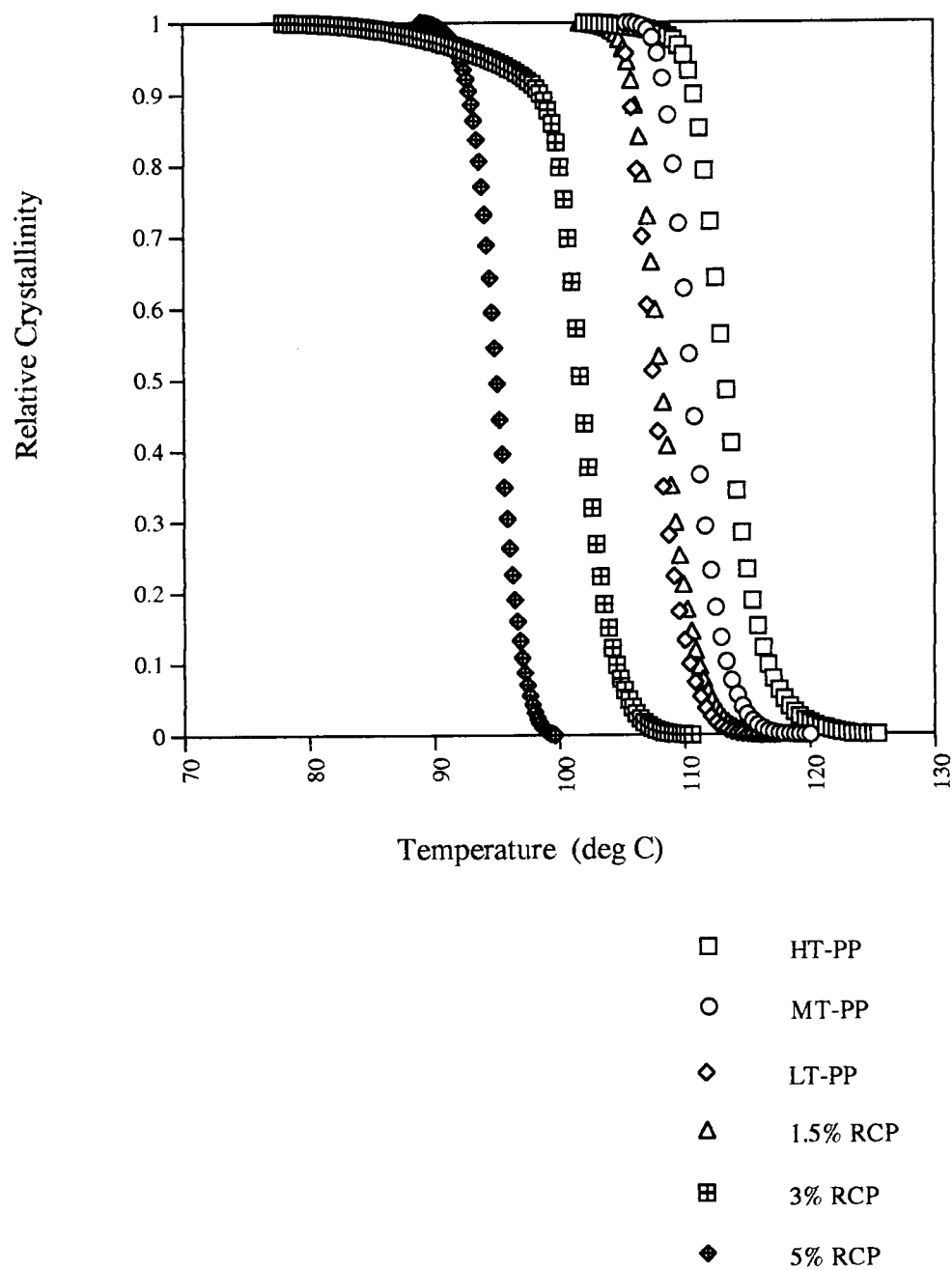


Figure 4.6. DSC data for purified samples cooled at a rate of 5 deg C/min.

expected crystallization trend. The resulting Avrami index values were slightly reduced overall, in the range of 2.8 to 4.9. The 3% RCP still yielded the highest value: $n=4.9$. Thus, it appears that some impurities may have been present in the as-received resins, but were removed by the purification procedure.

Isotacticity by FTIR

FTIR was used to estimate the percent isotactic content in the purified resins and to identify the removal of any specific fraction such as atactic polypropylene during the purification process. First, the isotacticity was determined for the purified samples in the same manner as described for the as-received resins. The ratios obtained here were calibrated against the data shown in Figure 4.1. The resulting values for isotacticity of the purified samples are listed in Table 4.5. These data indicate that the same trend in isotactic content as was previously seen still holds true. The homopolymers are ordered from low to high (92-99% isotactic), while the copolymers show increasingly lower percentages of isotactic material corresponding to increasing comonomer content. In direct comparison to the isotactic content results of the as-received resins, there appears to be a slight increase overall; however, this increase is within the estimated limits of error for this method ($\pm 2\%$). Consequently, it must be surmised that there was little change, if any, in the overall isotactic content due to purification.

Infrared studies of the xylene solutions obtained after precipitation of the polymer were conducted in order to determine if there was a concentration of a particular fraction of the whole polymer that remained in solution. These solutions showed little, if any, indication of polymer remaining in solution after the polymer

Table 4.5. Determinations of % isotactic PP in the purified samples according to FTIR. These values were calibrated against the results for the as-received samples.

Sample	Ratio of Peak Areas (974/995 cm ⁻¹)	Calculated % Isotactic PP
pure HT-PP	1.209	99
pure MT-PP	1.519	94
pure LT-PP	1.706	92
pure 1.5% RCP	1.375	96
pure 3% RCP	1.440	95
pure 5% RCP	1.640	93

was precipitated. Consequently, the remaining volume of each solution was allowed to evaporate completely. In the case of the MT-PP and HT-PP samples, residual trace solids were retrieved and analyzed. A summary of the observed absorption bands and their respective assignments is listed in Table 4.6. In both cases, a significant number of bands were identified as those characteristic of polypropylene (14) and assigned accordingly.

An infrared study of polypropylene conducted by Luongo (76) was utilized to characterize these solids as either atactic or isotactic polypropylene. Three bands in particular were noted to be especially sensitive to changes in tacticity: 1168, 974, and 895 cm^{-1} . These three bands were present in the spectrum of HT-PP, while two of the three (1168 and 895 cm^{-1}) were present in the MT-PP spectrum. Luongo reported the 1168 cm^{-1} band to be a sharp peak with a small shoulder at 1152 cm^{-1} in a 0% atactic sample, changing to a broader, slightly less intense peak at 1156 cm^{-1} in a 100% atactic sample. MT-PP and HT-PP showed peaks at 1169 and 1168 cm^{-1} (resolution=8) respectively, evidence of a low percentage of atactic material. Luongo also reported a sharp peak at 974 cm^{-1} and a very weak, broad peak at 895 cm^{-1} for 0% isotactic polypropylene; the HT-PP spectrum revealed such a weak peak at 973 cm^{-1} that it was difficult to compare the peak shape with Luongo's data. However, the peaks occurring at 898 cm^{-1} in both MT-PP and HT-PP samples, although weak, were distinctly seen as broad peaks; this is indicative of a lesser degree of isotacticity in the polymer.

Another test of the degree of isotacticity lies in the presence or absence of the absorption bands occurring at 1366, 1330, 1305, 1295, 1258, 1220, 1103, 1045, 995, 938, 895, 842, and 810 cm^{-1} (66). The MT-PP spectrum exhibited three of the thirteen peaks listed above, and the HT-PP showed six. Elimination of the majority

Table 4.6. Infrared peaks and band assignments for residual solids from concentrated xylene solutions.

Sample	Observed Peaks (cm ⁻¹)	Intensity *	Band Assignment
MT-PP	2944	broad, m	C-H (CH ₃) stretching
	2846	broad, m	C-H stretching
	1360	sharp, w	CH bend, CH ₂ twist
	1304	w	CH ₂ wag, CH ₂ twist
	1210	w	-
	1169	w	r _{cc} (axial), CH ₃ rock (axial)
	1008	w	-
	927	w	-
	898	w	CH ₃ rock (equatorial), CH ₂ rock
	842	w	CH ₂ rock
HT-PP	2960	sharp, w	C-H (CH ₃) stretching
	1365	w	CH bend, CH ₂ twist
	1304	w	CH ₂ wag, CH ₂ twist
	1256	sharp, m	-
	1168	w	r _{cc} (axial), CH ₃ rock (axial)
	1045	broad, m	-
	1019	broad, m	r _{cc} (equatorial), r _{cm}
	973	w	-
	898	w	CH ₃ rock (equatorial), CH ₂ rock
	842	w	CH ₂ rock

* Abbreviations: s=strong, m=medium, w=weak.

of the peaks characteristic of the 100% isotactic polypropylene spectrum in both of these cases is indicative of some degree of atactic polymer present. Although the actual percentage cannot be quantified, it is evident from the data presented that there is some percentage of both isotactic and atactic polymer present in these residual solids. Furthermore, the removal of some quantity of polymer by purification is clearly confirmed.

Determination of Sample Purity

FTIR was used to identify the presence of any additives or impurities in the as-received resins which may serve as nucleating agents, causing the unexpected shifts in crystallization trends noted earlier. Figure 4.7 shows the FTIR spectrum of the concentrated residual xylene solution obtained from the purification of the 1.5% RCP. Table 4.7 summarizes the band assignments for this sample. The absorption peaks which occurred in the range of $2850\text{--}2960\text{ cm}^{-1}$ are typically associated with C-H stretching. The 1726 cm^{-1} peak is characteristic of a carbonyl group, a species not found in the spectra of polypropylene or propylene-ethylene copolymers. The peaks occurring at 1271 and 1068 cm^{-1} are also seen to arise due to the vibration of a carbon-oxygen bond, in this case, =C-O . These bands are usually associated with ethers. Last, the bands at 1120 and 739 cm^{-1} were assigned as CH_2 out of plane wagging and $\text{-(CH}_2)_4\text{-O}$, respectively. It is unclear whether or not the 1120 cm^{-1} is due to a hydrocarbon, but the 739 cm^{-1} assignment clearly is not. All of these band assignments presented are only probable assignments and further investigation into the molecular structure by NMR and Mass Spectroscopy studies would be required to actually identify this unknown species. Based on this information, however, there is

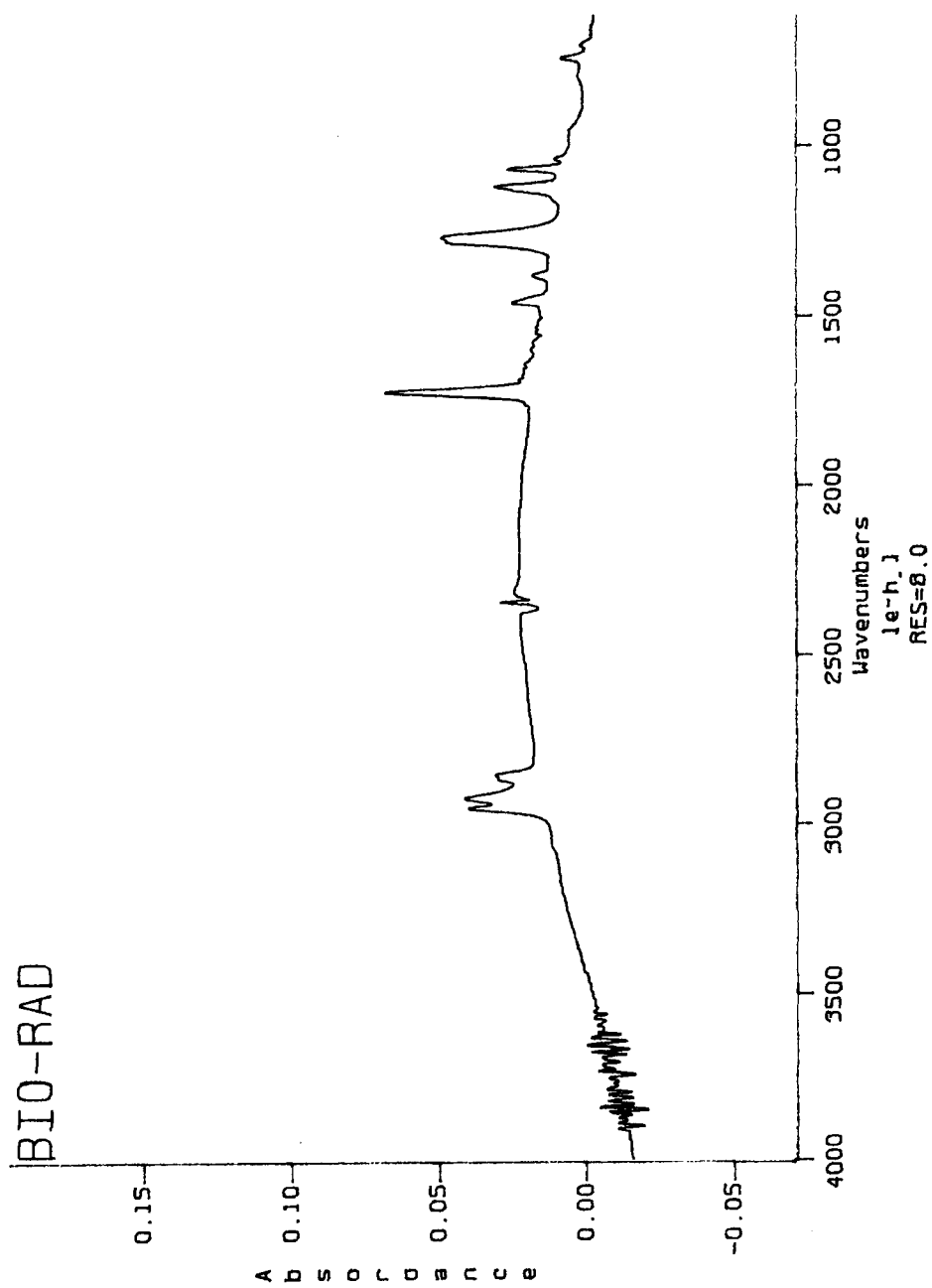


Figure 4.7. FTIR spectrum of the concentrated xylene solution obtained from the 1.5% RCP.

Table 4.7. Infrared peaks and possible band assignments for concentrated xylene solution remaining from purification process for 1.5% RCP.

Sample	Observed Peaks (cm ⁻¹)	Possible Assignment
Solution from 1.5% RCP	2955	C-H (CH ₂) stretching
	2926	C-H (CH ₂) stretching
	2855	C-H (CH ₂) stretching
	1726	C=O vibration
	1460	C-H (-CH ₂ -) deformation
	1271	=C-O (asymmetric vibration)
	1120	CH ₂ out of plane wagging
	1068	=C-O (symmetric vibration)
	739	-(CH ₂) ₄ -O skeletal (not hydrocarbons)

evidence of either an impurity or an additive present, since it is well-known that neither polypropylene nor PP-Ethylene copolymers contain oxidized species (11, 62, 66). Besides the C-H stretching shown by the peaks in the 2850-2960 cm^{-1} range, no evidence of atactic polymer was seen in this solution.

It was expected that absorption peaks uncharacteristic of polypropylene in the solutions obtained from the 5% RCP and the HT-PP would appear, similar to what was seen for the 1.5% RCP solution, since all three samples demonstrated a very high nucleation density in preliminary growth studies. However, all other solutions investigated, including the MT-PP (control sample), revealed no absorption peaks whatsoever. These data lead to three possible conclusions: 1) there are no additives or impurities in the 5% RCP or the HT-PP, 2) the additives or impurities are present but transparent in the region of 4000 - 400 cm^{-1} studied here by FTIR, or 3) the additives and impurities are present in such low concentration as to be undetectable by the technique used here.

4.2 Light Depolarizing Microscopy

Quiescent nonisothermal crystallization studies were conducted in order to compare the crystallization kinetics of the various resins under these conditions; hence, the effects of tacticity and ethylene content could be evaluated. LDM was used in conjunction with DSC to define the nonisothermal kinetics for a wide range of cooling rates, namely 5-4000°C/min.

Nonisothermal Crystallization Kinetics

The nonisothermal crystallization kinetics were defined using the LDM technique set forth by Ding and Spruiell (21) in Chapter 3. It is useful to begin with some typical data generated for PP by this technique. First, Figure 4.8 gives the measured cooling curves for six cooling rates for LT-PP. For a given cooling curve, a fast initial temperature drop occurs due to the large temperature difference between the polymer and the cooling medium. After this initial temperature drop, there is a plateau resulting from the heat of crystallization liberated during the crystallization process. The rate of temperature change is lower after the plateau due to smaller temperature differences between the polymer sample and the cooling medium. Finally, the temperature in the polymer approaches that of the cooling medium.

Second, the induction time, t_0 , defined as the total time spent below the equilibrium melting temperature but prior to the onset of crystallization, was determined in each case according to the I_0 (light intensity measured without analyzer) versus time curve (Figure 4.9). The first point at which a departure from the baseline occurs is due to a decrease in light intensity as a result of newly forming crystals; hence, this point ends the induction period and is indicative of the onset of crystallization. It is more useful to determine t_0 from the light intensity measured without the analyzer than from the intensity measured with the analyzer, since there is no interference in the reduction of light intensity due to light depolarization. The induction time determined for a given cooling rate should be shorter for a homopolymer than a copolymer, since homopolymers are known to crystallize faster and begin crystallization at higher temperatures than copolymers.

Third, the relationship between the average cooling rate ($^{\circ}\text{C}/\text{min}$) and the cooling rate factor, or CRF (1/sec), is defined in Figure 4.10. The average cooling

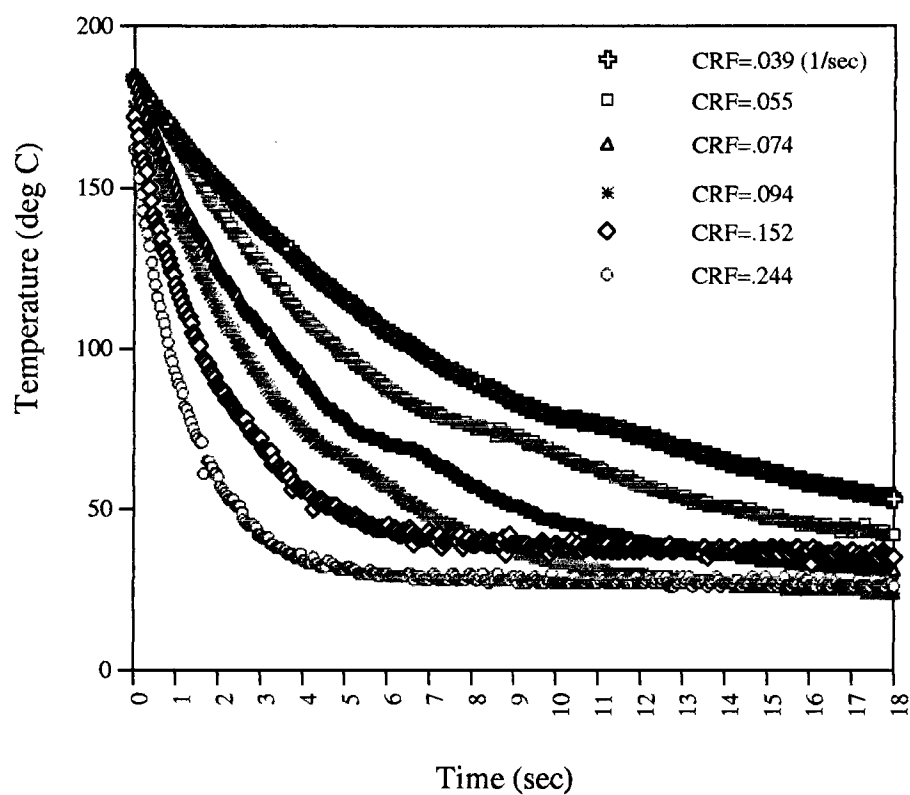


Figure 4.8. Cooling curves for LT-PP at various cooling rates.

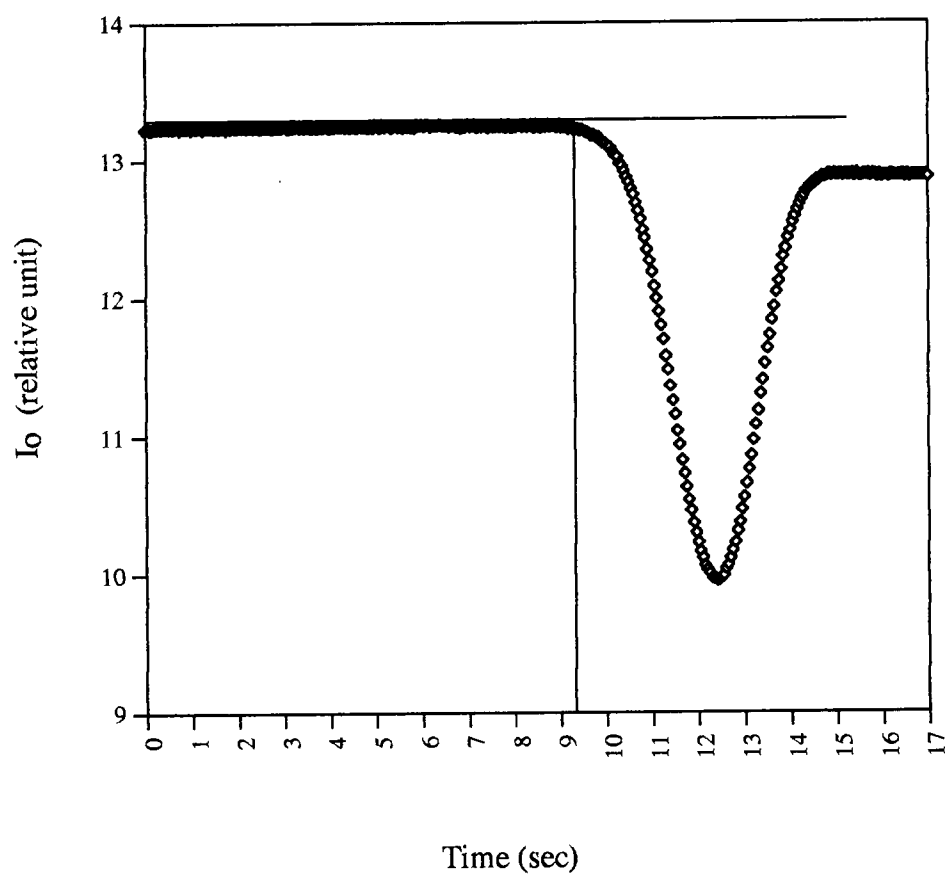


Figure 4.9. Typical light intensity vs time curve used for determining induction time.

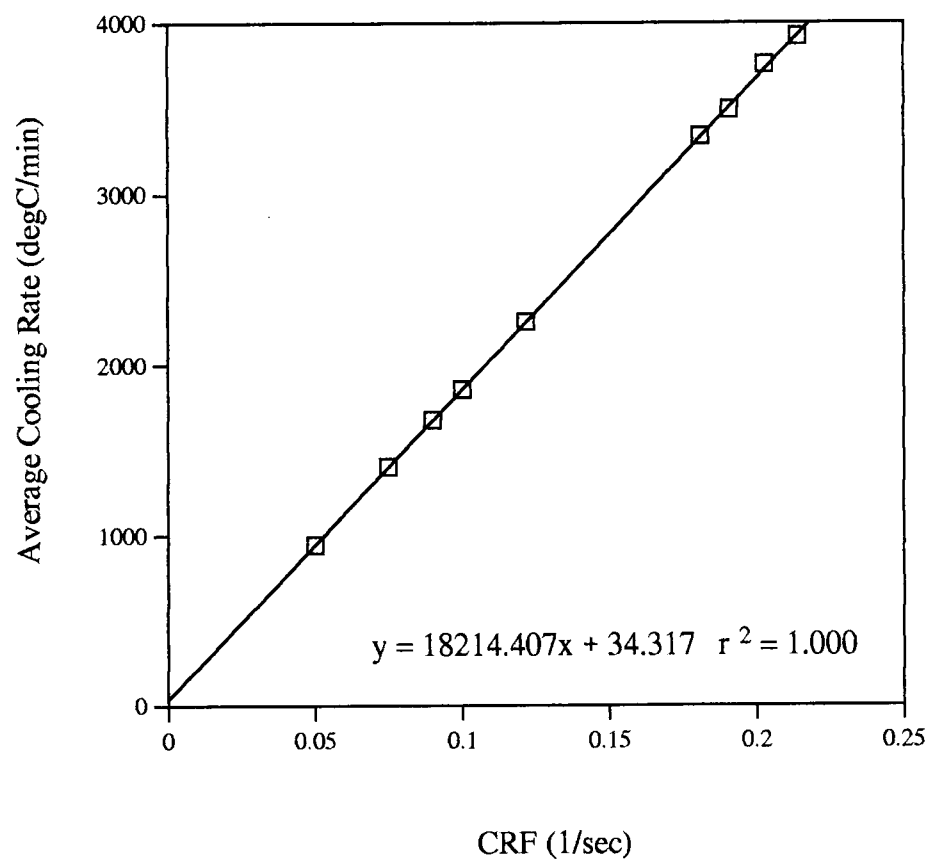


Figure 4.10. Average cooling rate prior to crystallization versus CRF.

rate was obtained by a linear regression of the experimental cooling curve for the time prior to the onset of crystallization. This same portion of the curve was regressed exponentially to yield the CRF. Recall that this relationship arises from the definition of CRF:

$$T - T_s = (T_o - T_s) \exp \{-(CRF)t\} \quad (4.1)$$

where T is the sample temperature, T_s the temperature of the cooling medium in the sample chamber, T_o the initial temperature at which the sample just begins to be cooled, and t the time. By controlling the air flow rates, cooling rates in the range of 200-4000°C/min were achieved.

Next, the relative crystallinity, θ , versus time for six cooling rates is given for the HT-PP sample in Figure 4.11. Here, θ is defined by

$$\theta = \frac{\chi_c}{(\chi_c)_\infty} = \frac{R - R_o}{R_\infty - R_o} \quad (4.2)$$

where χ_c and $(\chi_c)_\infty$ are the crystallinity at arbitrary time t and at $t=\infty$, respectively; R

is the relative light intensity ($R = \frac{(I - C)}{I_o}$), R_o the value of R when $\chi_c = 0$, and R_∞

the relative intensity at $t=\infty$. The relative crystallinity is equal to the fraction of transformed solid material. It can be readily seen that the onset of crystallization and the entire crystallization process is dependent on cooling rate. As the cooling rate increases, the induction period decreases, i.e. the sample crystallizes faster with

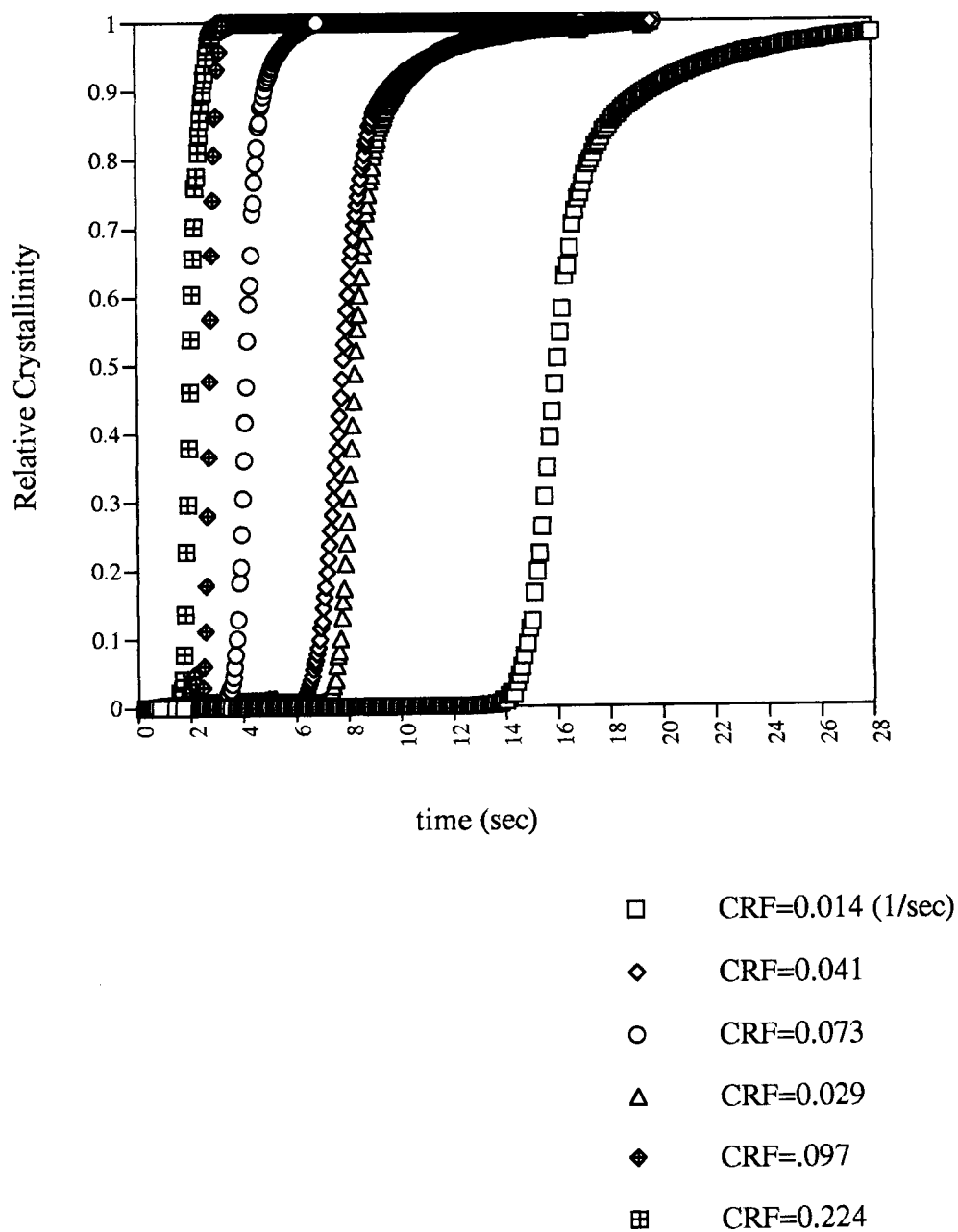


Figure 4.11. Changes in Relative Crystallinity for various cooling rates given by LDM for HT-PP.

increasing cooling rate. Once the crystallization process begins, the ensuing development occurs rapidly, and a final value is approached within a short period of time (usually 40 seconds or less depending on the polymer and the cooling rate condition). This period of rapid increase in crystallinity is referred to as primary crystallization. The slower process following this increase in which a final value of crystallinity is approached is termed secondary crystallization. The amount of secondary crystallization which can occur for a given sample is also cooling rate dependent. For a relatively low cooling rate ($CRF=0.014 \text{ sec}^{-1}$), more secondary crystallization occurs due to the reduced time constraints for the entire crystallization process. In contrast, the crystallization period is significantly shorter for $CRF=0.224 \text{ sec}^{-1}$, resulting in a lesser degree of secondary crystallization.

Figure 4.12 is the relative crystallinity versus temperature for several cooling rates. The onset temperature for crystallization clearly decreases with increasing cooling rate, resulting in a more narrow temperature range through which primary crystallization can occur.

The induction time, shown to be a function of cooling rate, is also significantly affected by variations in tacticity and comonomer content. This is demonstrated in Figure 4.13. The induction time is shorter for the homopolymers than for the copolymers over the range of cooling rates indicated. The induction time was seen to be shortest for the HT-PP, i.e. it crystallized faster than the MT-PP or LT-PP. LT-PP has a much lower degree of isotacticity (91%) than the HT-PP (99%), causing it to have the longest induction times of the three homopolymers. Of the copolymers, the 1.5% RCP had the shortest induction times over the range of cooling rates, followed by the 3% RCP, then the 5% RCP. This parameter, t_0 , is strongly

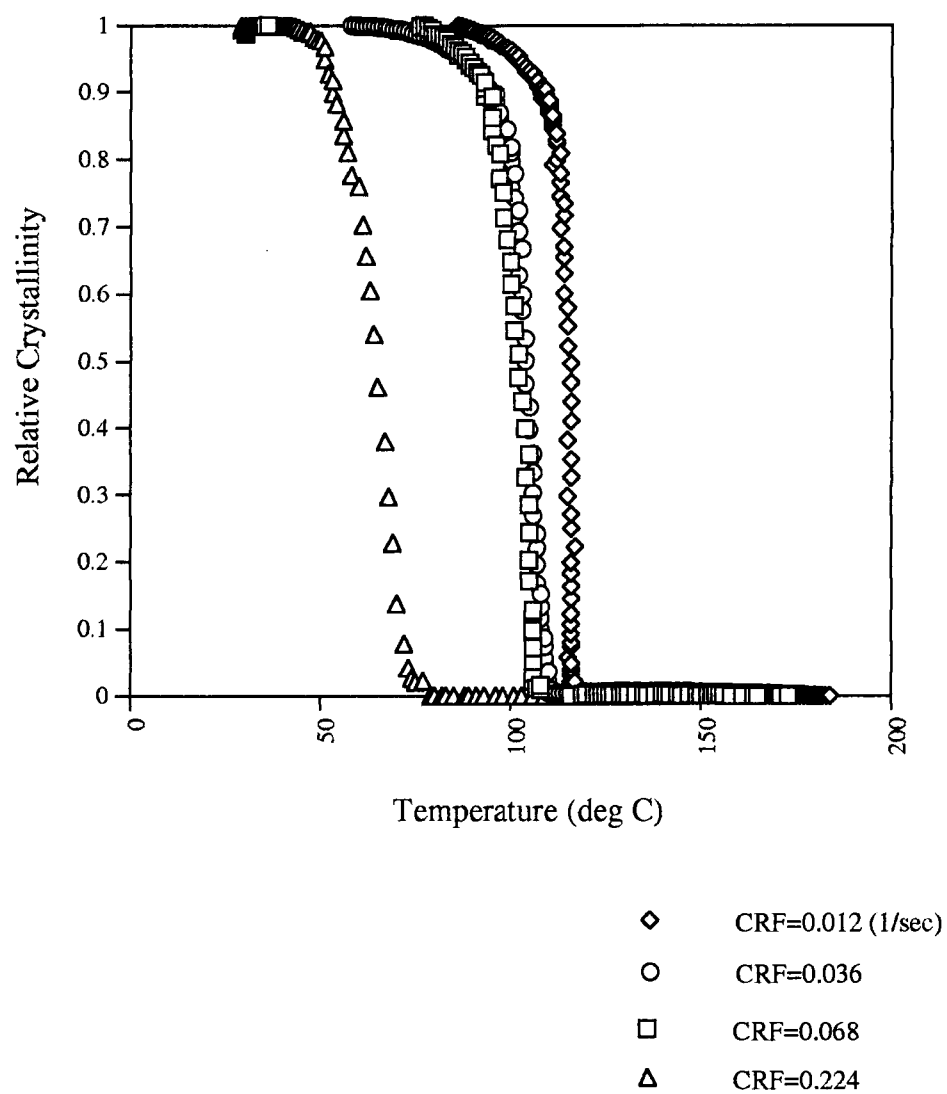


Figure 4.12. Relative crystallinity vs Temperature for various cooling rates for HT-PP.

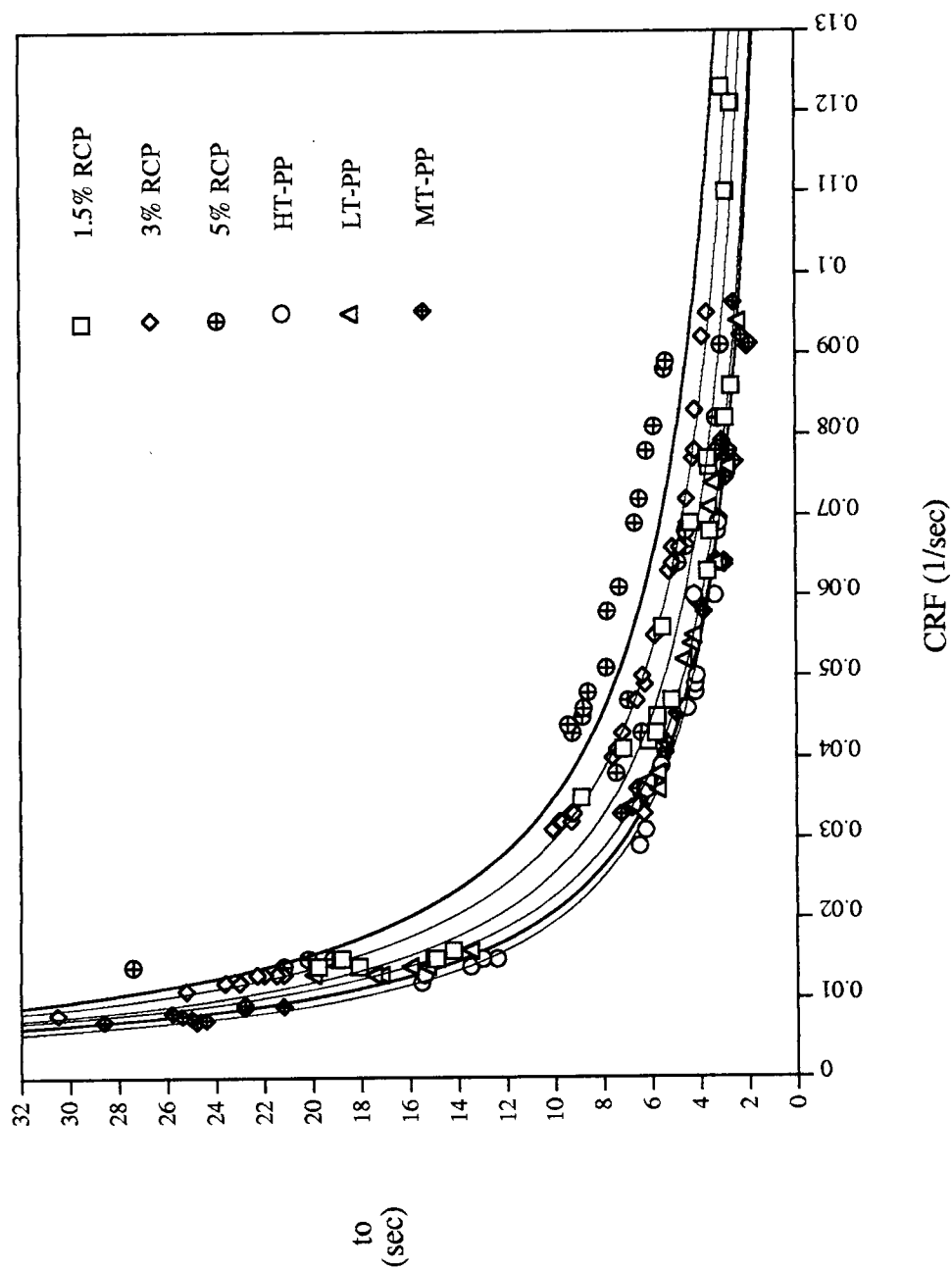


Figure 4.13. Effects of varying levels of ethylene comonomer and tacticity on induction time.

dependent on the initial nucleation process, as the end of the induction period is defined by the onset of crystallization.

Additional information on the crystallizability of these polymers is given by a plot of relative crystallinity versus time for a given cooling rate (Figure 4.14). CRF=0.041 for this plot and corresponds to an average cooling rate of 781°C/min. Here again, the homopolymers crystallize sooner than the copolymers, separated in the same manner as described for Figure 4.13. The HT-PP crystallizes before the LT-PP, while the MT-PP overlaps both of these samples and, as a result, is not particularly evident in this plot.

Avrami Analysis

Avrami theory was applied to further analyze the data. Plots of $\ln \ln [1/(1-\theta)]$ versus $\ln (t-t_0)$ were generated for each experimental run. The slope of the linear part of this curve yields the Avrami index. The rate constant k can be obtained from the y-intercept of the linear regression according to the following rearrangement of the Avrami equation:

$$\ln \ln \left(\frac{1}{1-\theta} \right) = \ln k + n \ln t \quad (4.3)$$

Values of the Avrami index are presented as a function of cooling rate in Figure 4.15. There is a fair amount of scatter in these values; however, the values seem to be concentrated in the range of 3 to 4.5, indicating three-dimensional growth. This is in accordance with the theoretical values of 3 and 4 for heterogeneous and homogeneous nucleation modes, respectively, and with values reported in the literature for isothermal crystallization studies of iPP: $n=3$ for $T_c < 137^\circ\text{C}$ (7, 34, 70,

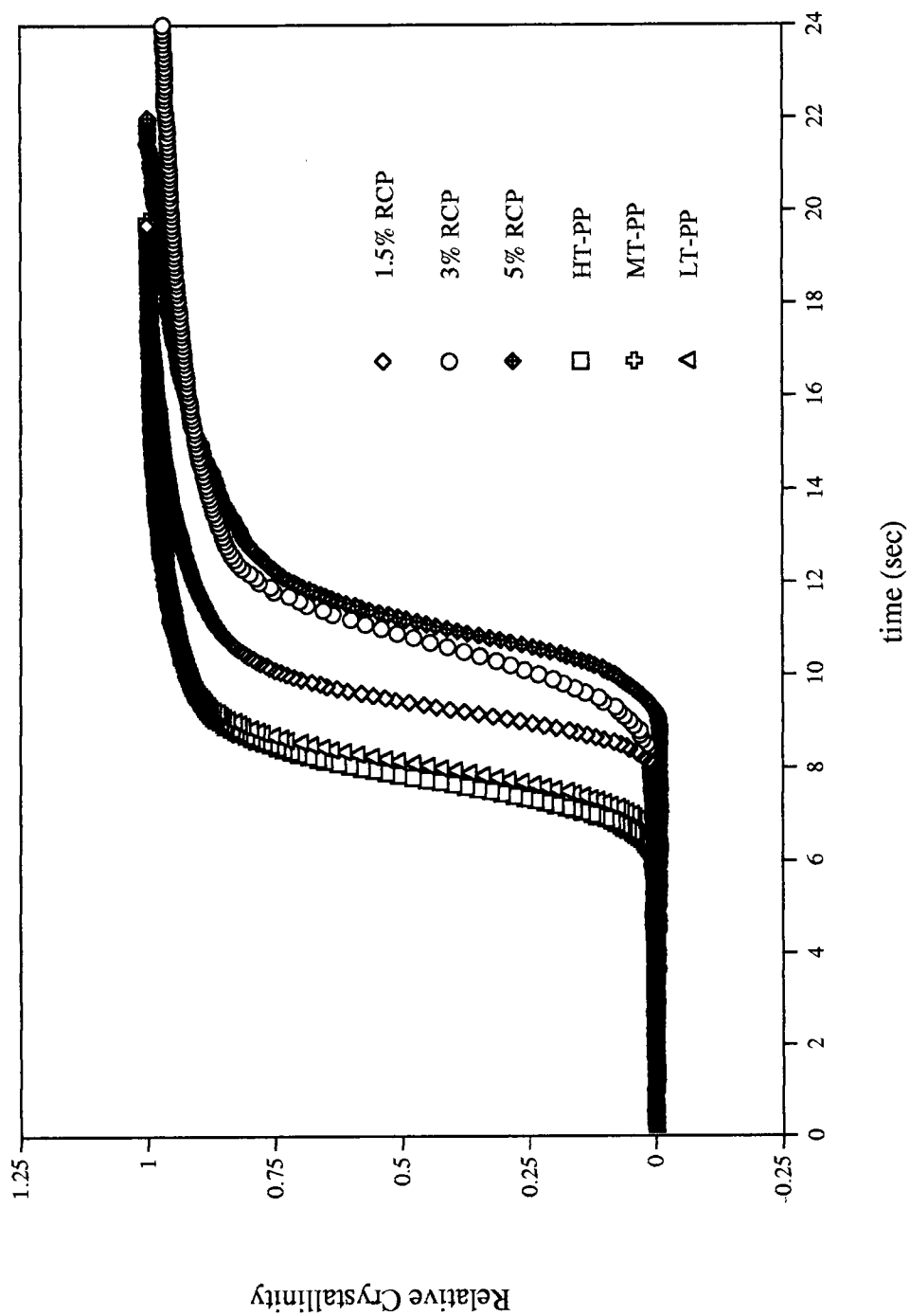


Figure 4.14. Changes in Relative Crystallinity with time as given by LDM for CRF = .041.

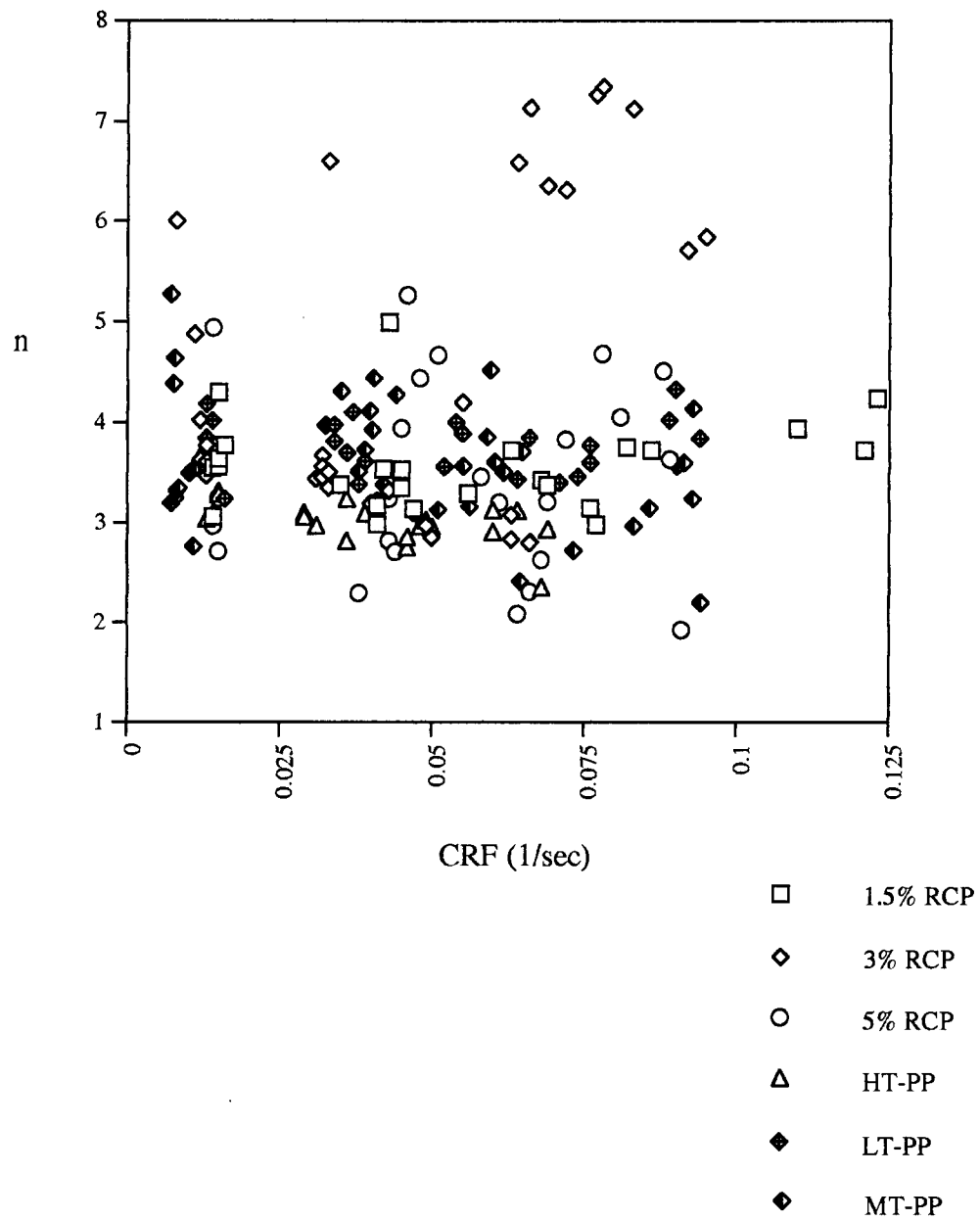


Figure 4.15. Dependence of Avrami index on CRF.

91), $n=4$ for $T_c < 128^\circ\text{C}$ (40), and $n=5$ or 6 for fast crystallization or lower T_c (7).

The most scatter appears to occur for the 3% RCP with values in the range of 3-5, as well as 6-7.5. Theoretical predictions of n are said to be dependent on both crystal geometry and nucleation mode; thus, the high values of n for the 3% RCP may be due to variations in these two parameters (78, 123). Furthermore, Avrami theory does not consider secondary crystallization, which actually accounts for a significant amount of polymer crystallization; hence, variations in both n and k may also be partially due to the secondary crystallization process. Further evidence to support either of these possibilities will be presented in the discussion of morphology.

The dependence of the rate constant, k , on cooling rate is illustrated for each polymer in Figure 4.16. Generally, it appears that k increases with higher supercoolings. Once again, however, the 3% RCP is unique in that its k values are nearly constant (within $\pm 0.05\%$) for all cooling rates. There is some difficulty in the interpretation of these data, since k is strongly related to both the nucleation and growth mechanisms. Furthermore, the uncertainty in the interpretation of n lends to that of the k parameter, since they are closely related.

One way of minimizing the variation in k due to that of n is by calculating k according to another transformation of the Avrami equation: $k = \frac{\ln 2}{(t_{1/2})^n}$. Here, an average n value is employed, and $t_{1/2}$ represents the half-time of the rate process equivalent to the light depolarization change measured at 50% crystallization. The resultant k values are given in Figure 4.17. It can be seen that much of the scatter in k is reduced and clearer trends are shown. The homopolymers have the highest values

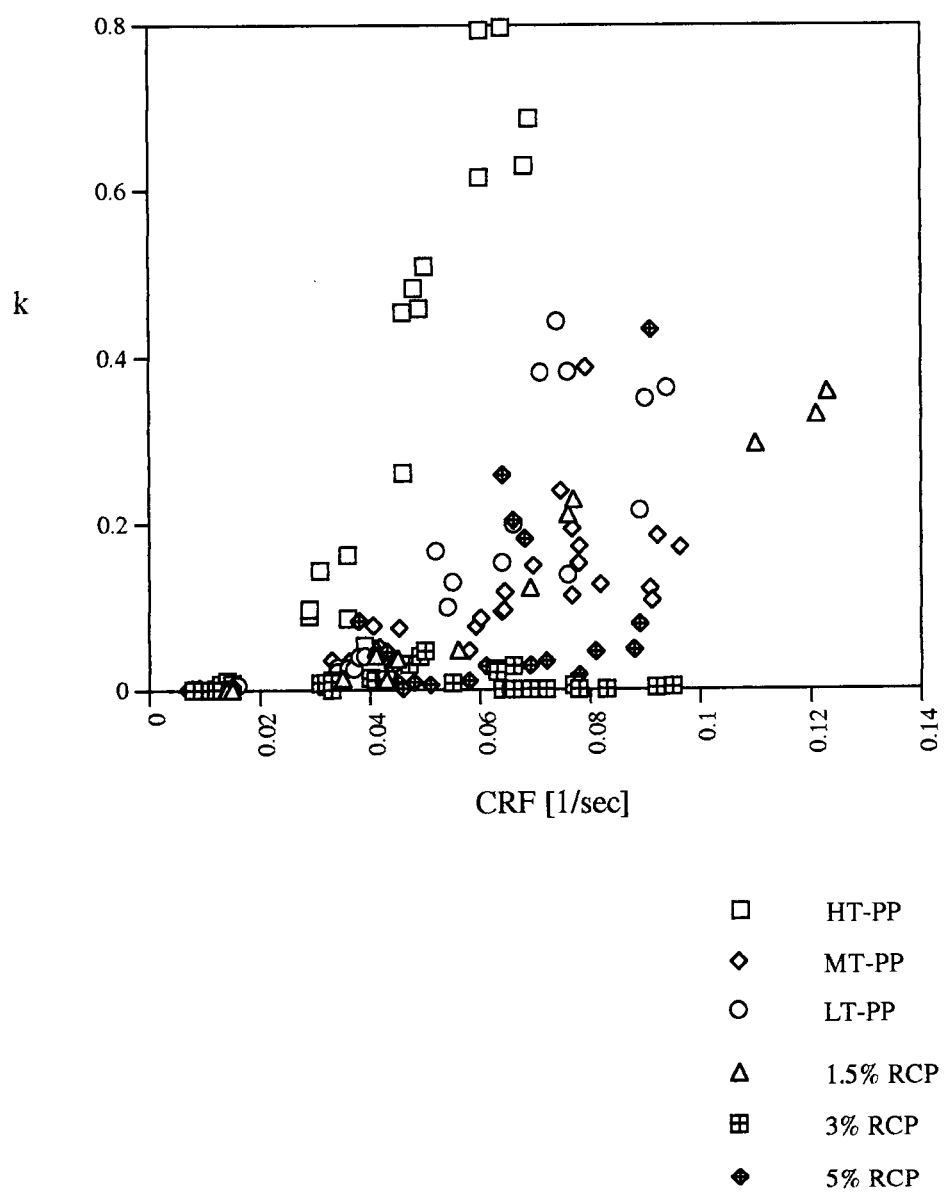


Figure 4.16. Rate constant k as a function of cooling rate.

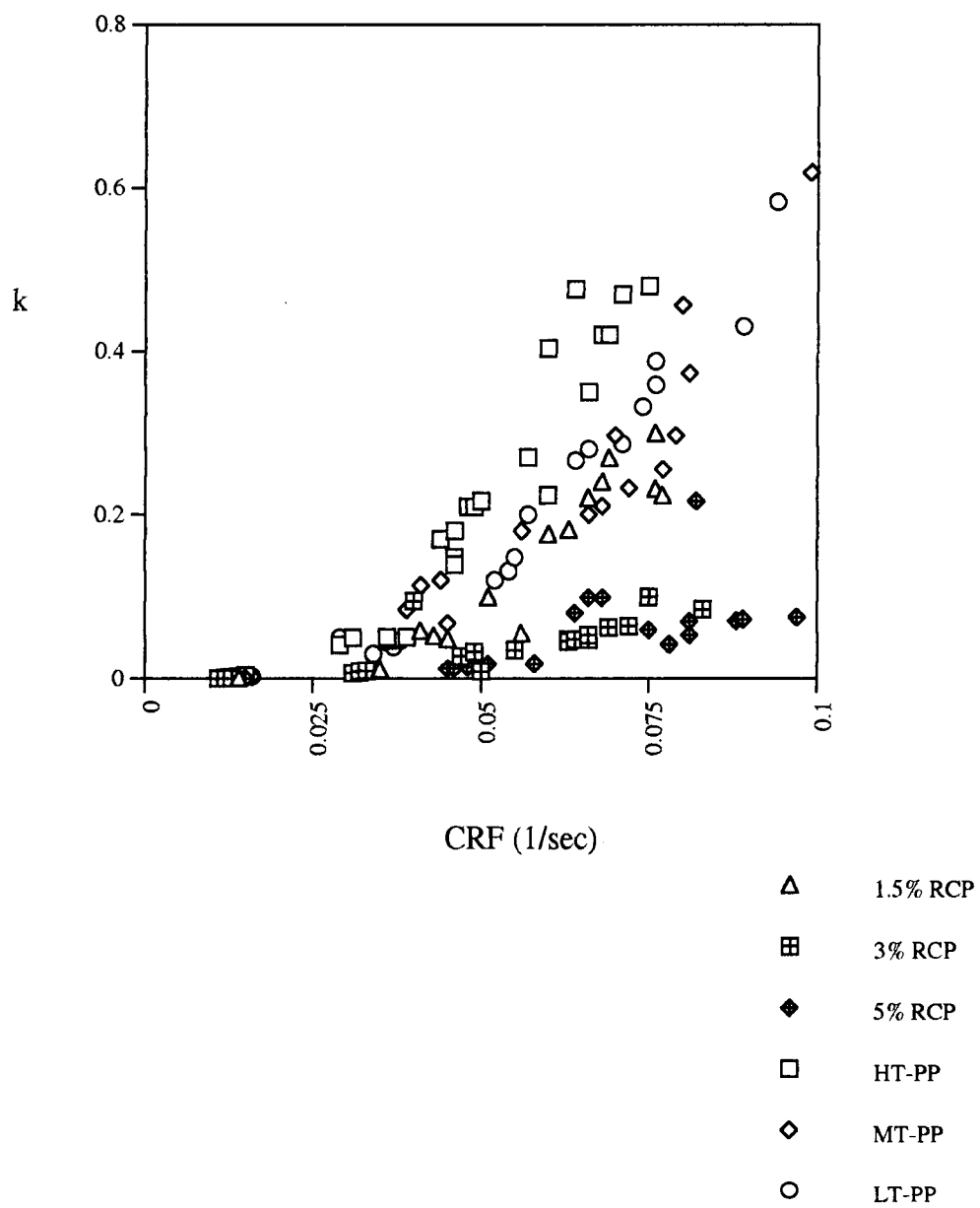


Figure 4.17. Rate constant k (determined from $t_{1/2}$) as a function of CRF.

of k over the range of cooling rates. The 1.5% RCP overlaps somewhat with the MT-PP and LT-PP, while the 3% RCP and 5% RCP values are in a lower range. Thus, there must be differences in either the nucleation or growth mechanisms (or both) of the homopolymers and the copolymers which are responsible for these trends in k .

Nucleation and Growth

Bulk crystallization data interpreted by Avrami theory can readily be related to the nucleation and growth rates of spherulites (82). To investigate nucleation behavior, primary nucleation densities were estimated for all samples at various cooling rates, or different crystallization temperatures, by counting the number of spherulites within a $3.9 \times 3.9 \mu\text{m}$ section of the field of view of the optical microscope as seen on the TV. Nucleation density measurements of these samples segregated the samples into two categories: those with a very high nucleation density (approximately 40 for the slowest cooling rate), and those with a relatively low nucleation density (approximately 10 for the slowest rate) (Figure 4.18). The HT-PP, 1.5% RCP, and 5% RCP fell into the category of high nucleation density; whereas, the LT-PP, MT-PP, and 3% RCP fell into the low nucleation density category. The homopolymers were expected to have similar nucleation densities to one another, while the copolymers would have similar values also, but slightly lower than those of the homopolymers; this decrease would be partly due to the presence of ethylene units which do not act as nucleation sites (14). However, this was not the case. Some differences between the nucleation densities may be attributed to differences in the catalyst systems used to produce these polymers (85) or nucleating impurities such as stabilizers and the like (40).

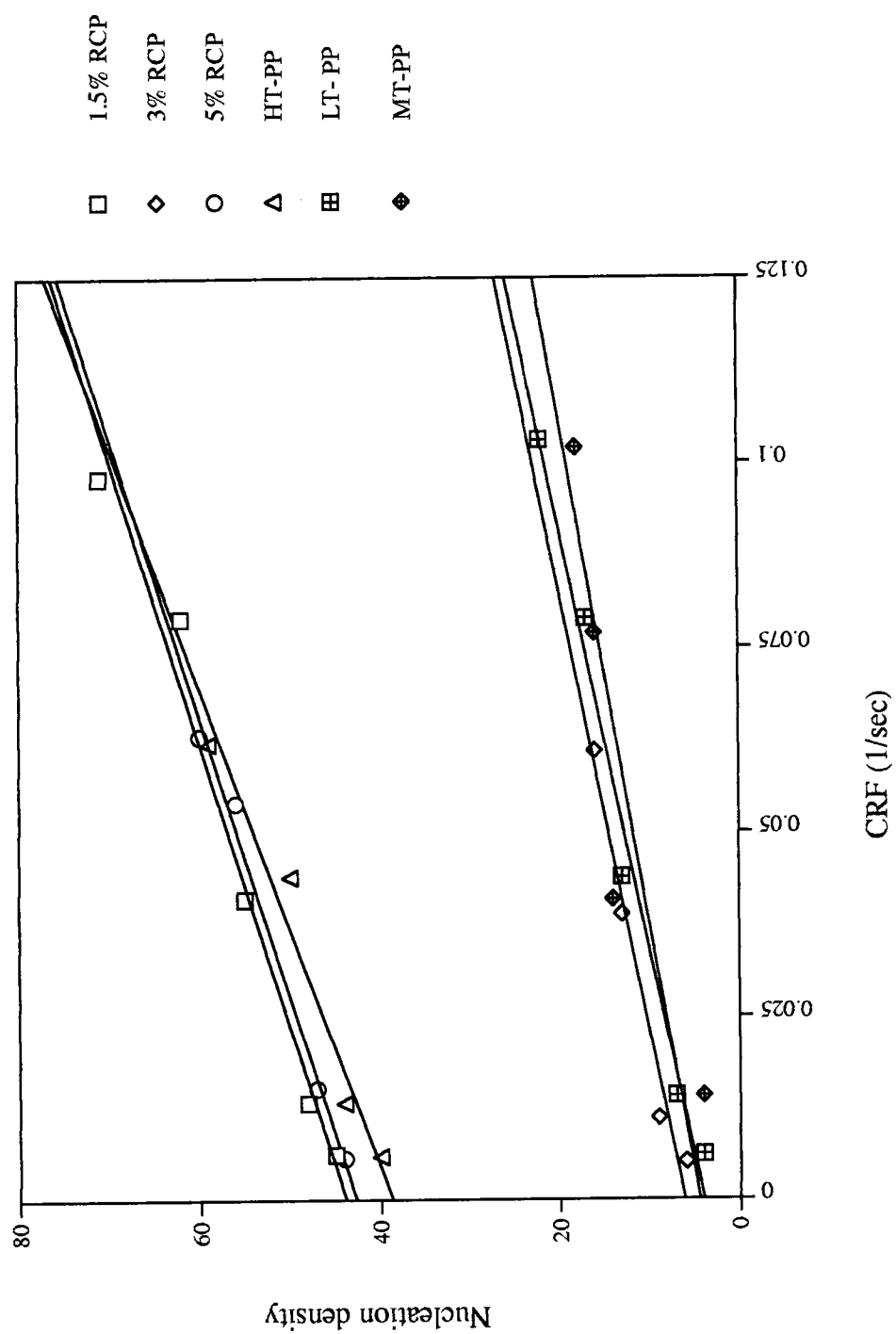
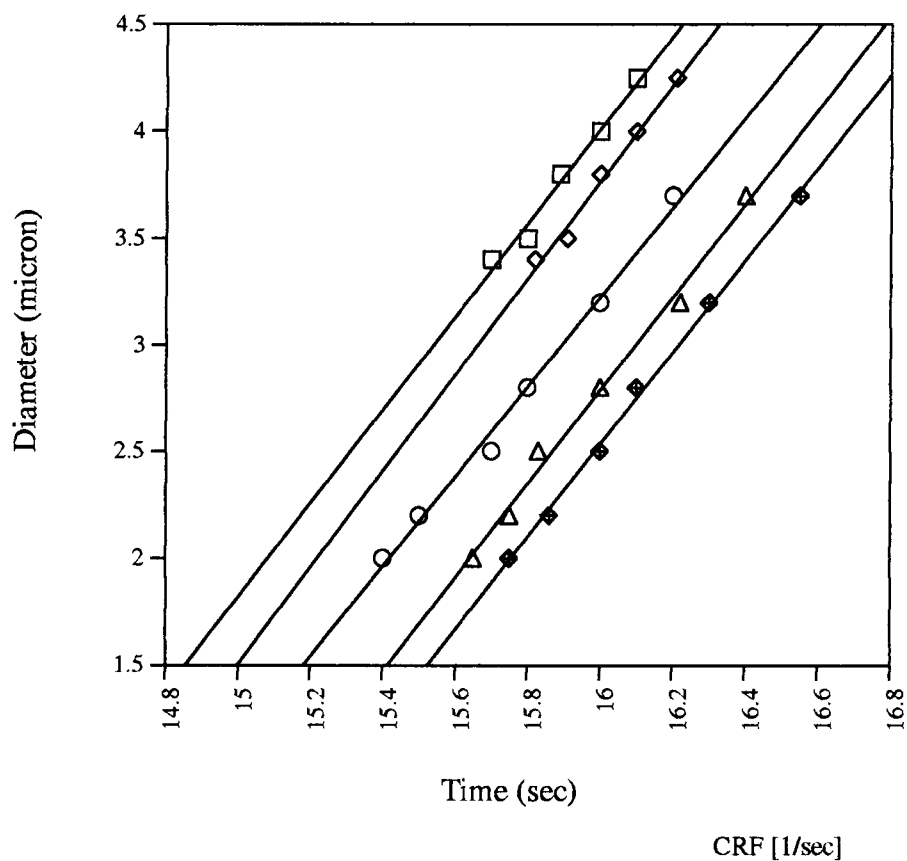


Figure 4.18. Comparison of Nucleation Density values for as-received samples.

Growth studies were conducted using the TV and VCR technique described in the experimental section. Measurements of spherulite diameters were taken as a function of time. Spherulite diameters were found to be linear with time at all crystallization temperatures until impingement for all samples. An example of this is shown in Figure 4.19. Three different randomly chosen spherulites were measured for each material in each cooling condition studied. This figure shows that the growth rates (slopes of the curves) are constant during crystallization. Each spherulite began growth at a slightly different time, indicating time-dependent, or sporadic, nucleation. This spherulitic growth corresponds both to the region of significant increase in light intensity for the Light Intensity versus time curve (Figure 4.20) and to the plateau region exhibited in the temperature versus time curve (Figure 4.21) in all cases. The relationship between the spherulitic growth and plateau temperature yields a partial explanation of the constant growth rates: the temperature remains almost constant during the growth. Further growth occurs after the plateau, however, while the temperature is decreasing; therefore, the constant growth cannot be solely attributed to a constant temperature. It must be noted that the average temperature is the quantity measured experimentally.

The average spherulite size is plotted against cooling rate in Figure 4.22. The average size was determined by directly averaging the spherulite diameter measurements obtained at the time just prior to impingement. The samples exhibiting low nucleation densities were seen to yield a much higher average spherulite diameter than did those with very high nucleation densities. Here, the lower degree of nucleation allowed for a longer time for spherulitic growth prior to impingement, effectively increasing final average spherulite size.



$$y = 0.219x - 31.142 \quad r^2 = 0.982 \quad \square \quad .0150$$

$$y = 0.219x - 32.529 \quad r^2 = 0.986 \quad \diamond \quad .0150$$

$$y = 0.221x - 30.539 \quad r^2 = 0.993 \quad \circ \quad .0150$$

$$y = 0.210x - 32.343 \quad r^2 = 0.992 \quad \triangle \quad .0148$$

$$y = 0.215x - 32.121 \quad r^2 = 0.997 \quad \blacklozenge \quad .0148$$

Figure 4.19. Spherulite diameter vs time for HT-PP.

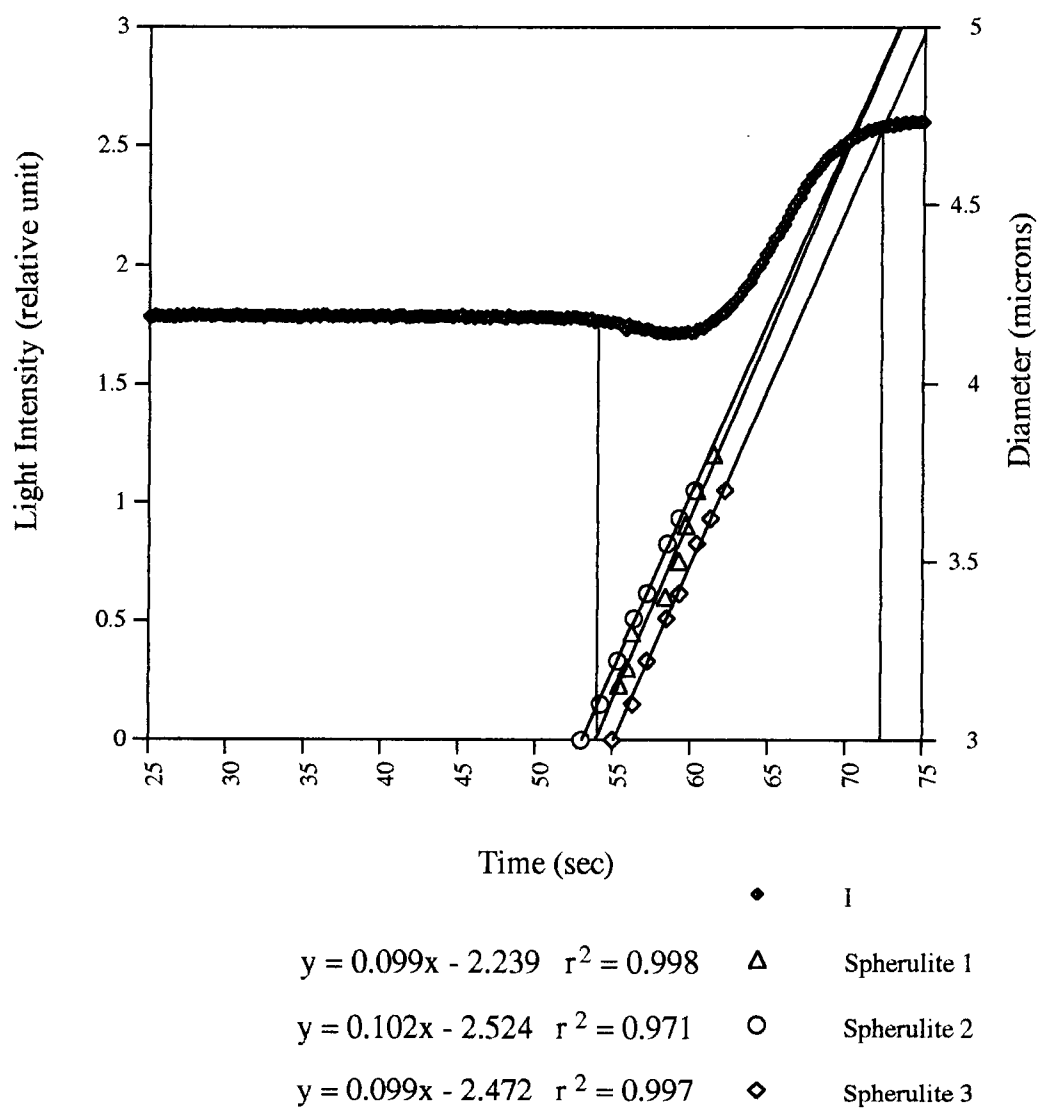


Figure 4.20. Spherulite diameter and light intensity vs time for 1.5% RCP for CRF=.004.

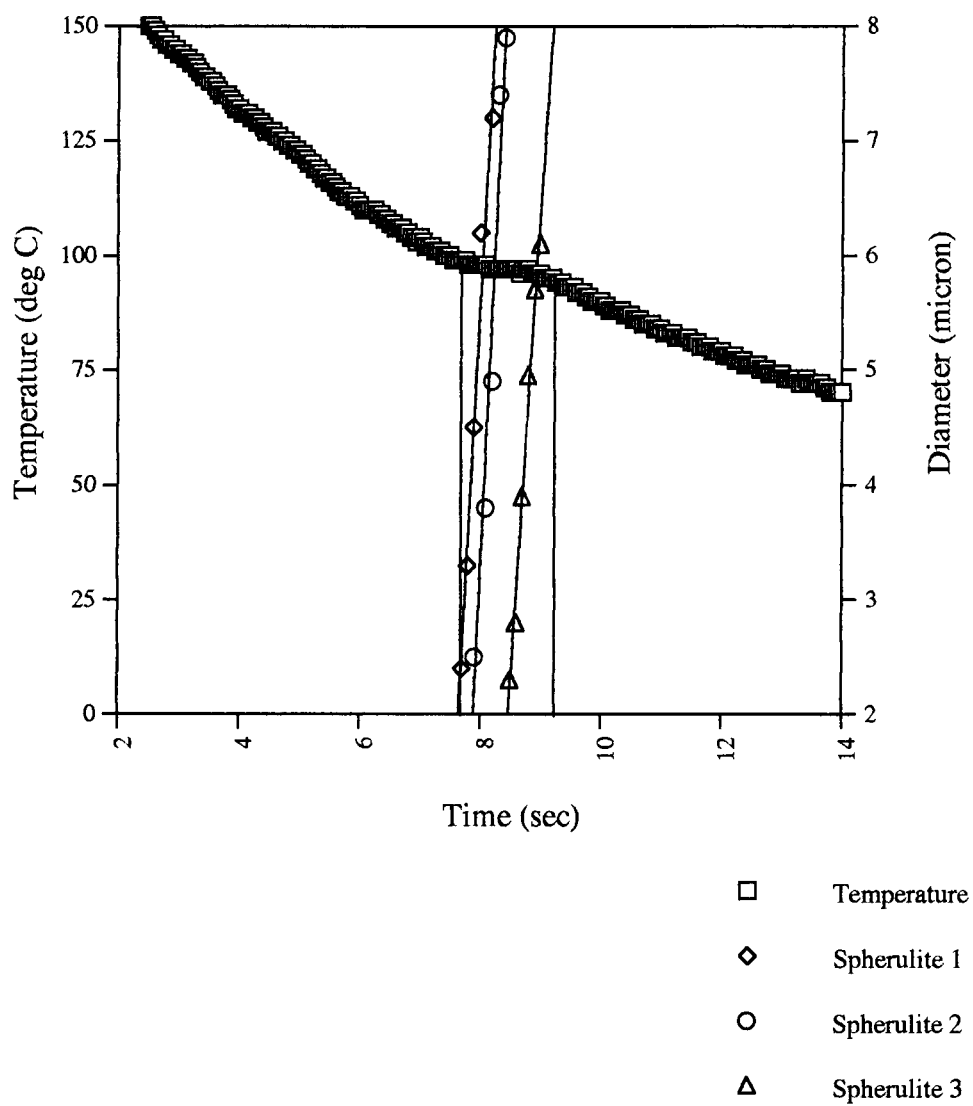


Figure 4.21. Spherulite diameter and temperature vs time for LT-PP for CRF=.037.

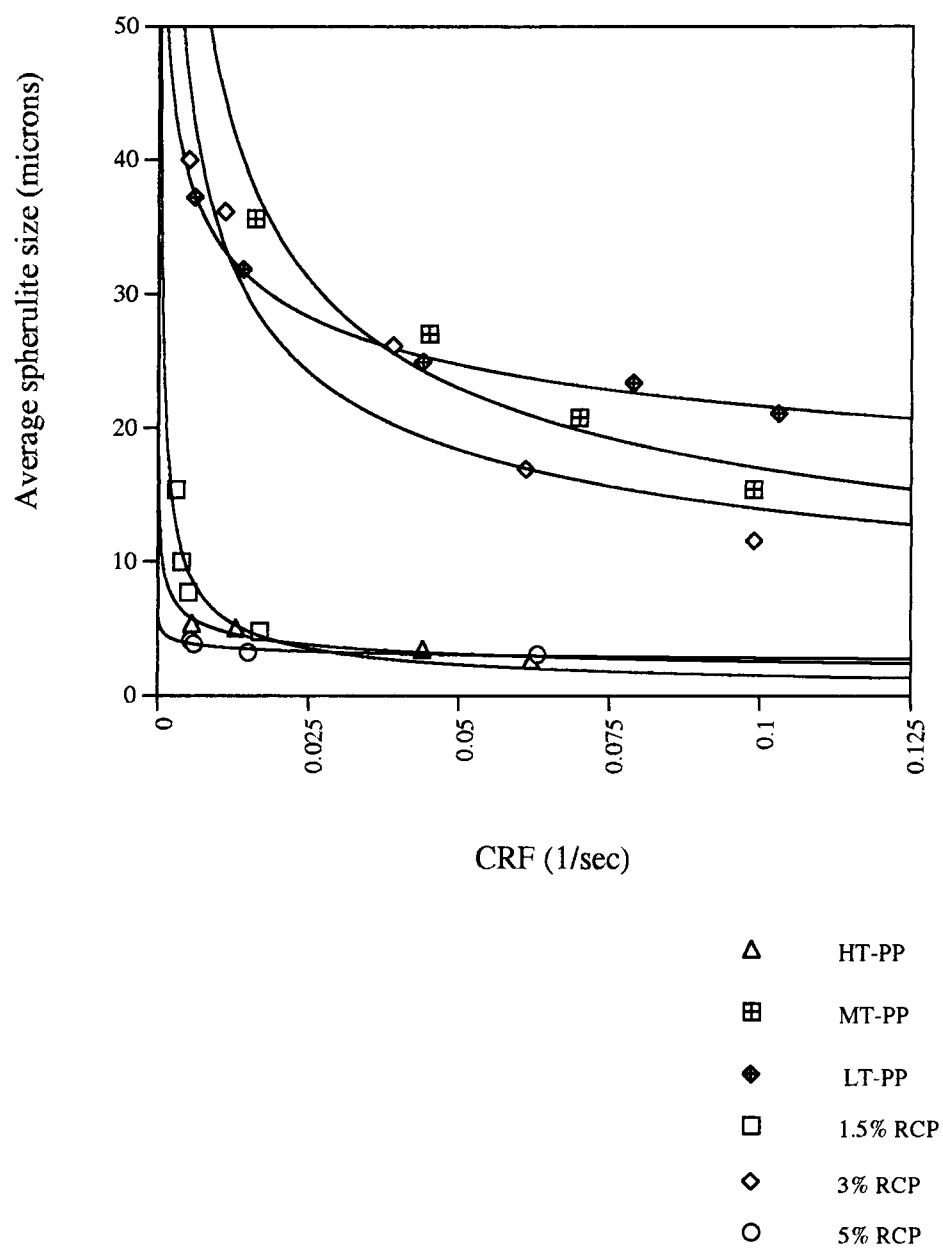


Figure 4.22. Average spherulite size as a function of cooling rate for as-received samples.

The growth rate for each measured spherulite is plotted as a function of cooling rate in Figure 4.23. The growth rate increases as cooling rate increases, which corresponds to a decreasing plateau temperature. These data, along with growth rate data obtained for the purified samples, were then applied to a Hoffman-Lauritzen plot, assuming the plateau temperature to be a reasonable representation of the crystallization temperature for a given cooling condition and $T_m^\circ = 186^\circ\text{C}$ for iPP (Figure 4.24). This figure indicates that this highly nonisothermal data does, in fact, follow the Hoffman-Lauritzen equation originally developed for isothermal crystallization. Further, the data presented falls into Regime III, since all crystallization temperature values were less than 137°C (50, 100).

The HT-PP was seen to have the highest growth rates, followed by the MT-PP and LT-PP which had nearly identical growth rates. Since the HT-PP has the highest degree of stereoregularity, this behavior was not surprising. The lesser degree of stereoregularity of the latter two polymers resulted in lower growth rates. The complementary effect of a lower degree of stereoregularity and high percentage of comonomer content caused the 5% RCP to yield the slowest growth rates of the three copolymers. In the same way, the 1.5% RCP exhibited the fastest growth of the copolymers studied due to the higher degree of isotacticity and smaller amount of comonomer.

It has been argued that the introduction of ethylene comonomer causes a reduction in the equilibrium melting temperature (2, 27, 46, 88). Thus, a Hoffman-Lauritzen plot was also constructed using experimental equilibrium melting data obtained for propylene-ethylene copolymers (88). The resulting plot showed slopes similar to those given by the first Hoffman-Lauritzen plot, but the curves were ordered differently. A shift occurred in the copolymer curves in which the 1.5% RCP

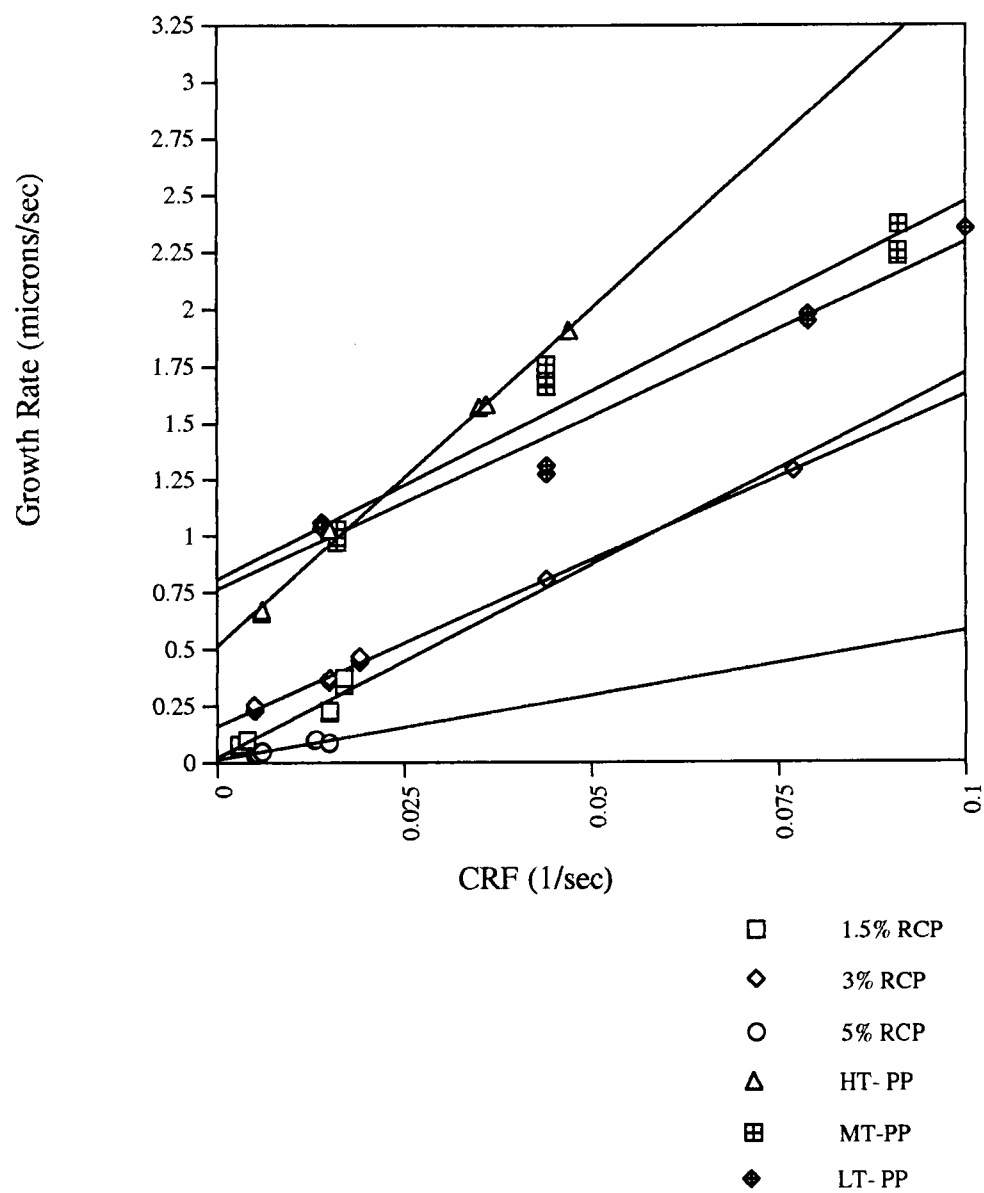
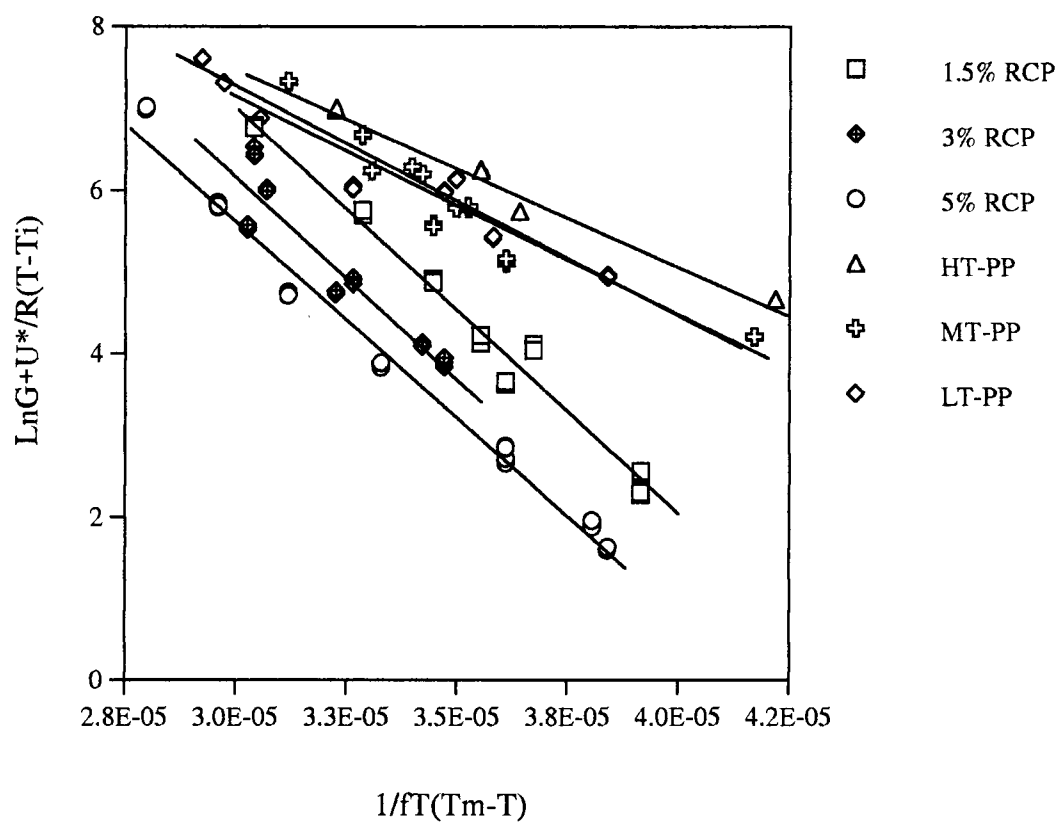


Figure 4.23. Comparison of Growth Rates for homopolymers and copolymers.



$$y = -499202.949x + 22.033 \quad r^2 = 0.979$$

$$y = -496785.103x + 21.072 \quad r^2 = 0.886$$

$$y = -483217.189x + 20.157 \quad r^2 = 0.985$$

$$y = -240887.373x + 14.710 \quad r^2 = 0.971$$

$$y = -283626.177x + 15.781 \quad r^2 = 0.904$$

$$y = -268191.628x + 15.187 \quad r^2 = 0.928$$

Figure 4.24. Hoffman-Lauritzen plot for as-received and purified sample data.

curve indicated the lowest growth rates, and the 5% RCP curve had the highest. The 3% RCP curve nearly coincided with the three homopolymer curves. This was not surprising since the new T_m° values were significantly reduced and decreased the value of the supercooling, hence increasing the calculated growth rate dependence on temperature. This effect was largest for the 3% RCP and 5% RCP due to the much lower T_m° values used in these cases. This plot, however, did not yield as clear a representation of the differences in the temperature dependencies of the growth rates as did the Hoffman-Lauritzen plot shown in Figure 4.24.

The growth studies also revealed some slight differences in the morphology of the various samples. Generally, all samples exhibited very spherical structures; however, in the case of the copolymers, there was a mixture of both spherical and elliptical structures. This effect was most predominant in the 3% RCP, appeared to a lesser degree in the 5% RCP, and was almost nonexistent in the 1.5% RCP. It is possible that the crystal geometry is actually a mixture of spheres and sheaves; this would account for the unusually high values of the Avrami index shown earlier (Fig. 4.15), since a sheaf geometry is predicted to yield an Avrami index value of 5 or 6, depending on nucleation mode. Similarly, this observation may account for the nearly constant k values demonstrated for the 3% RCP.

The birefringence of the spherulites produced at different cooling rates could not be ascertained due to the relatively high nucleation densities produced for the high cooling rate conditions studied. Many layers of spherulites formed during crystallization, even at low cooling rates (about 200°C/min), causing interference of the birefringence to occur. According to previous work, spherulites of mixed birefringence have been reported to be the most common for melt-crystallized iPP crystallized at any temperature less than 140°C (100, 103).

Effects of Purification (LDM data)

The purification procedure caused some changes in the crystallization behavior of the polypropylene resins. First, the induction times of the purified polymers revealed only small deviations from the previously well-defined curves: the induction times decreased slightly for the MT-PP, LT-PP, and 3% RCP, whereas they increased for the 1.5% RCP, 5% RCP, and HT-PP (Figure 4.25). The purified samples actually showed a lesser degree of scatter in the t_0 values than did the initial data. Second, the trend exhibited by the purified samples for changes in relative crystallinity with time showed the same result as was initially indicated by the samples not purified:

$$\text{HT-PP} > \text{MT-PP} > \text{LT-PP} > 1.5\% \text{ RCP} > 3\% \text{ RCP} > 5\% \text{ RCP}$$

Decreasing crystallization rate (increasing t_0) $\rightarrow$

Third, there was a slight change in the Avrami index and rate constant values. The exponent values decreased slightly overall, with a concentration in the range of 2 to 4 (Figure 4.26); most of the scatter outside of this range was given by the copolymers. The rate constant data appear to have shown either a slight increase or relatively no change, and there is more variability in the 3% RCP values overall. Last, a change in nucleation density was observed: the samples which had previously exhibited a high nucleation density now exhibited a decreased nucleation density (in the range already defined by the other samples) (Figure 4.27). This observation led to the conclusion that those samples (HT-PP, 1.5% RCP, and 5% RCP) contained a substance, functioning to increase nucleation significantly, which was removed upon purification. The growth rates and crystal geometry remained approximately the same. Therefore, the purification process slightly increased the measured

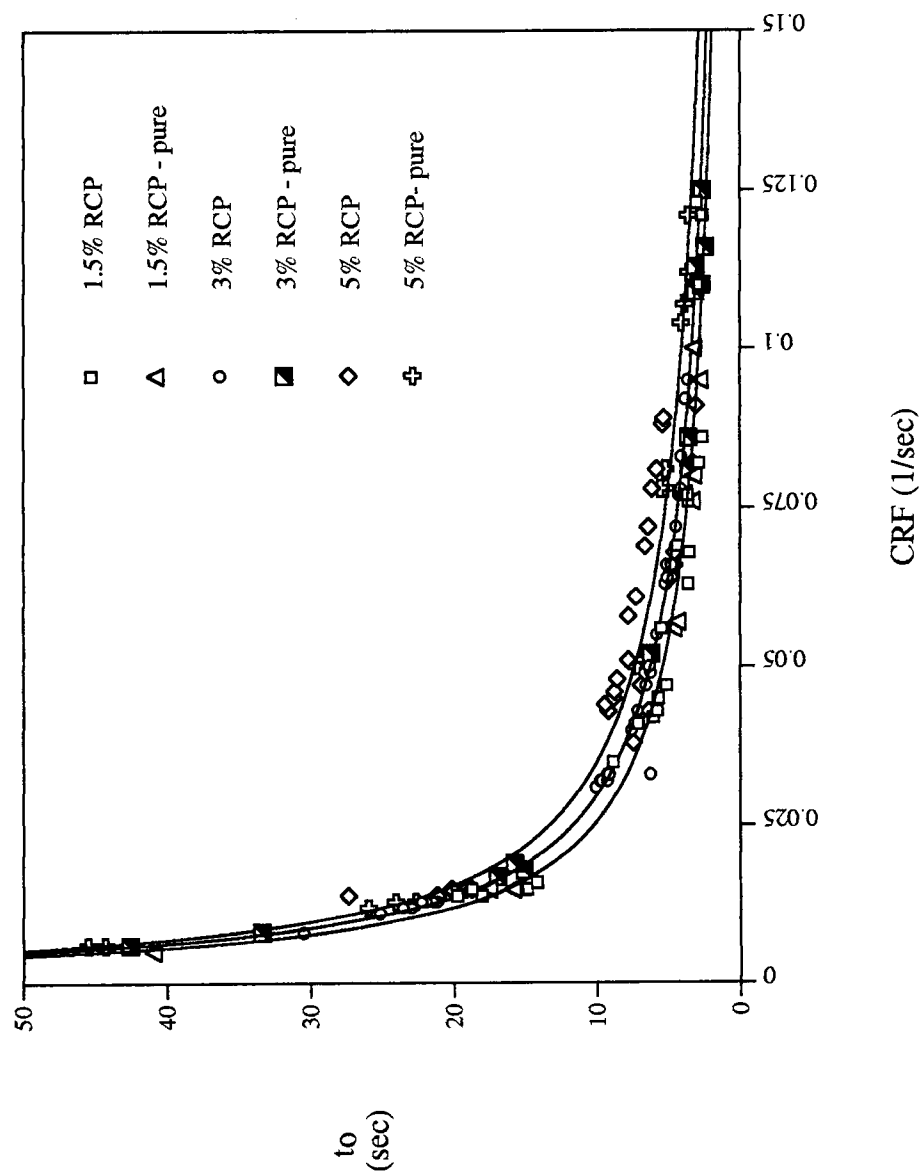


Figure 4.25. Comparison of Induction times for as-received samples and samples purified in xylene.

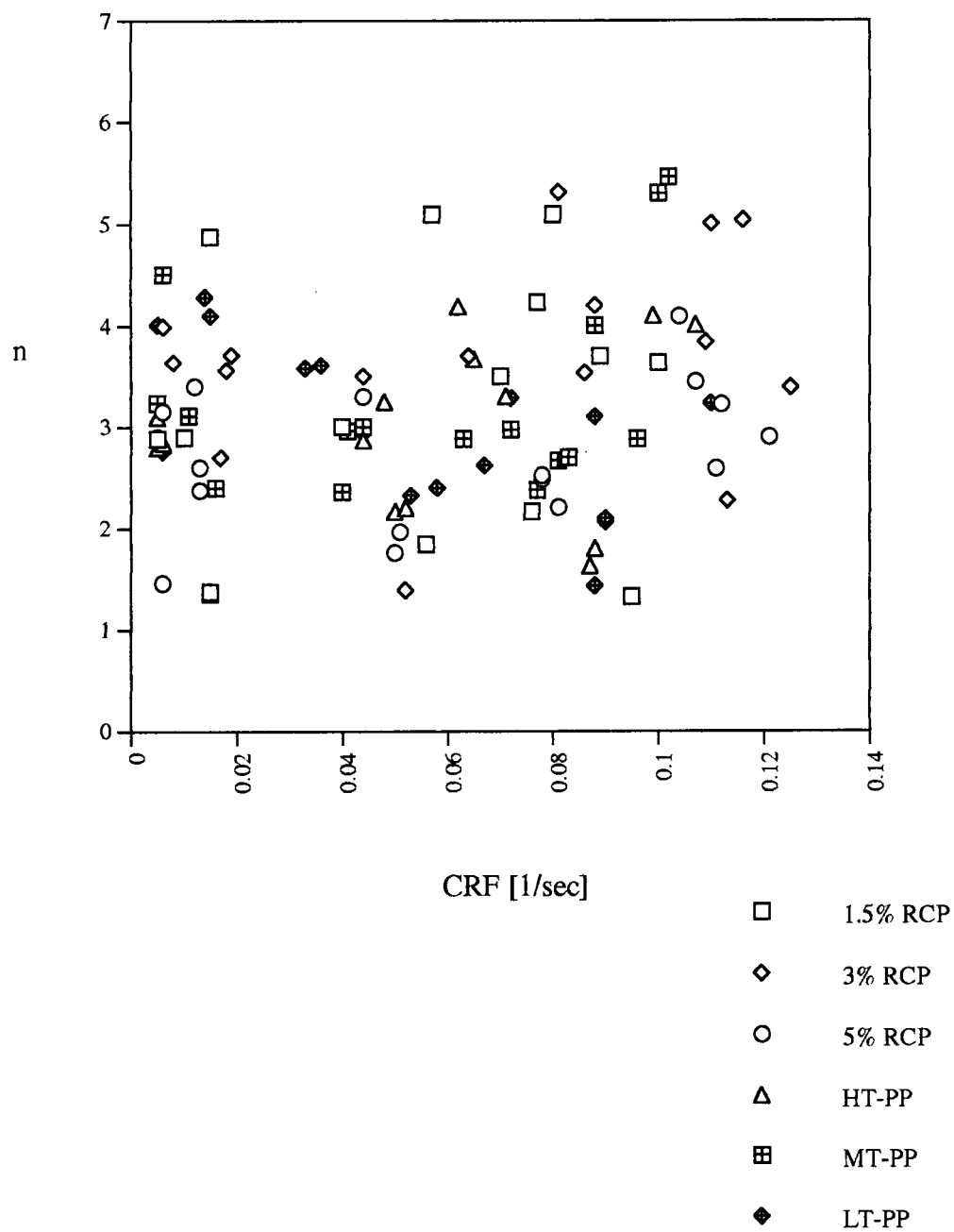


Figure 4.26. Avrami index values as a function of cooling rate for the purified samples.

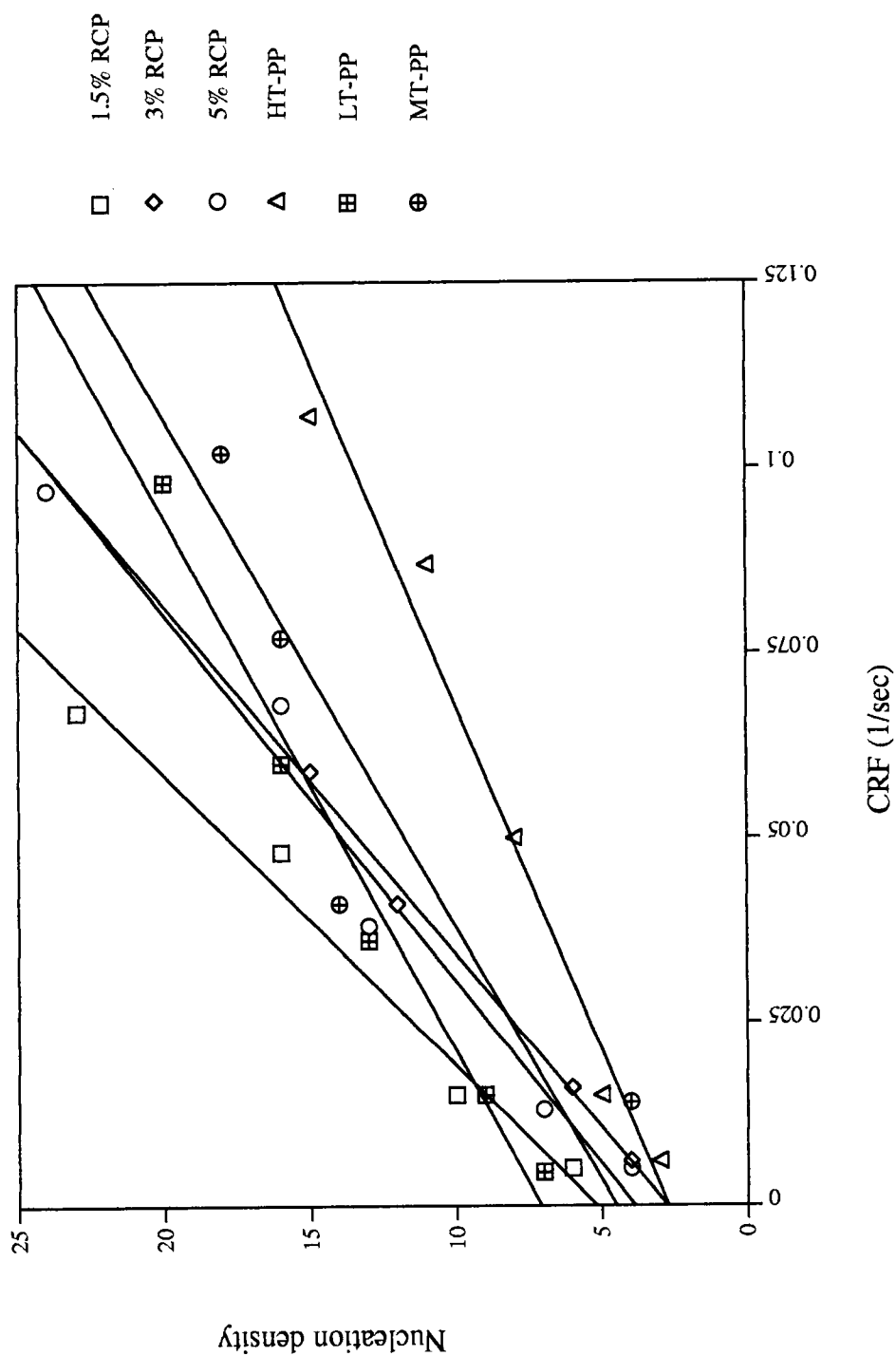


Figure 4.27. Comparison of Nucleation Density values for purified samples.

crystallization rates in the samples not originally exhibiting the nucleation effect, while decreasing the crystallization rates in the other samples by removal of the nucleation impurities. This was accomplished without affecting the crystal geometry or growth rates.

4.3 Morphology

X-ray Diffraction

The Wide Angle X-ray Diffraction patterns of each of the six polypropylenes cooled at both a low cooling rate (850 °C/min) and a high cooling rate (4000 °C/min) were recorded using a flat plate camera. A film pattern of MT-PP cooled at 7000°C/min was also obtained. The purpose of these x-ray diffraction studies was to identify the crystal phase present for each cooling rate.

The pattern of one homopolymer for a high cooling rate is shown in Figure 4.28. The patterns for all samples were quite similar; both the homopolymers and copolymers alike revealed seven rings. The ring diameters were measured and the d-spacings calculated according to the relationships $\tan 2\theta = \frac{D}{2R}$ and Bragg's Law ($\lambda = 2d \sin \theta$), where D=ring diameter, d= d-spacing, R the sample to film distance, and λ the wavelength of radiation used. This information is presented in Table 4.8 for the HT-PP only, since all patterns were nearly identical. The rings were numbered sequentially beginning at the center of the pattern, i.e. the innermost ring was numbered one. Table 4.9, which summarizes the observed d-spacings and corresponding Miller indices obtained from the literature (10, 57, 116) for the various crystal phases of polypropylene, was used to assign the crystal phases present.

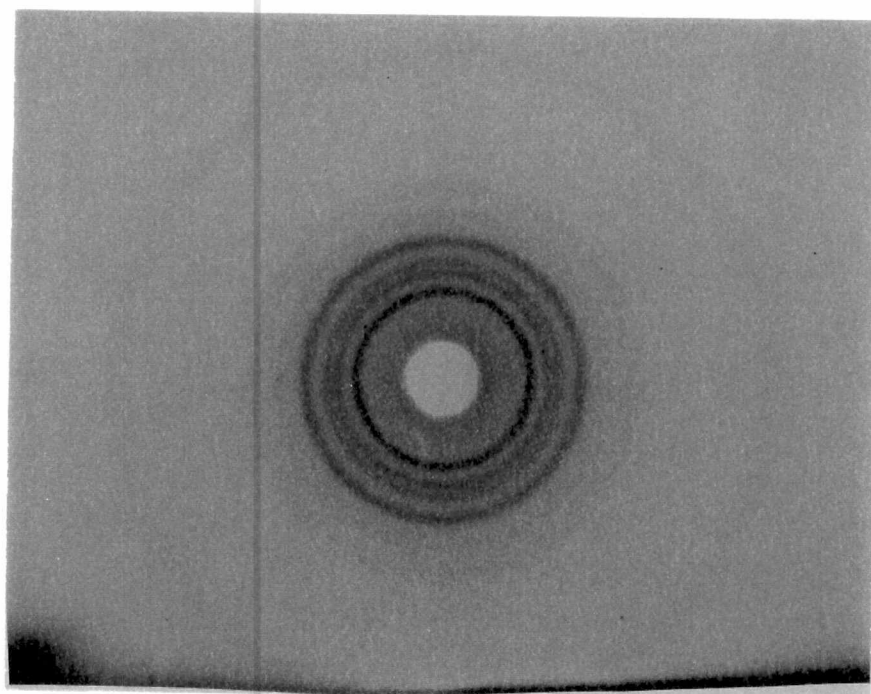


Figure 4.28. WAXD pattern of HT- PP at 4000 °C/min.

Table 4.8. X-ray diffraction results for HT-PP cooled at a rate of 4000 deg C/min.

Ring #	Ring Diam	d-spacing	Miller indices	Crystal
	(mm)		(hkl)	phase
1	18.2	6.26	110	α
2	21.8	5.22	040	α
3	24.5	4.69	130	α
4	28.5	4.09	041	α
5	34	3.50	060	α
6	38.5	3.15	220	α
7	66	2.12	-113	α

Table 4.9. Observed d-spacings and corresponding crystal phases given in the literature (10, 57, 116).

d-spacing	Crystal phase	hkl
6.370	γ	100
6.260	α	110
5.988	smectic	
5.900	γ	1 -1 0
5.514	β	300
5.290	γ	020
5.190	α	040
4.830	γ	022
4.770	α	130
4.415	γ	1 -2 0
4.190	γ, α	111
4.193	smectic	
4.050	γ	026
4.040	α	041
3.810	γ	119
3.513	α	060
3.310	γ	
3.140	α	220
3.101	smectic	
2.580	γ	2 -3 9
2.125	α	-1 1 3
2.123	smectic	

The first four rings observed are characteristic of four strong x-ray reflections of the α crystal form. Reflections typical of the γ phase corresponding to d-spacings of 6.37, 5.29, 4.415, and 4.19 Å are absent. Furthermore, β and γ reflections reported not to coincide with α reflections occur at 2θ values of 16.07° and 20.06° , respectively, neither of which were seen in these diffraction patterns. The pattern of the smectic phase shows two broad maxima at 14.8° and 21.2° and a more pronounced maximum at 28.8° (8, 110). None of the d-spacings corresponding to these angles were found to occur in this study. Consequently, the α phase was determined to be the only crystal form obtained.

The MT-PP sample cooled at a rate in the range of $7000^\circ\text{C}/\text{min}$ was quenched to 0°C and subsequently allowed to equilibrate at room temperature. This lower temperature was achieved due to the use of a setup in which liquid nitrogen cooled the air prior to its entrance into the sample chamber. This technique allowed this very high cooling rate to be reached. The x-ray pattern of this sample also indicates the presence of the α form, as it is similar to the other diffraction patterns obtained.

It was not unusual to identify the presence of the α crystal phase in these highly quenched PP resins, as evidence of the α phase in PP and PP-Ethylene copolymers has been documented by several authors (57, 88). Specifically, copolymerization of PP with ethylene has been seen to increase formation of the gamma phase at atmospheric pressure, but at low supercoolings. For higher supercoolings, the quantity of the γ phase has been shown to decrease substantially (88). Furthermore, evidence of the presence of the α form in microcrystalline and intercrystalline regions within a partially ordered phase of quench-cooled iPP has recently been presented by Caldas et al (13); this evidence is particularly applicable to

the present research in that the polypropylene used was also MT-PP produced by the Exxon Chemical Company.

Density and Crystallinity

The bulk crystallinity of a polymer can be determined by techniques such as density measurement, DSC, X-ray diffraction, and FTIR. In the present research, crystallinities were calculated from density and heat of fusion measurements. First, the crystallinity was calculated from density measurements of samples crystallized from the melt at various cooling rates given by LDM, according to the equation

$$X_c = \frac{\rho_c}{\rho} \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right) \text{ where } \rho \text{ is the sample density and } \rho_c \text{ and } \rho_a \text{ are densities of the}$$

crystalline and amorphous phases, respectively.

The values of percent crystallinity for all samples, listed in Tables 4.10 and Table 4.11, range from 39 to 63%. The density is plotted as a function of cooling rate (CRF) in Figure 4.29. This figure relates the dependence of density on cooling rate. For relatively high supercoolings, the samples achieved a much lower density than at low supercoolings due to the restricted time for crystallization to occur. It is evident that the HT-PP has the highest density (and highest crystallinity) over the range of cooling rates studied. The other two homopolymers are in the same range, 0.900 - 0.910 g/cm³, with the MT-PP having a higher density than the LT-PP overall. The figure shows the 1.5% RCP to have a slightly higher density than the LT-PP over the specified range of cooling rates. Based on LDM data, however, this result can be attributed to the nucleating effect observed for the 1.5% RCP.

Table 4.10. Density values and corresponding crystallinities from DGC measurements of as-received resins crystallized from the melt at different cooling rates.

Sample	CRF (1/sec)	Density (g/cc)	% Cryst
1.5% RCP	0.013	0.9028	57
	0.041	0.9014	56
	0.079	0.9008	55
	0.098	0.9004	55
	0.224	0.8999	54
3% RCP	0.011	0.8973	51
	0.039	0.8964	50
	0.061	0.8942	48
	0.099	0.8928	46
	0.234	0.8912	44
5% RCP	0.015	0.8929	46
	0.054	0.8919	45
	0.063	0.8910	44
	0.098	0.8909	44
	0.232	0.8899	43
LT-PP	0.014	0.9010	55
	0.044	0.9004	55
	0.079	0.8993	53
	0.103	0.8992	53
	0.227	0.8982	52
HT-PP	0.013	0.9079	63
	0.044	0.9064	61
	0.062	0.9050	60
	0.097	0.9035	58
	0.224	0.9021	56
MT-PP	0.016	0.9035	58
	0.045	0.9018	56
	0.070	0.9003	54
	0.099	0.8992	53
	0.223	0.8962	50

Table 4.11. Density values and corresponding crystallinities from DGC measurements of purified samples crystallized from the melt at different cooling rates.

Sample	CRF (1/sec)	Density (g/cc)	% Cryst
1.5% RCP pure	0.015	0.9018	56
	0.048	0.9005	55
	0.067	0.8986	53
	0.108	0.8983	52
	0.230	0.8979	52
3% RCP pure	0.016	0.8990	53
	0.041	0.8973	51
	0.059	0.8963	50
	0.093	0.8953	49
	0.230	0.8945	48
5% RCP pure	0.013	0.8910	44
	0.038	0.8903	43
	0.068	0.8886	41
	0.097	0.8874	40
	0.228	0.8868	39
LT-PP pure	0.015	0.9020	56
	0.036	0.9012	55
	0.060	0.9005	55
	0.098	0.9000	54
	0.235	0.8995	54
HT-PP pure	0.015	0.9059	61
	0.050	0.9044	59
	0.087	0.9036	58
	0.107	0.9025	57
	0.225	0.9014	56
MT-PP pure	0.014	0.9036	59
	0.041	0.9022	57
	0.077	0.9006	55
	0.102	0.8993	54
	0.230	0.8986	53

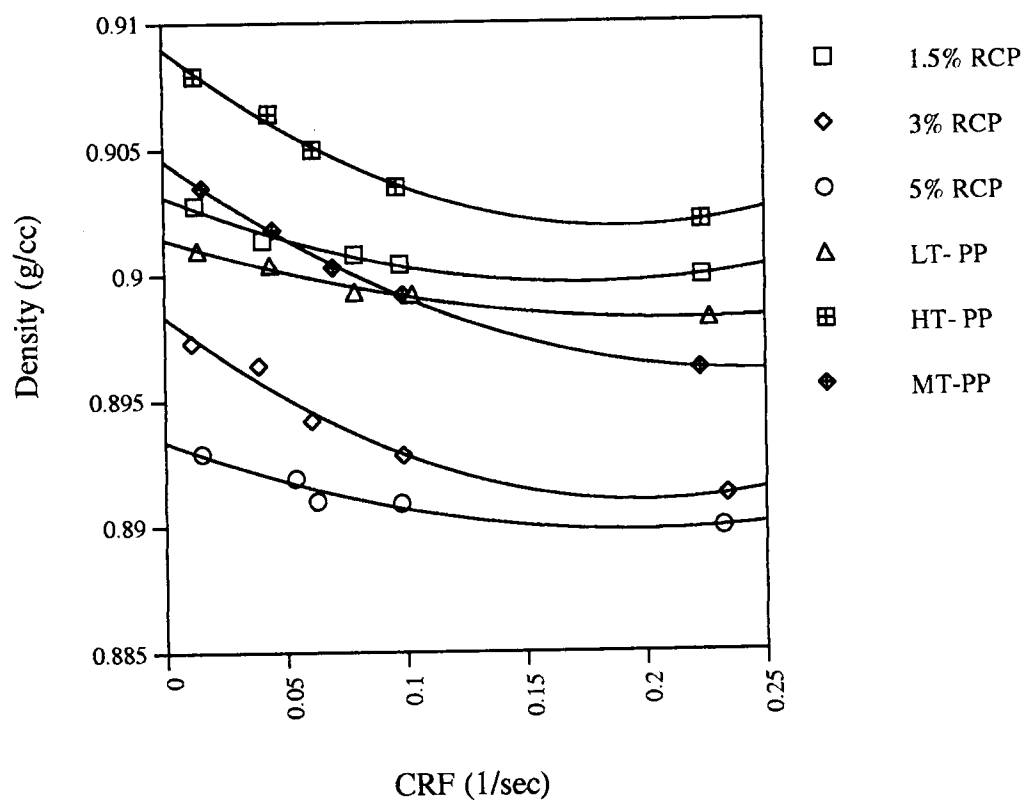


Figure 4.29. Density as a function of cooling rate for the as-received resins crystallized from the melt at various cooling rates.

The purification process appeared to have some effect on density. The density of the HT-PP showed a decrease upon purification, whereas the MT-PP and LT-PP each exhibited a slight increase in density (Figure 4.30). Of the three resins, the nucleating effect was observed only in the HT-PP; thus, it is reasonable to attribute the decrease in density to the removal of this nucleating effect (demonstrated by LDM) which resulted in a lower degree of crystallinity. The increase in density of the other homopolymers is likely to be due to the removal of some atactic material. Thus, the higher degree of homogeneity in the sample would allow for a higher degree of crystallinity to be achieved, indicated by increased density values.

Similar observations were made in the case of the copolymers. The 1.5% RCP and 5% RCP both demonstrated decreased density values upon purification, whereas the 3% RCP sample density increased (Figure 4.31). Once again, the 1.5% RCP and 5% RCP samples showed a nucleating effect which was removed by the purification process; the removal of this effect decreased the density, rendering a reduced percent crystallinity. The 3% RCP density increased upon purification; this was likely due to the removal of amorphous polymer as described above in the case of the two homopolymers.

The crystallinity calculated from density measurements is plotted as a function of the corresponding plateau temperature, i.e. the crystallization temperature given by LDM (Figure 4.32). For each resin, a higher cooling rate resulted in a lower plateau temperature. Thus, the data show that a higher cooling rate and lower crystallization temperature (T_p) result in lower crystallinity in each case. The effects of lower isotactic content and higher comonomer content each causing a lower ultimate crystallinity is evident when comparing the crystallinity of the homopolymers and copolymers for a given crystallization temperature. These comparisons can be made

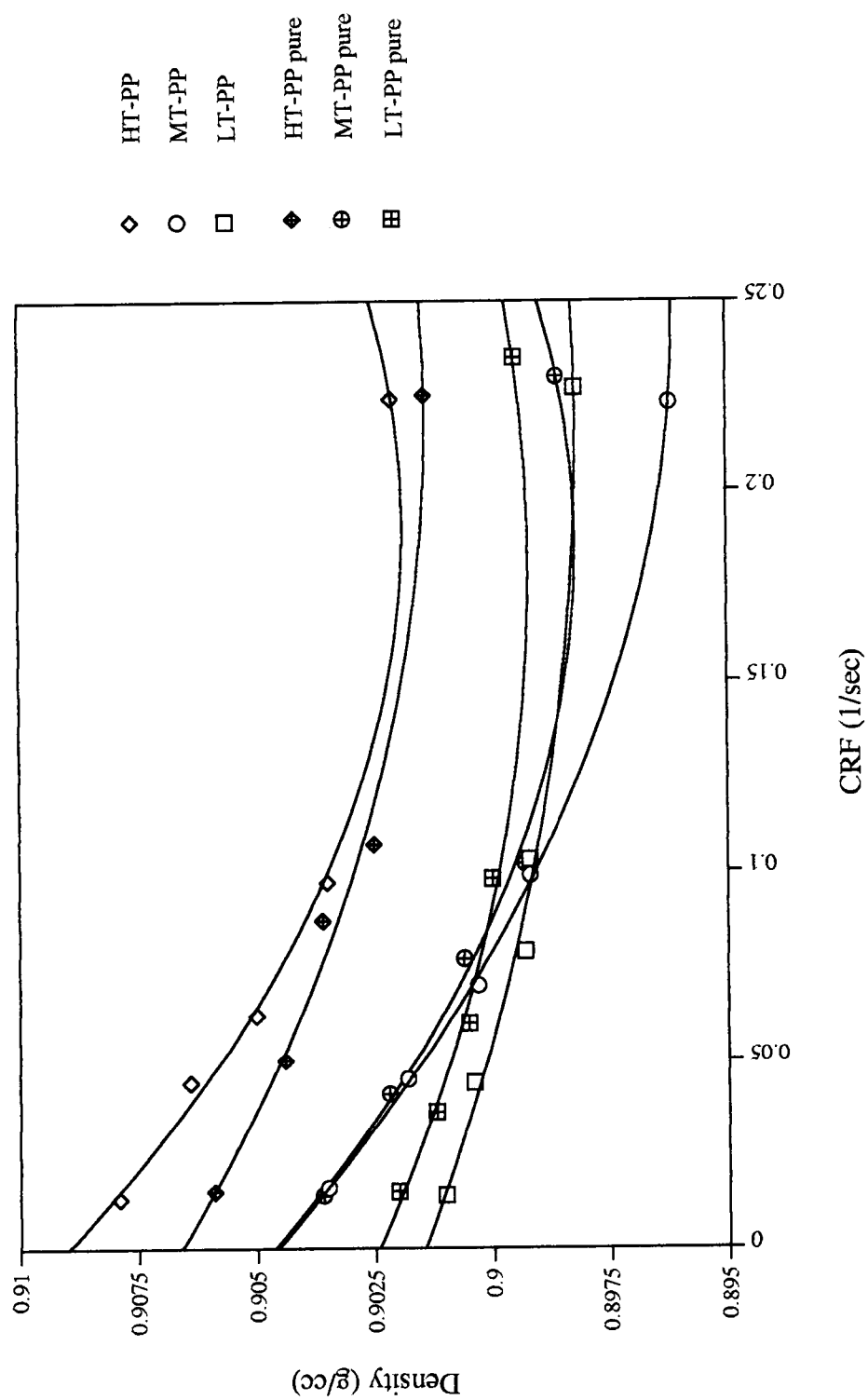


Figure 4.30. Density comparison of as-received and purified homopolymers crystallized from the melt at different cooling rates.

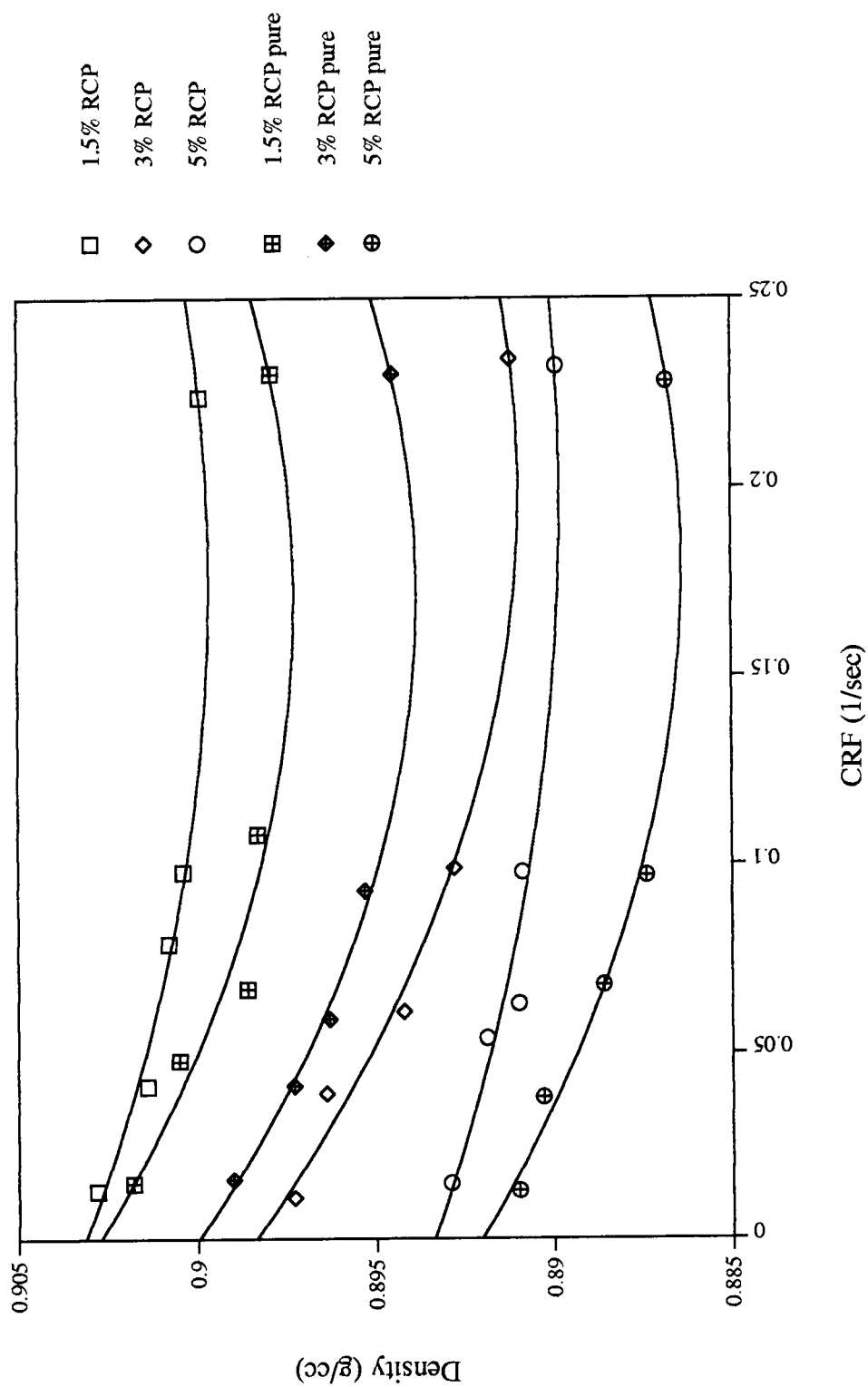


Figure 4.31. Density comparison of as-received and purified copolymers crystallized from the melt at different cooling rates.

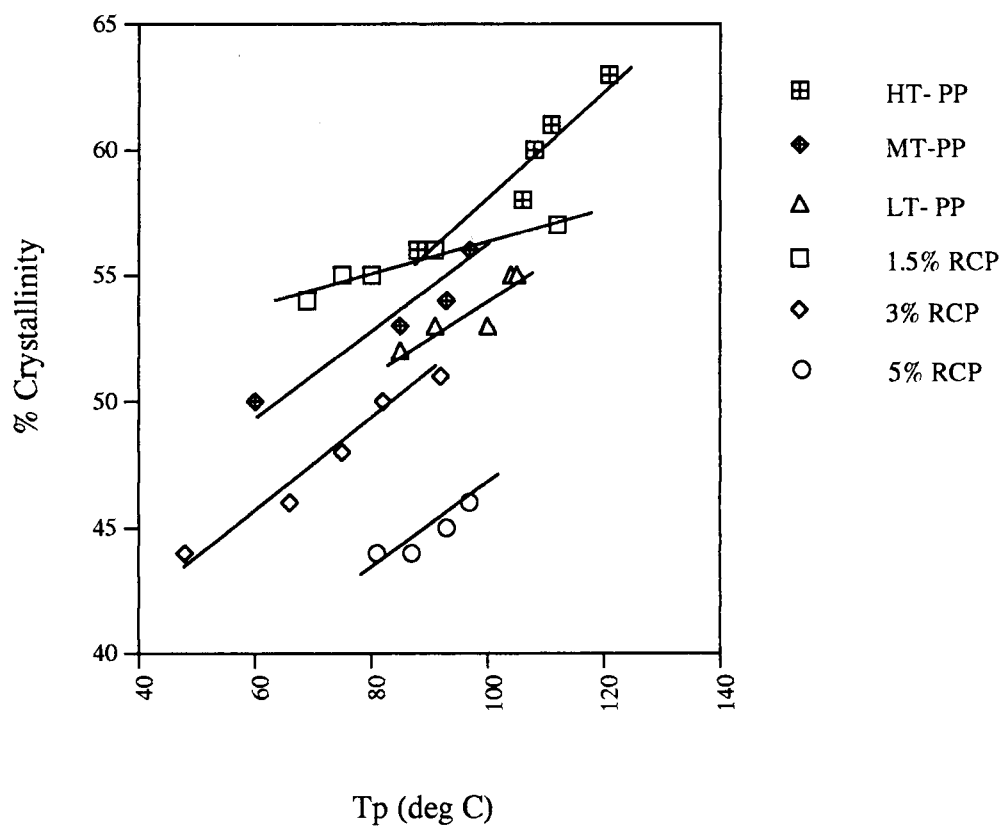


Figure 4.32. Percent crystallinity (from density) vs plateau (crystallization) temperature given by LDM for as-received samples.

since higher cooling rates for the homopolymers yielded crystallization temperatures comparable to those of the copolymers for lower cooling rates. Overall, the copolymerization of polypropylene with ethylene results in a lower density and ultimate degree of crystallinity. The observed nucleating effect appears to have only a slight effect in the case of the 1.5% RCP, increasing the density and final crystallinity slightly.

Percent crystallinity calculations from heat of fusion measurements by DSC ranged from 32 to 62% for the as-received resins crystallized from the melt at different undercoolings (Table 4.12), a slightly broader range than that defined by density measurements. This broader range is probably due to the differences in the physical property being measured and the significantly different cooling rates. In any case, the same trend was given by DSC as was defined by the DGC data, with the exception of the MT-PP yielding values nearly identical to the LT-PP and 1.5% RCP (Figure 4.33).

The purification process affected changes in the measured heats of fusion which resulted in a distinct separation of all the samples according to crystallinity (Figure 4.34). Here again, the differences in the crystallinity of the homopolymers can be attributed to differences in tacticity, while the effects of both comonomer content and tacticity influenced the observed separation of the copolymers.

4.4 Discussion and Summary of Results

Melting

The melting behavior exhibited by the various homopolymers and copolymers is summarized as follows: the homopolymers melted at higher temperatures than the copolymers, with increasing tacticity corresponding to a higher T_m , while the

Table 4.12. Degree of crystallinity as given by DSC.

Sample	Cooling Rate (deg C/min)	ΔH (J/g)	% Crystallinity
HT-PP	5	102.947	62
	10	101.027	61
	20	99.621	60
	40	97.115	59
MT-PP	5	83.655	51
	10	83.211	50
	20	82.301	50
	40	82.285	50
LT-PP	5	82.465	50
	10	82.256	50
	20	81.645	49
	40	81.317	49
1.5% RCP	5	83.990	51
	10	83.866	51
	20	82.937	50
	40	82.221	50
3% RCP	5	64.710	39
	10	64.560	39
	20	63.940	39
	40	61.994	38
5% RCP	5	58.491	35
	10	58.134	35
	20	54.907	33
	40	52.555	32

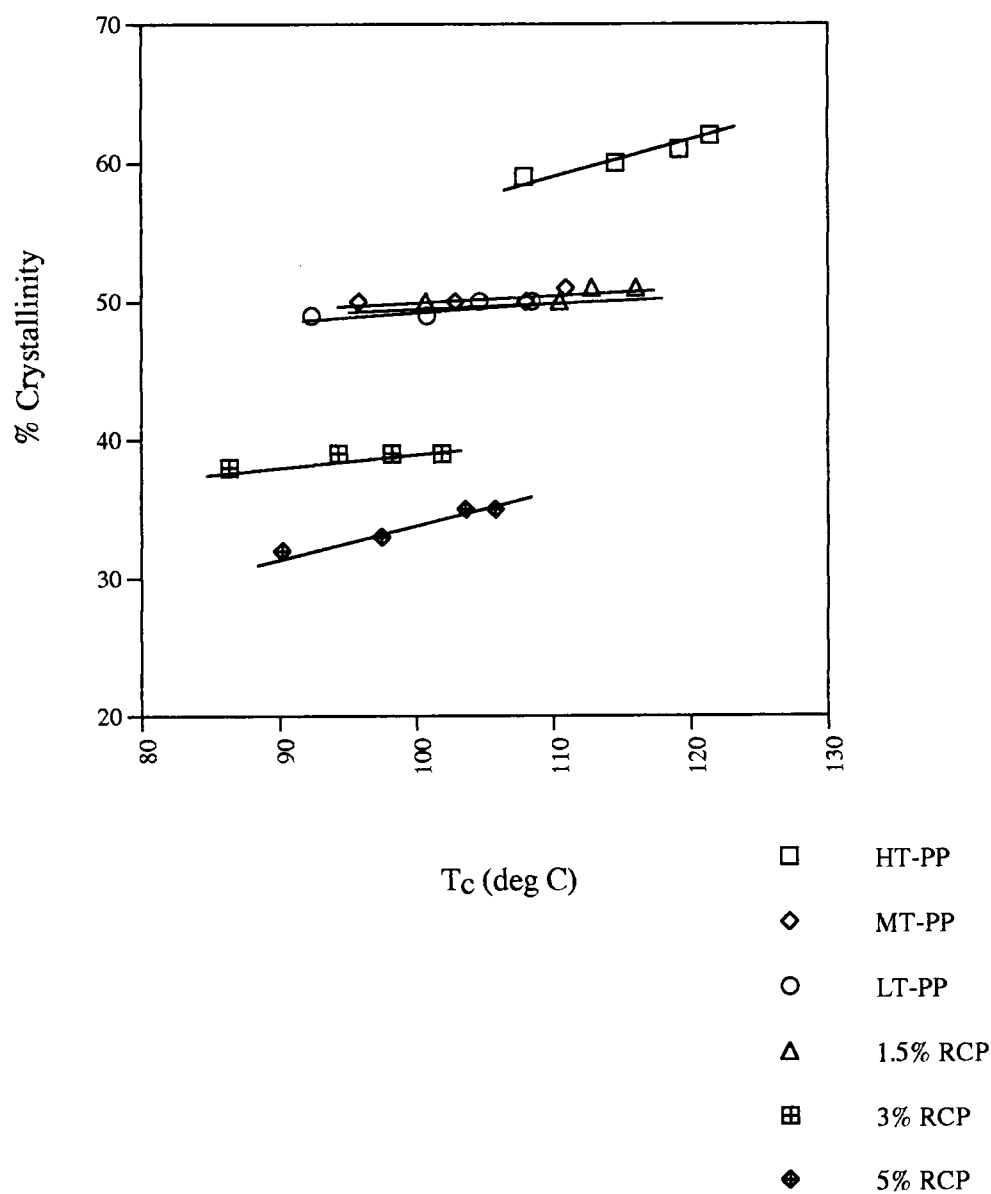


Figure 4.33. Percent crystallinity vs. Crystallization temperature as determined from heat of fusion measurements given by DSC.

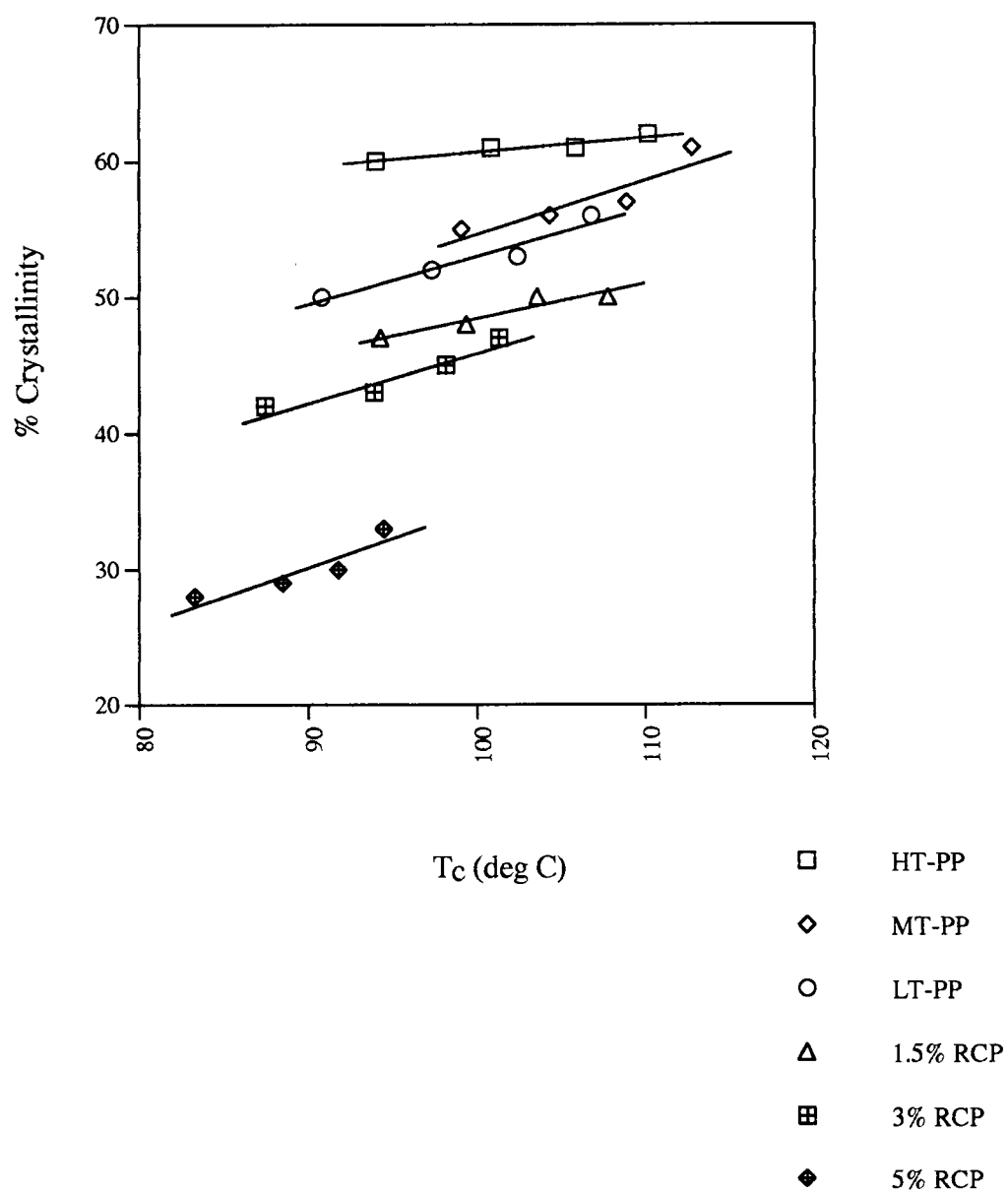


Figure 4.34. Percent crystallinity vs. Crystallization temperature as determined from DSC heat of fusion measurements of the purified samples.

copolymers melted at lower temperatures with increasing ethylene content. It is convenient to describe melting in thermodynamic terms at this point. Theoretically, melting takes place when the free energy of the liquid and solid phases are the same, so that they are in equilibrium with each other. At this point, the change in free energy on melting is zero:

$$\Delta G = \Delta H - T\Delta S = 0 \quad (4.4)$$

where $T=T_m^\circ$. Thus, the equilibrium melting temperature is defined as $T_m^\circ = \frac{\Delta H}{\Delta S}$

where ΔH and ΔS are the enthalpy and entropy of fusion, respectively. One explanation of the melting point depression observed for the copolymers is that preferential ordering of the copolymer chains is required for crystallization to occur and is manifested as an increase in entropy (27). However, a second argument is that of an enthalpy effect, resulting from the defective heat of fusion which accompanies crystallization in the copolymer case (107). Two very similar equations for the melting temperature as a function of crystal size for random copolymers (with low monomer concentrations) have been derived according to the entropy and enthalpy arguments; this similarity is said to imply that melting temperature data taken as a function of copolymer composition and crystal thickness does not distinguish between the inclusion and exclusion models (107).

The addition of comonomer units adds defects to the chain which may be included or excluded from the crystals. In either case, there is an increase in the surface free energy which can be illustrated with the following general equation:

$$\Delta G = \Delta G_v + \Delta G_s \quad (4.5)$$

where ΔG is the total free energy difference between the copolymer crystal and the melt, ΔG_V the free energy of the volume of the crystal, and ΔG_S the surface free energy. ΔG_S is always positive, while ΔG and ΔG_V must be negative to provide a driving force for either melting or freezing. Thus, ΔG_V must override the effect of ΔG_S . Assuming an exclusion model, for example, the ΔG_S term becomes much larger due to the addition of comonomer units to the crystal surface; hence, ΔG becomes larger according to equation 4.5. In this case, ΔG_V must be small enough to keep ΔG less than zero in order for the phase transition to occur.

The lamellar thickness plays a significant role in the melting of polymers. Theoretically, the actual melting temperature of a polymer is affected by its morphology. In particular, lamellar thickness is known to have a major influence on T_m based on the fact that thinner lamellae have a greater surface energy. This concept leads to the following relationship:

$$T_m = T_m^\circ - \frac{2\sigma_e T_m^\circ}{l\Delta H_f} \quad (4.6)$$

where T_m° is the equilibrium melting temperature, σ_e the fold surface energy, l the lamellar thickness, and ΔH_f the heat of fusion. Both equation 4.6 and experimental data have shown that isotactic polypropylene melts at decreasing temperatures with decreasing lamellar thickness (89). Since the present study yielded reduced melting

temperature values for the copolymers versus the homopolymers, it can be argued that the copolymer lamellae are thinner than the lamellae of the pure homopolymers.

Kinetics Analysis

The crystallization rates of the homopolymers were generally faster than those of the copolymers according to both DSC and LDM. Here, the homopolymers, consisting of one monomer type only, are driven thermodynamically to crystallize in order to lower their free energy. When comonomer units are incorporated, there is an addition of chain defects which increase the surface free energy according to equation 4.5. Note that this assumes that the defects are excluded from the crystal and occur on the surface. The result is a slower crystallization rate for the copolymer than the homopolymer. Further, increasing the amount of comonomer effectively increases the addition of chain defects, and hence the surface free energy. Therefore, the 5% RCP had a slower crystallization rate than the 1.5% RCP.

The crystallization data obtained from DSC, however, revealed some unexpected behavior, in that the 5% RCP crystallized faster than the 3% RCP, and the LT-PP crystallized faster than the MT-PP. The faster rate exhibited by the 5% RCP can be attributed to the unusually high nucleation density observed for this sample. The nucleating agent causing this effect may be functioning to reduce the surface free energy barrier to nucleation and cause a faster crystallization rate (74). In contrast, the LT-PP did not exhibit this nucleation effect. Hence, the LT-PP may have crystallized faster than the MT-PP as a result of a higher degree of isotactic content in some of the pellets analyzed. For example, the tacticity estimations were carried out on individual pellets initially, followed by bulk melt-pressed films. The latter gave a much higher

peak ratio than the former, indicating some degree of variability in tacticity on a pellet to pellet basis. These two cases of unexpected crystallization rates did not occur in the overall LDM data, although there was some degree of scatter in the data, evidence of some variation in the measured crystallization rates. It is possible that the effect of a very high supercooling lends to a lesser degree of sensitivity to small variations in crystallization rate in the LDM data than the DSC data.

The purification of the resins caused both slight increases and decreases in the crystallization rates. In particular, the crystallization rates of the samples initially exhibiting the nucleation effect decreased dramatically. The result was an ordering of the samples according to crystallization rate defined by DSC that was in agreement with that previously defined by LDM. These changes in crystallization rate for the samples originally demonstrating increased nucleation are likely to be caused by the removal of the nucleating agent. The surface free energy barrier would then increase and, consequently, reduce the crystallization rate. Overall, the crystallization rates were shown to be significantly influenced by tacticity variations and comonomer content.

The variations in crystal geometry, e.g. spherical and elliptical structures, observed in the 3% RCP and 5% RCP were unaffected by purification. The 3% RCP, in particular, exhibited the most variation in geometry and the most scattered and highest Avrami index values given by DSC and LDM. Hence, the nature of these values is probably largely due to the presence of spheres and sheaves, the latter of which yields a much higher Avrami index theoretically ($n=5$ or 6), while the effect of mixed nucleation mode (although not observed) may also be a contributing factor.

The growth rates were found to be constant for this highly nonisothermal process. This effect was previously reported to occur for iPP (121). The tacticity and

ethylene content seem to be dominating parameters controlling the growth rates. The homopolymer rates were higher than the copolymer rates with the HT-PP the highest and the 5% RCP the lowest. This influence of isotacticity is in agreement with previous documentation (55, 101). The differences observed for the copolymers are likely to be due to the random incorporation of ethylene units which sufficiently interrupt the crystallization process. For very high cooling rates, the crystallization temperature is lowered significantly. Thus, the ethylene units cannot be incorporated into the crystals due to time constraints and are rejected, resulting in lower growth rates (14). It is likely that this effect is increased with increasing ethylene comonomer, as was indicated in Figure 4.24. The crystallization temperature is much higher for low cooling rate conditions; consequently, it is possible that the ethylene units may be included in the crystals. In this case, faster growth rates would be expected.

Crystallinity

The differences in the bulk crystallinity values measured by DGC and DSC can be attributed to variations in tacticity and ethylene content. The HT-PP sample, 99% isotactic, yielded a higher crystallinity than did the MT-PP (93%), or the LT-PP (91%). Further, the copolymers, found to have decreasing tacticity with increasing ethylene content, yielded lower crystallinity values than the homopolymers for a given T_c . Specifically, the ethylene sequences act as chain defects which reduce crystallinity, resulting in a lower density. These data imply that the tacticity and the comonomer content both significantly influence the final crystallinity achieved by a polymer. This influence has previously been documented by several authors (43, 55, 107, 108).

It is unclear from these data alone whether the addition of a small amount of ethylene (1.5%) to an isotactic homopolymer causes more chain defects than does the inclusion of atactic sequences which function to decrease the amount of isotactic material in a homopolymer (LT-PP). The slightly higher crystallinity values obtained for the 1.5% RCP may be a result of the observed nucleating effect and the relatively high degree of tacticity estimated for the sample. First, a higher initial nucleation density in this sample would allow for an increased density and crystallinity due to the higher temperature of crystal nucleation, followed by a greater amount of time in the temperature range where crystal growth can occur. This argument is in agreement with that presented by Lu and Spruiell (75) for nucleated and neat polypropylene homopolymer data obtained by DGC and DSC. Second, the estimated isotacticity of the 1.5% RCP is actually higher than that of the LT-PP, and may be a contributing factor to its higher final crystallinity value.

The increase in density seen for the homopolymers not exhibiting the nucleation effect may be caused by the removal of a quantity of amorphous (atactic) polymer during the purification process, although this effect could not be conclusively demonstrated by FTIR. The smaller amount of amorphous polymer present in the pure resins allowed these homopolymers to undergo more efficient chain packing, resulting in higher crystallinity levels as indicated by higher densities.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The characterization of the polypropylene homopolymers and copolymers indicated that chain irregularities, such as atactic sequences and ethylene units, function to decrease the melting temperature. These parameters seem to influence melting behavior somewhat independently. The purification process introduced in this study also affected changes in melting temperature.

Nonisothermal crystallization experiments revealed that nucleation rates, growth rates, morphology, and the overall transformation kinetics were strongly dependent on the cooling condition employed, along with the tacticity, comonomer content, and purity of the polymers studied. The homopolymers were observed to crystallize faster than the copolymers and in order of increasing isotactic content. Similarly, the copolymers crystallized at slower rates corresponding to increasing comonomer content and decreasing isotacticity. The nucleation densities of the resins fell into the same range once the nucleating impurities were removed. The crystal growth geometries were distinctly different in the copolymers with high ethylene content (3 and 5%), although the crystal phase was the same (α -phase) for all materials at all cooling conditions.

The percent isotacticity and ethylene content both influenced the degree of crystallinity which could be obtained for a given cooling rate. In general, a higher percentage of isotactic content yielded a higher final crystallinity in both the

homopolymers and the copolymers. Furthermore, a higher percentage of comonomer units incorporated decreased the final degree of crystallinity. In all cases, the crystallinity values were affected by the cooling condition, where higher supercoolings reduced the percent crystallinity obtained.

Purification of the resins to remove nucleating impurities altered the crystallization rates slightly. However, the resulting trend was in accordance with previous LDM results which revealed distinct separations in crystallization rates corresponding to variations in tacticity and comonomer content.

The LDM and DSC techniques showed differences in sensitivity to the crystallization behavior. Although both techniques measured bulk crystallization, it is likely that the significantly higher cooling rates applied in LDM decreased the sensitivity of the technique to specific details of the crystallization process. This would account for the unexpected crystallization behavior initially indicated by DSC, but not by LDM. Despite this discrepancy, the LDM data demonstrated the same trends in crystallization rates as the purified DSC data. Furthermore, the crystallization data given by both techniques were quantitatively similar: $n=3 - 4.5$ for LDM and $n=3.5 - 4.7$ for DSC (with the exception of the unusually high value given for the 3% RCP).

Recommendations

It would be most useful to obtain NMR data characterizing the percent isotactic content, as well as the atactic content, for all the samples. This type of information would allow for a clearer comparison of all materials based on variations in isotactic content. Isothermal studies of the crystallization behavior of these polypropylenes

would be useful for comparison to the nonisothermal data presented here. It would allow for further definition of the overall crystallization kinetics of these materials. To further define the growth rate dependencies on temperature for these resins, it would be beneficial to determine the equilibrium melting temperature of the copolymers and to measure growth rates at higher supercoolings. A new VCR which can acquire more than 60 frames of images per second needs to be employed in the LDM technique in order to measure the increased growth rates which occur under very high cooling conditions due to the speed with which PP can crystallize. Last, it would be interesting to define the crystallization behavior at even higher supercoolings. This can only be achieved by modifying the present LDM system. The addition of a cooling apparatus would decrease the temperature of the cooling medium and increase the resultant cooling rates significantly.

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