CRYSTALLIZATION BEHAVIOR AND STRUCTURE PROPERTY BEHAVIOR
OF SELECTED THERMOPLASTIC POLYMERS

by

Brian G. Risch

Dissertation submitted to the faculty of
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY
in
Materials Engineering Science

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ABSTRACT

The crystallization behavior of poly(p-phenylene sulfide) PPS has been studied. Two PPS samples with $<M_w>$ = 43K and $<M_w>$ = 83K were fractionated to remove low molecular weight oligomers yielding fractionated PPS samples with $<M_w>$ = 57K and $<M_w>$ = 113K. The fractionated samples were then treated with an ion exchange process to allow control over the nature of endgroup counter-ion. Isothermal rates of bulk crystallization were analyzed as a function of molecular weight of PPS, fractionation, and chemical nature of the endgroup counter-ion. Additionally the spherulitic growth rates and nucleation densities were studied as a function of the chemical nature of the endgroup counter-ion for fractionated PPS with $<M_w>$ = 57K. As a function of endgroup counter-ion, crystal growth rates and overall rates of crystallization decreased in the following order: H > Zn > Na. No significant trends in nucleation density as a function of endgroup counter-ion were observed.
Bulk crystallization rates, nucleation density, general morphological features, equilibrium melting point, and absolute crystalline percentage of linear and star-branched nylon-6 have been studied as a function of branch-point functionality and crystallization temperature. Overall bulk crystallization rates were described in terms of the Avrami equation. The crystallization half-times of star-branched nylon-6 as a function of supercooling were reduced relative to those of linear nylon-6 of comparable molecular weight. Irregularities in lamellar structure were implied by SAXS experiments on samples with branch-point functionality as low as three.

The effects of changing the block length of poly(dimethylsiloxane), PSX, blocks in poly(etheretherketone)-poly(dimethylsiloxane), PEEK-PSX, multi block copolymers and their ketimine precursors, PEEKt-PSX, were investigated. A dramatic dependence on thermal history prior to crystallization was observed in both block copolymer systems. Block copolymers crystallized from the glassy state obtained a much higher degree of crystallinity at a much faster rate of crystallization than copolymers crystallized from the melt at identical crystallization temperatures.

Thermal and mechanical behavior of bisphenol-A polycarbonate was studied as a function of thermal history and absorbed mass fraction of CO₂. Mechanical testing and gas absorption experiments were performed on physically aged and unaged polycarbonate. Gas absorption studies indicated that although initial diffusion was somewhat retarded in the aged samples, both aged and unaged polycarbonate samples showed identical equilibrium absorbed gas values at 6500KPa and identical gas desorption behavior. Absorbed CO₂ was shown to plasticize polycarbonate.

Polymeric liquid crystalline foams were produced from star-branched polyoxybenzoate-polyoxyphenoxybenzoate copolymers (POB-co-POPB) via gas supersaturation followed by thermal blowing. Solid state CO₂ gas absorption well as melt processability of star-branched POB-co-POPB was increased relative to the linear polymer of comparable molecular weight. While CO₂ blown foams of linear POB-co-POPB produced by the gas supersaturation technique had a relatively high density and showed highly anisotropic bubble growth, well defined, nearly isotropic foams of star-branched POB-co-POPB with mean cell size from 200 to 400μ were made using the gas supersaturation technique.
ii.) ACKNOWLEDGEMENTS

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I also appreciate the support of this research by the National Science and Technology Center for High Performance Polymeric Adhesives and Composites at Virginia Polytechnic under contract number DMR8809714, as well as the Dow Chemical Company and Phillips Petroleum Company. I would also like to acknowledge the continued financial support from the Phillips fellowship at Virginia Polytechnic.
Dedicated to my father, Gordon Risch

whose guidance and support have been invaluable.
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i.) INTRODUCTION:

The physical behavior of polymeric materials is governed by a number of chemical and physical variables. Amongst these variables are chemical composition, chemical microstructure, molecular topology, molecular weight, molecular weight distribution, chemical additives, and the effects of processing history including thermal and mechanical history. The fact that there are so many variables influencing the physical behavior of polymeric materials makes the field of polymer science very broad indeed. This study investigates the effects of a number of key variables on the crystallization behavior and structure property behavior of a number of thermoplastic polymeric materials. Apart from the literature review chapters, the dissertation consists of several manuscripts which have either been accepted for publication in scientific journals (Chapters 4, 6, and 7) or submitted for publication (Chapters 3 & 5). Therefore, the writing style is somewhat different than what may be expected for a Ph.D. dissertation. Additionally, because additional co-authors contributed to the manuscripts, more than one author is implied at places in the dissertation as well, although the dissertation is primarily the work of the author.

The first part of this volume focuses primarily on the crystallization behavior and morphological features of three polymer systems. It begins with a general outline of quiescent crystallization of polymers in which models for the crystallization behavior
of polymeric materials are discussed and the effects of variables such as chemical composition, molecular weight, endgroup effects, and molecular topology are also summarized. The next two chapters discuss the crystallization behavior of poly(p-phenylene sulfide), PPS. Chapter 2 discusses previous literature on the chemistry, mechanical behavior, and crystallization behavior of PPS.

Chapter 3 is a study of the effects of molecular weight, fractionation, and endgroup counter-ion on the crystallization behavior of PPS. The effects of molecular weight, fractionation, and endgroup counter-ion on rheological behavior, crystalline growth rate, as well as nucleation density are examined. Two PPS samples with $<M_w> = 43K$ and $<M_w> = 83K$ were fractionated to remove low molecular weight oligomers yielding fractionated PPS samples with $<M_w> = 56K$ and $<M_w> = 113K$. The fractionated samples were then treated with an ion exchange process to allow control over the nature of endgroup counter-ion. Isothermal rates of bulk crystallization were analyzed as a function of molecular weight of PPS, fractionation, and chemical nature of the endgroup counter-ion. Additionally the spherulitic growth rates and nucleation densities were studied as a function of the chemical nature of the endgroup counter-ion for fractionated PPS with $<M_w> = 57K$. It was found that as a function of endgroup counter-ion, crystal growth rates and overall rates of crystallization decreased in the following order: H > Zn > Na. The order of decreasing crystal growth rates corresponded to a similar increase in melt viscosity as a function of endgroup counter-ion (ie. H < Zn < Na) suggesting
that the reason for increasing growth rates is decreasing secondary interchain interactions. No significant trend in nucleation density as a function of endgroup counter-ion were observed, but the nucleation density was observed to increase as a function of molecular weight by small-angle light scattering (SALS). Crystallinity determinations by WAXD and measurements of the heats of crystallization and melting illustrated that higher molecular weight PPS attained lower levels of crystallinity than PPS of lower molecular weight PPS when crystallized under identical conditions.

The next chapter discusses the effects of molecular topology on the crystallization behavior of nylon-6. The effects of changing molecular topology from linear to three-arm star to six-arm star while keeping total molecular weight constant are investigated in terms of the thermodynamic stability of the polymer crystals, crystallization kinetics, as well as rheological behavior. Bulk crystallization rates, nucleation density, general morphological features, equilibrium melting point, and absolute crystalline percentage of linear and star-branched nylon-6 were studied as a function of branch-point functionality and crystallization temperature. Overall bulk crystallization rates were described in terms of the Avrami equation. No significant difference in bulk crystallization rates as a function of crystallization temperature or absolute crystalline percentage was observed between linear, three-arm, and six-arm samples with identical thermal history and molecular weight. Equilibrium melting points obtained by Hoffman Weeks analysis were reduced in star-branched nylon-6
compared to the linear polymer of comparable molecular weight. In order to
deconvolute the effects of a decreased thermodynamic driving force for formation of
crystals of branched polymers, crystallization half times were measured as a function
of supercooling. The crystallization half-times of star-branchned nylon-6 as a function
of supercooling were reduced relative to those of linear nylon-6 of comparable
molecular weight. The general spherulitic superstructure appeared unaffected by
increasing branch-point functionality up to six. However irregularities in lamellar
structure were implied from SAXS experiments on samples with branch-point
functionality as low as three.

Chapter 5 examines the crystallization behavior and structure-property behavior
of poly(etheretherketone)-poly(dimethylsiloxane), PEEK-PSX, copolymers and their
ketimine precursors. The effects of varying the molecular composition and the
resulting changes in morphological features are investigated in terms of mechanical
behavior as well as crystallization behavior. The effects of changing the block length
of poly(dimethylsiloxane), PSX, blocks in poly(etheretherketone)-
poly(dimethylsiloxane), PEEK-PSX, multiblock copolymers and their ketimine
precursors, PEEKt-PSX, was investigated. It was found that the tensile modulus of
PEEK-PSX multiblock copolymers with amorphous PEEK blocks with $<MW> = 5000$
increased by 800% as the PSX block length was decreased from $<MW> = 5000$ to
$<MW> = 3000$, i.e. PSX mass fraction was decreased from 56% to 36%. After
crystallization of the PEEK blocks, the modulus of the copolymer with PSX block
<MW> = 3000 increased by ca. 500%, and the modulus of the copolymer with PSX block <MW> = 5000 increased ca. 200%. Both the rates of crystallization and the absolute crystallinity of the PEEK phase in these block copolymers was decreased relative to that of PEEK homopolymer of approximately the same molecular weight. Relative to PEEK homopolymer of approximately the same molecular weight, the crystallization half times for the multiblock copolymers when crystallized from the melt were increased by a factor of ca. 500 for the PEEK(5K)PSX(3K) system and by a factor of ca. 1000 for the PEEK(5K)PSX(5K) system. Crystalline volume fraction of the PEEK phase measured by WAXD was decreased from a maximum value of 41% in PEEK homopolymer crystallized under similar conditions to a maximum value of ca. 30% in the PEEK phase in the block copolymer systems. A dramatic dependence on thermal history prior to crystallization was observed in both block copolymer systems. Block copolymers crystallized from the glassy state obtained a much higher degree of crystallinity in the PEEK phase at a much faster rate of crystallization than copolymers crystallized from the melt at identical crystallization temperatures. Copolymers crystallized from the glass attained maximum levels of crystallinity of approximately 30% while those crystallized from the melt attained maximum levels of crystallinity of only 5-10%. The rate of crystallization for samples crystallized from the glass was approximately 30 times greater than that for samples crystallized from the melt at identical crystallization temperatures.
The second part of this volume investigates some of the aspects of processing polymers with pressurized gas. This section begins with a brief literature review outlining several important industrial applications for processing polymers with pressurized gas followed by a summary of several key experimental studies in the area.

Chapter 7 examines the effects of physical aging and carbon dioxide absorption on the thermal and mechanical properties of bisphenol-A polycarbonate. The effects of thermal and gas absorption history are investigated in terms of the gas absorption behavior, glass transition behavior, and the mechanical properties. Thermal and mechanical behavior of bisphenol-A polycarbonate was studied as a function of thermal history and absorbed mass fraction of CO₂. Physical aging at 120°C for one week produced dramatic changes in both the thermal and mechanical behavior. Gas absorption studies indicated that although initial diffusion was somewhat retarded in the aged samples, both aged and unaged polycarbonate samples showed identical equilibrium absorbed gas values at 6500KPa and identical gas desorption behavior. Absorbed CO₂ was shown to dramatically reduce the glass transition of polycarbonate. Additionally, samples which had been aged and absorbed a mass fraction of 0.07 to 0.10 of CO₂ showed thermal and mechanical behavior identical to that of a glass quenched from above Tg with identical adsorbed mass fraction. Once the absorbed gas was desorbed, the thermal and mechanical properties were similar

6
to those of a glass freshly quenched from above $T_g$. This study demonstrates that CO$_2$ gas absorption followed by desorption reverses physical aging in polycarbonate.

The final chapter discusses a novel technique for the production of liquid crystalline foams using a gas supersaturation technique. It examines several variables including processability and gas absorption behavior which must be controlled in order to produce a liquid crystalline foam. The study outlines how molecular weight and molecular topology as well as copolymer composition in poly(oxybenzoate)-poly(oxyphenoxybenzoate), POB-POPB, copolymers was modified in order to produce a liquid crystalline polymer which could be foamed using a gas supersaturation technique. Finally the effects of foam cell size and cell structure are discussed in terms of the mechanical properties of several POB-co-POPB foams. Linear and star-branched polyoxybenzoate-polyoxyphenoxybenzoate copolymers (POB-co-POPB) at 65/35 molar ratio were synthesized via melt acidolysis using AB type monomers and branching agents. By controlling the molecular weight and topology of these polymers, both melt processability and solid state CO$_2$ gas absorption behavior were enhanced. POB-POPB copolymers with molar ratio 65/35 showed a glass transition of 143°C and completion of melting at ca. 300°C. POB-POBP copolymers with systematically increasing branching agent content showed systematically decreasing peak intensity in wide angle x-ray diffraction, indicating that increasing branch-point concentration leads to a decrease in liquid-crystal ordering. Star-branched POB-POPB copolymers showed greatly enhanced carbon dioxide gas absorption behavior.
relative to their linear counterparts. While \( \text{CO}_2 \) blown foams of linear POB-co-POPB produced by the gas supersaturation technique had a relatively high density and showed highly anisotropic bubble growth, well defined, nearly isotropic foams of star-branched POB-co-POPB with mean cell size from 200 to 400\( \mu \)m were made using the gas supersaturation technique. Structural features were characterized via scanning electron microscopy, and mechanical properties were determined by indentation testing with a 0.25" ball indenter. These LCP foams exhibit relative mechanical properties similar to polystyrene and microcellular polycarbonate foams. A strong inverse relationship was noted between cell size and modulus for liquid crystalline foams with cell size below 400\( \mu \)m.
PART I:

CRYSTALLIZATION KINETICS AND MORPHOLOGICAL FEATURES

OF SELECTED THERMOPLASTIC POLYMERS
CHAPTER 1
Quiescent Crystallization Behavior of Polymers

Many factors influence the crystallization of polymeric materials such as the chemical composition and microstructure of the polymer chain, chain topology, molecular weight and weight distribution, chemical nature of endgroups, as well as the thermal and mechanical conditions during crystallization. As a result the crystalline morphology may be greatly varied depending on the aforementioned variables resulting in a wide range of thermodynamic and mechanical properties. The crystallization of polymers occurs at conditions far removed from thermodynamic equilibrium; therefore the crystalline morphology and resulting physical properties are determined by kinetic factors which are in competition with thermodynamic equilibrium. In many ways, polymer crystals violate the thermodynamic rules which govern crystal growth. For example usually little or no crystal growth occurs on the crystal surface with the highest surface energy, the fold surface. Additionally, polymer crystallization consistently leaves a second, often large, amorphous phase which violates the Gibbs phase rule. These anomalies are a consequence of the chain-like nature of polymer molecules.

A phase transformation, such as the crystallization of a polymer from its melt, occurs in two steps. First the new phase must be initiated within the parent phase,
and then the new phase grows. Initiation may occur homogeneously through statistical fluctuations or heterogeneously through the presence of impurities or residual nuclei, crystallites which have not completely melted. The second step, crystalline growth, is determined by the rate at which new polymer chains can be added onto the existing crystal faces.

Generally the phase boundary between the nuclei and melt is associated with a high surface energy, $\gamma$. Thus the energy associated with primary nucleation is:

$$G_{\text{nucleus}} = G_{\text{crystal}} + \gamma A \quad (1-1)$$

where $G_{\text{nucleus}}$ is the free energy associated with formation of a new crystalline nucleus, $G_{\text{crystal}}$ is the free energy associated with the crystalline phase, and $A$ is the surface area of the crystal. The total free energy change upon formation of a nucleus is:

$$\Delta G = G_{\text{nucleus}} - G_{\text{melt}} = \Delta G_B + \gamma A \quad (1-2)$$

where $\Delta G_B$ is the bulk free energy change for a constant volume transformation. At temperatures below the equilibrium melting point, $\Delta G_B$, is a negative quantity and thermodynamically stable nuclei may be formed. $\Delta G$ is, however, positive for small nuclei and the energy barrier for formation of a stable nucleus must be overcome by statistical fluctuations in the case of homogeneous nucleation. More often than not heterogeneous nucleation occurs due to the presence of residual nuclei and/or reduction of interfacial energies due to absorption onto impurities.
Several theories have been used to describe the bulk crystallization of polymers. The free-growth approximation\(^1\) assumes the evolution of an individual growth center is independent of other growth centers and the mass fraction already transformed. Clearly, this model is only applicable to the initial stages of crystallization. The Avrami relationship\(^2\) describes a phase transformation in which growth ceases upon impingement of growth centers. The Avrami relationship describes the normalized crystalline content, that is the amount crystallized relative to the amount crystallized upon cessation of crystallization, \(X_c\), as a function of time as well as geometrical and kinetic constants. In terms of the crystallization behavior of polymers the Avrami relationship is:

\[
1 - X_c = \exp(-Kt^n)
\]  

(1-3)

or equivalently:

\[
X_c = 1 - \exp(-Kt^n)
\]  

(1-4)

where \(K\) is a kinetic rate constant which is a function of temperature and \(n\) is the Avrami exponent. For three dimensional growth, \(K\) may be written in terms of the crystal growth rate, \(G\), and the nucleation density, \(N\):

\[
K = 4\pi NG^3/3.
\]  

(1-5)

Therefore by determining \(K\) and \(G\), the nucleation density, \(N\), may be determined assuming that \(N\) remains constant during the experiment. As illustrated in Table 1-1, the value of \(n\) may be related to the dimensionality of growth and the nucleation process, but the extraction of this information solely on the basis of the Avrami
exponent is not justified.\textsuperscript{3} The Avrami equation has been used to describe the crystallization of countless polymer systems with varying levels of success. In many polymer systems an Avrami exponent of 3 has been observed indicating that heterogeneous nucleation followed by three dimensional spherulitic growth is occurring.\textsuperscript{4} In some cases \( n \) is observed to be 4 suggesting homogeneous nucleation, and frequently an Avrami exponent of 2 is observed suggesting fibrillar or lamellar growth.\textsuperscript{4}

A more detailed look at the crystallization of polymer systems reveals that simple relationships between Avrami exponents and the actual processes of nucleation and growth may not always be justified. Nucleation is often not purely homogeneous or heterogeneous and may vary as a function of time. Complications such as lamellar thickening\textsuperscript{5,6} and the inability to achieve a constant volume transformation\textsuperscript{7} may produce deviations from the predicted values. Secondary crystallization and crystalline perfection occur, to varying extents, in almost all systems complicating the process of crystallization especially at high extents of conversion. Avrami exponents are often found to be fractional, and often at greater extents of conversion slower increases in crystallinity are observed than would be expected from initial data; this phenomenon is known as secondary crystallization.\textsuperscript{8} Significant effects of molecular weight on the crystallization kinetics of polymers have been observed.\textsuperscript{9} As the molecular weight increases, the level of crystallinity at which the rate of conversion deviates from that predicted by the Avrami relationship decreases.\textsuperscript{5} (Figure 1-1) This
phenomenon is not surprising since simplifications involved in the derivation of the Avrami relationship do not take into account the structure or topology of the residual melt. For example, at high levels of crystallinity or at rapid rates of crystallization there may be changes in the amorphous structure of the melt. If the sample is highly polydisperse the effects of segregation and diffusion also need to be discussed. Consequently the Avrami equation is often only useful in describing the crystallization behavior of polymers at relatively low degrees of crystallinity. In many cases the Avrami equation remains useful only because of cancellation of opposing effects.⁴
**TABLE 1-1:**
Values of the Avrami exponent for various types of nucleation and growth habits.\(^3\)

<table>
<thead>
<tr>
<th>Growth Habit</th>
<th>Linear Growth</th>
<th>Diffusion Controlled Growth</th>
<th>Linear Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-dimensional</td>
<td>4</td>
<td>5/2</td>
<td>n = 3</td>
</tr>
<tr>
<td>2-dimensional</td>
<td>3</td>
<td>2</td>
<td>n = 2</td>
</tr>
<tr>
<td>1-dimensional</td>
<td>2</td>
<td>3/2</td>
<td>n = 1</td>
</tr>
</tbody>
</table>
Figure 1-1:

An illustration of the effect of molecular weight on the isothermal crystallization of linear polyethylene. Theoretical Avrami relationship with n = 3;

•, $<\text{MW}> = 11,500; ; 14,000; ; 20,000; ; 47,000; \triangleleft, 76,000; \triangledown, 122,000; \nabla, 175,000;

○, 200,000; <, 600,000; <, $1.2 \times 10^6$. (from 8)
The Avrami relationship quantitatively describes the initial bulk transformation of a polymer melt to the crystalline state for a variety of polymer systems. However the Avrami equation does not take into account the specific details of how new polymer chains are added onto the growing crystalline faces. Spherulitic superstructures are most commonly observed in quiescently crystallized polymers. Spherulites are formed by stacks of lamellar crystals which grow radially from a central nucleation site. (Figure 1-2). Because these lamellar crystals are much thinner than the contour length of the polymer chains and polymer chains have been observed to traverse these lamellar crystals in their thin dimension (typically on the order of 100Å)\textsuperscript{10,11,12}, chain folding must occur. The exact nature of chain folding is an issue of some controversy, but statistical calculations for polymers with relatively flexible backbones, have shown that a large fraction of the polymer chains must reenter the crystal adjacent or be tightly folded.\textsuperscript{13,14,15} Various types of non-adjacent, reentry, however occur depending on the conditions of crystallization.\textsuperscript{16,17} Some examples illustrated in Figure 1-3 are cilia, tie-chains, and loose folds.

The nonequilibrium properties of polymer crystals results from the fact that polymers crystallized under quiescent conditions generally form thin lamellar chain-folded crystals. Nucleation theory suggests that the dimension of a secondary nucleus should scale as \(1/(\Delta T)\), where \(\Delta T\) is the degree of supercooling.\textsuperscript{18} If such crystals would grow in all dimensions they would melt very close to their equilibrium melting point; however, for kinetic reasons, polymer crystals often grow in a plane
Figure 1-2:

A schematic representation of spherulitic superstructure showing chain-folded lamellar crystals.
Figure 1-3:

An illustration of different types of folding which may occur in polymer crystals.

A.) Lamellar Crystal
B.) Interlamellar Links
C.) Non-Crystallized Chains
D.) Loose Fold
E.) Cilia
F.) Tie Chain
perpendicular to the fold plane. Because one dimension of the crystal is kept small, polymer crystals melt at temperatures distinctly below their equilibrium melting point, and the melting point of polymer crystals is a strong function of crystallization conditions since the thin dimension scales as $1/(\Delta T)$.

Directly measuring the equilibrium melting temperature of polymer crystals (i.e. crystallizing a polymer at temperatures very close to its equilibrium melting point) is virtually impossible due to kinetic restrictions. However, it is possible to extrapolate the equilibrium melting point of a lamellar, chain-folded crystal from non-equilibrium data. A method for determination of the equilibrium melting point for polymer crystals was developed by Hoffman and Weeks.\textsuperscript{18} In their derivation they assumed that one dimension of the growing, folded lamellar crystal retained a value close to that of a primary nucleus while the other two dimensions could become much larger.

The melting point for a lamellar crystal with lateral dimensions, $x$, thickness, $l$, (where $X >> l$) fold surface energy, $\sigma_e$, and enthalpy of fusion, $\Delta h_f$, may be described by the Thompson Gibbs equation:\textsuperscript{17}

$$T_m = T_m^0[1-(2\sigma_e/l(\Delta h_f))]$$

(1-6)

where $T_m^0$ is the polymer's equilibrium melting point. Since the lamellar thickness of such a crystal is very close to the limit set by nucleation theory, we may substitute $l'$ for $l$ in equation 1-6:

$$l' = 2\sigma_e T_m^0 / [\Delta h_f \Delta T] + \delta l$$

(1-7)
\[ T_m = T_c + \Delta T \left[ 1 - \frac{1}{(1 + C)} \right] \]  

(1-8)

where \( \Delta T = T_m^0 - T_c \) and \( C = \delta l [ (\Delta h_r) \Delta T / 2 \sigma_c T_m^0 ] \).

If \( \delta l \) is finite, a thermodynamic requirement for nucleus formation, the polymer crystal will melt at a temperature somewhat higher than the temperature at which it is formed. By crystallizing a polymer at several temperatures and extrapolating a plot of \( T_m \) vs. \( T_c \) to the point where \( T_m = T_c \) the equilibrium melting point may be determined. Deviation from the linear relationship predicted by Hoffman and Weeks may occur due to lamellar thickening or a variation in the thickness distribution of lamellar crystals as a function of temperature.

Two essentially different theoretical approaches have been taken to describe the role of chain folding in polymer crystallization. Secondary nucleation models\(^{19}\) assume that the additional enthalpy involved in the attachment of new chain segments onto the growing lamella is the rate limiting factor, while entropic models\(^{20,21,22}\) consider the significance of the degeneracy involved in the attachment process of a long chain molecule.

The simplest model which leads to predictions of lamellar thickness and growth rates and leads to a successful comparison between theory and experiment was developed by Lauritzen and Hoffman.\(^{23}\) This model assumes that the nuclei formed on the surface of the growing crystal are composed of stems (chain segments) of length, \( l \), thickness, \( b \), and width, \( a \). The nucleus grows by spreading in the direction, \( g \), to the edges of the crystal, leading to adding layers in the G
Figure 1-4:

Lauritzen and Hoffman's model for surface nucleation and growth of a chain-folded lamellar crystal. (from 19)
direction. An illustration of this model is shown in Figure 1-4. Several simplifications are assumed for this model. First, the fold period is assumed to fluctuate about a value very near the thermodynamic limit, \( l^* = 2(\sigma_e/\Delta f) + \delta l \), during isothermal growth. Additionally the polymer chains are assumed to reenter adjacent; this criteria becomes less and less valid at large undercoolings. Finally the effects of chain ends and defects are ignored.

The free energy of formation of \( \nu \) stems and \( \nu_f = \nu - 1 \) folds is:

\[
\Delta \Phi_\nu = 2b l \sigma + 2\nu_f ab \sigma_e - vabl \Delta f.
\]  
\(1-9\)

At finite undercoolings \( \Delta \Phi \) goes through a maximum at \( \nu = 1 \). As more and more stems are added, the value of \( \Delta \Phi \) decreases and approaches a region of stability. For large \( \nu \), \( \Delta \Phi \) becomes:

\[
\Delta \Phi_\nu = 2b l \sigma + vab(2\sigma_e - l\Delta f)
\]  
\(1-10\)

where \( \sigma \) is the lateral surface energy, \( \sigma_e \) is the fold surface energy, and \( \Delta f \) is the free energy of fusion.

The rate of nucleation is calculated in terms of the flux over the energy barrier in terms of flow over the barrier in one direction versus the other. Lauritzen and Hoffman derived the following expression for the total flux:

\[
S_T = N_0 \left( \frac{\beta}{l_o} \right) P \exp(2ab \sigma_e \Phi/kT) \exp(-4b \sigma \sigma_e / \Delta f kT)
\]  
\(1-11\)

where

\[
P = kT(2b \sigma - ab(\Delta f)\Phi)^{-1} - kT(2b \sigma + (1-\Phi)ab(\Delta f))^{-1}.
\]  
\(1-12\)
\( l_u \) is the monomer repeat unit length, \( \beta \) represents a retardation factor which accounts for the rate of transport of polymer molecules, \( N_0 \) is the occupation number, and \( \Phi \) is governed by the path by which the first nucleus element is attached to the surface. If the stem goes from the supercooled melt directly to the surface without any intermediate state, \( \Phi = 1 \). In many cases it is believed that there is an initial adsorption step before nucleation, hence \( 0 \leq \Phi \leq 1 \).

Polymers generally crystallize under conditions in which they are in an extremely viscous environment, thus the retardation factor, \( \beta \), is the controlling factor of the flux. \( \beta \) governs the rate at which polymer molecules or segments are transported to the site of crystallization. This retardation factor results from the necessity of moving the polymer chain through the melt via reptation and may be represented as:^{24,25}

\[
\beta = \left( \frac{\kappa}{n} \right) \left( \frac{kT}{h} \right) \left( \frac{\Delta T}{T_m} \right) \exp \left[ -\frac{Q'}{RT} \right]
\]  

(1-13)

where \( Q' \) is the activation energy for reptation, \( n \) is the number of units in the polymer chain, and \( \kappa \) is a numerical factor depending on the number of units which act cooperatively as an effective segment length in the liquid state. Experimental data on polyethylene fractions indicate that \( n \) in equation 1-13 should be considered as \( \langle n_z \rangle \), the \( z \)-average degree of polymerization.\(^{24} \)

There are several possible ways in which a new nucleus may be formed on the surface of a growing crystal. The stem may attach directly from the melt, or be adsorbed onto the growing crystal face in any number of conformations prior to the formation of a new stem.(Figure 1-5) In order to address the concept that several
Figure 1-5:

A possible path for surface absorption leading to subsequent nucleation. (from 19)
possible paths are possible for the initial attachment of a polymer stem, \textit{configurational path degeneracy}, a numerical factor, $P_{\bar{q}}$, is introduced by Hoffman into the expression for $N_0$. In the simple approximation where there are no fluctuations in initial stem attachment around $l'$, $P_{\bar{q}} = 1$. However, since many crystallization paths are available, $P_{\bar{q}} > 1$. Thus $N_0$ becomes:

$$N_0 = (zn_{\bar{q}})C_nP_{\bar{q}}$$  \hspace{1cm} (1-14)

where $z$ is the number of backbone units corresponding to a lamellar thickness $l'$, $n_{\bar{q}}$ is the number of stems in the substrate, and $C_n$ is a coordination factor corresponding to how many units on the surface to which a new unit attaches.

The nucleation rate, $i$, in nuclei per substrate length, $L = an_{\bar{q}}$, per second is given by:

$$i = S_T/an_{\bar{q}}$$  \hspace{1cm} (1-15)

Combining the above with our expression for the total flux, $S_T$:

$$i = (p_lz/a)(C_nP_0)(\kappa/n)(kT/h)\exp[-Q'/RT]\exp[-4\sigma_{\bar{q}}/(\Delta f)kT].$$  \hspace{1cm} (1-16)

If each nucleation act leads to completion of a growth strip of length, $L$, adding a layer of thickness $b$ before the next nucleation step occurs, the growth rate becomes\textsuperscript{18,22}:

$$G_1 = ibL$$  \hspace{1cm} (1-17)

or

$$G_1 = bS_Tn_{\bar{q}}/N = bLS_Tn_{\bar{q}}/aN$$  \hspace{1cm} (1-18)
where $N$ is Avagadro's number and $n_s$ is the number of sites or step segments corresponding to the length of a substrate. The polymer is said to be in Regime I if the growth rate of polymer crystals can be described by equations 1-17 and 1-18. Regime I crystallization is observed at temperatures close to the polymer's crystalline melting point.

At greater supercoolings, however, new nuclei form in larger and larger numbers on the substrate. Sanchez and DiMarzio\textsuperscript{26} noted that under appropriate conditions polymer crystal growth rate is proportional to the square root of the surface nucleation rate. In this case the growth rate becomes:\textsuperscript{23}

$$G_H = b(ig)^{1/2} = b(S_{ig}/aN)^{1/2}$$

(1-19)

If equation 1-19 describes the growth rate of the polymer crystals the system is in Regime II.

At still greater supercoolings the rate of formation of new stems becomes so great that the characteristic separation of stems approaches the width of a stem.\textsuperscript{27} In this case, Regime III, the crystal growth rate is controlled by the rate of deposition of new nuclei on the substrate, $i$, rather than $i^{1/2}$. Thus, an increase in the growth rate is observed as lower crystallization temperatures are reached. In comparison to growth in Regime I, growth in Regime II and III will lead to a rough, irregular growth front in which a substantial amount of irregular folding may occur. (Fig. 1-6) Crystallization in Regime III allows for non-adjacent reentry of polymer stems into the lamellar crystal on a large scale; thus, Regime III is the "worst case" for regular
Figure 1-6:

An illustration of the change in growth front morphology which occurs as the rate of formation of surface nuclei increases. (From 19)
chain folding with adjacent reentry. There are, however, strong restrictions on the fraction of non-adjacent chain folds, $p_{nir}$ for a lamellar crystal without a very large tilt of the chain axis to the fold plane.\textsuperscript{13} If $p_{nir}$ is greater than about 1/3 for such a system, a density paradox exists at the interphase between the fold surface of the crystal and the melt. In Regime III it is likely that small clusters of adjacently reenterant stems are connected to loose folds or cilia.\textsuperscript{25} It has been demonstrated that this model for chain folding, known as the variable cluster mode, is consistent with measurements of the radius of gyration for polymers crystallized at high undercoolings.\textsuperscript{15,16}

The overall growth rate for Regime III may be written as:

$$G_{III} = bi'L' = bi'n'_sa$$

(1-20)

where $i'$ is the nucleation rate and $n'_s$ is the small and roughly constant number of stems which are laid down between newly nucleated stems. $L'$ is an effective substrate length which is independent of $L$. In this case, unlike in the cases for Regimes I and II, the addition of only a small number of stems needs to be considered for determination of the total flux, $S_T$. As a result the expression for the total flux becomes:\textsuperscript{26}

$$S_T = N_0b \exp[-2b\sigma l/kT]$$

(1-21)

and $i'$ becomes:

$$i' = (N_0b\rho/an_s) \exp[-4b\sigma \sigma_c/(\Delta f)kT].$$

(1-22)

A general expression can be developed for crystallization in all three regimes:
\[ G_n = G_{0(n)} \exp[-Q'/RT] \exp[-K_n/T(\Delta T)f] \quad (1-23) \]

where in Regimes I and III:
\[ K_{I,III} = 4b\sigma\sigma_c T_m^0 / (\Delta h_f)k \quad (1-24) \]

and in Regime II:
\[ K_{II} = 2b\sigma\sigma_c T_m^0 / (\Delta h_f)k. \quad (1-25) \]

In these equations \( \Delta h_f(\Delta T)/T_m0f \) has been substituted for the \( \Delta f \) term which appears in eq. 1-22, where \( \Delta h_f \) is the enthalpy of fusion, \( T_m0 \) is the equilibrium melting point, \( \Delta T \) is the supercooling, and \( f \) is a correction factor for deviations from the free energy of crystallization from the approximate value of \( \Delta h_f/T_m0 \) at high supercoolings. Empirically \( f = 2T_c/(T_m0 + T_c) \). From examination of equations 3-24 and 3-25 it is apparent that \( K_I = K_{III} = 2K_{II} \).

Regimes I and III have identical nucleation exponents, but there is a large difference in the pre-exponential factor, \( G_{0(n)} \), between these two regimes:\textsuperscript{25}
\[ G_{0(I)}/G_{0(III)} = n_s/n_s'. \quad (1-26) \]

Experimentally the transition from Regime I - II and Regime II - III is determined by plotting the slope of \( \ln G + Q'/RT \) vs. \( 1/T(\Delta T) \); such a plot has a change in slope at the respective regime transitions.

Many factors may influence the growth rate or nucleation density for a given polymer system including previous thermal and mechanical history, molecular topology, as well as the effects of molecular weight and endgroups. Additionally if chemical changes occur during melt processing the crystallization behavior may be
especially sensitive to previous thermal history. Systems which possess strong secondary interactions such as hydrogen bonding in the melt are especially sensitive to melt processing. The crystallization behavior of nylon-6 has been studied for many years with varying results. Avrami exponents as high as $10^{28}$ and as low as $0.9^{29}$ have been reported for nylon-6. In some instances variation in the crystallization behavior of nylon-6 was attributed to the presence of ionic species which could interfere with the interchain hydrogen bonding in nylon-6$^{28}$. Other research has suggested that the presence of water may drastically effect both the crystalline and amorphous phase of nylon-6.$^{30}$ Disruption of interchain hydrogen bonding in nylon-6 has been attributed to the presence of water.$^{31}$ Further studies of nylon-6 by Reimschuessel, et. al., have revealed that polymers with strong secondary interactions, i.e. hydrogen bonding, retain orientation memory even at temperatures above their equilibrium melting point.$^{32,33,34,35}$ This retention of orientation memory was found to lead to local regions of order which subsequently acted as nucleation sites. Wilkes, et. al., had shown that a similar phenomenon occurred in a copolyester of lactic and glycolic acid when glassy films were strained prior to crystallization.$^{36}$ In this case molecular orientation was frozen in due to the fact that the films were in the glassy state prior to crystallization. A later study on the same material revealed that if complete melting did not occur, i.e. if samples were not processed above their equilibrium melting point, residual nuclei seeded new crystallites and led to a very high nucleation density.$^{37}$
Mandelkern and Devoy analyzed the effects of \( <M_n> \) on the spherulitic growth rate at low undercoolings.\(^{36}\) They considered the effects of molecular weight on the critical free energy for nucleation. Equation (1-23) may be rewritten:

\[
\ln G = \ln G_0 - (\Delta E/kT) - (\Delta F^*/kT). \quad (1-27)
\]

For a two-dimensional growth process involving unimolecular deposition of chain units on a crystalline face, the critical free energy for nucleation may be expressed as follows:

\[
\Delta F^* = 2\sigma_e \frac{2\sigma_c \cdot RT_c \cdot \ln[(x - \xi^* + 1)/x]}{[\Delta f_u - (RT_c/x)]} \quad (1-28)
\]

where \( \sigma_e \) is the interfacial free energy per sequence at the fold plane; \( \sigma \) is the lateral surface free energy; \( \xi^* \) is the number of units in the nucleus along the chain axis; \( x \) is the number of repeat units in the molecule; and \( \Delta f_u \) is the free energy of fusion per unit at \( T_C \). According to equations 1-27 and 1-28 a plot of \( \ln G \) \textit{versus} \( \Delta F/2\sigma T_C \) should produce straight lines for all molecular weights and intercept the \( \ln G \) axis at a common point. Fractions of linear polyethylene, poly(tetramethyl-p-silphenylene) siloxane, and trans-1,4-polyisoprene were found to obey this relationship. Following suggestions by Hoffman and Weeks\(^{39}\) and Maginn\(^{40}\), Lovering added a \( \ln <M_n> \) term to the left hand side of (1-27) to obtain:\(^{41}\)

\[
\ln G = \ln G_0 - \frac{\Delta F^*}{kT} - \ln <M_n> - \frac{\Delta E}{kT}. \quad (1-29)
\]

Growth rate data for t-1,4-polyisoprene was found to follow the above relationship for several fractions from \( <M_n> = 12,000 \) to \( <M_n> = 165,000 \).
Hser and Carr accounted for the reduced thermodynamic driving force for formation of crystals of lower molecular weight polymeric species by plotting crystallization data in terms of supercooling. They noted that the crystallization kinetics of highly monodisperse hydrogenated polybutadienes observed a similar exponential dependence on supercooling to commercially available polyethylenes with relatively broad molecular weight distributions. It was found that crystallization half-times, as a function of undercooling, went through a minimum as molecular weight was increased. They also noted that a four-arm star hydrogenated polybutadiene crystallized more rapidly than a linear molecule of comparable molecular weight.

Nucleation densities have been found to be affected by molecular weight and the chemical nature of the endgroups especially when ionic species are involved. The nucleation density of PPS has been observed to increase with increasing molecular weight. Additionally, as will be discussed later, the nature of endgroup counterion has been shown to effect both the nucleation density and crystalline growth rate of PPS. The effects of ionic endgroups on nucleation density were also observed in sodium carboxylate-terminated poly(ethylene terephthalate), and sodium phenoxide-terminated bisphenol-A polycarbonate. In these later studies it was found that the ionic-species formed phase separated domains which acted as nucleating species.
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CHAPTER 2
Poly (p-phenylene sulfide) - A Literature Review

I. Synthesis of Poly (p-phenylene sulfide)

In 1897 Grenvesse first assigned the poly-(p-phenylene sulfide) structure to an amorphous, insoluble resin produced by heating benzene with sulfur in the presence of aluminum chloride.¹ Similar products were also obtained after the turn of the century, but the presence of many byproducts such as thiophenol, phenyl sulfide, phenyl disulfide, and thianthrene resulted in very low polymer yields.²³⁴ In 1948 Macallum synthesized PPS by the melt reaction of p-dichlorobenzene with alkali and alkaline earth metal sulfides catalyzed by sulfur.⁵ (Figure 2-1) Polymers with molar ratios close to the theoretical values for pure PPS were obtained. Lenz, Handlovits, and Smith examined the Macallum procedure in detail and developed a more reliable preparative process. They prepared linear PPS by condensation polymerization of alkaline metal salts of p-halothiophenols in pyridine.⁶ Salts of p-I, p-Br, p-F, and p-Cl-thiophenols were utilized. The sodium salt of p-bromothiophenol gave more quantitative results, but side reactions resulted in low molecular weight polymers (DP ~ 20).

The first commercially feasible polymerization of PPS was developed by Edmonds and Hill.⁷ P-dichlorobenzene was polymerized with sodium sulfide in N-methyl pyrrolidone at elevated temperatures and pressures. PPS with molecular
Figure 2-1: Reaction mechanism proposed for the Macallum polymerization. (From 5)
weight between 15,000 and 20,000 were produced. It is believed that the mechanism of this reaction is a series of nucleophilic displacement reactions resulting in the formation of PPS and NaCl as a by-product. Recently, Yang, et. al., have developed a technique for controlling the chemical nature of the endgroups of PPS polymerized by the process of Edmonds and Hill. In their reaction scheme p-dichlorobenzene was added to give PPS with terminal chloro groups or sodium sulfide was added to give PPS with terminal sodium thiolate groups which were converted to terminal thiohydroxy groups. In this study it was found that compared with PPS with terminal thiohydroxy groups, PPS with terminal chloro groups attained higher levels of crystallinity.

Campbell developed an improved process for the synthesis of PPS with higher molecular weight. By reaction of p-dichlorobenzene with Na₂S in N-methyl pyrolidone with an alkaline metal salt of acetic acid, propanoic acid, or benzoic acid at elevated pressures and temperatures. Linear PPS with molecular weight in the range 35,000 to 65,000 was produced. By using 1,2,4-trichlorobenzene as a comonomer in this reaction, the molecular weight may be increased to 200,000 through branching; similarly the molecular weight of PPS may be increased by thermal curing, as will be discussed later. Originally the mechanism of the Campbell reaction was thought to be nucleophilic substitution; however Koch and Heitz proposed that the formation of poly(thio-1,4-phenylene) did not proceed by a normal polycondensation process since high molecular weight species were produced
early in the reaction. They proposed that the reaction mechanism was a one electron transfer process with radical-cations as reactive intermediates - see Figure 2-2. This type of polymerization may be classified as reactive intermediate polycondensation. The formation of PPS by this mechanism differs from conventional polycondensation reaction in the fact that the reactivity of the end groups is not independent of chain length. In the case of PPS a reactive intermediate is formed which is more reactive than the monomer and decreases in reactivity with increasing chain length - see Figure 2-3. Five types of intermediates may be formed during this reaction which include sulphenyl radicals, aromatic radicals, and radical cations. As a result of the mechanism, products with intermediate molecular weight are produced early in the reaction, and high molecular weight species are only produced near completion of the reaction. The dependence of molecular weight on conversion due to this mechanism is illustrated in Figure 2-4. Following the work of Koch and Heitz, Fahey and Ash performed a separate mechanistic study in which they concluded that the dominant mechanism of chain extension was through nucleophilic substitution; although competing side reactions could lead to endgroups with a different chemical structure than predicted.

Because of the varied reactive species involved in the polymerization of PPS, and the different possible methods of chain termination, the chemical nature of the endgroups may vary considerably. López, et. al., have studied the effects of varying endgroup counter-ion on the crystallization behavior of PPS. In this study an ion-
Figure 2-2: Reaction mechanism proposed for Campbell's synthesis of PPS by Koch and Heitz. (From 13)
Figure 2-3: Reaction mechanism proposed by Koch and Heitz for the synthesis of PPS by the method of Campbell. (From 13)

a.) Electron transfer from HS to the radical cation.

b.) Stabilization of the reactive intermediate by conjugation.
Figure 2-4: Schematic representation of the dependence of molecular weight on conversion from four types of polymerizations:
1.) Radical polymerization
2.) Polycondensation
3.) Living polymerization
4.) Reactive intermediate polycondensation
(From 13)
exchange process was used to selectively introduce specific metal counter-ions to chains terminated with ionic endgroups. Before introduction of the metal counter ions, the existing ionic species were removed. This process will be discussed in greater detail in the next chapter.

Novi, et. al., have recently used a novel approach to synthesize PPS. In this scheme p-bromobenzenethiolate was polymerized in DMSO at room temperature with catalytic amounts of solid arenediazonium tetrafluoroborate via a radical, radical-anion chain pathway in an argon environment. The reaction mechanism is summarized in Figure 2-5. Chain growth may be terminated by oxidation of a radical ion by residual initiator, radical/radical coupling, or hydrogen transfer to a radical from the medium. As discussed earlier, the different mechanisms for termination of chain growth may lead to endgroups with different chemical characteristics. As will be discussed in following sections, the chemical nature of PPS endgroups may lead to variation in crystallization behavior and crystallinity.

The exact nature of the endgroups of PPS is still not well understood. There is, however, justification for the ion-exchangable character of PPS. Chlorophenyl and mercaptan endgroups are expected from the polymerization scheme suggested by Koch and Heitz; although, of these two endgroups, only chlorophenyl endgroups have been spectroscopically observed on PPS - see Table 2-1. Several other endgroups have also been observed on PPS or on extracted oligomers.
Figure 2-5: Reaction mechanism proposed by Novi, et. al.  
(From 15)
<table>
<thead>
<tr>
<th>Expected Endgroups</th>
<th>Experimentally Observed?</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{S-CI} )</td>
<td>Yes</td>
</tr>
<tr>
<td>( \text{S-SH} )</td>
<td>No</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Unexpected Endgroups</th>
<th>Experimentally Observed?</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{S-CH-OH} )</td>
<td>Yes</td>
</tr>
<tr>
<td>( \text{S-CH-H} )</td>
<td>Yes</td>
</tr>
<tr>
<td>( \text{S-CH-NH-COCH} )</td>
<td>Yes</td>
</tr>
<tr>
<td>( \text{S-CH-NH-CH}_3 )</td>
<td>Yes</td>
</tr>
</tbody>
</table>
demonstrated that some of the endgroups consist of aromatic amines which may be ion-exchangable species. Reents and Kaplan also demonstrated that the unsubstituted endgroup is also observed.

II. Curing Behavior of PPS

Upon heating in the presence of oxygen PPS may undergo crosslinking reactions resulting in higher molecular weight, toughness, and ductility as well as increased solvent resistance.\textsuperscript{18,19} Thermal curing is used industrially to produce very durable and chemically resistant films of PPS. Curing of PPS may be performed either in the melt or in the solid state.\textsuperscript{20} The melt process involves heating the polymer at temperatures above its melting point for several hours in air until the polymer darkens and thickens. Eventually gelation occurs. The solid state process involves heating the polymer at temperatures above the glass transition but below the melting point in air. Figure 2-6 illustrates the change in melt flow associated with the curing reaction at different temperatures. The decrease in melt flow is indicative of an increase in molecular weight.

The thermal, mechanical, and structural properties of PPS are all affected by curing, and several studies have been undertaken to monitor the effects of curing in PPS. Wejchan-Judek and Zuk studied the curing of PPS with sulfur at 290°C in argon.\textsuperscript{21} They indicated that the impact resistance initially improved as the sulfur incorporated during the reaction, but after 0.94% sulphur was reacted a decrease in
Figure 2-6: Plot of melt flow as a function of curing time at different curing temperatures. (from 20)
impact resistance was observed. Thermogravimetric analysis showed that PPS containing higher amounts of sulfur was less thermally stable. X-ray diffraction measurements also showed a dramatic decrease in crystallinity as the amount of crosslinking increased. Brady also noted that the curing reaction inhibited the ability of PPS to crystallize. Zeng and Ho observed with a polarized optical microscope that cured PPS did not form the well developed spherulitic superstructure evident in uncured PPS. This study revealed little difference in the average size of the superstructures formed, but in the cured samples highly imperfect structures were formed. Joshi and Radhakrishnan noted that the crystallinity of PPS decreased with increasing curing temperature eventually reaching zero for samples cured for extended periods above their melting point. Recently, Bulakh, et. al., performed a more systematic study on the effects of the structural changes which occur in PPS during curing. They used differential scanning calorimetry, thermogravimetric analysis, infrared spectroscopy, and optical microscopy to monitor structural changes which occurred during curing, observing that thermal parameters such as melting point and heat of fusion are dramatically reduced due to the structural changes which occur during curing. (Figures 2-7A&B) They also noted, through changes in chemical structure observed via FTIR, that the rate of cure was substantially higher in air than in nitrogen.
Figure 2-7: Effects of curing at various times and temperatures on the thermal parameters of PPS:(From 23)
A: Variation of melting point.
B: Variation of heat of fusion.
Hawkins performed a detailed study of the mechanisms involved in the curing of PPS oligomers. He proposed that the following four types of reactions, as illustrated in Figure 2-8, occurred in PPS during curing:

1.) Chain extension.
2.) Oxidative crosslinking to form tri-substituted species.
3.) Thermal crosslinking to produce tri-substituted species.
4.) Oxygen uptake followed by loss of SO₂.

The results of Bulkah, et. al., as well as mass spectroscopy studies on PPS solid-state cured in air support the mechanisms proposed by Hawkins.
Figure 2-8: Reactions proposed by Hawkins for the curing of PPS. (From 26)
III. Crystallization Behavior of PPS

Numerous studies have been undertaken on the crystalline structure, morphology, thermodynamic stability, and kinetics of PPS. The first measurements of interplanar spacings in PPS through x-ray diffraction experiments were performed by Tsunawaki and Price in 1964,\textsuperscript{28} and in 1971 Tabor and co-workers provided the complete x-ray structure of PPS.\textsuperscript{29}(Figure 2-9) Tabor's measurements indicated that the unit cell was orthorhombic with unit cell dimensions $a = 8.67\text{Å}$, $b = 5.61\text{Å}$, and $c = 10.26\text{Å}$. The $c$-axis is parallel to the chain axis with two polymer chains and four repeat units passing through the unit cell. The sulfur atoms are arranged in a zig-zag manner with a bond angle of 110° in the (100) plane with the planes of the phenylene groups alternately rotated $+45°$ and $-45°$ relative to the base plane. Garbarczyk suggested a somewhat different structure,\textsuperscript{30} but Waddon, \textit{et. al.},\textsuperscript{31} observed a structure similar to that proposed by Tabor and compared the structure of PPS with poly(ether-ether ketone), PEEK, and poly(ether ketone), PEK, the three crystal structures were found to be similar.(Table 2-2)

Jones, \textit{et. al.}, performed wide angle x-ray scattering and model calculations to determine conformational and packing information on PPS.\textsuperscript{32} Their results suggested that the chain conformation in the glassy state was much like that in the crystalline state with the phenylene ring rotated about the bridging sulfur atom by 40°, 5° less than in the crystalline state. This conformation was found to persist for
Figure 2-9: The unit cell of PPS.
(from 29)
Table 2-2: Comparison of the Unit Cell Parameters of PPS, PEEK, and PEK.
(From 31)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Unit Cell</th>
<th>a-axis</th>
<th>b-axis</th>
<th>c-axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPS</td>
<td>Orthorhombic</td>
<td>8.67</td>
<td>5.61</td>
<td>10.26</td>
</tr>
<tr>
<td>PEEK</td>
<td>Orthorhombic</td>
<td>7.75</td>
<td>5.86</td>
<td>10.00</td>
</tr>
<tr>
<td>PEK</td>
<td>Orthorhombic</td>
<td>7.63</td>
<td>5.96</td>
<td>10.00</td>
</tr>
</tbody>
</table>

PPS
\[
\left[ \begin{array}{c} \text{S} \\ \sqrt{2} \end{array} \right]_n
\]

PEEK
\[
\left[ \begin{array}{c} \text{O} \\ \text{C} \\ \text{O} \\ \text{C} \end{array} \right]_x
\]

PEK
\[
\left[ \begin{array}{c} \text{O} \\ \text{C} \\ \text{O} \end{array} \right]_y
\]
about three repeat units (ca. 15Å). This study suggested that there was no preferential alignment of the chain axis, but there was limited range of "face-to-face" correlation of the phenylene groups. Other studies, however, on semicrystalline PPS indicate the presence of a significant quantity of a third, rigid amorphous, phase.\cite{33,34,35} This phase is attributed to the transition region between the ordered crystallites and the disordered amorphous phase. This phase has increased ordering of the polymer chains relative to the chain axis and has been shown to account for a substantial mass fraction in semicrystalline PPS, as much as 40\%.\cite{34,36,37}

Morphological studies of aggregates of PPS crystals grown from an α-chloronaphthalene solution revealed that the crystals had a fibrillar morphology with width of 30-40nm and thickness of 11.5nm.\cite{30,38,39} Both electron diffraction and x-ray diffraction experiments indicated that the c-axis is perpendicular to the basal plane and that growth occurred parallel to the b-axis. Information from the solution grown crystals was related to the spherulitic structures observed in melt crystallized PPS to indicate that crystallites were radially oriented within the spherulites with the b-axis aligned radially to the spherulite. The fact that polarized optical microscopy revealed spherulites with negative birefringence also indicate that the chain axis is perpendicular to the radius of the spherulites.

Chung and Cebe recently developed a two stage self seeding technique which allowed them to grow single crystals of PPS from 1-chloronaphthalene.\cite{40} From extensive analysis of these single crystals and crystal mats of PPS Chung and Cebe
were able to make several observations which have important implications concerning the crystal growth of PPS. PPS single crystals were observed to have a highly anisotropic needle-like growth habit with aspect ratios from 8 to 25 and width (15-20nm) only slightly larger than thickness (10-15nm). As in earlier studies, it was verified that the c-axis (chain axis) is parallel to the thin dimension of the crystals. The b-axis was also found to be aligned to the long axis of the crystal. Noting that there was no tendency for sectorization in these crystals Chung and Cebe decorated the fold surface of these crystals with rods of polyethylene to illustrate that the fold plane in PPS is perpendicular to the a-axis and parallel to the b-axis growth direction. (Figure 2-10) Noting the nature of folding in these crystals, it was suggested that the growth on the long dimension of the crystal would be controlled by both nucleation rate and crystal growth rate while growth on the short dimension should be controlled predominantly by nucleation rate. It was suggested that once a nucleation site was initiated on the (100) plane, the crystal grows along the long dimension by folding polymer chains along the b-axis direction. However, adjacent folding could be expected to be unlikely in a polymer with such a rigid backbone. Thermal analysis of these single crystals suggested that reorganization may occur during heating which can lead to a dual melting endotherm.
Figure 2-10: Sketch of the suggested polymer chain folding direction in PPS. PPS molecules fold parallel to the crystal growth direction which is also the long direction of the crystal. (From 38)
Chung and Cebe performed in depth studies on the dual melting behavior of PPS. Similar dual melt behavior has been observed in numerous other polymer systems and been explained either by dual crystal populations or reorganization of crystals upon heating. Based on findings from single stage and multi stage melt crystallization, they concluded that the multiple melt behavior was due to crystal reorganization during heating as well as differing levels of crystal perfection. (Figure 2-11) When PPS is crystallized at low undercoolings the crystal structure and morphology formed may result into two populations of different crystal perfection. In this temperature range the dual melting is due primarily to the melting of the two populations coexisting in the sample, and reorganization plays a minor role in the resultant melting behavior. PPS crystallized at large undercoolings forms relatively imperfect crystals from a state of low mobility. In this case, upon heating the mobility increases, and rearrangement to form more perfect crystals occurs. Therefore, at large undercoolings rearrangement plays a substantial role in the melting behavior of PPS. The existence of multiple crystal populations was demonstrated by multiple stage crystallization, where up to seven melting peaks were observed after a five stage crystallization. (Figure 2-12)

Numerous studies exploring many variables, have been undertaken on the crystallization behavior of PPS. Both isothermal and non-isothermal crystallization studies have been undertaken investigating, the effects of melt history, molecular
Figure 2-11: Endothermic response of PPS proposed by Chung and Cebe showing original endotherm reorganization and remelting endotherms, and the resultant dsc thermogram:
(A) High undercooling.
(B) Low undercooling.
(From 41)
Figure 2-12: Melting endotherms of Ryton V-1 PPS exposed to five successive step crystallization temperatures from the melt:
(A) Constant residence time at each temperature.
(B) Variable residence time at each temperature.
(From 42)
weight, branching, end-group counter ion, and the effect of fillers. Jog and Nadkarni found that in glass fiber filled PPS crystallization occurred more rapidly than in unfilled PPS and attributed the difference to more rapid heterogeneous nucleation at the fiber surface.\textsuperscript{51} They found the maximum crystallization rate to occur at 170\degree C. Furthermore the Avrami exponents were determined to be 2.5 for glass filled PPS and 2.2 for unfilled PPS. In another study, Jog and Ravindranath found the Avrami exponent for PPS to be between 2.0 and 2.2.\textsuperscript{52} They related fractional exponents to mixed modes of nucleation and secondary crystallization. Menczel and Collins studied the effect of molecular weight on the isothermal and non-isothermal crystallization kinetics of Fortron\textsuperscript{®} PPS produced by Hoechst Celanese.\textsuperscript{36,53} They observed Avrami exponents between 2 and 3 and an equilibrium melting point which varied from 320.5\degree C for the lowest molecular weight polymer to 348.5\degree C for the highest molecular weight polymer. Upon successively heating samples at 10\degree C/min to 350\degree C and cooling at 10\degree C in dry nitrogen, the crystallization exotherm was found to shift to lower temperatures and decrease in magnitude, a result which would be consistent with the earlier studies of Brady\textsuperscript{22}. These results suggest that keeping samples at an elevated temperature for extended periods of time when performing crystallization studies may lead to chemical degradation of the polymers which will subsequently bias experimental results. A more thorough study on the effect of melt history on the crystallization kinetics of PPS performed by Mehl and Rebenfeld\textsuperscript{54} revealed that crosslinking and chain extension reactions which occur at high
temperatures may significantly alter the crystallization kinetics and enthalpy of fusion of PPS. This trend was also found to be highly accelerated at melt temperatures above 320°C, and lower molecular weight species were found to be more susceptible. However, time in the melt was found to be a less important variable. Since the melt hold temperature will effect both the number of surviving crystalline nuclei and the rate at which chain extension and crosslinking reactions occur, this variable must be considered when comparing different crystallization studies.

Fagerburg, et. al., noted that PPS showed a noticeable increase in melt viscosity of PPS polymerized from p-diiodobenzene with time in the melt state. In order to determine whether this increase was primarily due to chain extension or chain branching, samples were prepared with a known degree of branching, and crystallization and rheological studies were performed. Increased branching content was found to dramatically effect the thermal characteristics of PPS. As branching was increased, the rate of crystallization as well as the heat of fusion and melting temperature were reduced. With as little as 1 mol% of branching agent added the ability of PPS to crystallize was nearly totally inhibited. This data contrasts later work by Lopez, et. al., but it is likely that the PPS produced from p-diiodobenzene is not as well chemically characterized as in the later study. Subsequent studies revealed that in some cases chain extension is the predominant chemical reaction which occurs during melt processing leading to higher molecular weight, mostly linear PPS.
The spherulitic growth rates of PPS with \( <M_w> = 15,000 \) and \( <M_w> = 51,000 \) were studies by Lovinger, et. al.\(^{59}\) As can be seen in Figure 2-13 the maximum growth rate was found to occur at about 180° C. Lovinger, et. al. observed a Regime II \( \rightarrow \) III transition at 208° C for PPS with \( <M_w> = 55,000 \), and for PPS with \( <M_w> = 15,000 \) Regime III kinetics were observed at low temperatures with a continual departure from Regime III kinetics without attaining Regime II kinetics at higher temperatures. The activation energy for chain motion was estimated to be 1400 cal/mol, the lateral-surface energy was estimated at 16.9 erg/cm\(^2\), and the fold surface energy was estimated to be 125 erg/cm\(^2\) for regime II and 130 erg/cm\(^2\) for regime III.

López, Wilkes, and Geibel studied the effects of molecular weight, branching, and endgroup counter-ion on the crystallization rates of PPS.\(^{60,61,62}\) Crystallization kinetics were studied using Avrami analysis, and from growth rate measurements, bulk nucleation densities were determined. The crystal growth rate of PPS was found to decrease as molecular weight increased (Figure 2-14) while the nucleation density was found to increase as molecular weight increased and crystallization temperature decreased (Figure 2-15). The nucleation density in PPS with \( <M_w> = 49,000 \) was found to be 32 times greater than that with \( <M_w> = 24,000 \). Increased branching content was found to reduce both crystalline growth
Figure 2-13: Plot of spherulite growth rates as a function of crystallization temperature for PPS:
LMW: $\langle M_w \rangle = 15,000$
MMW: $\langle M_w \rangle = 51,000$.
(From 59)
Figure 2-14: Crystal growth rate of PPS as a function of molecular weight and crystallization temperature. (From 60)
Figure 2-15: Nucleation density of PPS as a function of molecular weight and crystallization temperature. (From 60)
rate (Figure 2-16) as well as nucleation density (Figure 2-17). As illustrated in Figure 2-18, Hoffman-Weeks analysis indicated that increased branching content was also found to lower the equilibrium melting point of PPS. The heat of fusion of higher molecular weight PPS was also found to be significantly reduced in comparison to lower molecular weight PPS.

Studies on the effects of endgroup counter-ion on the growth rate of PPS indicated that the growth rate was, indeed, affected by the chemical nature of the endgroup counter ion. Figure 2-19 illustrates that crystal growth rates decreased as a function of endgroup counter-ion in the following order: calcium > hydrogen > zinc > sodium. In combination with measurements of the crystallization rate constant determined from Avrami analysis, the nucleation density of PPS was also found to be dramatically affected by the chemical nature of the endgroup counter-ion. Figure 2-20 illustrates that the nucleation densities increased in the following order H > Na > Zn > Ca. It is also interesting to note that the ion-exchange process used to control the chemical nature of the endgroup counter-ion increased the nucleation density of PPS by a factor of 20 and the bulk crystallization rate by a factor of 65 over comparable samples which had not undergone the ion exchange process.
Figure 2-16: Crystal growth rate of PPS as a function of branching content and crystallization temperature. (From 61)
Figure 2-17: Nucleation density of PPS as a function of branching content and crystallization temperature. (From 62)
Figure 2-18: Hoffman-Weeks plots used to determine the equilibrium melting point of PPS with different branching contents. (From 62)
Figure 2-19: Crystal growth rate of PPS as a function of endgroup counter-ion and crystallization temperature. (From 62)
Figure 2-20: Nucleation density of PPS as a function of endgroup counter-ion and crystallization temperature. (From 62)
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CHAPTER 3

Crystallization Behavior of Poly(\(p\)-phenylene sulfide):

Effects of Molecular Weight, Molecular Weight Distribution,

and the Chemical Nature of the Endgroup Counter-ion

INTRODUCTION:

Poly(\(p\)-phenylene sulfide) (PPS) is a high temperature semicrystalline engineering thermoplastic polymer that combines the properties of excellent chemical resistance, flame resistance, and mechanical strength\(^{1,2,3}\). Although PPS is a thermoplastic polymer, it may demonstrate some of the "curing" characteristics of a thermoset at high processing temperatures. PPS is known to undergo curing reactions which increase the polymer's molecular weight, toughness, ductility, and solvent resistance\(^{4}\). Due to this overall combination of properties, PPS is finding increased use as a moulding resin and has also been used as a matrix material for thermoplastic composites. Additional specific applications include pump impellers, ball valves, wear rings, electrical sockets, battery and telephone components, and electronic component encapsulants\(^{5,6}\). PPS may also be made conductive by the addition of dopants\(^{7,8,9}\).
The properties of semicrystalline polymers such as PPS depend on the crystallization behavior and morphological superstructure of the polymer. Numerous studies have been undertaken to investigate the crystalline structure, morphology, thermodynamic stability, and crystallization kinetics of PPS. Jog and coworkers studied the isothermal crystallization of PPS and found an Avrami exponent between 2.0 and 2.2. Lovinger, et. al. studied the spherulitic growth rates of PPS with $<M_w> = 15\ 000$ and $<M_w> = 51\ 000$ and found a maximum in the spherulitic growth rate of PPS at $180^\circ$C. López, Geibel, and Wilkes studied the effects of molecular weight, branching, and endgroup counter-ion on the crystallization behavior of PPS. The crystal growth rates were found to decrease as molecular weight increased while the nucleation density increased as molecular weight increased. Increasing branch content through the incorporation of a comonomer, 1,2,4-trichlorobenzene was found to reduce both the crystalline growth rate as well as nucleation density.

Due to the different possible mechanisms for termination of the polymerization of PPS, many endgroup species are present, some of which may possess an ionic character. On PPS samples which had undergone an effective ion exchange species to control the chemical nature of ionizable endgroups López and Wilkes noted that crystal growth rates decreased as a function of endgroup counter-ion in the following order: calcium > hydrogen > zinc > sodium. Nucleation densities were also found to increase in the following order: $\text{H} > \text{Na} > \text{Zn} > \text{Ca}$. 

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Several studies have been undertaken to investigate the effect of melt history on PPS. The melt history may have a profound influence on the crystallization rate of PPS since the melt hold temperature and residence time will affect both the number of surviving crystalline nuclei (commonly called residual nuclei) and the extent to which chain extension and crosslinking reactions occur. Menczel and Collins observed that upon successive heating to 350°C crystallization of PPS was retarded,\textsuperscript{16,17} a result consistent with the earlier findings of Brady.\textsuperscript{18} Fagerburg, et.al. noted that PPS prepared by a very different polymerization route showed a noticeable increase in melt viscosity with time in the melt state and attributed the increasing melt viscosity and decreasing crystallinity observed in samples subsequently crystallized to an increase in branching content and resulting increase in molecular weight.\textsuperscript{19,20} A more extensive study by Mehl and Rebenfeld on Fortoron\textsuperscript{®} PPS revealed that the crosslinking and chain extension reactions that occur at high temperatures significantly alter the rate of crystallization as well as crystallinity of PPS.\textsuperscript{21} This trend was found to be highly accelerated at melt temperatures above 320°C, and lower molecular weight species were found to be more susceptible to chain extension and crosslinking reactions. Koch and Heitz\textsuperscript{22} have proposed that the polymerization of PPS proceeds through reactive intermediates which decrease in reactivity with increasing molecular weight. As a consequence, the presence of low molecular weight species is likely to lead to decreased melt stability for PPS.
The present work investigates the effects of molecular weight and endgroup counter-ion on the nucleation density, crystalline growth rate, and bulk crystallization behavior of fractionated PPS by differential scanning calorimetry (DSC), optical polarized microscopy (OPM), small angle light scattering (SALS), and wide angle x-ray diffraction (WAXD). The results of crystalline growth rate measurements are correlated with rheological measurements. This study was undertaken in order to examine the effects that possible coupling and aggregation due to the ionizable character of some of the endgroups in PPS have on the rheological properties and crystallization behavior. By utilizing fractionated, ion-exchanged PPS, the results may be compared to the results of an earlier study by López, Geibel, and Wilkes, thus giving information about the effects of fractionation as well.

EXPERIMENTAL:

Materials:

The poly(p-phenylene sulfide) samples used in this study were synthesized via the process developed by Campbell. The characterization of weight average molecular weight and molecular weight distributions were obtained by means of a gel permeation chromatographic technique in α-chloronapthalene at 220°C developed by Stacy. In this study a flame ionization detector (FID) was used to measure polymer which elutes from the column. This type of detector has reduced sensitivity for species with molecular weights below about 1000g/mol because in the process of
solvent evaporation, the polymer passes through a heated region where some low molecular weight species may be volatilized. Since these low molecular weight species are most abundant in condensation polymerizations, it would be expected that number average molecular weights obtained from such a detector may be artificially high. Therefore only weight average molecular weights are reported in this study. The "Parent" samples were samples received "as polymerized". The high molecular weight parent sample (Parent #1 - see Table 3-1) was recovered from the reaction mixture by a process which gives this sample a slight fractionation of the low molecular weight oligomers, whereas the low molecular weight parent sample (Parent #2 - see Table 3-1) was recovered by a technique which removes no oligomers at all. Therefore there is a more prominent hump in the GPC scans for Parent #2 and the respective fractions than in those for Parent #1 and the respective fractions -see Figure 3-1. The "Fraction" samples were "Parent" samples which were fractionated, using a proprietary process, to remove low molecular weight oligomers. The specimens utilized to study the effects of endgroup counter-ion were prepared by using an effective ion-exchange procedure on the fractionated specimens. In an earlier study by López, et. al., the same ion-exchange procedure was performed on samples with $<M_w> = 63K$ which had not been fractionated. 15
Table 3-1: GPC and rheological characterization of the samples used in this study.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>(&lt;M_w&gt;)</th>
<th>(Poise, 1 rad/s)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent #1</td>
<td>64 000</td>
<td>13 100</td>
</tr>
<tr>
<td>Fraction #1</td>
<td>104 000</td>
<td>47 000</td>
</tr>
<tr>
<td>Acid Wash of Fraction #1</td>
<td>96 000</td>
<td>43 000</td>
</tr>
<tr>
<td>Na Exchange of Fraction #1</td>
<td>102 000</td>
<td>55 800</td>
</tr>
<tr>
<td>Zn Exchange of Fraction #1</td>
<td>106 000</td>
<td>55 900</td>
</tr>
<tr>
<td>Parent #2</td>
<td>44 000</td>
<td>2 800</td>
</tr>
<tr>
<td>Fraction #2</td>
<td>56 000</td>
<td>5 200</td>
</tr>
<tr>
<td>Acid Wash of Fraction #2</td>
<td>54 000</td>
<td>4 800</td>
</tr>
<tr>
<td>Na Exchange of Fraction #2</td>
<td>57 000</td>
<td>5 300</td>
</tr>
<tr>
<td>Zn Exchange of Fraction #2</td>
<td>60 000</td>
<td>5 500</td>
</tr>
</tbody>
</table>

* Data obtained at 300°C and 1 rad/s.
FIGURE 3-1: Molecular weight distributions obtained from GPC experiments:

A:  
 a - Parent #2  
 b - Fraction #2  
 c - Acid Wash of Fraction #2  
 d - Na Wash of Fraction #2  
 e - Zn Wash of Fraction #2  

B:  
 a - Parent #1  
 b - Fraction #1  
 c - Acid Wash of Fraction #1  
 d - Na Wash of Fraction #1  
 e - Zn Wash of Fraction #1
The existing metal ions present in the polymer were first removed by charging the PPS and a dilute solution of acetic acid (1% v:v) to a titanium autoclave. The reaction mixture was degassed by pressurizing to 200 psig with nitrogen and then releasing the pressure. This pressurization/release cycle was repeated six times. Doxygenating in this manner eliminates oxygen from the autoclave and minimizes the possibility of oxidative chain extension. The reaction mixture was then heated to 235°C with agitation for one hour. The polymer slurry was then cooled, filtered and the recovered polymer was washed with glass distilled water at room temperature to remove any residual adsorbed acetic acid solution. A sample of the acid washed polymer was analyzed for residual metal ions. To introduce specific metal ions to the acid-washed polymer, this polymer was again charged to the autoclave along with a dilute metal acetate solution (1% w:v). Doxygenating was performed as described earlier. The reaction mixture was heated to 235°C for 30 minutes, cooled and recovered as described above. All samples were dried in a vacuum oven at 100°C prior to analysis. Table 3-1 summarizes the samples used in this study. The apparent small increase in molecular weight as a function of endgroup counter-ion for the ion-exchanged species is not surprising and likely to be the result of aggregation of some of the ionic endgroups in the 1-chloronaphthalene solution.
Morphological Experiments:

PPS specimens were moulded into thin films between glass cover slips at 320°C prior to growth rate measurements. A Zeiss polarizing optical microscope equipped with a Leitz 350 heating stage and a 35mm camera were used for polarized optical microscopy experiments. Due to the fact that melt treatment of PPS at high temperatures (especially above 320°C) for extended periods of time, leads to thermal degradation, samples were heated to 320°C for only 4 minutes prior to crystallization. SALS experiments were also performed on the films cast between glass cover slips in order to determine if any differences in nucleation density from sample to sample were apparent. SALS experiments were performed in a lightproof room with a He Ne laser (λ = 6328 Å). An open-back camera was mounted 10cm from the sample in order to measure the Hv scattering pattern using the method described by Stein25.

Samples for WAXD experiments were compression moulded into plaques 10mm in diameter and 0.50mm thick. All WAXD experiments were performed on a Nicolet diffractometer operating at 40KV and 30mA and equipped with a STOE Bragg-Bernatto type goniometer. Cu-Kα X-rays (λ = 1.54 Å) were passed through a graphite monochromator prior to final collimation. Data was collected at 0.05° increments for 30s at each step between the angles of 10° and 35°. Data collection and analysis was performed using the Siemens Polycrystalline Software package.
**Thermal Analysis:**

A Seiko DSC 220C equipped with an auto cooler was used to obtain bulk crystallization information as well as heats of fusion and melting. Prior to all crystallization experiments samples were heated to 320°C for 4 minutes. Crystallization from the melt could be observed in the temperature range of 230°C to 270°C. The lower temperature limit was set by the time it took for the DSC signal to stabilize after the auto cooler rapidly cooled the DSC to the crystallization temperature. The upper limit was set by the long residence times encountered and the resulting limitations with temperature stability and heat transfer. Diffusion controlled crystallization experiments were performed by heating sealed 32mg DSC pans loaded with ca. 15mg of PPS to 320°C for four minutes and quenching the pan in liquid nitrogen. These pans were then placed in a DSC equilibrated at the crystallization temperature for data collection.

**Rheological Experiments:**

Samples were dried in a vacuum oven for 2 hours at 110°C and 15-20 in Hg and then compression moulded into 1" disks approximately 2.5mm thick. All measurements were performed on an RMS 800 shear rheometer under dry nitrogen. Samples were heated to 300°C for 8 minutes prior to data collection to ensure samples had reached thermal equilibrium. Frequency sweeps were performed from 0.1 to 100 rad/sec. with strain amplitudes on the order of 30%. Four data points were collected for each decade of frequency.
DATA ANALYSIS:

Growth Rate Measurements:

Spherulite growth was followed by taking photomicrographs with a 35mm camera which was attached to the polarizing optical microscope at fixed time intervals. The spherulite diameters, in microns, were subsequently determined from these photomicrographs. The radius was then plotted as a function of time which provided a straight line with slope equal to the crystal growth rate, G. The values of growth rate were then used to obtain the growth rates as a function of temperature as well as information on the nucleation density as a function of temperature when combined with the bulk crystallization rate constant, K, data. The relative error in growth rate measurements was no greater than 5% in most cases.

SALS:

Spherulitic structure, evident in many polymers, generally results in a SALS pattern under cross polarized light with fourfold symmetry. This pattern is known as the "four-leaf clover". At the intensity maximum of each lobe, the following relationship is satisfied:

\[ 4.09 = 4\pi R \sin(\Theta_{\text{max}}/2)/\lambda_m \]  

(3-1)

In this case \( R \) is the weight average spherulite radius, \( \Theta_{\text{max}} \) is the scattering angle at which an intensity maximum is observed, and \( \lambda_m \) is the wavelength of light in the material. In this case \( \lambda_m \) is calculated using 1.7 as the refractive index of PPS. Since \( \Theta_{\text{max}} \) is easily obtained from photographic measurements, SALS is a rapid
means of determining average spherulite size, and since these spherulites fill the volume of the material, SALS may also be used to determine changes in nucleation densities.

WAXD:

WAXD experiments were used to determine the crystalline fraction as a function of molecular weight. The classical method of Hermans and Weidinger\textsuperscript{28} was used to determine the crystalline fraction in samples of varying molecular weight. The method of peak deconvolution used in this study has been previously utilized by the authors to determine the crystallinity of LARC CPI\textsuperscript{29} and nylon-6.\textsuperscript{30} The amorphous scattering profile was obtained from a high molecular weight sample quenched from the melt in icewater.\textsuperscript{(Figure 3-2)} The amorphous scattering profile was then fitted to the total diffracted intensity and then subtracted to yield the scattering due to the crystalline peaks neglecting any effects such as thermal diffuse scattering. The ratio of the area under the crystalline peaks over the total diffracted intensity gives an estimate of the crystalline fraction. The experimental method of peak deconvolution is outlined in Figure 3-3.
FIGURE 3-2: Amorphous scattering profile of PPS.
FIGURE 3.3: Resolution of WAXD data into amorphous and crystalline components:
A - smoothed scattering pattern and raw data (points);
B - amorphous scattering profile;
C - crystalline peaks.
Thermal Analysis:

Crystallization kinetics: The overall rate of bulk crystallization may often be analyzed in terms of the well known Avrami equation\(^{31}\):

\[ X_C(t) = 1 - \exp(-Kt^n) \]  
(3-2)

where \( X_C(t) \) is the normalized crystalline content at time, \( t \), after the onset of crystallization. Often at low undercoolings an induction period may occur before the onset of crystallization. \( K \) is a rate constant which may be written in terms of the crystal growth rate, \( G \), and the nucleation density, \( N \). Assuming three dimensional growth, it can be shown that\(^{32}\):

\[ K = 4\pi NG^3/3. \]  
(3-3)

The Avrami exponent, \( n \), is a term dependent on the types of processes occurring during nucleation and growth.

By taking the double logarithm of equation (3-2) we obtain:

\[ \ln[-\ln(1-X_C(t))] = \ln K + n \ln t. \]  
(3-4)

Thus a plot of the double logarithm of amorphous content as a function of \( \ln(\text{time}) \), a classical Avrami plot, gives a straight line with slope \( n \) and intercept \( \ln K \). An alternative method of obtaining the same information involves the use of crystallization half-times. In this case the entire area under the crystallization exotherm represents a normalized crystalline content of unity. On a normalized basis the crystallization half-time, \( t_{1/2} \), is defined as the time at which the normalized
crystalline content is 0.5. From a graph of normalized crystalline content versus \( \ln(\text{time}) \) one may determine the Avrami exponent, \( n \), from the slope at \( t = t_{1/2}, S_{1/2} \).

Taking the logarithm of equation (3-2) at \( t = t_{1/2} \) one obtains:

\[
K = \ln(2)/t_{1/2}^n. 
\]  

(3-5)

The slope of the curve \( (1 - X_C(t)) \) as a function of \( \ln(\text{time}) \) may be written as:

\[
S = t[\delta(1-X_C(t))]/\delta t. 
\]  

(3-6)

From equation (3-2) \( \delta(1-X_C(t))/\delta t \) may be calculated:

\[
\delta(1-X_C(t))/\delta t = -Knt^{n-1}\exp(-Kt^n) 
\]  

(3-7)

at \( t = t_{1/2} \): \( S_{1/2} = n \ln(2)/2. \)  

(3-8)
RESULTS AND DISCUSSION:

When comparing crystallization information from polymers with different molecular weight or chemical microstructure (ie. endgroup counter-ion), it is useful to determine whether or not the equilibrium melting point of the species being investigated is affected. The method of Hoffman and Weeks\textsuperscript{34} was used to estimate the equilibrium melting points, $T_m^0$, of all specimens investigated in this study.

In an earlier study\textsuperscript{13} López and Wilkes found that the extrapolated values for equilibrium melting points of PPS with $<M_w> = 24$ 000, $<M_w> = 49$ 000, and $<M_w> = 63$ 000 varied as a function of molecular weight.(Figure 3-4) The extrapolated value of the equilibrium melting point was found to be 8°C higher for PPS with $<M_w> = 63$K than for PPS with $<M_w> = 24$K, an elevation higher than what would be expected based solely on theoretical considerations. In this earlier study, instrumental sensitivity limited the maximum temperature for crystallization to approximately 265°C, and the extrapolation was performed from crystallization temperatures in the 250°C to 265°C range.

Since the earlier work of Wilkes and López, Cebe and Chung have demonstrated that substantial reorganization may occur in PPS crystals especially as crystals heated from high undercoolings are melted.\textsuperscript{35,36} In such a case significant deviations from linearity in Hoffman Weeks plots may be observed especially for crystals formed at high undercoolings.
FIGURE 3-4: Hoffman - Weeks plots used to determine the thermodynamic melting points of PPS with $<M_w> = 24\,000$, $<M_w> = 49\,000$, $<M_w> = 63\,000$. (López and Wilkes)\textsuperscript{13}
Due to greater instrumental sensitivity for the experiments performed in this study, Hoffman Weeks data was extrapolated in the temperature range from 255°C to 270°C. Representative Hoffman Weeks data obtained for PPS samples of varying molecular weight, polydispersity, and endgroup counter-ion is shown in Figure 3-5. Apparent deviations from linearity are obtained at temperatures as high as 255°C. In this study, Hoffman Weeks extrapolations performed on data obtained in the 255°C to 270°C range produced equilibrium melting points of 320°C ± 2°C for all samples regardless of molecular weight or the chemical nature of the endgroup counter-ion. The fact that no significant deviation in equilibrium melting points as a function of endgroup counter-ion, polydispersity, or molecular weight was observed in this study, while López and Wilkes did observe deviation as a function of molecular weight in an earlier study is possibly due to the fact that the data used by López and Wilkes was obtained from lower molecular weight species where the role of molecular rearrangement during heating was more substantial and the fact that higher crystallization temperatures were available in this study.

The nucleation density was observed to vary strongly as a function of molecular weight for the PPS samples used in this study. SALS patterns for PPS samples crystallized at 245°C with $<M_w> = 44,000$, $<M_w> = 56,000$, $<M_w> = 63,000$, and $<M_w> = 104,000$ are shown in Figure 3-6. For PPS crystallized at 245°C, the spherulites in the lowest molecular weight PPS specimen grew to be four times as large as those for the highest molecular weight PPS specimen. As a function of
FIGURE 3.5: Hoffman-Weeks plots used to determine the thermodynamic melting points of PPS as a function of molecular weight and endgroup counter-ion:
A - Parent #2: $\langle M_w \rangle = 43 \, 000$;
B - Parent #1: $\langle M_w \rangle = 63 \, 000$;
C - Na washed Fraction #2: $\langle M_w \rangle = 56 \, 000$;
D - Zn washed Fraction #2: $\langle M_w \rangle = 56 \, 000$;
E - Acid washed Fraction #2: $\langle M_w \rangle = 56 \, 000$. 
FIGURE 3-6: SALS patterns obtained from PPS with $\langle M_w \rangle = 44,000$, A; $\langle M_w \rangle = 56,000$, B; $\langle M_w \rangle = 63,000$, C; $\langle M_w \rangle = 104,000$, D.
endgroup counter-ion, no variation in SALS patterns was observed. From the change in SALS patterns it is apparent that a great difference in weight average spherulite radius exists for different molecular weight PPS samples crystallized with identical thermal histories: this will be a key point with regard to this overall study. By combining the data from Figure 3-6 with equation (3-1) the weight average spherulite radius may be calculated as a function of molecular weight. These results are summarized in Table 3-2. Since more than adequate time was given for impingement of spherulites and completion of crystallization in each case, the much smaller average spherulite radius corresponds to a much higher nucleation density in the higher molecular weight species. In fact according to calculations based on the results of SALS, the nucleation density of the high molecular weight PPS is nearly 50 times that of the low molecular weight PPS crystallized under identical conditions.

Growth rate data was obtained from observing the radius of growing spherulites from optical micrographs at set time intervals. (Figure 3-7) This data was then plotted as spherulite radius as a function of time. Since different spherulites may nucleate at different times and the start of the timing for the experiment is arbitrary not all plots intercept the origin. The slope of such a plot, as shown in Figure 3-8, provides the linear crystalline growth rate. Crystal growth rate as a function of endgroup counter ion and temperature for fractionated PPS with \(<M_w> = 56,000\) is plotted in Figure 3-9. All species which had undergone the ion-exchange process had a crystalline growth rate approximately one in unit more rapid than the
Table 3-2: Results of SALS Patterns Obtained from PPS with Varying $<M_W>$

<table>
<thead>
<tr>
<th>$&lt;M_W&gt;$</th>
<th>$\theta_{max}$</th>
<th>Average Spherulite Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>44 000</td>
<td>4.6°</td>
<td>3.0μm</td>
</tr>
<tr>
<td>56 000</td>
<td>8.5°</td>
<td>1.6μm</td>
</tr>
<tr>
<td>63 000</td>
<td>13.0°</td>
<td>1.1μm</td>
</tr>
<tr>
<td>104 000</td>
<td>16.7°</td>
<td>0.8μm</td>
</tr>
</tbody>
</table>
FIGURE 3-7: Optical micrographs of PPS with $<M_w> = 56,000$ as a function of increasing crystallization time.
FIGURE 3-8: Data used to determine growth rate data for PPS.
FIGURE 3-9: Crystal growth rates as a function of endgroup counter-ion and temperature for fractionated PPS with $<M_w> = 56000$:

A - fractionated;
B - Na washed;
C - Zn washed;
D - Acid washed.
corresponding specimen which had not undergone the ion exchange process. For the species which had undergone the ion-exchange process, the growth rates increased in the following order: Na < Zn < H. The same trend was observed by López and Wilkes for unfractionated PPS.\textsuperscript{16}

Growth rates for the higher molecular weight fraction (\( <M_w> = 104\ 000 \)) as well as the ion-exchanged high molecular weight fractions were not attainable due to the extremely high nucleation density and extremely small average spherulite radius observed in this system. The trend towards substantially increased nucleation densities in higher molecular weight PPS is also consistent with earlier results obtained by López and Wilkes.\textsuperscript{16} The result for higher nucleation densities in these systems is likely due to the fairly low melt temperature used and the inability to fully destroy residual nuclei especially in the higher molecular weight species due to longer relaxation times. Melt hold temperatures as high as 265°C and hold times as long as 10 min., however, produced no noticeable differences in nucleation density by SALS or POM, but SALS patterns became more diffuse.

The variation in crystalline growth rate can potentially be explained by a similar trend observed in the viscosities of the polymer fractions as a function of endgroup counter ion. The viscoelastic behavior of commercially available Ryton\textsuperscript{*} PPS has been studied earlier by Eisenberg and Cayrol\textsuperscript{37} to temperatures as high as 340°C, but a study investigating the effects of ionic interactions in PPS has not previously been undertaken. Frequency sweeps were performed on all of the PPS specimens

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under a nitrogen atmosphere at 300°C and frequencies from 0.1 rad/s to 100 rad/s. As expected the viscosity of these specimens increased with $M_w$. (Figure 3-10) For both the high molecular weight and low molecular weight fractions there were distinct trends in viscosity as a function of endgroup counter-ion. (Figures 3-11 & 3-12) For both fractions the specimens which had not undergone the ion exchange process exhibited an increased viscosity over the entire frequency range. The ionic species exhibited an intermediate viscosity, while the acid washed specimens exhibited consistently decreased viscosities relative to all other species. Note, however, that the scales on these plots are expanded relative to Figure 3-10. These trends as well as the growth rate measurements and GPC results suggest that at least at the temperatures at which the experiments were performed, the presence of ionic species in the melt may lead to aggregation of ionic species which results in the formation of ion-clusters and effective chain extension.

The trends in viscosity may be explained by secondary interactions due to association through ionic endgroups. The unexchanged polymer has whatever metal ions are present after polymerization. The acid wash process was developed specifically to remove metal ions and promote ionizable endgroups; therefore the acid washed species exhibited less ionic interaction through decreased viscosity. The Na and Zn washed polymers had ionic species reintroduced and therefore exhibited a greater degree of association through increased viscosity. Melt rheological data associated with these materials is summarized in Table 3-1.
FIGURE 3-10: Shear viscosity of PPS as a function of frequency at 300°C
for PPS with:
A - $<M_w>$ = 44 000;
B - $<M_w>$ = 56 000;
C - $<M_w>$ = 64 000;
D - $<M_w>$ = 104 000.
FIGURE 3-11: Shear viscosity of PPS with $<M_w> = 104,000$ as a function of frequency at 300°C.
A - fractionated;
B - Acid Washed;
C - Zn washed;
D - Na washed.
FIGURE 3-12: Shear viscosity of PPS with $<M_w> = 56,000$ as a function of frequency at 300°C:
A - fractionated;
B - Acid washed;
C - Zn washed;
D - Na washed.
Crystallization Kinetics:

Crystallization exotherms for the acid washed fraction with $\langle M_w \rangle = 113,000$ for crystallization temperatures of 245°C, 250°C, 255°C, 260°C and 265°C are shown in Figure 3-13. Data from the isothermal crystallization experiments were put in the format for crystallization half-time analysis (Figures 3-14A & B) as well as classical Avrami analysis (Figures 3-15A & B). Figures 3-14 shows plots of normalized crystalline content as a function of ln(time) for PPS with $\langle M_w \rangle = 104,000$ and PPS with $\langle M_w \rangle = 44,000$ in both the nucleation and diffusion controlled temperature regimes. From these data and equations (3-5) and (3-8), the Avrami exponents, $n$, and rate constants, $K$, were determined as a function of temperature. Analysis on the Avrami plots (Figures 3-15) using equation (3-4) yielded the $n$ and $K$ values from the slope and the log of the intercept.

Both crystallization half-time analysis and Avrami analysis methods were performed on all specimens over the temperature ranges of 110°C to 125°C and 230°C to 270°C. The results obtained by these two separate techniques were equivalent within the limits of statistical deviation. Avrami exponents were found to vary between 2 and 3 depending on molecular weight and crystallization temperature. The higher molecular weight parent had an Avrami exponent value of nearly 3 at all crystallization temperatures whereas the low molecular weight parent had an Avrami exponent close to 2. (Figure 3-16) In both cases, fractionation reduced the Avrami exponent. There is a slight trend for slightly reduced Avrami exponents at lower
FIGURE 3-13: Crystallization exotherms as a function of temperature for acid-washed PPS with

\[ <M_w> = 104,000 \]: A, \( T_C = 240^\circ C \); B, \( T_C = 245^\circ C \); C, \( T_C = 250^\circ C \);
D, \( T_C = 255^\circ C \); E, \( T_C = 260^\circ C \).
FIGURE 3-14: Normalized crystalline content, $X_c$, vs. ln(time) for PPS with
A: $<M_w> = 44,000$:
A - Diffusion controlled temperature range;
B - Nucleation controlled temperature range.
B: $<M_w> = 104,000$:
A - Diffusion controlled temperature range;
B - Nucleation controlled temperature range.
FIGURE 3-15: Avrami plots for PPS with
A: $<M_w> = 44\ 000$:
A - Diffusion controlled temperature range;
B - Nucleation controlled temperature range.
B: $<M_w> = 104\ 000$:
A - Diffusion controlled temperature range;
B - Nucleation controlled temperature range.
FIGURE 3-16: Avrami exponents as a function of molecular weight:
A - Parent #1: \(<M_w> = 64\ 000;\)
B - Fraction #1: \(<M_w> = 104\ 000;\)
C - Parent #2 <M_w> = 44\ 000;
D - Fraction #2 <M_w> = 56\ 000.
crystallization temperatures possibly due to the inability for well developed sperulites to form before impingement occurs.

The effects of fractionation and the chemical nature of the endgroup counter-ion on crystallization rate constants and half-times for Parent #1 and Fraction #1 as well as the respective ion-exchanged samples are illustrated in Figure 3-17. In order to accommodate the large range of the data a log scale has been used for half times and kinetic rate constants. The raw data has been fitted with simple polynomials. For the high molecular weight species, the unFractionated species with $<M_w>$ = 64 000 crystallized more rapidly than the species with $<M_w>$ = 104 000 in the nucleation controlled temperature regime, but in the diffusion controlled temperature range the opposite trend was observed. Crystallization is often observed to occur more rapidly from the glass than from the melt due to higher nucleation densities. In this case the trend may be due to the fact that ionic association may be stronger at lower temperatures, leading to a larger effect on nucleation densities. Since fractionation greatly reduces the concentration of ionic endgroup species, the effects of ionic species would be expected to be greater for the unFractionated specimens. The acid washed sample with $<M_w>$ = 104 000 crystallized more rapidly than the ion-exchanged samples in both temperature ranges. The effects of both fractionation and the chemical nature of the endgroup counter-ion were distinctly more substantial for the low molecular weight species. As illustrated in Figure 3-18, the fractionated species with $<M_w>$ = 56 000 crystallized more rapidly than the parent species with
FIGURE 3-17: Effects of fractionation and endgroup counter-ion on crystallization half-times, $t_{1/2}$, and $\ln(K)$ for HMW PPS:
A - Parent #1: $<M_w> = 64,000$;
B - Fraction #1: $<M_w> = 104,000$;
C - Acid Washed Fraction #1;
D - Na Washed Fraction #1;
E - Zn Washed Fraction #1.
FIGURE 3-18: Effects of fractionation and endgroup counter-ion on crystallization half-times, $t_{1/2}$, and ln(K) for LMW PPS:
A - Parent #2: $<M_w>$ = 44 000;
B - Fraction #2: $<M_w>$ = 56 000;
C - Acid Washed Fraction #2;
D - Na Washed Fraction #2;
E - Zn Washed Fraction #2.
\( <M_w> = 44000 \). In this case the effects of endgroup counter ion were again more substantial than for the higher molecular weight species. All of the species which had undergone the ion-exchange process crystallized more rapidly than the fractionated sample which had not undergone the process, with the rates of crystallization increasing in the following order: Na < Zn < H. These trends are consistent with the trends observed by López and Wilkes in their earlier study.\(^{16}\)

When combined with growth rate data from Figure 3-9 and equation (3-3), assuming three dimensional growth, the rate constant data from Figure 3-17 may be used to calculate the nucleation density as a function of endgroup counter-ion and temperature. (Figure 3-19) Within the statistical deviation of the data, the effect of the chemical nature of the endgroup counter-ion on nucleation density is little or none for the fractionated samples with \( <M_w> = 56K \). Although spherulitic growth rates and consequently nucleation densities were unobtainable for the high molecular weight species, the effects of the chemical nature of the endgroup counter-ion are expected to be even less in this system due to the even lower concentration of ionizable species.

These experimental results, when taken in light of earlier observations by López, et. al., shed light on the role of low molecular weight oligomeric species on the process of nucleation in PPS. López, et. al., found that in unfractionated PPS specimens the nucleation density of Na washed PPS was found to be 20 times that
FIGURE 3-19: Effects of endgroup counter-ion on nucleation density, N, for PPS with \( <M_w> = 56'000\):

- A - Fractionated;
- B - Na Washed;
- C - Zn Washed;
- D - Acid Washed.
observed for PPS that had not undergone the ion exchange process, this suggests that
the presence of ionic species, especially in oligomeric PPS may lead to aggregates
which may act as nucleating species. In this earlier study the chemical nature of the
endgroup counter-ion was also found to substantially affect the nucleation density in
PPS. The fact that this trend was not observed in the present study suggests that removal of a great deal of the oligomeric species through fractionation
eliminated the effects due to the chemical nature of the endgroup counter-ion.
Therefore, the concentration of oligomeric species and the chemical nature of their
endgroups are important in determining nucleation density.

It has been previously reported that ionic endgroups in sodium carboxylate-
terminated poly(ethylene terephthalate) and sodium phenoxide-terminated
bisphenol-A polycarbonate were aggregated in a separate phase in the polymer
melt. In such a case, the authors proposed that aggregates may become nucleating
species due to the fact that they locally limit the mobility of the chains and lower the
activation energy for nucleation. Since the fractionation procedure used in this study
greatly reduced the number of ionic species in the melt, it is likely that the
subsequent effects of the ion-exchange process is greatly reduced. Therefore the
experimental findings are not surprising and provide a consistent interpretation.

The heat of bulk crystallization was measured for all samples which were
crystallized from the melt. Figure 3-21 illustrates the strong dependence of the heat
of crystallization on molecular weight which was observed. Higher molecular weight
FIGURE 3-20: Effects of endgroup counter-ion on nucleation density, $N$, for PPS with $<M_w> = 63 000$. (López and Wilkes)\textsuperscript{15}
FIGURE 3-21: Effect of molecular weight on the bulk heat of crystallization for PPS crystallized from the melt:

A - $<M_w> = 104\,000$;
B - $<M_w> = 64\,000$;
C - $<M_w> = 56\,000$;
D - $<M_w> = 44\,000$. 

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species showed consistently lowered heats of crystallization indicating a lower level of crystallinity in these samples. This effect was most noticeable for the highest molecular weight species in this study, $<M_w> = 104,000$. The effects of the chemical nature of the counter-ion on the heats of fusion were also measured. For the high molecular weight fraction, no significant effects of endgroup counter-ion were observed on the heat of crystallization. (Figure 3-22A) For the low molecular weight fraction the acid washed specimens showed a reduced heat of crystallization at higher undercoolings. (Figure 3-22B) It is likely that no endgroup counter-ion effect is observed in the high molecular weight species due to the fact that the concentration of the endgroups in this fraction is very low, which is consistent with data presented earlier. Table 3-3 summarizes the data obtained from these heat of crystallization measurements.

The effect of molecular weight on absolute crystallinity was also investigated by WAXD. Figure 3-23 illustrates the WAXD patterns obtained from species with varying molecular weight crystallized at 250°C for 2 hours. At this temperature, 2 hours was more than adequate time for these samples to reach their maximum value of crystallinity. After WAXD scans were performed on these samples and absolute crystallinity measurements were made, DSC specimens were prepared from each sample and heats of melting were also measured. (Figure 3-24) In each case the total melting exotherm was integrated which may introduce a potential error since dual melting behavior was observed in all samples, with samples of lower molecular

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FIGURE 3-22: Effect of endgroup counter-ion on the bulk heat of crystallization for:

I: PPS with $<M_w> = 104,000$:
A - Na washed;
B - Zn washed;
C - Acid washed.

II: PPS with $<M_w> = 56,000$:
A - Na washed;
B - Zn washed;
C - Acid washed.
FIGURE 3-23: WAXD patterns of PPS crystallized at 250°C for 2 hours:
A - $<M_w> = 44,000$;
B - $<M_w> = 56,000$;
C - $<M_w> = 64,000$;
D - $<M_w> = 104,000$. 
Table 3-3: Average Values of Heats of Crystallization for PPS as a Function of Molecular Weight and Endgroup Counter-ion

<table>
<thead>
<tr>
<th>$&lt;M_W&gt;$</th>
<th>Endgroup Counter-Ion</th>
<th>Average $\Delta Q_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>104 000</td>
<td>Unexchanged</td>
<td>6.9 J/g</td>
</tr>
<tr>
<td>&quot;</td>
<td>Na</td>
<td>6.5 J/g</td>
</tr>
<tr>
<td>&quot;</td>
<td>Zn</td>
<td>6.9 J/g</td>
</tr>
<tr>
<td>&quot;</td>
<td>Acid</td>
<td>7.0 J/g</td>
</tr>
<tr>
<td>63 000</td>
<td>Unexchanged</td>
<td>8.8 J/g</td>
</tr>
<tr>
<td>57 000</td>
<td>Unexchanged</td>
<td>10.1 J/g</td>
</tr>
<tr>
<td>&quot;</td>
<td>Na</td>
<td>10.1 J/g</td>
</tr>
<tr>
<td>&quot;</td>
<td>Zn</td>
<td>9.5 J/g</td>
</tr>
<tr>
<td>&quot;</td>
<td>Acid</td>
<td>7.9 J/g</td>
</tr>
<tr>
<td>43 000</td>
<td>Unexchanged</td>
<td>10.5 J/g</td>
</tr>
</tbody>
</table>
FIGURE 3-24: DSC scans at 10°C/min. of PPS crystallized at 250°C for 2 hours:
A - $<M_w>$ = 44 000;
B - $<M_w>$ = 56 000;
C - $<M_w>$ = 64 000;
D - $<M_w>$ = 104 000.
weight showing an increase in the height of the second melting peak. Earlier, Chung and Cebe made an in depth investigation of this dual melting behavior for PPS with $<M_w> = 15 000$ and $<M_w> = 60 000$ under isothermal and non-isothermal conditions. They suggested that for crystallization at low undercoolings the dual melting phenomenon was primarily due to dual populations of lamellar crystallites each of which melted at different temperatures. For crystallization at higher undercoolings they suggested that some crystallites may rearrange and melt at a higher temperature during heating in the DSC. The fact that the relative size of the higher temperature melting peak decreases with molecular weight in Figure 3-24 indicates that the population of crystallites which are more thermodynamically stable are less easily formed in higher molecular weight PPS, likely due to kinetic restraints due to reduced chain mobility. This finding would be consistent with the lower crystallinity observed by WAXD and lower heats of melting and fusion observed for PPS with increasing molecular weight. The increased size of the second melting peak in the lower molecular weight species and the fact that it is shifted to slightly higher temperatures may also be explained by the fact that more rearrangement may be possible during heating for lower molecular weight species. However it is unlikely that this phenomenon is occurring to a great extent in this study because the magnitude of the melting peak is not increased relative to that of the crystallization peak. For all of the samples studied the measured heats of fusion and melting did
not differ by more than what would be expected due to the small effect contribution of $T_e^{T_m}C_ldT$ (compare Figure 3-21 and Table 3-4).

Table 3-4 summarizes the measurements of heats of melting determined by DSC and absolute crystallinity determined by WAXD. Since, at this crystallization temperature, the value for the heat of melting and that for the heat of crystallization are nearly identical. The data from Table 3-4 may be used to extrapolate the heat of fusion for fully crystalline PPS.(Figure 3-25) Analysis of our data gives an experimental value of $22.1 \pm 0.7$ cal/g which is somewhat higher than the value obtained by Brady in a similar manner ($18.5$ cal/g)$^{18}$ and slightly lower than the value obtained by Cebe and Huo$^{40,41}$ ($26.7 \pm 0.8$ cal/g). Huo and Cebe made an independent measurement of the heat of fusion for fully crystalline PPS using density measurements and determined a value of $24.8 \pm 0.8$ cal/g.$^{35,36}$ Koch and Heitz extrapolated a value for fully crystalline PPS by extrapolating the values obtained from low molecular weight oligomers to infinite molecular weight.$^{42}$ Using this alternative method a value of $25 \pm 1$ cal/g was obtained. It is likely that the value for the heat of fusion of fully crystalline PPS is very close to this value, but determinations of this quantity by density measurements or x-ray analysis combined with thermal analysis may be complicated by the presence of an ordered amorphous phase.$^{39,40}$ Additionally the method of WAXD data analysis used in this study may

---

1 Menczel and Collins have determined the solid state heat capacity of PPS to be: $C_p [J^\circ C^{-1}g^{-1}] = 0.00317T[\circ C] + 0.954$ - see ref. 16.
Table 3-4: Results of WAXD Absolute Crystallinities and DSC Heats of Melting For Samples Crystallized at 250°C

<table>
<thead>
<tr>
<th>$&lt;M_w&gt;$</th>
<th>Absolute Crystallinity (WAXD)</th>
<th>Heat of Melting (DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>113 000</td>
<td>35 %</td>
<td>8.31 cal/g</td>
</tr>
<tr>
<td>83 000</td>
<td>48 %</td>
<td>10.61 cal/g</td>
</tr>
<tr>
<td>57 000</td>
<td>50 %</td>
<td>11.05 cal/g</td>
</tr>
<tr>
<td>43 000</td>
<td>53 %</td>
<td>11.75 cal/g</td>
</tr>
<tr>
<td>Amorphous Sample $&lt;M_w&gt; = 113 000$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
FIGURE 3-25: Data used to determine the heat of fusion for 100% crystalline PPS.
introduce a systematic error into the calculations since the contributions due to the atomic scattering factors, structure scattering factors, and contributions due to factors such as thermal diffuse scattering are ignored. These factors may be the reason why the extrapolated value in this study is somewhat lower than those determined in other studies.

CONCLUSIONS:

The effects of fractionation and the chemical nature of the endgroup counter-ion for PPS samples of varying molecular weight on the crystallization behavior of PPS were investigated. The nucleation density of PPS increased with increasing molecular weight, likely due to the fact that more residual nuclei survived the melt treatment in this system. Bulk crystallization rates were found to be more rapid for samples that had been fractionated than the "as polymerized" samples. The ion-exchange process used in this study increased the rate of bulk crystallization relative to samples which had not undergone the ion-exchange process. In all cases the acid washed samples were found to crystallize most rapidly. The effects of fractionation and the ion-exchange process was much more pronounced in the lower molecular weight species than in the high molecular weight PPS. Avrami exponents were found to be slightly reduced as a function of fractionation. Growth rates determined for PPS with $\langle M_w \rangle = 57000$ as a function of endgroup counter-ion were found to increase in the following order: Na < Zn < H. Nucleation densities for PPS with $\langle M_w \rangle =$
57,000 were found to be unaffected as a function of endgroup counter-ion. Since a strong effect was noted by an earlier study by one of the co-authors on unfractionated PPS of similar molecular weight, it was proposed that aggregates of ionic endgroups may be the nucleating species in this system. Since the number of ionic endgroups is greatly decreased due to the fractionation process used in this study, the effect of endgroup counter-ion on nucleation is, understandably, greatly reduced. A significant decrease in crystallinity with increasing molecular weight was observed through WAXD experiments, as well as through measurements of heats of fusion and melting by DSC. Trends in the dual melting behavior of PPS indicated that in high molecular weight PPS a greater percentage of the crystallites formed have a lower level of crystalline perfection than in PPS with lower molecular weight.
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CHAPTER 4

Crystallization Kinetics and Morphological Features of

Star-branched Nylon-6:

Effects of Branch-point Functionality

INTRODUCTION:

Linear nylon-6 has been a widely available, commercially important polymer for years. Star-branched nylon-6 varies from the linear variety in that it is characterized by a branch point from which a number of polymer chains or arms emanate. Recently, there has been increasing interest in starburst "dendrimers", a new class of molecules possessing extraordinary symmetry as well as high branching and terminal functionality.\textsuperscript{1,2,3,4} Star-branched nylon-6 with precisely controlled branching has been synthesized using starburst dendrimers as branch points.\textsuperscript{5} This new class of star-branched polymers offers significant reduction in melt viscosity compared to linear nylon-6 of comparable molecular weight. This reduction of melt viscosity allows for processing at lower temperatures and pressures as well as the ability to process higher molecular weight polymers. Additionally, reduced viscosity allows for improved extrudability as well as injection molding of nylon-6.

The solid state properties of both linear and star branched nylon-6 depend on the
crystallization behavior and morphology of the polymer. Extensive studies have been performed on the thermodynamic and structural properties of linear nylon-6. However, the effects of "dendrimer" star-branching on the crystallization kinetics and morphology of nylon-6 has, until now, remained uninvestigated. Mathias and Sikes have investigated the chemical structure and some of the physical properties of star-branched nylon-6 synthesized by an alternative means.\textsuperscript{14,15} Mathias and Sikes synthesized a star-branched polymer with branch point functionality of three, but had difficulty controlling molecular weight and preventing crosslinking reactions from occurring. An earlier study on the crystallization kinetics of hydrogenated polybutadiene (HPB) had found that star-branching in HPB with \((M_w/M_c)\approx 10\), where \(M_c\) is the average molecular weight between molecular entanglements, had the same effect as reducing the molecular weight by one-third.\textsuperscript{16} Both of these studies, however, lacked the precise control of branch-point functionality possible with starburst dendrimers. These studies also did not investigate the effects of increasing branch-point functionality on morphological features, as well as on equilibrium melting point and absolute crystallinity. The objective of this research has been to determine the effects, if any, that star-branching has on crystallization kinetics and morphology as well as thermodynamic properties such as heat of fusion and equilibrium melting point. While keeping the number average degree of polymerization constant, the effect of changing branch-point functionality from 2 (ie. linear) to 3 to 6 was investigated by
means of optical polarized microscopy (OPM), scanning electron microscopy (SEM),
small angle light scattering (SALS), wide angle x-ray diffraction (WAXD), small angle
x-ray scattering (SAXS), transmission electron microscopy (TEM), as well as
differential scanning calorimetry (DSC).

EXPERIMENTAL:

The samples utilized for the present study were prepared by a cation-initiated
ring opening polymerization of e-caprolactam with amine initiator functionality of
two, three, and six. The initiators for the three and six arm systems were the
forementioned starburst dendrimers first synthesized by Tomalia. The second
generation starburst polyethyleneimine used as an initiator for six-arm star-branched
nylon-6 is shown in

Figure 4-1. In the case of the linear polymer, 1,5-diamino pentane hydrochloride was
used as an initiator. In all cases the chemical structure of the initiator is substantially
different than that of the nylon-6 repeat unit. The unique nature of the branch-point
structure differentiates this type of regular-star-branching from conventional long
chain branching where the chemical structure of the branch point is similar to that
of the polymeric repeat unit.

Characterization information is outlined in Table 4-1. The number average
degree of polymerization, DP, was estimated from the product of the fractional
conversion and monomer to initiator ratio. GPC experiments were performed on
FIGURE 4-1:
Chemical structure of the second generation starburst polyethyleneimine used as an initiator in six-arm nylon-6.
TABLE 4-1:
Characteristics of samples utilized to study the effect of branch-point functionality on the crystallization kinetics and morphology of nylon-6

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Initiator Functionality</th>
<th>Number Average DP*</th>
<th>$M_n^{**}$</th>
<th>$M_w^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>2</td>
<td>270</td>
<td>16000</td>
<td>29000</td>
</tr>
<tr>
<td>Three Arm</td>
<td>3</td>
<td>300</td>
<td>19000</td>
<td>36000</td>
</tr>
<tr>
<td>Six Arm</td>
<td>6</td>
<td>270</td>
<td>21000</td>
<td>42000</td>
</tr>
<tr>
<td>Six Arm</td>
<td>6</td>
<td>1150</td>
<td>49000</td>
<td>105000</td>
</tr>
</tbody>
</table>

*Estimated from monomer to initiator ratio and fractional conversion.
**Measured by GPC analysis.
materials with similar nominal degrees of polymerization by Professor Saverio Russo using linear nylon-6 as a calibration standard.\textsuperscript{18} All nylon-6 samples were functionalized using a trifluoracetylation reaction, in order to facilitate solvation in methylene dichloride.\textsuperscript{19,20} M_n and M_w were estimated for the materials in this study by using the results obtained by Russo which were corrected for the reduced hydrodynamic volume of the star-branched polymers. Correction for hydrodynamic volume was necessary because the mean square radius of gyration for star-branched vs. linear polymers is known to scale as: $<R_g^2>_{\text{branched}}/ <R_g^2>_{\text{linear}} = (3f-2)/f^2$, where f is the branchpoint functionality.\textsuperscript{21} Polyamides functionalized using the trifluoracetylation procedure are easily hydrolyzed shifting the molecular weight distribution to lower values as well as increasing dispersity.\textsuperscript{20} On the other hand, the estimation of number average DP based on fractional conversion assumes that the polymerization reaction was a living polymerization. It is likely that the actual values of M_n for the samples lie somewhere between the values determined by GPC and those determined by fractional conversion. For convenience the samples will be referred to according to the number average degree of polymerization determined by fractional conversion.

Morphological Studies:

Reimschuessel \textit{et. al.} have shown that polymers with strong secondary interactions such as hydrogen bonding in nylon 6, retain orientation memory at temperatures even above their equilibrium melting point.\textsuperscript{7-10} In order to minimize the effects of
previous thermal and mechanical history, all samples were heated to 240°C, approximately 10 degrees above the equilibrium melting point, for 10 minutes prior to all morphological experiments. Samples were molded into thin films between glass microscope cover slides in order to determine any differences in morphological features as a function of branching functionality by means of OPM and SALS. A Zeiss polarizing microscope equipped with a Leitz 350 heating stage and a 35mm camera was utilized for OPM. SALS experiments were performed in a light proof room, with a HeNe laser (6328 Å). An open back camera was mounted 10cm from the sample within the heating stage to measure the scattering pattern.

Samples for WAXD, SAXS, TEM, and SEM were compression molded between PTFE films into plaques approximately 0.05cm x 5cm x 10cm. All WAXD experiments were performed on a Nicolet diffractometer operating at 40KV and 30mA and equipped with a STOE Bragg-Bernatto type goniometer. Cu-Kα x-rays (1.54 Å) were passed through a graphite monochrometer before final collimation. Data was collected at 0.1° increments between the scattering angles of 10° to 35°. For all runs two plaques were stacked to optimize thickness. Data collection and analysis was performed by the Siemens Polycrystalline Software Package.

SAXS measurements were performed using a Siemens Kratky camera system with an M. Braun position-sensitive detector from Innovative Technology, Inc. A Philips model PW 1729 tabletop generator was used. For all experiments the generator was set to 40 KV and 20 mA using the Cu Kα x-ray (1.54 Å). Lead Stearate was used for
angular calibration and Lupolen was used for absolute intensity calibration.

TEM samples were prepared from the same films that were used for WAXD and SAXS. Samples were microtomed at -20°C using a Reichert-Jung ultracut E43 ultramicrotome equipped with a diamond knife. Samples were cut to a thickness of 500Å - 1000Å. Samples were chemically stained with ruthenium tetroxide (RuO₄)²² by suspending them over a 0.5% solution of RuO₄ for 30-60 minutes. All TEM experiments were performed on a Phillips IL 420T STEM with an acceleration voltage of 100-120 KV.

After running WAXD and SAXS experiments on the compression molded plaques, they were cut into small pieces and etched using a permanganic acid permanganate solution.²³ The concentrated solution consisted of 0.5g of K₂MnO₄ dissolved in 20 ml of 85% H₃PO₄ diluted with 20 ml H₂O; the dilute solution differed from the concentrated solution in that it was diluted to a volume of 120mL. Following etching, all samples were sputter coated with gold in a Bio Rad E5400 high resolution SEM sputter coater to a thickness of approximately 210 Å. A Cambridge Instruments Stereoscan 200 scanning electron microscope with an operating voltage of 25KV was used for all scanning electron microscopy experiments.

Rheological Studies:

Samples for rheological experiments were compression molded into 1 inch x 1mm disks. All measurements were performed on an RMS 800 shear rheometer. For all
samples, melting was completed by the time the temperature had reached 240°C. Samples were held at 240°C for 10 minutes prior to rheological testing. During this period, no differences were noted in complex viscosity. Strain sweeps were performed from 1-10% strain at 240°C, frequency sweeps were performed from 0.1 to 100 radians per second at 240°C, and temperature sweeps were performed from 260°C to 200°C at 10 radians per second. Temperature sweeps were performed at a rate of 10°C/min. in order to obtain viscosity measurements in the supercooled melt before the onset of crystallization. The strain rate of 10 radians per second was chosen to keep torques high enough to be measurable in the branched systems which showed substantially reduced melt viscosities compared to linear samples of comparable molecular weight.

Bulk Crystallization Rate:

A Perkin-Elmer DSC-4 and a Seiko DSC 210 were used to obtain bulk crystallization information. In both cases, indium was used for temperature calibration. After being held in the melt for 10 minutes, all samples were isothermally crystallized in 2mg aluminum pans. Samples were held in the melt in order to correlate the thermal history of DSC experiments with that of experiments described earlier. Isothermal crystallization experiments were performed in the temperature range of 190°C to 207°C. The lower limit of 190°C was dictated by the maximum cooling rate available, for achievement of temperatures below 190°C before the onset of crystallization. The upper limit was set by the long induction
times before the onset of crystallization and the resulting problems with thermal stability and reduced signal to noise ratio. Due to the inability to rapidly but controllably quench samples from the melt, crystallization data from the diffusion controlled crystallization temperature range was not obtainable.

**DATA ANALYSIS:**

**SALS:**

Spherulitic structure, evident in many polymers, generally results in a (SALS) pattern under cross polarized light with fourfold symmetry. This pattern is known as the "four leaf clover" pattern. At the intensity maximum of each lobe, the following relationship is satisfied:

\[
4.09 = 4\pi \frac{R \sin(\Theta_{\text{max}}/2)}{\lambda_m}.
\] (4-1)

In this case \( R \) is the average spherulite radius, \( \Theta_{\text{max}} \) is the scattering angle at which an intensity maximum is observed, and \( \lambda_m \) is the wavelength of light in the material. Since \( \Theta_{\text{max}} \) is easily obtained from photographic measurements SALS is a rapid means of determining average spherulite size.

**WAXD:**

Wide angle x-ray diffraction was primarily used to determine whether any structural differences or differences in crystallinity were observable as a function of branch-point functionality. WAXD also allowed for an independent determination of absolute crystallinity which could later be correlated with heat of fusion measurements obtained by DSC.
The classical method of Hermans and Weidinger was used to determine absolute crystalline fraction in each of our three samples.\textsuperscript{25} This procedure involves the separation of x-ray scattering intensities into amorphous and crystalline components. Since our samples are homogeneous and isotropic, the crystalline fraction is the ratio of integrated intensity beneath the crystalline peaks over the integrated total intensity. The above procedure is based upon the assumption that the crystalline peaks can be deconvoluted from the amorphous scatter. The method of peak deconvolution that we selected was utilized by Vonk to determine absolute crystallinity in a number of polymers.\textsuperscript{26} It involves obtaining an amorphous scattering profile and subtracting the lineshape from the amplitude and baseline corrected total scattered intensity. The experimental method of peak resolution is outlined in Figure 4-2. Since no WAXD heating stage was available at our facility, and nylon-6 could not be adequately quenched to obtain an amorphous standard, the amorphous scattering profile of nylon-6 was obtained from an earlier study on linear nylon-6.\textsuperscript{27} Since no crystallographic differences were observable between our samples as a function of branch-point functionality, it was assumed that the linear nylon-6 standard was a valid standard for all branching architectures investigated.

The method of Hermans and Weidinger may underestimate the absolute crystallinity by 10\% or more due to its neglect of spatial and thermal disorder as well as amplitude corrections due to atomic scattering factors and structure factors.\textsuperscript{28} Although the effects of thermal diffuse scattering were not taken into account in this
FIGURE 4.2:
Resolution of WAXD data into amorphous and crystalline components.
A - Baseline corrected raw data points and Fourier fitted curve.
B - Baseline and amplitude corrected amorphous scattering profile.
C - Resolved crystalline peaks.
study, Ruland has shown that in polymers containing interchain hydrogen bonding, the effects of thermal disorder are not as significant as in polymers lacking strong secondary interactions. Preliminary calculations considering the effects of atomic scattering factors as well as structure factors suggest that the systematic error introduced by using the method of Hermans and Weidinger is less than 5%, on the order of our experimental uncertainty.

Thermal Analysis:

a.) DSC (Percent Crystallinity):

Percent crystallinity was determined from calorimetric data by integrating the entire region under the melting endotherm to obtain heat of fusion as a function of temperature. A molar heat of fusion of 21±2 KJ/molRpt. unit for Nylon 6 (100% crystalline material) was obtained by averaging several values obtained in earlier studies. The following equation was used to determine percentage crystallinity:

\[
\% \text{ xtal} = \left( \frac{\Delta H_{\text{measured}}}{\Delta H_{100\% \text{ xtal}}} \right) \times 100\% \tag{4-2}
\]

b.) DSC (crystallization kinetics):

The overall rate of bulk crystallization can often be analyzed in terms of the Avrami equation:

\[
X_c(t) = 1 - e^{-Kt^n} \tag{4-3}
\]

\(X_c(t)\) is the volume fraction of crystals at time, \(t\), after the onset of crystallization. Often at low values of supercooling an induction period may occur before the onset of crystallization. \(K\) is a rate constant including temperature dependent terms.
involving diffusion, growth, and nucleation density; and n, the Avrami exponent, is a constant depending on the types of processes occurring during nucleation and growth.

Taking the double logarithm of (4-3) we obtain:

\[ \ln[-\ln(1-X_c(t))] = \ln K + n \ln t. \quad (4-4) \]

Thus a plot of the double logarithm of amorphous content as a function of ln(time), a classical Avrami plot, gives a straight line with slope n and intercept ln K.

An alternative method of determining crystallization parameters involves the use of crystallization half-time. In this case the entire area under the crystallization exotherm represents a normalized crystalline content of unity. On a normalized basis the crystallization half time, \( t_{1/2} \), is defined as the time at which the normalized crystalline content is 0.5. From a graph of normalized crystalline content vs. ln(time) one may determine the Avrami exponent, n, from the slope at \( t = t_{1/2} \). \( S_{1/2} \).

Taking the logarithm of equation (4-3) at \( t = t_{1/2} \) one obtains:\(^{32}\)

\[ K = \frac{\ln(2)}{t_{1/2}^n}. \quad (4-5) \]

The slope of the curve \( 1-X_c(t) \) as a function of ln(time) may be written as:

\[ S = t^* [\delta(1-X_c(t))] / \delta t \quad (4-6) \]

From equation (4-3) \( \delta[1-X_c(t)] / \delta t \) may be calculated:

\[ \delta[1-X_c(t)] / \delta t = -Knt^{n-1}e^{-kt^n} \quad (7) \]

at \( t = t_{1/2} \):

\[ S_{1/2} = n \ln(2)/2. \quad (8) \]
RESULTS AND DISCUSSION:

The effect of branch functionality on equilibrium melting points, $T_m^0$, was determined using the method of Hoffman and Weeks. Figure 4-3 shows the data used to determine the equilibrium melting points as a function of branch point functionality while keeping DP nearly constant. This method gives equilibrium melting points of 236°C for linear nylon-6, 231°C for the three arm nylon-6, and 228°C for the six arm nylon-6. Melting points observed by DSC were consistently lowered as a function of increasing branch-point functionality. (Figure 4-4) A similar depression of melting points observed by DSC had been noted by Mathias and Sikes on a different star-branched nylon-6 system, but the equilibrium melting points were not determined for their polymers.

The origin of the depression of equilibrium melting points can be related to the nature of the lamellar crystals formed in the branched vs. linear systems. The enthalpy of formation for a chain-folded lamellar crystal is:

$$\Delta H_{\text{crystal}} = 4xl\sigma + 2x^2\sigma_e - x^3)(\Delta f).$$  \hspace{1cm} (4-9)

In this case, $x$ is the lateral dimension of the crystal, $l$ is the lamellar thickness, $\sigma$ is the lateral surface energy, $\sigma_e$ is the fold surface energy, and $\Delta f$ is the bulk free energy of fusion. For crystals with $x >> l$, it can be shown that the melting temperature may be estimated by:

$$T_m = T_m^0 \left[ 1 - 2\sigma_e/(\Delta h_l) \right];$$  \hspace{1cm} (4-10)

Equation 4-10 predicts a melting point depression of $(2T_m^0\sigma_e/\Delta hl)$ for a thin
FIGURE 4.3:
Effect of branch-point functionality on Hoffman Weeks Plots
lamellar crystal below that of an infinitely thick crystal. Since it will be shown later that the average thickness of lamellar crystals of nylon-6 is not greatly effected by branch-point functionality, the data in Figure 4-3 suggests that the ratio \((\sigma_e/\Delta h)\) for crystals of star-branched nylon-6 is less than that for linear nylon-6 by 26% for six-arm nylon-6 and 22% for three-arm nylon-6. An expected result of the entropic constraint imposed on the branched molecules would be to promote an increased equilibrium melting point for crystals of branched polymers when compared to their linear counterparts. Since the observed trend is in the opposite direction, the effects of the additional entropic constraint appears to be minimal. The observed depression of melting points may be attributed to differences in bulk enthalpy of fusion and greater fold surface energies in crystals of branched polymers due to local defects. The enthalpy of formation of a crystal will be decreased if bulky branch-points and end groups are included within or near the surface of a crystal. End groups lack the spatial symmetry necessary to pack into the crystal lattice, and noting that the chemical structure of the branch-points is substantially different than that of nylon-6, it is unlikely that such a structure can pack into lamellar crystals. As the concentration of branch points and end groups increases, the equilibrium melting point of the polymer crystals should decrease as well.

In order to substantiate the above arguments, the equilibrium melting point of six-arm nylon-6 with a considerably higher DP (1150) was determined. Since the concentration of branchpoints and endgroups in this higher molecular weight system
FIGURE 4-4:
Effect of branch-point functionality on DSC melting endotherms
for samples isothermally crystallized at 200°C:
A - linear nylon-6; $T_m = 222.5$
B - three-arm nylon-6; $T_m = 221.5$
C - six-arm nylon-6; $T_m = 219.5$
is decreased compared to the lower molecular weight six-arm system by a factor of four, the equilibrium melting point should be nearer to that of the linear system. Indeed, the equilibrium melting point of star-branched nylon-6 with DP = 11500 was determined to be 232°C, six degrees higher than six-arm nylon-6 with DP = 270. Thus as an effect of branching, the melting point depression in our system appears to be directly correlated to changes in bulk crystallization enthalpy and steric interactions resulting in higher fold surface energy. Recently Roland and Buckley have used the above arguments to attribute changes in the thermodynamic stability, i.e. equilibrium melting point, of polytetrahydrofuran networks to crosslink density. On a local scale the branchpoints in star-branched nylon-6 behave much like a crosslink in terms of decreasing the thermodynamic stability of a crystal.

Data from isothermal crystallization experiments were put in the format for crystallization half-time analysis (Figure 4-5a,b,&c) as well as classical Avrami analysis (Figures 4-6a,b,&c). Figures 4-5a,b,&c are plots of the normalized crystalline content of linear nylon-6, three-arm nylon-6, and six-arm nylon-6 as a function of ln(time). From this data and equations (4-5) and (4-8) the Avrami exponents, \( n \), and rate constants, \( K \), were determined as a function of temperature (Figures 4-7 and 4-8). Analysis on the Avrami plots using equation 4-4, Figures 4-6a,b,&c, yielded the \( n \) and \( K \) values from the slope and the log of the intercept (Figures 4-9 and 4-10). In experiments where an induction period was observed, star-branched nylon-6 showed substantially shorter induction periods before the onset of crystallization

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FIGURE 4.5:
Normalized crystalline content vs. time:
A - linear nylon-6, B - three arm nylon-6, C - six arm nylon-6
FIGURE 4-6:
Avrami plots: A - linear nylon-6, B - three arm nylon-6, C - six arm nylon-6.
FIGURE 4-7:
Avrami exponent, $n$, vs. $T_c$: effect of branch-point functionality as determined by crystallization half-time analysis.
FIGURE 4-8:
Rate constant, $K$, vs. $T_c$: effect of branch-point functionality as determined by crystallization half-time analysis.
**FIGURE 4-9:**
Avrami exponent, $n$, vs. $T_c$: effect of branch-point functionality as determined by classical Avrami analysis.
FIGURE 4.10:
Rate constant, $K$, vs. $T_c$: effect of branch-point functionality as determined by classical Avrami analysis.
when compared to the linear polymer crystallized at the same temperature.

Both analysis methods revealed a decrease in the Avrami exponent with decreasing temperature in all samples. Earlier studies on the crystallization kinetics of linear nylon six revealed Avrami exponents that ranged from 2 to 3 for isothermal crystallization temperatures ranging from 150°C to 190°C. Magill noted through microscopy and optical depolarization experiments that heterogeneous nucleation was prominent at temperatures below 190°C, but at temperatures above 190°C sporadic, homogeneous nucleation became evident and Avrami exponents approaching 4 were observed. No significant changes in the Avrami exponent as a function of branch-point functionality were evident; however Avrami exponents showed a definite increase at temperatures above 197°C. Avrami exponents had an average value of 2.8 in the temperature range of 190°C-197°C; for temperatures above 197°C the average Avrami exponent increased to about 4. Theoretically, this increase in Avrami exponent may correspond to the transition from heterogeneous nucleation with three dimensional spherulitic growth to homogeneous nucleation with three dimensional spherulitic growth.

The effect of branch-point functionality on crystallization half-times is shown in Figure 4-11. Plotting crystallization half-times as a function of supercooling eliminates the observed effect of branching on equilibrium melting point that would be present if these values were plotted as a function of crystallization temperature. Carr and Hser observed that star branched polyethylene showed significantly lower
FIGURE 4-11:
Effect of branch-point functionality on crystallization half-times vs. supercooling:
a.) linear nylon-6, □ b.) three-arm nylon-6, X, c.) six-arm nylon-6, ◊.
crystallization half times as a function of supercooling compared to linear polyethylenes of equivalent molecular weight. A similar but less pronounced effect is seen in the Nylon-6 utilized in this study. The crystallization half-times for the linear polymer are nearly twice those observed for the six-arm system at equivalent supercooling. The branched systems also appear to display an increased dependence of crystallization half-times on supercooling relative to the linear polymer: this increased supercooling dependence is also consistent with data obtained by Carr and Hser. Decreased crystallization half-times are desirable for most applications since a higher degree of absolute crystallinity can be obtained in less time with equivalent supercooling - other factors being equivalent.

When discussing the effects of chain branching on crystallization it is important to consider that branching may have two counteracting effects on the rate at which polymer chains may be deposited on the surface of a growing lamellar crystal. For most polymers of relatively low molecular weight, the dominant mode of diffusion is reptation. de Gennes has shown that branching tends to increase reptation times by a factor that is exponential in the number of entanglements per branch compared to the power law dependence observed for linear chains. A counteracting effect arises from the fact that branched chains tend to have a much smaller radius of gyration than linear chains of similar molecular weight. Reduced hydrodynamic volume is evident in star-branched polymers through reduced intrinsic viscosity. Branched chains, thus, tend to be more compact and form
entanglements with fewer neighbors than linear polymers of equivalent molecular weight. Further complicating the picture are the considerations that constraint release and coupling parameters, a measure of the extent to which the average polymer molecule is entangled with its neighbors, may vary considerably depending on branch-point functionality. Ngai, et. al. have shown that coupling parameters may vary considerably depending on branch-point functionality. Lodge, on the other hand, has shown that coupling parameters for star polymers with arm lengths well above the entanglement length are nearly constant as a function of branch-point functionality. Viovy, et. al. as well as Roovers have proposed that constraint release in polymer melts may vary greatly as a function of macromolecular topology; however the exact nature of this process in nonlinear systems is still not well understood.

In order to measure the effects of star-branching on diffusion times and entanglement coupling, viscosity vs. temperature sweeps were performed from 260°C to 200°C. (Figure 4-12) By performing a downward temperature sweep at 10°C per minute, viscosities of the supercooled melt could be measured before the onset of crystallization. As suggested by crystallization half-time measurements, viscosities of the supercooled melts were greatly reduced as a function of increasing branch-point functionality. The behavior of both linear and star-branched nylon-6 may be explained by the coupling model for entangled polymer melts. At temperatures well above the glass transition the viscosity of a polymer may be represented by: \(^{41}\)
FIGURE 4.12:
Effects of branch-point functionality on complex viscosity; temperature sweeps at 10 radians/sec: □ - Linear nylon-6; \( <M_n> = 30 900 \), X - Three-arm nylon-6; \( <M_n> = 31 500 \), ▲ - Six-arm nylon-6; \( <M_n> = 30 900 \), ◼ - Six-arm nylon-6; \( <M_n> = 130 000 \).
\[ \zeta = M^*[\zeta(T)] = M^*[\zeta_0(T)]^{(1/(1-n(f))} \]

where the monomeric friction factor, \(\zeta(T)\), can be expressed in the Arrhenius form as:

\[ \zeta(T) = Ce^{E_a/[1/(1-n(f))RT]} \]

Where \(n(f)\) is the coupling parameter. Ngai and Plazek have shown that the primitive flow activation energy, \(E_a\), of polymers is more a function of bond rotational energies than topology.\(^{41}\) Therefore, the coupling parameter, \(n(f)\), of a linear or star-branched systems may be calculated from the temperature dependence of viscosity.\(^{41}\) A plot of \(\ln(n)\) vs. \(1/T\) has slope \(E_a/(1-n(f))R\). Since \(E_a\) is essentially a function of bond rotational energy, independent of topology, \(n(f)\) may be determined. The value of \(E_a\) was estimated from that of a methylene group in linear polyethylene as determined by Ngai and Plazek since this is the most flexible link in the nylon-6 chain.\(^{41}\) The true value of \(E_a\) in nylon-6 is likely to be somewhat larger than that for the methylene linkage due to the presence of amide linkages.

In this way the coupling parameters of the three arm and linear polymer with molecular weight (ca. 30 000) were found to be nearly identical as predicted by Lodge, et. al.; however the coupling parameter of the six-arm system was found to reduced by nearly a factor of two when compared to that of the linear system -see Table 4-2. When similar measurements were performed on a six-arm nylon-6 with four times the molecular weight, the coupling parameter was found to agree with the linear value.
**TABLE 4-2:**
Coupling parameters as measured from temperature dependence of shear viscosity

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Branch-point Functionality</th>
<th>M_\infty</th>
<th>Δ\log\eta/Δ(T^{-1})</th>
<th>n_f</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>2</td>
<td>29 000</td>
<td>3290</td>
<td>0.39</td>
</tr>
<tr>
<td>three-arm</td>
<td>3</td>
<td>36 000</td>
<td>3120</td>
<td>0.35</td>
</tr>
<tr>
<td>six-arm</td>
<td>6</td>
<td>42 000</td>
<td>2720</td>
<td>0.26</td>
</tr>
<tr>
<td>six-arm</td>
<td>6</td>
<td>105 000</td>
<td>3290</td>
<td>0.39</td>
</tr>
</tbody>
</table>
The average molecular weight between entanglements, $M_e$, in Nylon-6 is approximately 5000.\(^{42}\) From this value we would expect an average of six entanglements per molecule for the samples in this system with weight average molecular weight of 30 000. However the weight average molecular weight of each arm in the six arm system is only 7000, very close to the critical length for entanglements, $(M_w/M_e)\sim 1$. Since the weight average molecular weight per arm is so close to the critical molecular weight between entanglements, it is expected that only about half of the arms in this system are effectively entangled with neighbors due to the distribution of arm lengths and lengths between entanglements. The end result is that the coupling parameter in this system should be significantly reduced compared to that of the linear polymer. This hypothesis is further verified by the fact that the coupling constant increases for the six-arm stars when the molecular weight of the arms increases above the average critical length for entanglements, $(M_w/M_e) >> 1$.

Ngai and Plazek have shown that in entangled polymer melts the zero-shear viscosity of branched polymers may be substantially greater than that for the linear counterpart due to the exponential dependence of viscosity on the number of entanglements per arm in branched polymers. This study, however, suggests that if the number of entanglements per arm is kept low, melt viscosities of branched polymers may be reduced substantially when compared to their linear counterpart. Due to the exponential dependence of melt viscosity on the number of entanglements
in branched polymers versus the power law dependence for linear polymers, the
effects of regular branching on the viscosity of a polymer is dependent on the ratio
\((M_w/M_c)\). If this ratio is kept low, the effect of star branching is to reduce reptation
times; when this ratio becomes large, i.e. \((M_w/M_c)_{swm} > 4\),\(^{43,44}\) the rapidly
increasing exponential dependence produces slowed reptation times and thus greater
viscosities. As a consequence, the increased molecular weight dependence on
reptation times for branched polymers means that molecular weight and
polydispersity must be more precisely controlled in order to produce consistent melt
viscosities for industrial applications.

The self-diffusion coefficient for a polymer melt may be represented in an
Arrhenius form analogous to (4-12) above:

\[
D_t = Ce^{-Ea/[(\gamma-\lambda)RT]}
\]

(4-13)
The average terminal relaxation time of the polymer melt may, thus, be expressed
as:\(^{39}\)

\[
<\tau> = <R_g^2>/D_t
\]

(4-14)
For high molecular weight, flexible polymers, the effects of regular star-branching on
the average radius of gyration may be approximated by:\(^{45}\)

\[
<R_{g,f}^2> / <R_g^2> = (3f^{-1.2})^{f2} / (3f^{-2})^{f^{-2}}
\]

(4-15)
Where \(f\) and \(f'\) are branchpoint functionalities of polymers with equivalent molecular
weight. In order for star-branching to slow terminal relaxations, the coupling
parameter must be large enough to offset the effect of reduced hydrodynamic
volumes. This may only occur at molecular weights well above the critical molecular weight for entanglement, $M_c$.

Star branching reduces reptation times in nylon-6 in the range of molecular weights used in this study. This reduction in reptation times is responsible for the greatly reduced melt viscosities of star-branched nylon-6 compared to its linear counterpart with comparable molecular weight; even for the six-arm stars with high molecular weight the melt viscosity was reduced to that of the linear polymer of much lower number average molecular weight. Due to reduced terminal relaxation times, polymer chains may more easily diffuse onto the surface of growing lamellar crystals. Assuming that spherulitic growth and nucleation are otherwise identical, the result of reduced reptation times is to also reduce crystallization half-times as a function of supercooling for nylon-6 with increasing branch-point functionality. The exact nature of spherulitic nucleation and growth in linear vs. star-branched polymers will be discussed later in this paper.

It can be argued that the cause of the lower equilibrium melting points in star-branched nylon-6 is the local effect that a branchpoint has on the thermodynamic stability of crystal. A branchpoint cannot be packed into a crystal lattice without causing a defect and topologically constraining its neighbors. Inclusion of such defects might also tend to reduce the absolute crystallinity measured by x-ray and DSC. In each of the polymers investigated in this study, the initiator chemistry was somewhat different from that of nylon-6. Therefore even in the linear system,
initiated by a difunctional amine, it is unlikely that this chemically different portion of the polymer chain could pack into a crystal lattice; although the topological constraints in this case would be negligible.

Values of the heat of fusion as a function of crystallization temperature were obtained by integration under the entire melting endotherm. These values were then used in combination with (4-2) to determine absolute crystallinity. Figure 4-13 shows the effect of branch-point functionality as well as temperature on measured heat of melting. There appears to be a slight reduction in measured heat of melting of crystals of star-branched nylon-6 compared to crystals of linear nylon-6. This reduction may be attributed to higher fold surface energies of lamellar crystals or a decrease in bulk crystalline enthalpy due to inclusion of bulky branch-points at or near the surface of such crystals, since no significant change in absolute crystallinity was measured by WAXD (Table 4-3). The reduced heat of melting for crystals of star-branched nylon-6 relative to linear nylon-6 is consistent with depressed melting points for star-branched nylon-6. The trend towards lower values of heat of melting at high $T_c$ is likely due to the fact that these crystals were not held at at the crystallization temperature long enough for secondary crystallization to be completed.

In this system both chain ends and branch-points may cause crystalline defects. As molecular weight is kept constant and branch-point functionality increases, the concentration of both types of defects in a crystal increases. The melting point of a crystal may be described by:
FIGURE 4-13:
Effect of branch-point functionality on the heat of melting vs. temperature.
FIGURE 4-14:
Wide angle x-ray diffraction patterns of samples crystallized at 200°C:
A - Linear nylon-6, B - Three-arm nylon-6, C - Six-arm nylon-6.
**TABLE 4-3:**
Effect of branch-point functionality on the absolute crystallinity determined by WAXD and DSC

<table>
<thead>
<tr>
<th>Sample</th>
<th>% crystallinity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DSC ±1%</td>
<td>WAXD ±2%</td>
</tr>
<tr>
<td>linear</td>
<td>33</td>
<td>31</td>
</tr>
<tr>
<td>three-arm</td>
<td>31</td>
<td>30</td>
</tr>
<tr>
<td>six-arm</td>
<td>31</td>
<td>31</td>
</tr>
</tbody>
</table>
\[ T_m^o = \frac{\Delta H_{\text{fus}}}{\Delta S_{\text{fus}}} \]  

where \( \Delta H_{\text{fus}} \) is the bulk enthalpy of fusion, and \( \Delta S_{\text{fus}} \) is the bulk entropy of fusion. If the entropic effect of the additional constraint in a star-branched system were significant, the expected result would be an increase in equilibrium melting point. Since the contrary is observed, it is apparent that enthalpic effects are much more significant. The inclusion of a defect such as an endgroup or branch-point at or near the surface of a crystal lattice would be expected to reduce the enthalpy of fusion of such a crystal. Enthalpy of fusion measurements were performed on six-arm nylon-6 with DP = 1 150 in order to determine if the lower concentration of endgroups and branch-points in this system would lead to an enthalpy of fusion closer to that of linear nylon-6. However, the detected difference in enthalpy of fusion was not beyond experimental uncertainty (60.4 mJ/mg for the sample with DP = 270 vs. 60.7 mJ/mg for the sample with DP = 1150). The results obtained while keeping molecular weight constant, and changing branch-point functionality alone, are enough to suggest that bulk enthalpies of fusion of crystals containing star-branched polymers are, indeed reduced compared to their linear counterparts.

Depressed equilibrium melting points as well as lowered enthalpies of fusion in crystals containing star-branching is consistent with the greater number of possible defects within crystals of star-branched polymers; however no appreciable differences between the crystal structure of linear vs. branched systems were observed by WAXS(Figure 4-14). Absolute crystallization measurements by WAXS and DSC
reveal only small differences for samples with identical thermal history - see Table 4-3. Since the observed depression of equilibrium melting points is small, the effects of star-branching may lie at the limits of sensitivity of our instruments. Additionally WAXS measurements are less sensitive to defects at the edges of lamellar crystals and corresponding increases in fold surface energy due to steric interactions. The agreement between absolute crystallinity measured by WAXS and DSC suggest that the value used in this study for the molar heat of fusion of nylon-6 (21KJ/mol_{Rpt. unit.}) is an accurate value.

Since the values of the bulk crystallization constant, K, contain information about growth rate as well as nucleation density, it was imperative to see whether any differences in morphological features, i.e. nucleation density, were evident. Morphological studies were also needed to confirm our assumptions about nucleation and growth processes based on the Avrami exponent.

Optical polarized microscopy measurements, summarized in Figures 4-15a-f, revealed changes in nucleation density and average spherulite size as a function of temperature. Average spherulite diameter for specimens crystallized at 200°C were on the order of 10μm apparently with a rather broad distribution of spherulite sizes. Optical polarized microscopy also revealed a trend towards slightly smaller spherulites in the three-arm system. The size of the spherulitic structures, however, were difficult to estimate from OPM measurements.

Small angle light scattering, H_{\alpha}, patterns were used to get a more accurate
FIGURE 4.15:
Optical micrographs of star-branched nylon-6 between cross polarizers:
A,B - linear, crystallized at 191°C and 200°C respectively,
C,D - three arm, crystallized at 191°C and 200°C,
E,F - Six arm, crystallized at 191°C and 200°C.
indication of average spherulite radius as a function of branch-point functionality and temperature. These experiments revealed $\Theta_{\text{max}}$ values in the 3 to 9 degree range indicating an average spherulite radius on the order of 2 to 5 $\mu$M - see Figure 4-16. The average angle at which the maximum in the light scattering pattern, $\Theta_{\text{max}}$, occurred did not vary appreciably as a function of branch-point functionality except for the case of the three-arm system which tended to show a consistently higher value of $\Theta_{\text{max}}$. Since six separate samples were run to verify the reproducibility of results it is believed that the spherulites in the three-arm system were statistically slightly smaller than those in the linear and six-arm systems. The results of SALS experiments are provided in Table 4-4. In the cases where two values are given, the high and low values of several experiments are given.

Scanning electron microscopy was used to obtain further detail of themorphological features of the star-branched nylon system. By varying etching time and etchant concentration, differences between bulk and surface morphology could be better clarified. The systematic effects of etching on the six arm system are evident in Figures 4-17a-c. The dilute solution appeared to etch away a spherulitic layer, approximately 10$\mu$m, in ten minutes of etching while the concentrated etchant solution appeared to have the same effect after only one minute. Thus, a sample etched ten minutes in concentrated solution reveals morphology approximately 100$\mu$m beneath the surface. Comparison of spherulitic size, size distribution, and shape reveal no significant differences as a function of star-branching. Spherulitic
FIGURE 4-16:
Hν SALS patterns obtained from star-branched nylon-6:
A,B - linear, crystallized at 191°C and 200°C respectively,
C,D - three arm, crystallized at 191°C and 200°C,
E,F - Six arm, crystallized at 191°C and 200°C.
TABLE 4-4:
Results of H$_v$ SALS experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Theta_{\text{max}}$</th>
<th>Spherulite Radius (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>5.7</td>
<td>2.7</td>
</tr>
<tr>
<td>three-arm</td>
<td>8.5</td>
<td>1.8</td>
</tr>
<tr>
<td>six-arm</td>
<td>5.7</td>
<td>2.7</td>
</tr>
</tbody>
</table>

A: Samples crystallized at 191°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Theta_{\text{max}}$</th>
<th>Spherulite Radius (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear</td>
<td>2.9</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>3.6</td>
</tr>
<tr>
<td>three-arm</td>
<td>4.3</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>5.7</td>
<td>2.7</td>
</tr>
<tr>
<td>six-arm</td>
<td>2.9</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>3.6</td>
</tr>
</tbody>
</table>

B: Samples crystallized at 200°C
FIGURE 4-17:
Effects of chemical etching time on six-arm nylon-6 observed by SEM:
A - Etched 1 minute in dilute etchant solution,
B - Etched 2 minutes in dilute etchant solution,
C - Etched 5 minutes in dilute etchant solution.
FIGURE 4-18:
Morphological features of etched linear, three-arm, and six-arm nylon-6
as observed by SEM: A - Linear nylon-6, B - Three-arm nylon-6, C - Six-arm nylon-6.
structure suggests three dimensional growth with an average spherulite diameter on the order of 10 \( \mu m \) for samples crystallized at 200\(^\circ\)C- see Figures 4-18a,b,c. The observed Avrami exponent at 200\(^\circ\)C was 3.8. When compared to samples etched 1 minute with concentrated solution, no morphological differences are seen in samples etched 10 minutes as shown by Fig. 4-17c, thereby indicating that no noticeable differences are present in bulk vs. surface morphology on samples cast between PTFE films. The fact that no differences were evident, suggests that no major surface nucleation effects are present. The concave surfaces evident on some of the spherulites are the sites of impingement. The fact that these surfaces are nonplanar suggests that the spherulites were not nucleated simultaneously, i.e. homogeneous nucleation may have occurred. Three dimensional growth by homogeneous or self nucleation would be a phenomenon consistent with an Avrami exponent of four and results obtained earlier by Magill.\(^{13}\) Lack of surface-nucleation may be accounted for by the rapid rate of self-nucleation observed.

The small difference in average spherulite diameter observed in OPM and SALS may be related to differences in the level of impurities or branch-point chemistry, either of which could act as nucleation sites, thereby slightly increasing nucleation density. In any case, the slight variation in nucleation density observed in the three-arm system vs. the linear and six arm systems may account for the trend towards slightly higher K values in the three-arm system.

Although no major differences were noted in the size and shape of spherulites,
reduced equilibrium melting points in star-branched nylon-6 suggests that some type of structural differences may be present within the crystalline structure of these polymers due to the presence of branch-points. WAXD failed to reveal any differences in crystal structure or order. SAXS experiments performed on samples isothermally crystallized at 200°C reveal a broadening and decrease in intensity in the scattering peak(Figure 4-19). The linear system displays a strong peak in the smeared SAXS pattern corresponding to an approximate long spacing of 110Å. Although no significant change in long spacing was observed, the star-branched systems displayed a decreased peak prominence as a function of branch-point functionality. The trend shown in this series of SAXS scans suggests that star branching disrupts spatial regularity in lamellar structure. The average extended chain length for the linear nylon-6 with DP = 270 is approximately 2300Å,\(^\text{46}\) in a lamellar crystal 110Å thick, such a polymer chain could be folded approximately 20 times if both regular folding and adjacent reentry took place. Since the bulky branchpoints are difficult to pack into a crystal lattice, and no differences in lattice structure were observed as a function of branch-point functionality, it is expected that these branchpoints exist at the fold surface of the lamellar crystals. Since the initiator chemistry was different than that of nylon-6 for all samples investigated, it is expected that regular folding may continue only until a branch-point is reached. At this point some disruption of regular folding is expected. The linear system may make up to 10 such regular folds until a chemically different unit is encountered.
FIGURE 4-19:
Smoothed, smeared SAXS profiles obtained from nylon-6:
A - Linear nylon-6, B - Three-arm nylon-6, C - Six-arm nylon-6.
The three-arm polymer may only make about six regular folds before inclusion of a branch point and the six-arm polymer with DP = 270 may only make about 3. Although there is certainly some question as to just how regularly polymer chains are folded in lamellar crystals, it should be noted that each time a fold is made at a branchpoint, considerable disruption of regular folding must occur in order to include the rest of the branches. This disruption of regular folding will, most likely, lead to increased fold energies and decreased order at and near the lamellar fold surface. Besides lowering the melting point of a lamellar crystal, branch points at the fold surface lead to a broader interphase between lamellar crystals and intervening amorphous material. Mandelkern and Popli have shown that small concentrations of branch-points in polyethylene may double the amount of polymer in interfacial regions.\textsuperscript{47} Recently Lee, Lin, and Phillips have shown that increasing the thickness of the interfacial layer between crystalline and amorphous material, while keeping total crystalline percentage constant, leads to substantial attenuation of SAXS peaks.\textsuperscript{48} An increase in interfacial material would be consistent with all of our experimental findings. Irregularities in the fold surface are consistent with depressed melting points for branched polymer crystals as well as broadened and attenuated SAXS peaks.

The results of SAXS experiments raised new questions concerning the nature of structural disorder introduced by the inclusion of branch-points within crystalline structure. TEM experiments were performed in order to clarify the details of the
lamellar structure in linear vs. branched nylon-6. No differences were evident in
spherulitic superstructure at low magnification. (Figure 4-20) Upon higher
magnification and even after staining for extended periods of time with RuO₄, no
lamellar structure was resolvable in this study. Interestingly, earlier experiments
performed by Trent, et. al, using RuO₄ on nylon-11 also failed to reveal lamellar
structure.⁴⁹
FIGURE 4-20:
Spherulitic superstructure of nylon-6 stained with RuO$_4$ as observed by TEM:
A - Linear nylon-6: crystallized at 200°C,
B - Three-arm nylon-6: crystallized at 200°C,
C - Six-arm nylon-6: crystallized at 200°C.
CONCLUSIONS:

The effect of star branching functionality on the morphology, crystallization kinetics, equilibrium melting point, and heat of fusion of nylon-6 was studied by OPM, SALS, SEM, WAXS, SAXS, TEM, and DSC. The crystallization kinetics of all three systems could be described by an Avrami equation with exponent, on average, between 2.8 and 4.5. As first noted by Magill, a transition from heterogeneous nucleation to homogeneous nucleation of spherulites at 197°C is consistent with the observed change in Avrami exponent of linear and star-branched nylon-6. No significant differences in either Avrami exponent or rate constant as a function of temperature were observed as a function of increasing branch point functionality; however crystallization half-times were reduced by one-half in the branched systems for equivalent values of supercooling. Crystallization half-times may be effected by reduced reptation times in star-branched systems. Although melting points appeared to be systematically lowered with increasing branch-point functionality, no significant differences were observed in absolute crystalline percentages. SAXS measurements suggest irregularities at or near the surface of lamellar crystals containing branched macromolecules may be responsible for the observed depression of melting points. If the ratio ($M_w/M_e$) is kept low star branching may be a feasible way in which the melt viscosity and crystallization half-times of nylon-6 can be substantially reduced. Controlled star-branching of polymers may lead to improvements in both processability and bulk crystallization rates.
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CHAPTER 5

Structure-Property Behavior of Poly(etheretherketone).

Poly(dimethylsiloxane) Block Copolymers and Their Ketaline Precursors

INTRODUCTION:

Block or segmented copolymers have long sequences (blocks) of one type of repeat unit joined at one or both ends to blocks of a chemically different repeat unit. Block copolymerization is a way in which two chemically different repeat units with different chemical and physical properties may be joined into the same molecule thus resulting in a molecule which may possess surface and bulk properties quite different from the corresponding homopolymers. Block copolymers are especially attractive in the fact that their molecular design may be tailored to a specific application by controlling such features as the chemical nature of the blocks, the architecture of the copolymer (i.e. diblock, triblock, or multiblock), as well as the block length of the respective blocks resulting in a much broader range in properties than would be possible with a homopolymer.

In the case where the chemical units within the backbone of the block copolymer are incompatible, these systems tend to form submicroscopic (1-100nm), phase-separated domains.\(^1\) In block copolymer systems where crystallization of one or both
of the blocks does not occur or in the case where microphase separation occurs before crystallization and no morphological change occurs upon crystallization of one or both of the phases, microsphere, cylinder, lamella, and bicontinuous microstructures are commonly observed. In this case the morphology depends on the chemical nature of the blocks, the film preparation technique (melt vs. solvent casting as well as the type of solvent used), and the volume fraction of each block type in the particular system.\(^2\)\(^3\) However, when crystallization may occur concurrently with or before phase separation, the resulting morphology is determined by crystallization, phase separation, or the competition between the two processes.

Theoretical predictions of equilibrium morphologies of crystallizable block copolymer systems have been made by Di Marzio, \textit{et al.},\(^4\) Whitmore and Noolandi,\(^5\) and Vilgis and Halperin\(^6\). In each of these cases, the amorphous segments are attached to crystalline segments in lamellar crystals. The equilibrium morphology is determined by the energy associated with the thermodynamics of phase separation combined with the energy associated with crystallization within the semi-crystalline blocks. In such a case the most thermodynamically favorable state is determined by balancing the contributions due to the entropic effects of microphase separation, combined with the free energy of crystal formation, the free energy of the crystal surface, and the elastic energy associated with deformation of the grafted covalently coupled segments. These models, however, are purely thermodynamic and no considerations are given to the complicated competition between the kinetics of
crystallization and phase separation. In the case where the chemical nature of the blocks is highly dissimilar the blocks are strongly segregated and subsequent crystallization within one or both of the phases is unlikely to affect morphology. In the case where the chemical incompatibility of the two blocks is only minimal, the blocks are only weakly segregated, and crystallization in one or both of the blocks may result in significant morphological changes.

A great deal of research has been undertaken to investigate the domain structure and crystalline morphology of crystallizable block copolymers. Gervais, et. al. investigated the morphology of triblock copolymers including poly(ethylene oxide) or poly(e-caprolactone) as the crystallizable block and polystyrene or polybutadiene as the amorphous block. A lamellar morphology of alternating crystalline and amorphous layers was observed. Cohen and co-workers have recently observed a strong path dependence on the final morphology of block copolymers cast from solvents. They observed that in poly(dimethylsiloxane)-nylon-6 diblock copolymers with varying block lengths, the morphology is highly dependent on sample history. In the case where a solvent was highly selective, phase separation occurred before crystallization and a lamellar morphology was observed. In the case where a less selective solvent was used, phase separation and crystallization occurred concurrently and a spherulitic morphology was observed. Once the samples were annealed above the melting point of nylon-6, microphase-separated polydimethylsiloxane domains were observed within these structures.
Recently research has been undertaken to investigate the nature of chain folding in crystallizable block copolymer systems. Douzinas and Cohen\textsuperscript{16} have recently postulated that in a diblock copolymer of ethylene-co-butylene-b-ethylethylene orientation of the crystallized chains is surprisingly perpendicular to lamellar normal, 90° from the orientation predicted from thermodynamic theories of crystallization of block copolymers. This is an example of a strongly segregated system in which microphase-separation occurs prior to crystallization. In this case the unusual chain folding was attributed to the influence of topological constraints on the crystallizable blocks which are constrained to crystallize in microphae-separated domains. Rangarajan and Register\textsuperscript{17} have found that in ethylene-(ethylene-\textit{alt}-propylene) block copolymers, a system which phase separates upon crystallization of the polyethylene blocks, that chain folding occurs parallel to the lamellar normal as predicted by theory.

Aromatic poly(arylene ether ketones) have been of interest as a high performance engineering thermoplastic due to a combination of good mechanical properties and solvent resistance as well as a high use temperature. Siloxane polymers offer properties such as low surface energy, hydrophobicity, low dielectric constant, low $T_g$ as well as good chemical stability at elevated temperatures. Poly(etheretherketone)-poly(dimethylsiloxane), denoted PEEK-PSX in this paper have been successfully synthesized using a relatively stable imide link between segments.\textsuperscript{18} In this study, the effects of crystallization of the PEEK block in PEEK-
PSX multiblock copolymers is investigated. In this system the glass transition (and crystalline melting point) of PSX is low enough so that this segment is a "fluid" during the crystallization of the PEEK phase and during mechanical testing at room temperature. Additionally the difference between electron densities of these polymers facilitates easy monitoring of phase behavior through small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM). Since the electron density distribution functions of the two polymers is also substantially different, changes in the crystallinity of the PEEK phase are easily measured through wide angle x-ray diffraction (WAXD) measurements since the scattering due to the amorphous PSX phase is easily deconvoluted from that of the PEEK phase. While keeping the PEEK block length at 5K the effects of changing the PSX block length from 5K to 3K were observed in terms of structure, mechanical properties and crystallization behavior. Additionally the effects of crystallinity within the PEEK phase on both structural features and dynamic mechanical behavior were investigated.
EXPERIMENTAL:

Materials:

Perfectly alternating copolymers of PEEK-PSX were synthesized by first preparing oligomers of norbornene anhydride terminated poly(dimethylsiloxane) (PSX) - Figure 5-1. These functionalized PSX oligomers were then reacted with aryl amine terminated poly(etheretherketimine) (PEEKt) in a condensation reaction. The resultant polymer was a perfectly alternating copolymer of PSX and PEEKt containing a protected ketone group. Rapid hydrolysis of the ketimine in solution resulted in a perfectly alternating copolymer of PEEK and PSX which precipitated in the semicrystalline form. (Figure 5-2) Further details of the synthetic scheme are published elsewhere.19,20

In this study two PEEKt-PSX copolymers and their two hydrolyzed PEEK-PSX copolymers were studied. (Table 5-1) The precursor PEEKt-PSX copolymers had a PEEKt block number average molecular weight of 4900 (5K) and PSX block number average molecular weights of 3200 (3K) and 4900 (5K). It is expected that the polydispersity of the PEEK blocks is roughly 2 since these blocks were polymerized via a polycondensation reaction however this information was not available. The PEEK-PSX copolymers formed by hydrolysis of the ketimines had a PEEK block molecular weight of 3900 (4K), due to loss of mass during hydrolysis of the ketamine. In this study the ketimine copolymers will be referred to as PEEKt(5K)PSX(3K) and PEEKt(5K)PSX(5K) and the ketone polymers will be

200
FIGURE 5-1: Synthesis of anhydride terminated poly(dimethylsiloxane) oligomers via a ring opening polymerization of D4 ($\text{Si}_4\text{H}_8\text{O}_4$).
FIGURE 5-2: Synthesis and hydrolysis of perfectly alternating poly(etheretherketone)-poly(dimethylsiloxane) block copolymers.
TABLE 5-1: Characteristics of Samples Used in This Study.

<table>
<thead>
<tr>
<th>Sample Designation:</th>
<th>Block Lengths</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PSX</td>
</tr>
<tr>
<td>PEEKt(5K)PSX(3K)</td>
<td>3 200</td>
</tr>
<tr>
<td>PEEKt(5K)PSX(5K)</td>
<td>4 900</td>
</tr>
<tr>
<td>PEEK(4K)PSX(3K)</td>
<td>3 200</td>
</tr>
<tr>
<td>PEEK(4K)PSX(5K)</td>
<td>4 900</td>
</tr>
</tbody>
</table>
referred to as PEEK(4K)PSX(3K) and PEEK(4K)PSX(5K).

Films of the copolymers (PEEKt-PSX) prior to hydrolysis were cast from chloroform. PEEK-PSX polymers were compression moulded between copper sheets at 360°C for 6 minutes utilizing a 3 step moulding procedure. First the sample was placed in the mould between copper sheets for two minutes during which time the sample became viscous. After the initial two minute equilibration period low pressure (<5 PSI) was placed on the fluid sample for 2 minutes to produce a film ca. 0.5mm thick. Then the pressure was released, and the sample was kept in the heated mould for an additional two minutes to allow relaxation of any residual stress which occurred during moulding. After this relaxation period, the sample was rapidly quenched in an icewater bath. Both WAXD and differential scanning calorimetry indicated that such a treatment produced totally amorphous samples for both PEEK-PSX copolymers investigated.

**Structural Characterization:**

All WAXD experiments were performed on a Nicolet diffractometer operating at 40KV and 30mA and equipped with a STOE Bragg-Bernatto type goniometer. Cu-Kα X-rays (1.54Å) were passed through a graphite monochromator prior to final collimation. Data was collected at 0.05° increments between the angles of 10° and 35° for samples of PEEK-PSX copolymers and the amorphous PEEK homopolymer.
For the PSX homopolymer a scan range of 5° to 35° was used. At each step a data acquisition time of 15s was used. Data collection and analysis was performed using the Siemens Polycrystalline Software package.

SAXS measurements were performed on films before and after dynamic mechanical testing using a PAAR Kratky camera system with an M. Braun position-sensitive detector from Innovative Technology, Inc. A Phillips model PW 1729 tabletop generator was used. For all experiments the generator was set to 40KV and 20mA using the Cu-Kα X-ray (1.54Å). Lead stearate was used for angular calibration and Luopolen for absolute intensity calibration.

Transmission electron microscopy, TEM, samples were prepared from films of the PEEKt-PSX copolymers, amorphous films PEEK-PSX copolymers and PEEK-PSX films that had been crystallized in a dynamic mechanical spectrometer, DMS. Samples were ultramicratomed at -140°C using a Reichert-Jung ultracut E43 ultramicrotome equipped with a diamond knife in three normal directions. Samples were cut to a thickness of ca. 500Å. All were performed on a Phillips IL 420T STEM with an acceleration voltage of 100-120KV.

Mechanical Testing:

Stress-strain behavior of the samples was obtained using an Instron Model 1122 tensile tester interfaced to a computer for data collection and stress calculation. Dogbone specimens with cross sectional areas of 1.75mm² were tested with a gauge length of 10mm and a crosshead speed of 2mm/min. under ambient conditions. In
each case three samples were run to insure reproducibility.

Dynamic mechanical testing was performed on samples with cross sectional areas of ca. 4 mm$^2$ and initial gauge length of 10 mm with a Seiko DMS 200 equipped with an auto cooler at frequencies of 1, 10, and 20 Hz using a heating/cooling rate of 1°C/min and a maximum force amplitude of 20 g.

*Thermal Analysis:*

A Seiko DSC 220 C equipped with an auto cooler was used to obtain bulk crystallization information as well as heats of fusion as a function of sample composition and thermal history. Amorphous films were heated to 360°C at a rate of 10°C/min under dry nitrogen and held at 360°C for 6 minutes before being quenched to the isothermal crystallization temperature. *Crystallization from the melt occurred very slowly and was only observable by this method in a very narrow temperature range between 225°C and 235°C for the PEEK(4K)PSX(3K) copolymer and in the temperature range of 229°C to 232°C for the PEEK(4K)PSX(3K) copolymer.* Isothermal crystallization experiments at higher and lower temperatures were not possible at higher and lower temperatures due to limitations of temperature stability and sensitivity of the DSC used in this study. Isothermal crystallization experiments were also performed on amorphous films quenched from the melt in an ice water bath by placing these films in a DSC cell equilibrated at the crystallization temperature. After all isothermal crystallization runs, samples were again heated to 360°C at 10°C/min. in order to determine the heat of melting.
DATA ANALYSIS:

Thermal Analysis:

DSC (Percentage Crystallinity) percentage crystallinity was determined from calorimetric data by integrating the entire region under the melting endotherm to obtain the heat of melting as a function of temperature and prior thermal history; the difference between the heats of fusion and heats of melting, $(T_m - T_c) C_p$, was assumed to be negligible. This value was then normalized by the mass fraction of PEEK within the copolymer and the molar heat of fusion of PEEK homopolymer to obtain the percentage crystallinity within the PEEK phase. A value of 130J/g was assumed as the heat of fusion of perfectly crystalline PEEK.  

WAXD:

Wide angle x-ray diffraction was used to determine whether structural differences between the crystalline phase of the block copolymers and PEEK homopolymer were evident. WAXD experiments also allowed for an independent determination of crystallinity which could later be correlated with heat of melting measurements obtained by DSC.

Yao has recently developed procedures for resolution of overlapping WAXS curves and subsequently determining the apparent crystallinity relative to the entire sample as well as the relative crystallinity within the crystallizable phase. He has used his procedure to determine the crystallinity of poly(ethylene oxide)-polystyrene block and graft copolymers, poly(methyl acrylate)-poly(ethylene oxide) graft
copolymers, as well as poly(methyl methacrylate) graft copolymers and their ionic complexes. In each of these cases the peak deconvolution procedure was complicated due to the fact that the scattering profiles due to the amorphous components of the respective blocks were similar; thus, it was difficult to deconvolute the scattering contributions due to the amorphous phases.

In our case a slight modification of the procedures used by Yao was possible due to the great differences that were evident in the WAXD scattering profiles of amorphous PEEK and PSX homopolymers. Figures 5-3A&B illustrate the differences evident in the scattering profiles of amorphous PEEK homopolymer and 1200 centipoise, methyl-endcapped poly(dimethylsiloxane). PEEK has an amorphous halo with a maximum intensity at 18.75° and FWHM (Full Width Half Max) of 7.4° while PSX has an amorphous halo with maximum intensity at 11.4° and FWHM of 3.5°. The scattering profile of the amorphous PEEK-PSX copolymers are shown in Figure 5-4. By subtracting the scattering profile of PEEK from the raw data of the two copolymers in the 10°-35° degree range, the scattering profile of the PSX phase in this range of angles is obtained normalized as a function of PSX volume fraction. (Figure 5-5) This data may then be subtracted from the raw data along with the background scattering to obtain
FIGURE 5-3: A: WAX scattering pattern obtained from 1200 cPoise, methyl endcapped poly(dimethylsiloxane).
B: WAX scattering pattern obtained from amorphous PEEK.
FIGURE 5-4: Wide angle x-ray scans of amorphous PEEK-PSX copolymers:
A - PEEK(5K)PSX(5K),
B - PEEK(5K)PSX(3K).
FIGURE 5-5: Deconvoluted wide angle x-ray scattering pattern due to the PSX component in PEEK-PSX block copolymers:
A - PEEK(5K)PSX(5K),
B - PEEK(5K)PSX(3K).
the scattering contribution due to the PEEK phase alone.

Once the above method of peak subtraction was used, the crystallinity determinations were performed on the PEEK phase using the classical method of Hermans and Weidinger.\textsuperscript{26} The method of peak deconvolution used in this study has been previously been utilized by the authors to determine the crystallinity of LARC CPI\textsuperscript{27} and nylon-6.\textsuperscript{28} The amorphous scattering profile was fitted to the total scattered intensity and subtracted from the total scattered intensity of the PEEK phase yielding the scattering peaks due to the crystalline phase alone. The ratio of the integrated intensity under these peaks compared to the total scattered intensity gave the crystallinity of the PEEK phase. In this technique, of course, atomic and structural scattering factors and effects such as those due to thermal diffuse scattering are ignored. The experimental method of peak resolution is outlined in Figure 5-6.
FIGURE 5-6: Resolution of WAXD data into amorphous and crystalline components:
A - smoothed amorphous scattering profile;
B - smoothed crystalline peaks.
RESULTS AND DISCUSSION:

Mechanical testing was performed on both the PSX-PEEKt precursor polymers and amorphous PSX-PEEK polymer to investigate the effects of the conversion of the ketimine groups to ketone groups. As illustrated in Figure 5-7 conversion of the ketimine to a ketone resulted in a significant decrease in modulus as well as an increase in elongation to break in both samples. Additionally the conversion of the ketimine groups to ketone groups caused a much more significant decrease in modulus in the case of the samples with a PSX block length of 5K. The results of these mechanical tests are summarized in Table 5-2. It is expected that the differences in mechanical properties between the PEEKt-PSX copolymers and the PEEK-PSX copolymers are due to differences in microstructural features due to the differences in the chemical nature of the two species and the mass loss of ca. 20% of the hard phase during hydrolysis. The microstructure, in each case determines the level of continuity in each phase and, thus the resulting mechanical properties. As will be discussed later, the glass transition of the ketimine precursor and the resulting PEEK phase is hardly affected by the conversion.

Both transmission electron microscopy and SAXS experiments were easily facilitated due to the differences in the densities of PEEK and PSX: 1.400 g/cc for crystalline PEEK, 1.263 g/cc for amorphous PEEK and 0.98 g/cc for poly(dimethyl siloxane). Transmission electron micrographs performed on the
FIGURE 5-7: Stress strain curves obtained from tensile testing of PEEKt-PSX and PEEK-PSX copolymers:
A - PEEKt(5K)PSX(5K)
B - PEEKt(5K)PSX(3K)
C - PEEK(4K)PSX(5K)
D - PEEK(4K)PSX(3K)
FIGURE 5-8: A: TEM of PEEKt(5K)PSX(5K) copolymer.  
B: TEM of PEEKt(5K)PSX(3K) copolymer.
TABLE 5-2: Results of Mechanical Testing on PEEKt-PSX and PEEK-PSX Copolymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus (MPa)</th>
<th>Elongation to Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEKt(5K)PSX(3K)</td>
<td>690 ± 15</td>
<td>30 ± 5</td>
</tr>
<tr>
<td>PEEKt(5K)PSX(5K)</td>
<td>390 ± 30</td>
<td>40 ± 5</td>
</tr>
<tr>
<td>PEEK(4K)PSX(3K)</td>
<td>290 ± 5</td>
<td>55 ± 15</td>
</tr>
<tr>
<td>PEEK(4K)PSX(5K)</td>
<td>36 ± 2</td>
<td>60 ± 15</td>
</tr>
</tbody>
</table>
PEEKt-PSX copolymers revealed a lamellar like morphology in the PEEKt(5K)PSX(5K) copolymer (Figure 5-8A) and a morphology with a more continuous PEEKt phase and microdomains of PSX in the PEEKt(5K)PSX(3K) copolymer (Figure 5-8B). Smear SAXS scans on the PEEKt-PSX copolymers indicated an estimated interdomain spacing of approximately 225Å for the PEEKt(5K)PSX(5K) copolymer and 240Å for the PEEKt(5K)PSX(3K) copolymer. (Figure 5-9)

The notable decrease in modulus for the PEEK(4K)PSX(5K) system is believed to be due to a disruption of continuity in the PEEK phase in this system. Transmission electron micrographs of the amorphous PEEK(4K)PSX(5K) copolymer in three normal directions (Figure 5-10A,B,&C) reveal that the sample possesses an isotropic, bicontinuous morphology notably different from that of its ketimine precursor. Continuity in the PSX phase in this sample is, therefore, consistent with the low modulus observed. TEMs performed on the crystalline sample (Figure 5-11) revealed no change in morphology due to crystallization of the PEEK phase. Thus, in this system the morphology attained while pressing the film becomes locked in prior to crystallization and subsequent crystallization must take place in isolated microdomains as will be discussed later. SAXS patterns performed on the PEEK(4K)PSX(5K) copolymer indicate an approximate interdomain spacing of 250Å for both the crystalline and amorphous samples. (Figure 5-12) This peak is, however somewhat distorted due to its nearness to the beam stop.
FIGURE 5-9: SAXS patterns obtained from PEEKt-PSX copolymers:
A - PEEKt(5K)PSX(5K)
B - PEEKt(5K)PSX(3K)
FIGURE 5-10: TEMs of amorphous PEEK(4K)PSX(5K):
A: Normal to film surface.
B,C: Perpendicular sections parallel to film surface.
FIGURE 5-11: TEM of semicrystalline PEEK(5K)PSX(5K) copolymer.
FIGURE 5-12: SAXS patterns obtained from PEEK(4K)PSX(5K):
A - Amorphous sample
B,C - Semicrystalline sample in perpendicular directions.
This value corresponds closely to the interdomain spacing observed in the TEMs. The only differences evident in the SAXS scans of the crystalline and amorphous PEEK(4K)PSX(5K) was a slight reduction in peak intensity and the development of a shoulder on the peak. This is likely due to the low levels of crystallinity attained in these materials upon crystallization, as will be discussed later.

Transmission electron micrographs normal and perpendicular to the surface of an amorphous film of the PEEK(4K)PSX(3K) copolymer reveal a lamellar morphology intermixed with less defined structures. Similar morphological features have been observed by Hashimoto in systems near the cylindrical-lamellar transition composition\(^3\).\(^{(23)}\) The fact that the lamellar structure in this system is not as well defined than in the 5K-5K system, may be attributed to the fact that the volume fraction of the two phases for this copolymer may be nearer to the transition composition for formation of cylindrical microdomains of PSX. TEMs of crystalline PEEK(4K)PSX(3K) reveal that the lamellar structure is retained in this system during crystallization however the interlamellar spacing appears to change due to crystallization.\(^{(24)}\) The change evident in the smeared SAXS patterns of the PEEK(4K)PSX(3K) copolymer is consistent with development of more highly ordered lamellar structure; however this is smeared data and gives shifted s values as well as broadened peaks.\(^{(25)}\)
FIGURE 5-13: TEMs of amorphous PEEK(4K)PSX(3K):
A: Normal to the film surface.
B: Parallel to the film surface.
FIGURE 5-14: TEMs of semicrystalline PEEK(4K)PSX(3K) copolymer.
A: Normal to the film surface.
B: Perpendicular to the film surface.
FIGURE 5-15: SAXS patterns obtained from PEEK(4K)PSX(3K):
A - Amorphous sample
B,C - Semicrystalline sample in perpendicular directions.
Dynamic Mechanical Testing:

Dynamic mechanical tests were performed on both the ketamine precursors and the PEEKt-PSX copolymers. These tests were performed on the PEEKt-PSX copolymers from the temperature range of -150°C to approximately 150°C at which point the samples softened. The modulus data obtained from these tests at 1Hz is illustrated in Figure 5-16A and the corresponding tan δ data is presented in Figure 5-16B. At 20°C the modulus for the PEEKt(5K)PSX(3K) copolymer was ca. 800MPa and the modulus for the PEEKt(5K)PSX(3K) copolymer was ca. 400MPa. These values are slightly higher than those obtained from simple stress-strain curves due to the higher strain rate in this case. Two distinct glass transitions are evident at ca. -130°C and 145°C which is consistent with the phase separation indicated in these systems by TEM and SAXS. No crystallization was noted in the PSX phase in either of the ketimine copolymers.

Similar tests were performed on the amorphous PEEK-PSX copolymers, however due to the ability of these polymers to crystallize, these tests were carried to temperatures of approximately 330°C at which point the PEEK phase melted. Figure 5-17A illustrates the modulus data obtained at a frequency of 1Hz and Figure 5-17B illustrates the corresponding tan δ behavior. The dynamic mechanical behavior in these cases, is complex due to both the crystallization and melting of the PEEK phase. Additionally, in the PEEK(4K)PSX(5K) copolymer crystallization and melting of the PSX phase also occurred, a phenomenon
FIGURE 5-16: Dynamic mechanical testing of PEEKt-PSX copolymers:

A:  A - Storage modulus, $E'$, of PEEKt(5K)PSX(3K),
     B - Storage modulus, $E'$, of PEEKt(5K)PSX(5K).

B:  A - Tan $\delta$ behavior for PEEKt(5K)PSX(3K),
     B - Tan $\delta$ behavior for PEEKt(5K)PSX(5K).
interestingly not observed in the corresponding PEEKt-PSX copolymer. Besides the two glass transition temperatures due to the PSX and PEEK phases at -130°C and 145°C respectively, crystallization of the PEEK phase occurs in the temperature range between 145°C and 200°C, and in the 4K-5K system crystallization and melting of the PSX phase occurs in the temperature range of -130°C to -50°C. It is interesting to note that the glass transition between the PEEKt phase and the PEEK phase is only slightly affected by conversion, both samples begin to soften at approximately 145°C. Scans were also made in the temperature range of 0°C to 230°C for samples which were crystallized from the glass at 230°C for 30 minutes. The modulus values obtained from these tests at 1 Hz are summarized in Table 5-3. Figures 5-18A and 5-18B compare the dynamic mechanical behavior and corresponding tan δ behavior of an amorphous PEEK(4K)PSX(3K) sample and a sample which had been crystallized. Figures 5-19A and 5-19B compare the dynamic mechanical behavior and corresponding tan δ behavior of an amorphous PEEK(4K)PSX(5K) copolymer and a sample which had been crystallized. The PEEK(4K)PSX(3K) sample showed an increase in the modulus at 20°C from 300MPa for the amorphous sample to 500MPa for the semicrystalline sample. The PEEK(4K)PSX(3K) sample showed an increase in modulus at 20° from 4MPa for the amorphous sample to 20MPa for the semicrystalline sample, a fivefold increase! In both cases the presence of crystallinity shifted the maximum value in the tan δ curves approximately 15°C.
FIGURE 5-17: Dynamic mechanical testing of PEEK-PSX copolymers:

A:  A - Storage modulus, $E'$, of PEEK(4K)PSX(3K),
     B - Storage modulus, $E'$, of PEEK(4K)PSX(5K).

B:  A - Tan $\delta$ behavior for PEEK(4K)PSX(3K),
     B - Tan $\delta$ behavior for PEEK(4K)PSX(5K).
TABLE 5-3: Results of Dynamic Mechanical Testing at 20°C (1 Hz):
Effects of Crystallinity Within the PEEK Phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus Amorphous</th>
<th>Modulus Semi-Crystalline</th>
<th>Percentage Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK(4K)PSX(3K)</td>
<td>300 MPa</td>
<td>500 MPa</td>
<td>167%</td>
</tr>
<tr>
<td>PEEK(4K)PSX(5K)</td>
<td>4 MPa</td>
<td>20 MPa</td>
<td>500%</td>
</tr>
</tbody>
</table>
FIGURE 5-18: Dynamic mechanical testing of PEEK(4K)PSX(5K):
A:  A - Storage modulus, $E'$, of amorphous sample,
    B - Storage modulus, $E'$, of sample crystallized at 230.5°C.
B:  A - Tan $\delta$ behavior for amorphous sample,
    B - Tan $\delta$ behavior for sample crystallized at 230.5°C.
FIGURE 5-19: Dynamic mechanical testing of PEEK(4K)PSX(3K):

**A:**
- A - Storage modulus, $E'$, of amorphous sample,
- B - Storage modulus, $E'$, of sample crystallized at 230.5°C.

**B:**
- A - Tan $\delta$ behavior for amorphous sample,
- B - Tan $\delta$ behavior for sample crystallized at 230.5°C.
higher for the semicrystalline samples than for the amorphous samples. The reduction of the amplitude of the \( \tan \delta \), \( T_g \) peak also is indicative of a smaller fraction of the material being in the amorphous state, and therefore undergoing a glass transition.

The large difference between the glass transition temperatures of the components in these copolymers results in a large temperature range where the modulus of the copolymer remains roughly constant. Additionally the ability of the PEEK-PSX copolymers to crystallize extends their effective use temperature and allows, depending on thermal history, further control of mechanical properties.

**X-Ray Diffraction:**

In order to determine the amount of crystallinity actually attained in the PEEK phase in these copolymers WAXD experiments were performed on the PEEK(4K)PSX(3K) and the PEEK(4K)PSX(5K) copolymer. As discussed earlier, the scattering due to the PSX phase was subtracted from the total scattering profile of the block copolymers and the resulting scattering profile was compared to PEEK homopolymer with a number average molecular weight of approximately 30K. Addressed earlier, Figure 5-4 illustrates the wide angle x-ray scattering behavior for the two amorphous PEEK-PSX copolymers. As the compositions change from the 4K-5K polymer to the 4K-3K polymer the scattered intensity corresponding to the PEEK phase increases and the scattered intensity due to the PSX phase decreases according to the copolymer compositions. Additionally, peak
integrations performed on the deconvoluted peaks agree well with the respective weight fractions. WAXD scans were performed on the PEEK(4K)PSX(3K) and PEEK(4K)PSX(5K) copolymers which were crystallized from the glass at 230°C for 30 minutes as well as the PEEK homopolymer which was crystallized at 230°C from the melt. (Figure 5-20) Absolute crystallinity of the PEEK phase was determined from the x-ray data to be ca. 40% for both copolymers while the homopolymer attained approximately the same level of crystallinity when crystallized under similar circumstances.

The FWHM breadth of various peaks was measured to determine if peak broadening due to changes in long range ordering or crystallite sizes occurred. Hindeleh and Johnson have measured peak breadths in polyamide, polyester, and cellulose fibers and related these measurements to weight-average crystallite sizes normal to the \((h\ k\ l)\) diffracting planes.\(^ {32,33}\) Their analysis as well as ours, however, neglected the effects of thermal and structural disorder. Similar analysis performed on the \((1\ 1\ 0)\), \((1\ 1\ 1)\), and \((2\ 0\ 0)\) peaks in the PEEK-PSX copolymers illustrated that substantial peak broadening occurred in these polymers relative to that of PEEK homopolymer. (Tables 5-4A,B,C). In this case it is likely that a substantial contribution of peak broadening is due to disruption of structural order due to the attachment of non-crystallizable PSX blocks onto the surface of PEEK crystallites. The fact that the \((1\ 1\ 0)\) and \((2\ 0\ 0)\) peaks
<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\Theta$ (°)</th>
<th>Breadth FWHM (rad.)</th>
<th>Broadening</th>
</tr>
</thead>
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<td>0.01553</td>
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<td>0.01606</td>
<td>1.74</td>
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<th>Broadening</th>
</tr>
</thead>
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<td>0.0138</td>
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<td>1.24</td>
</tr>
<tr>
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<td>0.0162</td>
<td>1.17</td>
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<th>$2\Theta$ (°)</th>
<th>Breadth FWHM (rad.)</th>
<th>Broadening</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
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<td>0.0129</td>
<td>1</td>
</tr>
<tr>
<td>PEEK(4K)PSX(3K)</td>
<td>22.90°</td>
<td>0.0197</td>
<td>1.53</td>
</tr>
<tr>
<td>PEEK(4K)PSX(5K)</td>
<td>22.90°</td>
<td>0.0176</td>
<td>1.36</td>
</tr>
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</table>
FIGURE 5-20: WAXD scans of, A - semi-crystalline PEEK homopolymer, B - Deconvoluted scattering due to the PEEK phase of PEEK(4K)PSX(3K) C - Deconvoluted scattering due to the PEEK phase of PEEK(4K)PSX(5K).
are more substantially broadened than the (1 1 1) peak indicate that fewer structural irregularities occur along the c-axis. These structural irregularities are almost certainly associated with the short nature of the PEEK blocks since both the (1 1 0) and the (2 0 0) planes are parallel to the direction in which the polymer molecules traverse the unit cell in PEEK. It is unlikely that any substantial amount of chain folding occurs at all in or copolymers since the domain spacing from SAXS measurements is on the order of 200 to 250Å which is nearly identical to the number average length of the crystallizable PEEK blocks. Also since the distribution of PEEK block lengths is rather broad, there are likely to be many short PEEK blocks which may substantially disrupt the crystalline order.

**Crystallization Behavior:**

Isothermal crystallization experiments performed on PEEK-PSX block copolymer powders indicated that these block copolymers crystallized at much slower rates than PEEK homopolymer molecular weight on the order of the PEEK block length. This result is likely due to two contributing factors. First, the crystallizable PEEK blocks in this system are connected to PSX blocks in segregated domains which greatly inhibit the mobility of the crystallizable PEEK blocks. Additionally the PEEK phase is segregated into microdomains in which the likelihood of nucleation events is decreased. Since the PSX segments are highly fluid in this system, the likelihood of nucleation at domain interfaces is very low. Analysis of crystallization in this block copolymer system must address both chain mobility and crystal nucleation.
Typical Avrami analysis could not be used to accurately describe the crystallization behavior of these phase separated copolymers. The assumption of impingement of growth centers associated with the derivation of the Avrami relationship does not account for the complication introduced due to the possibility of impingement of growing crystals with domain interfaces which may occur in a phase separated system. Due to the very slow rates of crystallization and the small volume of crystallizable material in these samples crystallization could only be accurately monitored over a very small temperature range. Crystallization of the PEEK(4K)PSX(3K) copolymer could only be experimentally monitored in the narrow temperature range from 225°C to 235°C. At temperatures higher and lower than this, the rates of crystallization became so slow that the heat flow measured by DSC due to crystallization could not be resolved from the background noise. Crystallization of the PEEK(5K)PSX(5K) copolymer was extremely difficult to monitor due to the even lower volume fraction of crystallizable polymer as well as the extremely low crystallization rates observed in this system. Crystallization in this copolymer could only be experimentally monitored in a temperature range from 229°C to 232°C. For both copolymers a maximum in the bulk crystallization rate was observed at a temperature of 230.5°C, very close to the temperature at which low molecular
FIGURE 5-21: Normalized crystalline content vs. time for PEEK(4K)PSX(3K):
A - Crystallized at 228°C,
B - Crystallized at 230.5°C,
C - Crystallized at 232.5°C,
D - Crystallized at 235°C.
FIGURE 5-22: Effect of PSX block length on crystallization of PEEK-PSX block copolymers at 230.5°C:
A - PEEK(4K)PSX(3K); $t_{1/2} = 260s$,
B - PEEK(4K)PSX(5K); $t_{1/2} = 1200s$. 
weight PEEK homopolymer crystallizes most rapidly. Figure 5-21 illustrates the effects of changing crystallization temperature on the rate of crystallization of PEEK(4K)PSX(5K). Figure 5-22 illustrates the effect of changing block length on the rate of crystallization for both PEEK-PSX block copolymers at 230.5°C. At this temperature PEEK(4K)PSX(3K) has a crystallization half-time of 260s while PEEK(4K)PSX(5K) has a crystallization half-time of 1200s; a 10% change in the volume fraction of PSX decreases the rate of crystallization by a factor of 5! This large change in crystallization rate is likely due to the great decrease in continuity observed in the PEEK phase which is evident as the volume fraction of PEEK is decreased from 51% to 38%. As will be discussed later, the change in the continuity of the PEEK phase has dramatic effects on the rates of nucleation in the microdomains. Crystallization half-times as a function of temperature and copolymer composition are plotted in Figure 5-23; again the dramatic effect of changing block length is evident. After crystallization experiments were performed, samples were heated at a rate of 10°C to determine the heat of melting, Q_m, as a function of temperature.(Figure 5-24) This data was then normalized by PEEK volume fraction and divided by the enthalpy of melting for perfectly crystalline PEEK (130 J/g)\textsuperscript{17} to estimate the crystalline fraction of the PEEK phase.(Figure 5-25) The PEEK(4K)PSX(3K) copolymer developed up to 20% crystallinity in the PEEK phase while the PEEK(4K)PSX(3K) copolymer only developed 6% crystallinity in the PEEK phase even when crystallized over
FIGURE 5-23: Crystallization half-times vs. copolymer composition and crystallization temperature:
A - PEEK(4K)PSX(3K),
B - PEEK(4K)PSX(5K).
FIGURE 5-24: Effect of copolymer composition and crystallization temperature on the heat of melting:
A - PEEK(4K)PSX(3K),
B - PEEK(4K)PSX(5K).
FIGURE 5-25: Effect of copolymer composition and crystallization temperature on crystallinity of the PEEK phase:
A - PEEK(4K)PSX(3K),
B - PEEK(4K)PSX(5K).
far longer time periods.

The effects of previous thermal history on the crystallization behavior of PEEK-PSX copolymer were also studied. Since varying levels of structural continuity may occur as a function of block copolymer composition, the process of nucleation within phase separated domains is likely to very strongly affect the rate of bulk crystallization. As less and less continuity within the PEEK occurs, more and more nucleation events must occur within separate domains to achieve the same level of crystallinity. If nucleation occurs heterogeneously, it is quite likely that many of the small domains contain no such heterogeneities and crystallization may not occur within these domains within the time scale of our experiments. As early as 1952, Price had noted that upon successive melting and recrystallization at relatively low undercoolings crystalline nuclei reformed repeatedly at fixed locations in the melt presumably at heterogeneities. At higher supercoolings, additional nuclei were formed. Subsequently a variety of droplet experiments were performed on various polymer systems to investigate the effects of dividing the melt into such small droplets that most would not contain heterogeneities. These experiments showed that not only was the rate of nucleation greatly inhibited in these microdroplets but at low undercoolings only a small fraction of the droplets crystallized. Since the crystallizable phase in block copolymer systems may be separated into microdomains similar to those in the droplet experiments, thermal history may be especially important in determining the crystallization rates and
absolute crystallinity in crystallizable block copolymers.

Crystallization exotherms as a function of previous thermal history for PEEK(4K)PSX(3K) films crystallized isothermally at 230.5°C are plotted in Figure 5-26. Curve A is an exotherm for PEEK(4K)PSX(3K) crystallized from the glass; Curve B is an exotherm for PEEK(4K)PSX(3K) crystallized from the melt. It is clearly evident that previous thermal history has a very dramatic effect on the rate of crystallization. When normalized crystalline content, Xc, is plotted against time the effect of thermal history on crystallization half-times can be determined. (Figure 5-27) The crystallization half time for PEEK(4K)PSX(3K) crystallized from the glass is 56s compared to 1560s for that crystallized from the melt. Thus quenching a sample before crystallization increases the rate of crystallization by nearly a factor of 30! Quenching the samples prior to crystallization brings these samples into a temperature range where homogeneous nucleation may occur more readily which would enhance the rate of crystallization.

If phase separation retarded nucleation of crystallites within the PEEK microdomains it is likely that during crystallization from the melt some of these domains may not crystallize at all during our experimental time frame. Therefore the heats of melting of samples crystallized from the glass would be likely to be greater than for samples crystallized from the melt. Additionally this difference
FIGURE 5-26: Effect of previous thermal history on the crystallization exotherm for PEEK(4K)PSX(3K):
A - Crystallized from the glass,
B - Crystallized from the melt.
FIGURE 5-27: Normalized crystalline content vs. time for PEEK(4K)PSX(3K) crystallized at 230.5°C; effect of previous thermal history:
A - Heated from the glass; $t_{1/2} = 56$ s,
B - Quenched from the melt; $t_{1/2} = 1560$ s.
should become more and more pronounced as the PEEK phase becomes less and less continuous. For the PEEK(4K)PSX(3K) copolymer the heat of melting for a sample crystallized from the melt at 230.5°C for 3 hours was 12.5 J/g while the heat of melting for a sample crystallized from the glass under identical conditions was 25 J/g. (Figure 5-28) For the PEEK(4K)PSX(5K) copolymer the heat of melting for a sample crystallized from the melt at 230°C for 3 hours was 3 J/g while the heat of melting for a sample crystallized from the glass under identical conditions was 16.5 J/g. (Figure 5-29) The heats of melting were then used to calculate the percentage crystallinity as a function of previous thermal history and compared to the values obtained by WAXD. (Table 5-5) The crystallinity determination from heats of melting agreed fairly well with the WAXD results. The slight disagreement in these measurements may be due to the high surface energies of these crystals which would decrease the heat of melting or the fact that the method of crystallinity determination used in this study did not account for atomic or structural scattering factors. In the PEEK(4K)PSX(3K) copolymer the sample crystallized from the glass attained 2 times the crystallinity of the sample crystallized from the melt. In the PEEK(4K)PSX(5K) copolymer crystallizing the sample from the glass resulted in a fivefold increase in the amount of crystallinity relative to the same sample crystallized from the melt. Like in the droplet experiments discussed earlier, it is likely that the samples
FIGURE 5-28: Effect of previous thermal history on the melting behavior of PEEK(4K)/PSX(3K) crystallized at 230.5°C:
A - Crystallized from the glass; $\Delta Q_m = 25\text{J/g}, T_m = 315\text{°C}$.
B - Crystallized from the melt; $\Delta Q_m = 12.5\text{J/g}, T_m = 306\text{°C}$.
FIGURE 5-29: Effect of previous thermal history on the melting behavior of PEEK(4K)PSX(5K) crystallized at 230.5°C:
A - Crystallized from the glass; $\Delta Q_m = 16.5\text{J/g}$, $T_m = 312^\circ\text{C}$.
B - Crystallized from the melt; $\Delta Q_m = 3.0\text{J/g}$, $T_m = 303^\circ\text{C}$.
**TABLE 5-5:** Crystalline Fraction of the PEEK Phase in PEEK-PSX Block Copolymers as Determined by WAXD and Thermal Analysis: Effects of Prior Thermal History.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$Q_m$ (DSC)</th>
<th>% Xtal (DSC)</th>
<th>% Xtal (WAXD)</th>
</tr>
</thead>
<tbody>
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<td>Crystallized From The Melt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEEK(4K)PSX(3K)</td>
<td>12.5 ± 1 J/g</td>
<td>20 ± 2 %</td>
<td>-</td>
</tr>
<tr>
<td>PEEK(4K)PSX(5K)</td>
<td>3.0 ± 1 J/g</td>
<td>6 ± 2 %</td>
<td>-</td>
</tr>
<tr>
<td>Crystallized From The Glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEEK(4K)PSX(3K)</td>
<td>25.0 ± 1 J/g</td>
<td>39 ± 2 %</td>
<td>37 ± 4 %</td>
</tr>
<tr>
<td>PEEK(4K)PSX(5K)</td>
<td>16.5 ± 1 J/g</td>
<td>32 ± 2 %</td>
<td>37 ± 4 %</td>
</tr>
</tbody>
</table>
crystallized from the melt were never brought to sufficient undercoolings for homogeneous nucleation to occur in all of the PEEK microdomains. The fact that the crystallinity determined by DSC was substantially lower in the case of the PEEK(4K)PSX(5K) copolymer may be related to the fact that small crystallites surrounded by attached PSX chains may be associated with a high surface energy, thereby leading to a decreased heat of formation. Additionally, the fact that the phase separated morphology formed prior to crystallization in this system is locked into place is likely to make crystallization a less energetically favorable phenomenon than in the case of the homopolymer.

The results obtained in this study are contrary to trends observed in PEEK homopolymer. As may be expected, Cebe and Hong39 observed that PEEK homopolymer crystallized from the glass obtained levels of crystallinity on the order of one-half that obtained from the melt. They attributed this difference to the formation of crystals with less perfection when samples were quenched prior to crystallization. The results of crystallization of PEEK-PSX copolymers illustrate that decreasing continuity within the crystallizable phase may drastically impair a polymer's ability to crystallize from the melt due to a decreasing probability for nucleation of crystallites. Due to the very low glass transition temperature of the PSX phase the likelihood of nucleation at domain interfaces is very low. Furthermore the flexible nature of the PSX blocks allows a substantial amount of the PEEK phase to crystallize at lower crystallization temperatures. In this case the

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crystalline fraction of the PEEK phase in PEEK-PSX block copolymers crystallized from the glass was greater than that observed in PEEK homopolymers crystallized under similar conditions.

CONCLUSIONS:

Structural features and mechanical properties of two PEEKt-PSX and PEEK-PSX block copolymers as well as crystallization behavior of PEEK-PSX block copolymers were studied as a function of copolymer composition. The phase behavior obtained as a result of film casting, thermal history, and copolymer composition dramatically affects both the mechanical properties and crystallization behavior of these block copolymers. A dramatic decrease in modulus was observed as the continuity of the PSX phase was increased. The rate of crystallization in PEEK-PSX block copolymers is extremely sensitive to both copolymer composition and thermal history. As PSX block length was changed from 3K to 5K (a 12.5% increase in PSX mass fraction) the rate of crystallization decreased by a factor of 5. Thermal history had a far more dramatic effect, when crystallized from the glass PEEK-PSX copolymers crystallized 30 times faster than from the melt at the same crystallization temperature. The fact that lower crystallinities were observed in samples crystallized from the melt indicated that due to the fact that the crystallizable phase in PEEK-PSX copolymers were segregated into micro-domains, the probability of heterogeneous nucleation within these domains was greatly reduced, and at high crystallization temperatures some domains were unable to crystallize due to the inability of primary nuclei to
form at these higher temperatures. This hypothesis was further verified by the fact that as the PEEK phase became less continuous, the crystallinity of the PEEK phase when crystallized from the melt became greatly reduced.
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PART II:

SOME ASPECTS OF PROCESSING POLYMERS WITH PRESSURIZED GAS
CHAPTER 6
Processing Thermoplastic Polymers With Pressurized Gas
A Literature Review

I. Introduction

Many applications have been developed for processing polymers with compressed and supercritical fluids.\textsuperscript{1,2,3} Fluid diluents have been used to concentrate polymer solutions by facilitating lower critical solution temperature phase separation\textsuperscript{2,4} and to fractionate polymers.\textsuperscript{5,6,7} Supercritical fluid diluents have been used to extract residual monomers, oligomers, and solvent.\textsuperscript{8,9,10} Fluid diluents may also be used to plasticize polymers,\textsuperscript{11,12,13,14,15,16,17} to reduce the viscosity of polymer melts and solutions\textsuperscript{18}, to condition polymeric membranes,\textsuperscript{19} and to produce microcellular foams,\textsuperscript{20,21} microspheres,\textsuperscript{22,23} and fibers.\textsuperscript{24,25} Replacing alkane solvents with compressed fluid diluents is becoming especially attractive because no environmentally hazardous substances are used. Recently CO\textsubscript{2} has been used to replace alkane solvents for coatings applications.\textsuperscript{26,27}

Compressed fluid diluents offer several advantages over conventional solvents despite the need for elevated pressures. The fact that environmentally friendly gases may be used eliminates concerns about the environmental effects of residual solvents.
Since the gas molecules are smaller than typical organic solvent molecules, absorption kinetics are generally enhanced, and both pressure and temperature may be adjusted to control absorption kinetics. In coming years, mainly due to increasing environmental concerns, the replacement of typical organic solvents with compressed fluid diluents in many industrial processes is bound to increase.

II. Glass Transition Behavior and Plasticization

Depending on the nature and pressure of the gas, compressed fluid diluents may have profound effects on polymer morphology and physical properties. While a gas with low solubility at high pressure may act to produce an isostatic pressure and thus reduce the glass transition temperature of a polymer,\textsuperscript{28} soluble polymers have been shown to decrease the glass transition temperature in many polymer systems.\textsuperscript{11-14,29,30} Depressions of over 100°C have been observed. In some cases, depending on the temperature, both effects may be observed.\textsuperscript{12}

Two general approaches have been used to describe the glass transition behavior of a polymer in the presence of a compressed fluid diluent. These general approaches involve lattice fluid models\textsuperscript{13,15,31} and the Gibbs-Di Marzio criterion of the glass transition temperature.\textsuperscript{32,33,34} More recently Johnston, \textit{et. al.}, developed a model to predict the glass transition behavior of polymers in the presence of a compressed fluid diluent which combines elements of lattice fluid theory and the Gibbs-Di Marzio criterion.\textsuperscript{35,36} Their model treats solubility, density, pressure, and temperature as independent variables and predicts a previously unknown
phenomenon where a polymer undergoes a liquid to glass transition with an increase in temperature, a process known as retrograde vitrification.\textsuperscript{35,36} This model allows the generation of a pressure-glass transition temperature phase diagram with a minimum of experimental data. As illustrated in Figure 2-1, four fundamental types of glass transition temperature behaviors as a function of pressure have been predicted, but despite the complicated nature of the various $T_g$ vs. pressure curves, a simple, near linear sorption vs. $T_g$ behavior is observed in each case - see Figure 6-2. This simple linear behavior is consistent with the phenomenological models used to describe $T_g$ behavior.\textsuperscript{37} The near linear dependence of $T_g$ on absorbed gas has been experimentally observed on many occasions.\textsuperscript{13,15,29}

Accompanying the changes observed in the glass transition behavior of polymers to an absorbed gas are changes in mechanical properties. CO\textsubscript{2} has been observed to be a strong plasticizer for both polysulfone\textsuperscript{38} and bisphenol-A polycarbonate\textsuperscript{29}. Plasticization of the polymer matrix by absorbed gas has been invoked to explain the complicated absorption behavior observed in polymers in the presence of a pressurized gas\textsuperscript{16}, but in some cases where there is strong evidence that a gas acts as a plasticizer for a certain polymer system, a decrease in gas absorption kinetics with increasing gas pressure is observed.\textsuperscript{38} This evidence suggests that the molecular motions responsible for the bulk physical and mechanical properties of a polymer are not necessarily those responsible for the diffusion of small penetrant molecules.
Figure 6-1:

Types of $T_g$ behavior as a function of pressure predicted by the model. (From 35)
Figure 6-2:

Predicted $T_g$ behavior as a function of weight fraction of absorbed gas in the polymer for the four cases shown in Figure 6-1. (From 35)
III. Gas Absorption Behavior

Anomalous, non-Fickian gas absorption behavior has been observed in many polymer systems.\textsuperscript{39,40,41,42,43,44,45} The gas absorption, in these cases underwent a two stage gas absorption process - see Figure 6-3. In the initial stages of absorption, rapid, Fickian absorption was observed. This stage was followed by a slower rate of absorption in which rearrangement of polymer molecules was presumed to occur. Kovacs noted that the absorption of gas molecules as a result of an increased external gas pressure corresponded to a swelling of the polymer matrix due to sorption of small molecules. Berens and Hoffenberg extended these earlier studies to study the free volume dependence of gas absorption kinetics due to prior thermal and gas absorption history.\textsuperscript{44,46} Their analysis showed that not only was the gas absorption behavior of a polymer dependent on the magnitude of the deviation of free volume from the equilibrium state but on changes in the effective free volume due to penetrant molecules.\textsuperscript{\textcopyright{(Figure 6-4)} While the initial stages of gas absorption are most strongly governed by a polymer's excess free volume, the final "relaxation limited" absorption behavior is more a function of polymer-permeant interactions.

At temperatures well below the glass transition temperature of a polymer, the rate of diffusion of permeant molecules is far greater than that of polymer backbone molecules; therefore penetrant molecules may escape from a polymer no longer held at high pressure, leaving some additional effects on the excess free volume of the
Figure 6-3:

Absorbed mass fraction vs. time for vinyl chloride in PVC powder at 50°C. (From 44)
Figure 6-4:

Effects of sample history on absorption isotherms for vinyl chloride in PVC powder at 30°C. (From 46)
polymer. Due to this fact, the subsequent gas absorption behavior may be a function of the type and amount of gas which was present in the polymer prior to an experiment. Koros, et. al, have investigated the effects of gas exposure histories on the selectivity and permeability of polymeric membranes.\textsuperscript{19,47,48} Their results suggest that pretreatment with a pressurized gas allows for non-equilibrium packing configurations with higher energies than those in untreated polymers. Work by Sanders, et. al, suggests that specific interactions are involved in the nonequilibrium packing mechanisms involved in a polymer permeant system.\textsuperscript{49}

**IV: Microcellular Foams**

Recently considerable industrial interest in processing polymers has arisen from the development of a process to produce microcellular foams using pressurized gas. Foams with a very small cell size were first envisioned by Professor Nam P. Suh of the Massachusetts Institute of Technology. The rationale was that if bubbles smaller than the critical flaws which already existed in the material were produced density could be reduced without significantly reducing modulus and toughness. The basic process for development of microcellular foams involves two steps\textsuperscript{50}: First the polymer is saturated by a non-reacting gas at an elevated pressure - see Figure 6-5. Following saturation, the pressure is released, and the (now supersaturated) polymer is heated to its foaming temperature. At this point gas bubbles nucleate and grow in the polymer. The foaming temperature is some temperature above the $T_g$ of the polymer fluid diluent system. As discussed earlier this temperature may be below the
Figure 6-5:

An illustration of the supersaturation process used to produce microcellular foams.
$T_g$ of the polymer alone due to the significant depression of $T_g$ due to the presence of the fluid diluent. The process for production of microcellular foams was patented in 1984 by a consortium of the Massachusetts Institute of Technology and several U.S. companies including Eastman Kodak Co.\textsuperscript{51} In 1988 Kodak developed and patented a continuous process for producing microcellular foams using supercritical CO$_2$ - see Figure 6-6.\textsuperscript{51}

The forementioned procedure known as the "microcellular process"\textsuperscript{52} or "supersaturation process"\textsuperscript{29} has been used to produce foams of many polymeric materials. Including polystyrene\textsuperscript{50}, polycarbonate\textsuperscript{21}, poly vinyl chloride\textsuperscript{52}, polyethylene terephthalate\textsuperscript{59,60}, and poly methyl-methacrylate\textsuperscript{53}. Microcellular polystyrene has been investigated in a number of studies.\textsuperscript{50,54,55,56,57} Nitrogen has been the most effective gas for production of microcellular polystyrene although other gases have been tried. It was found in this system that density could be controlled continuously in this system due to an exponential increase in nucleation density of bubbles observed with increasing saturation pressure.\textsuperscript{56} Bubble growth was modeled by modifying the Newtonian model for growth of a single bubble in a polymer matrix to account for non-newtonian effects caused by the power law fluid dynamics of the polymer.\textsuperscript{57}

Microcellular polycarbonate was first produced by Kumar, Weller, and Hoffer in 1990 using CO$_2$.\textsuperscript{21} Due to the high solubility of CO$_2$ in polycarbonate, a great reduction in relative density is possible in this system. A mass fraction of up to 10%
Figure 6-6:

A schematic of the continuous process for producing microcellular foams using supercritical CO₂.
CO₂ at a pressure of 6500KPa was observed²⁹ with resultant foam densities of 0.1 g/cc.²¹ Nucleation density in microcellular polycarbonate was found to be independent of foaming temperature in the temperature range of 60°C to 160°C suggesting that the Arrhenius type temperature dependence predicted for typical nucleation theories was not obeyed in this case.²¹,⁵⁸ The constant nucleation density in the polycarbonate CO₂ system suggested that at temperatures near the glass transition temperature, heterogeneous nucleation is the dominant mechanism of nucleation.

Microcellular polyethylene teraphthalate (PET) has been produced using CO₂.⁵⁹,⁶⁰ It was found that upon sufficiently long exposure to CO₂ PET became plasticized enough to begin crystallization. Most likely due to orientation during the blowing process, PET foams have been observed to have a significantly higher crystalline fraction than PET thermally processed in otherwise identical conditions.

Although the data available from the mechanical testing of microcellular polymers produced by the supersaturation process is limited, models have been developed to predict the initial modulus in compression and tension as well as initial collapse stress.⁶¹,⁶²,⁶³ As illustrated in Figure 6-7, the relative modulus at a given relative density is comparable to that of conventional structural foams. Microcellular foams, however offer the advantage of being able to continually control the density over a wide range of densities. Energy to failure for microcellular polystyrene has
Figure 6-7:

Modulus vs. density for microcellular polycarbonate and other structural foams as a function of foam density. (From 60)
been shown to increase by five to seven fold in uniaxial tension suggesting that the impact strength and ductility of these materials is enhanced.\textsuperscript{52} Fatigue testing of microcellular polycarbonate shows that the fatigue life of microcellular polycarbonate may exceed that of solid polycarbonate by up to a factor of 17 - see Figure 6-8.\textsuperscript{64}
Figure 6-8:
Fatigue life of Microcellular Polycarbonate Foams with High Relative Densities.
(From 51)
V. Conclusion:

In the last decade many new applications for processing polymeric materials with pressurized gases have been developed. Because these processes offer the advantages of using no environmentally hazardous, organic solvents and greater control over processing variables, a great deal of research has been undertaken to investigate the physical and mechanical changes which may occur when a polymer is exposed to a pressurized gas. Although this is a new field, it is already clear that using compressed fluid diluents instead of conventional solvents or plasticizers may result in physical or mechanical properties which were previously unavailable to the polymer industry.
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CHAPTER 7

Effects of Physical Aging and Carbon Dioxide Absorption in Bisphenol-A Polycarbonate

INTRODUCTION:

The well known process of physical aging is a phenomenon associated with the non-equilibrium nature of the glassy state.\(^1\) As an amorphous polymer is cooled from above its glass transition temperature both the segmental mobility and the molar volume of the polymer decrease. When the glass transition temperature is reached there is a dramatic decrease in segmental relaxation. At this point the segmental relaxation rate may no longer accommodate volume relaxation to the equilibrium value within a reasonable time frame. As a result excess free volume is frozen into the system. Even at temperatures below the glass transition temperature, however, some localized segmental relaxation may occur over a much longer time frame. As a result the equilibrium glassy state is approached and a decrease in excess free volume occurs through the process of physical aging. Bartos, \textit{et. al.}, have observed the rate of volume relaxation in polycarbonate, and illustrated that the rate of volume relaxation increases rapidly with storage temperature at temperatures below \(T_g\).\(^2\)
Physical aging has been shown to dramatically influence the mechanical properties of glassy polymers due to the increase in relaxation times associated with decreased free volume.\textsuperscript{3,4} Lee has shown that the logarithm of the permeability coefficient decreases linearly with the inverse of the specific free volume of glassy polymers,\textsuperscript{5} and Kapur and Rogers have shown that physical aging decreases the diffusion coefficient of glassy polymers.\textsuperscript{6} Therefore, it is well documented that physical aging affects the gas absorption properties of glassy polymers.

Recently interest has increased in processing polymers with compressed gases especially in the production of thermoplastic microcellular foams.\textsuperscript{7,8,9} Bisphenol polycarbonate, PC, has been used in these studies due to its good impact strength and high glass transition temperature. The effects of physical aging on the glass transition and mechanical properties of PC have been studied earlier by several others.\textsuperscript{3,5,10} A great deal of research has been undertaken to determine the effects of processing polymers with pressurized gas especially for polymer applications as gas permeable membranes. Depending on the solubility and pressure of the gas, the effects of the pressurized gas on the physical properties of the polymer may be varied. If a polymer is placed in the presence of a non-soluble pressurized gas or in a soluble pressurized gas at pressures well above the saturation pressure, the effect is to impose an isostatic pressure on the polymer reducing segmental mobility and increasing the glass transition.\textsuperscript{11} However, if a polymer is placed in the presence of a soluble pressurized gas near or below saturation pressure, the gas diffuses into
the polymer and acts as a low molecular weight diluent. Condo, *et al.*, have shown that polymers with compressed fluid diluents may exhibit significantly depressed glass transition temperatures.\(^{12,13}\) Berens noted that depending on the previous thermal and/or vapor treatment of a polymer, sorption kinetics may be widely varied.\(^{14}\) The work of Berens and others led to the development of kinetic sorption models which included contributions due to conventional Fickian diffusion, a relaxation-controlled contribution, plus the role of the absorbed gas as a plasticizer.\(^{14,15,16,17}\) Studies on the sorption and dilatation in polycarbonate indicated that previous conditioning with various pressures of carbon dioxide led to dramatic effects in sorption and dilatation behavior.\(^{18,19}\) Sanders studied the effects of penetrant induced plasticization in the CO\(_2\) - polyethersulfone (PES) system.\(^{20}\) Sanders illustrated that CO\(_2\) plasticized polyethersulfone by observing a dramatic depression of the glass transition temperature which accompanied decreased tensile modulus and increased elongation to break with increasing amounts of absorbed CO\(_2\).\(^{20}\) Sanders also noted that exposing PES to high pressure CO\(_2\) altered the nonequilibrium state of the polymer, altering the effects of physical aging. This study addresses the effects of processing physically aged and unaged polycarbonate with pressurized CO\(_2\) on physical and mechanical properties.

**EXPERIMENTAL:**

Samples utilized in this study were General Electric LEXAN® bisphenol-A polycarbonate slabstock (2.5mm) and thin films (15 mil.). To ensure samples were
not plasticized by atmospheric gases (CO₂ or H₂O) all samples were stored in a vacuum desiccator for one week at room temperature before experiments unless otherwise specified. Samples were then heated to 160°C (ca. 10°C above Tₑ) for 5 minutes and then rapidly cooled to room temperature before physical aging or testing of unaged samples. Physical aging was carried out in a vacuum oven for one week at either 100°C and 120°C. All DSC runs were performed on a Seiko DSC 220C or DSC 210 at a heating rate of 10°C/min. unless otherwise specified. The instruments were calibrated with indium and sapphire standards. Samples were thick enough so that negligible gas desorption occurred during experimentation.

The stress-strain behavior of the PC films were made using a Model 1122 Instron tensile tester interfaced to a computer for data collection and stress calculation. Dogbone specimens were cut from films of thickness ranging from 15 to 18 mils. The stressed, cross-sectional area of the samples was 10mm by 2.5mm. A guage length of 1cm was used with a crosshead speed of 2mm/min. Three to five samples were tested in each case to note reproducibility.

Gas absorption behavior was measured by placing from 5-10 aged and freshly quenched samples in a cylindrical high pressure cell of interior diameter of 50mm and height 150mm. Samples were pressurized with Coleman grade 4 CO₂ (99.99% Purity) at a pressure of 6500KPa (900PSI). Before pressurization the pressure cell was evacuated with a vacuum pump.
RESULTS AND DISCUSSION:

The extent of physical aging was indicated by the area of the well known exothermic peak occurring at the glass transition. Figure 7-1 illustrates the effects of physical aging for 1 week at 100°C and 120°C. As expected, the effect of physical aging on the glass transition was much more notable in the samples aged at 120°C than those aged at 100°C. In order to determine the effects of physical aging on gas absorption and permeability, absorbed gas mass fraction was measured as a function of time and previous thermal history -see Figure 7-2. For a given thermal history, the values of absorbed mass fraction obtained from each of the 5-10 samples measured varied by no more than 0.1%. Within the sensitivity of our measurements, differences in absorbed mass fraction as a function of thermal history were only noticeable at short times; after gas absorption occurred for 72 hours, no differences were evident in absorbed gas mass fraction. At this point no further significant additional gas absorption occurred; thereby indicating that all three samples had nearly identical equilibrium values. As seen in Figure 7-3, when similar measurements were made to follow the desorption of CO₂ no difference was noted in the desorption behavior of the three samples indicating that the effect of previous thermal history on the permeability of the samples was eliminated. Carbon dioxide desorption occurred very rapidly in the initial stages, where significant gas desorption occurred in a matter of minutes. No significant amount of CO₂ was measurable after a week of desorption. The rapid initial rate of CO₂ desorption and the fact that
FIGURE 7-1:
DSC scans of polycarbonate as a function of thermal history
A - Quenched from 160°C
B - Quenched from 160°C and annealed for 7 days at 100°C
C - Quenched from 160°C and annealed for 7 days at 120°C
FIGURE 7-2:
Absorption of CO₂ in polycarbonate: effects of physical aging
A - Quenched from 160°C
B - Quenched from 160°C and annealed for 7 days at 100°C
C - Quenched from 160°C and annealed for 7 days at 120°C
FIGURE 7-3:
Desorption of CO$_2$ from polycarbonate: effects of physical aging
A - Quenched from 160°C
B - Quenched from 160°C and annealed for 7 days at 100°C
C - Quenched from 160°C and annealed for 7 days at 120°C
samples with different thermal histories showed identical behavior suggested that absorbed CO₂ plasticized the samples as well as erased the previous effects of physical aging. This hypothesis was verified by observing the glass transition in a freshly quenched sample and comparing it to a sample that had been annealed at 120°C for 7 days and then saturated with CO₂ gas which was then allowed to desorb for 190 hours. As seen in Figure 7-4 no differences were evident in the glass transition temperature of the two samples and the characteristic exothermic thermic peak was eliminated. Figures 7-5 and 7-6 illustrate the systematic effects of absorbed mass fraction of CO₂ on the glass transition temperature of polycarbonate as observed by DSC. These DSC experiments were performed at a heating rate of 20°C to minimize gas desorption during heating. (The increased heating rate shifted the observed Tᵣ from 150°C at a rate of 10°C/min. to 152.5°C at a rate of 20°C/min.) As shown in Figure 7-6 the depression of the glass transition temperature of polycarbonate suggests a strong linear dependence on absorbed mass fraction of CO₂ (R² = 0.97). The onset of foaming at temperatures slightly above Tᵣ prevented the runs from being continued beyond this point, note runs E, F, and G were therefore stopped at temperatures below those of runs A-D. Significant Tᵣ depressions due to high levels of dissolved gas in other glassy polymers have recently been observed experimentally in other studies.²¹,²²,²³ The results obtained for CO₂ in polycarbonate agree very well with theoretical predictions of the glass transition temperature of polymer/fluid diluent systems based on the phenomenological models
FIGURE 7-4:
Effects of gas absorption and desorption on the glass transition of polycarbonate
A - Freshly quenched from 160°C
B - Quenched from 160°C, annealed at 120°C for 7 days, saturated with CO₂ gas at 900PSI (absorbed mass fraction = 0.10), and then desorbed for 190 hrs.
FIGURE 7-5:
Systematic decrease in glass transition of polycarbonate as a result of absorbed CO$_2$
A - Absorbed mass fraction = 0.015; $T_g = 143^\circ$C
B - Absorbed mass fraction = 0.024; $T_g = 134^\circ$C
C - Absorbed mass fraction = 0.033; $T_g = 123^\circ$C
D - Absorbed mass fraction = 0.040; $T_g = 106^\circ$C
E - Absorbed mass fraction = 0.055; $T_g = 94^\circ$C
F - Absorbed mass fraction = 0.073; $T_g = 78^\circ$C
G - Absorbed mass fraction = 0.090; $T_g = 73^\circ$C

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FIGURE 7-6:
Effect of absorbed CO$_2$ on the glass transition of polycarbonate:
T$_g$ vs. absorbed mass fraction
used to describe $T_g$ behavior.\textsuperscript{11,24} Thus, the $T_g$ of a polymer/gas system is governed by the absorbed mass fraction which, in turn, is governed by the temperature, pressure, and solubility of the gas in question. Extrapolation of our data leads to a ca. 100°C depression of the glass transition of polycarbonate with an absorbed mass fraction of only 10% CO$_2$.

The results of the gas absorption, gas desorption, and thermal analysis experiments suggested that CO$_2$ gas would plasticize polycarbonate samples and gassupersaturation followed by desorption could eliminate the effects of physical aging. Figure 7-7 illustrates the dramatic change in stress-strain behavior caused by physical aging for one week at 120°C. For our testing conditions, samples quenched from above the glass transition temperature show an average yield stress of 58MPa while those aged for 1 week at 120°C show an average yield stress of 73MPa, an increase of 26%! The aged samples also showed decreased elongation to break at this crosshead speed. Figure 7-8 illustrates the effect of absorbed CO$_2$ on the stress-strain behavior of aged and unaged polycarbonate. The stress-strain behavior showed no dependence on previous thermal history for samples containing a mass fraction of CO$_2$ greater than or equal to 7%. Although there was a 10% difference in absorbed mass fraction between samples placed in the pressure cell for 24 hours at 900PSI and those which were saturated at 900PSI (one week), there were no significant difference in yield stress -see Figure 7-8. In both cases an average yield stress of about 40 KPa was observed, a decrease of 31% when compared to the value
FIGURE 7-7:
Stress strain behavior for polycarbonate: effects of physical aging
A - Quenched from 160°C and annealed for one week at 120°C:
  Yield Stress = 73MPa
B - Freshly quenched from 160°C: Yield Stress = 58MPa
FIGURE 7-8:
Stress strain behavior for polycarbonate: effects of gas absorption
A - Quenched from 160° and held at a CO₂ pressure of 900PSI for 7 days: absorbed mass fraction = 0.10
B - Annealed for 7 days at 120°C and held at a CO₂ pressure of 900PSI for 7 days: absorbed mass fraction = 0.10
C - Quenched from 160° and held at a CO₂ pressure of 900PSI for 24 h: absorbed mass fraction = 0.078
D - Annealed for 7 days at 120°C and held at a CO₂ pressure of 900PSI for 24 h: absorbed mass fraction = 0.070
for a freshly quenched sample and a decrease of 45% when compared to the value for a sample physically aged at 120°C for one week. Samples which were saturated with CO₂ showed an increased elongation to break compared to samples which were allowed to absorb CO₂ for 24 hours, although scatter of roughly 10% was observed in these values. This behavior may be attributed to the significant plasticization effect of CO₂ on polycarbonate. Similarly, as illustrated in Figure 7-9, after desorption for 1 week there were no appreciable differences between samples saturated with CO₂ gas at 900PSI and those pressurized for 24 hours, although slight differences in elongation to break were observed. Once desorption was essentially complete (after one week), the yield stress of the samples increased to 45MPa, a value 22% less than a freshly quenched sample! In all cases, once significant gas absorption occurred, no distinction could be made between aged and unaged samples based on mechanical behavior. Figures 7-7, 7-8, and 7-9 dramatically illustrate the effects of gas supersaturation on aged and unaged polycarbonate samples. As illustrated in Figures 7-7 and 7-8, once an appreciable amount of CO₂ enters the system, the system becomes plasticized. As saturation is reached, the effects of previous thermal history are eliminated. This is due to the increase in segmental relaxation rates caused by the CO₂ plasticizer. Since the system is still well below its glass transition temperature, gas diffusion rates are still much more rapid than segmental relaxation rates. Thus, as the CO₂ gas desorbs from the supersaturated polymer diluent system, excess free volume, and a small fraction of the original gas
FIGURE 7-9:
Stress strain behavior for polycarbonate: effects of gas absorption and desorption
A - Quenched from 160°, held at a CO₂ pressure of 900PSI for 7 days (absorbed mass fraction = 0.10), and desorbed for one week
B - Annealed for 7 days at 120°C, held at a CO₂ pressure of 900PSI for 7 days (absorbed mass fraction = 0.10), and desorbed for 1 week
C - Quenched from 160°C, held at a CO₂ pressure of 900PSI for 24 hours. (absorbed mass fraction = 0.078), and desorbed for one week
D - Annealed for 7 days at 120°C, held at a CO₂ pressure of 900PSI for 24 hours. (absorbed mass fraction = 0.070), and desorbed for one week
molecules, are left in the sites once occupied by gas molecules. As a result some "excess" free volume may be "pumped" into a glassy polymer by gas absorption and desorption. The presence of increased excess free volume and residual CO$_2$ molecules is indicated by the dramatic decrease in yield stress observed in samples which were gassed and degassed.

CONCLUSIONS:

The effects of physical aging and gas supersaturation were studied for the bisphenol A-polycarbonate CO$_2$ system. Samples which were aged at 120°C for one week and quenched showed dramatic evidence of physical aging in thermal as well as in mechanical behavior. Gas absorption studies indicated that although initial diffusion was somewhat retarded in physically aged samples, both aged and unaged polycarbonate samples showed identical equilibrium absorbed gas values at a pressure of 6500KPa as well as essentially identical gas desorption behavior. Absorbed CO$_2$ was shown to dramatically reduce the glass transition temperature of polycarbonate with a linear dependence on absorbed mass fraction. Additionally, samples which had been aged and absorbed a mass fraction of 0.07 to 0.10 of CO$_2$ showed thermal and mechanical behavior identical to that of a quenched glass with identical adsorbed mass fraction. Once absorbed gas was nearly totally desorbed, samples behaved as if they were freshly quenched from above $T_g$. The effects of physical aging and gas absorption are important when processing polymers with
pressurized gases such as in the production of microcellular foams. This study suggests that although mechanical and thermal properties of aged and unaged polycarbonate may be markedly different, after processing with pressurized CO₂ properties are independent of previous physical aging and only a function of absorbed mass fraction of CO₂. In the case where pressurized CO₂ is used to produce microcellular polycarbonate, it is important to recognize the effects of physical aging, the effects of the absorbed gas as a plasticizer, as well as the effects that the processing history may have on the excess free volume of the system. Finally, this study suggests that gas absorption followed by desorption is a feasible method of reversing physical aging in glassy polymers.
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CHAPTER 8

Generation and Structure-Property Behavior of Novel Liquid Crystalline Foams

Produced via a Gas Supersaturation Technique

INTRODUCTION:

The motivation to produce polymeric liquid crystalline foams arises from the fact that due to the ease of molecular orientation in these materials under melt flow, it is difficult to produce liquid crystalline materials with isotropic or nearly isotropic physical properties. If a polymeric liquid crystalline foam could be produced, the foaming process could produce a more isotropic low density material, since foaming tends to promote biaxial extension in the cell walls. Furthermore, a liquid crystalline foam could possess the high stiffness characteristic of conventional liquid crystalline polymers on a localized scale combined with more isotropic physical properties on a larger scale. While high molecular orientation is likely to occur in liquid crystalline foams within the cell walls during blowing, if bubbles nucleate and grow isotropically within the material the resultant structure should possess globally isotropic orientation. (Figure 8-1) Unlike many conventional foams, these materials could be well suited for high temperature applications and possibly possess improved barrier properties if the foam is a closed cell foam. An additional advantage this class of
FIGURE 8-1: A simplified illustration of globally isotropic orientation in liquid crystalline foams.
materials offers is that no environmentally hazardous gases are used in the CO₂ supersaturation technique of foam production.

The gas supersaturation process has been recently used to produce microcellular foams of several polymers including polystyrene and polycarbonate.¹² Two variables which are essential in utilization of the gas supersaturation technique are adequate processability as well as good gas solubility and permeability in the polymer-gas system. In this study, linear and star branched liquid crystalline polyoxybenzoate-polyoxyphenoxybenzoate copolymers (POB-co-POPB) at 65/35 molar ratio were produced via melt acidolysis using AB type monomers and tetrafunctional branching agents. By controlling the molecular weight and topology of these polymers, both processability and gas absorption behavior of these materials were enhanced. The motivation behind using a star-branched topology in this liquid crystalline system was that a star branched topology might enhance melt processability, and the branch-points within the star-branched LCPs might disrupt some of the liquid crystalline order resulting in improved gas permeability and solubility. (Figure 8-2) As will be shown, well defined, liquid crystalline foams of star-branched POB-co-POPB with mean cell size from 140 to 800μ were produced by the gas supersaturation technique.
Linear liquid crystal polymer:
- Highly ordered system-

Branched liquid crystal polymer:
- Disrupted order-

**FIGURE 8.2:** An illustration of disruption of order due to inclusion of branch-points.
EXPERIMENTAL:

Materials

While further details of the synthesis of the POB-co-POPB polymers utilized will be published later, the synthetic scheme utilized to produce branched POB-co-POPB is summarized in Figure 8-3. In order to control the branching topology within these polymers, an A-B monomer combined with either A type endgroups for a linear topology or branchpoints with A type functionality for a star-branched topology were used. The molecular weight and topology were controlled by adding the branching or end-capping agents in appropriate stoichiometric ratio. The predicted molecular weight and topology of the four copolymers used in this study based on stoichiometric ratio are: linear (10K), 4-arm (10K), linear (20K), and 4-arm (20K), see Table 8-1. The 4-arm (10K) LCP had a mole fraction of 1.56% branching agent and the 4-arm (20K) LCP had a mole fraction of 0.77% branching agent. Throughout this paper, the samples will be referred to according to the topology and molecular weight predicted by stoichiometric offset via the well known Carothers equation.4

Rheological Characterization

These polymers were also characterized according to their melt viscosities. Samples for rheological experiments were compression molded into 25mm x 1mm discs. All measurements were performed on an RMS 800 shear rheometer. Time sweeps were performed for approximately 5 minutes at a shear rate of 10 rad/s at
Synthesis of Branched POB-POPB Copolymers

\[
\begin{align*}
\text{H}_2\text{C}-\text{C}-\text{O} & \quad \text{C}-\text{OH} \\
4\text{-acetoxystyrene acid} & \\
PABA(65) \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C}-\text{C}-\text{O} & \quad \text{O}\text{-C} & \quad \text{O}_{\text{Ac}} \\
4(4\text{-acetoxystyrene})\text{benzoic acid} & \\
POPB(33) \\
\end{align*}
\]

* 2,2',4,4'-Tetraacetoxystyrene (branching agent)

\[
\begin{align*}
\text{Chlorobenzene} \\
290^\circ\text{C}, 2.5 \text{ hrs, Ar flow} \\
340-350^\circ\text{C}, 1.5 \text{ hrs, in vacuum} \\
\end{align*}
\]

\[
\text{Branched POB-co-POPB}
\]

\[
\begin{align*}
\text{4-acetoxystyrene (end cap for linear LCPs)} & \\
\text{AcO-} & \quad \text{C} & \quad \text{AcO} \\
\end{align*}
\]

FIGURE 8-3: An outline of the synthetic scheme used to produce branched POB-co-POPB.
TABLE 8-1: Characteristics of Samples

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Mol. % of Branching Agent</th>
<th>Molecular Wt.</th>
<th>Topology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear (10K)</td>
<td>0%</td>
<td>10 000</td>
<td>Linear</td>
</tr>
<tr>
<td>Linear (20K)</td>
<td>0%</td>
<td>20 000</td>
<td>Linear</td>
</tr>
<tr>
<td>4-Arm (10K)</td>
<td>0.77%</td>
<td>10 000</td>
<td>Four-Arm</td>
</tr>
<tr>
<td>4-Arm (20K)</td>
<td>1.56%</td>
<td>20 000</td>
<td>Four-Arm</td>
</tr>
</tbody>
</table>
350°C to ensure that the rheological behavior of the materials did not change substantially during the course of the experiments due to chemical reactions (Figure 8-4). During this time period, only a slight increase in melt viscosity was noted, however this change was not significant. Strain sweeps were performed from 0.5% to 5% strain at 350°C no effect of strain on viscosity on any of the samples was noted. Frequency sweeps were performed from 0.1 to 100 radians per second also at 350°C (Figure 8-5). Temperature sweeps were performed from 370°C to 300°C at a rate of 3°C per minute and at a frequency of 1 radian per second (Figure 8-6). Although the data from the temperature sweeps was not in the Newtonian region of the frequency response, data from the temperature sweeps was put into the form of Arrhenius plots to determine information about the relative molecular weight of the polymers as well as flow activation energy (Figure 8-7).

**Foam Generation:**

As illustrated in Figure 8-8, the gas supersaturation technique of producing liquid crystalline foams involves three steps: First, compression molded plaques of POB-co-POPB polymers with dimensions of 2mm thickness and 25mm diameter were placed in a high pressure cell filled with Coleman grade 4 CO₂ (99.99% Purity) at a pressure of 6500KPa (950PSI) at 23°C. Samples were periodically removed and weighed on a Mettler balance to monitor mass uptake of CO₂. After one week, at which point gas saturation was approached in all samples, these samples were removed from their high pressure environment and placed in an oven equilibrated at a foaming
FIGURE 8-4: Viscosity-time sweeps at 10rad/sec. and 350°C:
A: Linear (20K) POB-co-POPB
B: 4-Arm (10K) POB-co-POPB
FIGURE 8-5: Viscosity-frequency sweeps at 350°C:
A: Linear (20K) POB-co-POPB
B: Linear (10K) POB-co-POPB
C: 4-Arm (20K) POB-co-POPB
D: 4-Arm (10K) POB-co-POPB
FIGURE 8-6: Viscosity-temperature sweeps at 1 rad./sec. and 3°C/min.:
A: Linear (20K) POB-co-POPB
B: Linear (10K) POB-co-POPB
C: 4-Arm (20K) POB-co-POPB
D: 4-Arm (10K) POB-co-POPB
**FIGURE 8-7:** Arrhenius plots obtained from temperature dependence of viscosity:

- **A:** Linear (20K) POB-co-POPB
- **B:** Linear (10K) POB-co-POPB
- **C:** 4-Arm (20K) POB-co-POPB
- **D:** 4-Arm (10K) POB-co-POPB
FIGURE 8-8: A schematic of the supersaturation process used to produce liquid crystalline foams.
temperature above the crystalline melting point of the LCPs. At this point bubbles nucleated and grew within the LCP melts. After being held at the foaming temperature for 60s, the LCPs were removed from the oven and quickly solidified as they cooled to room temperature.

**Structural Characterization**

All WAXD experiments were performed on a Nicolet diffractometer operating at 40KV and 30mA and equipped with a STOE Bragg-Bernatto type goniometer. Cu-Kα X-rays (1.54 Å) were passed through a graphite monochromator prior to collimation. Data was collected at 0.05° increments between scattering angles of 10° and 30°. Data collection and analysis was performed using the Siemens Polycrystalline Software Package.

Samples for polarized optical microscopy (POM) experiments were microtomed from the foams using a razor blade. A Zeiss polarizing optical microscope equipped with a 35mm camera was used for all POM experiments.

Samples were prepared for SEM by either sectioning with a razor blade (low mag.) or fracturing them after freezing them in liquid nitrogen for 60s (high mag.). Prior to microscopy, samples were sputter coated with gold to a depth of ca. 210Å in a Bio Rad E5400 high-resolution SEM sputter coater. All SEM experiments were performed on a Cambridge Instruments Stereoscan 200 scanning electron microscope set at an operating voltage of 15KV.

**Mechanical Testing**

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Indentation testing was performed on a Model 4505 Instron mechanical tester interfaced to a Macintosh computer. The test geometry consisted of a steel plate upon which samples would rest and a 0.25" stainless steel spherical ball indenter which was driven into the samples at a rate of 1mm/sec (Figure 8-9). The data collected in this geometry is in the form of load on the indenter head, $P$, vs. displacement of the indenter head, $h$. Sample thickness did not vary greatly from a mean value of approximately 3mm so that the strain rate in each case varied little from sample to sample. To insure homogeneity within each sample and reproducability of experimental results, each sample was indented in three locations. All tests were performed at 23°C.

DATA ANALYSIS:

Rheological Behavior

The behavior of both linear and star-branched polymers has been explained by the entanglement coupling model for polymer melts. At temperatures well above the glass transition temperature the zero shear viscosity of a polymer may be represented by:

$$\eta_0 = M^e[\zeta(T)] = M^e[\zeta_o(T)]^{[1/(1-n(f))]}$$

(8-1)

where the monomeric friction factor, $\zeta(T)$, can be expressed in the Arrhenius form as:

$$\zeta(T) = Ce^{Ea/[1-n(f)RT]}$$

(8-2)

where $n(f)$ is the coupling parameter. Ngai and Plazek have shown that the
FIGURE 8-9: A schematic of the instron indentation test fixture
primitive flow activation energy, $E_a$, is more a function of bond rotational energies than of topology. Therefore, the coupling parameter, $n(f)$, of linear or star branched systems may be determined from the temperature dependence of viscosity. A plot of $\ln(n)$ versus $1/T$ has slope $E_a^*/R$, $E_a^* = E_a/(1-n(f))$. Since $E_a$ is essentially a function of bond rotational energy and independent of topology, $n(f)$, a measure of the effective interaction between polymer chains, may be determined.

_Mechanical Behavior_

Gibson and Ashby have identified deformation mechanisms within a variety of foams and applied their knowledge in conjunction with simple models of cell structure to arrive at equations relating mechanical properties to a foam's material composition and structural features.\(^7\) Gibson and Ashby based their model of closed cell foam behavior on two parameters: the density of the foam, $p^*$, relative to that of the solid polymer, $p_s$, and the proportion of material in the cell edges (struts) $\Phi$.\(^8\)(Figure 8-10) The indentation tests performed in this study give a measure of the initial modulus of a foam and a foam's behavior in compressive collapse.

_Foam Modulus:_ The contributions to foam modulus, $E^*$, for a closed cell foam come from bending of cell edges, stretching and bending of cell walls, and gas compression. These factors are considered in the following equation:

$$
E^* = E_s\{(\Phi^2p_r^2 + (1-\Phi)p_r) + (P_o/E_s)[(1-2\mu^*)/(1-p_r)]\} \\
$$

(8-3)

where $p_r = p^*/p_s$.  

$$
\text{where } p_r = p^*/p_s. \\
$$

(8-4)

$E_s$ is the modulus of the bulk polymer, $P_o$ is the initial gas pressure in the foam,
FIGURE 8-10: Interpretation of Φ; cell walls vs. cell edges:
A: Cell wall
B: Cell edge
approximately 1 bar, and $\mu^*$ is the Poisson's ratio of the foam, ca. 0.33.$^8$

_Compressive Collapse:_ The stress at which elastic collapse takes place, $\sigma_{el}^*$, is dictated by the polymer modulus$^7$:

$$\sigma_{el}^* = (0.05)E_0(p^*/p_0)^2. \quad (8-5)$$

The stress at which plastic collapse occurs, $\sigma_{pl}^*$, is governed by the polymer yield stress$^7$:

$$\sigma_{pl}^* = \sigma_{yield}(0.3)(p^*/p_0)^{3/2}. \quad (8-6)$$

Equations 8-5 and 8-6 define the onset of compressive collapse. Elastic collapse occurs when elastic deformation leads to cell wall collapse while plastic collapse occurs when plastic deformation leads to cell wall collapse. Often cell wall collapse involves both plastic and elastic deformation. Post collapse behavior is more complicated, but the rise in stress above the collapse value, $\Delta \sigma^*$, may be given as a function of initial gas pressure, $P_0$ and total strain, $\varepsilon$:

$$\Delta \sigma^* = P_0\varepsilon/(1-p^*/p_0).$$

$$d = D : h \geq D/2 \quad (8-9)$$

where $D$ is the diameter of the ball indenter. The average stress is calculated from:

$$\sigma = P/A_c = 4P/\pi d^2 \quad (8-10)$$

where $A_c$ is the contact area of the indenter with the sample. Note that $\sigma$ is an average value due to the parabolic like-load distribution produced by the ball indenter for elastic deformation.(Figure 8-11) The load distribution, however, no longer remains parabolic after cell wall collapse begins. The peak value of stress occurs at the center of the indenter; it has a value $\sigma_{peak} = 1.5\sigma$.$^9$ The strain, in this
FIGURE 8-11: The load distribution produced by a spherical indenter.
case, is represented as the ratio of penetration depth, $h$, to sample thickness due to the fact that the sample thickness is on the order of the size of the indenter radius. The Young's modulus of the material may be estimated by the following equation which describes the elastic contact behavior developed by Hertz for a spherical indenter:\textsuperscript{10}

$$E = (3\pi/4)\sigma/e.$$  (8-11)
RESULTS AND DISCUSSION:

Rheological testing was performed on these samples in order to extract information about how adding the branching agent affected the interchain interactions in the polymer melt as well as to extract relative information about the molecular weight of these polymers since GPC experiments could not be performed due to their insolubility - recall Figures 8-5&6. The decreased frequency dependence of star-branched POB-co-POPB on viscosity relative to that of linear POB-co-POPB is not surprising since recent studies have shown that the relaxation spectra of star-branched polymers are broader than those for linear polymers.\textsuperscript{11} The broadened relaxation spectra and exponential dependence of viscosity on arm length for star-branched polymers are attributed to modes of diffusion based primarily on chain retraction.\textsuperscript{11,12,13} The differences in temperature dependence between linear and star-branched polymers is likely due to competition between chain retraction and constraint release. Watanabe, \textit{et. al.} have shown that in low molecular weight star-branched polymers the characteristic relaxation time associated with constraint release can be comparable to that for the terminal chain retraction mode, i.e. constraint release may have a significant contribution to the viscoelastic response of low molecular weight star-branched polymers.\textsuperscript{14} This picture is complicated by the fact that our system may possess liquid crystalline ordering as well. These phenomena may also be responsible for the slightly nonlinear response at high temperatures in
the Arrhenius plots. Noting the nonlinear response at higher temperatures, Arrhenius slopes and intercepts were obtained from the data in the 310°C to 350°C range for the linear polymers and from the 310°C to the 335°C range for the star-branched polymers - recall Figure 8-7. Although all the samples did not show zero-shear viscosity behavior at the strain rate used, 1 rad/sec, regression analysis combined with equations 1 and 2 can provide at least semi-quantitative information about molecular weight and flow activation energy. Regression analysis in these regions produced $R^2$ values of at least 0.99 indicating that at least in this region the entanglement coupling model describes the molecular dynamics in this system well. The greater than exponential dependence of viscosity on temperature observed in the star-branched polymers at higher temperatures is likely due to a mechanism of diffusion with a higher activation energy such as constraint release\textsuperscript{14} or to the loss of liquid crystalline ordering. A significant increase in the slope of the Arrhenius plot was noted in this region. Since a linear fit to the Arrhenius plots reflects diffusion based modes of reptation, activation energies and intercepts extracted from the high temperature region are inaccurate. The data extracted from the Arrhenius plots are summarized in Table 8-2. Relative molecular weights for the polymers were extracted from the Arrhenius intercept. Since there is little difference in the Arrhenius slope as a function of topology and molecular weight, this indicates that the flow activation energies of POB-co-POPB vary little as a function of topology in
### TABLE 8-2: Parameters Determined from Arrhenius Plots

<table>
<thead>
<tr>
<th>SAMPLE DESIGNATION</th>
<th>ARRHENIUS INTERCEPT</th>
<th>$E^*$ (KCal/mol.)</th>
<th>RELATIVE MOLECULAR WEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear 10K</td>
<td>-8.7 ± 0.1</td>
<td>17.4 ± 0.8</td>
<td>1</td>
</tr>
<tr>
<td>Linear 20K</td>
<td>-7.93 ± 0.05</td>
<td>20.0 ± 0.3</td>
<td>2.15</td>
</tr>
<tr>
<td>4-Arm 10K</td>
<td>-10.2 ± 0.1</td>
<td>20.1 ± 0.8</td>
<td>0.23</td>
</tr>
<tr>
<td>4-Arm 20K</td>
<td>-8.0 ± 0.1</td>
<td>18.7 ± 0.8</td>
<td>1.95</td>
</tr>
</tbody>
</table>
this molecular weight range. In each case the flow activation energy measured in this manner was much greater than that measured for flexible chain polymer in the same manner. The flow activation energies for the POB-co-POPB polymers used in this system (ca. 20 Kcal/mol.) were approximately 3 times that measured for linear polyethylene with $<M_w> = 10^5$ (6.40 Kcal/mol.)\textsuperscript{15} The increased dependence of Arrhenius intercept on molecular weight may well be partially due to the exponential dependence of viscosity on the number of entanglements per arm for star-branched polymers.\textsuperscript{13,14} Nonetheless, the results of the viscosity measurements suggest that the relative molecular weights predicted by stoichiometric offset are consistent with the rheological data.

The extent to which the liquid crystalline order was disrupted within POB-co-POPB is evident through the attenuation of the wide angle x-ray diffraction (WAXD) peak at $\sim20^\circ$ (Figure 8-12). The intensity of this peak systematically decreases with increasing branch-point concentration indicating that the branch-points cause a disruption of the liquid crystalline order. Although the order is disrupted, however, the WAXD patterns still indicate that liquid crystalline order is present, even in the samples with 1.56% branch-point content.

The presence of liquid crystalline ordering in these systems is further supported by the granular texture observed in POM experiments - see Figures 8-13A&B. The granular texture characteristic of liquid crystalline polymers was observed in samples
FIGURE 8-12: WAXD scans of POB-co-POPB: effects of branching
A: Linear (20K) POB-co-POPB; 0% branching agent.
B: 4-Arm (20K) POB-co-POPB; 0.77% branching agent.
C: 4-Arm (20K) POB-co-POPB; 1.56% branching agent.
FIGURE 8-13: Polarized optical photomicrographs of branched LCPs:
A: 4-Arm (20K) POB-co-POPB.
B: 4-Arm (10K) POB-co-POPB.
with both 0.77% and 1.56% branching agent content.

Differential Scanning Calorimetry (DSC) scans performed at 10°C/min. indicated a decrease in the magnitude of the melting transition between 280°C and 300°C with increasing branch-point concentration (Figure 8-14). The decrease in this melting endotherm also suggests disrupted order within the LCPs containing branch-points.

The WAXD results suggested that gas permeability and solubility within the branched LCPs might be expected to be enhanced. Figure 8-15 shows the gas absorption behavior as a function of molecular weight and topology. The linear LCPs both showed significantly poorer gas absorption behavior with the 20K molecular weight LCP absorbing a mass fraction of only 1.4% CO₂ and the 10K molecular weight LCP absorbing a mass fraction of 1.6% CO₂ after one week. In the same time period the 20K molecular weight LCP with 0.77% branch-point content absorbed a mass fraction of 3.5% CO₂ and the 10K molecular weight LCP with 1.56% branch-point content absorbed a mass fraction of 7.5% CO₂! Thus the inclusion of branch-points and the resulting disruption of liquid crystalline order dramatically increases the absorption of CO₂ in these POB-co-POPB copolymers.

Although the linear POB-co-POPB polymers produced foams with relatively high densities and highly anisotropic bubble nucleation and growth, both the 10K and 20K molecular weight star-branched POB-co-POPB polymers produced well defined foams with densities from 0.3 to 0.4 g/cc, ca. 30% of the initial density of the compression molded plaques (1.24g/cc) (Figure 8-16). These foams contained both
FIGURE 8-14: DSC scans of POB-co-POPB: effects of branching
A: Linear (20K) POB-co-POPB; 0% branching agent.
B: 4-Arm (20K) POB-co-POPB; 0.77% branching agent.
C: 4-Arm (20K) POB-co-POPB; 1.56% branching agent. open and closed cells
FIGURE 8-15: Gas Absorption in POB-co-POPB: effects of branching.
A: Linear (20K) POB-co-POPB
B: Linear (10K) POB-co-POPB
C: 4-Arm (10K) POB-co-POPB
D: 4-Arm (20K) POB-co-POPB
FIGURE 8-16: Cross section of a liquid crystalline foam.
although the cells were predominately closed. The nucleation density of bubbles in the 4-arm (10K) foam was greater than that in the 4-arm (20K) foam, and the mean cell size in the 4-arm (10K) foam was less than half that of the 4-arm (20K) foam. The nucleation density also appeared to increase with increasing temperature in both systems (Figure 8-17). Highly anisotropic cell shape near the outer skins of these foams suggests that some molecular orientation which occurred during compression molding may have persisted through the subsequent processing of these materials. The characteristic sheet-like structure of liquid crystalline polymers was clearly evident in the cell walls of the liquid crystalline foams suggesting that liquid crystalline order and molecular orientation occurred within the cell walls. (Figure 8-18) Additionally, optical photomicrographs obtained from microtomed sections of the foams revealed the granular texture characteristic of liquid crystalline ordering in the cell walls - see Figures 8-13A&B.

One of the primary goals of this study were to determine the effects that high orientation within cell walls on the mechanical behavior of foams. Since the cell sizes produced in POB-co-POPB foams via the gas supersaturation technique varied substantially, the effects of cell size on mechanical properties was also studied. Representative data from indentation tests in the form of stress strain plots are shown in Figure 8-19. This figure compares the mechanical response of a POB-co-POPB foam (mean cell size = 140μm) with that of microcellular polycarbonate foam produced by the authors (mean cell size = 10μm) and that of a standard commercial
FIGURE 8-17: Effects of blowing temperature on nucleation density and cell size:

A: 4-Arm (20K) POB-co-POPB foamed at 310°C.
B: 4-Arm (20K) POB-co-POPB foamed at 325°C.
C: 4-Arm (20K) POB-co-POPB foamed at 350°C.
D: 4-Arm (10K) POB-co-POPB foamed at 310°C.
E: 4-Arm (10K) POB-co-POPB foamed at 325°C.
F: 4-Arm (10K) POB-co-POPB foamed at 350°C.

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FIGURE 8-18: Enlargement of a cell edge showing the sheet-like structure characteristic of liquid crystalline polymers.
FIGURE 8-19: Indentation tests; comparison of different foams:
A: POB-co-POPB foam
B: Polycarbonate microcellular foam
C: Polystyrene foam
polystyrene foam produced by DOW (mean cell size = 75μm). The low values of stress achieved for testing in the polystyrene foam are due to its much lower density ($p^* = 0.05\text{g/cc}$) compared to that of the other foams tested (ca. 0.35g/cc). None of the foams showed a definite yield point but all three showed a significant decrease in the slope of the stress strain curve indicative of cell wall collapse between 5% and 10% strain.

While the polystyrene and polycarbonate foams showed the onset of densification at relatively high strains (ca. 70% - 80%) the POB-co-POPB foams appeared to begin densification much earlier in the test. The foams with cell sizes greater than 400μm appeared to begin densification as early as 40% strain - see Figure 8-20. As cell size increased in the POB-co-POPB foams the initial modulus decreased and densification occurred earlier in the test. Both of these trends are attributed to a higher number of irregularities and defects within the foam structure. To compensate for differences in foam densities the specific modulii (modulus/density) of foams was compared as a function of chemical composition, thermal history, and mean cell size in Table 8-3. The POB-co-POPB foams showed specific modulus values between 650 and 1000 MPa(g/cc)$^{-1}$ with a strong dependence on cell size. The effects of foam cell size on the mechanical response of POB-co-POPB foams are illustrated in Figure 8-21. There appears to be a strong inverse dependence between specific modulus and cell size for cells between cells of mean diameter 100μm to 450μm, but there is little or no noticeable effect of cell size on specific modulus for
**TABLE 8-3:**
Specific Modulus vs. Foam Composition and Microstructure

<table>
<thead>
<tr>
<th>FOAM</th>
<th>MODULUS (MPa)</th>
<th>DENSITY (g/cm³)</th>
<th>MEAN CELL SIZE (µm)</th>
<th>SPECIFIC MODULUS (MPa*cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>48 ± 1</td>
<td>0.05</td>
<td>75</td>
<td>970 ± 18</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>500 ± 20</td>
<td>0.317</td>
<td>10</td>
<td>1 580 ± 60</td>
</tr>
<tr>
<td>4-Arm POB-co-POPB Foams</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10K) 350°C</td>
<td>330 ± 10</td>
<td>0.336</td>
<td>140</td>
<td>980 ± 30</td>
</tr>
<tr>
<td>(10K) 325°C</td>
<td>310 ± 15</td>
<td>0.355</td>
<td>240</td>
<td>870 ± 40</td>
</tr>
<tr>
<td>(10K) 310°C</td>
<td>250 ± 30</td>
<td>0.371</td>
<td>430</td>
<td>670 ± 80</td>
</tr>
<tr>
<td>(20K) 350°C</td>
<td>250 ± 30</td>
<td>0.368</td>
<td>430</td>
<td>680 ± 80</td>
</tr>
<tr>
<td>(20K) 325°C</td>
<td>255 ± 50</td>
<td>0.370</td>
<td>650</td>
<td>690 ± 140</td>
</tr>
<tr>
<td>(20K) 310°C</td>
<td>260 ± 50</td>
<td>0.370</td>
<td>800</td>
<td>700 ± 140</td>
</tr>
</tbody>
</table>
FIGURE 8-20: Indentation tests; effects of cell size:
A: 4-Arm (10K) POB-co-POP B foam: mean cell size = 140μm
B: 4-Arm (10K) POB-co-POP B foam: mean cell size = 430μm
FIGURE 8-21: Effect of cell size on specific modulus of POB-co-POPB foams
cells larger than 450µm. This effect of cell size is not addressed in Gibson and Ashby's approach to describing the mechanical response of foams. An effect of the same magnitude was also noticed by Benning as well as Clutton and Rice in EVA and LDPE foams with densities of 0.045g/cc, but no explanation was proposed for the observed dependence. In our case, it appears that this cell size effect may be due to a combination of factors. Since the POB-co-POPB foams become increasingly irregular in structure with increasing cell size, it is likely that defects and an increasing number of open cells may lead to a decreased initial modulus. Additionally, this effect may be due to a different distribution of material between cell walls and struts as a function of cell size, an effect which is accounted for by Gibson and Ashby.

Table 8-4 compares modulus values predicted by eq. 8-3 with the experimental values. The amount of material in cell edges or struts for a given foam, \( \Phi \), is estimated by examination of the respective SEM micrograph, and the modulus of the solid polymers are determined by running indentation tests on standards of solid polymers. Indentation tests were performed on solid polycarbonate, polystyrene, and the POB-POPB copolymers used in this study. From the indentation tests, the initial Young's modulus of the polymers was determined from the initial slope of stress-strain curves. Our results agreed well with modulus values obtained from the literature for polystyrene and polycarbonate. With reasonable estimates of \( \Phi \), the predicted values of initial modulus for microcellular polycarbonate and polystyrene
TABLE 8-4: Comparison Between Observed and Predicted Foam Modulus:
Effects of Foam Composition and Structure

<table>
<thead>
<tr>
<th>FOAM</th>
<th>CELL SIZE (μm)</th>
<th>$E^*$&lt;sub&gt;Observed&lt;/sub&gt; (MPa)</th>
<th>$E^*$&lt;sub&gt;Predicted&lt;/sub&gt; (MPa)</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>75</td>
<td>48 ± 1</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>10</td>
<td>500 ± 20</td>
<td>507</td>
<td>0.45</td>
</tr>
<tr>
<td><strong>4-Arm POB-co-POPB Foams</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10K) 350°C</td>
<td>140</td>
<td>330 ± 10</td>
<td>320</td>
<td>0.5</td>
</tr>
<tr>
<td>(10K) 325°C</td>
<td>240</td>
<td>310 ± 15</td>
<td>302</td>
<td>0.6</td>
</tr>
<tr>
<td>(10K) 310°C</td>
<td>430</td>
<td>250 ± 30</td>
<td>250</td>
<td>0.8</td>
</tr>
<tr>
<td>(20K) 350°C</td>
<td>430</td>
<td>250 ± 30</td>
<td>350</td>
<td>0.9</td>
</tr>
<tr>
<td>(20K) 325°C</td>
<td>650</td>
<td>255 ± 50</td>
<td>350</td>
<td>0.9</td>
</tr>
<tr>
<td>(20K) 310°C</td>
<td>800</td>
<td>260 ± 50</td>
<td>350</td>
<td>0.9</td>
</tr>
</tbody>
</table>
foams agree well with the experimental values. The predicted modulus for the foams produced from the 4-Arm 10K POB-co-POPB also agree well with the experimental values, but the experimental values for the foams produced from the 4-Arm 20K POB-co-POPB foams fell 40% below the predicted values. The predicted modulus of these foams was greater than that of the foams produced from the 4-Arm 10K due to the fact that the experimental values of shear modulus for the higher molecular weight solid polymer obtained by indentation testing was ca. 40% greater. This may be due to greater ease of molecular relaxation in the lower molecular weight system since molecules in this system are not as likely to be entangled with as many neighbors. Additionally, there may be less molecular orientation in the cell walls of the 4-Arm 10K foam. The failure of Gibson and Ashby's model, in these cases, is attributed to the irregularities in structure and high number of structural defects.

The results of indentatation testing imply that the effects of cell size on initial modulus may be explained in terms of structural features encompassed by the model of Gibson and Ashby. The POB-co-POPB foams generated in this study showed an increase in the amount of material in cell edges with decreasing cell size leading to an increase in modulus as predicted by eq. 8-3. Foams with large, irregular cells failed to behave as predicted by eq. 8-3. Several earlier studies have observed a reduction in the modulus of microcellular foams relative to that predicted by the simple equation:17,18,19,20
\[ E^* = E_s (p^*/p_s)^2 \]  

(8-12)

This reduction of modulus was attributed to structural defects within the foams. This simple equation, however does not account for the structural features of the foam. Figure 8-22 shows the structure of microcellular polycarbonate and polystyrene foams. Both foams are uniform, apparently defect free, well characterized and consist of essentially all closed cells; however the cells in the microcellular polycarbonate foam have a significantly greater percentage of material in the cell edges relative to that in the cell walls. If the material in the cell edges is not considered when predicting modulus, eq. 8-3 overestimates the modulus of microcellular polycarbonate. Conventional foams usually have a very low density with a very small amount of material in the cell edges; thus eq. 8-10 does a good job at explaining the behavior. Since the equation developed by Gibson and Ashby considers the effects of structural features as well as foam density, it may applicable for foams regardless of cell size as long as the structural features of the foam are fairly regular.

In explaining the differences in the collapse and densification behavior of the different foams it is instructive to examine SEMs of the damage left by the indenter.(Figure 8-23) In both the microcellular polycarbonate and polystyrene foams, foam collapse and densification and collapse occurred through the buckling of cell walls. In the POB-co-POPB foams this buckling of cell walls was also accompanied by cracking in cell walls and at the sample's surface. Crack propagation
FIGURE 8-22: Structural features of microcellular polycarbonate and polystyrene foams:

A: Microcellular polycarbonate foam; 573X
B: Polystyrene foam; 543X

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**FIGURE 8-23**: Structural damage produced by indentation testing:
- **A**: POB-co-POPB foam
- **B**: Polystyrene foam
- **C**: Microcellular polycarbonate foam
often leads to failure in conventional liquid crystalline materials, however in these liquid crystalline foams cracks are arrested at cell edges leading to enhanced toughness. This cracking eliminates some of the contribution due to the compression of gas within the cells, however according to eq. 8-3 this should only account for about 0.05% of the initial modulus observed for these foams (ca. 47KPa).

Table 8-5 illustrates the plastic and elastic collapse stresses predicted for the foams based on eqs. 8-4 and 8-5 compared to the actual collapse stresses observed for the foams studied. Although the predicted values of plastic and elastic collapse varied little for the POB-co-POPB foams (due to a slight increase in density for the larger cell foams) there was a significant increase in the observed value of collapse stress as cell size decreased. The observed collapse stress of the foams increased from roughly 2 to 3 MPa for the foams with cell size greater than 400μm to 5MPa for the foam with a mean cell size of 140μm. For the POB-co-POPB foams with mean cell size over 400μm the predicted value for plastic collapse stress were close to the experimentally observed values, although the determination of collapse stress was difficult due to increased linearity in the stress strain behavior in these samples. For the polystyrene, microcellular polycarbonate, and POB-co-POPB foams with small cells the observed collapse stress was intermediate between the values predicted for plastic and elastic collapse. It is apparent, since a significant effect of cell size was observed in collapse stress, that eqs. 8-5 and 8-6 do not adequately explain the collapse behavior of foams as a function of structure and cell size. The
TABLE 8-5: Comparison Between Observed and Predicted Collapse Stress: Effects of Foam Composition and Structure

<table>
<thead>
<tr>
<th>FOAM</th>
<th>CELL SIZE (µm)</th>
<th>$\sigma^*_{\text{Observed}}$ (MPa)</th>
<th>$\sigma^*_{\text{E1}}$ (MPa)</th>
<th>$\sigma^*_{\text{F1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>75</td>
<td>0.6</td>
<td>3.4</td>
<td>0.06</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>10</td>
<td>6</td>
<td>10.0</td>
<td>2.4</td>
</tr>
<tr>
<td>4-Arm POB-co-POPB Foams</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10K) 350°C</td>
<td>140</td>
<td>5.0</td>
<td>10.0</td>
<td>2.5</td>
</tr>
<tr>
<td>(10K) 325°C</td>
<td>240</td>
<td>3.5</td>
<td>11.0</td>
<td>2.8</td>
</tr>
<tr>
<td>(10K) 310°C</td>
<td>430</td>
<td>2.3</td>
<td>12.3</td>
<td>2.8</td>
</tr>
<tr>
<td>(20K) 350°C</td>
<td>430</td>
<td>2.3</td>
<td>13.4</td>
<td>3.0</td>
</tr>
<tr>
<td>(20K) 325°C</td>
<td>650</td>
<td>2.3</td>
<td>13.2</td>
<td>2.9</td>
</tr>
<tr>
<td>(20K) 310°C</td>
<td>800</td>
<td>2.3</td>
<td>13.3</td>
<td>2.9</td>
</tr>
</tbody>
</table>
data obtained from indentation tests, however is unlikely to give a very accurate measure of collapse stress due to the fact that the load distribution is non-uniform before the onset of collapse and the fact that the load distribution changes as collapse is initiated first in the regions under the greatest stress.

**CONCLUSIONS:**

Closed cell liquid crystalline foams have been produced by supersaturation with CO₂ gas followed by thermal blowing. In order to enhance processability and maximize CO₂ absorption, 4-arm branching agents were added giving the polymer molecules a star- branched topology. The modification of the topology was found to substantially alter the rheological behavior of these polymers relative to their linear counterparts of comparable molecular weight. A decrease in liquid crystalline ordering due to inclusion of the branch-points was observed through both WAXD and DSC experiments. Star-branched POB-co-POPB was found to absorb up to 8.5% CO₂ by mass. By varying thermal blowing temperature and molecular weight, foam cell size was varied from 100μm to 800μm. The LCP foams produced by the supersaturation process exhibited mechanical behavior comparable to polystyrene and microcellular polycarbonate foams. The mechanical behavior of the foams was found to agree quite well with the general model proposed by Gibson and Ashby for initial foam modulus of a closed cell foam if the foams had a fairly regular and defect free structure. A strong inverse relationship between modulus and cell size was attributed to differences in the amounts of materials in cell edges vs. cell walls and structural
irregularities. The collapse stress observed for the foams fell between the values predicted by Gibson and Ashby for elastic and plastic collapse. The results of this study imply that if structural features such as cell size and the fraction of material in cell edges can be controlled. Foam properties may be controlled as a function of structure as well as density. This study also illustrates that irregularities and inhomogeneities within a foams structure lead to decreased initial modulus and yield stress.
REFERENCES (Chapter 8)


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CHAPTER 9

RECOMMENDATIONS

This work consists of five independent research topics; three of which deal primarily with the crystallization behavior of polymers and two of which deal primarily with processing pressurized gas. In general, the major research goals for each project were accomplished satisfactorily, and in some cases some very interesting additional information was obtained. However in the course of analyzing the data questions often arise which for, one reason or another remain unanswered generally because of limitations on available facilities or limitations due to the nature of the polymeric systems involved.

In general, the study of the crystallization behavior of PPS answered many questions which had arisen in earlier studies. There are, nonetheless, several additional questions which remain unresolved. First of all, although the nature of the chemical nature of PPS and its endgroups has been extensively studied, there is still a lot to learn about the chemistry of PPS. In this study accurate number average molecular weights and values for polydispersity could not be obtained. The GPC data in this study was obtained with the use of a flame ionization detector which has limitations in quantifying species with molecular weight under 1000 g/mol which would be expected to be quite abundant especially in the unfractionated species. The use of a GPC detector with higher sensitivity towards
lower molecular weight species would give more quantitative information about the effects of fractionation on the molecular weight distribution and the actual concentration of endgroups for each sample. Additionally, more extensive melt rheological studies could be performed on PPS. First of all, the melt hold temperature used for the rheological studies was rather low (300°C), it would be instructive to perform temperature sweeps to determine the temperature dependence of viscosity and possibly extract flow activation energies as a function of molecular weight and endgroup counter ion through Arrhenius plots.

The study of PEEK-PSX block copolymers and their ketamine precursors uncovered several interesting morphological features, structure-property relationships, and aspects of crystallization behavior. The scope of this study, however, was limited mainly due to sample availability. It would be instructive to expand the study by varying block length and copolymer composition to a greater extent to change the structure of the microphase-separated domains and observe how changes in domain connectivity affect mechanical behavior as well as crystallization behavior. Possibly the PSX block length could be increased to 10K in order to observe even further decreased connectivity of the PEEK domains. A similar effect could be investigated by decreasing the PEEK block length in these polymers to 2K and keeping the PSX block length at 5K in this copolymer system to see the combined effects of a low PEEK block length and decreased PEEK domain connectivity. If our conclusions are correct crystallization should be

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slowed and crystalline fraction of the PEEK phase should be decreased relative to the samples already studied.

In the study of the crystallization behavior of nylon-6, it would be instructive to obtain a complete series (i.e. linear, three-arm, and six-arm) of nylon-6 of varying molecular weights. Arguments made based on the analysis of the materials investigated in this study suggest that the effects of star-branching for higher molecular weight nylon-6 would be reduced, and perhaps, in the case of very high molecular weight nylon-6 these trends may be reversed. If a complete series with \( <M_N> = 49000 \) as well as a series with \( <M_N> = 100000 \) were studied, the conclusions obtained in this study would be further verified.

The development of a process to produce liquid crystalline foams provided an interesting new class of materials; however little was known about the actual molecular weight of the POB-POPB polymers used in this study. Due to insolubility in GPC solvents, molecular weight distributions were unobtainable for these materials, and the only information on molecular weight was based on stoichiometric offset and rheology data. Some questions about the rheology data are still apparent: such as what is the entanglement molecular weight, \( M_e \), for these systems? How accurately does the flexible chain viscosity model predict the rheological behavior of these relatively rigid molecules? and does the same model apply to both linear and star-branched molecules? To answer these questions
more rheology data on higher and lower molecular weight linear and star-branched specimens needs to be run. Additionally the effects of changing block copolymer composition on foam structure and mechanical behavior was never studied. Theoretically by changing copolymer composition the use temperature of these foams could be enhanced. In any case, sample availability ultimately prevented these additional questions to be answered.
VITA

Brian G. Risch was born in Yankton, South Dakota on September 13, 1967. He was raised in Woodbury, Minnesota and attended elementary and secondary school there. He graduated from Woodbury High School in 1986 where he was active in a number of extracurricular activities including football and track. From 1986 to 1990 he attended Carleton College in Northfield, Minnesota where he lettered in collegiate varsity football for four years and was team captain for the 1989 football season. In 1990 he received a bachelors degree in physics after which he went to Virginia Polytechnic Institute and State University and enrolled in the Materials Science and Engineering program. In May, 1994 he received his Doctor of Philosophy.

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