

SOLVENT-INDUCED CRYSTALLIZATION OF POLY(ETHER ETHER KETONE)

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(ABSTRACT)

The purpose of this study was learn how the diffusion, swelling, and crystallization processes are coupled during solvent-induced crystallization of poly(ether ether ketone) (PEEK). Unoriented amorphous PEEK films were immersed in aprotic organic liquids at ambient temperature and bulk properties or characteristics were monitored as a function of immersion time. The sorption behavior, T_g and T_m , suppression, crystallinity, and dynamic mechanical response were correlated as a function of solvent chemistry and immersion time.

The saturation time of methylene chloride, 1,3-dichloropropane, tetrahydrofuran, cyclopentanone, chlorobenzene, toluene, diethyl ketone, and ethylbenzene in amorphous PEEK films were found to range from hours to days depending on the level of polymer-solvent interactions. *In-situ* isochronal DMA spectra show that the T_g of PEEK was suppressed from 150 °C to below ambient temperature such that crystallization was kinetically feasible during ambient immersion. In addition, an increase in viscoelastic dispersion was attributed to the presence of crystallinity.

From dynamic mass uptake and wide-angle x-ray diffraction (WAXD) results, it was found that the bulk sorption rate was equal to the bulk crystallization rate for all solvent systems that promoted SINC and PEEK exhibited diffusion-limited crystallization, irrespective of the nature of the transport mechanism. In addition, the solvent-induced crystals exhibit preferred orientation as supported by photographic WAXD. A distinct sorption front, observed with scanning electron microscopy, further

supports the scenario of diffusion-controlled crystallization and one-dimensional diffusion.

Isothermal DMA spectra for THF, cyclopentanone, and chlorobenzene, indicate that, as the solvent diffuses into the films, the stiffness of the polymer decreases at short times, begins to increase, and then reaches a relatively time-independent value. It was determined that the initial decrease in the storage modulus was due to the incredible plasticization of the amorphous phase. When the films contained greater than 60 % of the ultimate crystallinity, the storage modulus was observed to increase as a result of the reinforcing effect of the solvent-induced crystals. WAXD and mass uptake results confirm that the plateau in the storage modulus coincides with the completion of bulk crystallization and saturation of the amorphous phase.

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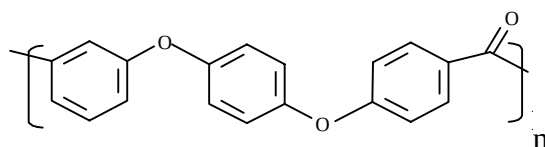
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1. INTRODUCTION

Poly(ether ether ketone) (PEEK), a “high-performance” semicrystalline thermoplastic is used as a matrix material for structural components and in applications requiring thermal stability and chemical resistance. The repeat unit of PEEK is shown below:



The aromatic nature of the backbone leads to the relative stiffness of the polymer and its high glass transition temperature of 145 °C. The crystallinity of PEEK ranges from zero (amorphous) to ~50 % depending on the thermal history or the method of crystallization.¹

In its semicrystalline form, PEEK has excellent chemical resistance and has been used for pumps, filters, bearings, and seals where the polymer is exposed to fuels, refrigerants, paints, coatings, and other liquid or vapor environments.^{2,3} It has been found that amorphous, unoriented PEEK will plasticize and crystallize in the presence of common organic liquids and vapors (e.g. methylene chloride, tetrahydrofuran (THF), toluene, and acetone)^{4, 5, 6, 7, 8} and supercritical fluids (e.g. freon-22 and CO₂).⁹ Cornélis¹⁰ determined that semicrystalline PEEK plasticizes and crazes while under stress and in the presence of the same solvents that crystallized amorphous PEEK. The morphology and the mechanical properties are altered as a consequence of polymer-solvent interactions within the amorphous phase. These results emphasize the importance of studying the effect of liquid environments on the performance of polymeric materials.

Swelling, crystallization, solvent stress cracking or crazing, and dissolution can result from favorable solvent interactions within the amorphous phase; higher density crystals in a semi-crystalline polymer are considered to be impermeable to low molecular

weight liquid molecules.¹¹ Subsequently, specific interactions within the amorphous phase can promote changes in the morphology and mechanical properties.

One example of a detrimental interaction was in the case of an injection molded automotive air-conditioning compressor valve that was found to develop micro-cracks after limited exposure to refrigerants. It was later determined from differential scanning calorimetry that solvent-induced crystallization (SINC) of the PEEK valve had occurred; further crystallization caused shrinkage and the development of cracks in the precision-machined valve. A thermal annealing step was added to the molding process to relax internal stresses and enhance the level of crystallinity (i.e. the degree of constraint on the amorphous phase) and the problem was resolved.¹²

Solvent-induced crystallization is a complex phenomena involving the coupled processes of diffusion, swelling, and crystallization. Several intrinsic and extrinsic variables can affect the rate and/or extent of each process and the development of morphology. Internal/external stresses, temperature, pressure, thickness, initial crystallinity/orientation, molecular weight distribution, and solvent chemistry are the most common experimental variables. By immersing one polymer in a series of solvents and holding all other variables constant, the effect of the chemical nature of the solvent on the properties of a polymer can be isolated.

The purpose of this study was to learn how sorption, swelling, and crystallization are coupled during the development of solvent-induced crystallinity in PEEK. Unoriented/unstressed amorphous PEEK films (same thickness and molecular weight) were immersed in liquid organic solvents at ambient temperature and bulk properties or characteristics were monitored as a function of immersion time. Sorption kinetics were determined from dynamic mass uptake experiments at ambient temperature. Bulk crystallization kinetics and crystallinity indices were evaluated via differential scanning calorimetry and wide-angle x-ray diffraction. The rate-limiting factor for the crystallization process was inferred from the relative rates of sorption and crystallization. An *in-situ* dynamic mechanical technique was used to determine the effects of

plasticization (swelling) and crystallization on the glass transition and the mechanical response of the polymer.

Chapter 2 presents a literature review of diffusion, crystallization, T_g and T_m suppression, and morphology. Chapter 3 introduces the bulk characterization techniques including mass uptake, wide-angle x-ray diffraction, and *in-situ* dynamic mechanical analysis. Chapter 4 presents the important experimental results. Chapter 5 discusses the relevance of the results. The conclusions and future work are summarized in Chapter 6 and Chapter 7, respectively.

2. BACKGROUND

The concepts of segmental mobility of polymer chains are well understood in terms of the effects of temperature on polymer properties. Typically, as temperature is increased, thermal energy induces segmental mobility. Below the glass transition temperature, T_g , molecular motions are restricted to side chain rotation and non-cooperative motion in the polymer backbone and the material is hard and glassy. Above T_g there is sufficient thermal energy for cooperative, large-scale molecular motion in the amorphous domains and the material is soft and rubbery. Upon heating a crystallizable polymer above T_g , crystallization becomes kinetically favorable.¹³

In addition to thermal means of molecular mobility, chemical environments can also promote structural rearrangements via the interaction between chemical species and polymer chains. Stuart and Williams^{4,14} used Raman Spectroscopy to compare solvent and thermal effects on PEEK. They found that the changed frequency values of the carbonyl stretching mode of PEEK, after exposure to tetrachloroethane, corresponded to the values for the unsolvated polymer at a temperature near 250 °C. The solvent induced molecular relaxation processes in PEEK were comparable to the processes induced via thermal means at temperatures well above the T_g of unsolvated PEEK. This implies that thermal and chemical energy can promote a similar degree of chain mobility.

In general, if a liquid encounters an unstressed glassy polymer, the small molecules may disrupt the intermolecular cohesive forces between polymer chains, enhance chain mobility in the amorphous phase, and lower the glass transition temperature.¹³ Consequences of polymer-liquid interactions include swelling, crystallization (SINC), solvent stress cracking or crazing, and possibly dissolution. When the interactions are strong enough to suppress the T_g below the exposure temperature, crystallization becomes kinetically favorable. If a glassy polymer (that is capable of crystallizing) is exposed to a solvent between T_g and the melt temperature, T_m° , crystallization ensues. A high degree of swelling allows easier movement of the polymer molecules and there is less steric hindrance restricting the movement and reorientation of

the chains.¹³ Typically, T_g is suppressed more than T_m° and the crystallization temperature regime, defined by $\Delta T = (T_m^\circ - T_g)$, is broadened and shifted to lower temperatures.^{13, 15}

The polymer-solvent interaction is defined by the chemical and molecular nature of the solvent molecules relative to the polymer chains, the initial state of the polymer (e.g. crystallinity, orientation, and molecular weight distribution), temperature, pressure, and stress state. Important properties of the solvent include its activity, molar volume, solubility parameter, acid-base character, polarity, and hydrogen bonding ability. Generally, an increase in temperature corresponds to an increase in the kinetics of sorption. In addition, the greater the initial crystallinity present in a given polymer, the less solvent the system can absorb, and the less likely SINC will occur due to the impermeability of the crystalline entities.^{13,16} Arzak *et al.*¹⁷ established that amorphous PEEK absorbs methylene chloride faster and to a greater extent than highly crystalline PEEK (~30 % crystallinity). The authors determined from WAXD and density results that there is no significant solvent-induced crystallinity in semicrystalline PEEK. These results were explained by the hindrance of the crystalline phase to the diffusion of solvent through the polymer.

Solvents that have similar chemical moieties as the polymer chains will often exhibit specific interactions with the polymer (i.e. "like dissolves like"). A common indicator of polymer-solvent interactions is the square of the cohesive energy density, or the solubility parameter. Polymers tend to dissolve in solvents having solubility parameters within one unit of their own.^{18,19} However, the solubility parameter is only meaningful if there is athermal mixing; the theory is not applicable when specific interactions (e.g. attraction between species of opposite polarities, acid-base attractions, and hydrogen bonding) occur. Hansen proposed a method more suitable for polar and hydrogen-bonding systems where the total cohesion parameter is divided into dispersion (δ_d), polar (δ_p), and hydrogen-bonding (δ_h) contributions as shown in Equation 2.1.²⁰

$$\delta = \sqrt{(\delta_d^2 + \delta_p^2 + \delta_h^2)} \quad \text{Equation 2.1}$$

Hybrid maps were developed by Hansen and others to establish two or three-dimensional zones of polymer-solvent solubility/interaction.

Stober and Seferis²¹ suggest that only those penetrants within a narrow range of solvent properties can affect PEEK. Their study was based on whether or not the solvents promoted solvent induced crystallization in neat amorphous PEEK at 20 °C. A two-phase model was used to evaluate the crystallinity from density measurements. The hydrogen-bonding index was plotted as a function of the solubility parameter and a zone was established wherein SINC was found to occur. However, it was later discovered by Kalika *et al.*⁵ and Cornélis¹⁰ that acetone, which lies outside of this zone, does promote SINC of amorphous PEEK during ambient temperature exposure.

The Flory-Huggins theory introduces a lattice model to predict the equilibrium thermodynamic properties of concentrated polymer solutions. The theory provides a measure of the change in free energy accompanying the formation of a one-phase polymer-solvent mixture.²² The assumptions are as follows: flexible chains, all chains are the same molecular weight, random mixing, only nearest neighbor interactions, concentrated solutions, and weak specific interactions. According to the lattice model, the mixing process is random in nature so the entropy is purely statistical; Flory-Huggins derived the maximum entropy of the system excluding specific interactions ($\Delta H \geq 0$ and $\Delta V = 0$). Realistically, polymers have various configurations including branched or rigid structures not accounted for in the derivation of ΔG_{mix} ; there are additional restrictions on chain dimensions due to steric hindrance and excluded volume that lower the entropy of the system. The interaction energy should be a free energy term to account for cases where interactions lead to local ordering and render the mixing process non-random.

An interaction parameter, χ , introduced by Flory to account for the effects of specific interactions, is a temperature-independent dimensionless quantity which contains entropic (χ_s) and enthalpic (χ_H) components.

$$\chi = \chi_s + \chi_H \quad \text{Equation 2.2}$$

$$\chi_H = \frac{V_s}{RT} (\delta_p - \delta_s)^2 \quad \text{Equation 2.3}$$

where V_s is the molar volume of the solvent, R is the universal gas constant, T is temperature in Kelvin, δ_p and δ_s are the solubility parameters of the polymer and solvent, respectively. The χ_s component is equal to the inverse number of nearest neighbors of a molecule or segment in solution and is a constant equal to 0.34.²³

Despite the oversimplifying assumptions, the solubility/cohesion parameter and the Flory interaction parameter serve as good qualitative predictors of polymer-solvent interactions. Quantitatively, these theories work best where there are non-polar or weakly polar polymer-solvent interactions.

Many researchers have focused on individual aspects of SINC such as the transport behavior of the solvent,^{4,5,6,7,8,24,25,26,27} crystallization behavior of the polymer,^{15,26,28} or the development of crystalline morphology.^{4,15,27,29,30} Some authors have rationalized why polymer-solvent interactions occur based on the chemical nature of the molecules.^{4,14,31} Other authors have done more comprehensive analyses of SINC in PET.^{15,26}

The purpose of this research was to learn how the sorption, swelling, and crystallization processes are coupled during the SINC of PEEK. The objective was reached by studying the effect of a series of organic solvents on the bulk sorption and crystallization behavior, T_g and T_m° suppression, and dynamic mechanical response. A literature review is presented below and comparisons are made between SINC and thermal-induced crystallization. Note that the term ‘solvent’ will be used interchangeably with diluents, penetrants, and interactive fluids even though the interactions are not strong enough to solvate the polymer.

2.1. Diffusion/Solvent Transport

Diffusion is a molecular process whereby a concentration gradient induces a flux of penetrant molecules from regions of high concentrations to regions of low concentration. The flux of penetrant is calculated as³²

$$J = -M \frac{d\mu}{dz} \quad \text{Equation 2.4}$$

where J is flux, M is a constant, μ is chemical potential, and z is position. Fick's first and second laws were developed to describe the diffusion process. Fick's first law describes the local rate of change in the concentration of a diffusing species and Fick's second law provides the governing differential equation for changes in concentration with respect to distance and time. If it is assumed that penetrant diffusion behaves as an ideal solution then chemical potential is proportional to concentration via Henry's law, resulting in Fick's second law,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right) \quad \text{Equation 2.5}$$

where C is concentration, t is time, and D is the diffusion coefficient.

One particular solution to Fick's second law can be obtained if the geometry of the system is known. In the case of diffusion through a polymer film, an assumption can be made that diffusion is only through the thickness of the film (i.e. in the z -direction); diffusion is negligible through the edges of the film. Fick's second law can be solved for semi-infinite slab geometry.³³ If it is assumed that the initial concentration of the penetrant is zero through the film thickness, the surface concentration remains constant at all times, and D is only a function of temperature, Equation 2.5 can be rewritten as

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial z^2} \right) \quad \text{Equation 2.6}$$

The sorption behavior of the system as a whole can be determined if the solution is integrated over the sample volume; hence, the molecular process of diffusion can be

related to the experimental observation of sorption. Assuming Fickian diffusion, an apparent diffusion coefficient D_z was estimated for each solvent and sorption temperature using the following equation³⁴

$$D_z = \pi \left(\frac{z_0}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad \text{Equation 2.7}$$

where z_0 is the average specimen thickness prior to solvent immersion, M_m is the effective moisture equilibrium content (i.e. when the rates of absorption and desorption become equal)¹³ expressed in weight percent, and the latter part of the equation represents the slope from a plot of mass uptake versus normalized time ($\sqrt{t} / z_0$).

Liquid diffusion in glassy polymer films is often non-Fickian and the simple transport model previously described is invalid. Diffusion is a complex process for the following reasons: 1) the diffusion mechanism and/or rate is sensitive to intrinsic and extrinsic properties of the system³³ (e.g. degree of crystallinity, exposure temperature relative to T_g , molar volume of the solvent, free volume of the polymer, film thickness, and specific interactions), 2) SINC can occur, 3) the boundary conditions may be time-dependent, and 4) the diffusion coefficient often varies with concentration (e.g. as swelling occurs, glassy polymers transition to the rubbery state and the diffusivity increases³⁵).

2.1.1. Molecular mechanisms of diffusion in glassy polymers

In general, the diffusion of small molecules, those smaller than the monomer units of a given polymer, have been interpreted in terms of free volume concepts.^{13,18,36} Diffusion occurs by local, activated jumps of the penetrant molecules from one unoccupied site to another in the polymer. No major redistribution of the polymer free volume is necessary and Fickian behavior is observed. This is true for the diffusion of simple gases through solid polymers and the diffusion coefficient is independent of concentration.¹³ One of the fundamental criterion for Fickian sorption is that the surface concentration is constant throughout the sorption process. This implies that the polymer chain segments in the surface layers must instantaneously equilibrate. Typically, there

are finite rates by which changes in polymer structure (e.g. chain rearrangements) can occur in response to the stresses that develop in the polymer during sorption. Diffusion of liquids in glassy polymers is often anomalous.

Anomalous behavior is evidenced by significant deviations from the linear relationship between absorption and the square root of time and can be attributed to a time-dependence of polymer chain relaxation in the presence of penetrant molecules.²⁵ A plasticizing solvent lowers the T_g of the polymer sometimes below the environmental temperature and enhances molecular motion in the polymer. It is known that diffusion rates above T_g are significantly higher than below T_g .³⁷ In this case, diffusion may depend on the concentration of the penetrant. If D_z is dependent on concentration, the minimum void size necessary for solvent transport is larger than the average free volume in the polymer; the polymer segments have to rearrange to create a passageway for the solvent molecules.¹³

Thomas and Windle³⁸ developed a theory to explain the transport behavior of organic liquids in glassy polymers in terms of the diffusivity of the liquid and the viscous flow rate of the glassy polymer. The existence of a sharp front is shown to result from the time-dependent mechanical deformation of the polymer (i.e. viscous resistance of the polymer to an increase in volume and change of shape) in response to the thermodynamic swelling stress. The plasticization front movement is limited by the kinetics of the glassy to rubbery transition. In addition, an induction period often precedes sorption behavior; the mass uptake is initially linear with time. The induction period and the plasticization front are representative of a limiting type of non-Fickian behavior referred to as Case II sorption.

In general, the fractional weight gain can be expressed as⁷

$$\frac{M_t}{M_m} = Kt^n \quad \text{Equation 2.8}$$

where M_t is the mass uptake at time t and K is a constant that depends upon the structural characteristics of the polymer and the polymer-solvent interaction. The value of the exponent, n , indicates the nature of the transport mechanism. When Equation 2.8 is rewritten as

$$\text{Log}\left(\frac{M_t}{M_m}\right) = \text{Log}K + n\text{Log}(t) \quad \text{Equation 2.9}$$

the slope of a log-log plot is n (according to Equation 2.9). For planar geometry, if $n = \frac{1}{2}$, the diffusion is classified as Fickian or pseudo-Fickian when the criteria are not met for classical Fickian diffusion. If $\frac{1}{2} < n < 1$, $n = 1$, or $n > 1$, the diffusion is classified as anomalous, Case II, or super Case II, respectively.⁷

The diffusion theories which describe swelling must be modified to account for the existence of SINC. Theories describing the coupling of plasticization and crystallization processes will be described in a later section.

2.1.2. Sorption of organic liquids in PEEK

The sorption of organic swelling agents that promote SINC in a variety of polymers with relatively stiff backbones has been studied. Such polymers include poly(ethylene terephthalate) (PET)^{15,26,27}, poly(butylene terephthalate)/polyarylate²⁸, Nylon 6I³¹, and PEEK.^{4,5,6,7,8,24,25,30,39} Several different sorption behaviors (e.g. sorption kinetics, solubility, and transport mechanism) have been noted for PEEK depending on the chemical nature of the liquid and its concentration/activity, film thickness, sorption temperature, molecular weight, and initial degree of crystallinity.^{25, 39}

Mensitieri *et al.*²⁵ found that the controlling transport mechanism changes with sorption temperature for liquid methylene chloride sorption in amorphous PEEK. At -32°C , the weight uptake is linear with time and is indicative of Case II behavior. At 36°C , the weight uptake is linear with the square root of time and is indicative of Fickian behavior. These results suggest the existence of two competing effects, diffusive control of the penetrant concentration and polymer relaxation at the swelling front, the latter being the rate-determining step at lower temperatures. Osmotic stresses arise from a difference in solvent content between the penetrated and unpenetrated polymer and promote relaxation of the polymer chains in the presence of the solvent. At elevated sorption temperatures, the rate of viscoelastic response to the osmotic stresses increases more than the diffusion rate. Hence, above a certain temperature, polymer chains are

able to relax instantaneously in the presence of the solvent and the diffusive resistance in the swollen shell becomes the controlling factor.

In addition, Mensitieri *et al.*²⁵ found that the exposure of amorphous PEEK films of varying thickness to liquid and vapor penetrants at several activities exhibited a broad range of sorption behavior from ideal Fickian to Case II. They determined that methylene chloride/hexane solutions, with moderate to high methylene chloride activity, exhibited transport behaviors characterized by diffusion-controlled relaxation. Lower temperatures, thinner films, and higher solvent activities led to higher maximum sorption uptakes. Overshoots in the sorption curve were attributed to the expulsion of solvent from the crystals leading to a super-saturation of the amorphous phase.

The aim of this study was to compare the rate of sorption to the rate of crystallization, regardless of the exact mechanism of diffusion, to determine the rate-limiting factor for the crystallization process. The polymer, film thickness, and sorption temperature were kept constant and only the chemistry of the solvent was varied to study the effect of solvent chemistry on the phenomenon of SINC. Classical Fickian behavior was assumed to determine pseudo-Fickian diffusion coefficients (assuming D is a constant during isothermal immersion) and to compare the relative rates of sorption for a given series of solvents.

2.2. T_g/T_m Suppression

The depression of T_g and T_m° that is induced by the solvent depends on the amount of solvent absorbed in the polymer. In addition, the amount of solvent absorbed will depend on the degree of interaction of the solvent with the polymer. Gordon and Taylor presented a relationship⁴⁰, based on free volume concepts, that characterizes the T_g depression of a purely amorphous polymer in the presence of a penetrant. It is assumed that there is at least partial miscibility of the diluent and the polymer; there is true dissolution on a local scale. The T_g according to Gordon and Taylor is defined as:

$$T_g = \frac{(KW_1T_{g1} + W_2T_{g2})}{(KW_1 + W_2)} \quad \text{Equation 2.10}$$

where T_g , T_{g1} , T_{g2} represent the glass transition temperatures of the system, diluent, and polymer, respectively, and W_1 and W_2 are the weight fractions of the diluent and polymer, respectively. The constant K is given by the following relationship:

$$K = \frac{\Delta\alpha_2}{\Delta\alpha_1} \quad \text{Equation 2.11}$$

where $\Delta\alpha$ is the difference in the expansion coefficients of the pure components in the glassy and molten state.

Fox⁴¹ introduced a simpler approach to estimating T_g suppression. The Fox equation assumes an additive relationship between the free volume of the mixture and the free volume of the system; the addition of a low molecular weight species increases the volume of the system and lowers T_g .

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad \text{Equation 2.12}$$

The Fox equation will give a first-order approximation of the T_g of a polymer at equilibrium in a plasticizing liquid. The major assumptions are that the solvent and polymer are at least partially miscible on the molecular level and that no other phases are present. Unfortunately, this approximation is not applicable when SINC occurs because a second phase develops during sorption. This equation can significantly overestimate the suppression in T_g when SINC occurs. However, the experimentally determined will be correlated to the estimate from the Fox equation.

The glass transition temperature of polymers can be measured via a variety of thermal and mechanical techniques. A few common examples are differential scanning calorimetry, dilatometry, dielectric methods, and dynamic mechanical analysis (DMA). The glass transition temperature depends on the time allotted for the experiment; the heating/cooling rate of static or quasistatic experiments, and the frequency of dynamic

experiments.⁴² Typically, as the frequency is increased, T_g increases because the molecules cannot respond as quickly at higher test frequencies until the polymer reaches a higher temperature.⁴³ The glass transition is often thought of as a kinetic transition or a pseudo-second order transition. For this study, the glass transition of solvent-saturated PEEK will be determined via an in-situ dynamic mechanical analysis technique at a frequency of 1 Hz. It is important to note, however, that this method would suffer if solvent desorption occurs during heating.

Since the melting temperature of a solvent-saturated polymer cannot be experimentally obtained, the depression of T_m° in the presence of a solvent will be estimated using the following relationship⁴⁴:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{RV_2}{\Delta H_2 V_1} (\phi_1 - \chi \phi_1^2) \quad \text{Equation 2.13}$$

where R is the gas constant, V_1 and V_2 are the molar volumes of the diluent and polymer repeat unit respectively, ϕ_1 is the volume fraction of the diluent, and ΔH_2 is the heat of fusion per mole of repeat unit of polymer. This relationship is based on the assumption that the diluent does not enter the crystalline phase and there are non-polar or slightly polar interactions. In this study, the Flory-Huggins interaction parameter, χ_1 , will be estimated using Equations 2.2-2.3 and Hansen solubility parameters.

Since a swelling solvent primarily interacts with the amorphous phase, the suppression of T_g is much greater than the suppression of T_m° . Subsequently, the window of crystallization, defined by $(T_m^\circ - T_g)$, is broadened and crystallization becomes kinetically favorable at lower temperatures relative to the dry, unswollen polymer.

2.3. Crystallization

Before SINC can be discussed in terms of crystallization kinetics and morphological development, a discussion of thermal induced crystallization is presented.^{45,46} Keith and Padden developed a qualitative theory to address the kinetics of spherulitic growth in crystallizing polymers. Since the rate of crystal growth is typically in the radial direction, a radial growth rate equation was developed. The growth rate can be separated into nucleation and growth terms. The limiting factors for thermal-induced crystallization are the diffusion of the polymer chains at temperatures near T_g and the rate of nucleation at temperatures near T_m° . The growth rate passes through a maximum when the two competing factors are approximately equal in magnitude.

A more quantitative theory was developed by Hoffman to provide enhanced detail regarding spherulite nucleation and growth rate (designated i and g , respectively).⁴⁶ Hoffman defined three regimes of crystallization kinetics from the melt: 1) at temperatures near T_g (Regime I), $i \gg g$, 2) at intermediate temperatures (Regime II), $i \sim g$ and, 3) at temperatures near T_m (Regime III), $g \gg i$. Hence, the degree of supercooling, $\Delta T = T_m^\circ - T_c$ where T_m° is the equilibrium melt temperature, determines the extent of nucleation and growth. A large ΔT corresponds to the development of smaller and more numerous spherulites.

The most common description of the initial stages of bulk crystallization has been interpreted or modeled in terms of the Avrami⁴⁷ equation

$$1 - X(t) = \exp(-Kt^n) \quad \text{Equation 2.14}$$

where $X(t)$ is the fraction of the total volume of material that has undergone crystallization after a given amount of time t , K is the crystallization rate constant which contains information about the nucleation and growth processes, and n is the time exponent which serves to indicate the geometry of the growing crystalline entities. SINC studies of undeformed PET suggest that the nucleation is athermal and the crystalline texture is three-dimensionally spherulitic.²⁶

Makarewicz and Wilkes¹⁵ used a modified Avrami model (Zachmann and Konrad) to predict and explain the overall diffusion-limited crystallization kinetics

observed experimentally for the case of liquid-induced crystallization. The model states that the overall volume fraction of material crystallized in the entire film specimen, $X(t')$ can be given by a dimensionless Avrami-type relation

$$X(t') = \int_0^{b'\sqrt{t'}} \left\{ 1 - \exp \left[- \left(t' - \frac{Z'^2}{b'^2} \right)^3 \right] \right\} dZ', \text{ where } Z = b\sqrt{t} \quad \text{Equation 2.15}$$

where Z is the distance of penetration of the plasticized front from the film surface, b is a rate constant proportional to the diffusivity, $Z' = Z/a$, a is the half thickness of the polymer film, $t' = 3K_2^{1/2}t$, and $b'^2 = b^2/a^2 3K_2^{1/2}$. When $b't'^{1/2}$ is greater than or equal to one, the upper limit of the integral reduces to one and the entire film contains the penetrant at the saturation concentration.

When the time scale for crystallization, t_c , is much greater than the time scale for diffusion, t_d , the entire film should crystallize simultaneously with no diffusional limitations. Conversely, when the crystallization rate far exceeds the diffusion rate ($t_d \gg t_c$), each volume element crystallizes immediately on contact with the diffusion front.¹⁵ It is suggested that the thicker the polymer film, the greater the diffusional limitation on the observed crystallization kinetics and the more likely Fickian behavior is observed.¹⁵ A sorption overshoot might be expected for thin films where diffusion is completed before extensive crystallization takes place. Qualitatively, the relationships developed by Zachmann and Konrad are indicative of the dimensionality of growth and the kinetic limitations of diffusion and crystallization.

Durning and Russel⁴⁸ proposed a mathematical model (abbreviated as DR) with two adjustable parameters to describe coupled transport, crystallization, and macrovoid development. The major simplifying assumptions of the DR model are: 1) the average concentration of penetrant in the amorphous regions governs the crystallite growth rate, 2) penetrant transport occurs only in the amorphous regions, 3) the amount of diluent trapped in the developing crystallites is negligible, and 4) the time dependence of polymer relaxation is confined to the immediate vicinity of the moving boundary; the penetrated portion of the polymer is highly plasticized and the polymer response time is

relatively short. The amount of penetrant in the glassy region ahead of the moving boundary is small.

For SINC, solvent diffusion (defined by the sorption behavior) and crystalline growth are the two rate processes that govern the overall crystallization rate; consequently, the experimentally measured crystallization rates are discussed in terms of a rate-limiting process.^{15,48} According to Durning and Russel⁴⁸, the rate-limiting factors for solvent uptake and SINC are defined in Table 2.1. The DR model successfully predicts a variety of experimental behaviors where the existence of a glassy-swollen interface (and a chemical potential discontinuity) is postulated. The model predicts four limiting regimes of behavior according to the values of the dimensionless crystallization rate and the dimensionless sample half thickness (Table 2.1). The most common experimentally observed behaviors include relatively thick films with fast crystallization (Behavior type A) and relatively thin films with slow crystallization (Behavior type B).

Table 2.1 Rate limiting factors for SINC of glassy polymers.

Behavior Type	Relative Film Size	Relative Crystallization Rate	Mass Uptake*	Crystallization (rate-limiting factor)
A	thick	fast	Fickian, $r \propto t^{1/2}$	Diffusion control, $r \propto t^{1/2}$
B	thin	slow	Case II, $r \propto t$	Crystal Growth control
C	thin	fast	Case II, $r \propto t$	Diffusion control, $r \propto t$
D	thick	slow	Fickian, $r \propto t^{1/2}$	Crystal Growth control

* Alternate terminology: Waywood and Durning²⁸ refer to Fickian sorption as diffusion-controlled uptake, Case II sorption as swelling-controlled uptake, and diffusion-controlled crystallization (Type C) as swelling-controlled crystallization.

If the crystallization rate, r_c , is fast relative to the sorption rate, r_s , crystallization will occur instantaneously upon contact with the moving diffusion front. If the crystallization rate is relatively slow, regardless of the sorption behavior, the forming crystals have more time to develop and are predicted to be more perfect/ordered than in the former case. In this study, the rate-limiting factor for SINC will be inferred from bulk sorption and crystallization kinetics (i.e. from experimentally observed rates: r_s^* and r_c^*). In addition, qualitative observations of the induced morphology will be presented.

Almost a decade later, Kalospiros *et al.*⁴⁹ developed a continuous morphology model (abbreviated KOAM) to predict when the travelling discontinuity develops. A dimensionless adjustable parameter, defined as the ratio of the crystallization time to the mass flux-relaxation time, is introduced to describe the time scale for crystallization relative to the time-scale to reach equilibrium saturation. The KOAM model predicts a broader range of experimentally observed crystallization and sorption behaviors than the DR model does. However, for cases where a distinct moving front/discontinuity is observed, the KOAM model reduces to the DR model and the DR model will adequately predict the behavior of the SINC process.

Several techniques (quantitative and qualitative) have been utilized in the literature to determine crystallinity in polymer films. Unfortunately, many of these techniques do not apply to systems that have undergone SINC. In general, the onset of crystallization in amorphous polymer films is accompanied by an increase in opacity. However, opacity can be a result of the presence of crystalline entities, cavitation/voids, or fluctuations in optical anisotropy on the order of the wavelength of visible light. If the crystals are small relative to the wavelength of light, the films may appear translucent or transparent regardless of the presence of crystallinity. Therefore, a visual assessment of SINC is unreliable.

Crystallinity measurements from density or specific volume methods may produce misleading results especially if void formation occurs during the SINC process, residual solvent remains in the structure after drying and/or, further crystallinity is induced during the desorption process. Wolf *et al.*²⁹ found that the degree of crystallinity via x-ray was significantly greater than the value obtained via density measurements.

The authors suggest that the discrepancy is due to the presence of voids. Desai and Wilkes²⁶ observed an initial zone of fast diffusion from their mass uptake curves. Subsequent SEM observation confirmed the presence of surface cavitation, especially for solvents with similar solubility parameters to PET.

Another common technique for determining polymer crystallinity is differential scanning calorimetry (DSC). The degree of crystallinity is calculated as the ratio of the experimentally measured heat of fusion (area under the endothermic melt peak) to the theoretical heat of fusion of the polymer if it were 100 % crystalline. DSC may not be useful for determining crystallinity from SINC if the heat scans are performed at slow heating rates. During the DSC heating scan, the T_g increases as residual solvent is driven out of the system and the SINC crystals can melt and recrystallize at any temperature between the immersion temperature and T_m . In addition, if the SINC films are pre-dried at higher temperatures to remove residual solvent, additional thermal crystallization may occur; the degree of perfection and extent of crystallization may be altered during the drying process. In this case, the morphology is no longer representative of the morphology that was induced solely from SINC. To limit the aforementioned affects in this study, a faster heating rate was employed and relative changes in crystallinity with immersion time were determined from changes in the crystallization enthalpy.

Wide-angle x-ray diffraction (WAXD) is the most direct method of determining crystallinity because it analyzes the unit cell structure. The technique has been used to determine the diffraction spectra of PEEK following solvent immersion. The specimens are air-dried to remove as much solvent as possible; Wolf *et al.*⁸ determined that a small amount (2-3 wt %) of residual liquid in PEEK films, following desorption, had little or no effect on the x-ray analysis but added a substantial error to the determination of crystallinity from density measurements

WAXD has been used to investigate the bulk crystalline content and crystallinity kinetics of SINC by obtaining diffraction profiles in symmetric transmission geometry. Desai and Wilkes²⁶ have shown, for amorphous undrawn PET, that changes in the peak intensity of a given reflection with immersion time are directly related to changes in the crystallinity of the polymer. Cornélis¹⁰ estimated a crystallinity index for solvent-crystallized PEEK by correcting the diffraction patterns for absorption incoherent

scattering and then integrating the area under the Gaussian peaks obtained by curve fitting.

In this study, the crystallinity index was evaluated from the integrated areas under the crystalline and amorphous WAXD patterns. This technique is thought to give better estimates of crystallinity for systems that exhibit changes in crystalline orientation; changes in the integrated area of a WAXD pattern will be less dramatic than changes in the relative ratios of the diffraction peaks in terms of calculating an index of crystallinity. For this study, a modification of a method by Justi *et al.*⁵⁰ was used to scale the diffraction pattern of an experimental amorphous standard into the semicrystalline pattern. This method was used to examine the crystallinity at different stages of solvent-induced crystallization in amorphous PEEK films. DSC was used as a secondary method to determine relative changes in crystallinity for a given system.

2.4. Dynamic mechanical analysis (DMA)

When viscoelastic materials are subjected to cyclic stresses/strains, some of the input energy is stored as potential energy (elastic behavior) and the remaining energy is dissipated in the form of heat (viscous dissipation). The quantity E' , the storage modulus, is a measure of the energy stored elastically and E'' , the loss modulus, is a measure of the energy lost as heat. A viscoelastic polymer undergoing cyclic loading will display a finite phase angle, δ , between the stress and strain response whose magnitude is dependent on both the frequency and temperature. $\tan\delta$ is called the loss tangent, δ being the angle between the in-phase and out-of-phase components in the cyclic motion. Figure 2.1 shows the generalized behavior of the phase relationship between stress and strain in a sinusoidal loading experiment of a viscoelastic material. Measurement of the viscous component (E'') and/or $\tan\delta$, via dynamic mechanical techniques, provides a means of studying molecular motions within polymers.⁵¹

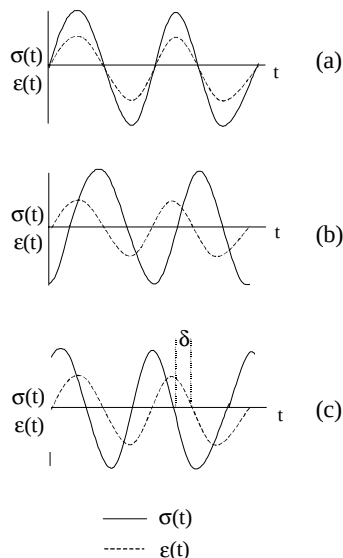


Figure 2.1 A schematic of the relationship between stress and strain for sinusoidal loading.⁵¹ (a) pure elastic behavior, (b) pure viscous behavior, (c) viscoelastic behavior.

At specific rates and temperatures, the loss modulus and $\tan\delta$ will display maximas, or distinct “loss peaks” indicative of mechanical resonance; local modes of motion are in-phase with the applied dynamic loading. At low temperatures, below T_g , local-scale motions such as rotations of side groups and oscillations or rotations of backbone components can be detected. Low temperature loss peaks are important because they represent molecular means by which energy can be dissipated in the glassy state (e.g. impact properties at low temperatures). At temperatures at or above T_g , there is sufficient thermal energy for large-scale cooperative molecular motion of the backbone. The storage modulus exhibits at least an order of magnitude decrease upon heating through T_g and the $\tan\delta$ is on the order of 1.0 or higher.⁵¹

The presence of crosslinks, crystallinity, or a reinforcing phase will inhibit molecular motions in the amorphous phase. Hence, the change in E' through the glass transition will be smaller than that of a purely amorphous version of the same polymer. In addition, the breadth of the mechanical response at T_g (i.e. viscoelastic dispersion) increases; it takes more thermal energy to relax the highly constrained amorphous regions. Often the peak in $\tan\delta$ is located at a substantially higher temperature than E''

when this broadening effect occurs and the presence of a reinforcing crystalline phase suppresses the magnitude of the loss transition and $\tan\delta$ at T_g .⁴³ When the temperature range of the glass transition is small, either the peak temperature of $\tan\delta$ or E'' is defined as T_g . If the temperature range of the glass transition is broad, one has to define a range instead of a single temperature. In this study, the glass transition will be defined as a temperature range spanning from the onset of the initial drop in E'' to the peak in $\tan\delta$.

Amorphous PEEK shows a large drop in E' over a small temperature range (10 °C) through T_g , unlike thermally crystallized PEEK. It is expected that the glass transition of solvent-saturated semicrystalline PEEK will be located below room temperature, a criterion necessary for crystallization to occur, and it will span a broad temperature range due to the constraining effect of the crystals. In addition, the presence of crystallinity will have the effect of increasing the modulus and therefore the modulus will not drop sharply above T_g , as might be expected if the polymer were completely amorphous.⁵¹ Similar to thermally crystallized PEEK, it is expected that any increase in crystallinity will lower the amplitude of $\tan\delta$.²⁴

To date, only a few DMA studies have been performed on polymer specimens while immersed in a fluid. Dillman and Seferis⁵² introduced a technique to determine the true dynamic mechanical properties of polymeric materials in fluid environments. They subtracted the viscous drag effects to obtain fluid-independent dynamic mechanical properties. Stober and Seferis²¹ presented an isothermal spectrum from the real-time immersion of semicrystalline PEEK in methylene chloride but did not quantitatively relate the dynamic mechanical properties to the sorption process. Desai and Wilkes⁵³ utilized a modified Rheovibron to investigate the effect of SINC on the dynamic mechanical properties of PET in organic liquids. Several different behaviors, indicative of differing degrees of crystallinity and differences in morphology, were noted for initially amorphous PET that was immersed in methanol at a temperature below the T_g of the swollen polymer and then crystallized at higher temperatures. The breadth, magnitude, and location of T_g , as indicated by a peak in $\tan\delta$, changed as a function of crystallization temperature.

Browne *et al.*⁵⁴ determined the relaxation characteristics of PEEK, after immersion to equilibrium at ambient temperature, via dynamic mechanical analysis in the

vicinity of the α -relaxation. The specimens were tested immediately after removal from the solvent to minimize solvent loss and it was found that the glass transition temperature (defined by the peak in $\tan\delta$) was suppressed to 77 °C in toluene. Toluene, chloroform, acetone, and dichloromethane (MC) exhibited broader and lower maxima $\tan\delta$ peaks than amorphous PEEK indicating the presence of crystallinity. The authors emphasize that this T_g is not representative of the specimen at equilibrium uptake due to desorption during the heat scan. However, the suppression of the glass transition temperature of PEEK illustrates the plasticization effect of the solvent.

The dynamic mechanical properties of amorphous PEEK were studied during ambient temperature immersion in organic solvents that promote crystallization. A sinusoidal strain was imposed on film specimens in three-point bend mode and the storage modulus, E' , was monitored as a function of temperature or time while immersed in solvent. Two *in-situ* experiments were performed, an isochronal (constant frequency, temperature sweep) and an isothermal (constant frequency, constant temperature) test. An isochronal test was utilized, on a PEEK film that was crystallized in a solvent at ambient temperature, to determine the T_g of the plasticized polymer. An isothermal test was developed to follow changes in the stiffness (E') of the polymer with immersion time in a solvent at a given temperature. This method is valid only if: (a) the T_g of the polymer-solvent system is between T_m and T_b of the solvent and, (b) the polymer has a high enough bending modulus to retain mechanical integrity above T_g .

2.5. Morphology

The crystal structure of thermal-induced PEEK crystals has been studied and reported in the literature. Dawson and Blundell⁵⁵ report the orthorhombic unit cell parameters to be $a = 7.75 \text{ \AA}$, $b = 5.86 \text{ \AA}$, and $c = 10.00 \text{ \AA}$. The molecules adopt a zig-zag conformation defined by their ether and carbonyl groups. The diffraction peaks are located at scattering angles of 18.7, 20.7, 22.6, and 28.7°, for (110), (113), (200), and (213) planes, respectively.

Blundell and Osborn¹ determined that thermally-crystallized PEEK exhibits spherulitic superstructure and to a first approximation, their data are consistent with a two-phase crystal/amorphous structure consisting of lamellae, whose thickness increases with crystallization temperature. Olley *et al.*⁵⁶ determined, via scanning electron microscopy, that PEEK crystallized isothermally from the glassy state exhibits smaller spherulites (in agreement with a higher nucleation density) and thinner lamellae than PEEK crystallized isothermally from the melt.

To date, only small-angle x-ray scattering has been utilized to estimate the size of the solvent-induced crystalline lamellae in PEEK.^{5,30} Kalika *et al.*³⁰ revealed markedly smaller long-spacings and a broader distribution of interlamellar thicknesses for solvent-crystallized specimens compared to specimens crystallized from the glassy state. Recently, it has been found that acetone vapor⁵ and dichloromethane vapor⁶ crystallize amorphous PEEK and the resultant crystals are of small dimensions and/or very disordered compared to thermal-induced crystals. Wolf *et al.*²⁹ determined from WAXS measurements that solvent-crystallized PEEK exhibited relatively broad diffraction peaks indicating small crystals.

It is expected that the superstructure of solvent-crystallized PEEK will be similar in nature to that of solvent-crystallized PET since both polymers are rigid, the unit cell structures are similar (i.e. orthorhombic), and the thermal properties are closely analogous¹. Desai and Wilkes²⁶ established the nature of the crystalline superstructure of unoriented, amorphous PET immersed in various organic solvents to be spherulitic. In addition, small-angle light scattering (SALS) patterns were obtained in the presence of solvent to verify that the spherulitic texture developed during the swelling process rather than during the desorption process. In all cases where spherulitic morphology was found, the average size of the spherulites showed weak temperature dependence and little change with different solvents. However, a slight increase in SALS pattern intensities were noted for the more interactive solvents; good solvents possibly enhance chain mobility and lead to more perfect packing and higher anisotropy. The small size of the spherulites formed from SINC, relative to those formed via thermal methods, can be explained in terms of the large degree of supercooling. One noteworthy conclusion from the SINC of PET is that similar crystalline superstructures were obtained for the range of

solvents studied regardless of the kinetics of sorption. This suggests that solvents that promote crystallization with different kinetics, regardless of the rate-limiting factor for crystallization, may have similar crystal sizes and morphological texture.

In this study, qualitative observations were made as to the fine structure of solvent-crystallized PEEK from WAXD and DSC data. The width of the diffraction peaks contains information about crystal size and perfection, photographic WAXD indicates the presence of orientation, and calorimetry spectra contain information about crystal size distribution. Atomic Force Microscopy was originally investigated to directly image the lamellae of solvent-crystallized PEEK. However, the images were not reproducible and Chapter 7 addresses this issue further.

3. EXPERIMENTAL

3.1. Materials

3.1.1. Poly(aryl ether ether ketone) (PEEK)

In the initial stages of the project, commercially extruded amorphous PEEK films were obtained from Westlake Plastics (Victrex®, grade 450). Orientation, high molecular weight, and the presence of additives and processing aids in the commercial films were undesirable characteristics for this study. Residual orientation induced by extrusion could be minimized by compression molding the films, but at the expense of adding another heat cycle to the material. PEEK degrades at temperatures above 385 °C; self-nucleation is suppressed but the polymer can exhibit decreases in the crystallization rate and in the attainable crystallinity depending on the environment (e.g. air or nitrogen) and the residence time in the melt.⁵⁷ Secondly, since molecular weight affects both the diffusion and crystallization rates, it was advantageous to obtain a low molecular weight grade to increase the kinetics of the SINC process.

Infrared analysis was performed to determine if any low molecular weight species leached out of the commercial films during solvent immersion. No significant species were found. Thermogravimetric results corroborated the infrared results since there was less than 0.3 % loss in mass below 300 °C. However, small percentages of nucleating agents, undetectable by these experiments, could drastically alter the crystallization kinetics of the polymer.

To eliminate the aforementioned experimental variables, a low molecular weight PEEK powder was obtained from ICI (Victrex®, grade 150PF). It had an intrinsic viscosity of ~0.15 Pa-s and weight and number average molecular weights of 33,500 and 11,700 g/mol, respectively. No known additives are present.

PEEK is used commercially in its semicrystalline form because the presence of crystals promotes enhanced stiffness, strength, and chemical resistance. For this study, however, it was necessary to start with an amorphous version of a semicrystalline

polymer to follow the development of SINC without restrictions on chain mobility and barriers to diffusion.

Unoriented, amorphous films (0.30-0.50 mm thickness) were prepared by compression molding powder at 400 °C for 15 minutes at 50 psi in a Carver Laboratory hot press. Air bubbles were removed by oscillating the pressure between 50 and 100 psi for 30 seconds before quenching the molten polymer plaque in ice water. The resultant films were visually transparent and no distinct crystalline diffraction peaks were observed via wide-angle x-ray diffraction. The glass transition and melting temperatures, as determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min, were 140 °C and 345 °C, respectively. The films were stored in a laboratory environment and tested within two months of processing.

3.1.2. Organic solvents

Literature studies show that amorphous PEEK absorbs insignificant amounts of protic solvents including water and aliphatic alcohols; swelling is minimal.⁷ These results suggest that the size of the solvent molecules, which could hamper the penetration of solvent in the polymer, does not dominate the sorption behavior. For example, water, which is the smallest of the molecules examined, yields the smallest amount of mass uptake (0.2 wt. % at ambient temperature) and degree of swelling and does not crystallize PEEK. Therefore, hydrogen bonding does not play a major role in the solvent-induced crystallization of PEEK. Small polar alkyl halides (e.g. methylene chloride, chloroform, and trichloroethane)⁴ and saturated ring structures containing similar chemical moieties as PEEK (e.g. tetrahydrofuran, benzene, and toluene)⁷ promote swelling and crystallization in amorphous PEEK. It is therefore proposed that dipole-dipole or acid-base interaction between the solvent molecules and polymer chains promote SINC of PEEK.

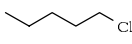
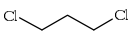
For this study, amorphous PEEK films were immersed in a series of aprotic organic solvents at ambient temperature to determine the effect of chemical structure on the overall SINC process. Important characteristics of the solvents, obtained from the Merck Index⁵⁸, are listed in Table 3.1. Dynamic solvent uptake experiments were

performed at 23 °C with all of the solvents listed. DMA and WAXD experiments were performed on THF, cyclopentanone, chlorobenzene, toluene, and diethyl ketone.

The ACS grade organic solvents, obtained from Aldrich, were selected for the following reasons: 1) four of the solvents (tetrahydrofuran (THF), chlorobenzene, toluene, and methylene chloride (MC)) have been shown in the literature to crystallize amorphous PEEK at ambient temperature, 2) each solvent possesses similar chemical moieties as PEEK (e.g. phenyl ring, ether or ketone linkages) or are acidic in nature (e.g. chlorinated solvents), 3) the series of solvents exhibits a systematic change in chemical structure, 4) the boiling temperatures are above ambient temperature and, 5) the melting temperatures are below the solvent-plasticized T_g of PEEK. The latter two reasons are necessary requirements for determining the glass transition via an *in-situ* dynamic mechanical technique.

Bulk property trends will be correlated to differences in solvent chemistry. The systematic changes in structure, as shown in Table 3.1, are as follows: (a) different phenyl substituents, (b) phenyl versus aliphatic halide, (c) saturated ring structures, ether versus ketone, with similar molar volumes, (d) ring versus aliphatic ketone with the same number of carbon atoms, and (e) dichlorinated aliphatic solvents with different hydrocarbon chain lengths.

Table 3.1 Characteristics of organic solvents utilized in this study.⁵⁸

Solvent	Chemical Structure	Molar Volume, V_m , (cm ³ /mol)	Density, 23 °C (g/cm ³)	Melting Point, T_m (°C)	Boiling Point, $T_{b,760}$ (°C)
ethylbenzene ^(a)		122.6	0.866	-95	136.25
toluene ^(a)		106.5	0.866	-95	110.6
chlorobenzene ^{(a),(b)}		101.8	1.107	-45	132
<i>n</i> -amyl chloride ^(b)		120.8	0.8828	-99	107.8
tetrahydrofuran ^(c)		81.1	0.8892	-108.5	66
cyclopentanone ^{(c),(d)}		88.5	0.9509	-58.2	130.6
diethyl ketone ^(d)		105.6	0.816	-42	101.5
methylene chloride ^(e)		64.0	1.3266	-95.1	40
1,3 dichloropropane ^(e)		95.1	1.1878	-99.5	120.4

3.2. Dynamic mass uptake

Wolf *et al.*⁷ found that the swelling of PEEK film in the presence of toluene is highly anisotropic with the largest dimensional change in the thickness direction (i.e. perpendicular to the plane of the film). In addition, a distinct sorption front can be seen via SEM. These results reinforce the idea that solvent diffusion is one-dimensional. Figure 3.1 illustrates the formation of a pseudo-composite during the sorption of solvent

through a film specimen where z_i is the initial film thickness and z_g is the thickness of the unpenetrated glassy region. The x and y directions are assumed to be identical.

The solvent molecules diffuse from the surface inwards causing the polymer to become highly plasticized. Diffusion into the plasticized region is rapid compared with diffusion into the unplasticized region, and a sharp boundary is created²⁵; a swollen rubbery region reinforced with SINC crystals develops behind the moving boundary. As immersion time increases, the glassy amorphous region diminishes and disappears once the sorption fronts meet in the middle of the film. However, sorption is not necessarily complete at this point; it has been shown for PET that a nontrivial amount of sorption can occur after the fronts have met.³⁶ This observation implies that a steep but finite gradient in concentration exists at the liquid front-dry polymer interface. This situation is shown schematically in Figure 3.2.

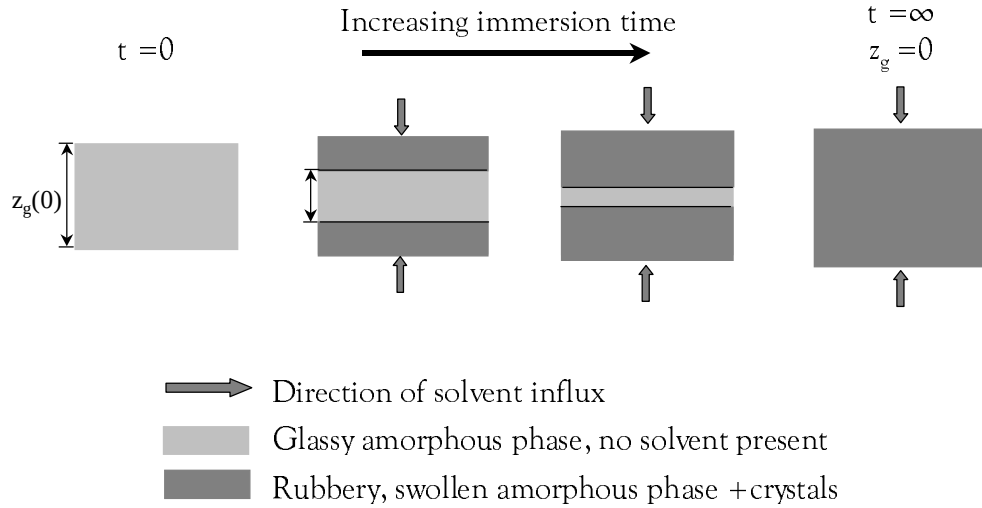


Figure 3.1 Film cross-sections illustrating solvent front location with immersion time.

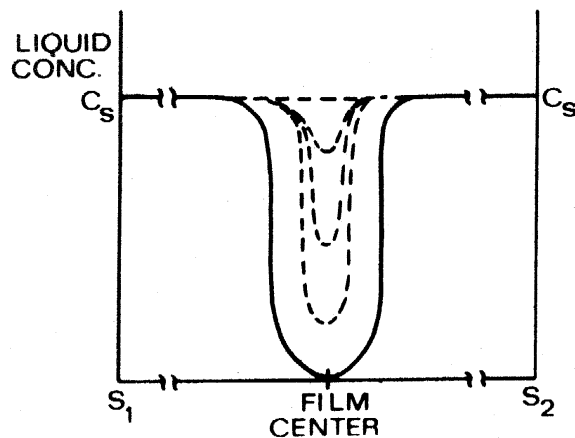


Figure 3.2 A schematic of the potential liquid concentration distribution near the film center as the diffusion process nears completion.³⁶

Film specimens are placed in vials of solvent at room temperature, periodically removed, blotted with a tissue to remove excess solvent, and weighed using a Mettler AE50 millibalance. The entire weighing process takes less than 30 seconds to minimize solvent evaporation. Solvent uptake is calculated as

$$\% \text{ solvent} = \frac{[M_t - M(0)]}{M(0)} \times 100 \quad \text{Equation 3.1}$$

where M_t is the mass at time t and $M(0)$ is the initial mass.

Mass uptake data is plotted as a function of immersion time normalized to the film thickness. This universal time-scale is necessary because the sorption is proportional to the film thickness in the range of 0.30 to 0.50 mm; the greater the film thickness, the longer the time to reach equilibrium sorption. For comparison purposes in this research, the diffusion process is assumed to be Fickian and the mass uptake is plotted as a function of $\sqrt{t}$; for all solvents studied, the sorption is linear with $\sqrt{t}$ during short immersion times. The experimental rate of sorption, r_s^* , is the slope of a linear fit to the data in the initial stage of uptake. Figure 3.3 illustrates a case where the sorption is linear with $\sqrt{t}$ prior to reaching a maximum mass uptake, M_m . To estimate a diffusion coefficient, with units of m^2/sec , Equation 2.7 can be rewritten as

$$D_z = \frac{\pi}{16} \frac{(r_s^*)^2}{M_m^2} \quad \text{Equation 3.2}$$

where r_s^* has units of $\%-m/\text{sec}^{1/2}$.

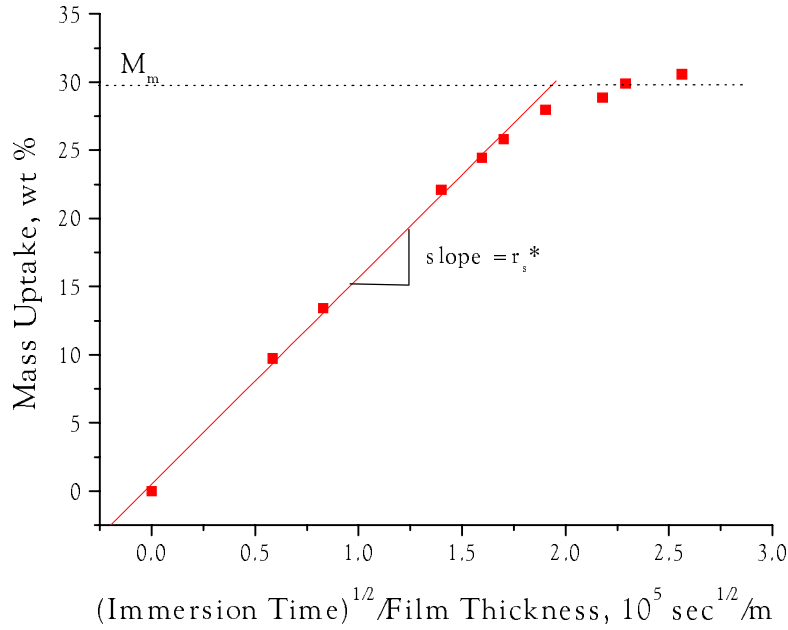


Figure 3.3 Solvent uptake plot for amorphous PEEK immersed in THF at 23 °C.

3.3. Wide-angle x-ray diffraction (WAXD)

Separate pieces of amorphous PEEK films are immersed in a solvent at ambient temperature for given amounts of time to attain a specific level of sorption between initial immersion and equilibrium saturation (i.e. maximum in the mass uptake). Sorption and crystallinity values were calculated from a series of 15-20 individual film specimens, each representative of the state of amorphous PEEK at a specific point in time during sorption. For each film specimen, the immersion time was calculated from the value of normalized time, representing a given mass uptake, multiplied by the film thickness.

Upon removal from the solvent, the films were weighed to get a mass uptake then air dried for 24 hours followed by drying for several days at 50 °C to minimize the amount of residual solvent prior to WAXD analysis. The solvent uptake data from the dynamic uptake experiment was found to coincide with the WAXD specimen uptake data (Figure 3.4). This confirms that the normalized time-scale represents a universal time-scale for sorption.

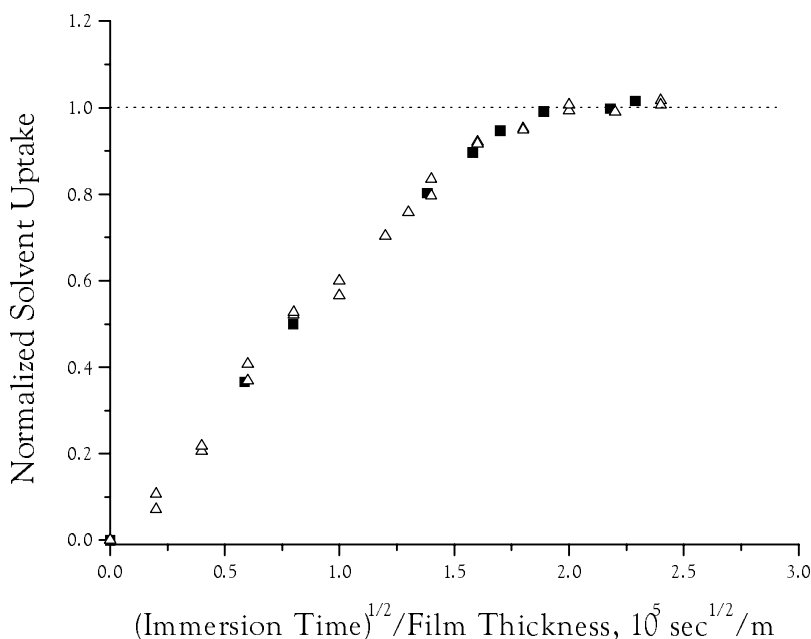


Figure 3.4 Dynamic uptake data for THF in amorphous PEEK from a single specimen (■) and from individual WAXS specimens (Δ).

WAXD profiles were obtained for each film specimen using a Rigaku Ultima+ x-ray diffractometer equipped with a monochromator (1.0/1.0/0.15 mm slits). Symmetric θ -2 θ scans were performed at room temperature in transmission mode for scattering angles of 10 to 35 degrees and fixed time steps at 0.6 °/min and 0.04° intervals. Amorphous PEEK was analyzed to obtain an amorphous reference spectrum (i.e. a broad halo indicative of short-range order). The amorphous spectrum was scaled to each individual diffraction spectrum via a similar technique used by Justi *et al.*⁵⁰ Figure 3.5 is

a schematic showing the contribution of the amorphous and crystalline portions to the diffraction spectrum.

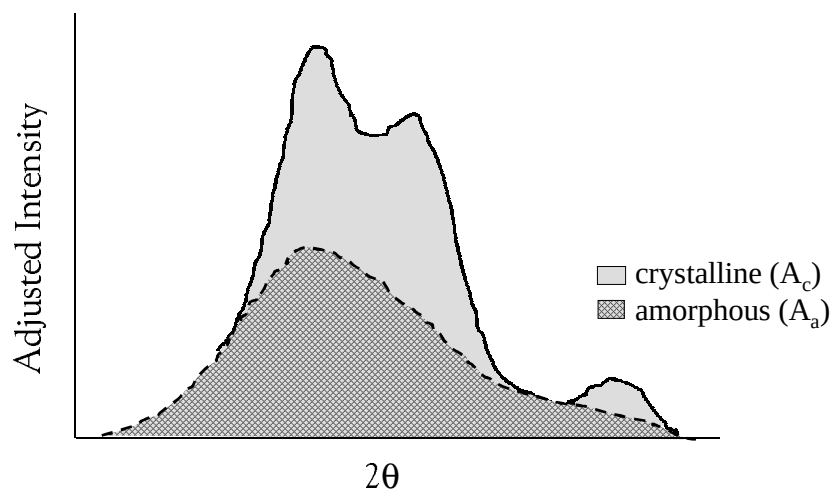


Figure 3.5 Schematic overlay of diffraction spectra for solvent-crystallized PEEK and amorphous PEEK.

An index of crystallinity, CI, was calculated from a ratio of the areas under the curves

$$CI = \frac{A_c}{A_c + A_a} \quad \text{Equation 3.3}$$

A_c and A_a represent the integrated areas under the crystalline and amorphous WAXD patterns, respectively. The crystallinity index was plotted on the same normalized time-scale as the mass uptake data.

3.4. Differential scanning calorimetry (DSC)

DSC was used as an alternate method for determining relative changes in crystallinity. DSC scans were performed on the same film pieces used for WAXD. Scans were performed on a Perkin-Elmer Pyris1 DSC at a heating rate of 100 °C/min to limit structural reorganization on heating⁵⁹; slow heating rates may lead to an increase in

the degree of crystallinity during the heat scan. The temperature range was 50 °C to 400 °C and the purge gas was nitrogen with a flow rate of 20 ml/min. The temperature and heat-flow were calibrated with pure standards of indium and zinc using the same heating rate.

Figure 3.6 shows the effect of heating rate on the thermodynamic transitions of amorphous PEEK. Note that increasing the heating rate does not significantly change the crystallization and melting enthalpy or the location of the melt peak. The faster heating rate does raise the crystallization peak temperature due to rate effects on the mobility of the polymer chains.

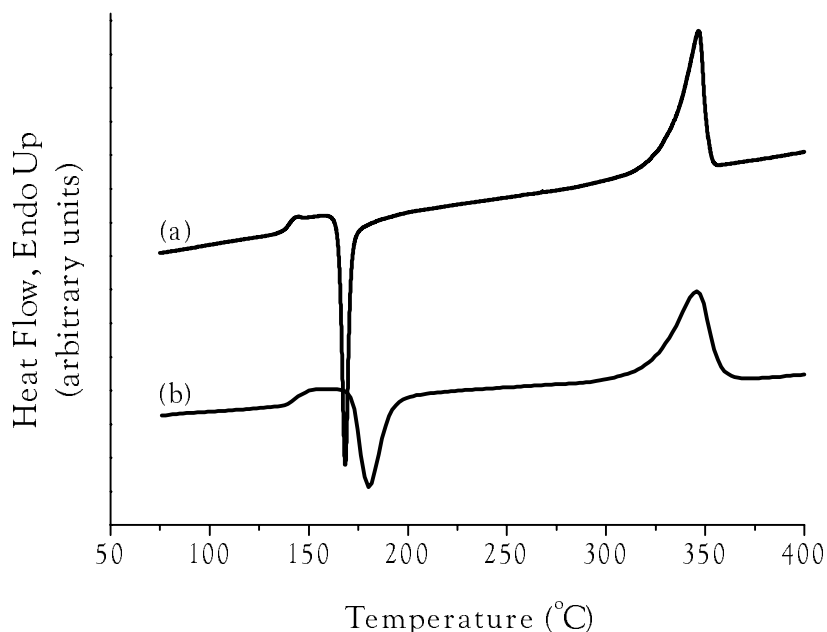


Figure 3.6 DSC plot of amorphous PEEK at (a) 10 °C/min and (b) 100 °C/min.

The standard method to evaluate the crystallinity of a polymer via DSC is to subtract the heat of crystallization from the heat of melting and divide by the theoretical heat of fusion per gram for a 100 % crystalline version of the polymer. However, absolute crystallinity indices could not be obtained in this study because of the presence of multiple melting and recrystallization phenomena in the melting range (300-350 °C).

Therefore, the enthalpy of crystallization was used as a measure of crystallinity. As shown in Figure 3.7, the enthalpy decreases with immersion time indicating the development of solvent-induced crystallinity.

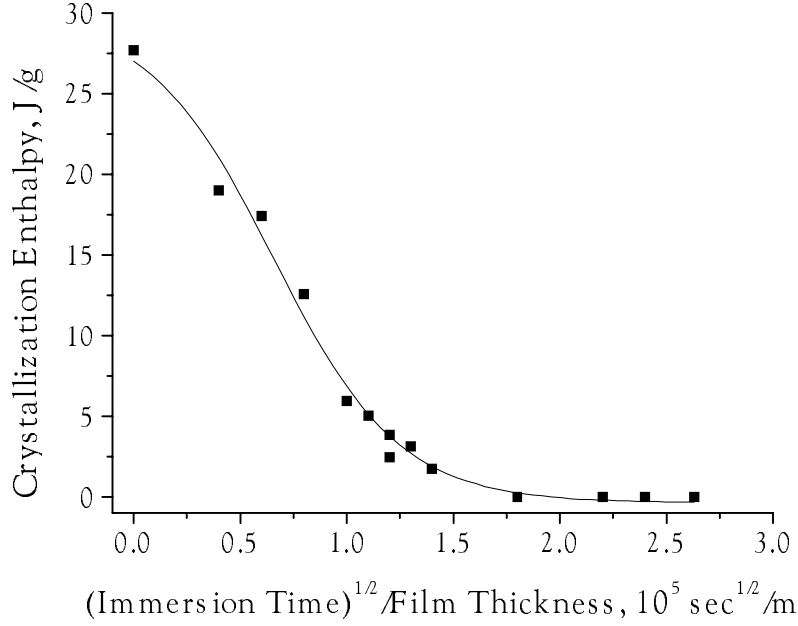


Figure 3.7 Plot of the crystallization enthalpy of PEEK with immersion time in THF.

To compare DSC and WAXD results, it is necessary to present the data in a normalized form. Therefore, the enthalpy of crystallization, $\Delta H_c(t)$, is normalized to the enthalpy of crystallization for a completely amorphous PEEK specimen, $\Delta H_c(0)$. The normalized crystallinity index is calculated as

$$1 - \frac{\Delta H_c(t)}{\Delta H_c(0)} \quad \text{Equation 3.4}$$

The normalized crystallinity index is plotted as a function of immersion time as shown in Figure 3.8. Maximum crystallinity is reached when the value becomes 1.0.

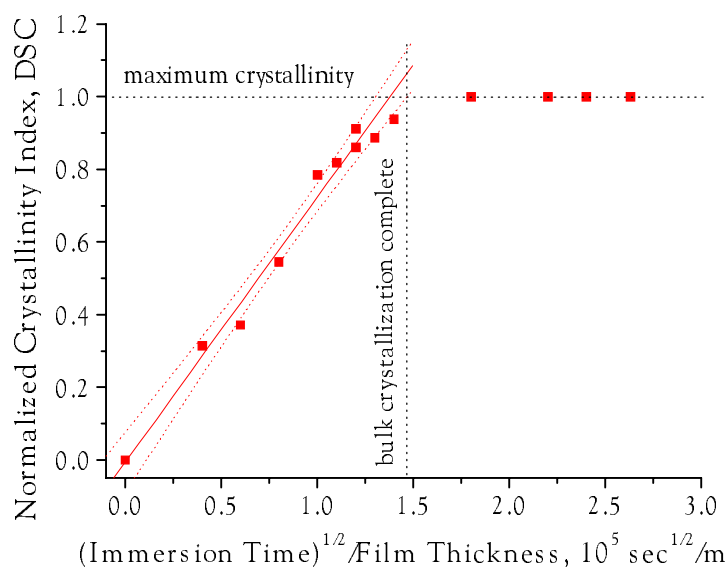


Figure 3.8 Plot of normalized crystallinity index calculated from DSC data versus normalized immersion time in THF at 23 °C. The dashed lines represent the 95% confidence interval of the linear fit.

3.5. Dynamic mechanical analysis (DMA)

A Perkin-Elmer DMA-7, as shown in Figure 3.9a, equipped with a solvent sleeve attachment, was used to analyze the glass transition and follow changes in the storage modulus, $E'(t \text{ or } T)$, of PEEK while immersed in solvent. The three-point bending fixture, as shown in Figure 3.9b, consists of a 5 mm platform and a knife-edge probe that oscillates in the z-direction. A frequency of 1.0 Hz was chosen to minimize viscous drag and inertial effects of the fluid on the film specimens. Complete immersion of the sample stage occurs with the furnace assembly in the raised position; a stainless steel cylinder filled with solvent fits directly into the furnace opening.

Dynamic and static controls were enforced at the beginning of each test run to maintain displacement through the glass transition and to ensure continuous contact between the probe tip and the specimen. The static force was set at a value 20 % higher than the dynamic force and the amplitude of the dynamic displacement was held constant at 10.0 μm . An isochronal (i.e. constant frequency) scan was performed with a heating

rate of 2 °C/min between the melting and boiling points of the solvent (T_m and T_b , respectively) (Table 3.1.).

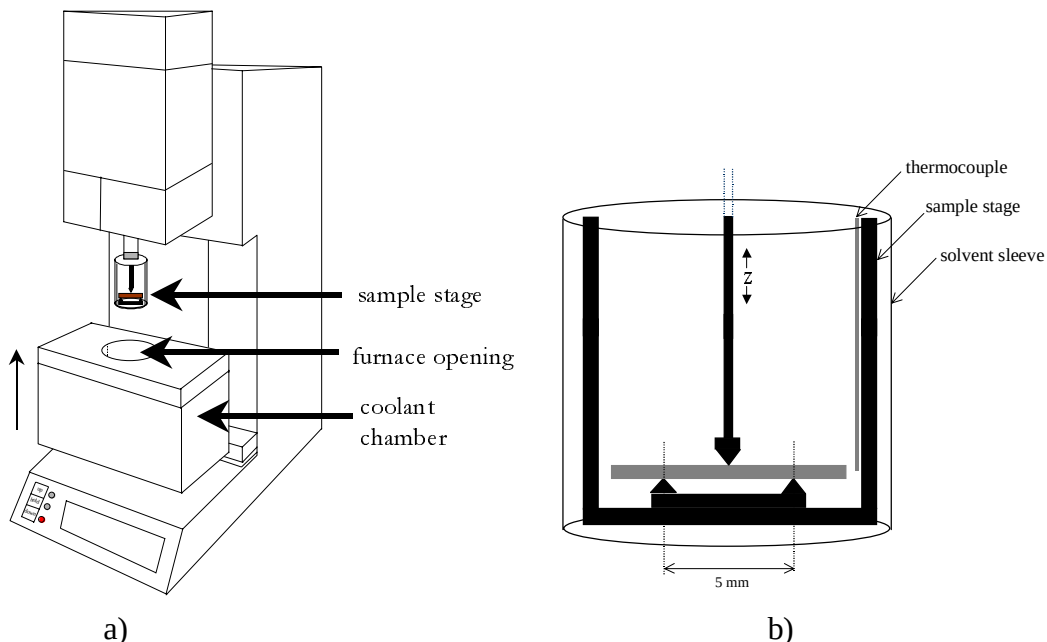


Figure 3.9 Schematic of the Perkin-Elmer DMA-7 a) analyzer and b) sample stage.

3.5.1. Isochronal Scan

The purpose of this experiment was to analyze the glass transition of PEEK/solvent systems at equilibrium solvent uptake (refer to the scenario in Figure 3.1 where $t = \infty$). Specimens are removed from their vial of solvent, transferred to the DMA, re-immersed in solvent via the solvent sleeve, and given time to re-equilibrate in the solvent prior to testing. Long-range molecular mobility of PEEK was characterized as a function of solvent type and solvent content by heating the PEEK/solvent systems between the freezing and boiling points of the solvent at 2 °C/min. The location, magnitude, and breadth of the glass transition exhibit the effects of plasticization and crystallization. The glass transition of the saturated polymer, defined as a temperature range spanning from the peak in E'' to the peak in $\tan\delta$, should be detected at or below the immersion temperature for crystallization to be thermodynamically feasible.

The T_g of amorphous PEEK was difficult to obtain in three-point bend mode because the polymer loses its mechanical stability when heated through T_g . Subsequently, PEEK was molded directly onto an aluminum sheet (0.5 mm thickness) to add the necessary rigidity and the glass transition was determined to be between 150-159 °C as shown in Figure 3.10a. This value is approximately 10 °C higher than the DSC value, as expected, due to frequency effects. Figure 3.10b shows that the storage modulus increases after T_g due to crystallization from the glassy state during the DMA scan.

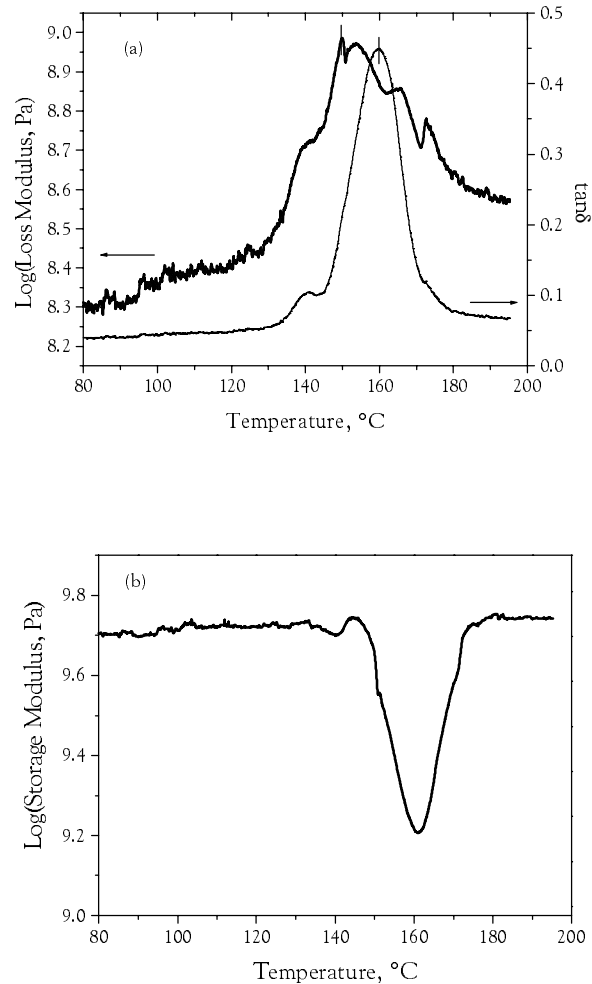


Figure 3.10 DMA isochronal scan of amorphous PEEK showing the (a) analysis of the glass transition (from E'' and $\tan\delta$) and (b) storage modulus when heating through T_g .

3.5.2. Isothermal Scan

Changes in the storage/elastic modulus, E' , are followed as a function of immersion time (i.e. solvent content) for all solvents at ambient temperature. Only the PEEK/THF system was tested at a different temperature, 5 °C, to show the effect of temperature on the kinetics of SINC. The isothermal tests were initiated on a dry, amorphous film at ambient temperature to obtain a glassy modulus. After a few minutes into the test, the furnace assembly was raised and the entire sample stage and thermocouple were immersed in solvent. The storage modulus was monitored *in-situ* as a function of immersion/diffusion time. The time-dependent moduli, $E'(t)$, were normalized to the reference modulus, $E'(0)$, and plotted on the same normalized time-scale as the solvent uptake data for comparison purposes (Figure 3.11). In general, decreases in $E'(t)$ are attributed to plasticization, degradation, or dissolution, whereas increases in $E'(t)$ are attributed to reinforcing phenomena such as crosslinking or crystallization.

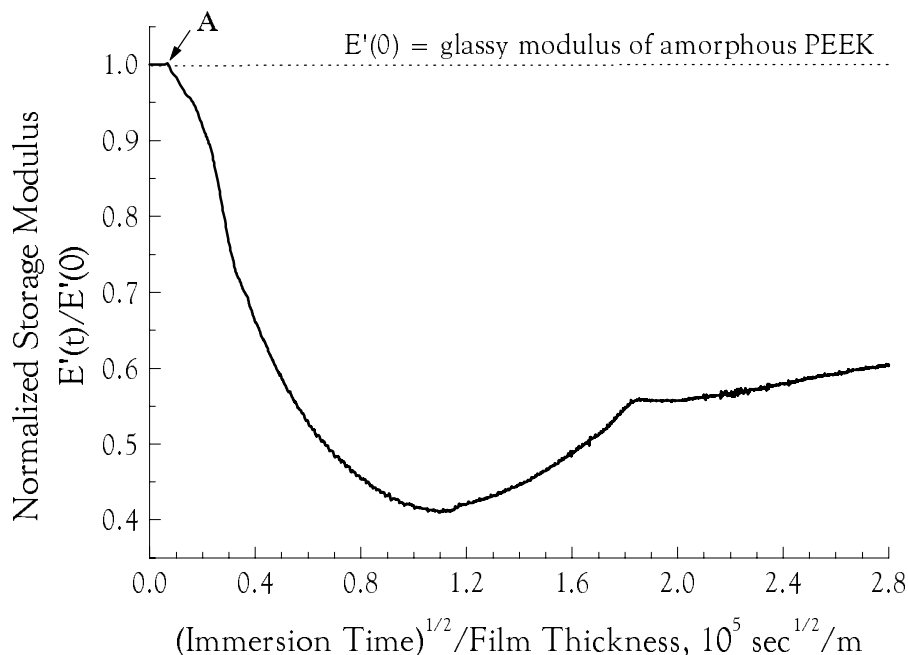


Figure 3.11 Isothermal DMA scan of amorphous PEEK immersed in THF at 23 °C. The solvent is introduced at A, after a stable glassy modulus is obtained.

3.6. Scanning electron microscopy

One PEEK/solvent system was used to analyze the progression of the sorption front with immersion time. The WAXD specimens from the THF immersion at 23 °C were prepared for SEM analysis. Each film specimen was scored with a razor blade and fractured in liquid nitrogen. The specimens were placed in a potassium permanganate solution described by Olley *et al.*⁵⁶ to etch away the top layer of the fractured surface. The surface was sputtered with 300 Å of gold and the stainless steel specimen fixture was grounded with silver paint to help minimize charging effects in the SEM. The ISI-SX-40 SEM was operated at 20 kV with a 10 mm working distance to image the fracture surfaces.

Aside from the location of the solvent front, interesting crack patterns were observed via SEM (Figure 3.12). The cracking behavior was attributed to residual stresses in the films as a result of the tremendous volume changes that have occurred in the polymer. Swelling causes expansion while crystallization leads to shrinkage (i.e. the density of PEEK increases upon crystallization). Prior to etching, solvent is removed; deplasticization causes the swollen regions to shrink leaving the boundary between the swollen and unpenetrated glassy regions in tension. There is a discontinuity at the interface between the swollen and the unpenetrated glassy regions causing the two regions to be in different stress states.

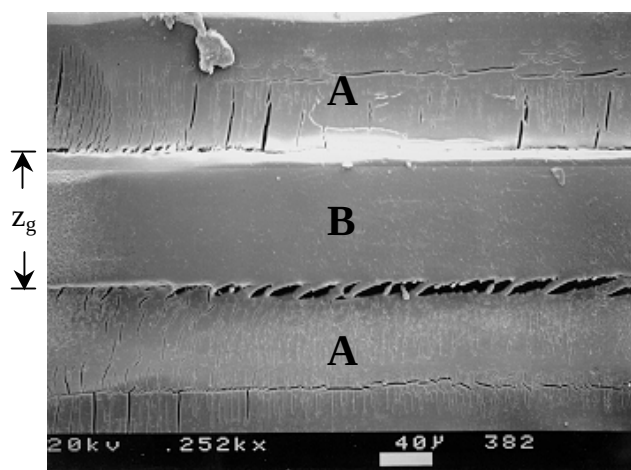


Figure 3.12 SEM image of a cross-section of PEEK film through the thickness (350 µm). The boundary between region A and B represents the progression of THF into the film during immersion where region B is the glassy, amorphous polymer of thickness z_g .

The relative penetration depth, $Z'(t)$, was calculated as

$$Z'(t) = 1 - \left(\frac{z_g(t)}{z_0} \right) \quad \text{Equation 3.5}$$

where $z_g(t)$ is defined as the thickness of the unswollen amorphous region located in the center of the polymer film. The relative penetration depth is zero prior to solvent penetration of the surface layers and 1.0 when the sorption fronts meet in the center of the film (i.e. $Z'(\infty) = z_0/2$). The films may continue to absorb solvent even after the sorption fronts have met; the disappearance of the glassy zone does not ensure that the film is at equilibrium saturation.

4. RESULTS

This chapter presents important experimental results from the characterization of SINC in amorphous PEEK. The kinetics of sorption, the solubility, and pseudo-Fickian diffusion coefficients were obtained from dynamic uptake experiments. The bulk crystallization kinetics and crystalline indices were determined from wide-angle x-ray diffraction. Differential scanning calorimetry was used as a secondary method to follow changes in crystallinity with immersion time. *In-situ* isochronal and isothermal DMA techniques were utilized to determine the effect of solvents on the glass transition and the storage modulus of PEEK, respectively. The progression of the solvent front through the film thickness was observed via SEM.

4.1. Dynamic Mass Uptake

Dynamic mass uptake curves are shown in Figure 4.1. Amorphous PEEK absorbs each solvent at a different rate (r_s^*) and to a different extent (M_m) depending on specific polymer-solvent interactions. A comparison was made between four sets of solvents, as described in Table 3.1 of Chapter 3, and the data is shown in Figures 4.2-4.5 and summarized in Tables 4.1-4.2. The data were fit to a Boltzman function and the 95% confidence bands, shown as dashed lines, represent the precision of the curve fits. These results illustrate how simple variations in the polarity/acidity and/or structure of the solvent can significantly change the sorption kinetics and the solubility in amorphous PEEK. All of the small molecule ethers, ketones, and substituted benzenes (e.g. THF, cyclopentanone, chlorobenzene, toluene, and diethylketone) used in this study promoted some degree of sorption, swelling, and crystallization of amorphous PEEK at ambient temperature. The interactions are thought to be acid/base in nature.

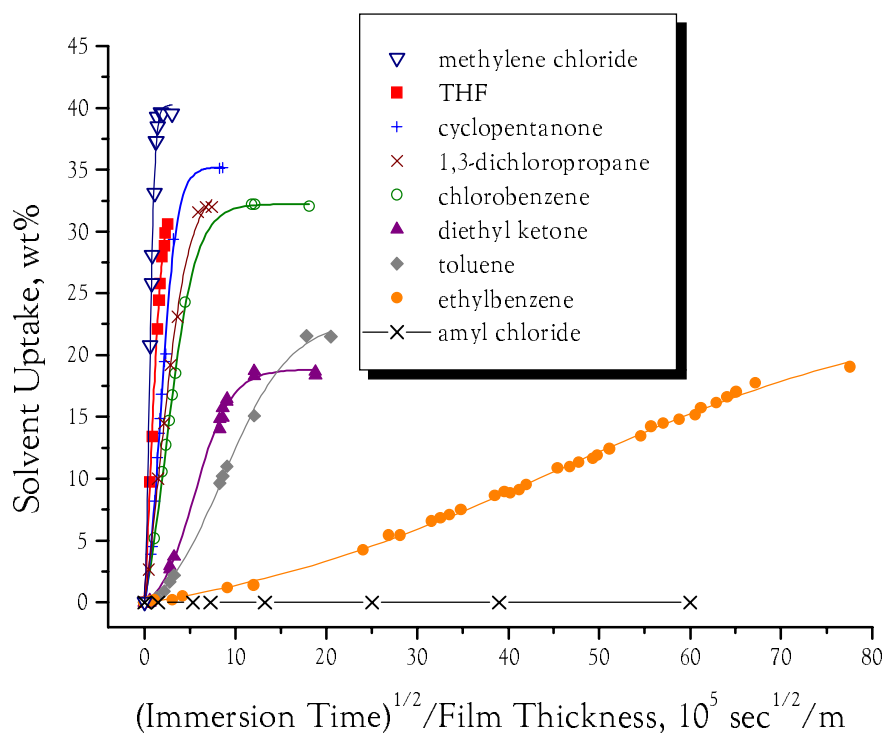


Figure 4.1 Dynamic solvent uptakes in amorphous PEEK films at 23 °C.

Stuart and Williams⁴ interpreted the effect of certain chlorinated hydrocarbons on PEEK in terms of Lewis acid-base interactions between the polymer and the solvent. PEEK acts as a soft base, due to the ether, carbonyl, and aromatic groups along the backbone which act as electron donors. They concluded that the chlorinated solvents affect PEEK to varying degrees depending on their relative acidities. In this research it was found that amyl chloride, a linear chlorinated solvent, did not show any significant interactions with PEEK; amorphous PEEK did not absorb amyl chloride at ambient temperature (Figure 4.2a). This could be because the hexane chain can assume many conformations⁶⁰, which may cause the substituent chain to physically shield the acid sites on the solvent from interacting with the basic sites on PEEK. However, solvents such as methylene chloride and 1,3-dichloropropane promote rapid swelling and crystallization of amorphous PEEK (Figure 4.2b). These solvents possess more acidic sites for interactions

to occur and they have smaller molar volumes than amyl chloride; the hydrogen atoms adjacent to the chlorine atoms are partially positive due to inductance effects.⁶⁰

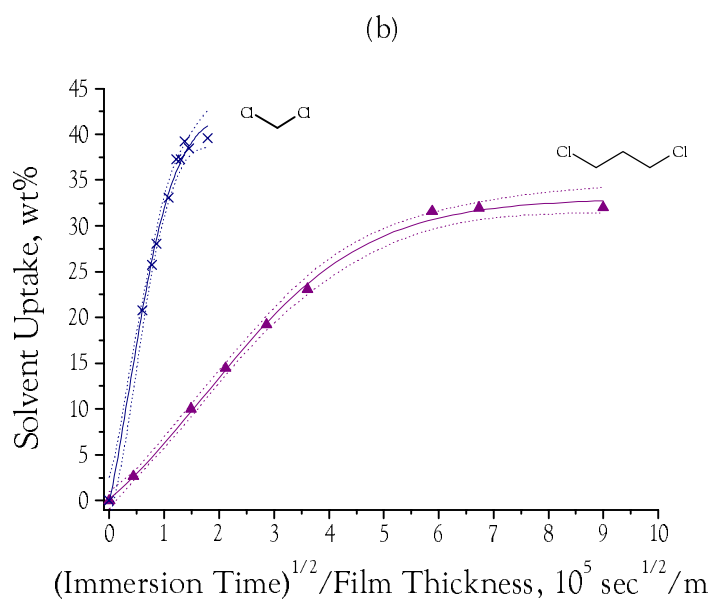
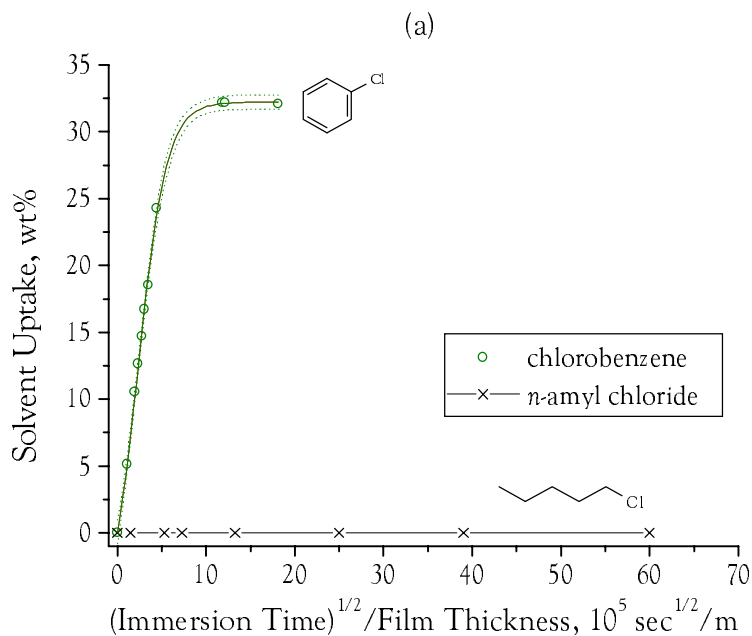


Figure 4.2 Mass uptake of (a) monochlorinated and (b) dichlorinated solvents in amorphous PEEK at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

For the benzene-derivative solvents (e.g. toluene and ethylbenzene), the rate of transport and the degree of interaction with PEEK decrease with the chain length of the hydrocarbon substituent, or an increase in the molar volume of the solvent. The geometry of the penetrating molecule may play a major role in the transport into the polymer. The chlorine atom in chlorobenzene is electron withdrawing; the phenyl hydrogens are acidic primarily because of inductive effects.⁶⁰ The sorption rate (r_s^*) and mole fraction solvent absorbed per polymer repeat unit, as shown in Figure 4.3, were observed as follows: ethylbenzene < toluene < chlorobenzene.

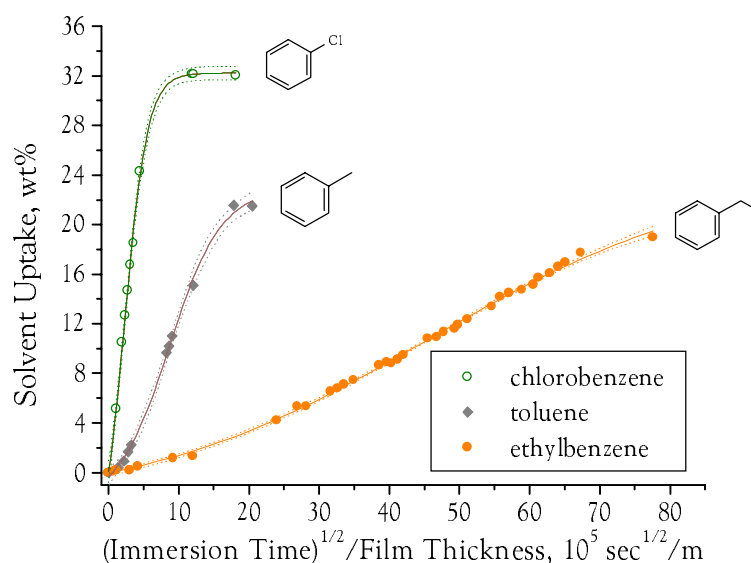


Figure 4.3 Comparison mass uptake plot for benzene derivatives. The dashed lines represent the 95% confidence interval of the curve fit.

Aliphatic and cyclic solvents with ether and ketone linkages exhibited significant differences in the nature of their sorption behavior (Figure 4.4-4.5). The hydrogen atoms in THF are acidic due to an inductive effect from the oxygen atom; the oxygen atom is partially negative and the hydrogen atoms are partially positive. The carbon atom bonded to the oxygen atom in cyclopentanone possesses a positive charge and the hydrogen atoms on the adjacent carbons are partially positive.⁶⁰ However, the acid sites on

cyclopentanone are less accessible for interactions because of steric hindrance from the oxygen atom. In the case of diethyl ketone, the aliphatic ethyl groups on the carbonyl carbon can assume conformations that physically shield the acid sites. The sorption rate (r_s^*) and mole fraction solvent absorbed per polymer repeat unit were observed as follows: THF > cyclopentanone >> diethyl ketone.

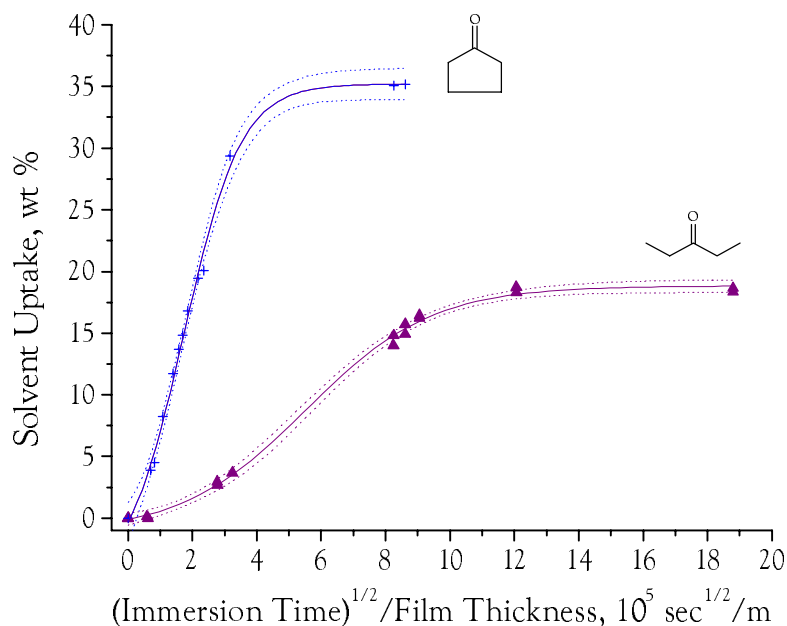


Figure 4.4 Mass uptake of aliphatic and cyclic ketones at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

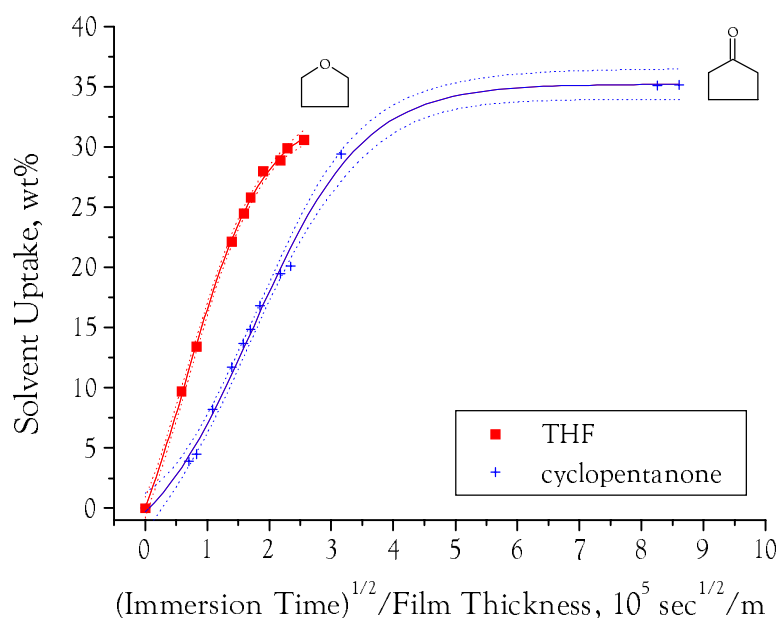


Figure 4.5 Mass uptake of cyclic solvents (ether versus ketone) at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

The nature of the sorption process was assumed to be pseudo-Fickian, for comparison purposes, to calculate diffusion coefficients for each PEEK/solvent system. The term “pseudo” is used when sorption varies with the square root of time but the criteria are not met for ideal Fickian diffusion. However, the calculated n values, obtained from a log-log plot of fractional weight gain (M_t/M_m) versus time (refer to Equation 2.9), suggest that most of the solvents exhibit anomalous behavior (i.e. $0.5 < n < 1.0$) at ambient temperature (Figure 4.6-4.8). It was found that the solvents that promoted the greatest extent of plasticization at the fastest rates exhibited pseudo-Fickian sorption (i.e. chlorobenzene, THF, MC, and 1,3-dichloropropane). Within each series of solvents (i.e. benzene derivatives, ketones, and dichlorinated alkanes), the shift from anomalous transport behavior to pseudo-Fickian is observed (via a decrease in the n value towards 0.5) as the degree of polymer-solvent interactions increases.

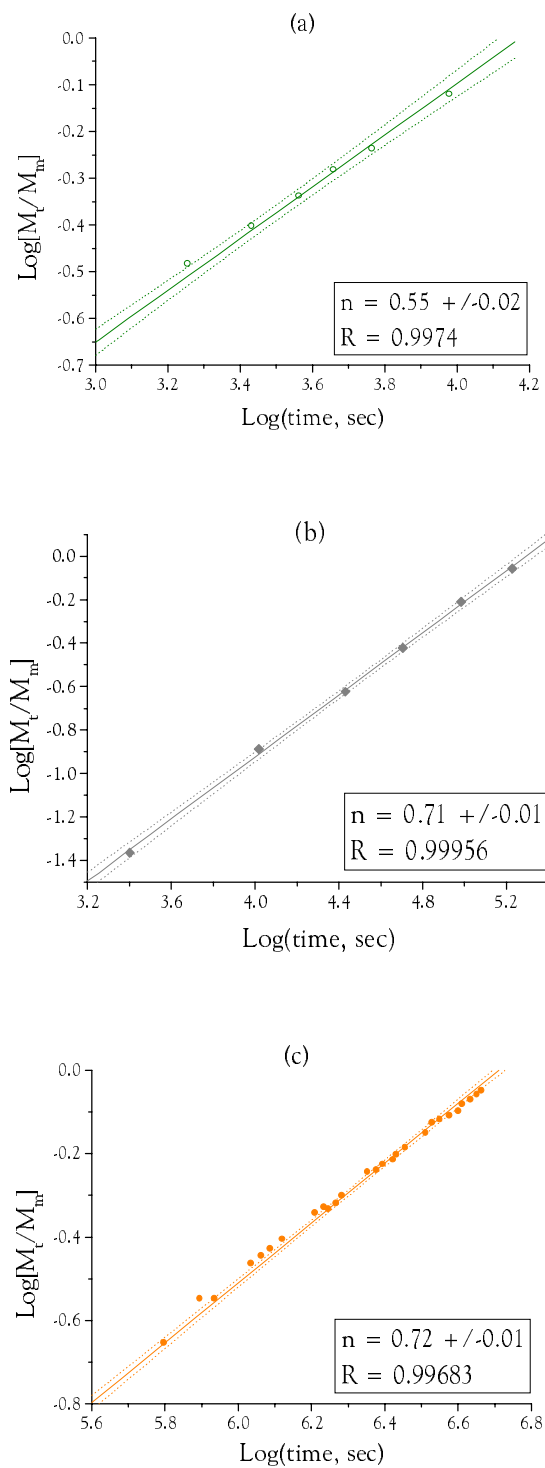


Figure 4.6 Determination of n for benzene derivative solvents: (a) chlorobenzene, (b) toluene, and (c) ethylbenzene. The dashed lines represent the 95% confidence interval of the curve fit.

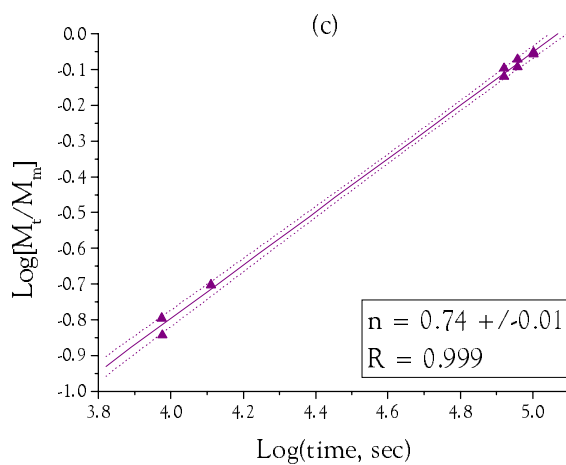
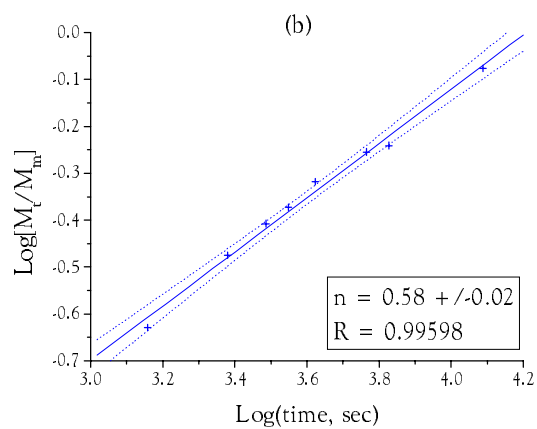
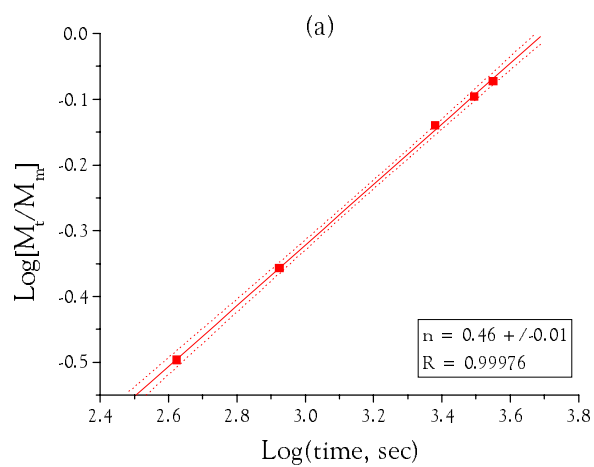


Figure 4.7 Determination of n for solvents with ether and ketone groups: (a) THF, (b) cyclopentanone, and (c) diethyl ketone. The dashed lines represent the 95% confidence interval of the curve fit.

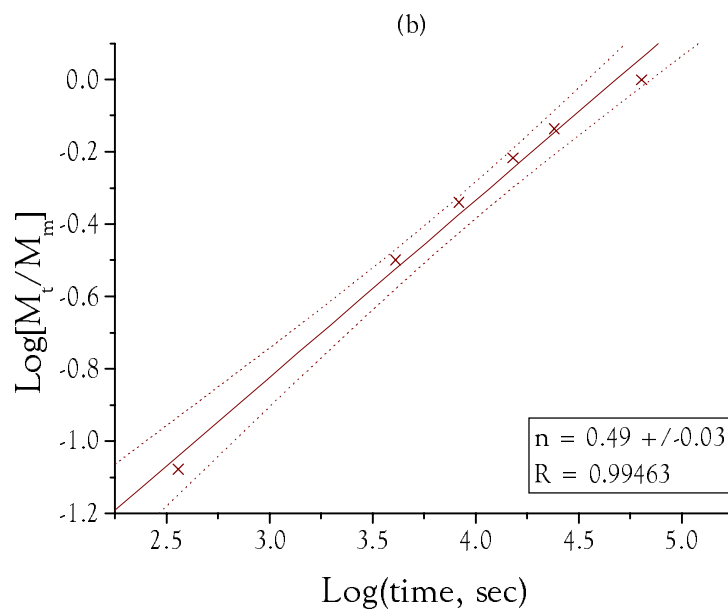
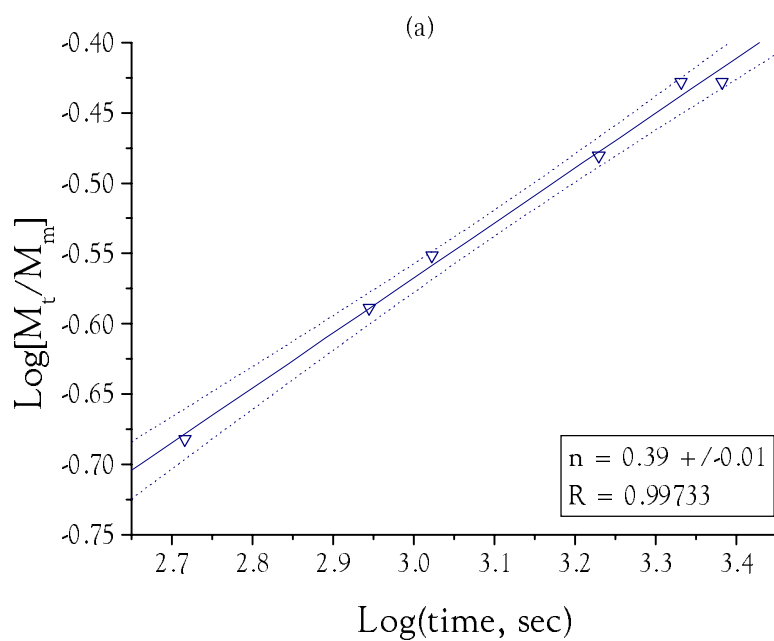


Figure 4.8 Determination of n for aliphatic dichlorinated alkanes: (a) methylene chloride and (b) 1,3-dichloropropane. The dashed lines represent the 95% confidence interval of the curve fit.

The sorption of THF in amorphous PEEK was performed at ambient temperature and 5°C to show the effect of temperature on the nature of solvent transport (Figure 4.9). By lowering the sorption temperature, it was found that the sorption behavior changed from pseudo-Fickian to anomalous (Figure 4.10). In other words, the controlling transport mechanism shifted from diffusive resistance in the swollen shell to chain relaxation at the boundary with a decrease in sorption temperature.²⁵ The activation energy of the diffusive mechanism is lower than that of chain relaxation; the rate of viscoelastic response to osmotic stresses decreases more than the diffusion rate with decreasing temperature.

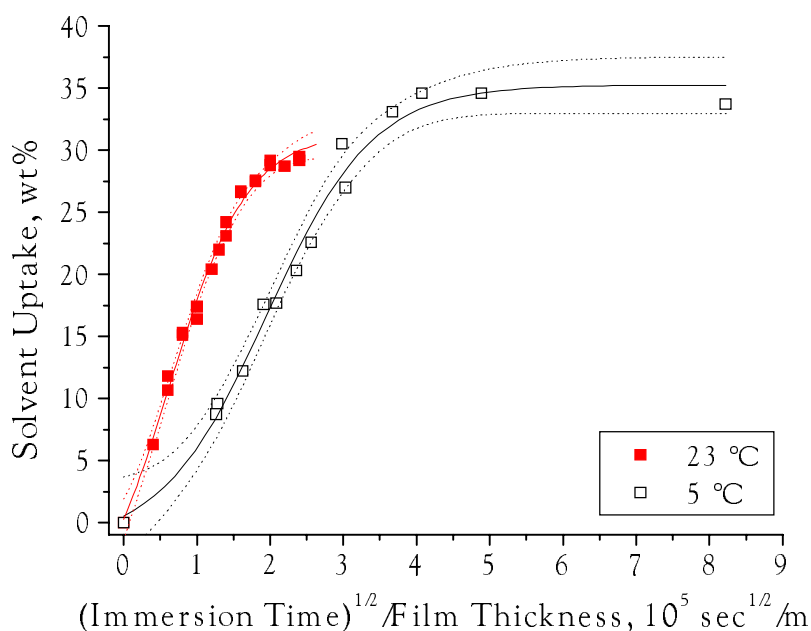


Figure 4.9 Mass uptake of THF at ambient temperature versus 5 °C. The dashed lines represent the 95% confidence interval of the curve fit.

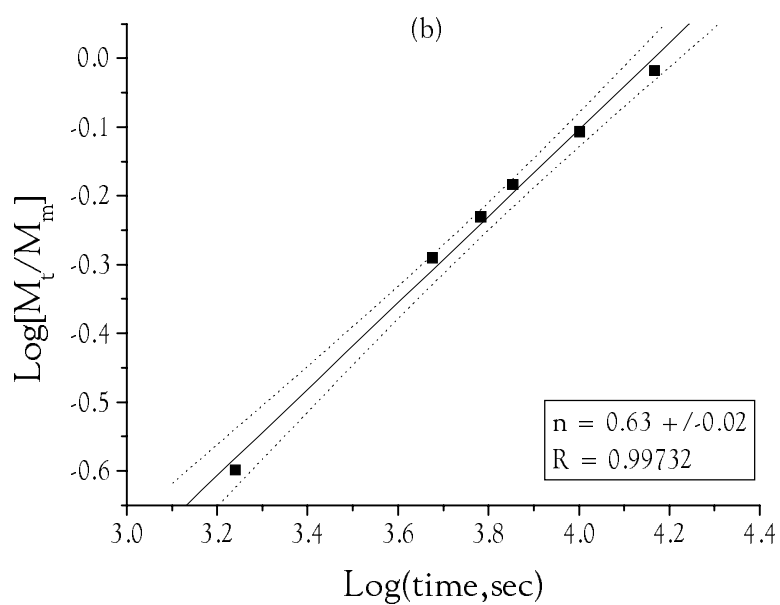
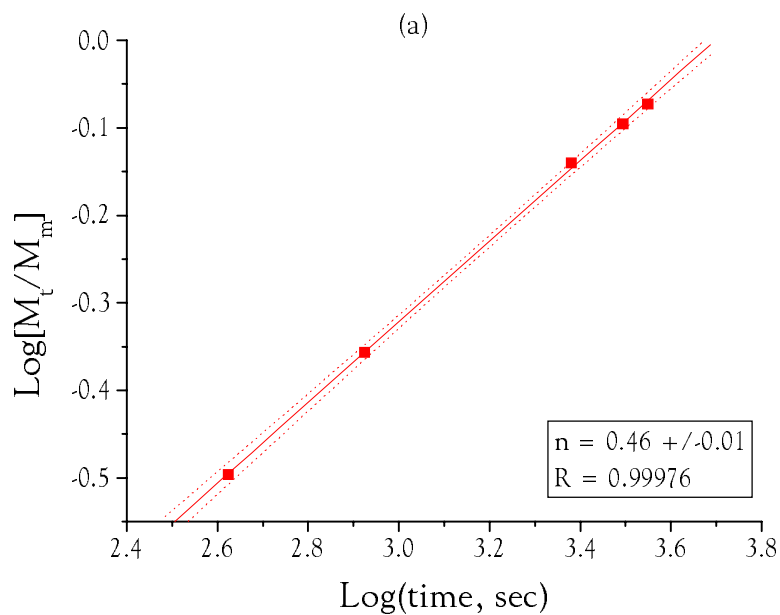


Figure 4.10 Plot to determine n for THF sorption at temperatures of (a) 23 °C (b) 5 °C. The dashed lines represent the 95% confidence interval of the curve fit.

A rate of sorption, r_s^* was calculated for each PEEK/solvent system from the slope of the mass uptake plot as described in Section 3.2 and shown in Figures 4.12-4.19. Several of the solvent systems exhibited an induction period in the beginning stages of sorption that was not linear with the square root of time. Similarly, these systems were found to have n values indicative of anomalous transport behavior.

Assuming pseudo-Fickian behavior for comparison purposes, the average diffusion coefficients were calculated to be in the range of 10^{-14} to 10^{-11} m²/s. Wolf and Grayson⁷ determined that the diffusion coefficient for toluene in amorphous PEEK at 35 °C was 0.16×10^{-12} m²/s, approximately an order of magnitude smaller than the value calculated in this study at 23 °C. Intuitively the diffusivity should increase with temperature. However, Wolf and Grayson used the film half thickness for z_0 in Equation 2.6 thereby decreasing D_z by a factor of four. In addition, they studied the diffusivity in a higher molecular weight amorphous PEEK film; increasing the molecular weight may lead to a lower diffusivity.

For the benzene-derivative solvents, the diffusion coefficient was two orders of magnitude smaller for ethylbenzene than for toluene, presumably due to an increase in the chain length of the phenyl substituent. Of the solvents with ketone character, amorphous PEEK absorbed half as much of the aliphatic ketone (diethyl ketone) than the cyclic ketone (cyclopentanone). The diffusivity of the cyclic ether (THF) in PEEK was three times faster than the diffusivity of cyclopentanone. Interestingly, a larger mole fraction of solvent per repeat unit of amorphous PEEK correlated to a higher rate of sorption and diffusivity. In addition, there was an exponentially decreasing trend in the rate of sorption with increasing solvent molar volume as shown in Figure 4.11. The equation used to generate the curve fit was

$$(r_s^*)^2 \approx 100e^{\frac{-V_m}{13}} \quad \text{Equation 4.1}$$

which provides an approximate empirical correlation between r_s^* and V_m . However, no clear distinction could be made between solvents, in terms of SINC promotion, based solely upon molar volume.

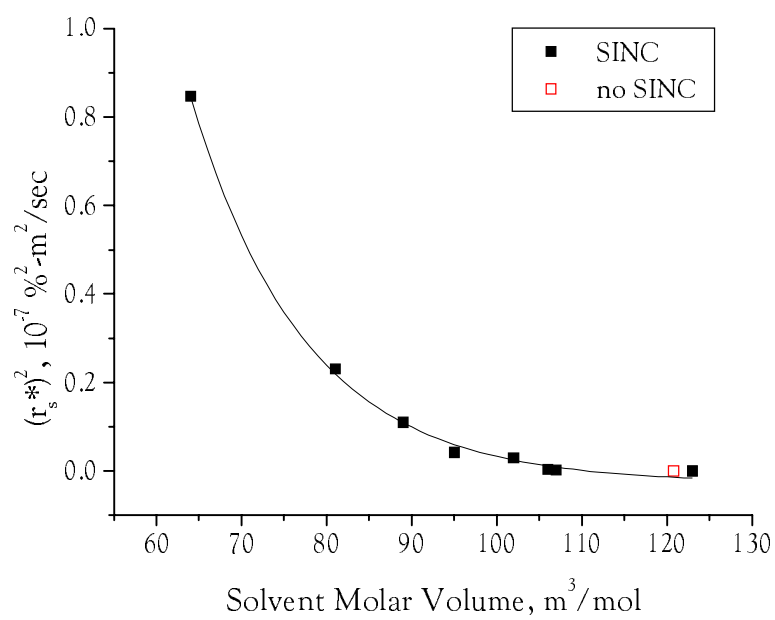


Figure 4.11 Rate of sorption as a function of solvent molar volume.

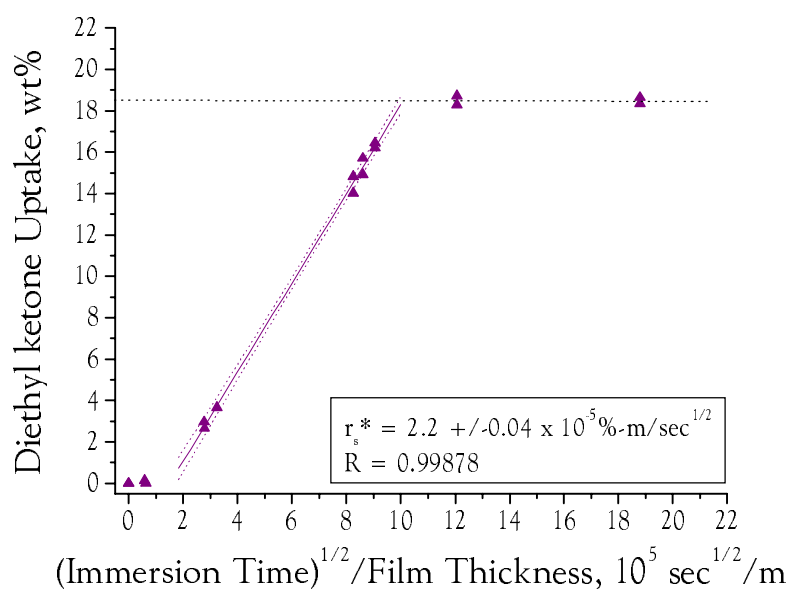


Figure 4.12 Determination of r_s^* for diethyl ketone sorption. The dashed lines represent the 95% confidence interval of the curve fit.

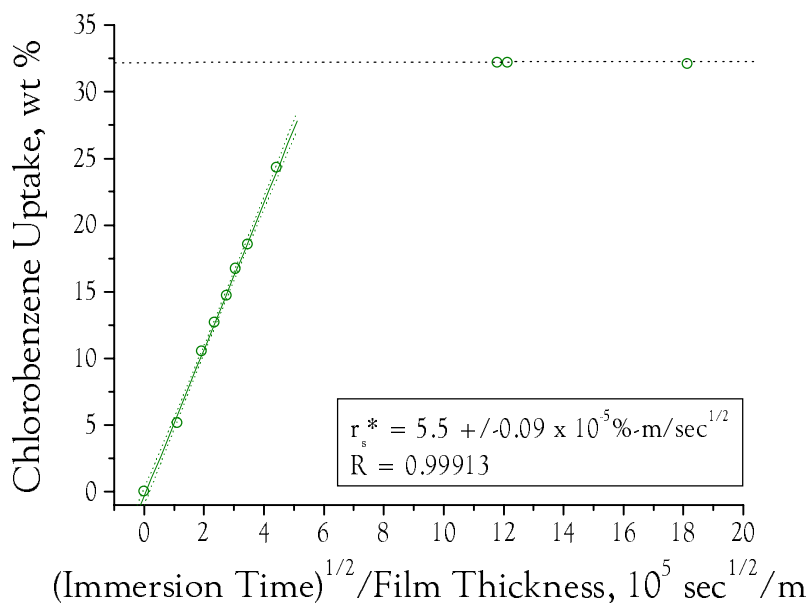


Figure 4.13 Determination of r_s^* for chlorobenzene sorption. The dashed lines represent the 95% confidence interval of the curve fit.

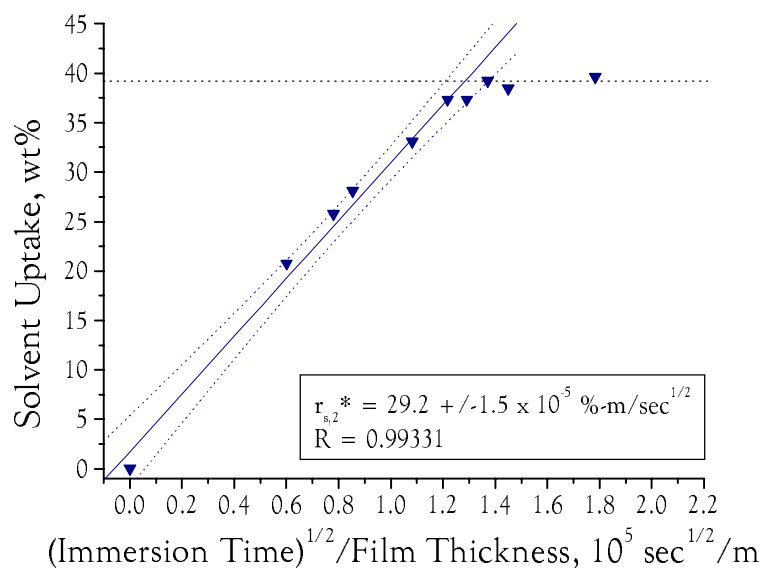


Figure 4.14 Determination of r_s^* for MC sorption at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

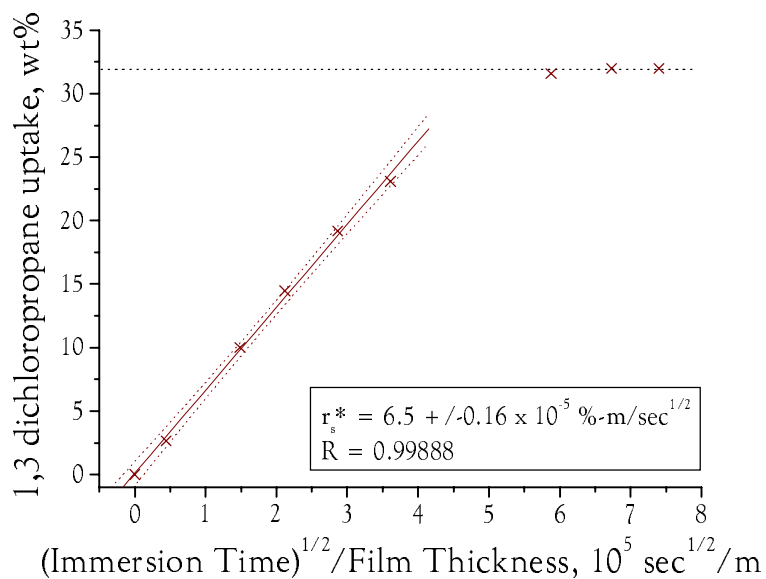


Figure 4.15 Determination of r_s^* for 1,3-dichloropropane sorption at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

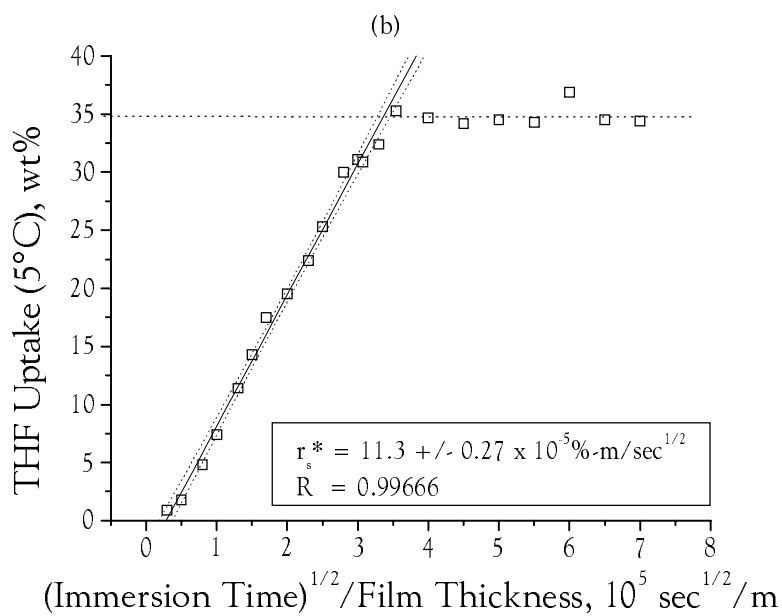
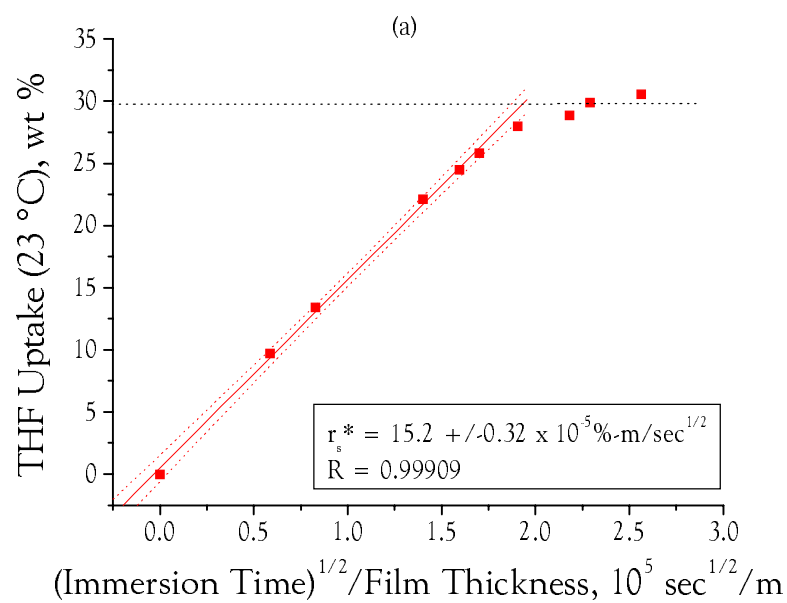


Figure 4.16 Determination of r_s^* for THF at sorption temperatures of (a) 23 °C (b) 5 °C. The dashed lines represent the 95% confidence interval of the curve fit.

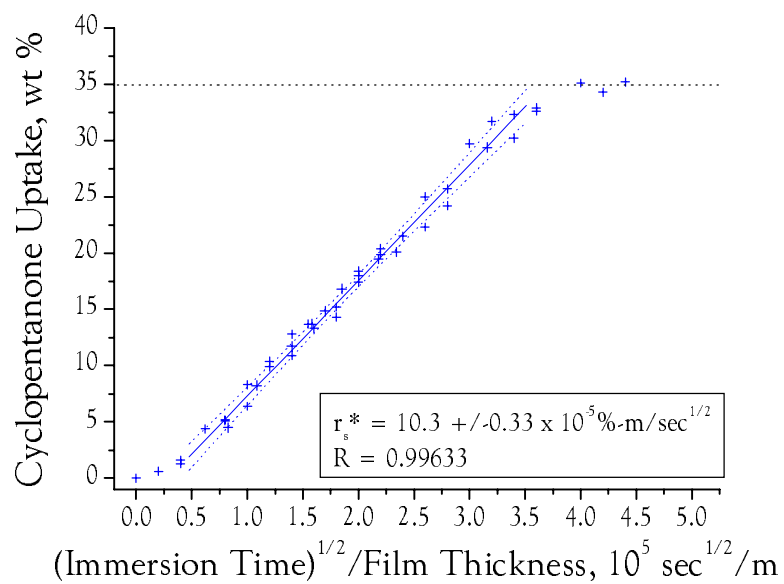


Figure 4.17 Determination of r_s^* for cyclopentanone sorption at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

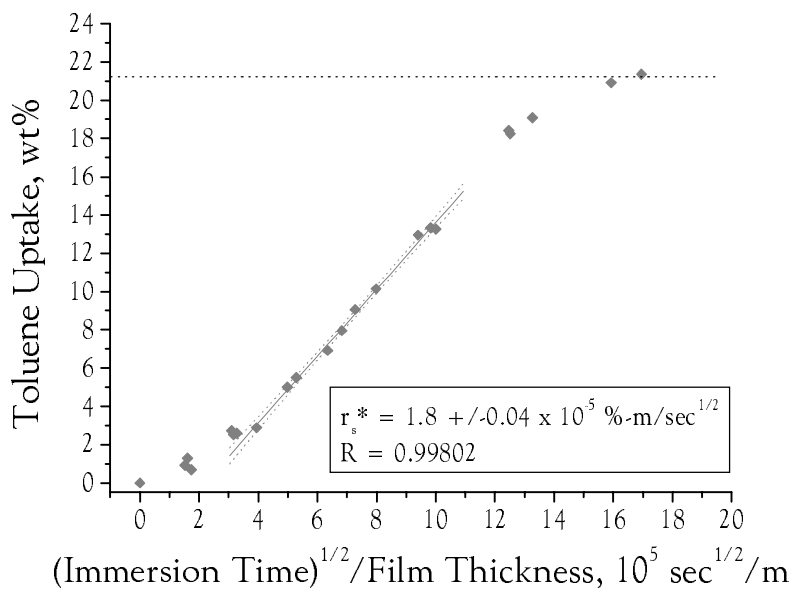


Figure 4.18 Determination of r_s^* for toluene sorption at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

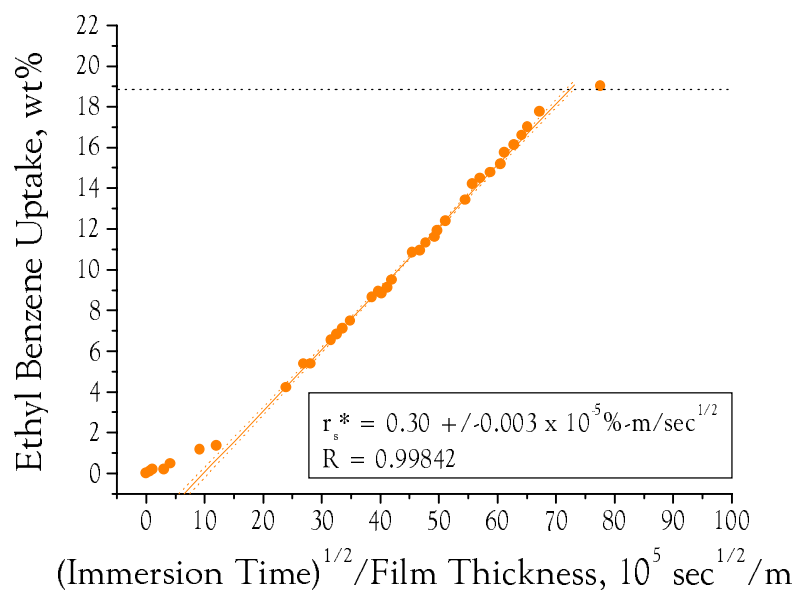


Figure 4.19 Determination of r_s^* for ethylbenzene sorption at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

Table 4.1 Summary of results obtained from dynamic uptake experiments.

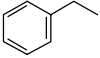
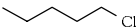
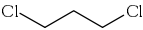
Solvent	Chemical Structure	M_m , 23 °C (wt %)	n_{avg}
ethylbenzene		19	0.66
toluene		21	0.66
chlorobenzene		32	0.55
<i>n</i> -amyl chloride		0	—
diethyl ketone		18	0.74
cyclopentanone		35	0.57
tetrahydrofuran		30	0.45
1,3 dichloropropane		31.5	0.49
methylene chloride		39.5	0.39

Table 4.2 Summary of the sorption rates and average diffusion coefficients with error calculations.

Solvent	$r_s^{* (a)}$, (10^{-5} %-m/sec$^{1/2}$)	Error in r_s^{*} (10^{-5} %-m/sec$^{1/2}$)	$D_z^{(b)}$ (10^{-12} m^2/sec)	Error in $D_z^{(c)}$ (10^{-12} m^2/sec)
ethylbenzene	0.30	0.003	0.049	0.0011
toluene	1.8	0.04	1.3	0.061
chlorobenzene	5.5	0.09	5.8	0.20
diethyl ketone	2.2	0.04	2.8	0.10
cyclopentanone	10.5	0.33	17	1.1
tetrahydrofuran	15.2	0.32	50	2.1
1,3 dichloropropane	6.5	0.16	8.4	0.40
methylene chloride	29.2	1.5	100	11

(a) Slope of the linear fit to the mass uptake versus time curves (Figure 4.11-4.18)

(b) Equation 3.2

(c) Error calculated from the derivative of Equation 3.2

4.2. Wide-angle x-ray diffraction

Figure 4.20 shows the diffraction spectra for solvent-crystallized and thermally crystallized PEEK. After subtraction of the amorphous contribution, the net crystalline spectra of thermal and solvent crystallized films are compared in Figure 4.21. There is an arbitrary vertical offset to separate the diffraction spectra. Dotted lines are positioned at the scattering angles for the (110) and (200) diffracting planes as a visual guide to show that the crystal unit cell dimensions are the same regardless of the method of crystallization. A detailed analysis was not performed to determine the exact location of the diffraction peaks. The diffraction peaks for solvent-crystallized PEEK are broad suggesting that the crystal size is relatively small and/or the crystals are disordered. It is interesting to note that the (113) peak is indiscernible in the diffraction spectra of the solvent crystallized specimens. This may be due to the overlapping of the broad (110) and (200) diffraction peaks and a lower relative intensity of the (113) peak.

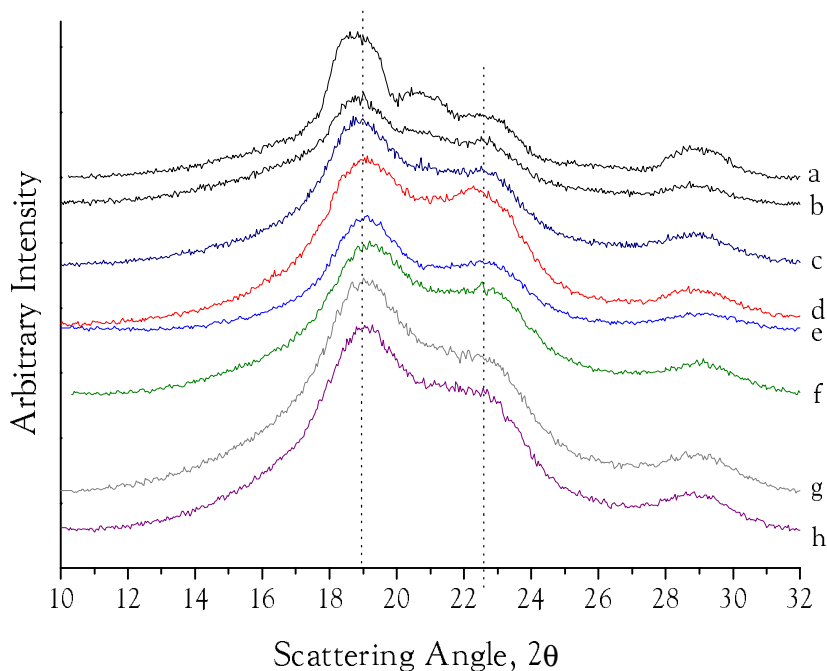


Figure 4.20 WAXD spectra for thermal and solvent-crystallized PEEK films. (a) melt crystallized at 320 °C/1hr, (b) crystallized from the glassy state at 190 °C/1hr, (c) MC, (d) THF, (e) cyclopentanone, (f) chlorobenzene, (g) toluene, and (h) diethyl ketone.

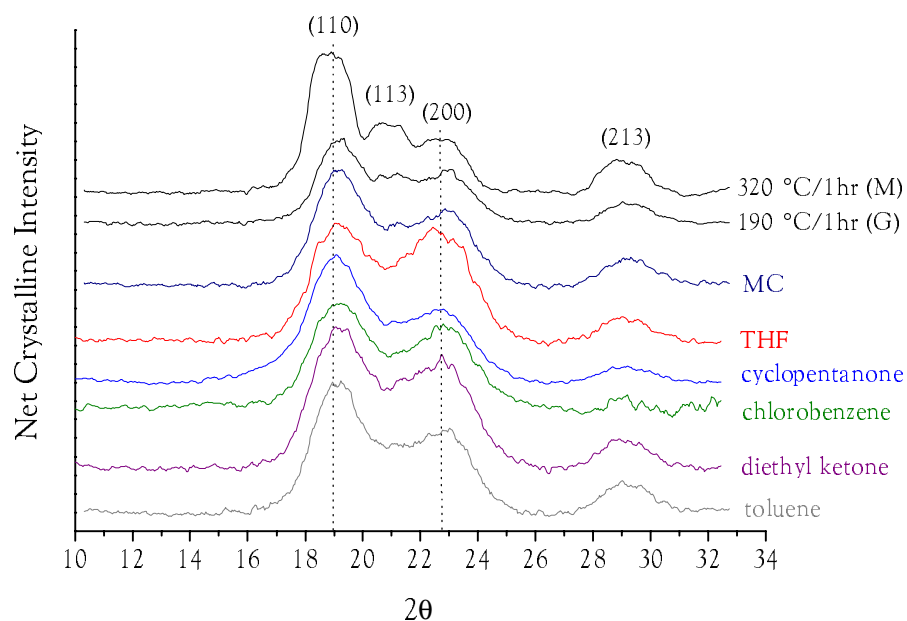


Figure 4.21 WAXD spectra of thermal and solvent-crystallized PEEK after subtracting the amorphous contribution from the diffraction data.

Figure 4.22 shows the net crystalline diffraction spectra, after subtraction of the amorphous contribution, for PEEK following immersion in THF for a range of times. The intensity of the diffraction peaks increases with immersion time; the scattering increases with amount of bulk crystallinity.

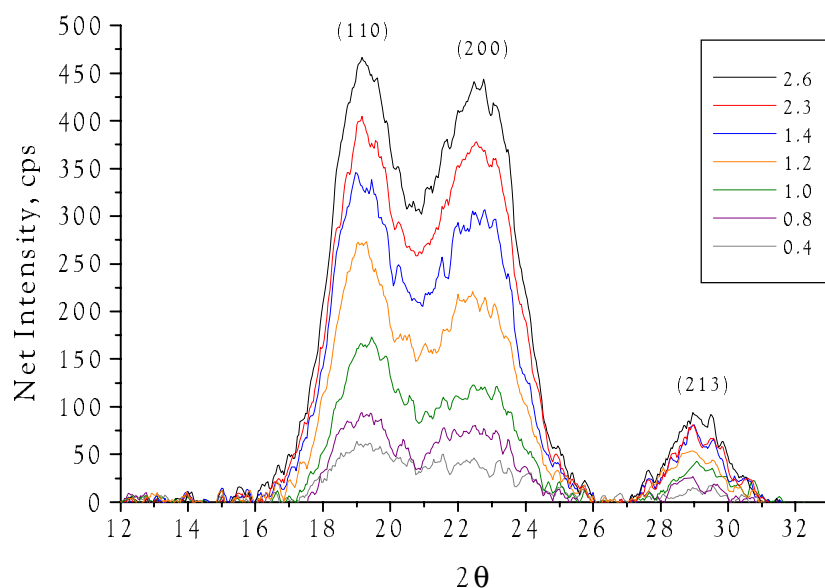


Figure 4.22 WAXD spectra of THF-crystallized PEEK after subtracting the amorphous contribution. The immersion times are listed in units of $10^5 \text{ sec}^{1/2}/\text{m}$.

A crystallinity index (CI) was determined for each PEEK/solvent system from a compilation of 15-20 specimens, each representing a different point in time during diffusion. Subsequently, crystalline indices were plotted as a function of normalized immersion time to obtain crystallization profiles. A Boltzman function was used to generate a curve fit to the data. The crystallinity indices for PEEK, after ambient crystallization in toluene, chlorobenzene, THF, cyclopentanone, and diethyl ketone ranged from 0.35-0.49 (Figures 4.23-4.27). These values are comparable to the crystalline fractions given in the literature for thermally crystallized PEEK¹, even though corrections were not made to the WAXD patterns for absorption incoherent scattering. The symmetrical-transmission technique has the advantage over normal-beam transmission techniques in that the diffraction pattern may be measured at angles up to $2\theta = 90^\circ$ without the absorption correction becoming excessive.⁶¹

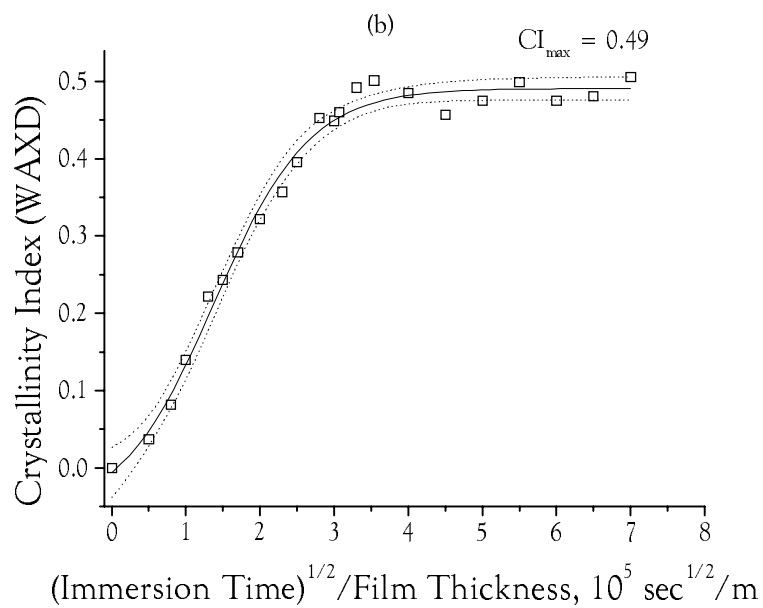
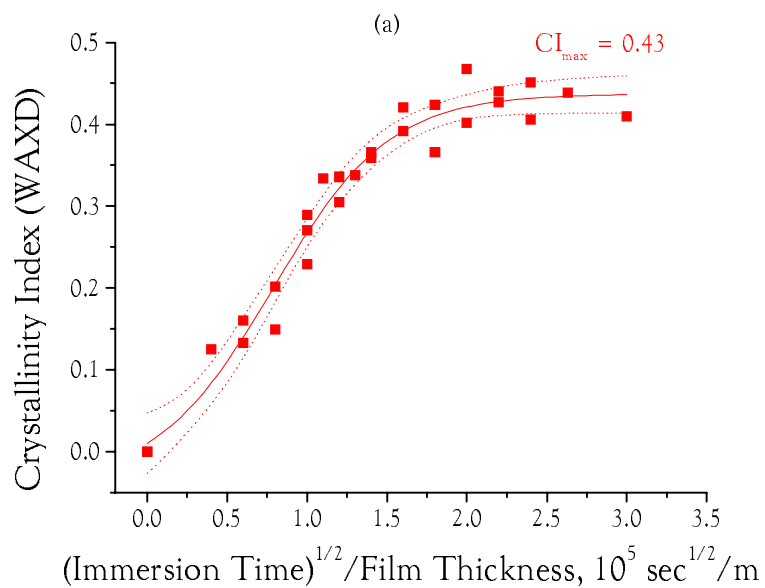


Figure 4.23 Crystallinity indices for PEEK after immersion in THF at (a) 23 °C and (b) 5 °C. The dashed lines represent the 95% confidence interval of the curve fit.

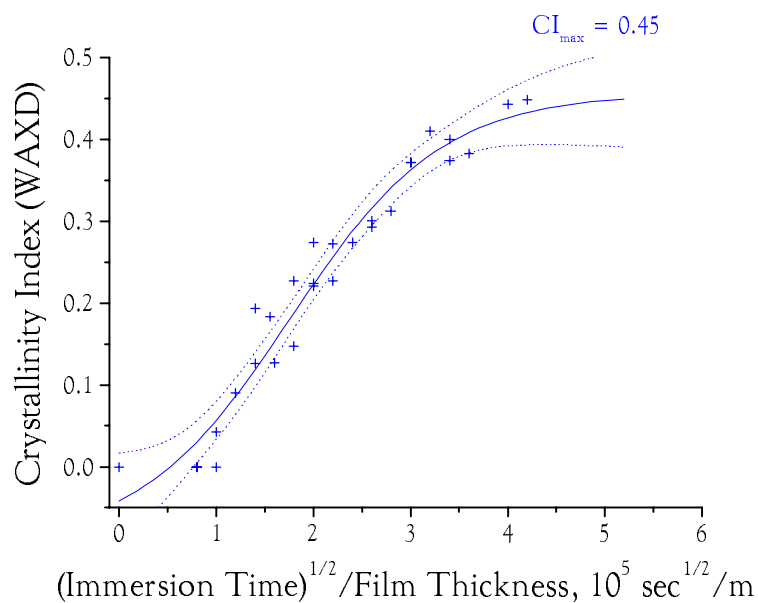


Figure 4.24 Crystallinity indices for PEEK after immersion in cyclopentanone. The dashed lines represent the 95% confidence interval of the curve fit.

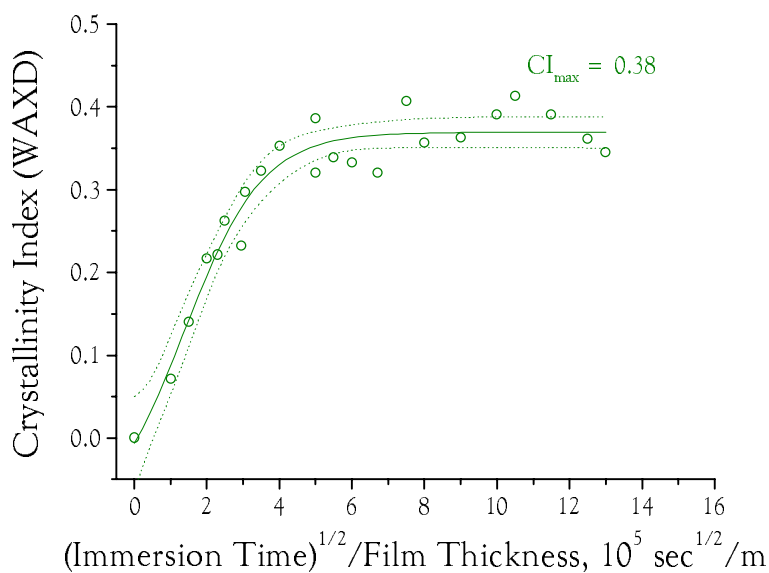


Figure 4.25 Crystallinity indices for PEEK after immersion in chlorobenzene. The dashed lines represent the 95% confidence interval of the curve fit.

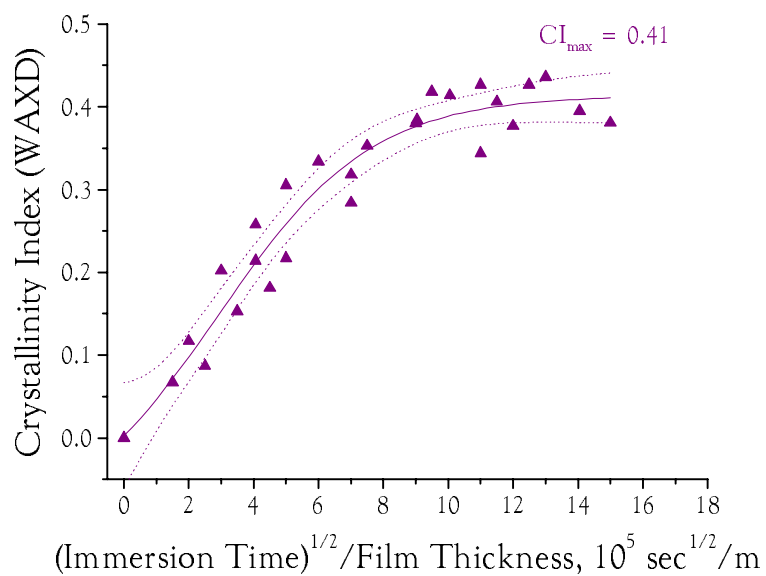


Figure 4.26 Crystallinity indices for PEEK after immersion in diethyl ketone. The dashed lines represent the 95% confidence interval of the curve fit.

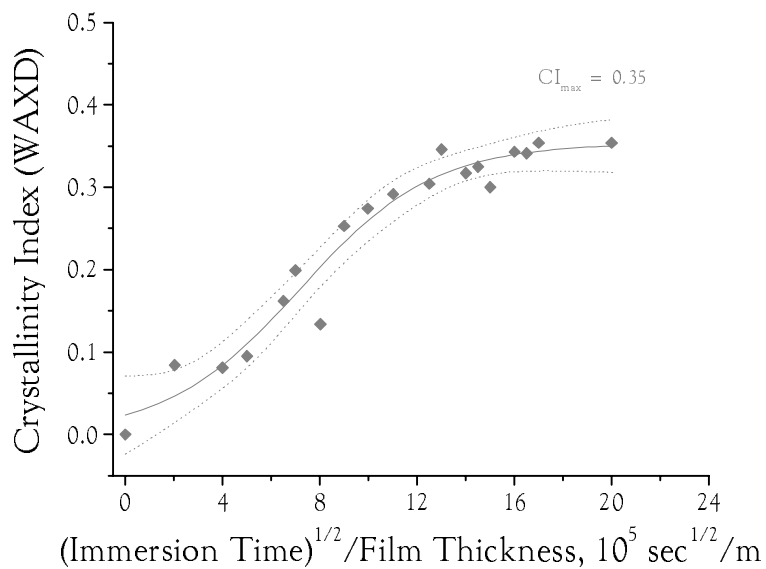


Figure 4.27 Crystallinity indices for PEEK after immersion in toluene. The dashed lines represent the 95% confidence interval of the curve fit.

4.3. DSC

It has been shown that isothermally crystallized PEEK exhibits two distinct melt peaks.^{62,63,64} Three hypotheses exist as to the origin of the double melting behavior: (i) they are due to two separate crystal structures; (ii) they are due to the existence of lamellae of different thickness; (iii) they are attributable to recrystallization effects during the DSC heat scan. There has been supporting evidence for the latter two hypotheses from x-ray, DSC, and microscopy data. Blundell⁶³ suggests that the dual melting behavior results from different components of the morphology, formed in two stages of crystallization. The author has shown, for melt crystallized PEEK, that the upper melting peak represents the melting of primary lamellae and the lower melting peak represents the melting of thinner lamellae that form at a later time between the primary lamellae. Similarly, for PEEK crystallized from the glass, it is expected that the lower peak represents the melting of crystals that were reorganized at T_c and of additional crystals that developed during the isothermal hold.

The main purpose for performing DSC heat scans at 100 °C/min was to limit the extent of melting/recrystallization during the heat scan. The melt peak would be representative of the melting of the original crystals that formed during solvent immersion. In addition, the enthalpy of the crystallization exotherm was used to determine relative changes in crystallinity with immersion time. With a heating rate of 10 °C/min, there exists only one melt peak (Figure 4.28). However, two melt peaks were observed at heating rates of 100 °C/min in the melting range indicating the presence of two distinct populations of crystals (Figure 4.29). The DSC scans for THF immersion times of 0.0, 0.6, 1.0, and 2.2 ($\times 10^5 \text{ sec}^{1/2}/\text{m}$) are highlighted in both figures to show the effect of heating rate on the melting range. Presumably, smaller crystals form during solvent-induced crystallization and subsequently melt at a lower temperature. Figure 4.30 shows the presence of dual melt peaks for the PEEK/cyclopentanone system at a heating rate of 100 °C/min.

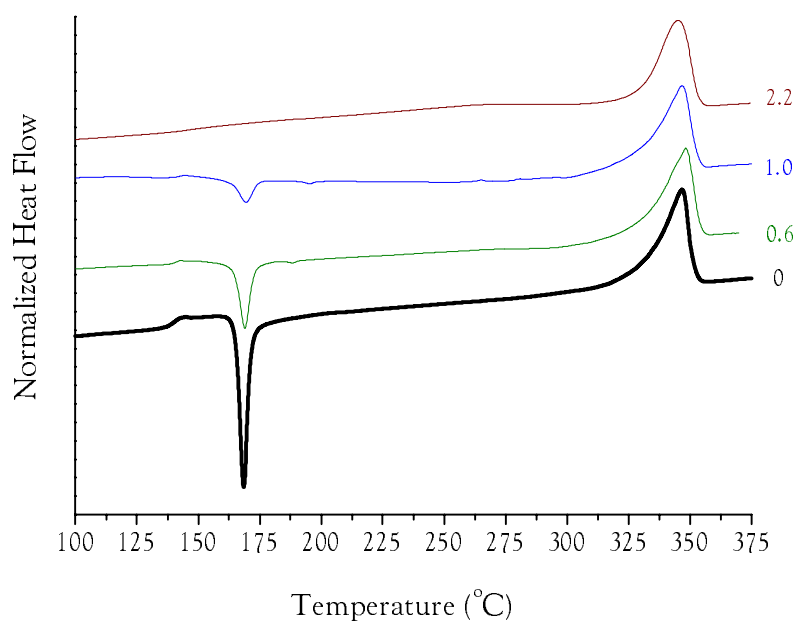


Figure 4.28 DSC scans at a heating rate of 10 °C/min of PEEK after immersion in THF for different times ($10^5 \text{ sec}^{1/2}/\text{m}$).

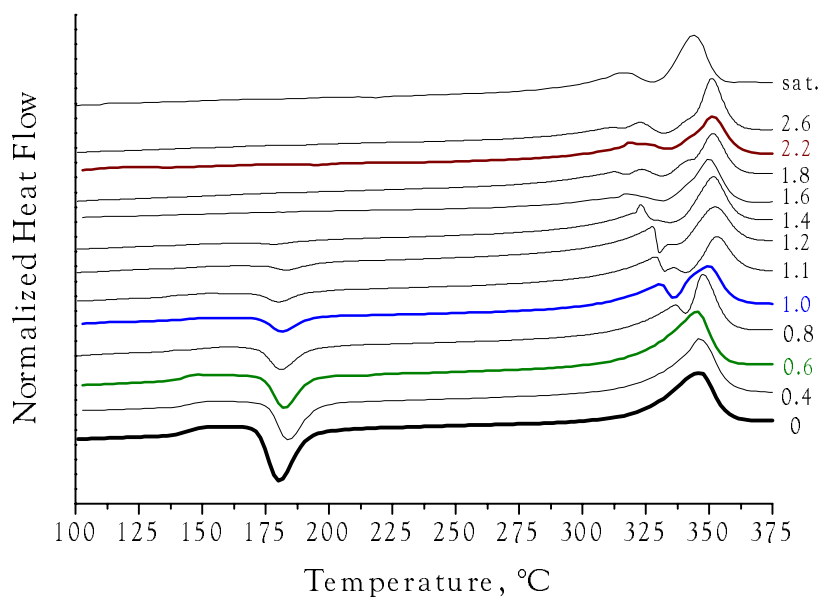


Figure 4.29 DSC scans at heating rates of 100 °C/min of PEEK after immersion in THF for different times ($10^5 \text{ sec}^{1/2}/\text{m}$).

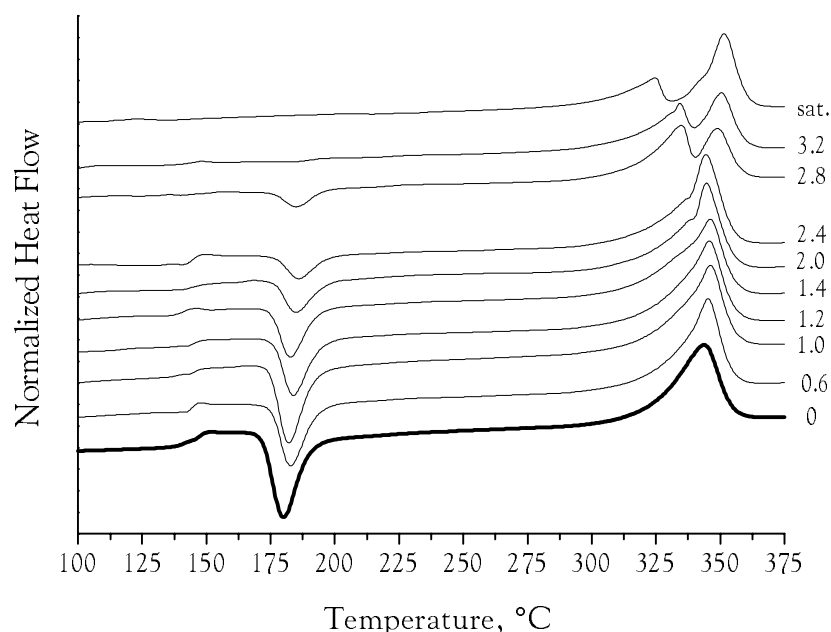


Figure 4.30 DSC scans at heating rates of 100 °C/min of PEEK after immersion in cyclopentanone for different times ($10^5 \text{ sec}^{1/2}/\text{m}$).

Although these results indirectly suggest that more than one population of crystal sizes are present in solvent-crystallized PEEK, no conclusions can be drawn here.

The crystallization enthalpy was measured from the integrated area under the crystallization exotherm. As immersion time increased, the amount of crystallinity in the polymer film increased. Subsequently, there was less amorphous material available to crystallize as the crystallization of the polymer film progressed and the residual exotherm decreased. Figures 4.31a and 4.32a represent the enthalpy changes for THF and cyclopentanone. The enthalpy values were normalized according to Equation 3.4 and plots of normalized crystallinity index versus immersion time are shown in Figures 4.31b and 4.32b. The underlying assumption is that bulk crystallization is complete when the crystallization enthalpy becomes zero.

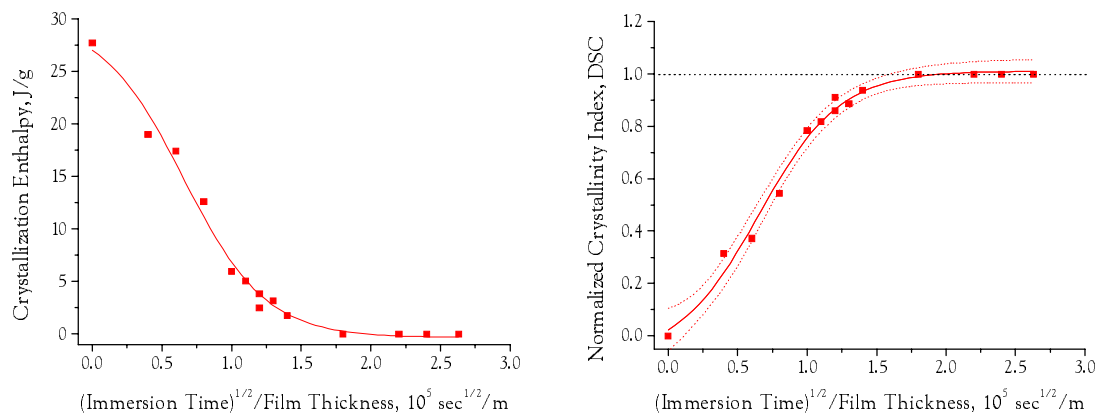


Figure 4.31 (a) Residual crystallization enthalpy and (b) normalized crystallinity index for PEEK crystallized in THF at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

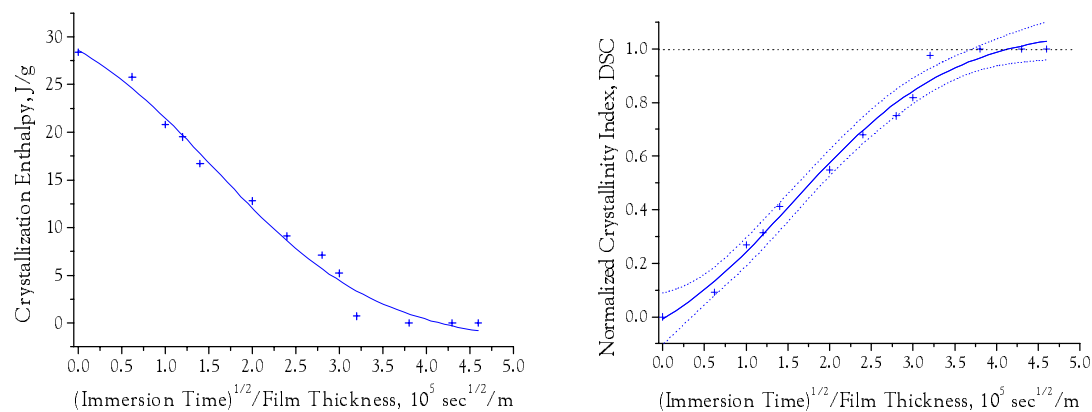


Figure 4.32 (a) Residual crystallization enthalpy and (b) normalized crystallinity index for PEEK after immersion in cyclopentanone at 23 °C. The dashed lines represent the 95% confidence interval of the curve fit.

4.4. Isochronal DMA (1 Hz)

Isochronal DMA scans were performed at 1 Hz as described in Section 3.5. The glass transition for each PEEK/solvent system is shown in Figure 4.33 as a broad step transition in the storage modulus. Amorphous PEEK is shown as a reference. At low temperatures, prior to the onset of cooperative motion in the amorphous phase, all of the spectra converge to the same value of storage modulus. Unreinforced polymers typically exhibit moduli on the order of 2.0-3.0 GPa in the glassy state.

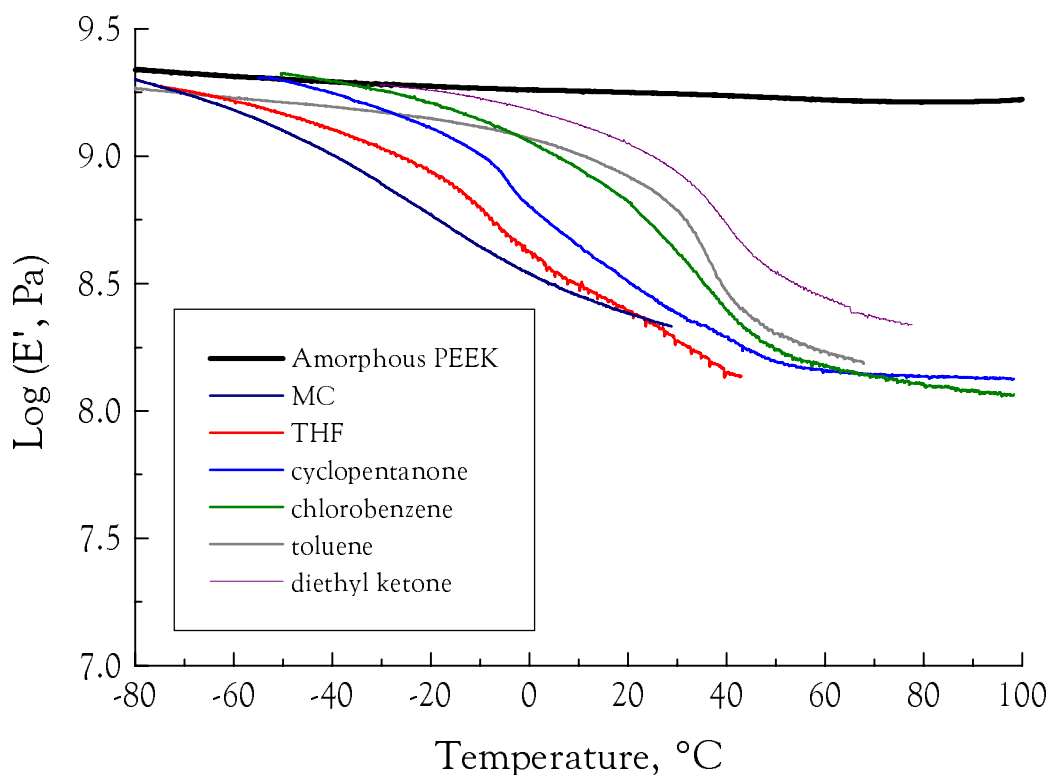


Figure 4.33 *In-situ* isochronal (1 Hz) DMA heat scans of solvent-saturated PEEK.

The glass transition was defined as a range in temperature spanning from the onset in the decrease in the loss modulus to the peak in tan delta. It was found that the glass transition of amorphous PEEK was suppressed to below ambient temperature during solvent immersion; hence, crystallization is kinetically feasible during ambient immersion. Plots of loss modulus and tan delta versus temperature are shown in Figures 4.34-4.39 for each PEEK/solvent system and the results are summarized in Table 4.3. Solvent-crystallized PEEK shows a glass transition that spans as much as 60 degrees in temperature whereas amorphous PEEK shows a glass transition that spans 10 degrees in temperature (Figure 3.9a).

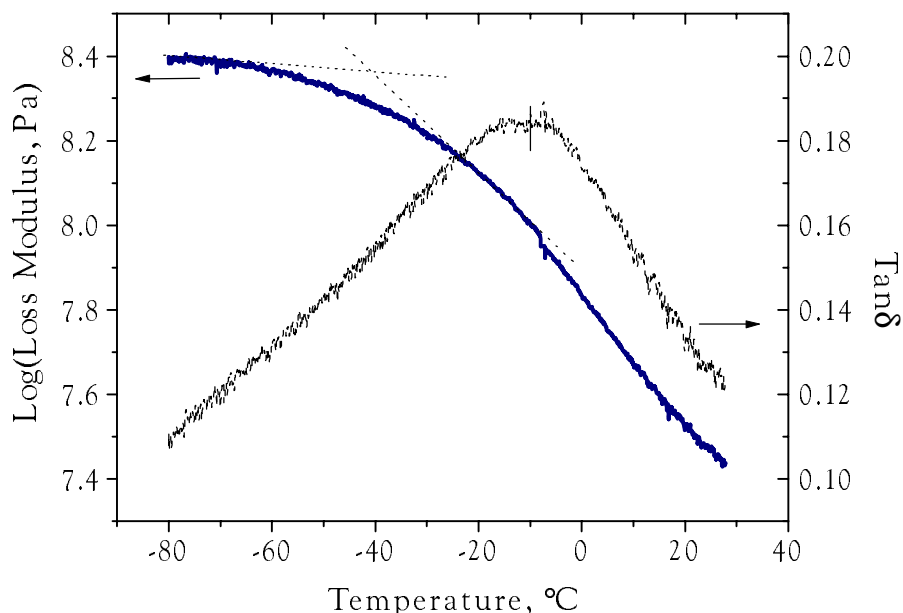


Figure 4.34 *In-situ* glass transition of PEEK saturated with MC.

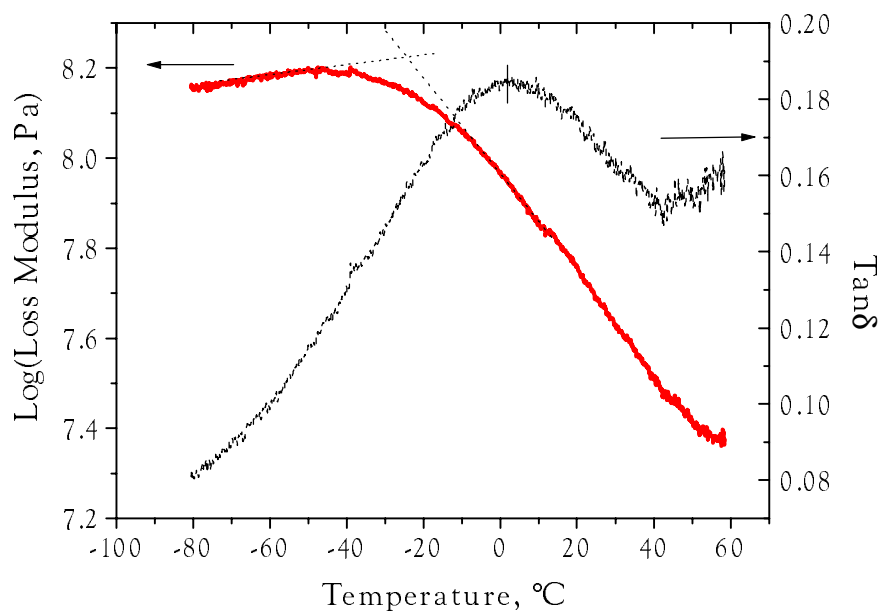


Figure 4.35 *In-situ* glass transition of PEEK saturated with THF.

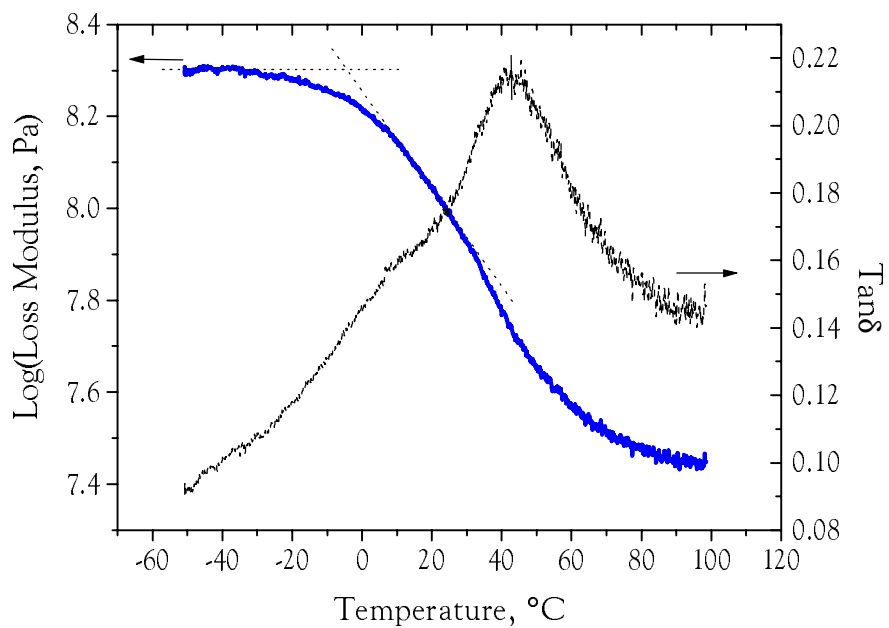


Figure 4.36 *In-situ* glass transition of PEEK saturated with cyclopentanone.

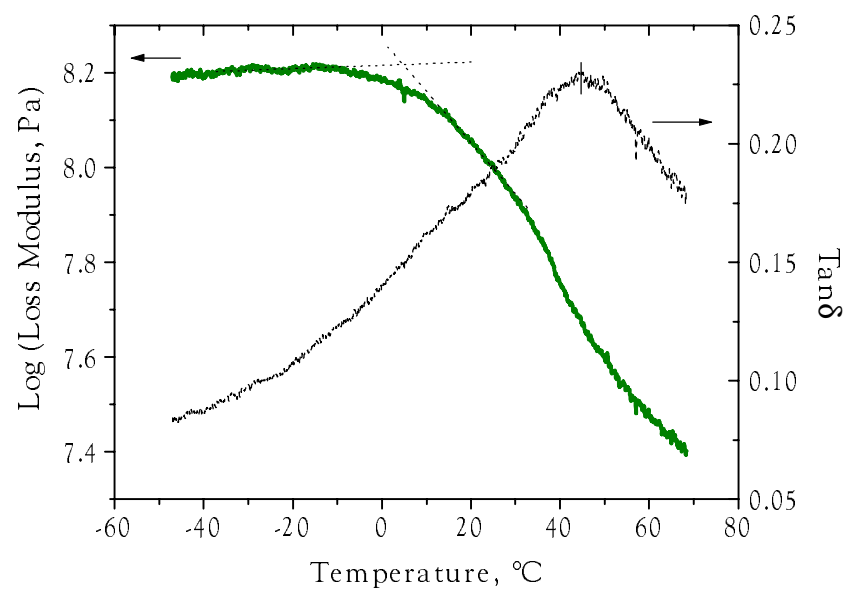


Figure 4.37 *In-situ* glass transition of PEEK saturate with chlorobenzene.

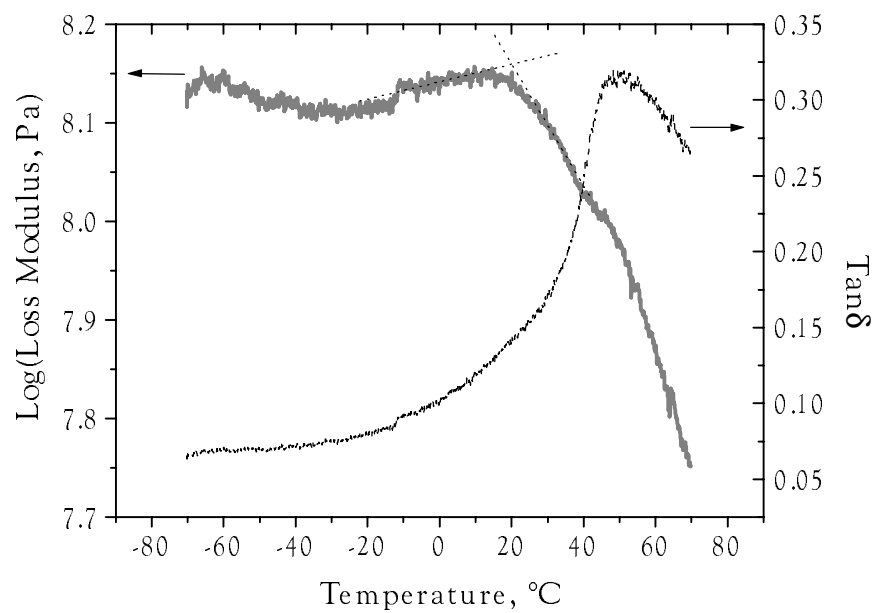


Figure 4.38 *In-situ* glass transition of PEEK saturate with toluene.

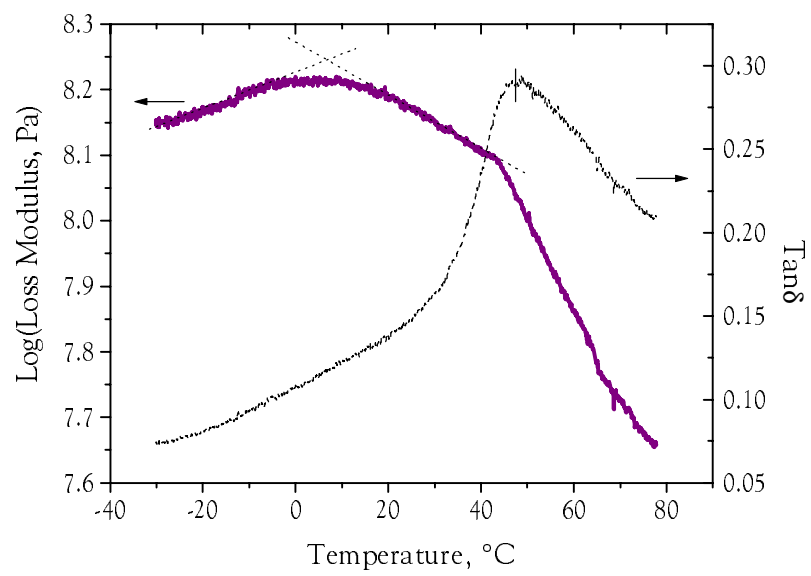


Figure 4.39 *In-situ* glass transition of PEEK saturate with diethylketone.

Table 4.3 Glass transition ranges for solvent-saturated PEEK via DMA at 1 Hz.

System	Glass Transition (1Hz)	
	E'' onset, °C	tan δ peak, °C
toluene	20	50
chlorobenzene	5	45
diethyl ketone	10	50
cyclopentanone	-5	40
THF	-25	0
MC	-40	-10
Amorphous PEEK	150	160

The storage modulus of solvent-saturated PEEK decreases an order of magnitude when heating through the glass transition unlike amorphous PEEK, which becomes highly compliant in the rubbery state (above 150 °C). Amorphous PEEK films, tested in three-point bend mode, fail to maintain sufficient mechanical stiffness above T_g . The results suggest that there is a significant degree of crystallinity present in the solvent-crystallized films; crystallinity strongly enhances the modulus in the rubbery region above T_g .⁵¹ The PEEK films consist of two phases at ambient temperature: a rubbery amorphous phase and a reinforcing crystalline phase.

4.5. Isothermal DMA (23 °C)

Isothermal DMA spectra are shown in Figure 4.40 for ambient immersion of amorphous PEEK in MC, THF, cyclopentanone, chlorobenzene, and toluene. The solvent was introduced at $t = 0$ and the relative storage moduli were monitored as a function of immersion time. The storage moduli were normalized to the glassy modulus of amorphous PEEK (i.e. the storage modulus at $T = 23$ °C). All solvents promoted some degree of plasticization as indicated by the decrease in stiffness with immersion time. Immersion of amorphous PEEK in methylene chloride resulted in a 70 % decrease in stiffness with solvent penetration. A slight increase and eventually a plateau value followed a distinct minimum. This trend was observed for all solvents except toluene; the time frame of sorption for toluene was much greater than the time frame of the DMA experiment (2 days versus 5 hours, respectively). An explanation of these results is presented in Chapter 5.

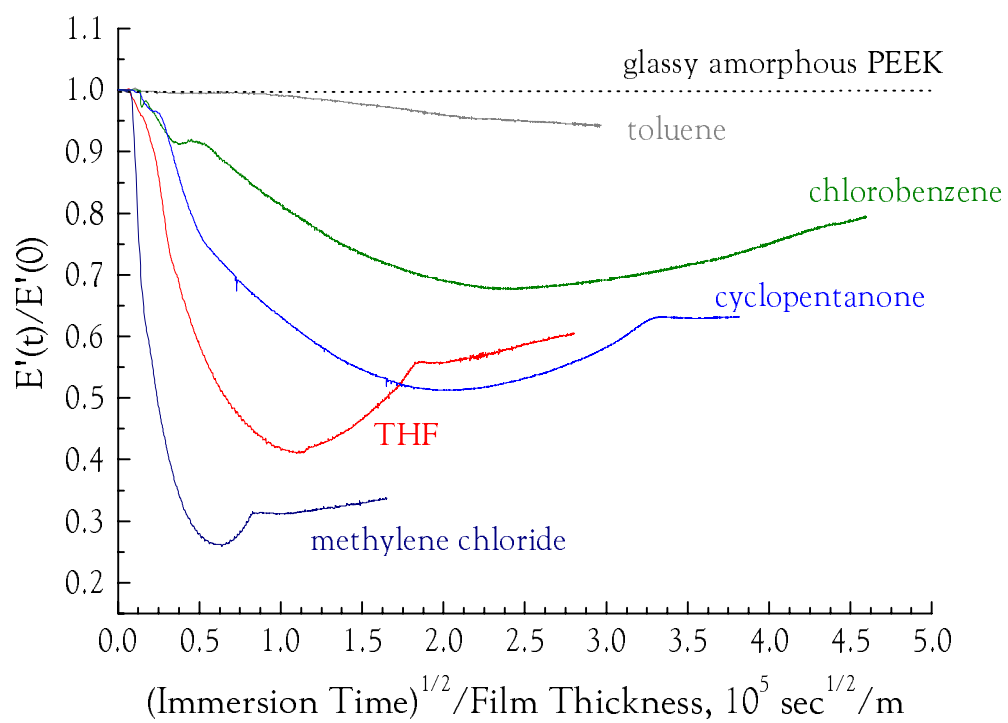
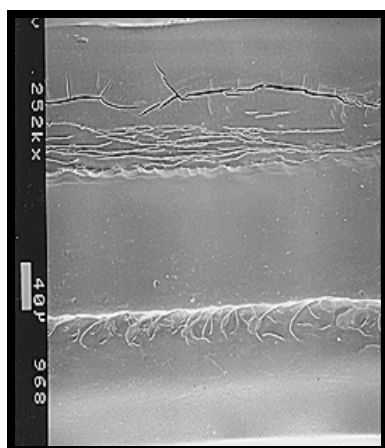


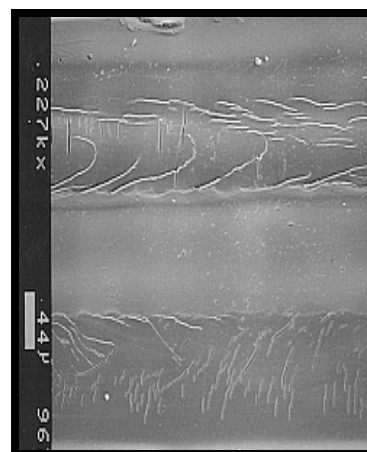
Figure 4.40 Isothermal DMA of PEEK during solvent immersion (23 °C).

4.6. SEM

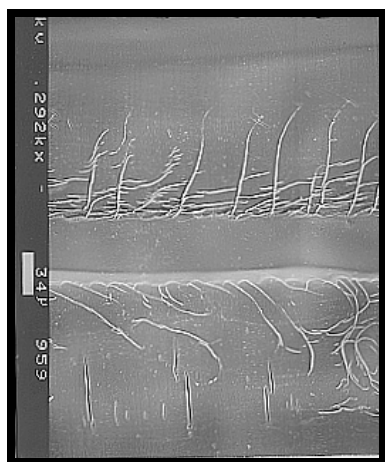
As the solvent diffuses into the film, large osmotic swelling stresses promote a discontinuity at the glassy-swollen interface. This interface was observed via SEM following desorption of residual solvent. Figure 4.41 shows the location of the solvent front in amorphous PEEK films after immersion in THF at 23°C for intermediate times between $M(0)$ and M_m . The cracks were observed only after etching and did not develop during solvent sorption or desorption. The penetration depth of THF in amorphous PEEK at 23 °C was found to vary linearly with the square root of time. These results are discussed in more detail in Chapter 5.



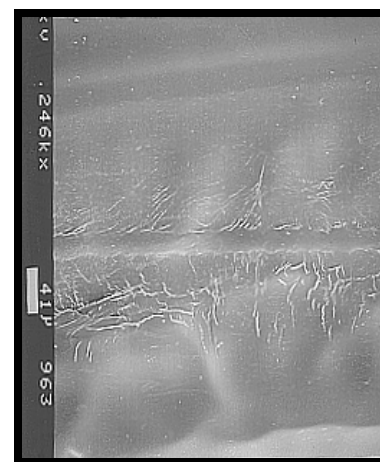
(a)



(b)



(c)



(d)

Figure 4.41 SEM micrographs of film cross-sections after immersion in THF for normalized times of (a) 1.1 (b) 1.3 (c), 1.4 (d) 1.6 ($10^5 \text{ sec}^{1/2}/\text{m}$).

5. DISCUSSION

The glass transition was suppressed below room temperature for all PEEK/solvent systems, as shown via isochronal DMA. However, the transition spanned a broad temperature range and was therefore defined in terms of a temperature range (between the onset of decrease in E'' and the peak in $\tan\delta$) instead of a single temperature. The T_g calculated from the Fox equation was significantly lower than the low temperature end of the glass transition range determined from *in-situ* DMA as summarized in Table 5.1. This can be explained in terms of the presence of crystallinity.

A two-phase system develops as the solvent diffuses into the film, where solvent molecules are intimately mixed with the amorphous phase but excluded from the crystals. Hence, the overall weight fraction of solvent within the amorphous phase is greater than the weight fraction in the bulk. However, crystallinity tends to broaden the glass transition and shift it to higher temperatures due to constraints on chain motion within the amorphous phase.⁶⁵ In this respect, the Fox equation overestimates T_g suppression.

The melting temperature suppression is relatively small as compared to T_g suppression (Table 5.1). In a parallel study, of absorption of organic solvents in amorphous undeformed PET, Makarawicz and Wilkes¹⁵ found that the maximum variation in T_m depression was estimated to be only 20 °C. In the case of amorphous, undeformed PEEK, the melting point suppression was estimated to be as much as 85 °C in MC. However, the T_g suppression was estimated to be as much as 245 °C, indicating the tremendous plasticization effect of the solvents. The crystallization temperature regime of PEEK, defined as $T_m^\circ - T_g$, was effectively increased in the presence of the solvents. The solvents that promoted SINC of PEEK were estimated to increase the breadth of the crystallization temperature regime of PEEK by at least 100 °C.

Table 5.1 Summary of the T_g and T_m° suppression of PEEK

Solvent	M_m	$T_g^{(a)}$, °C	T_g range ^(c) (°C)	$\delta^{(d)}$ (MPa ^{1/2})	$\chi_1^{(e)}$	T_m° , ^(f) (°C)	$(T_m^\circ - T_g)^{(g)}$, °C
ethylbenzene	0.19	-27.5	40, 50	17.3	0.78	368	395
toluene	0.21	-37.7	20, 50	17.4	0.66	361	399
chlorobenzene	0.32	-47.5	5, 45	19.4	0.15	349	397
diethyl ketone	0.18	11.0	10, 50	18.0	0.47	360	349
cyclopentanone	0.35	-65.3	-5, 40	20.2	0.04	333	398
THF	0.30	-85.1	-25, 0	18.6	0.24	335	420
MC	0.395	-103.2	-40, -10	22.4	0.03	321	424

PEEK		145 ^(b)	150, 160	21.3		395	250
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(a) Equation 2.12

(b) Measured via DSC at a heating rate of 10 °C/min

(c) Measured via DMA at 1 Hz

(d) Hansen total solubility parameter, Equation 2.1

(e) Equation 2.3

(f) Equation 2.13

(g) Difference between estimated T_m° and T_g values

SINC morphology is discussed qualitatively in terms of melt features from DSC and photographic WAXD patterns. DSC scans, performed at a heating rate of 100 °C/min, show two distinct melt peaks for all solvent-crystallized films. This indicates the presence of two main populations of crystal sizes. The lower temperature peak may be associated with the melting of crystals that formed during the isothermal crystallization in the solvent at 23 °C. The degree of supercooling, $\Delta T = T_m^{\circ} - T_c$, was calculated to be much greater for PEEK immersed in SINC-promoting solvents at ambient temperature than for PEEK crystallized from the glassy state or melt crystallization at a low temperature (near T_g). Regardless of the method of crystallization, a large ΔT promotes a high degree of nucleation and limited growth so the resultant crystals are numerous and small.

Makarewicz and Wilkes¹⁵ determined that the relatively small long-spacings observed in SINC specimens of PET were associated with the degree of supercooling which is significantly larger than that observed for thermal-induced crystallization. In addition, the same authors verified by small-angle light scattering that the liquids induced a spherulitic texture. Desai and Wilkes²⁶ determined from SEM observation that the size of the spherulites ranged from 1-3 μm , regardless of solvent. Kalika *et al.*⁵ concluded from SAXS analysis of solvent-crystallized PEEK that the long-spacings are smaller than those observed for thermally-crystallized PEEK and are independent of penetrant type. In addition, Wolf and coworkers²⁹ proposed from WAXS studies that solvent-induced PEEK crystals are smaller and more tightly organized as compared to thermally annealed specimens. Corn  lis¹⁰ confirmed that the crystal structure of PEEK is the same, regardless of the method of crystallization.

If crystallization is limited by diffusion and the diffusion is primarily in one dimension (i.e. through the thickness of the films), orientation of the crystalline phase may be influenced by the direction of the mass flux. To test this hypothesis, photographic WAXD spectra were obtained for SINC and thermally crystallized PEEK films in two orthogonal directions. The diffraction spectra were collected in transmission mode with a Philips PW 1720 x-ray generator. Flat-film diffraction spectra were obtained after 2.5-3 hours of exposure time to Cu- $k\alpha$ radiation at operating conditions of 40 kV and 20 mA. To obtain spectra with the x-y plane of the film oriented

perpendicular to the incident beam, the PEEK films were laid flat over the pinhole of the diffractometer. To obtain spectra with the x-z plane oriented perpendicular to the incident beam, thin strips were cut and stacked to cover the diameter of the pinhole (0.051 mm) (Figure 5.1). The x and y directions of the films are assumed to be identical.

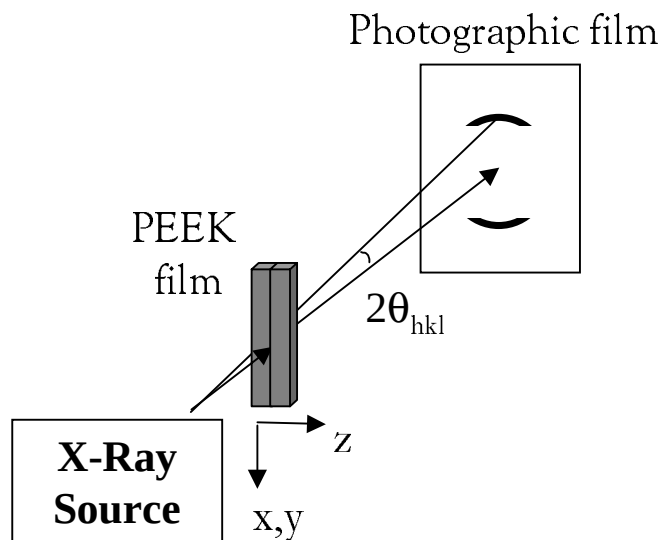


Figure 5.1 Schematic showing the photographic WAXD experimental set-up where the incident X-ray beam is oriented normal to the diffusion direction.

In support of the diffusion-limited scenario, photographic WAXD patterns show that indeed there is preferred orientation of the solvent-induced crystals formed during THF, MC, and toluene immersion. When the incident beam was oriented perpendicular to the x-y plane of the solvent-crystallized films (i.e. parallel to the z-direction), no preferred crystal orientation was detected as shown in Figure 5.2a. When the incident beam was oriented perpendicular to the x-z plane of the solvent-crystallized films, some diffraction rings exhibited azimuthal dependence in the meridional regions as shown in Figure 5.2b and 5.3. Films that were crystallized from the glassy state or the melt-state exhibited sharp uniform diffraction rings, regardless of the orientation of the film specimens to the incident beam (Figure 5.4). Qualitatively, these results suggest that

crystals formed via thermal means are randomly oriented. The intensity of the diffraction rings is irrelevant because the film thicknesses were not the same.

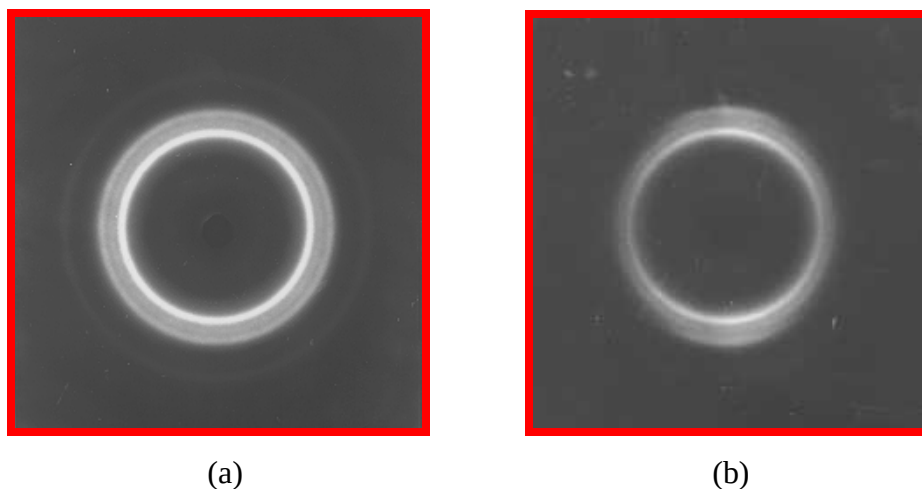


Figure 5.2 Photographic WAXD of PEEK film saturated in THF at 23 °C where the beam is oriented orthogonal to (a) the x-y plane and (b) the x-z plane of the film.

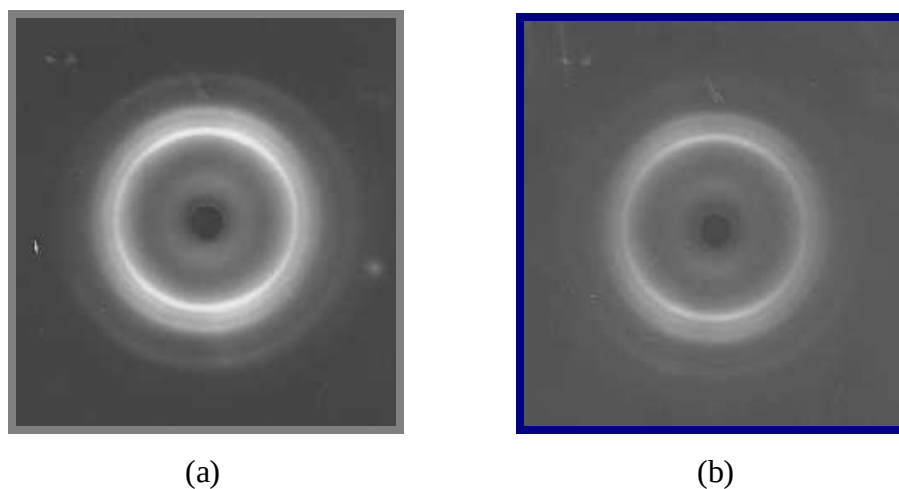


Figure 5.3 Photographic WAXD of PEEK films (beam oriented orthogonal to the x-z plane of the film) after saturation in (a) toluene and, (b) methylene chloride.

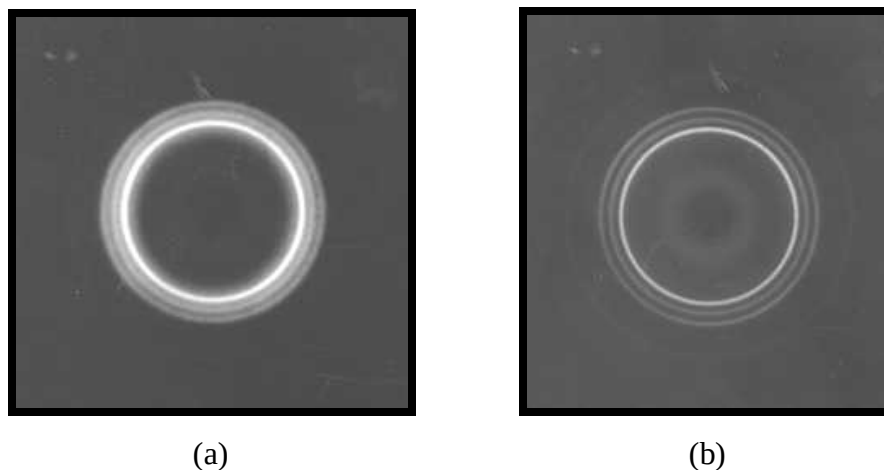


Figure 5.4 Photographic WAXS of PEEK films (beam oriented orthogonal to the x-z plane of the film) (a) isothermally crystallized from the glassy state (190 °C/1hr) and, (b) isothermally crystallized from the melt (320 °C/1hr).

To determine if the film is saturated once the solvent fronts meet in the middle of the film, the mass uptake, swelling, and SEM front location were followed for the diffusion of THF in amorphous PEEK at ambient temperature. The mass uptake, swelling, and SEM front location were determined from individual film specimens at each time interval. Each property was normalized to vary from zero to the maximum value of the property; a normalized property value of one represents the point of saturation, maximum degree of swelling, and the disappearance of the observed front location. Figure 5.5 shows the normalized property plot where the error bars represent the precision of the measurements.

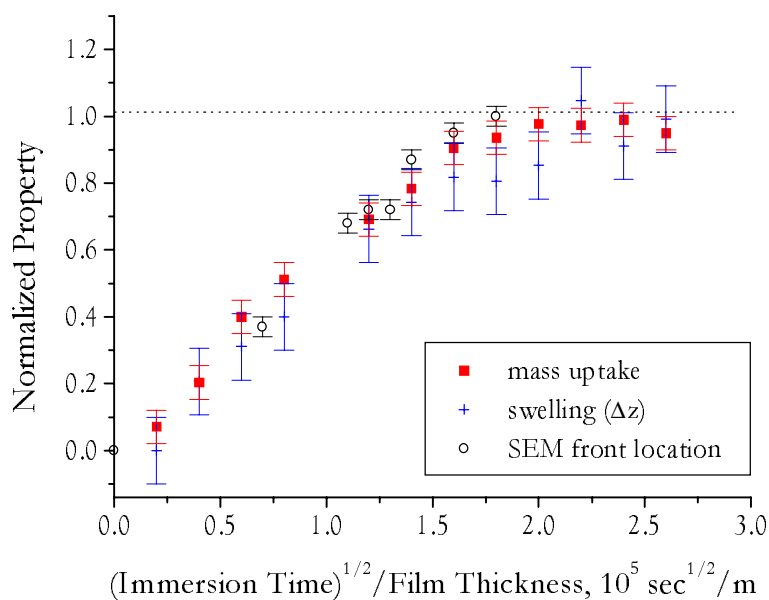


Figure 5.5 Normalized property plot showing the mass uptake, swelling, and SEM front location during immersion of amorphous PEEK in THF at 23 °C.

Within the scatter of the experimental data, the sorption of THF and the concomitant swelling of the amorphous PEEK film are coincident. In addition, sorption and swelling are complete when the fronts meet in the center of the film. It is important to note, however, that swelling, sorption, and front location may not coincide for immersion in different solvents or immersion at different temperatures. For example, there has been evidence in PET for swelling to continue after the fronts have met in the center of the film.³⁶

To verify the development of solvent-induced crystallinity during diffusion, the normalized WAXD and DSC data were compared for THF and cyclopentanone and found to coincide within experimental error (Figures 5.6 and 5.7, respectively). This means that bulk crystallinity is complete when the residual crystallization exotherm is no longer detected via DSC.

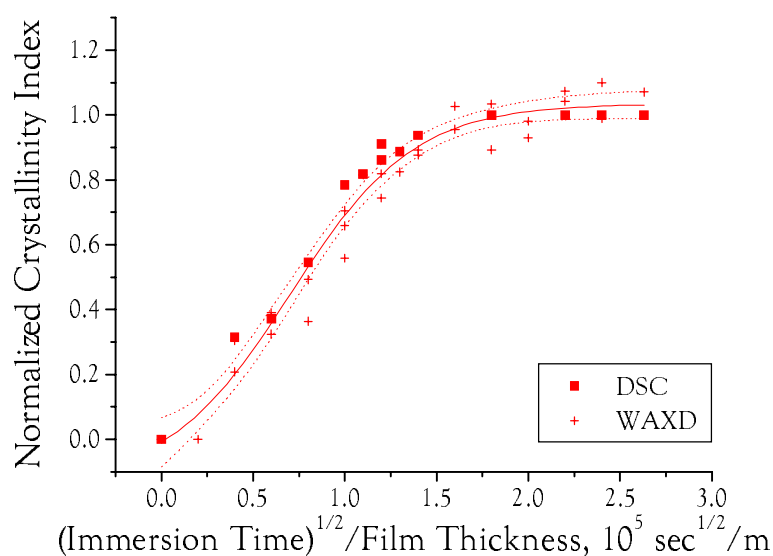


Figure 5.6 Verification of crystallinity development during THF immersion via DSC and WAXD. The dashed lines represent the 95% confidence interval of the curve fit.

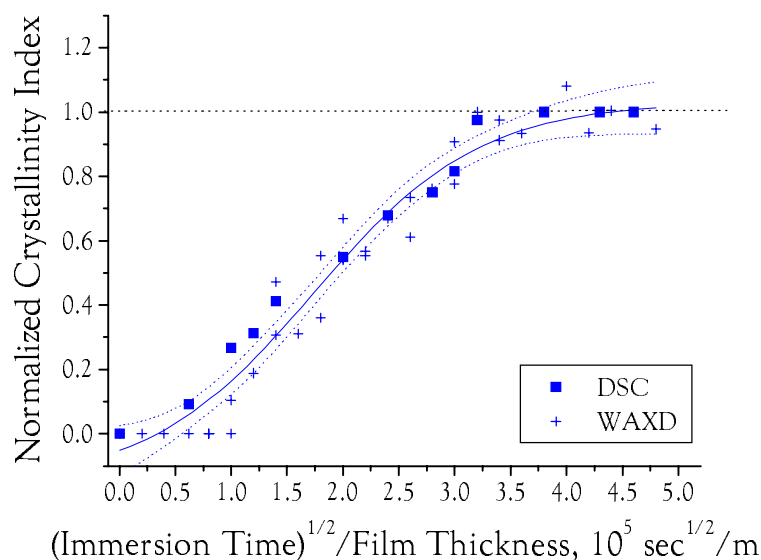


Figure 5.7 Verification of crystallinity development during cyclopentanone immersion via DSC and WAXD. The dashed lines represent the 95% confidence interval of the curve fit.

The rate-limiting factor for crystallization depends on the relative kinetics of sorption and crystallization. In this study, experimentally observed rates of bulk sorption, r_s^* , and crystallization, r_c^* , were determined. It was assumed that the r_c^* can be less than or equal to the actual rate of crystallization; the polymer is capable of crystallizing faster than the rate of sorption, however crystallization cannot occur ahead of the sorption front. In this study, it was assumed that crystallization cannot occur ahead of the advancing liquid front and the crystals are distributed homogeneously through the thickness of the film at saturation. If r_c^* is equal to r_s^* , the crystallization process is defined as diffusion-limited (Figure 5.8a). This suggests that crystallization occurs simultaneously with the movement of the crystallization front (i.e. instantaneously in the presence of solvent, once the glass transition is suppressed below the immersion temperature). The schematic in Figure 2.1 is representative of diffusion-limited crystallization where the advancing front separates a rubbery amorphous phase reinforced with crystals from an unpenetrated glassy core. The second scenario is the case where diffusion occurs faster than crystallization (Figure 5.8b). In this case, crystallization is controlled by the mobility of the polymer chains in the presence of the solvent and the crystallization process is kinetics-limited.

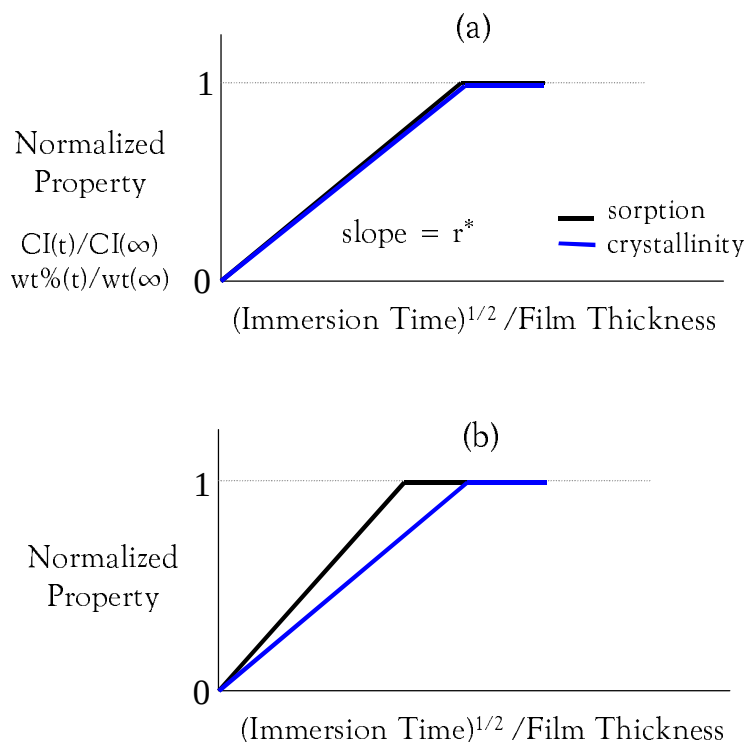


Figure 5.8 Rate-limiting scenarios for SINC (a) diffusion-limited vs. (b) kinetics-limited.

All of the solvents listed in Table 3.1, except amyl chloride, promoted diffusion-limited crystallization of amorphous PEEK at ambient temperature. Figures 5.9-5.13 show the overlay of mass uptake and crystallinity data as a function of normalized time. Linear fits to the initial stages of sorption and crystallinity, in addition to the 95 % confidence bands associated with each fit, are shown in Chapter 4. The crystallinity indices were normalized to the crystallinity index of PEEK after solvent saturation and the sorption values were normalized to the solubility, M_m . Thus, when the normalized value equals one, the degree of sorption and crystallinity has reached a maximum, time-independent value.

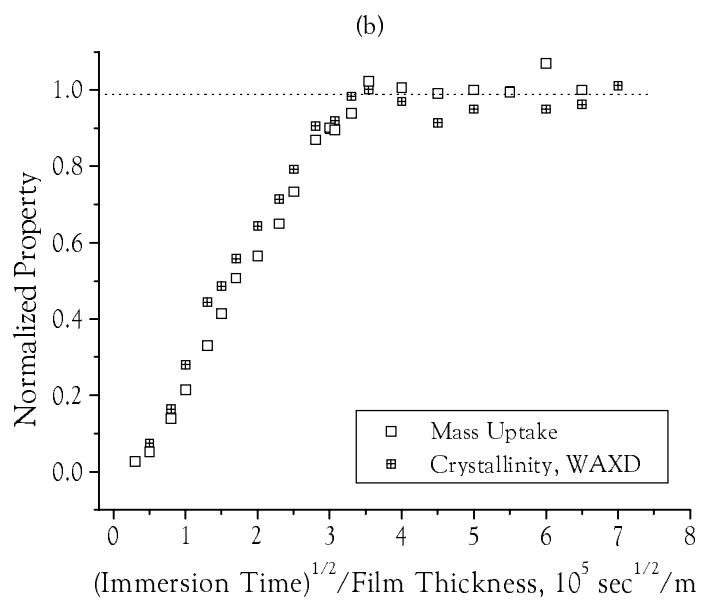
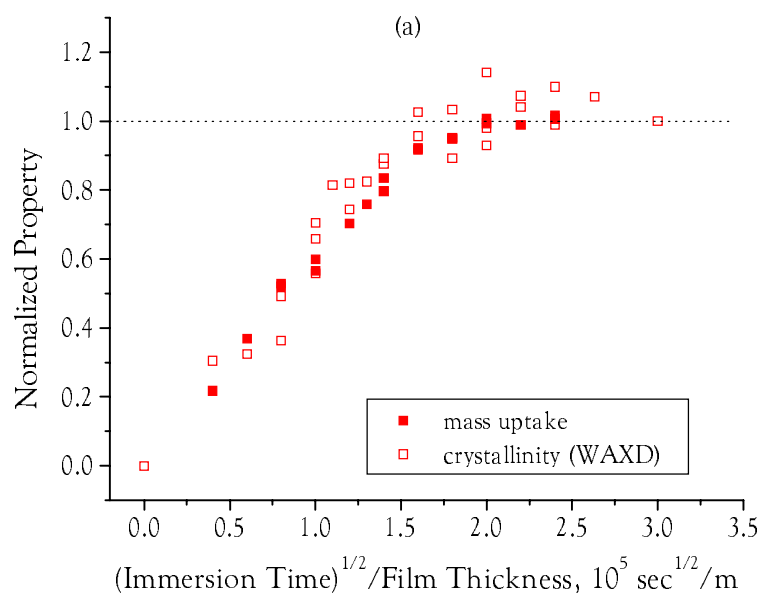


Figure 5.9 Comparison of sorption and crystallization rates for THF at (a) 23 °C and (b) 5 °C.

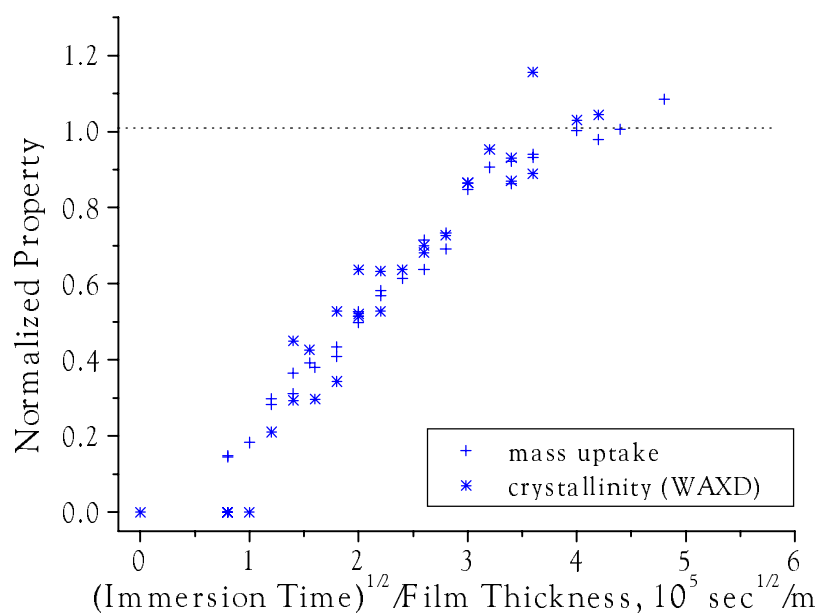


Figure 5.10 Comparison of sorption and crystallization rates for PEEK/cyclopentanone.

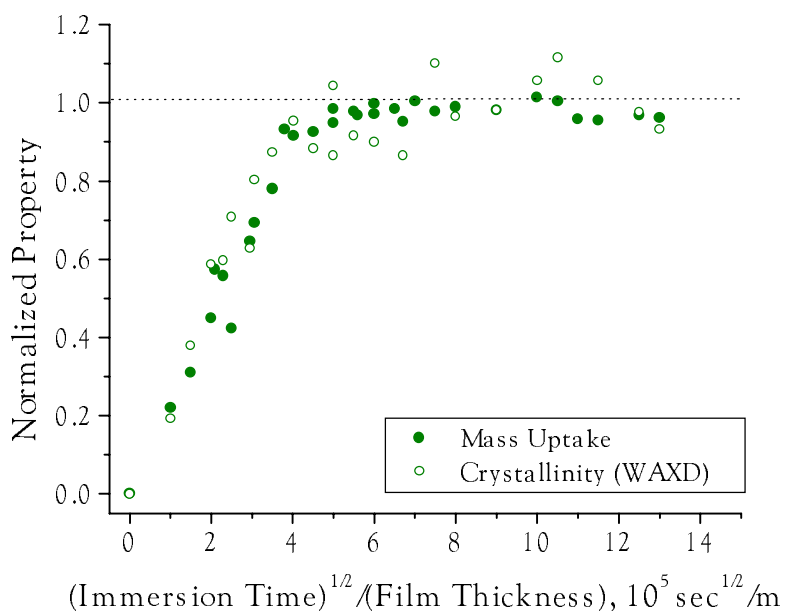


Figure 5.11 Comparison of sorption and crystallization rates for PEEK/chlorobenzene.

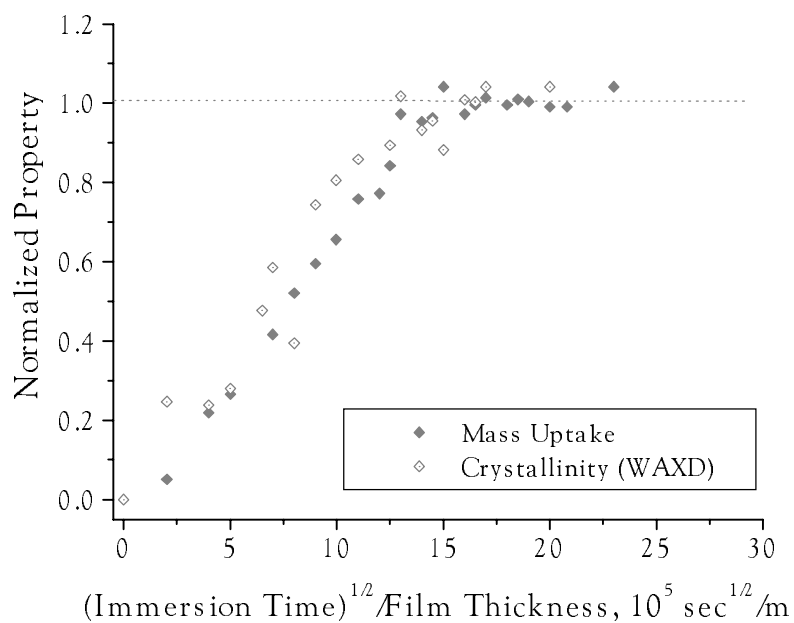


Figure 5.12 Comparison of sorption and crystallization rates for PEEK/toluene.

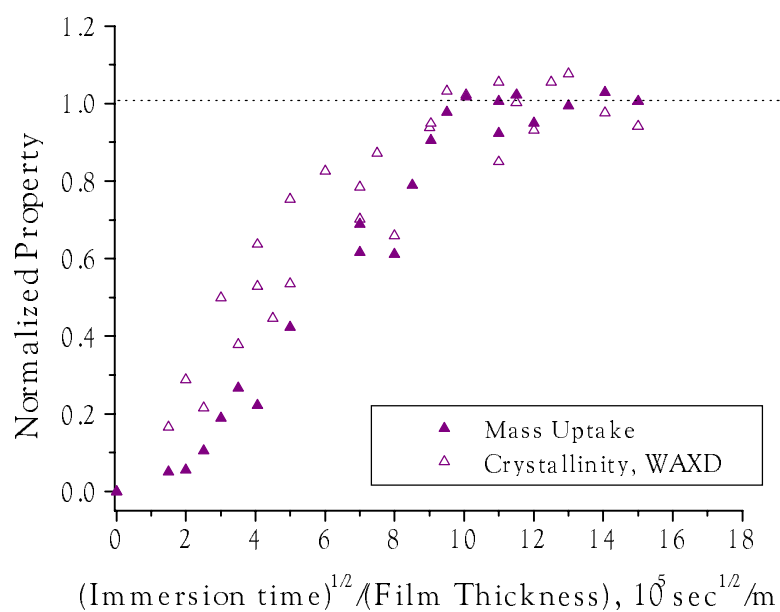
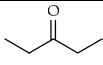
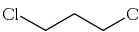


Figure 5.13 Comparison of sorption and crystallization rates for PEEK/diethyl ketone.

Each PEEK/solvent system exhibited different SINC kinetics and apparent solubility at equilibrium, which indicate the varying degree of polymer-solvent interactions. MC and THF plasticize amorphous PEEK to the greatest extent and at faster rates than diethyl ketone and toluene. Table 5.2 lists the crystallinity indices for PEEK after immersion in different solvents. In addition, the mole fraction of solvent molecules per polymer repeat unit was calculated to distinguish between each solvent in terms of the number of molecules interacting with the polymer chains in the amorphous phase.

Lowering the immersion temperature by approximately 15 °C from ambient temperature changed the kinetics of the SINC process and the solubility of THF at equilibrium. However, the ultimate fraction of solvent-induced crystallinity which resulted, calculated in terms of an index of crystallinity, was relatively independent of penetrant and temperature (at least with a small temperature difference as shown for THF). Kalika *et al.*⁵ arrived at a similar conclusion for the exposure of amorphous PEEK to acetone and MC vapor. Desai and Wilkes²⁶ determined that the “supercooling” concept may not be as critical a parameter as in thermally induced crystallization since the spherulite size of PET was found to be independent of the diffusion rates and the SINC temperature.

Table 5.2 Summary of sorption and crystallinity data at equilibrium saturation.

Solvent	Chemical Structure	M_m , 23 °C (wt %)	CI_{max}	Mole Fraction* (solvent/r.u.)
ethylbenzene		19	0.28	0.72
toluene		21	0.35	1.02
chlorobenzene		32	0.38	1.32
diethyl ketone		18	0.41	1.02
cyclopentanone		35	0.45	2.18
tetrahydrofuran		30	0.43	2.18
1,3 dichloropropane		31.5	0.35	1.23
methylene chloride		39.5	0.40	2.27

$$* \text{ Mole Fraction} = \frac{M_m \left(\frac{m_p}{m_s} \right)}{(1 - CI_{max})}$$

m_p = molar mass of the repeat unit of PEEK = 288 g/mol

m_s = molar mass of the solvent (Table 2.1)

CI_{max} = maximum crystallinity index

A normalized property plot was constructed for the THF, cyclopentanone, and chlorobenzene systems (Figures 5.14-5.16) which included mass uptake, bulk crystallinity, and dynamic mechanical response. It was determined from the bulk sorption and crystallinity studies that solvent-induced crystallization of PEEK is diffusion-limited in these systems. In addition, the storage modulus reaches a relatively time-independent value at the same time that bulk crystallization and mass uptake are complete, within experimental scatter.

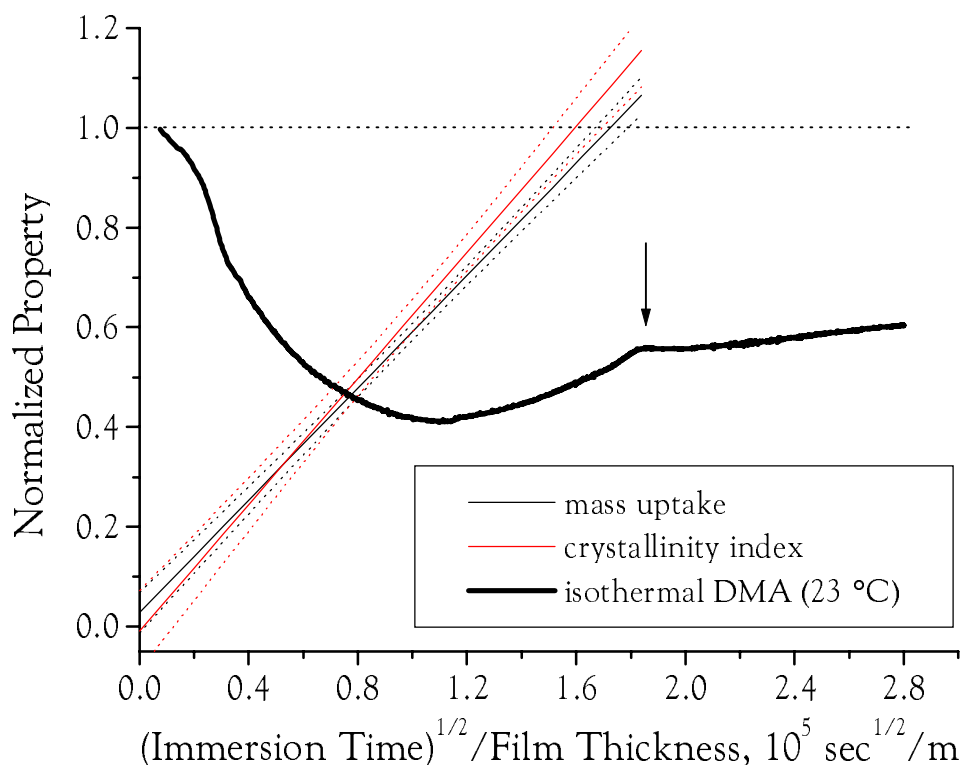


Figure 5.14 Normalized property plot for PEEK immersion in THF at 23 °C. The linear fits to the sorption and crystallinity data are presented with 95% confidence bands. The arrow points to the onset of a relatively time-independent E' which corresponds to the completion of bulk crystallization.

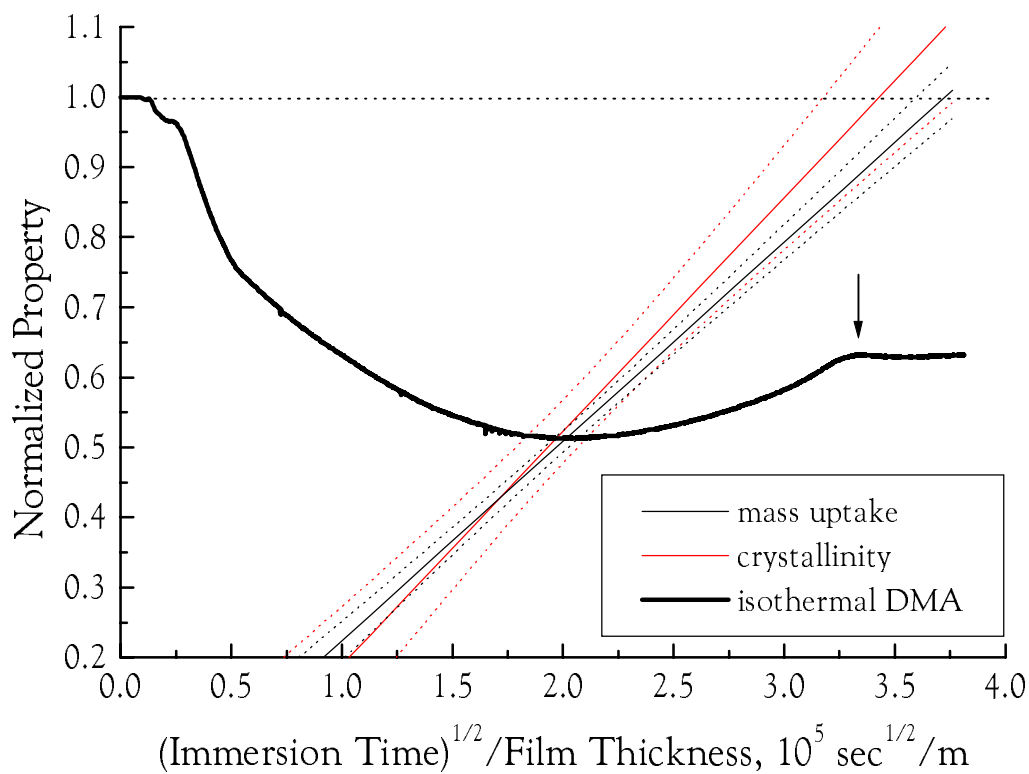


Figure 5.15 Normalized property plot for PEEK immersion in cyclopentanone. The linear fits to the sorption and crystallinity data are presented with 95% confidence bands. The arrow points to the onset of a relatively time-independent E' which corresponds to the completion of bulk crystallization.

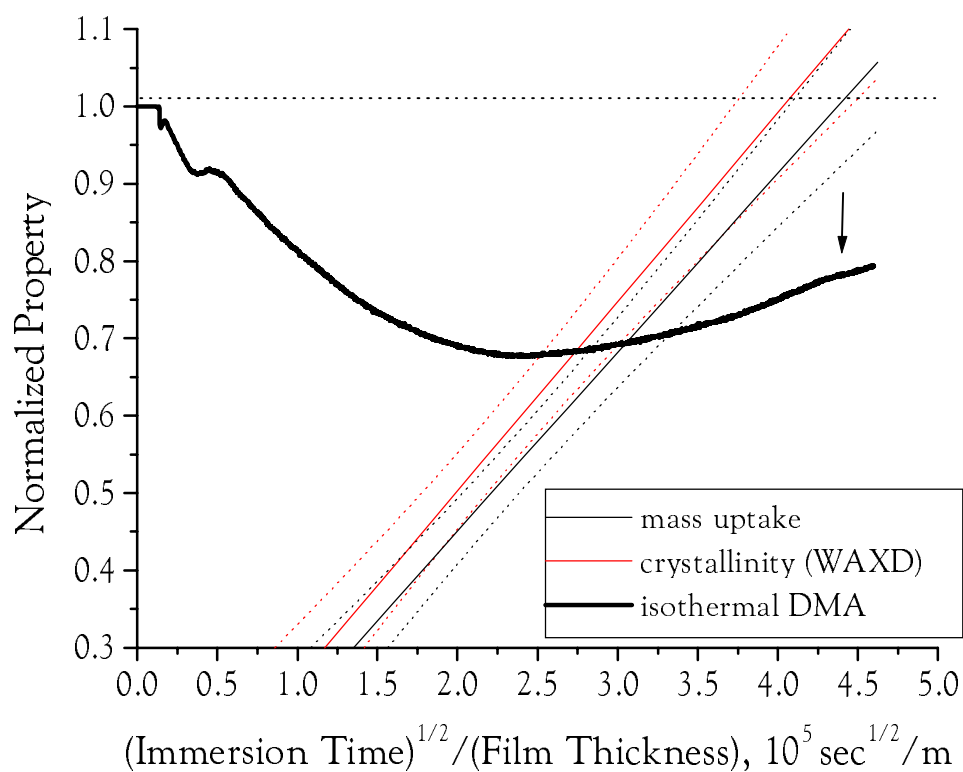


Figure 5.16 Normalized property plot for PEEK immersion in chlorobenzene. The linear fits to the sorption and crystallinity data are presented with 95% confidence bands. The arrow points to the onset of a relatively time-independent E' which corresponds to the completion of bulk crystallization.

In the early stages of sorption, a large volume of the PEEK film is glassy and minimal plasticization has occurred. If the Fox equation is used to estimate the average T_g in the bulk of the film, it is shown that plasticization (i.e. T_g suppression) dominates the dynamic mechanical response at short times (Figure 5.17). The underlying assumptions are that the solvent molecules are dispersed throughout the entire volume of amorphous phase and no crystallinity is present. The bulk T_g of PEEK decreases rapidly at short immersion times, concomitant with a decrease in the storage modulus, and reaches a plateau value once the entire film is saturated with solvent. Therefore, the plasticization effect is greatest in the early stages of the sorption process.

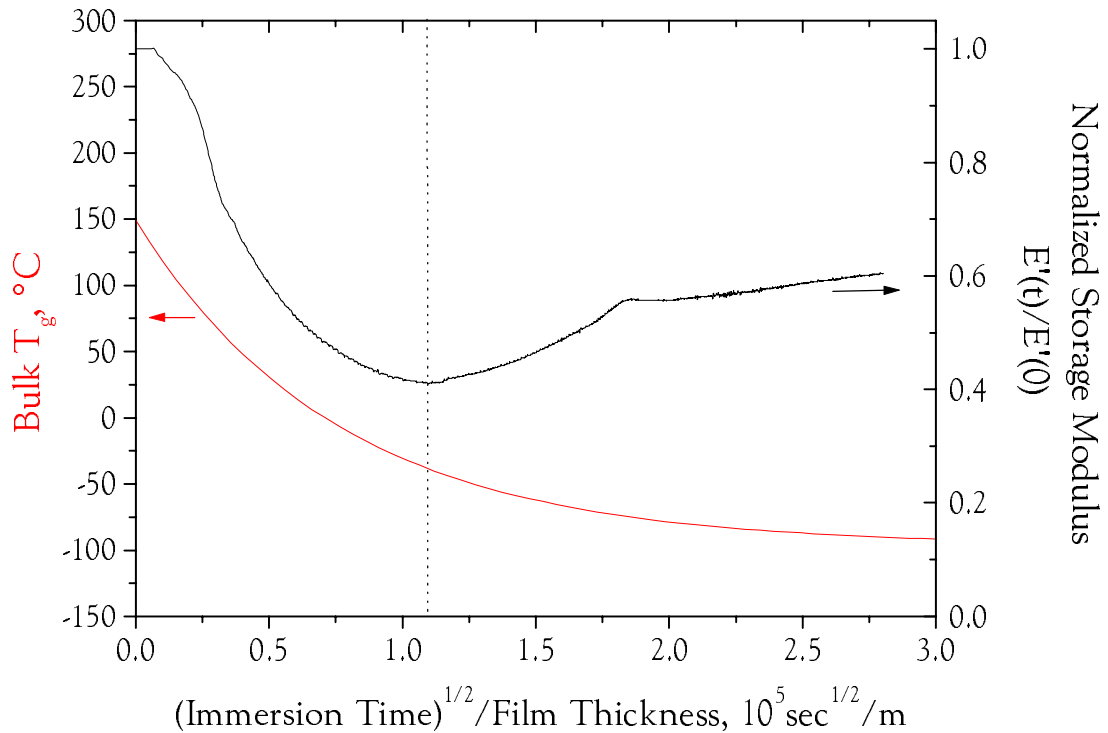


Figure 5.17 The effect of plasticization on the dynamic mechanical response of amorphous PEEK during isothermal immersion.

As the amount of bulk crystallinity increases, the reinforcing effect of the crystals begins to dominate the mechanical response. The minimum in the storage modulus occurs when approximately 60 % of the total system crystallinity is attained; the unaffected glassy region (z_g) represents 40 % of the initial volume of the PEEK film when the storage modulus is observed to increase. The plateau in the modulus at longer times coincides with the completion of bulk crystallization (Figure 5.18). It is speculated that the gradual increase in the storage modulus beyond this point is due to secondary crystallization.

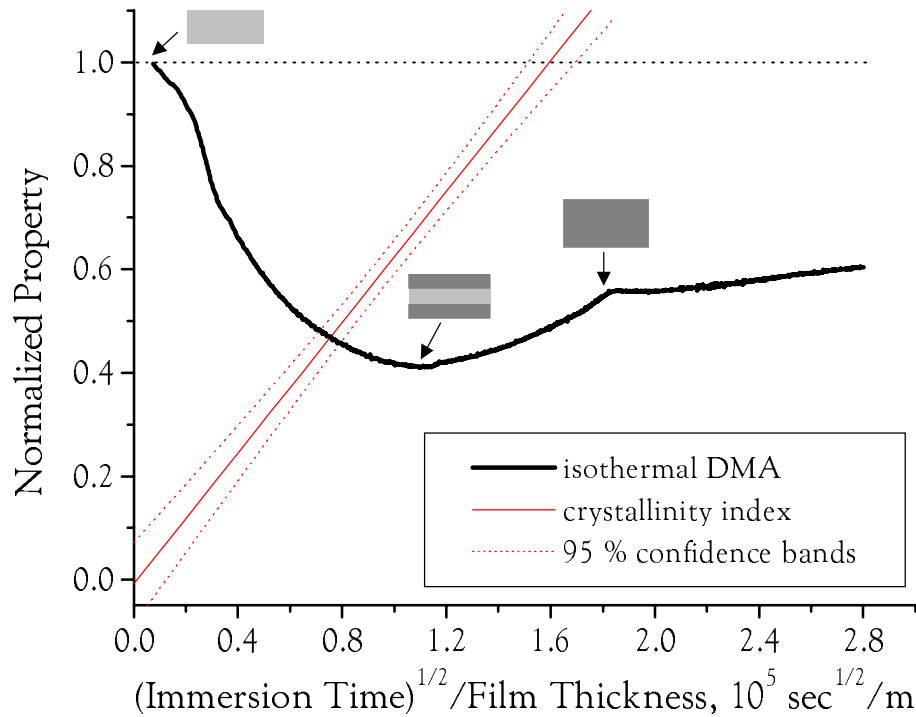


Figure 5.18 The effect of crystallinity on the dynamic mechanical response of PEEK during isothermal immersion.

6. CONCLUSIONS

Poly(aryl ether ether ketone) (PEEK) is used in applications such as filters, valves, and pump liners due to its excellent chemical resistance. However, it has been found that several common organic solvents cause swelling, crystallization, or environmental stress cracking/crazing to occur which lead to failure in-service. This study was aimed at learning how the diffusion, swelling, and crystallization processes are coupled during solvent-induced crystallization of PEEK. The objective was reached by correlating bulk properties or characteristics such as sorption, swelling, crystallinity, and dynamic mechanical response as a function of solvent chemistry and immersion time. The geometry of the specimens was such that the diffusion was constrained to one dimension (i.e. through the thickness of thin films from the surface inwards).

The kinetics of sorption, the solubility, and pseudo-Fickian diffusion coefficients were obtained from mass uptake experiments. The bulk crystallization kinetics and crystalline indices were determined from wide-angle x-ray diffraction. Differential scanning calorimetry was used as a secondary method to follow changes in crystallinity with immersion time. *In-situ* isochronal and isothermal DMA techniques were developed to analyze the glass transition and changes in the storage modulus of PEEK, respectively. The magnitude, breadth, and location of the glass transition were determined for each PEEK/solvent system at saturation. The progression of the solvent front through the film thickness was observed via SEM. Qualitative trends were observed based upon the chemical nature and molar volume of the solvents.

For all of the solvents studied, excluding amyl chloride, which did not absorb into amorphous PEEK, the rate of sorption increased with decreasing molar volume and increasing solubility. However, the molar volume alone does not determine which solvents will promote SINC. It was proposed that the polymer-solvent interactions that promoted SINC were acid-base in nature. The dichlorinated alkanes (MC and 1,3-dichloropropane) and the cyclic ether and ketone (THF and cyclopentanone, respectively) exhibited the fastest diffusivity/crystallization rates. In addition, the same four solvents

were estimated to suppress the glass transition the greatest and have the largest crystallization regime.

In-situ isochronal DMA spectra show that methylene chloride, toluene, tetrahydrofuran, cyclopentanone, chlorobenzene, and diethyl ketone suppress the T_g of PEEK from 150 °C to below ambient temperature. Subsequently, when the T_g of the polymer decreases below the experimental exposure temperature, the system is at a temperature between T_g and T_m and crystallization becomes kinetically favorable. The glass transition spans a 30-50 °C temperature range and the storage modulus exhibits an order of magnitude decrease. The modulus maintains a relatively high value in the rubbery state due to the presence of the reinforcing crystals.⁵³

In-situ isothermal dynamic mechanical tests for MC, THF, cyclopentanone, and chlorobenzene show that the storage modulus decreases at short times, subsequently increases, then reaches a plateau value. Results confirm that plasticization of the amorphous phase causes the modulus to decrease. As the degree of crystallinity increases with immersion time, the precipitation of crystals acts to reinforce the amorphous phase and the storage modulus begins to increase. This was found to occur when the film was crystallized to 60 % of its maximum value in a given solvent. When the storage modulus became time-independent, bulk crystallization was complete. The storage modulus is representative of a polymer that consists of a rubbery amorphous matrix reinforced with crystals (Figure 3.1 at $t = \infty$).

It was found that the bulk sorption rate was equal to the bulk crystallization rate for all PEEK/solvent systems and PEEK exhibited diffusion-limited crystallization, regardless of the nature of the transport mechanism. Thus, crystallization occurred simultaneously behind the advancing solvent front regardless of the time-scale for saturation (e.g. 20 minutes for MC versus two days for toluene). In addition, an increase in the extent of polymer-solvent interactions corresponded to a shift in the transport behavior from anomalous towards pseudo-Fickian. The rate of polymer chain relaxation

(i.e. molecular rearrangements in the presence of the solvent) was greater than the diffusion rate for the most interactive solvents.

WAXD photographs suggest that there is a preferred orientation of the crystals through the thickness of the films and no preferred orientation in the plane of the film. In addition, a distinct sorption front was observed further supporting the scenario of diffusion-controlled crystallization and one-dimensional diffusion. These results suggest two possible morphologies: (1) the crystalline superstructure that develops in the presence of the solvent is non-spherulitic or (2) spherulites develop during immersion and deformation occurs during the desorption process. Further analysis is necessary to verify the origin of the crystal orientation.

It is concluded that the low molecular weight aprotic liquid solvents in this study promoted solvent-induced crystallization of unoriented, amorphous PEEK at ambient temperature. Diffusion occurred from the surface of the films inwards and a discontinuity (i.e. sorption front) was observed at intermediate immersion times via SEM. The crystallization process was determined to be diffusion-limited as crystallization occurs simultaneously with the advancing front. Indirectly, WAXD results suggested that the solvent-induced crystals are small and/or imperfect and they exhibit preferred orientation. In addition, The *in-situ* storage modulus of PEEK is controlled by the competing effects of plasticization and crystallization during solvent immersion and a time-dependent value is attained when bulk crystallization is complete.

7. FUTURE WORK

In this study, the major research objective was accomplished satisfactorily and some additional information was obtained regarding the effect of organic solvents on the crystallization of amorphous PEEK. However, several questions remain unanswered due to limitations in characterization techniques or limitations in time. Therefore, the following experiments are proposed to extend the current work.

In particular, only relative changes in the storage modulus were necessary for analyzing the effect of solvents on the real-time dynamic mechanical response of amorphous PEEK in the presence of organic solvents. For this technique to measure absolute storage moduli, the effect of solvent density, solvent viscosity, and frequency will have to be quantitatively determined and subtracted from the DMA spectra.

One experiment would be to determine the effect of solvent density on the absolute storage moduli. Possibly, a higher density solvent may exert an upward force on the film specimen (due to buoyancy), and lead to erroneously high values of the moduli. To test this, a polymer such as polyethylene, which is relatively inert to most organic solvents, could be placed in solvents with lower and higher densities than itself. Isothermal DMA runs could be performed at ambient temperature and the storage modulus monitored as a function of immersion time. The first several minutes will establish if the density of the solvent affects the moduli. In this study, all the solvents had a lower density than PEEK except methylene chloride. At short immersion times, the bulk density was closer to that of amorphous PEEK and the polymer was less dense than MC. At longer times, the bulk density surpassed the density of MC.

Another defining experiment would be to determine the effect of chain structure on the solubility, sorption, crystallinity, and dynamic mechanical response in the same organic liquids. Polymers from the poly(aryl ether ketone) family would be ideal to study since they have similar chemistry as PEEK (e.g. PEEKK or PEKEKK have stiffer backbones and higher Tgs than PEEK due to a higher ketone:ether ratio). The polymer

should have a similar molecular weight average as PEEK 150PF used in the current study.

The ultimate experiment would involve directly imaging the fine structure of the crystals via AFM. To image the crystalline superstructure of the bulk polymer (i.e. in the center of the solvent-crystallized films) via AFM, it is necessary to obtain a flat surface of the film cross-section. In this study, SINC and thermally crystallized film specimens were prepared for AFM but unreproducible images were obtained. The specimens were mounted in epoxy and cut through the thickness with a clean razorblade to expose a section of the film cross-section. The surfaces were microtomed at -100 °C in an ethanol bath for 20 minutes, air-dried overnight, and placed in the AFM for observation. Some specimens, including the amorphous PEEK reference, had an oil-like substance on the surface that promoted interactions between the polymer surface and the silicon AFM tip. Regardless of the source of the PEEK films (e.g. commercially extruded or compression molded from powder), thermal or solvent-crystallized, good images could not be obtained in tapping mode. For AFM to provide useful/reproducible information regarding the bulk crystalline morphology of SINC films, it will be necessary to obtain a consistent surface with no artifacts. Surface moisture, contamination, or residual solvent may be causing surface-tip interactions.

It was originally hypothesized that the morphology may depend on the rate-limiting factor for crystallization. If r_s^* is greater than r_c^* then crystallization will occur homogeneously behind the sorption front and crystallization is limited by the mobility of the polymer chains in the presence of the liquid. If r_s^* is equal to r_c^* then crystallization, as was shown for the PEEK/solvent systems in this study, occurs instantaneously and the solvent front and crystallization front coincide and the crystallization process is diffusion-limited. It is expected that the diffusion-limited scenario would promote less perfect crystals. The next experiment would be to force the crystallization to be kinetics-limited by performing the same set of experiments with one solvent on thinner films and compare the morphology via AFM.

The presence of preferred orientation of the SINC crystals suggests the following two possibilities: 1) the superstructure is not spherulitic and crystal growth/arrangement are limited by the diffusion process or 2) the superstructure that develops during immersion is spherulitic but the desorption process causes deformation of the spherulites. Small-angle light scattering (SALS) on the solvent-crystallized PEEK films would determine if spherulitic morphology is present after desorption. Since turbidity becomes an issue at high levels of crystallinity/opacity, SALS will have to be performed on specimens that have been removed from solvent in the early stages of the sorption process (i.e. when minimal crystallinity has developed). In addition, an ideal test would be to perform photographic WAXD on a saturated film while it is immersed in solvent to determine if the orientation develops during the sorption process.

It is important to note that the melting behavior observed with DSC could not be explained in this study. The current speculation is that the lower temperature melt peak is representative of the melting of crystals that formed during isothermal immersion, similarly to the dual melting behavior exhibited for PEEK that has been isothermally crystallized near T_m . The polymer could be heated rapidly to a temperature above the lower melt peak and quenched below T_g to remove one population of crystals. Next, the morphology could be imaged via AFM and compared to a SINC specimen to determine the origin of the lower melt peak.

Now that a systematic series of experimental data has been obtained for solvent-crystallized PEEK, the next step would be to utilize the DR model, as described in Section 2.3, to quantitatively describe the concentration and crystallization behavior of PEEK. The DR mathematical model for SINC postulates a morphological discontinuity at the diffusion front. More recent models, are capable of predicting when such discontinuities develop. When distinct sorption fronts are observed for a given polymer/solvent system, as they were for the PEEK/solvent systems in this study, the DR model is valid, as a first approximation.

The DR mathematical model can quantitatively predict the sorption and crystallinity behavior if the following unknown constants are measured/estimated/calculated:

- film thickness (λ_p)
- threshold swelling concentration
- swelling kinetic exponent
- dimensionless crystallization rate (Ω)
- initial crystallinity (> 0 ; representative of nuclei)
- ultimate crystallinity (< 1)
- crystallinity at saturation
- volume fraction of solvent in the amorphous phase at saturation

The unknown functions in the DR model are concentration, $\gamma(\epsilon, \tau)$, crystallinity, $f(\epsilon, \tau)$, void fraction, $\epsilon(\epsilon, \tau)$, the location of the swelling front, $\lambda(\tau)$, and the location of the saturation front, $\lambda_s(\tau)$, where ϵ is the position from the surface of the film and τ is the immersion time. The best way to model the behavior is to set up an algorithm which increments the front position by $\Delta\lambda$, calculates the amount of time to reach that position, and determines the concentration and crystallinity profile. The profiles would be determined from $\lambda(0)$ (i.e. the surface of the PEEK film) to $\lambda(\tau)$ where $\lambda(\tau)$ is the location of the front at a given immersion time. Ahead of the front, the concentration and crystallinity are zero. The concentration at the film surface is constant and equal to the saturation concentration. As the solvent front progresses into the film, there will be some sort of concentration and crystallinity gradient from $\lambda_s(\tau)$ to $\lambda(\tau)$ that varies from the equilibrium value at the surface to zero at the solvent front. Void formation can occur behind $\lambda_s(\tau)$. The fronts meet in the middle of the film when $\lambda(\tau) = \lambda_p$. A schematic of an arbitrary concentration profile at a given time is shown in Figure 7.1.

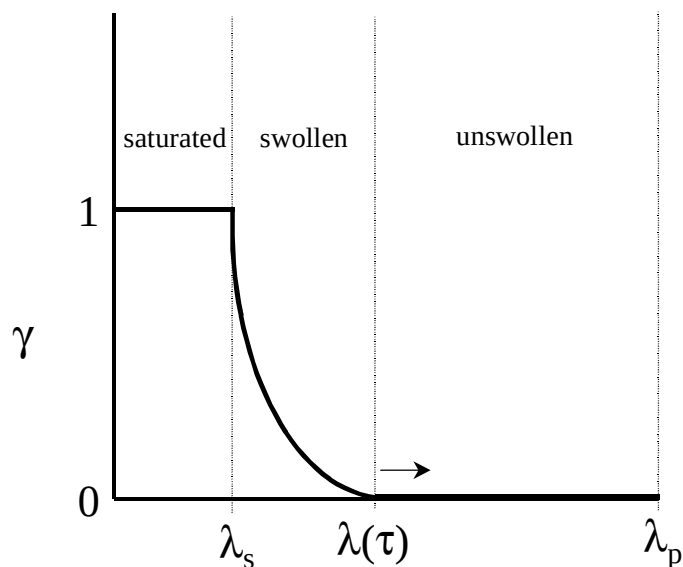


Figure 7.1 An arbitrary concentration profile at an intermediate immersion time.

One of the original objectives of this study was to define a quantitative indicator of SINC promoting solvents for a given polymer. There appeared to be a trend of decreasing sorption rates and solubility with increasing solvent molar volume for the series of aprotic solvents studied. However, amyl chloride, which did not promote SINC of amorphous PEEK, could not be discerned from the other solvents based solely on molar volume (refer to Figure 4.11). It is suggested that the dissociation constant (i.e. a measure of acidity) or dipole moment of the solvent may provide a better indication of which solvents will promote SINC of PEEK. A wider range of solvents needs to be investigated to establish a more comprehensive database.

REFERENCES

- ¹ D.J. Blundell and B.N. Osborn, "The morphology of poly(aryl-ether-ether ketone)", *Polymer*, Vol. 24, pp. 953 (1983)
- ² Ingersoll-Dresser Pumps Brochure, Form 71031-B
- ³ V. Hillyard, "Tough plastics make the grade", *Machine Design*, vol. 65, no. 24, pp. 66-70 (1993)
- ⁴ B.H. Stuart and D.R. Williams, "A study of the absorption of chlorinated organic solvents by poly(ether ether ketone) using vibrational spectroscopy", *Polymer*, vol. 36, pp. 4209-4213 (1995)
- ⁵ D.S. Kalika, J.C. Nickell, R.K. Krishnaswamy, and B.F. Barton, "Dynamic relaxation behavior of solvent-crystallized poly(ether ether ketone)", *J. of Poly. Sci.: Part B: Poly. Phys.*, Vol. 32, pp. 759 (1994)
- ⁶ A. Michele and V. Vittoria, "Transport properties of dichloromethane in glassy polymers: 5. poly(aryl ether ether ketone)", *Polymer*, Vol. 34, No. 9, pp. 1898 (1993)
- ⁷ C.J. Wolf and M.A. Grayson, "Solubility, diffusion and swelling of fluids in thermoplastic resin systems", *Polymer*, Vol. 34, No. 4, pp. 746 (1993)
- ⁸ C.J. Wolf, J.A. Bornmann, and M.A. Grayson, "Absorption of toluene in poly(aryl-ether-ether-ketone)", *J. Poly. Sci.: Part B: Poly. Phys.*, Vol. 30, pp. 113 (1992)
- ⁹ J.R. Lee and R.G. Kander, Supercritical Fluid Technology and Polymers, Ch.8, American Chemical Society, pp. 131 (1995)
- ¹⁰ H.T. Cornélis, Ph.D. Dissertation, "Effect of intermediate solvents on poly(ether ether ketone)", Virginia Polytechnic Institute and State University (1995)
- ¹¹ J.H. Hildebrand and R.L. Scott, Solubility of Nonelectrolytes, Reinhold, New York, (1950)
- ¹² Personal communication with Dr. Ronald G. Kander, Associate Professor, Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University (1999)

-
- ¹³ L. Rebenfeld, P.J. Makarewicz, H.-D. Weigmann, and G.L. Wilkes, "Interactions between solvents and polymers in the solid state", *J. Macro. Sci.-Rev. Macro. Chem.*, Vol. C15, No. 2, pp. 279-393 (1976)
- ¹⁴ B.H. Stuart and D.R. Williams, "The solvent-induced swelling of poly(ether ether ketone) by 1,1,2,2-tetrachloroethane", *Polymer*, Vol. 35, No. 6, pp. 1326-1328 (1994)
- ¹⁵ P.J. Makarewicz and G.L. Wilkes, "Small-angle x-ray scattering and crystallization kinetics of poly(ethylene terephthalate) crystallized in a liquid environment", *J. Poly. Sci.: Poly. Phys. Ed.*, Vol. 16, pp. 1559-1582 (1978)
- ¹⁶ A. Peterlin, *J. Macromol. Sci., Phys. Ed.*, vol. B11, pp. 57 (1975)
- ¹⁷ A. Arzak, J.I. Eguiazabal, and J. Nazabal, "Effects of methylene chloride sorption on the properties of poly(ether ether ketone)", *J. Poly. Sci.: Part B: Poly. Phys.*, Vol. 32, pp. 325-331 (1994)
- ¹⁸ Encyclopedia of Polymer Science and Engineering, 2nd ed., Vol.15, John Wiley & Sons, Inc., New York, pp. 394 (1989)
- ¹⁹ L.H. Sperling, Introduction to Physical Polymer Science, 2nd ed., John Wiley & Sons, Inc., New York, pp. 67 (1992)
- ²⁰ CRC Handbook of Solubility Parameters and Other Cohesion Parameters
- ²¹ E.J. Stober and J.C. Seferis, "Fluid sorption characterization of PEEK matrices and composites", *Poly. Eng. Sci.*, Vol. 28, No. 9, pp. 634 (1988)
- ²² P.C. Hiemenz, Polymer Chemistry, Marcel Dekker, Inc., New York, pp. 513-537 (1984)
- ²³ P.C. Painter and M.M. Coleman, Fundamentals of Polymer Science, 2nd Ed., Technomic Publishing Company, Inc., Pennsylvania, pp. 318-321 (1997)
- ²⁴ E.J. Stober, J.C. Seferis, and J.D. Keenan, "Characterization and exposure of polyetheretherketone (PEEK) to fluid environments", *Polymer*, Vol. 25, pp. 1847 (1984)
- ²⁵ G. Mensitieri, M.A. Del Nobile, A. Apicella, and L. Nicolais, "Time and temperature dependent sorption in poly-ether-ether-ketone (PEEK)", *Poly. Eng. and Sci.*, Vol. 29, No. 24, pp. 1786-1795 (1989)
- ²⁶ A.B. Desai and G.L. Wilkes, "Solvent-induced crystallization of polyethylene terephthalate", *J. Poly. Sci.*, Symposium No. 46, pp. 291-319 (1974)

-
- ²⁷ H. Ouyang and C-C. Chen, "Acetone transport in poly(ethylene terephthalate)", *J. Appl. Phys.*, Vol. 81, No. 10, pp. 6680 (1997)
- ²⁸ W.J. Waywood and C.J. Durning, "Solvent-induced crystallization of a compatible polymer blend", *Poly. Eng. Sci.*, Vol. 27, pp. 1265 (1987)
- ²⁹ C.J. Wolf, J.A. Bornmann, M.A. Grayson, and D.P. Anderson, "Solvent-induced crystallinity in poly(aryl-ether-ether-ketone) (PEEK)", *J. Poly. Sci.: Part B: Poly. Phys.*, Vol. 30, pp. 251 (1992)
- ³⁰ D.S. Kalika, D.G. Gibson, D.J. Quiram, and R.A. Register, "Relationship between morphology and glass transition temperature in solvent-crystallized poly(aryl ether ketones)", *J. Poly. Sci.: Part B: Poly. Phys.*, Vol. 36, pp. 65 (1998)
- ³¹ W. Liu, B. Breault, and J. Brisson, "Solvent-induced crystallization of Nylon-6I", *J. Poly. Sci.: Part B: Poly. Phys.*, Vol. 33, pp. 1559 (1978)
- ³² Shewmon, Paul G., *Diffusion in Solids*, McGraw-Hill Publishing, New York, pp. 124 (1963)
- ³³ R. McGregor., Diffusion and Sorption in Fibers and Films, Vol. 1, Academic Press, London (1974)
- ³⁴ ASTM D5229
- ³⁵ J. Crank and G.S Park, Diffusion in Polymers, Academic Press, New York (1968)
- ³⁶ P.J. Makarewicz and G.L. Wilkes, "Diffusion studies of poly(ethylene terephthalate) crystallized by nonreactive liquids and vapors", *J. Poly. Sci.: Poly. Phys. Ed.*, Vol. 16, pp. 1529-1544 (1978)
- ³⁷ L.H. Sperling, pp. 147 (1992)
- ³⁸ N.L. Thomas and A.H. Windle, "A theory of Case II diffusion", *Polymer*, Vol. 23, pp. 529 (1982)
- ³⁹ M.A. Del Nobile, G. Mensitieri, P.A. Netti, and L. Nicolais, "Anomalous diffusion in poly-ether-ether-ketone", *Chem. Engin. Sci.*, Vol. 49, No. 5, pp. 633-644 (1994)
- ⁴⁰ M. Gordon and J.S. Taylor, *J. Appl. Chem.*, Vol. 2, pp. 493 (1952)
- ⁴¹ T.G. Fox, *Bull. Am. Phys. Soc.*, Vol.1, pp. 123 (1956)
- ⁴² L.H. Sperling, pp. 330 (1992)

-
- ⁴³ R. P. Chartoff, P.T. Weissman, and A. Sircar, ASTM STP 1249, "The application of dynamic mechanical methods to T_g determination in polymers: An overview", pp. 88-107 (1994)
- ⁴⁴ L. Mandelkern, R.R. Garrett, and P.J. Flory, *J. Am. Chem. Soc.*, Vol. 74, pp. 3949 (1952)
- ⁴⁵ L.H. Sperling, pp. 229-244 (1992)
- ⁴⁶ "The Rubbery State and Crystalline State of Polymers", course notes on crystallization kinetics, Dr. G.L. Wilkes, Department of Chemical Engineering, VPI & SU
- ⁴⁷ P. Meares, Polymers: Structure and Bulk Properties, Van Nostrand, New York, Ch. 5 (1965)
- ⁴⁸ C.J. Durning, C.J. and Russel, W.B., "A mathematical model for diffusion with induced crystallization: 1", *Polymer*, Vol. 26, pp. 119 (1985)
- ⁴⁹ N.S. Kalospiros, G. Astarita, and M.E. Paulaitis, "Coupled diffusion and morphological change in solid polymers", *Chem. Engin. Sci.*, Vol. 48, no. 1, pp. 23-40 (1993)
- ⁵⁰ S. Justi, E.S. Sherman, and M. Olariu, "Degree of crystallinity calculations for polymer and catalyst materials", *Mat. Sci. Forum*, Vols. 166-169, pp. 109 (1994)
- ⁵¹ G.L. Wilkes, Encyclopedia of Physical Science and Technology, "Polymers, mechanical behavior", Vol.11 (1987)
- ⁵² S.H. Dillman and J.C. Seferis, "Dynamic mechanical analysis of polymeric systems in liquid environments", *Poly. Eng. Sci.*, Vol. 31, No. 4, pp. 253 (1991)
- ⁵³ A.B. Desai and G.L. Wilkes, "A method for evaluating the dynamic mechanical properties of a polymer fiber or film in a liquid environment", *Textile Research Journal*, Vol. 45, pp. 173-178 (1975)
- ⁵⁴ M.M. Browne, M. Forsyth, and A.A. Goodwin, "The effect of solvent uptake on the relaxation behavior, morphology, and mechanical properties of a poly(ether ether ketone)/poly(etherimide) blend", *Polymer*, Vol. 38, No. 6, pp. 1285-1290 (1997)
- ⁵⁵ P.C. Dawson and D.J. Blundell, *Polymer*, Vol. 21, pp. 577 (1980)
- ⁵⁶ R.H. Olley, D.C. Bassett, and D.J. Blundell, "Permanganic etching of PEEK", *Polymer*, Vol. 27, pp. 344-348 (1986)

-
- ⁵⁷ A. Jonas and R. Legras, "Thermal stability and crystallization of poly(aryl ether ether ketone)", *Polymer*, Vol. 32, No. 15, pp. 2691 (1991)
- ⁵⁸ The Merck Index, 11th Ed., Merck & Co., Inc., New Jersey (1989)
- ⁵⁹ C. Bas, P. Battesti, and N.D. Alberola, "Crystallization and melting behaviors of poly(aryletheretherketone) (PEEK) on origin of double melting peaks", *J. Appl. Poly. Sci.*, Vol. 53, pp. 1745-1757 (1994)
- ⁶⁰ R.T. Morrison and R.N. Boyd, Organic Chemistry, 5th Ed., Allyn and Bacon, Inc., New York (1987)
- ⁶¹ L.E. Alexander, X-Ray Diffraction Methods in Polymer Science, John Wiley & Sons, New York, pp. 71 (1969)
- ⁶² Y. Lee and R.S. Porter, "Double-melting behavior of poly(ether ether ketone)", *Macromolecules*, Vol. 20, No. 6, pp. 1336-1341 (1987)
- ⁶³ D.J. Blundell, "On the interpretation of multiple melting peaks in poly(ether ether ketone)", *Polymer*, Vol. 28, pp. 2248-2252 (1987)
- ⁶⁴ D.C. Bassett, R.H. Olley, and I.A.M. Al Raheil, "On crystallization phenomena in PEEK", *Polymer*, Vol. 29, pp. 1745-1754 (1988)
- ⁶⁵ R.P. Chartoff, P.T. Weissman, and A. Sircar, ASTM STP 1249, "The Application of Dynamic Mechanical Methods to Tg Determination in Polymers: An Overview", pp. 78-107, (1994)

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