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Solvent-induced crystallization of amorphous poly(ether ether ketone) by acetone

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A 0.3 mm thick amorphous poly(ether ether ketone) (PEEK) film was exposed to acetone until equilibrium in the weight uptake was recorded, and was then dried in a vacuum oven at 70°C. The resulting structure was compared to the initial structure by means of differential scanning calorimetry (d.s.c.), wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS), and infra-red (i.r.) spectroscopy. Although the exposed film remained translucent, all of these complementary techniques suggested the presence of crystallinity which was induced by the exposure of the amorphous PEEK film to the solvent. Copyright © 1996 Elsevier Science Ltd.

(Keywords: PEEK; solvent-induced crystallization; X-ray scattering study)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a high-performance semicrystalline thermoplastic which is widely used in composite and aerospace applications. PEEK has a high glass transition temperature, T_g, of 143°C and a high melting temperature, T_m, in the range from 330 to 350°C. The chemical resistance of PEEK was first believed to be very good, but recent studies have shown that PEEK can be swollen by either benzene derivatives (e.g. tetrahydrofuran) or small chlorinated hydrocarbons (e.g. 1,1,2,2-tetrachloroethane and methylene chloride), which can cause plasticization and further crystallization[1-9].

If the cooling rate from the melt is sufficiently high, PEEK can also be produced in the amorphous state. This permits the solvent-induced crystallization (SINC) process to be studied in greater detail, as there is essentially no crystallinity in the polymer before it is exposed to solvents.

In this present study, the effect of a very common solvent, namely acetone, on the structure of amorphous PEEK is studied by means of several complementary techniques. Acetone was found to induce crystallization in amorphous PEEK, as shown by differential scanning calorimetry (d.s.c.), wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS), and infra-red (i.r.) spectroscopy.

EXPERIMENTAL

Materials

PEEK powder was purchased from ICI (Victrex®, grade 150PF). It has a reported intrinsic viscosity of 0.15, with weight- and number-average molecular weights of 33 500 and 11 700, respectively. This PEEK powder is a commercial grade, which may contain additives, such as stabilizers for processing (antioxidants) and for use (ultra-violet (u.v.) stabilizers). The acetone used was an h.p.l.c. grade, purchased from Fisher.

Film preparation

The PEEK powder was compression moulded between metal plates by using a Carver laboratory hot press at 385°C for 5 min. A mould release agent (Frekote 800-NC, from Dexter Corporation) was used to prevent the PEEK melt from sticking to the metal plates and the Kapton sheets. The PEEK melt was quenched in ice water in order to obtain ~0.3 mm thick amorphous films. These amorphous films were physically aged in an oven at 135°C (8°C below the glass transition temperature of PEEK) for 66 h. Absence of orientation in the amorphous film was verified by using wide-angle X-ray scattering (WAXS) with a CuKα radiation source ($\lambda = 1.54$ Å) and a Warhus camera. Two broad amorphous haloes were obtained in both directions (perpendicular and parallel to the surface of the film) suggesting that no orientation was present in the amorphous PEEK film. The effect of the mould release agent on the solvent diffusion in the specimens was minimized by a mild polishing of the sample surface using a silicon carbide sandpaper (600 grit), which also minimized any damage to the surface of the films.

Dynamic solvent uptake measurements

The dynamic solvent uptake measurements consisted of placing a piece of the PEEK film in a solvent and periodically removing the specimen from the solvent and weighing it by using a Mettler AE30 millibalance. The sample was placed in a scintillation vial (total volume

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of 20 ml) with acetone, which was then stored at room temperature during the entire period of experimentation. Before each weight measurement, the surface of the sample was carefully wiped to eliminate any residual solvent. When the measurements were completed, the sample was promptly put back in its scintillation vial, with the entire process taking place over 20 to 30 s.

Desorption methods

The technique used to desorb the completely swollen PEEK samples consisted of first putting the samples in a desiccator under vacuum at room temperature until equilibrium in the weight loss was recorded and then placing the partly desorbed samples in a vacuum oven at 70°C, which is above the boiling point of acetone ($T_b = 56.5°C$), but far below the T_g of PEEK (143°C). Therefore, this technique permits drying of the samples without inducing further crystallization or other structural changes.

Some residual solvent ($\sim 2\%$ residual weight) remained in the structure even after equilibrium in the weight loss was recorded at 70°C. This residual solvent would be removed from the structure if drying was performed at a temperature above the T_g of the polymer. However, this high temperature would permit further crystallization to occur, which would then interfere with our morphological study of the solvent-induced crystallinity.

Differential scanning calorimetry

Differential scanning calorimetry (d.s.c.) runs were performed with a Mettler TA3000 DSC30 machine using 5 to 20 mg samples placed into a d.s.c. pan. The latter were heated from 100 to 400°C at a rate of $10°C\,min^{-1}$. The crystallinity indices were estimated by integrating the area under the melting peak and dividing this area by the theoretical value of $130\,J\,g^{-1}$ for the 100% crystalline PEEK heat of fusion[10]. For clarity in presenting the d.s.c. data, the curves were shifted on the *y*-axis (i.e. heat flow axis) and no values on the *y*-coordinates are given.

Wide-angle X-ray scattering

WAXS measurements on the films were performed with a PW 1720 X-ray generator (Philips Co.) at room temperature for scattering angles of 5 to 40°. The crystallinity index for each sample was estimated by integration of the area under the Gaussian peaks obtained by curve fitting. The crystallinity index is calculated as follows:

$$\text{crystallinity index} = \frac{A_c}{A_a + A_c} \qquad (1)$$

where A_c is the area under the crystalline peaks and A_a is the area under the amorphous halo. For clarity in presenting the WAXS data, the patterns were shifted on the *y*-axis (i.e. intensity axis) and no values on the *y*-coordinates are given.

Small-angle X-ray scattering

SAXS profiles were obtained using a Kratky camera equipped with a position-sensitive detector from Innovative Technology. A PW-1729 X-ray generator (Philips Co.) operating at 40 kV and 20 mA was used to produce CuKα radiation of wavelength 1.54 Å. The scattering intensity was obtained by subtracting the parasitic scattering from the sample scattering. Scattering intensities for all of the samples were normalized by the thickness of the sample and the intensity of the X-ray beam. The intensities reported here are absolute intensities based on the standard Lupollen.

Infra-red spectroscopic analysis of PEEK films

The compression moulded PEEK films were too thick for infra-red spectroscopic analysis to be performed, as the aromatic structure of PEEK is strongly absorbing in the mid-i.r. range[11]. Therefore, the PEEK film used for the infra-red spectroscopic analysis was a Stabar K200 film, which is an extruded non-crystallized film from ICI, made from Victrex®, with a thickness of 1 mm. The infra-red spectroscopic technique is used to study the effect of solvent exposure on the morphology of the amorphous PEEK film. Therefore, the PEEK film was used as received, or exposed to acetone until equilibrium in the weight uptake was recorded and then dried by using the desorption technique described above. It should be noted that the thin PEEK film used for the infra-red spectroscopic analysis was found to contain some amount of orientation that may affect the crystallinity, crystal orientation, and diffusion of the solvents in the polymeric films. Therefore, a direct comparison between the other characterization techniques for SINC (i.e. d.s.c., WAXS, and SAXS) is not possible. However, a relative comparison is appropriate here.

The infra-red spectrometer was a Nicolet 510 machine equipped with a triglycine sulfate (TGS) detector. Attenuated total reflectance (ATR) measurements were taken with a Seagull® variable angle accessory (Harrick Scientific Corporation). The ATR crystal was zinc selenide and the incident angle was 45°. The spectrometer bench was purged with dry nitrogen, and 400 scans were collected and averaged at a resolution of $4\,cm^{-1}$.

RESULTS

Figure 1 gives the weight percentage uptake of acetone by amorphous PEEK as a function of the square root of time (i.e. Fickian plot), as obtained from the dynamic solvent uptake measurements. From this figure, two important parameters can be obtained, namely the maximum solvent uptake and the time needed for equilibrium in the weight uptake to be reached. These are 14% and 12.5 days, respectively, for a 0.3 mm thick PEEK sample. No morphological changes (i.e. solvent-induced crystallization) were *visually* observed upon exposure of the amorphous sample to acetone at room temperature. Specifically, the films remain translucent. However, further analysis of the acetone-exposed amorphous PEEK sample revealed some morphological changes, as will be shown below. All results from the experiments that follow were obtained on amorphous PEEK samples that had been swollen with acetone until equilibrium in the weight uptake was reached and then dried by using the above-mentioned desorption technique.

The d.s.c. curves of the initial and acetone exposed samples are shown in *Figure 2*. The initial amorphous sample shows a distinct T_g transition at around 143°C. Note the endothermic peak around T_g that corresponds to physical ageing induced by heating the amorphous sample at 135°C for 66 h. An exothermic peak situated between 155 and 180°C corresponds to the crystallization process which occurs upon heating in the

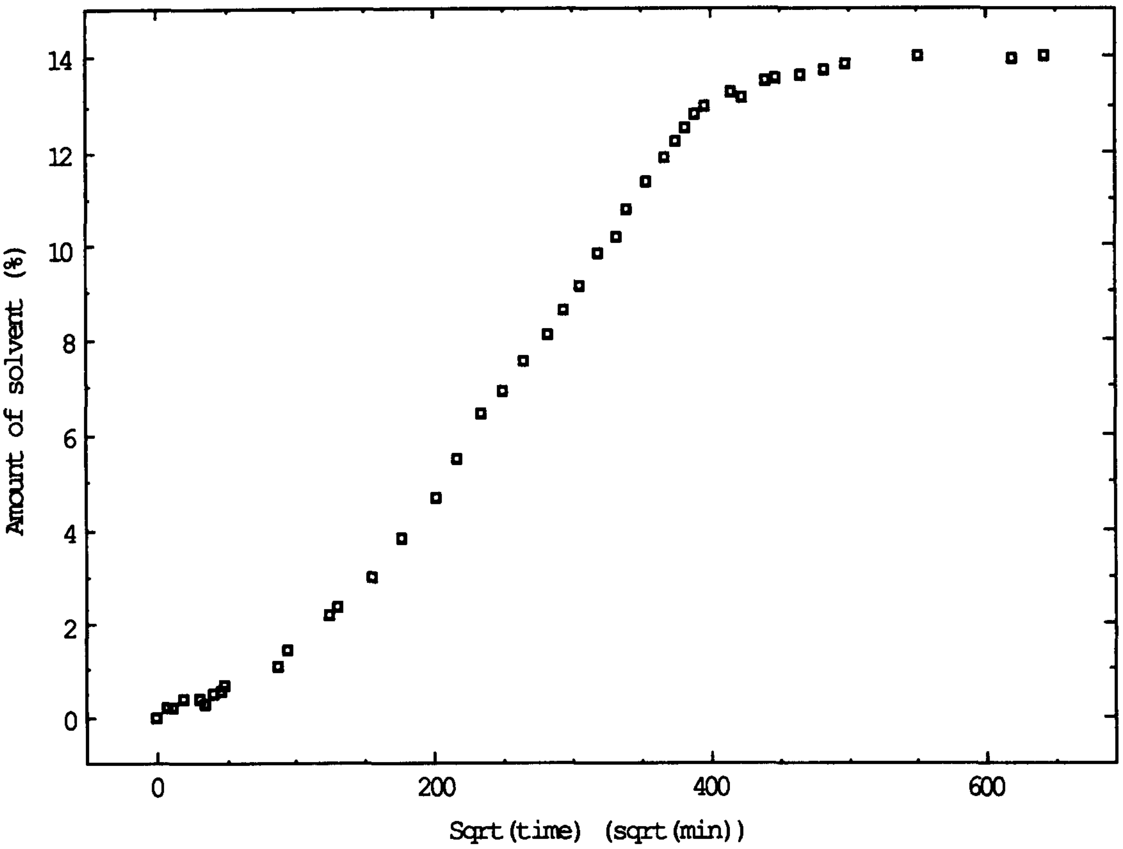

Figure 1 Acetone percentage uptake in PEEK *versus* the square root of time

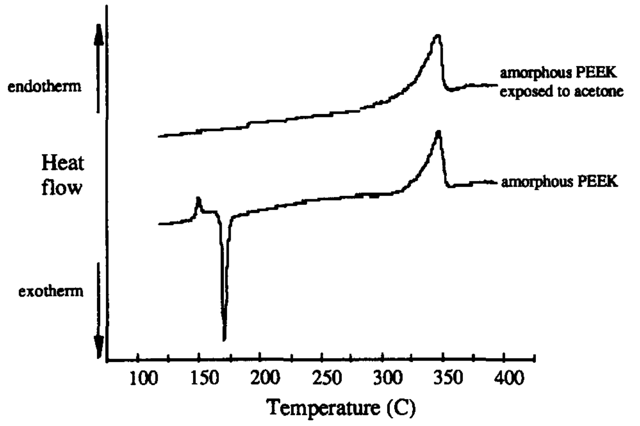

Figure 2 D.s.c. curves of initial and acetone-exposed PEEK samples

calorimeter, and is followed by an endothermic melting peak with a peak melting temperature of 344°C. This melting temperature falls inside the 330–350°C range reported in the literature. The disappearance of the crystallization exothermic peak after exposure to acetone, with the melting peak still being present, suggests that crystallinity was induced by the presence of acetone.

WAXS patterns of the initial and acetone-exposed samples are shown in *Figure 3*. The initial amorphous PEEK(0/0) displays a very broad amorphous hump, with no sharp peaks that are characteristic of a totally amorphous sample. The presence of crystalline peaks in the WAXS pattern of the amorphous PEEK samples exposed to acetone confirms the existence of SINC by acetone in the specimens. These crystalline peaks are less intense than those of thermally crystallized specimens[10,12–14], but the scattering angles at which they occur correspond to the scattering angles at which the crystalline peaks of thermally crystallized samples occur. The crystal structure of the solvent-induced PEEK crystals should therefore correspond to the crystal structure of thermally-induced PEEK crystals. The crystalline peaks of PEEK crystallized from the melt have been found to correspond to an orthorhombic unit cell, with the following crystal parameters: $a = 7.781$, $b = 5.922$, and $c = 10.056$ Å, with the c-axis being in the chain direction[15]. The crystallinity index, as evaluated by integrating the area under the Gaussian peaks from the WAXS pattern for this sample, is $\sim 5.9\%$.

SAXS patterns of the initial and acetone-exposed amorphous PEEK samples are given in *Figure 4*. The initial amorphous PEEK sample does not display any peaks, which is consistent with the absence of crystallinity. In the case of the sample exposed to acetone, a relatively broad peak appears with a maximum at a scattering vector of ~ 0.01 Å^{-1}, which corresponds to a long spacing of the order of 100 Å. Blundell and Osborn[10] have reported that the long spacing of PEEK crystallized from the melt is ~ 160 Å. Therefore, the long spacing of the solvent-crystallized PEEK samples is somewhat smaller than that of thermally crystallized samples. Moreover, the crystalline peak of the acetone-exposed sample is very broad, suggesting that the crystal morphology encountered in this sample must have a low degree of ordering.

Infra-red spectroscopy was also used for determining solvent-induced crystallization in the amorphous PEEK

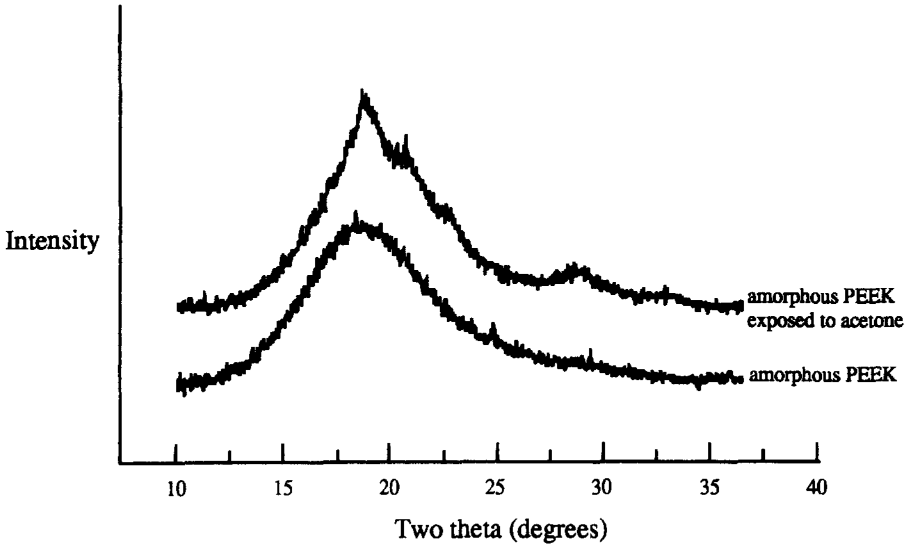

Figure 3 WAXS patterns of initial and acetone-exposed amorphous PEEK

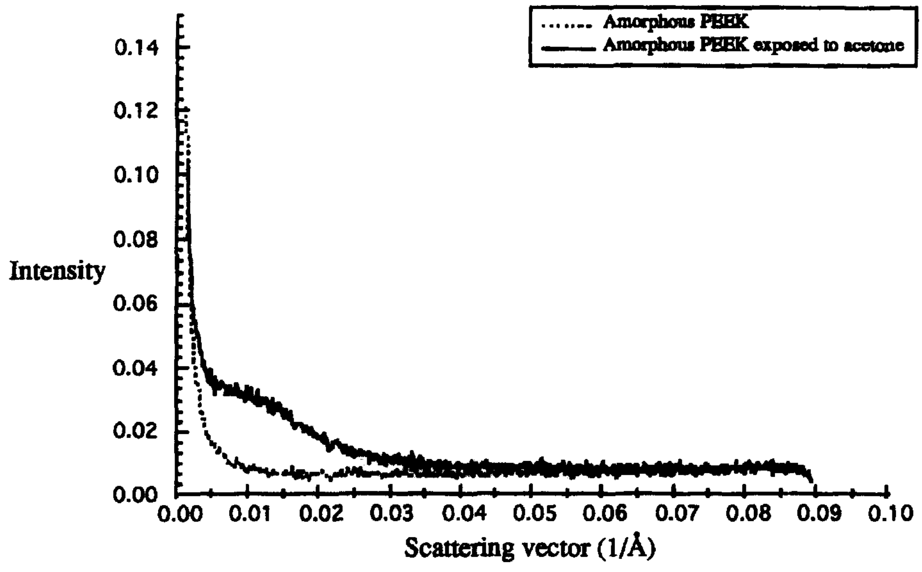

Figure 4 SAXS patterns of initial and acetone-exposed amorphous PEEK

sample. *Figure 5* shows the mid-i.r. spectra of the initial and acetone-exposed samples. According to Chalmers *et al.*[11], some bands in the mid-i.r. spectrum become both sharper and more intense with increasing crystallinity, as a result of the molecular units in the correct conformation crystallizing, while other bands decrease in intensity. Two band ratios are used in the study of crystallinity in PEEK by i.r. spectroscopy, namely 1305 cm^{-1}/1280 cm^{-1} and 970 cm^{-1}/952 cm^{-1}. Band ratios have been used since the intensity of mid-i.r. spectra are dependent on the area of contact between the sample and the reflection element.

Chalmers *et al.*[11] developed correlation graphs between each absorbance ratio and the crystallinity index of the polymeric films. Following their analysis, it is possible to evaluate the crystallinity indices of the acetone-exposed sample. A thermally crystallized PEEK sample was used as a reference. This sample was thermally crystallized from the glass state at 190°C for 60 min, and had a crystallinity index of 20.9% from the WAXS data. By extrapolating the crystallinity indices obtained by WAXS and the band ratios obtained by i.r. spectroscopy, the crystallinity indices could thus be obtained for the amorphous PEEK sample exposed to acetone. *Table 1* gives the band ratios and the crystallinity indices of amorphous PEEK, acetone-exposed amorphous PEEK, and thermally crystallized PEEK for both the 1305/1280 and 970/952 band ratios. The crystallinity indices correspond to a depth of penetration of the i.r. radiation of $\sim 1\,\mu m$, and therefore they may not correspond to the crystallinity indices encountered in the bulk of the polymer. The crystal morphologies may also be different in the surface layer to those in the bulk of the polymer. The diffusion of the solvent in a thin film (as used for the i.r. spectroscopy study) may be different to that in a thicker film, as the stresses induced by the solvent may be of different natures (i.e. plane stress vs. plane strain). However, the infra-red spectroscopic analysis of the solvent-exposed amorphous PEEK specimens confirmed the d.s.c., WAXS, and SAXS results in that *solvent-induced crystallization was induced by acetone in amorphous PEEK.*

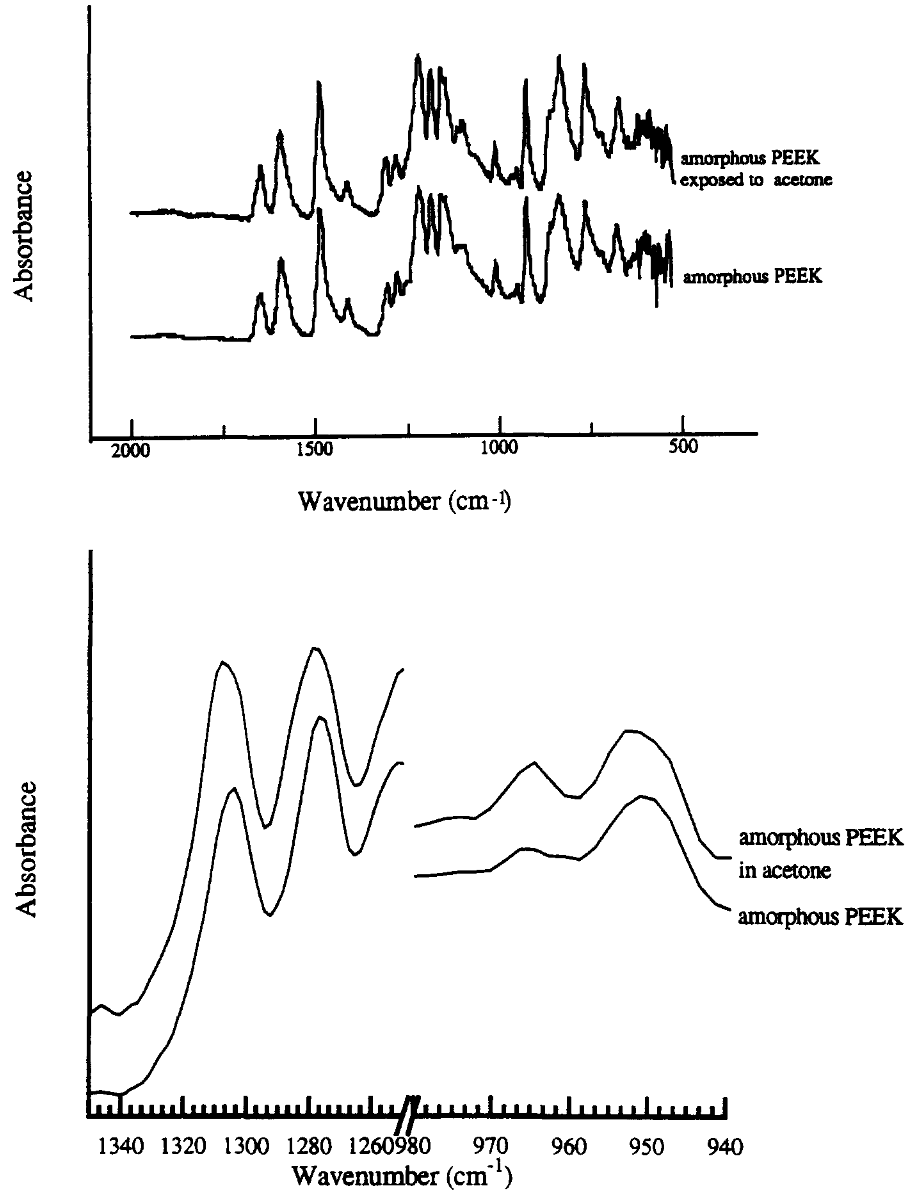

Figure 5 Infra-red spectra of initial and acetone-exposed amorphous PEEK films

Table 1 Values for the band ratio and crystallinity index of initial and acetone-exposed amorphous PEEK and thermally crystallized PEEK samples obtained by infra-red spectroscopy

	970/952 Band ratio		1305/1280 Band ratio	
Sample	Band ratio	x_c (%)	Band ratio	x_c (%)
Amorphous PEEK	0.539	0	0.811	0
Acetone-exposed amorphous PEEK	0.708	17.5	0.950	24.2
Thermally crystallized PEEK	0.741	20.9	0.931	20.9

DISCUSSION

All four of the techniques used in this study (i.e. d.s.c., WAXS, SAXS, and i.r. spectroscopy) showed that SINC is induced by acetone in amorphous PEEK. However, no information on the morphology of the solvent-induced crystals could be obtained by these four complementary techniques. In typical SINC processes, the samples become opaque upon exposure to the solvents. In this present study, the samples remained translucent upon exposure to acetone at room temperature. Small-angle light scattering (SALS) performed on the acetone-exposed sample did not show any scattering peaks. Thus, the crystal ordering is large enough to be detected by SAXS, but it is too small to be detected by SALS. Further study in our laboratory is under way to determine the scale of the ordered structure in this system.

When amorphous PEEK is exposed to acetone at a slightly higher temperature (i.e. 45°C), the sample becomes opaque. This suggests that the crystal entity becomes bigger as the temperature of solvent exposure is increased.

Solvent-induced crystallization is due to the plasticization of the polymeric chains by the presence of the solvent molecule, which disrupts the intermolecular forces between the macromolecules[16]. Such an effect causes the glass transition temperature to be depressed so that the experimental temperature becomes situated between the glass transition temperature and the melting point of the polymer. If the polymer is crystallizable, then crystallization ensues. The glass transition temperature of the system, T_g, can be estimated by the Fox equation[17], which takes the following form:

$$\frac{1}{T_g} = \frac{w_p}{T_g^o} + \frac{w_s}{T_g^s} \qquad (2)$$

where w_p and w_s are the weight fractions of the polymer and solvent, respectively, and T_g^o and T_g^s are the glass transition temperatures of the polymer and solvent, respectively. The glass transition temperature of PEEK is 416 K. The glass transition temperature of a solvent is not readily available; however, it can be estimated from its melting point. For low-molecular weight polar molecules, we find that the following relationship applies:

$$T_g \cong \tfrac{1}{2} T_m \qquad (3)$$

The melting point of acetone is 178.4 K, giving an estimated value for the glass transition temperature of 89.2 K. Using the weight fraction obtained from the dynamic solvent uptake measurements (i.e. $w_s = 0.14$ for acetone in amorphous PEEK) and the glass transition temperatures that we have just obtained gives a glass transition temperature of 1.97°C for the acetone/amorphous PEEK system. This value suggests that SINC is indeed induced at room temperature. However, this process takes place in a system that is poorly plasticized (i.e. the T_g of the system is only about 20°C lower than room temperature) and thus should give very low crystallinity, in addition to poorly organized crystal structures, as found with the d.s.c., WAXS, and SAXS data.

CONCLUSIONS

Exposure of an amorphous PEEK sample to acetone was found to induce crystallization. Even if this SINC process could not be seen visually (i.e. the sample remained translucent upon exposure to the solvent), it was detected by four complementary techniques, i.e. d.s.c., WAXS, SAXS, and i.r. spectroscopy. However, even if the spatial scale of the crystal ordering obtained by the acetone exposure was large enough to be detected by SAXS, it was too small to be detected by small-angle light scattering. This suggested that a relatively small crystal morphology was obtained, which is now under further investigation in our laboratory.

The Fox equation allowed the glass transition temperature of the system to be estimated. This T_g is ~ 20°C lower than room temperature (i.e. the temperature at which the exposure was performed in this study); therefore, the system is poorly plasticized, thus resulting in a very low crystallinity index (as shown by the WAXS and d.s.c. results) and poorly organized crystal structures (as shown by the SAXS results).

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