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Structure–property behaviour of poly(ether ether ketone)–polydimethylsiloxane block copolymers and their ketamine precursors

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The influence of changing the block length of the polydimethylsiloxane block on the structure/property behaviour of two poly(ether ether ketone)–polydimethylsiloxane (PEEK–PSX) multiblock copolymers and their amorphous (non-crystallizable) ketamine precursors (PEEKt–PSX) was investigated. In the precursor block copolymer form, as well as the reduced amorphous and its corresponding semicrystalline form, a microphase morphology was noted from transmission electron microscopy (TEM) studies. For the solution cast precursor or the compression moulded reduced amorphous systems, the materials displayed two T_gs at ca. -130 and $+145°C$, indicating strong phase separation. It was found that the room temperature tensile modulus of the PEEK–PSX multiblock copolymers with amorphous PEEK blocks of $\bar{M}_n = 4000$ increased by 800% as the PSX block length was decreased from $\bar{M}_n = 5000$ to $\bar{M}_n = 3000$, i.e. the PSX mass fraction was decreased from 56 to 45%. This increase in stiffness resulted from developing a more continuous phase of the PEEK block component. After crystallization of the PEEK blocks, the room temperature modulus of both of the PEEK–PSX copolymers increased by 200–500% in contrast to their amorphous forms. Relative to the PEEK homopolymer of approximately the same molecular weight, the melt crystallization half-times for the multiblock copolymers were increased by a factor of 500 for the PEEK(4K)PSX(3K) system and by a factor of 1000 for the PEEK(4K)PSX(5K) system. A dramatic dependence of crystallization behaviour on thermal history prior to crystallization was observed in both microphase-separated block copolymer systems. Block copolymers thermally crystallized from the glassy state obtained a distinctly higher degree of crystallinity at a much faster rate of crystallization than the same copolymers crystallized from the melt at identical crystallization temperatures. Copolymers crystallized from the glass attained maximum levels of PEEK crystallinity of ~ 40%, while those crystallized from the melt attained a maximum level of crystallinity of only 5–20%. The rate of crystallization for samples crystallized from the glass was ~ 30 times greater than that for samples crystallized from the melt at identical crystallization temperatures. Possible explanations for these observations are presented.

(Keywords: block copolymer; ketamine precursor; block length)

INTRODUCTION

Block or segmented copolymers have long sequences (blocks) of one type of repeat unit joined at one or both ends to blocks of a chemically different repeat unit. Such molecules often possess surface and bulk properties quite different from the corresponding homopolymers of the respective blocks. These copolymers are especially attractive in the fact that their molecular design may be tailored to a specific application by controlling such features as the chemical nature of the blocks, the architecture of the copolymer (i.e. diblock, triblock, or multiblock), as well as the block length of the respective blocks.

In the case where the chemical units within the backbone of the block copolymer are incompatible, these systems tend to form submicroscopic (1–100 nm), phase-separated domains[1]. In block copolymer systems where crystallization of one or both of the blocks does not occur, or in the case where microphase separation occurs before crystallization and no morphological change occurs upon crystallization of one or both of the phases, microsphere, cylinder, lamella, and bicontinuous microstructures are commonly observed. In this case the morphology achieved also depends on the chemical nature of the blocks, the film preparation technique (melt vs. solvent casting as well as the type of solvent used), and the volume fraction of each block type in the particular system[2,3]. However, when crystallization may occur concurrently with or before phase separation, the resulting morphology can be strongly influenced by crystallization, phase separation, or the competition between the two processes[4].

Theoretical predictions of equilibrium morphologies of crystallizable block copolymer systems have been made by Di Marzio *et al.*[5], Whitmore and Noolandi[6], and Vilgis and Halperin[7]. In each of these cases, the amorphous segments were considered to be attached to

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crystalline segments in lamellar crystals. The equilibrium morphology was determined by the energy associated with the thermodynamics of phase separation combined with the energy associated with crystallization within the semicrystalline blocks. In such a case the most thermodynamically favourable state is determined by balancing the contributions due to the entropic effects of microphase separation, combined with the free energy of crystal formation, the free energy of the crystal surface, and the elastic energy associated with the deformation of the covalently coupled segments. These models, however, are purely thermodynamic and no considerations were given to the complicated competition between the kinetics of crystallization and phase separation. However, in the case where the chemical nature of the blocks is highly dissimilar,the blocks are strongly segregated and subsequent crystallization within one or both of the phases is unlikely to affect the morphology. In the case where the chemical incompatibility of the two blocks is only minimal, the blocks are only weakly segregated, and crystallization in one or both of the blocks may result in significant morphological changes.

Considerable research has been undertaken to investigate the morphology of crystallizable block copolymers[4,8,9]. Gervais and coworkers investigated triblock copolymers including poly(ethylene oxide) or poly(ϵ-caprolactone) as the crystallizable block and polystyrene or polybutadiene as the amorphous block[10–13]. A lamellar morphology of alternating crystalline and amorphous layers was observed. Cohen and coworkers have recently observed a strong path dependence on the final morphology of block copolymers cast from solvents[14,15]. They observed that in polydimethylsiloxane–nylon-6 diblock copolymers with varying block lengths, the final morphology is highly dependent on sample history. In the case where a solvent was highly selective for one of the blocks, microphase separation occurred before crystallization and a lamellar morphology was observed. In the case where a less selective solvent was used, phase separation and crystallization occurred concurrently and a spherulitic morphology containing spherical siloxane microdomains was observed.

Recently research has also been undertaken to investigate the nature of chain folding in crystallizable block copolymer systems. Douzinas and Cohen[16] have recently postulated that in a diblock copolymer of ethylene-*co*-butylene-*b*-ethylethylene orientation of the folded crystallized chains is surprisingly parallel to the direction of lamellar orientation, i.e. 90° from the orientation predicted from thermodynamic theories of crystallization of block copolymers! This system is an example of a strongly segregated system in which microphase separation occurs prior to crystallization. In this case the unusual chain folding was attributed to the influence of topological constraints on the crystallizable blocks which are constrained to crystallize in microphase-separated domains. In contrast, Rangarajan and Register[17] have found that for ethylene–(ethylene-*alt*-propylene) block copolymers, a system which phase separates upon crystallization of the polyethylene blocks, chain folding occurs parallel to the lamellar normal. Hence, with regard to chain folding features, controversy exists and further work is needed to address this issue.

Aromatic poly(arylene ether ketones) are important as high-performance engineering thermoplastics due to a combination of good mechanical properties and solvent resistance, as well as a high-use temperature. Siloxane polymers offer properties such as low surface energy, hydrophobicity, low dielectric constant, low T_g (ca. -125°C), as well as good chemical stability at elevated temperatures[18]. Poly(ether ether ketone)–polydimethylsiloxane, multiblock copolymers, denoted as PEEK–PSX in this paper, have been successfully synthesized by using a relatively thermally stable imide link between the segments[19]. Using these materials we now investigate the effects of crystallization of the PEEK block. In this system the glass transition (and crystalline melting point) of PSX is low enough for this segment to act as a 'fluid' during the crystallization of the PEEK phase and during mechanical testing at ambient temperature. Additionally, the difference between the electron densities of these polymers facilitates easy monitoring of phase behaviour through small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Since the electron density distribution functions of the two polymers are also substantially different, changes in the crystallinity of the PEEK phase are easily measured through wide-angle X-ray diffraction (WAXD) measurements since the scattering due to the amorphous PSX phase is easily deconvoluted from that of the PEEK phase. While keeping the PEEK block length at 4K, the effects of changing the PSX block length from 5K to 3K were observed in terms of structure, mechanical properties and crystallization behaviour. Additionally, the effects of crystallinity within the PEEK phase on both structural features and dynamic mechanical behaviour were investigated.

EXPERIMENTAL

Materials

Perfectly alternating copolymers of PEEK–PSX were synthesized by first preparing oligomers of norbornene anhydride terminated polydimethylsiloxane (PSX) (*Figure 1*). These functionalized PSX oligomers were then reacted with aryl amine terminated poly(ether ether ketimine) PEEKt) in a condensation reaction. The resultant polymer was a perfectly alternating copolymer of PSX and PEEKt containing a protected ketone group. Rapid and complete hydrolysis of the ketimine in solution resulted in a perfectly alternating copolymer of PEEK and PSX which precipitated in the semicrystalline form (*Figure 2*). Further details of the synthetic scheme are published elsewhere[18,20].

In this study two PEEKt–PSX copolymers and the two corresponding hydrolysed PEEK–PSX copolymers were studied (*Table 1*). The precursor PEEKt–PSX copolymers had a PEEKt block number-average molecular weight of 4900 (5K) and PSX block number-average molecular weights of 3200 (3K) and 4900 (5K). It is expected that the polydispersity of the PEEK blocks is approximately 2 since these blocks were polymerized via a polycondensation reaction. The PEEK–PSX copolymers formed by hydrolysis of the ketimines had a PEEK block molecular weight of 3900 (4K), due to a loss of mass during hydrolysis of the ketamine. In this study the non-crystallizable precursor ketimine copolymers will be referred to as PEEKt(5K)PSX(3K) and PEEKt(5K) PSX(5K) and the reduced crystallizable ketone polymers

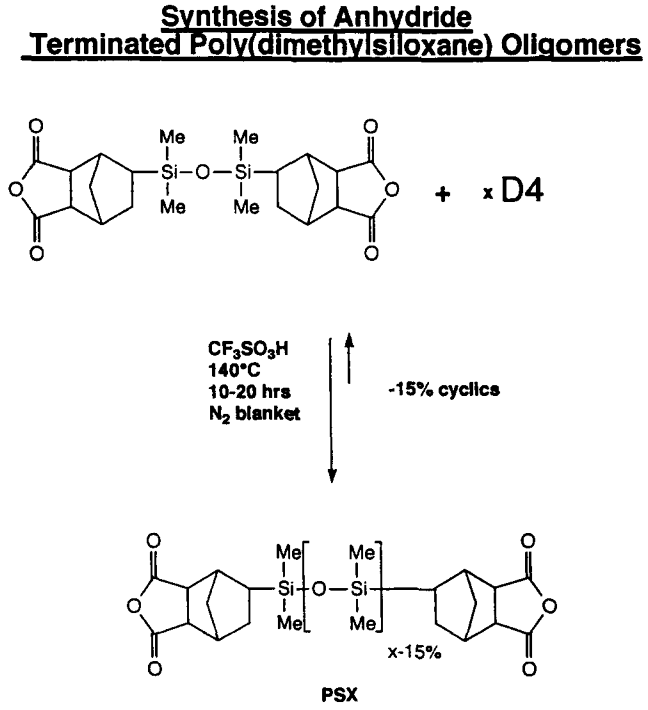

Figure 1 Synthesis of anhydride terminated polydimethylsiloxane oligomers via a ring-opening polymerization of D4 ($Si_4H_8O_4$)

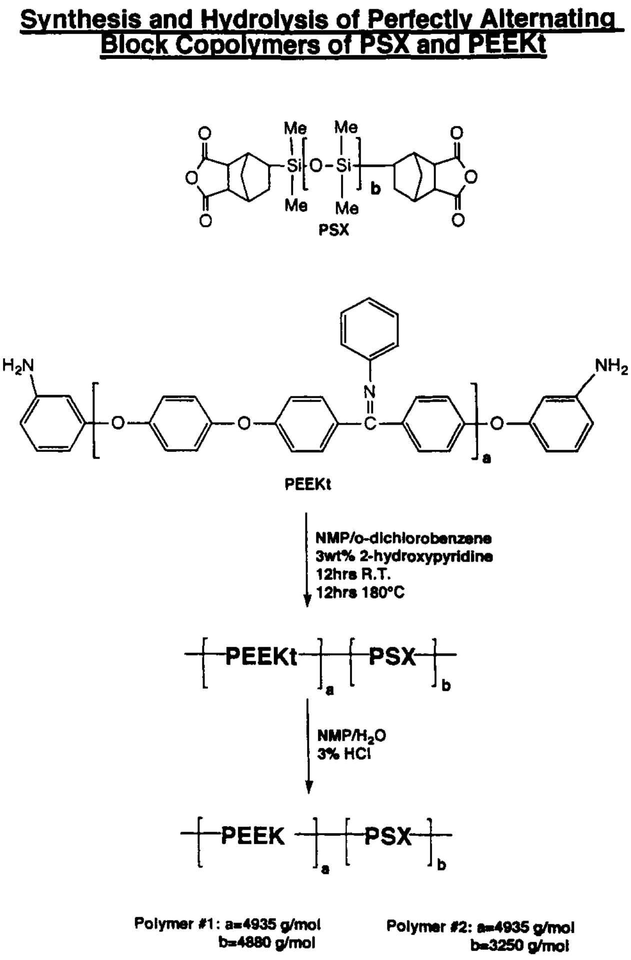

Figure 2 Synthesis and hydrolysis of perfectly alternating poly(ether ether ketone)–polydimethylsiloxane block copolymers

Table 1 Number-average molecular weights of the blocks in the copolymers studied in this work

Sample	PSX	PEEKt	PEEK
PEEKt(5K)PSX(3K)	3 200	4 900	–
PEEKt(5K)PSX(5K)	4 900	4 900	–
PEEK(4K)PSX(3K)	3 200	–	3 900
PEEK(4K)PSX(5K)	4 900	–	3 900

will be referred to as PEEK(4K)PSX(3K) and PEEK(4K)PSX(5K).

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

Structural characterization

All WAXD experiments were performed on a Nicolet model Stoe/V-2000 diffractometer operating at 40 kV and 30 mA. CuKα X-rays (1.54 Å) were passed through a graphite monochromator prior to final collimation. Data were collected at 0.05° increments between the angles of 10 and 35° for samples of PEEK–PSX copolymers and the amorphous PEEK homopolymer. For the PSX homopolymer a scan range of 5 to 35° was used. At each step a data acquisition time of 15 s was used. Data collection and analysis was performed using the Siemens Polycrystalline Software package.

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

Transmission electron microscopy (TEM) samples were prepared from films of the PEEKt–PSX copolymers, amorphous films of PEEK–PSX copolymers and PEEK–PSX films that had been directly crystallized in a dynamic mechanical spectrometer at 230°C for 30 min. Samples were ultramicratomed at −140°C, using a Reichert-Jung ultracut E43 ultramicrotome equipped with a diamond knife, in three normal directions. Samples were cut to a thickness of ca. 500 Å. All TEM studies were performed on a Phillips IL 420T scanning transmission electron microscope with an acceleration voltage of 100–120 kV.

Mechanical testing

The stress–strain behaviour of the samples was examined by using an Instron Model 1122 tensile tester interfaced to a computer for data collection and stress calculation. Small dog-bone specimens, stamped from either the films of the solution-cast precursor or from the compression moulded PEEK–PSX systems, with cross sectional areas of 1.75 mm^2, were tested with a gauge length of 10 mm and a crosshead speed of 2 mm min^{-1} under ambient conditions. In each case three samples were run in order to determine reproducibility.

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

Thermal analysis

A Seiko 220C differential scanning calorimeter equipped with an auto cooler was used to obtain bulk crystallization information as well as the heat of crystallization as a function of sample composition and thermal history. Amorphous films were heated to 360°C at a rate of 10°C min^{-1} under dry nitrogen and held at 360°C for 6 min before being quenched to the isothermal crystallization temperature. *Crystallization from the melt occurred very slowly and was only observable in a reasonable time frame by this method in a very narrow temperature range between 225 and 235°C for the PEEK(4K)PSX(3K) copolymer and in the temperature range of 229 to 232°C for the PEEK(4K)PSX(3K) copolymer.* Isothermal crystallization experiments were not possible at either higher or lower temperatures to these due to limitations of the long-term temperature stability and sensitivity of the calorimeter used in this study. Isothermal crystallization experiments were also performed on amorphous films that had been quenched from the melt in an ice/water bath by placing these films in a differential scanning calorimetry (d.s.c.) cell equilibrated at the crystallization temperature. After all isothermal crystallization runs, samples were again heated to 360°C at 10°C min^{-1} in order to determine the heat of melting.

DATA ANALYSIS

Thermal analysis

Percentage crystallinity was determined from the d.s.c. data by integrating the entire region under the melting endotherm to obtain the heat of melting as a function of temperature and prior thermal history. Assuming the difference between the heat of crystallization and heat of melting to be negligible, this value was then normalized by the mass fraction of PEEK within the copolymer and the molar heat of fusion of the PEEK homopolymer to obtain the percentage crystallinity within the PEEK phase. A value of 130 J g^{-1} was assumed as the heat of fusion of perfectly crystalline PEEK[21].

WAXD

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

Yao has recently developed procedures for resolution of overlapping WAXD curves and for subsequently determining the apparent crystallinity relative to the entire sample as well as the relative crystallinity within the crystallizable phase. He has used this procedure to determine the crystallinity of poly(ethylene oxide)–

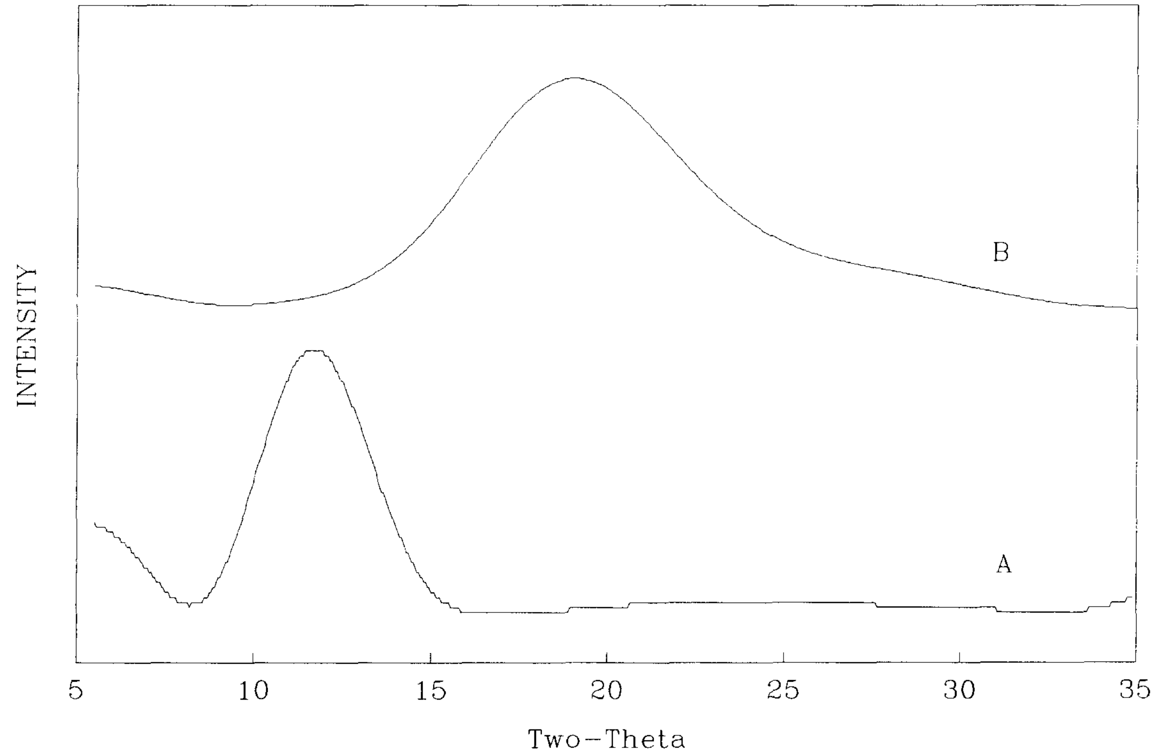

Figure 3 WAXD scattering profiles obtained from: (A) 1200 CP, methyl-endcapped polydimethylsiloxane; (B) amorphous PEEK

polystyrene block and graft copolymers[22,23], and poly(methyl acrylate)–poly(ethylene oxide) graft copolymers[24], as well as poly(methyl methacrylate) graft copolymers and their ionic complexes[25]. In each of these cases the peak deconvolution procedure was complicated due to the fact that the scattering profiles due to the amorphous components of the respective blocks were similar; thus, it was difficult to deconvolute the scattering contributions due to the amorphous phases.

In our case a slight modification of the procedures used by Yao was possible due to the great differences that were evident in the WAXD scattering profiles of amorphous PEEK and PSX homopolymers. *Figure 3* illustrates the differences evident in the scattering profiles of amorphous PEEK homopolymer with that of 1200 cP, methyl-endcapped polydimethylsiloxane. PEEK has an amorphous halo with a maximum intensity at 18.75° and a f.w.h.m. (full width at half maximum) of 7.4°, while PSX has an amorphous halo with maximum intensity at 11.4° and a f.w.h.m. of 3.5°. The scattering profiles of the amorphous PEEK–PSX copolymers are shown in *Figure 4*. By subtracting the scattering profile of PEEK from the raw data of the two copolymers in the 10–35 degree range, the scattering profile of the PSX phase over this range of angles is obtained and is then normalized as a function of the PSX volume fraction (*Figure 5*). These data may then be subtracted from the raw data along with the background scattering to obtain the scattering contribution due to the PEEK phase alone.

Once the above method of peak subtraction had been carried out, the crystallinity determinations were performed on the PEEK phase by using a similar approach to that of Hermans and Weidinger[26]. The method of peak deconvolution used in this study has been previously utilized by the present authors to determine the crystallinity of LARC CPI[27] and nylon-6[28]. The amorphous scattering profile was fitted to the total scattered intensity and subtracted from the total scattered intensity of the PEEK phase, thus yielding the scattering peaks due to the crystalline phase alone. The ratio of the integrated intensity under these peaks compared to the total scattered intensity gave the crystallinity of the PEEK phase. It is recognized, however, that this technique does not take into account any minor corrections for differences in atomic

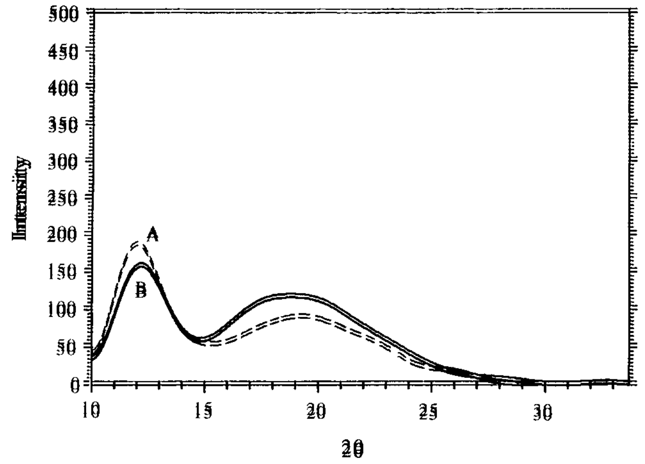

Figure 4 WAXD scattering profiles of amorphous PEEK–PSX block copolymers: (A) PEEK(4K)PSX(5K); (B) PEEK(4K)PSX(3K)

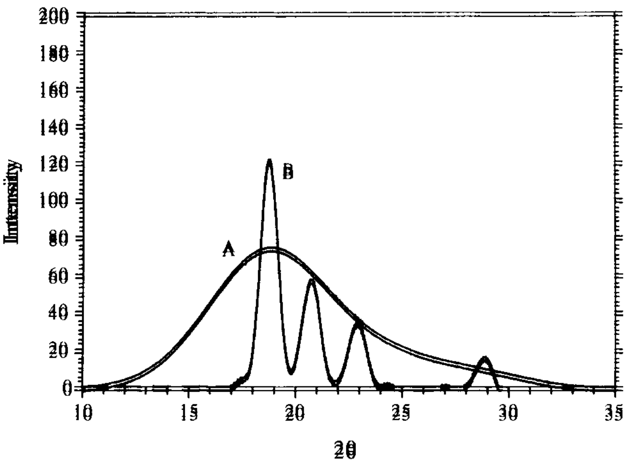

Figure 6 Resolution of WAXD data into amorphous and crystalline components: (A) smoothed amorphous scattering profile; (B) smoothed crystalline peaks

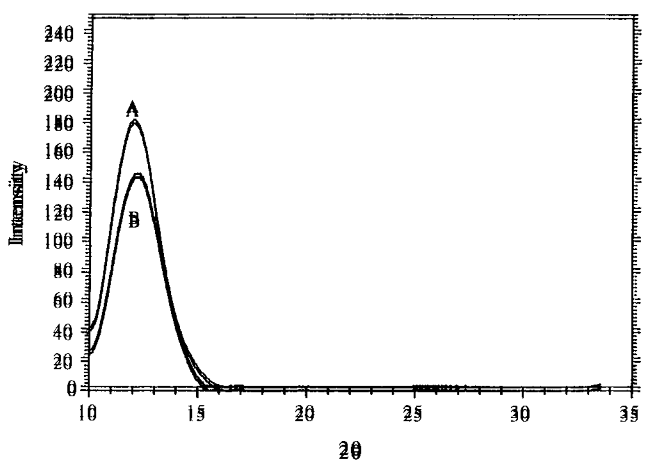

Figure 5 Deconvoluted WAXD scattering profiles due to the PSX component in PEEK–PSX block copolymers: (A) PEEK(4K)PSX(5K); (B) PEEK(4K)PSX(3K)

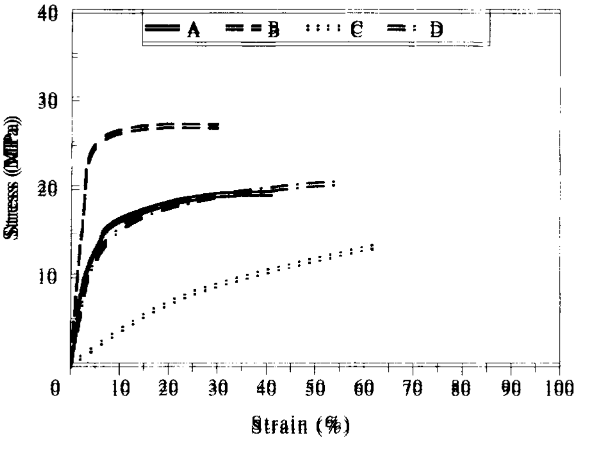

Figure 7 Stress–strain curves obtained from tensile testing of PEEKt–PSX and amorphous PEEK–PSX copolymers: (A) PEEKt(5K)PSX(5K); (B) PEEKt(5K)PSX(3K); (C) PEEK(4K)PSX(5K); (D) PEEK(4K)PSX(3K)

Table 2 Results of stress–strain testing on PEEK–PSX and amorphous PEEK–PSX copolymers at 23°C

Sample	Modulus (MPa)	Elongation-to-break (%)
PEEKt(5K)PSX(3K)	690 ± 15	30 ± 5
PEEKt(5K)PSX(5K)	390 ± 30	40 ± 5
PEEK(4K)PSX(3K)	290 ± 5	55 ± 15
PEEK(4K)PSX(5K)	36 ± 2	60 ± 15

and thermal diffuse scattering. The experimental method of peak resolution is outlined in *Figure 6*.

RESULTS AND DISCUSSION

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

Transmission electron microscopy experiments were easily facilitated, due to the differences in the densities of PEEK and PSX: 1.40 g cm^{-3} for crystalline PEEK, 1.26 g cm^{-3} for amorphous PEEK[29] and 0.98 g cm^{-3} for

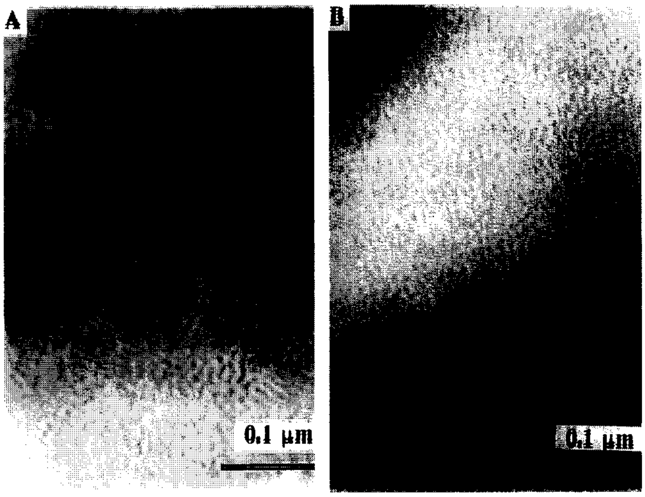

Figure 8 Transmission electron micrographs of PEEKt–PSX copolymers: (A) PEEKt(5K)PSX(5K); (B) PEEKt(5K)PSX(3K)

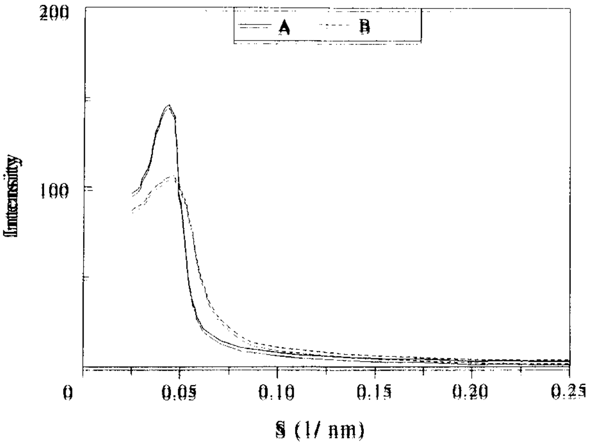

Figure 9 SAXS profiles obtained from PEEKt–PSX copolymers: (A) PEEKt(5K)PSX(5K); (B) PEEKt(5K)PSX(3K)

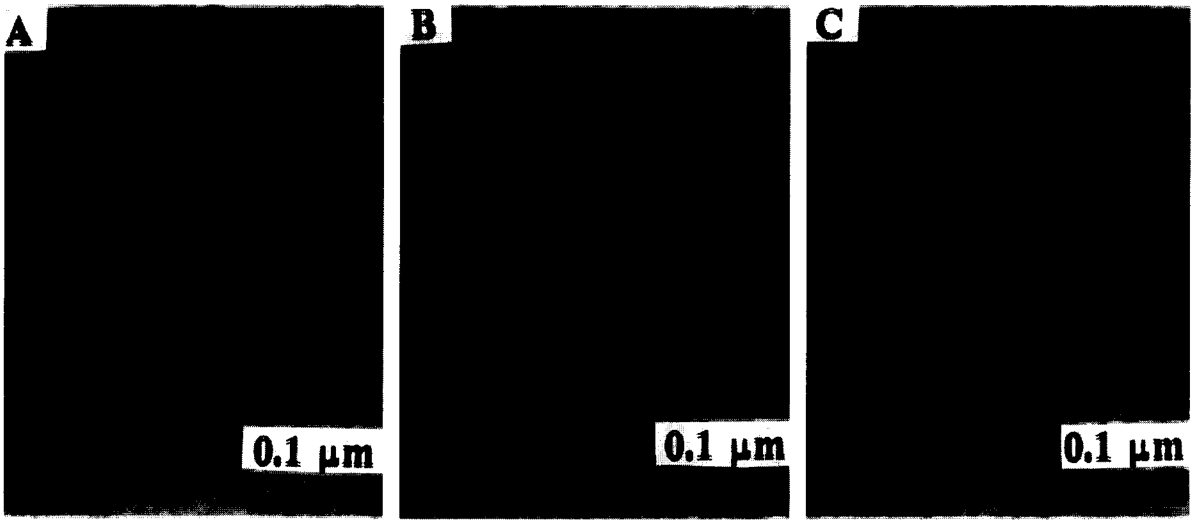

Figure 10 Transmission electron micrographs of the PEEK(4K)PSX(5K) copolymer: (A) observation normal to film surface; (B, C) perpendicular sections, with observations parallel to the film surface

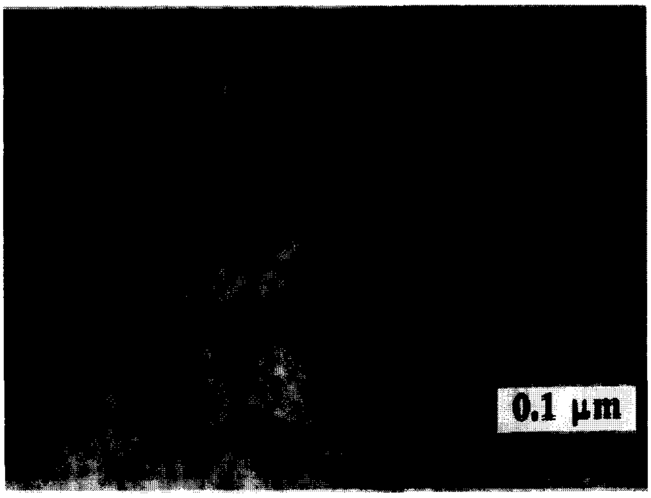

Figure 11 Transmission electron micrographs of the semicrystalline PEEK(4K)PSX(5K) copolymer

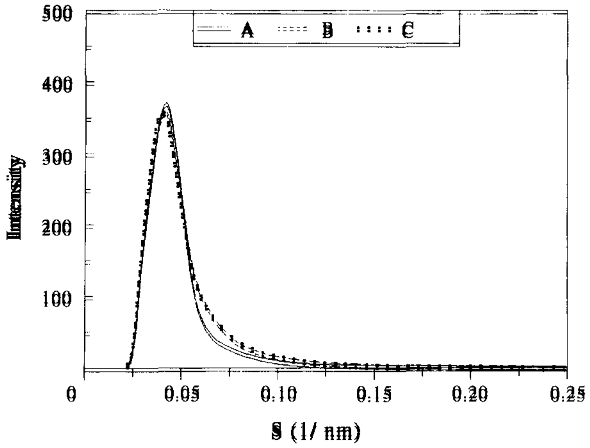

Figure 12 SAXS profiles obtained from the PEEK(4K)PSX(5K) copolymer: (A) amorphous sample; (B, C) semicrystalline sample with beam parallel and perpendicular to the film normal, respectively

polydimethylsiloxane[30]. Transmission electron micrographs obtained for the PEEKt–PSX copolymers revealed a lamellar-like morphology in the PEEKt(5K)PSX(5K) copolymer (*Figure 8A*) and a morphology with a more continuous PEEKt phase and microdomains of PSX in the PEEKt(5K)PSX(3K) copolymer (*Figure 8B*). Smeared SAXS scans on the PEEKt–PSX copolymers indicated an estimated interdomain spacing of ≈ 225 Å for the PEEKt(5K)PSX(5K) copolymer and 240 Å for the PEEKt(5K)PSX(3K) copolymer (*Figure 9*).

The notable decrease in modulus for the PEEK(4K) PSX(5K) system relative to the corresponding ketamine precursor is believed to be due to a disruption of continuity in the PEEK phase in this system. Transmission electron micrographs of the amorphous PEEK(4K) PSX(5K) copolymer in three normal directions (*Figures 10A–C*) reveal that the sample possesses an isotropic, bicontinuous morphology which is notably different from that of its ketimine precursor. Continuity of the PSX phase in this sample is, therefore, consistent with the low modulus observed. *TEM performed on the crystalline sample* (Figure 11) *revealed no change in morphology due to crystallization of the PEEK phase. Thus, in this system where strong segregation is expected, the morphology attained while pressing the film becomes locked-in prior to crystallization and subsequent crystallization must take place in isolated microdomains, as will be discussed later.* SAXS patterns obtained for the PEEK(4K)PSX(5K) copolymer indicate an approximate smeared interdomain spacing of 250 Å for both the crystalline and amorphous samples (*Figure 12*). This peak, however should be interpreted cautiously for it is somewhat distorted due to its nearness to the beam stop. However, this value corresponds closely to the interdomain spacing observed in the transmission electron micrographs. The only differences evident in the SAXS scans of the crystalline and amorphous PEEK(4K)PSX(5K) copolymer was a slight reduction in peak intensity and the development of a shoulder on the peak corresponding to a possible change in the microdomain long spacing. This may be due to the low levels of crystallinity attained in these materials upon crystallization, as will be discussed later.

Transmission electron micrographs, normal and perpendicular to the surface of an amorphous film of the PEEK(4K)PSX(3K) copolymer, reveal a more lamellar-like morphology intermixed with less defined textures (*Figures 13A* and *B*). Similar morphological features have been observed by Hashimoto in systems near the cylindrical-lamellar transition composition[31]. The fact that the lamellar structure in this system is not as well defined as in the 4K–5K system, may possibly be attributed to the fact that the volume fraction of the two phases for this copolymer may be nearer to the transition composition for formation of cylindrical microdomains of PSX. Transition electron micrographs of crystalline PEEK(4K)PSX(3K) reveal that the lamellar structure is retained in this system during crystallization; however, the interlamellar spacing appears to change due to crystallization (*Figure 14*). The change evident in the smeared SAXS patterns of the PEEK(4K)PSX(3K) copolymer is consistent with the development of a more highly ordered lamellar structure: however, the SAXS data are smeared data and this causes peak broadening (*Figure 15*).

Dynamic mechanical analysis (d.m.a.)

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

Similar tests were performed on the amorphous PEEK–PSX copolymers; however, due to the ability of these polymers to crystallize during the d.m.a. experiments, these tests were carried out up to temperatures of ≈ 330°C, at which point the PEEK began to melt. *Figure 17A* illustrates the storage modulus data obtained at a frequency of 1 Hz and *Figure 17B* illustrates the corresponding tan δ behaviour. For these copolymers the dynamic mechanical behaviour is more complex due to both the crystallization and the melting of the PEEK phase. Additionally, in the PEEK(4K) PSX(5K) copolymer, crystallization and melting of the PSX phase also occurred, a phenomenon not observed in the corresponding PEEKt–PSX copolymer. Besides the two glass transition temperatures, due to the PSX and PEEK phases, at −130 and 145°C, respectively, crystallization of the PEEK phase occurs in the temperature range between 145 and 200°C, while in the PEEK(4K) PSX(5K) system crystallization and melting of the PSX phase occurs in the temperature range from −130 to −50°C. It is interesting to note that the glass transition of the PEEKt phase is only slightly affected by conversion to the PEEK phase, i.e. both samples begin to soften at ≈ 145°C. D.m.a. scans were also made in the temperature range from 0 to 230°C for samples which were crystallized from the glass at 230°C for 30 min. The storage modulus values obtained from these tests at 1 Hz are summarized in *Table 3*. The PEEK(4K)PSX(3K) sample shows an increase in the modulus at 20°C from 300 MPa for the amorphous sample to 500 MPa for the semicrystalline sample. The PEEK(4K)PSX(3K) sample shows an increase in modulus at 20°C from 4 MPa for the amorphous sample to 20 MPa for the semicrystalline sample, i.e. a fivefold increase! *Figures 18A* and *B* compare the storage modulus and corresponding tan δ behaviour of an amorphous PEEK(4K)PSX(3K) sample with a semicrystalline sample. The presence of crystallinity shifts the maximum value in the tan δ curve

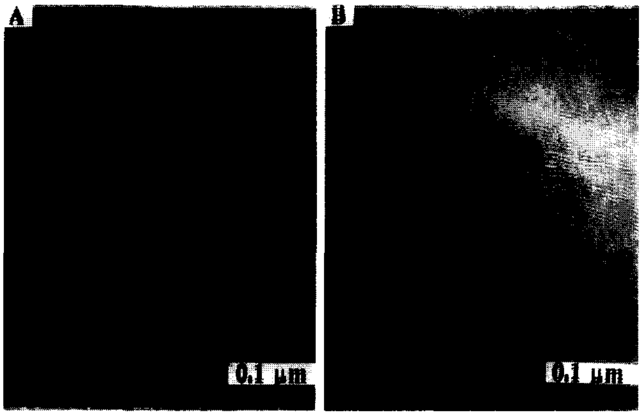

Figure 13 Transmission electron micrographs of the amorphous PEEK(4K)PSX(3K) copolymer: (A) observation normal to film surface; (B) observation parallel to film surface

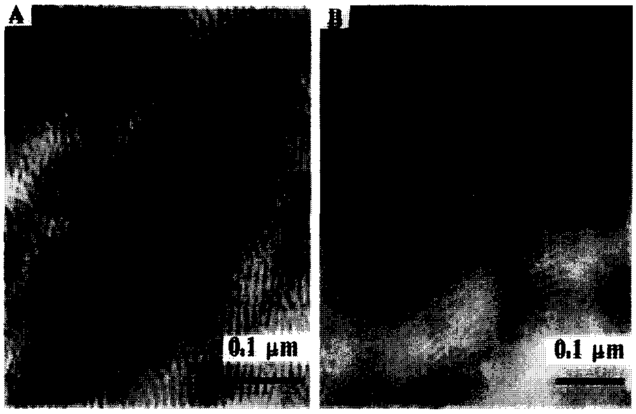

Figure 14 Transmission electron micrographs of the semicrystalline PEEK(4K)PSX(3K) copolymer: (A) observation normal to film surface; (B) observation perpendicular to film surface

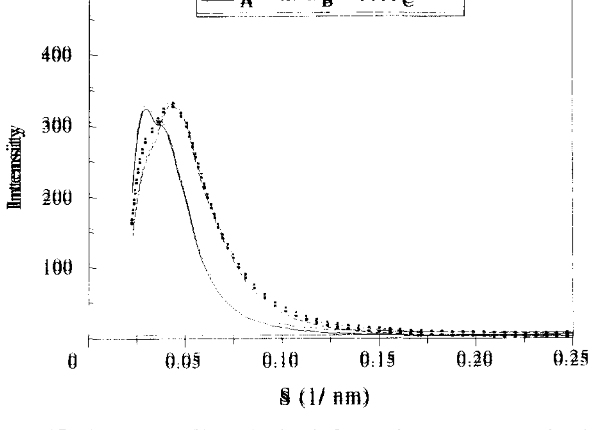

Figure 15 SAXS profiles obtained from the PEEK(4K)PSX(3K) copolymer: (A) amorphous sample; (B, C) semicrystalline sample with beam parallel and perpendicular to the film normal, respectively

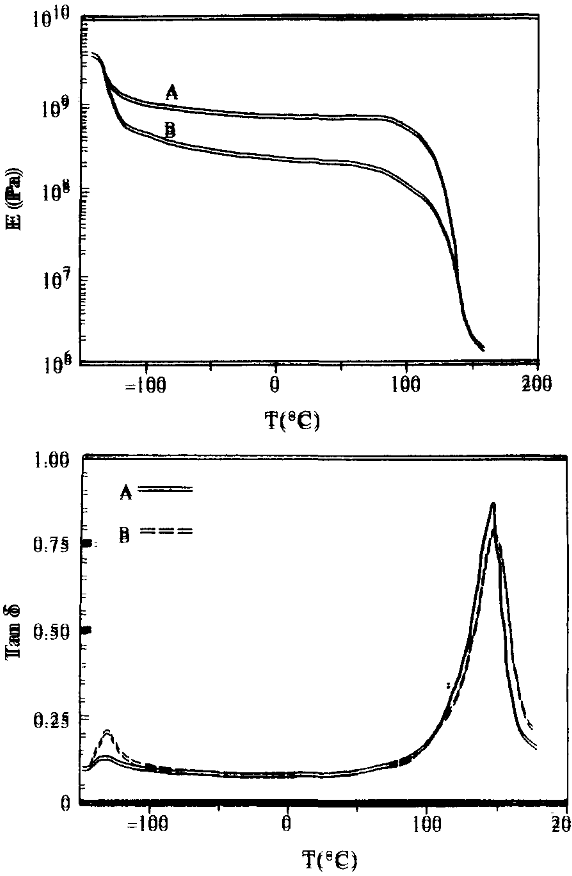

Figure 16 Dynamic mechanical testing of PEEKt–PSX copolymers showing storage modulus (E') data (A) and tan δ data (B): (A) PEEKt(5K)PSX(3K); (B) PEEKt(5K)PSX(5K)

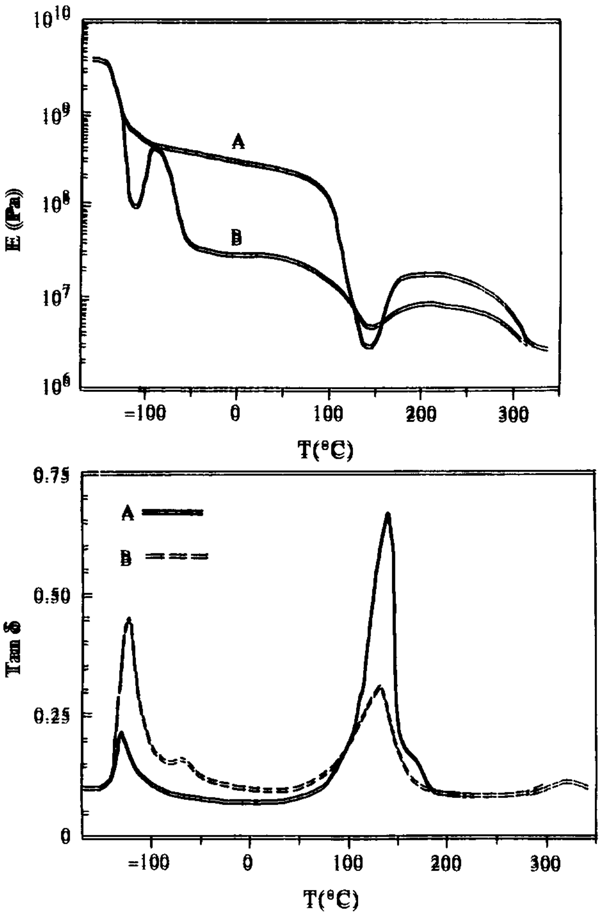

Figure 17 Dynamic mechanical testing of PEEK–PSX copolymers showing storage modulus (E') data (A) and tan δ data (B): (A) PEEK(4K)PSX(3K); (B) PEEK(4K)PSX(5K)

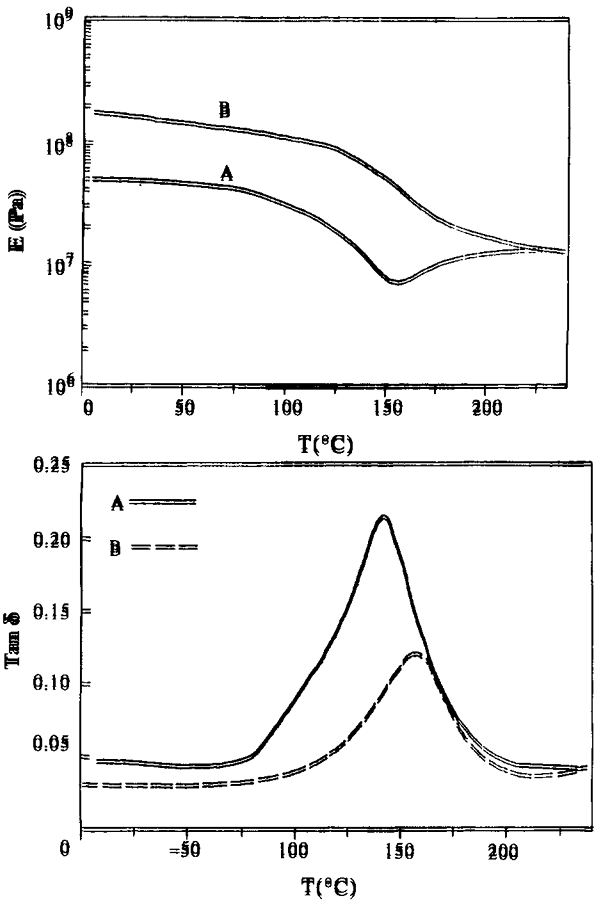

Figure 18 Dynamic mechanical testing of the PEEK(4K)PSX(5K) copolymer showing storage modulus (E') data (A) and tan δ data (B): (A) amorphous sample; sample crystallized at 230.5°C

approximately 15°C higher for the semicrystalline sample than for its amorphous counterpart. The reduction of the amplitude of the tan δ peak at the T_g is also indicative of a smaller fraction of the material being in the amorphous state, and therefore undergoing a glass transition.

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

X-ray diffraction

In order to determine the amount of crystallinity actually attained in the PEEK phase in these copolymers WAXD experiments were performed on the PEEK(4K) PSX(3K) and PEEK(4K)PSX(5K) copolymer. As discussed earlier, the scattering due to the PSX phase was subtracted from the total scattering profile of the block copolymers and the resulting profile was then compared to that obtained from a PEEK homopolymer with a number-average molecular weight of ≈ 30K. As addressed earlier, *Figure 4* illustrates the wide-angle X-ray scattering behaviour for the two amorphous PEEK–PSX copolymers. As the compositions change from the 4K–5K polymer to the 4K–3K polymer, the scattered intensity corresponding to the PEEK phase increases and the scattered intensity due to the PSX phase decreases, according to the copolymer compositions. Additionally, peak integrations performed on the deconvoluted peaks agree well with the respective weight fractions. WAXD experiments were performed on the PEEK(4K)PSX(3K) and PEEK(4K)PSX(5K) copolymers, which *were crystallized from the glass* at 230°C for 30 min, as well as the PEEK homopolymer which was crystallized at 230°C from the melt (*Figure 19*). Crystallinity of the PEEK

Table 3 Results of dynamic mechanical testing at 20°C (1 Hz) showing effects of crystallinity within the PEEK phase

Sample	Modulus (MPa)		Percentage increase (%)
	Amorphous	Semicrystalline	
PEEK(4K)PSX(3K)	300	500	167
PEEK(4K)PSX(5K)	4	20	500

phase was determined from the X-ray data to be ca. 40% for both copolymers, while the homopolymer attained approximately the same level of crystallinity when crystallized under similar circumstances.

The f.w.h.m. breadth of various peaks was measured to determine if peak broadening occurred due to changes in the long-range ordering or crystallite sizes. Hindeleh and Johnson have measured peak breadths in polyamide, polyester, and cellulose fibres and related these measurements to weight-average crystallite sizes normal to the (*h k l*) diffracting planes[32,33]. Their analysis as well as ours, however, neglected the effects of thermal and structural disorder. Similar analysis performed on the 1 1 0, 1 1 1, and 2 0 0 peaks in the PEEK–PSX copolymers illustrated that substantial line broadening occurred in these polymers relative to that of the PEEK homopolymer (*Table 4*). In this case it is likely that a substantial contribution of line broadening is due to disruption of structural order due to the attachment of non-crystrallizable polydimethylsiloxane blocks on to the surface of PEEK crystallites. The fact that the 1 1 0 and 2 0 0 peaks are more substantially broadened than the 1 1 1 peak indicate that fewer structural irregularities occur along the *c*-axis. These structural irregularities are almost certainly associated with the short nature of the PEEK blocks, since both the (1 1 0) and the (2 0 0) planes are parallel to the direction in which the polymer molecules traverse the unit cell in PEEK. It is likely that less chain folding occurs in these copolymers since the domain spacing observed from SAXS measurements and TEM experiments is of the order of 200 to 250 Å, which is very close to the average length of the crystallizable PEEK blocks. In addition, since the distribution of the PEEK block lengths is rather broad due to their development by a step-growth reaction, as indicated above, there are likely to be many short PEEK blocks which may also substantially disrupt the crystalline order.

Crystallization behaviour

Isothermal crystallization experiments performed on PEEK–PSX block copolymer powders indicated that these block copolymers crystallized at much slower rates than the corresponding PEEK homopolymer with a molecular weight on the order of the PEEK block length or even PEEK homopolymers with much higher molecular weights. This result is likely to be due to two contributing factors. First, the crystallizable PEEK blocks in this system are connected to PSX blocks in segregated domains. While the PSX blocks are liquid-like in the crystallization range of the PEEK blocks, the high chemical incompatability of these two blocks will place a restriction on the ease of chain transport in the PEEK phase during crystallization. Additionally, the PEEK phase is segregated into microdomains in which the likelihood of heterogeneous nucleation events is decreased. Furthermore, since the PSX segments are highly fluid in this system, the likelihood of self nucleation at the domain interfaces may be very low. Analysis of crystallization in this block copolymer system must therefore address both chain mobility and crystal nucleation.

Typical Avrami analysis could not be used to accurately

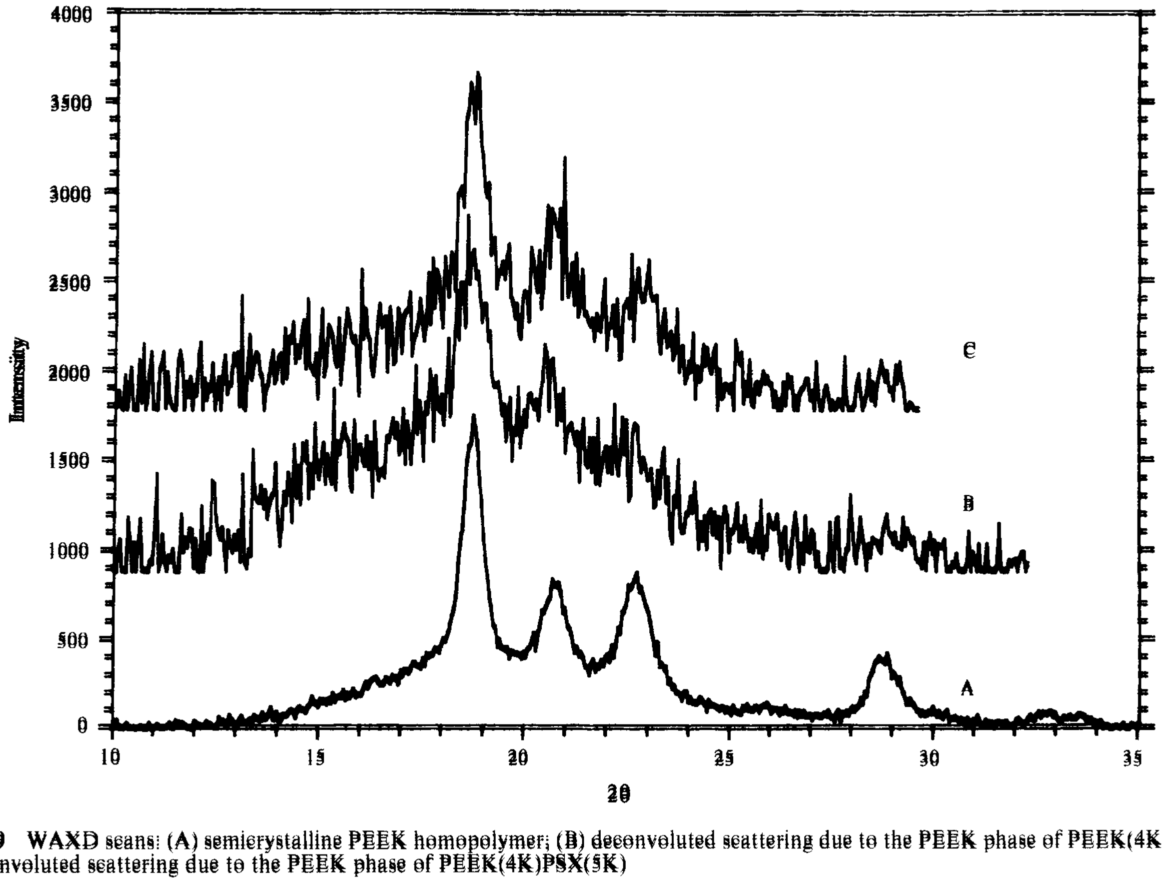

Figure 19 WAXD scans: (A) semicrystalline PEEK homopolymer; (B) deconvoluted scattering due to the PEEK phase of PEEK(4K)PSX(3K); (C) deconvoluted scattering due to the PEEK phase of PEEK(4K)PSX(5K)

Table 4 X-ray line broadening in the PEEK phase of PEEK-PSX copolymers

Peak	Sample	2θ (deg)	F.w.h.m. breadth (rad)	Broadening (%)
110	PEEK	18.75	0.00925	1
110	PEEK(4K)PSX(3K)	18.70	0.01553	1.68
110	PEEK(4K)PSX(5K)	18.75	0.01606	1.74
111	PEEK	20.75	0.0138	1
111	PEEK(4K)PSX(3K)	20.70	0.0171	1.24
111	PEEK(4K)PSX(5K)	20.75	0.0162	1.17
200	PEEK	22.90	0.0129	1
200	PEEK(4K)PSX(3K)	22.90	0.0197	1.53
200	PEEK(4K)PSX(5K)	22.90	0.0176	1.36

describe the crystallization behaviour of these phase-separated copolymers. The assumption of impingement of growth centres associated with the derivation of the Avrami relationship does not account for the complication introduced due to the possibility of impingement of growing crystals with domain interfaces which may occur in a phase-separated system. *Due to the very slow rates of crystallization and the small volume of crystallizable material in these samples, crystallization could only be accurately monitored over a very narrow temperature range.* Crystallization of the PEEK(4K)PSX(3K) copolymer could only be experimentally monitored by d.s.c. in the narrow temperature range from 225 to 235°C. At temperatures higher and lower than this, the rates of crystallization became so slow that the heat flow measured by d.s.c. due to crystallization could not be resolved from the background noise. Crystallization of the PEEK(5K)PSX(5K) copolymer was also *extremely difficult* to monitor due to the even lower volume fraction of crystallizable polymer, as well as the *extremely low crystallization rates* observed in this system. Crystallization in this latter copolymer could only be experimentally monitored in a temperature range from 229 to 232°C, the range where the maximum growth rate was expected. For both copolymers a maximum in the bulk crystallization rate was observed at a temperature of 230.5°C, very close to the temperature at which low-molecular-weight PEEK homopolymer crystallizes most rapidly[34]. *Figure 20* illustrates the effects of changing the crystallization temperature on the rate of crystallization of PEEK(4K)PSX(5K). *Figure 21* illustrates the influence of block length on the rate of crystallization for both of the PEEK-PSX block copolymers at 230.5°C. At this temperature PEEK(4K)PSX(3K) has a crystallization half-time of 260 s while PEEK(4K)PSX(5K) has a crystallization half-time of 1200 s; a 12% change in the volume fraction of PSX decreased the rate of crystallization by a factor of 5! This large change in crystallization rate is believed to be due to the great decrease in continuity observed in the PEEK phase, which is evident as the volume fraction of PEEK is decreased from 51 to 38% (recall the earlier TEM data). As will be discussed later, the change in the continuity of the PEEK phase has dramatic effects on the rates of nucleation in the microdomains. Crystallization half-times as a function of temperature and copolymer composition are plotted in *Figure 22*; again the dramatic effect of changing the block length is evident. After crystallization experiments were performed, samples were heated at a rate of 10°C min^{-1} to determine the heat of melting, Q_m, as a function of temperature. These data were then normalized by PEEK volume fraction and divided by the enthalpy of melting[21] for perfectly crystalline PEEK (130 J g^{-1}) in order to estimate the crystalline fraction of the PEEK phase (*Figure 23*). The PEEK(4K)PSX(3K) copolymer developed up to 20% crystallinity in the PEEK phase, while the PEEK(4K)PSX(3K) copolymer only developed 6% crystallinity in

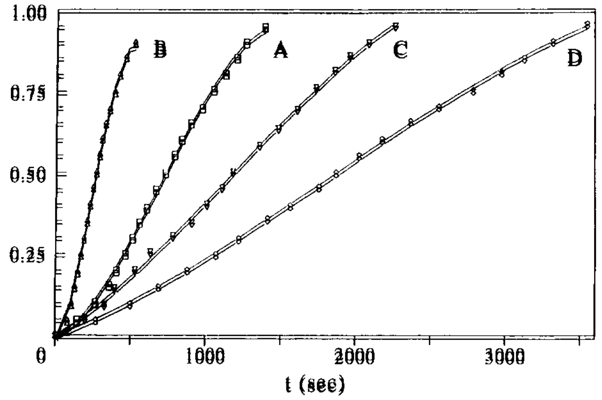

Figure 20 Normalized crystalline content vs. time for PEEK(4K)PSX(3K): (A) crystallized at 228; (B) crystallized at 230.5; (C) crystallized at 232.5; (D) crystallized at 235°C

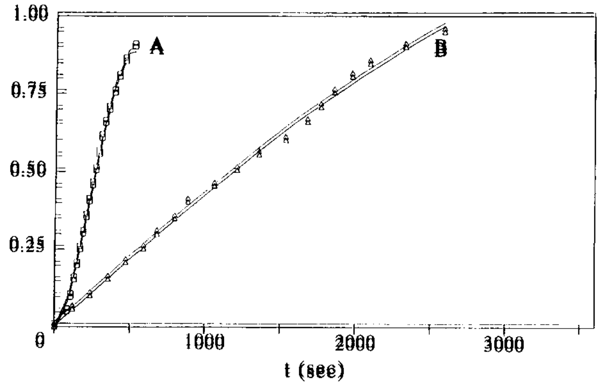

Figure 21 Effect of PSX block length on crystallization of the PEEK-PSX block copolymers at 230.5°C: (A) PEEK(4K)PSX(3K), $t_{1/2}$ = 260 s; (B) PEEK(4K)PSX(5K), $t_{1/2}$ = 1200 s

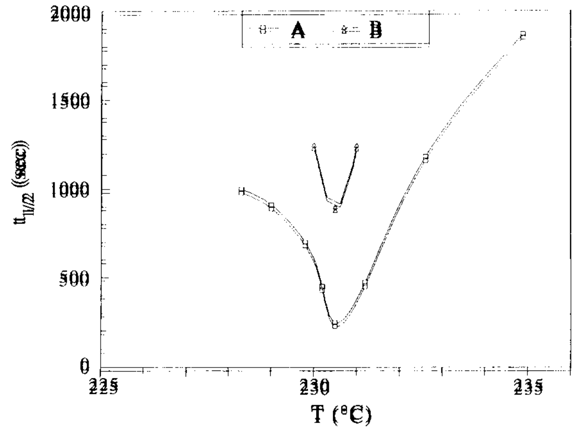

Figure 22 Crystallization half-times as a function of copolymer composition and crystallization temperature: (A) PEEK(4K)PSX(3K); (B) PEEK(4K)PSX(5K)

this phase, even when crystallized over far longer time-periods.

The effects of previous thermal history on the crystallization behaviour of PEEK–PSX copolymers were also studied. Since varying levels of structural continuity may occur as a function of block copolymer composition, the process of nucleation within phase-separated domains is likely to strongly affect the rate of bulk crystallization. As less continuity within the PEEK occurs, more and more nucleation events must occur within separate domains in order to achieve the same level of crystallinity. If nucleation occurs heterogeneously, it is likely that many of the small domains contain no such heterogeneities and crystallization may not occur within these domains within the time-scale of our experiments. As early as 1952, Price had noted that upon successive melting and recrystallization at relatively low undercoolings crystalline nuclei reformed repeatedly at fixed locations in the melt, presumably at heterogeneities[35]. At higher supercoolings, additional nuclei were formed. Subsequently, a variety of droplet experiments were performed on various polymer systems in order to investigate the effects of dividing the melt into such small droplets that most of these would not contain heterogeneities[36–38]. These experiments showed that not only was the rate of nucleation greatly inhibited in these microdroplets but at low undercoolings only a small fraction of the droplets crystallized in the time-frame investigated. Since the crystallizable phase in block copolymer systems may be separated into microdomains similar to those in the droplet experiments, thermal history may be especially important in determining the crystallization rates and absolute crystallinity in crystallizable block copolymers.

Crystallization exotherms as a function of the previous thermal history for PEEK(4K)PSX(3K) films crystallized isothermally at 230.5°C are plotted in *Figure 24*: curve A is an exotherm for PEEK(4K)PSX(3K) crystallized from the glass; curve B is an exotherm for PEEK(4K)PSX(3K) crystallized from the melt. It is clearly evident that previous thermal history has a very dramatic effect on the rate of crystallization. When the normalized crystalline content, X_c, is plotted against time, the effect of thermal history on crystallization half-times can be determined (see *Figure 25*). The crystallization half-time for PEEK(4K)PSX(3K) crystallized from the glass is 56 s compared to 1560 s for a sample crystallized from the melt. Thus, quenching a sample before crystallization increased the rate of crystallization by nearly a factor of 30! Quenching the samples prior to crystallization brings these samples into a temperature range where homogeneous nucleation may occur more readily, which would enhance the rate of crystallization.

If phase separation retarded the nucleation of crystallites within the PEEK microdomains, it is likely that during crystallization from the melt some of these domains may not crystallize at all during our experimental time-frame. Therefore, the heat of melting for samples crystallized from the glass is likely to be greater than for samples crystallized from the melt. Additionally, this difference should become more and more pronounced as the PEEK phase becomes less and less continuous. For the PEEK(4K)PSX(3K) copolymer the heat of melting for a sample crystallized from the melt at 230.5°C for 3 h was 12.5 J g^{-1}, while the heat of melting for a sample crystallized from the glass under identical conditions was 25 J g^{-1}. For the PEEK(4K)PSX(5K) copolymer the heat of melting for a sample crystallized from the melt at 230°C for 3 h was 3 J g^{-1}, while the heat of melting for a sample crystallized from the glass under

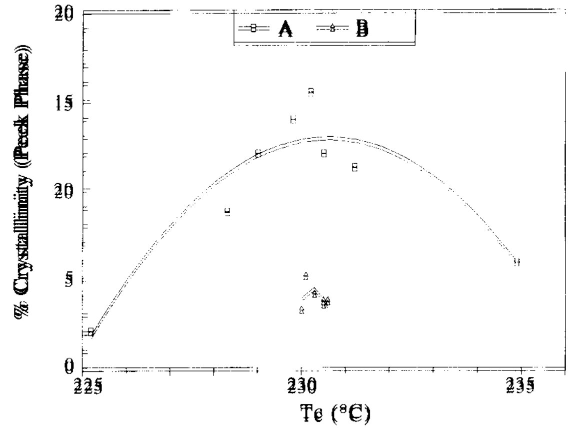

Figure 23 Effect of copolymer composition and crystallization temperature on the crystallinity of the PEEK phase: (A) PEEK(4K) PSX(3K); (B) PEEK(4K)PSX(5K)

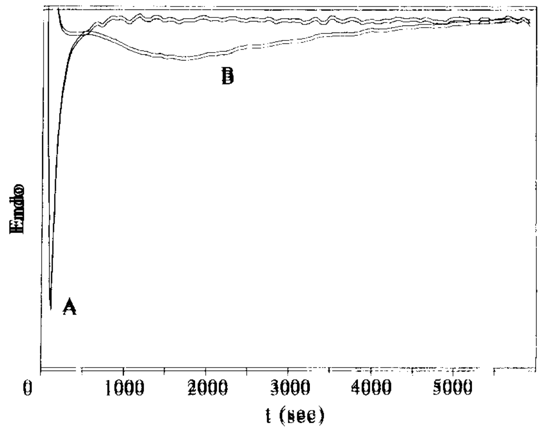

Figure 24 Effect of previous thermal history on the crystallization exotherm for PEEK(4K)PSX(3K): (A) crystallized from the glass; (B) crystallized from the melt. Both crystallizations were at 230.5°C

identical conditions was 16.5 J g^{-1}. The heats of melting were used to calculate the percentage crystallinity as a function of the previous thermal history and were then compared to the values obtained by WAXD (*Table 5*). The crystallinity determination from the heat of melting data agreed fairly well with the WAXD results. The slight disagreement in these measurements may be due to the high surface energies of these crystals which would decrease the heat of melting, or the fact that the method of crystallinity determination used in this study did not account for atomic or structural scattering factors. In the PEEK(4K)PSX(3K) copolymer the sample crystallized from the glass attained twice the crystallinity of the sample crystallized from the melt. In the PEEK(4K) PSX(5K) copolymer, crystallizing the sample from the glass resulted in a fivefold increase in the amount of crystallinity relative to the same sample crystallized from the melt. As in the droplet experiments of Price discussed earlier[33], it is likely that the samples crystallized from the melt were never brought to sufficient undercoolings for homogeneous nucleation to occur in all of the PEEK microdomains. The fact that the crystallinity determined by d.s.c. was substantially lower in the case of the PEEK(4K)PSX(5K) copolymer may be related to the fact that small crystallites surrounded by attached PSX chains may be associated with a high surface energy, thus leading to a decreased heat of melting. Additionally, the fact that the phase-separated morphology formed in this system is locked into place prior to crystallization is likely to make crystallization a less energetically favourable phenomenon than in the case of the homopolymer.

The results obtained in this study are contrary to trends observed in PEEK homopolymer. As may be expected, Cebe and Hong[39] observed that PEEK homopolymer crystallized from the glass obtained levels of crystallinity on the order of one-half of that obtained from the melt. They attributed this difference to the formation of crystals with less perfection when samples were quenched prior to crystallization. The results obtained from crystallization of the PEEK–PSX copolymers illustrate that decreasing continuity within the crystallizable phase may drastically impair a polymer's ability to crystallize from the melt, due to a decreasing probability for nucleation of crystallites. Due to the very low glass transition temperature of the PSX phase, the likelihood of nucleation at domain interfaces is expected to be very low. Furthermore, the flexible nature of the PSX blocks allows a substantial amount of the PEEK phase to crystallize at lower crystallization temperatures. In this case, the crystalline fraction of the PEEK phase in the PEEK–PSX block copolymers crystallized from the glass was greater than that observed in PEEK homopolymers crystallized under similar conditions.

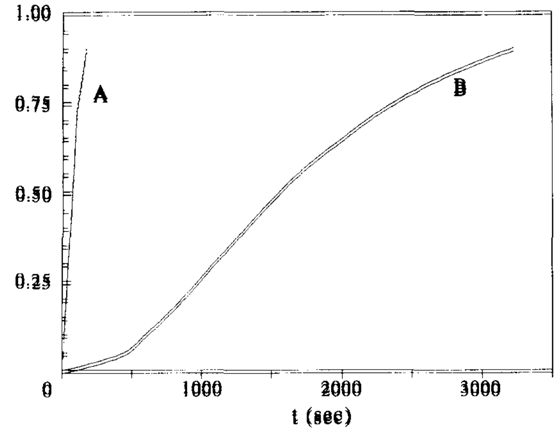

Figure 25 Normalized crystalline content vs. time for PEEK(4K) PSX(3K) crystallized at 230.5°C, showing the effect of previous thermal history: (A) heated from the glass, $t_{1/2} = 56$ s; (B) quenched from the melt, $t_{1/2} = 1560$ s

CONCLUSIONS

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

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Table 5 Crystalline fraction of the PEEK phase in PEEK–PSX block copolymers as determined by WAXD and thermal analysis, showing the effects of prior thermal history

Sample	Q_m[a] (J g^{-1})	Crystallinity[a] (%)	Crystallinity[b] (%)
Crystallized from the melt			
PEEK(4K)PSX(3K)	12.5 ± 1	20 ± 2	–
PEEK(4K)PSX(5K)	3.0 ± 1	6 ± 2	–
Crystallized from the glass			
PEEK(4K)PSX(3K)	25.0 ± 1	39 ± 2	37 ± 4
PEEK(4K)PSX(5K)	16.5 ± 1	32 ± 2	37 ± 4

[a] Data obtained from d.s.c.
[b] Data obtained from WAXD

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