Polymorphism in poly(aryl ether ketone)s*

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Polymorphism in poly(aryl ether ketone)s (PEKs) has been studied by X-ray diffraction as a function of the chemical structure and the crystallization conditions. Two types of chemical variations were investigated: (1) the molar ratio of the keto/ether linkages (expressed as % ketone linkages) was varied from 33 to 67% using the wholly 1,4-substituted forms of poly(aryl ether ether ketone) (PEEK), PEK, poly(aryl ether ketone ether ketone ketone) (PEKEKK) and poly(aryl ether ketone ketone) (PEKK) and (2) the partial replacement of 1,4-substituted phenyl residues with their 1,3-substituted counterparts of PEKK and PEKEKK. As-polymerized polymers and materials prepared by melt crystallization, cold crystallization and crystallization induced by exposure to methylene chloride (solvent crystallization) were used. For all of the polymers investigated, the conventional structure, known as form 1, was observed in samples prepared by melt crystallization. In contrast, for polymers crystallized under one of the other conditions, the second polymorph, known as form 2, was sometimes observed. The occurrence of form 2 was found to be dependent on chain stiffness, which was systematically modified by changing the 1,3-substituted/1,4-substituted isomer ratio and/or by changing the ether/keto linkage ratio and molecular mobility during crystallization. With the increase of chain stiffness and the decrease of crystallization mobility, the ability to form the second polymorph was significantly enhanced. Polymorphism in poly(aryl ether ketone)s may be due to the nucleation control: the stable, form 1 phase has a slower nucleation rate, and thus a higher crystal surface free energy than the metastable form 2 phase.

(Keywords: polymorphism; poly(aryl ether ketone)s; X-ray diffraction)

INTRODUCTION

Polymorphism is a common phenomenon in crystalline polymers. Different polymorphs are observed as a result of the variation in molecular conformation, chain packing and the coexistence of different crystallizing components. Several reviews are available which deal with this subject[1-3].

Recently, we reported that a second crystalline polymorph (form 2) can be obtained in poly(aryl ether ketone ketone)s (PEKKs), and other poly(aryl ether ketone)s by solvent-induced crystallization or cold crystallization of non-crystalline samples[4-9]. The form 2 structure differs from the more stable form 1 structure (normally induced by melt crystallization) in the relative placement of the chains and, consequently, the inter-chain interactions. There is no evidence to indicate that a change in chain conformation is associated with the polymorphism. Projections of the two unit cells (viewed down the chain axes) are shown in *Figure 1*. Form 1 has a two-chain orthorhombic unit cell with chains located at the corner and centre of the unit cell and is characterized by edge-to-face phenyl interactions. In contrast, form 2 has been assigned a one-chain (metrically) orthorhombic unit cell with face-to-face phenyl interactions[9]. (An alternative unit cell has been proposed by Blundell and Newton[10], and this also has face-to-face phenyl interactions.) The two polymorphs have different melting temperatures, and, in some cases, the form 2 structure is capable of converting into form 1 after melting. These two polymorphic forms are similar to those found in poly(*p*-phenylene terephthalamide)[11-13].

The second crystalline form has not been reported for poly(phenylene oxide) (PPO), poly(phenylene sulfide) (PPS), or PEEK. Changes in the inter-chain dipole–dipole interactions, as a result of the different linkages are not responsible for the occurrence of the second polymorph, since many polymers exhibit similar chain polarizabilities of the unit cells. The above observation suggests that, for wholly aromatic polymers that can be represented by –P–Li– where P represents a 1,4-substituted phenyl moiety and Li represents a linkage group such as ketone, ether, sulfide or amide, the occurrence of form 2 becomes more favourable as the linkage stiffness increases; i.e. in the order sulfide < ether < ketone < amide. To help test this hypothesis, we have chosen four poly(aryl ether ketone) samples with different ether/keto ratios, namely PEEK (33% keto linkage), PEK (50% keto linkage), PEKEKK (60% keto linkage) and PEKK (67% keto linkage) (see *Table 1*) to be crystallized under different conditions. Both from changes in the T_g[9] and from molecular modelling[14], the chain stiffness is known to increase with an increase in the keto content. An alternative approach was also adopted for changing the chain stiffness by replacing some of the 1,4-substituted phenyl residues with their 1,3-substituted counterparts. Previously, we have studied PEKK copolymers prepared from diphenylether (DPE), terephthalic acid (T) and isophthalic acid (I). Ordered polymers

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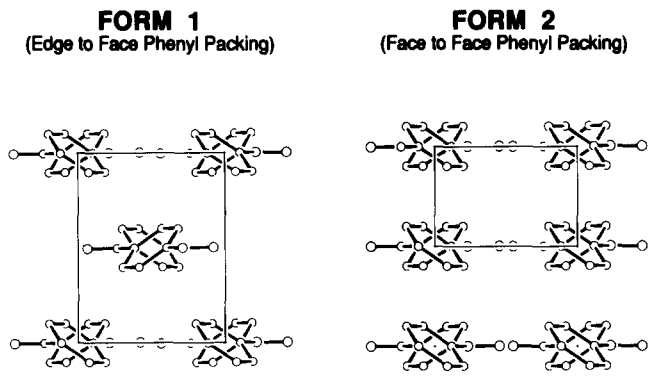


Figure 1 Projections of the unit cells and chain packing for the two polymorphs of PEKK (diagram reproduced from ref. 9)

were prepared that consist of phthalate 'diads' containing –DPE–T–DPE–T– (TT) and –DPE–T–DPE–I– (TI)[9], or –DPE–T–DPE–I– (TI) and –DPE–I–DPE–I– (II)[15]. In all of the copolymers, except for those with T/I ratios $<40\%$, the 1,3-substituted residue (I) was observed to be incorporated into the crystalline structure where it acts as a conformational or entropic defect that effectively decreases the equilibrium melting temperature and the crystallization rate. The content of the 1,3-substituted residues was also observed to affect the ability to form the second polymorph.

In this work, two aspects of polymorphism and polymorphism stability are studied. The first is chain stiffness: systematic changes in molecular stiffness have been accomplished by modifying the keto/ether linkage ratio and the fraction of 1,4-substituted residues that are replaced by 1,3-substituted moieties in the molecular backbone. The second aspect is chain mobility during crystallization: several conditions have been investigated: as-polymerized, crystallization from the molten state (melt crystallization), crystallization from a quenched glassy sample (cold crystallization) and crystallization induced by exposing glassy samples to a low-molecular-weight solvent, in this case, methylene chloride (solvent crystallization).

EXPERIMENTAL

Poly(aryl ether ether ketone) (PEEK), poly(aryl ether ketone) (PEK), poly(aryl ether ketone ether ketone ketone) (PEKEKK), and poly(aryl ether ketone ketone) (PEKK), were investigated as part of this study. The chemical structures and keto/ether linkage ratio for these polymers are shown in *Table 1*. In addition to the all-1,4-substituted polymers, PEKK and PEKEKK polymers incorporating 1,3-substituted residues were also prepared. The chemical structures and the fraction of 1,3-substituted moieties in the monomer repeat units of these polymers are shown in *Tables 2* and *3*. All of the polymers, except PEEK (ICI grade 150G), were specially prepared by one of us (K. Faron): the syntheses of the polymers are described elsewhere[16]. All of the polymers have number-average molecular weights (M_n) and weight-average molecular weights (M_w) of $\sim 10\,000$ and 30 000, respectively.

Samples for X-ray diffraction experiments (125 μm thick), were equilibrated at approximately 10°C above the equilibrium melting temperature and then either quenched to the glassy state (by a water quench) or melt crystallized at 200°C for 24 h. The quenched samples were either solvent crystallized (by exposure to methylene chloride), or cold crystallized at 200°C for 24 h. Polymer which was recovered from the polymerization medium was cold pressed into samples with an equivalent thickness to the melt pressed samples.

X-ray diffractometry scans were collected in the symmetrical transmission mode using an automated Philips diffractometer (curved crystal monochrometer, 1° divergence and receiving slits, sample rotating) with CuKα radiation. Data were collected from $2\theta = 4°$ to 65°, in a fixed time mode with a step size of 0.05°. The processing of the raw data has been described previously[9].

Table 1 Chemical structures and keto/ether linkage ratios for all 1,4-substituted poly(aryl ether ketone)s investigated in this study

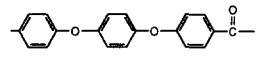
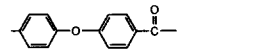
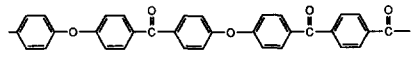
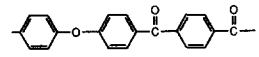
Structure	Name	Ketone (%)
	PEEK	33
	PEK	50
	PEKEKK	60
	PEKK	67

Table 2 Chemical structures and amounts of 1,3-substituted residues in the monomer repeat unit for the three homopolymers of PEKK

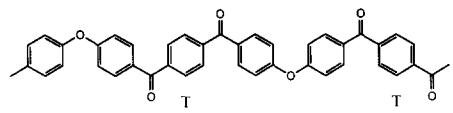
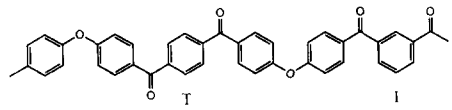
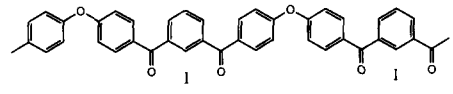
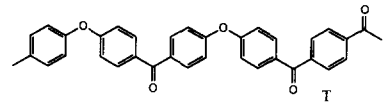
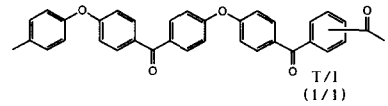
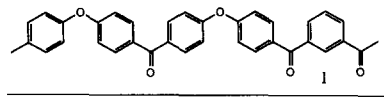
Structure	Residue (%)
	0
	17
	33

Table 3 Chemical structures and amounts of 1,3-substituted residues in the monomer repeat unit for the three PEKEKK polymers studied in this work

Structure	Residue (%)
	0
	10
	20

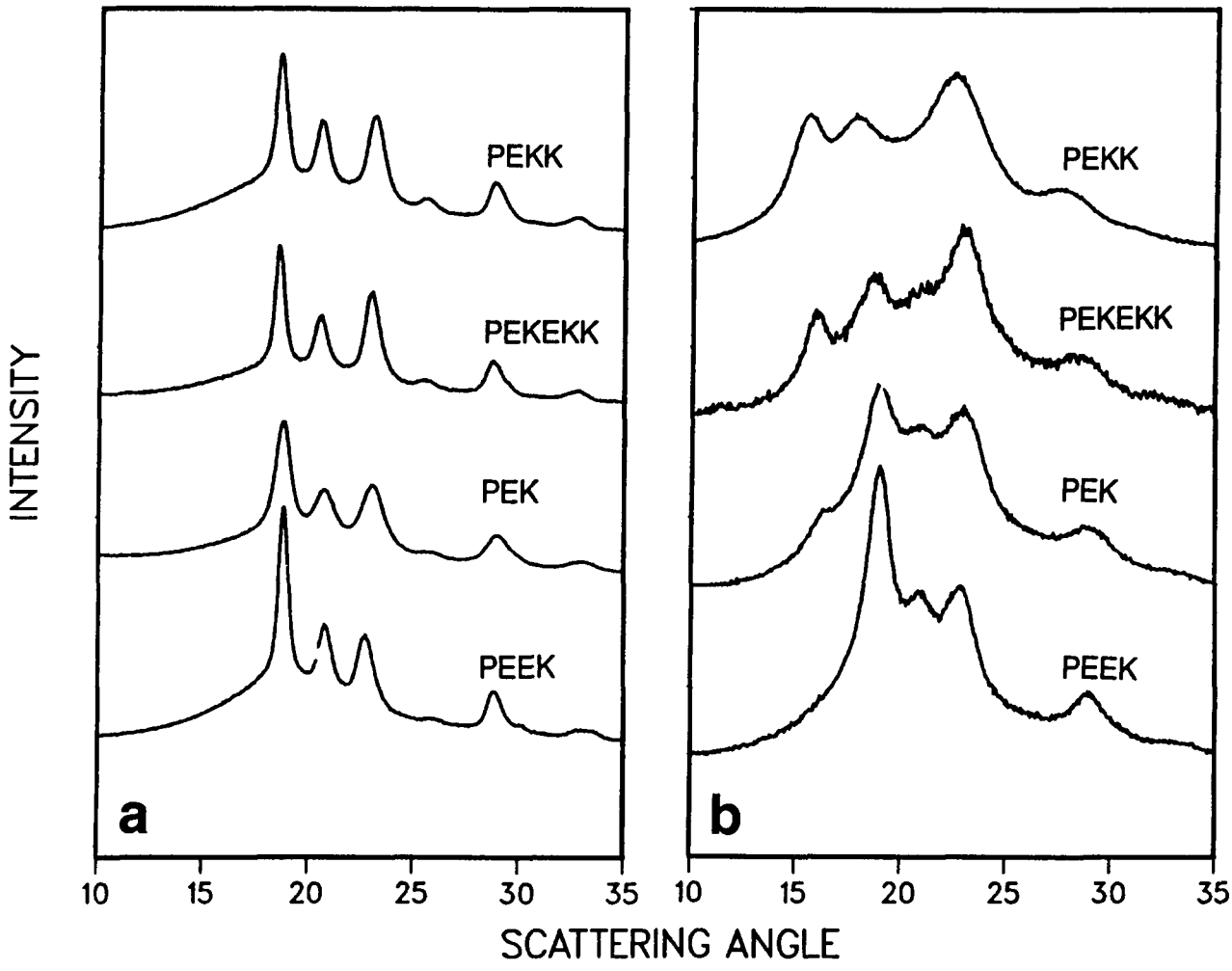


Figure 2 Powder diffraction patterns obtained from (a) melt crystallized and (b) solvent crystallized all-1,4-substituted PEEK, PEK, PEKEKK and PEKK

RESULTS AND DISCUSSION

Effect of keto/ether linkage ratio

Powder diffraction patterns of melt crystallized and solvent crystallized, all-1,4-substituted PEEK, PEK, PEKEKK and PEKK are shown in *Figures 2a* and *2b*, respectively. The diffraction patterns for the melt crystallized samples are generally similar but exhibit a small shift in the peak positions to a lower angle with an increase in the keto content. This shift reflects a systematic change in the unit cell parameters with increasing keto content. These patterns are characteristic of the form 1 structure.

In solvent crystallized PEKK (67% keto linkages), a different diffraction pattern is observed, which is associated with the form 2 structure. The pattern is characterized by a new peak located at $2\theta = 15.6°$, which has been indexed as the 010 reflection of the form 2 structure. (A different cell structure was characterized by Blundell and Newton[10].) In contrast, the diffraction pattern obtained from solvent crystallized PEEK (33% keto linkages) shows only the pattern characteristic of form 1. The diffraction pattern from PEK and PEKEKK (50 and 60% keto linkages, respectively) show diffraction characteristics of both polymorphs, indicating that the samples have both phases present. The intensity of the 010 reflection (form 2) increases with the increasing keto content, indicating that both the formation and stability of form 2 are enhanced by an increasing chain stiffness, i.e. form 2 is the minor phase in PEK, but the major phase in PEKEKK. The one polymer with a keto content less than 50% (PEEK) does not form this structure.

Effect of incorporating 1,3-substituted phenyl moieties

Incorporation of 1,3-substituted residues into the polymer chain was also observed to affect the ability to form different polymorphs. *Figure 3a* shows the diffraction patterns obtained for three melt crystallized PEKK homopolymers with T/I ratios of 100/0 (TT), 50/50 (TI) and 0/100 (II). These compositions correspond to the polymers described in *Table 2*. The diffraction patterns for the melt crystallized polymers are characteristic of form 1. The reflection positions are unaffected by the change in polymer composition, indicating that the unit cell parameters are unchanged by incorporation of the 1,3-substituted residues. However, there is a decrease in the relative intensity of the 111 reflection ($2\theta = 20.6°$) with increasing isophthalate content. This decrease has been attributed to the inclusion of the 1,3-substituted moiety into the crystalline phase[9]. *Figure 3b* shows the diffraction patterns of the solvent (methylene chloride) crystallized polymers. While the TT and TI homopolymers show the form 2 diffraction pattern, the II polymer is observed to adopt the form 1 structure. [Copolymers of TT/TI and TI/II have been prepared and examined for the occurrence of form 2. The latter is observed in solvent

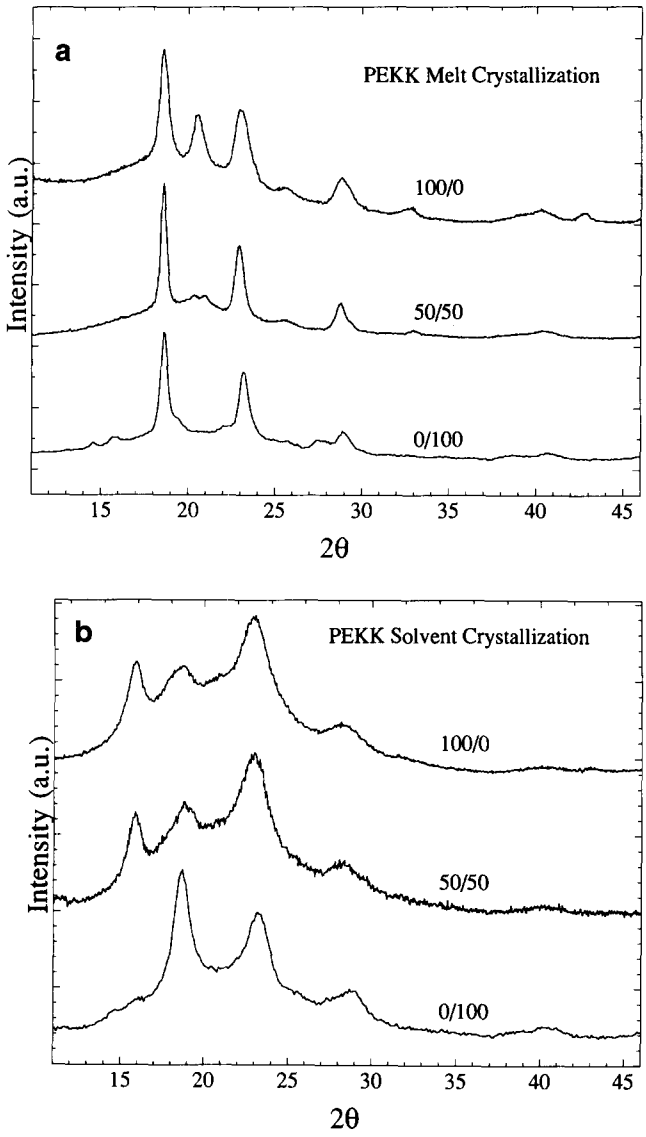


Figure 3 Powder diffraction patterns obtained from (a) melt crystallized and (b) solvent crystallized PEKK homopolymers with T/I ratios of 100/0 (TT), 50/50 (TI) and 0/100 (II)

crystallized PEKKs with TT-like structures (T/I ratios from 100/0 to 70/30) and TI-like structures (T/I ratios from 60/40–40/60). PEKKs with II-like structures (T/I ratios from 30/70 to 0/100) show only form 1.] Similar observations of this polymorph occurrence were made for the as-polymerized PEKK crystals and also for cold crystallized material.

Figure 4 shows a 'phase diagram' that summarizes the occurrence of the two polymorphs in the PEKK copolymers as a function of the degree of incorporation of 1,3-substituted residues (via the T/I ratio) and the crystallization conditions. As the T/I ratio is changed, the inherent chain stiffness is altered, with the chain flexibility increasing with an increasing content of 1,3-substituted residues. In a similar manner, the crystallization conditions can be ranked in terms of polymer mobility. Melt crystallization conditions offer the least restriction on chain mobility, and all compositions show only the form 1 crystals. In contrast, for samples prepared by solvent crystallization at room temperature, where the chains probably have the most restrictive mobility, form 2 is observed, but only in polymers having limited 1,3-substituted moiety concentrations. Under conditions of intermediate mobility, such as cold crystallization, those compositions that crystallized as form 2 crystals now display the diffraction characteristics of both the form 1 and form 2 species. In the more flexible polymers that have high concentrations of isophthalate, form 2 is not observed, i.e. the increase in the 1,3-substituted isomer content is observed to decrease the possibility of form 2 crystal formation. It appears that while the form 1 structure is the thermodynamically stable crystalline form, the polymers can be trapped, under certain conditions, in the less stable form 2. The polymer chains are 'trapped' as form 2 crystals when the molecular mobility is low and the chain stiffness is high.

Figures 5a and *5b* show the diffraction patterns of melt crystallized and solvent crystallized PEKEKK containing 0, 10 and 20% 1,3-substituted residues (see *Table 3*) (referred to as the 100/0, 50/50 and 0/100 samples, respectively). While the melt crystallized samples show the characteristic diffraction patterns of form 1, in the solvent crystallized materials the diffraction patterns of the 100/0 and 50/50 samples are dominated by the pattern attributed to the crystalline form 2. In contrast, the diffraction pattern of the 0/100 sample shows only form 1.

Thermodynamic and kinetic considerations

In a previous study[9], we have shown that the two polymorphs in PEKK (50/50) have different melting temperatures. The melting temperature of the form 2 structure is lower than that of form 1, which indicates that form 2 is thermodynamically less stable and/or has a smaller crystal size. This latter feature may be a characteristic of form 2 since its diffraction patterns are generally broader than those of form 1 (see *Figures 2* and *3*). In *Figure 6* (in the case of PEKK (50/50)), the degree of supercooling between the cold crystallization and the melt crystallization processes is the same, but the former condition always produces form 2, while the latter does not. This suggests that production of different polymorphs may be due to nucleation control. The form 2 structure is clearly favoured under fast nucleation conditions, such as cold crystallization with a large degree of supercooling, solvent induced crystallization, and crystallization from an as-polymerized solution. In contrast, form 1 is favoured in an environment of slow

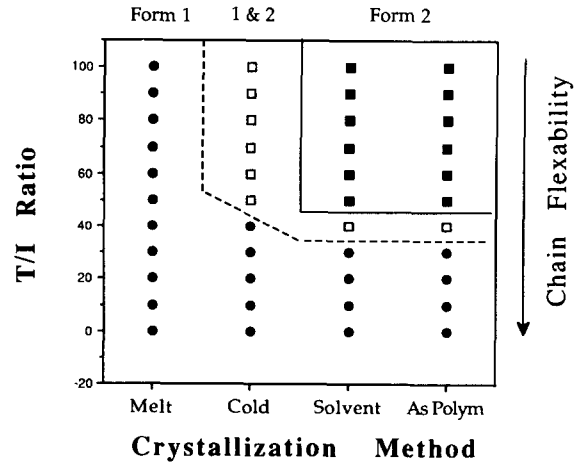


Figure 4 'Phase diagram' summarizing the occurrence of the two crystalline polymorphs in PEKK as a function of the degree of incorporation of 1,3-substituted residues (via the T/I ratio) and the crystallization conditions

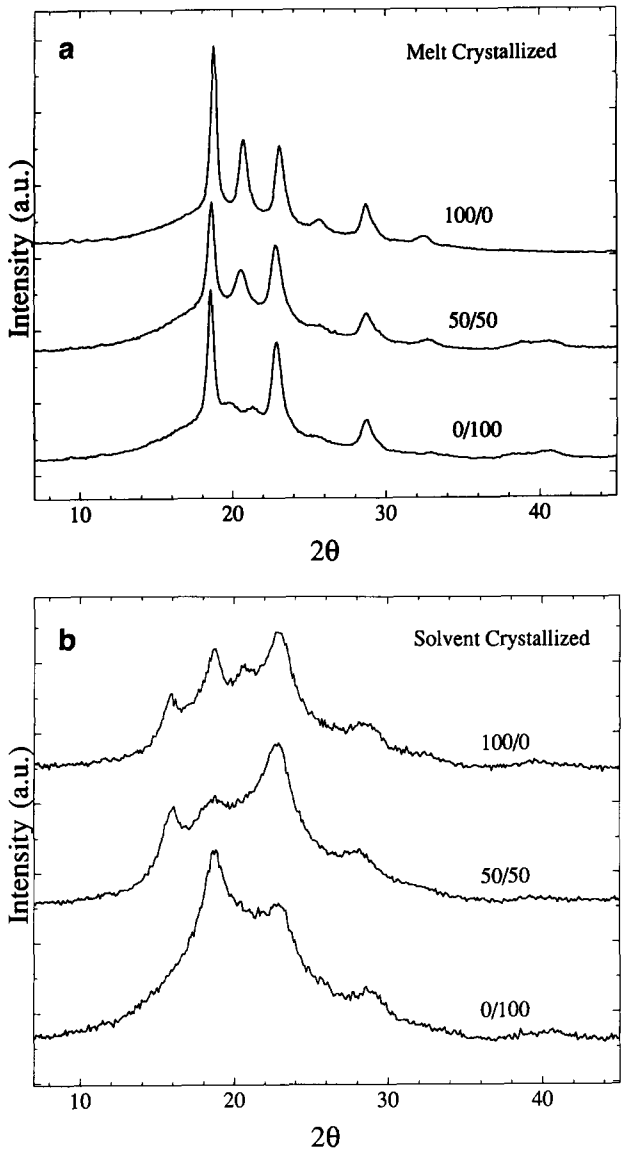


Figure 5 Powder diffraction patterns obtained from (a) melt crystallized and (b) solvent crystallized PEKEKK copolymers containing 0, 10 and 20% 1,3-substituted residues (referred to as the 100/0, 50/50 and 0/100 samples, respectively)

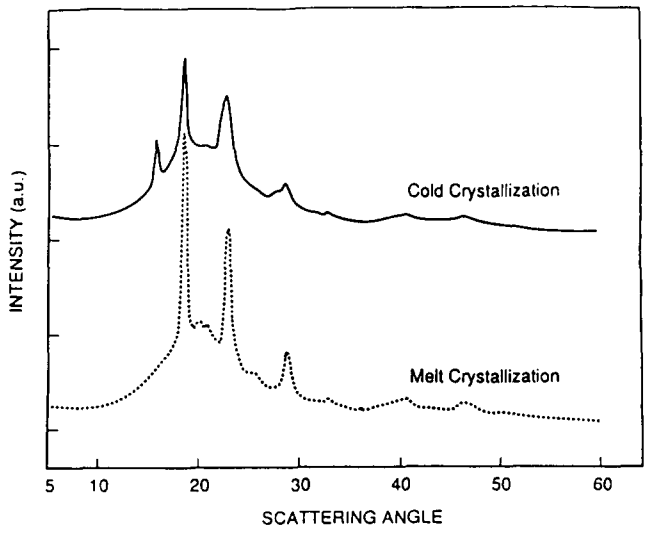


Figure 6 Powder diffraction patterns of cold crystallized and melt crystallized PEKK (50/50), with a crystallization temperature of 200°C in both cases (diagram reproduced from ref. 9)

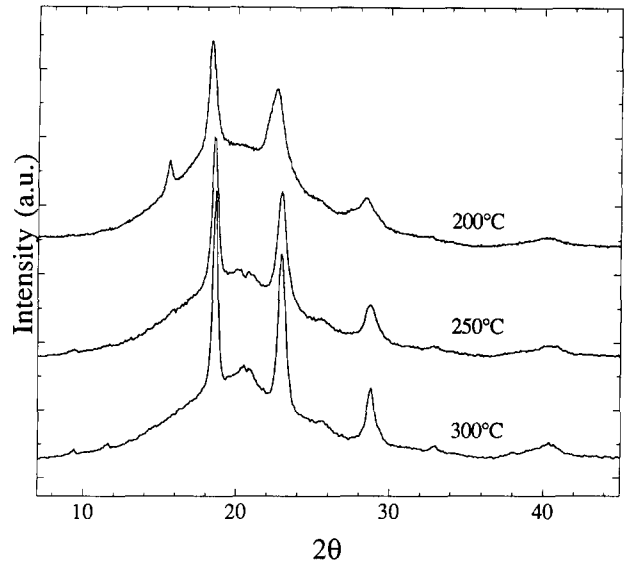


Figure 7 Powder diffraction patterns of PEKK (50/50) prepared with the application of three different degrees of supercooling (crystallization temperatures: 200, 250 and 300°C). Only the sample with the highest degree of supercooling (i.e. 200°C) shows the presence of form 2

nucleation, such as melt crystallization with a small degree of supercooling. We have confirmed this hypothesis by the following experiments. When three different degrees of supercooling (crystallization temperatures: 200, 250 and 300°C) were applied to cold crystallized PEKK (50/50), the samples with the lower degree of supercooling (i.e. 300°C) did not show any form 2 phase (*Figure 7*).

If we assume that the difference in the heat of fusion between forms 1 and 2 is negligible (this can be justified by the same unit cell dimensions for the two forms[9]) and the degree of supercooling is the same (cold *versus* melt crystallization), then the different nucleation rates of the two polymorphs imply, according to the nucleation theory[17], that the surface free energy for the two crystal forms is different. Since form 2 is favoured under fast nucleation conditions, it should have a higher crystal surface free energy than form 2. A similar explanation has been given by Keller[18] for the polymorphism (the normal orthorhombic phase *versus* the high pressure hexagonal phase) observed in polyethylene.

CONCLUSIONS

To summarize, we have found that the polymorphism observed in poly(aryl ether ketone)s is dependent on two factors: (1) chain stiffness that can be modified by changing the ether/keto linkage ratio and/or by changing the *meta/para* isomer (or 1,3-/1,4-substitution) ratio, and (2) molecular mobility during the crystallization process. The polymers investigated included PEEK, PEK, PEKEKK and PEKK, with the latter two systems having different compositions of 1,3-substituted moieties incorporated in their structures. The crystallization conditions investigated included as-polymerized, melt crystallized, cold crystallized and solvent crystallized (by using methylene chloride). We have concluded that the ability to form the second crystalline phase, i.e. form 2, is significantly enhanced by increasing the chain stiffness and/or decreasing the chain mobility. In fact, chain stiffness directly affects the crystallization kinetics, so the

polymorphism may also be a consequence of the crystallization rate difference. This is consistent with the argument that the occurrence of different polymorphs is due to nucleation control. We believe that the form 2 phase is favoured under fast nucleation conditions, while the form 2 phase is favoured under slow nucleation conditions, which implies that form 2 has a lower surface free energy than form 1.

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