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Crystallization behaviour of poly(ether ether ketone)/poly(ether sulfone) block copolymer

Junkui Cao*, Wencheng Su and Zhongwen Wu
Department of Chemistry, Jilin University, Changchun, China, 130023

and Jingjiang Liu
Changchun Institute of Applied Chemistry, Academia Sinica, China, 130022

and Tatsuki Kitayama and Koichi Hatada
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

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The crystallization and melting behaviours of a multiblock copolymer comprising poly(ether ether ketone) (PEEK) and poly(ether sulfone) (PES) blocks whose number average molecular weights ($\bar{M}_n$'s) were 10 000 and 2900, respectively, were studied. The effect of thermal history on crystallization was investigated by wide-angle X-ray diffraction measurement. A differential scanning calorimeter was used to detect the thermal transitions and to monitor the energy evolved during the isothermal crystallization process from the melt. The results suggest that the crystallization of the copolymer becomes more difficult as compared with that of pure PEEK. The equilibrium melting point of the copolymer was found to be 357°C, about 30°C lower than that of pure PEEK. During the isothermal crystallization, relative crystallinity increased with crystallization time, following an Avrami equation with exponent $n \approx 2$. The fold surface free energy for the copolymer crystallized from the melt was calculated to be 73 erg cm^{-2}, about 24 erg cm^{-2} higher than that of pure PEEK. Copyright © 1996 Elsevier Science Ltd.

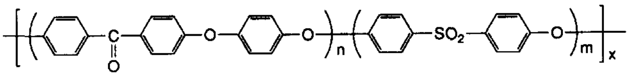
(Keywords: PEEK/PES block copolymer; crystallization behaviour; differential scanning calorimetry)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a semicrystalline high-performance thermoplastic with a glass transition temperature (T_g) of *ca* 143°C and a melting point of the main crystallites of *ca* 334°C, and is well known for its high chemical resistance, excellent thermal stability and good mechanical properties. These excellent properties make PEEK an attractive high-performance polymer potentially used as a structural adhesive and composite matrix[1–3].

Crystal structure, morphology, crystallization and melting behaviour of PEEK have been extensively studied by several authors[4–12]. PEEK was found to exhibit crystallization behaviour and spherulitic growth similar to poly(ethylene terephthalate)[4]. The crystal structure of PEEK is similar to that of poly(*p*-phenylene oxide), and the orthorhombic unit cell of PEEK crystal has lattice constants of *a*, *b* and *c* in the range of 7.75–7.78, 5.89–5.92 and 9.88–10.06 Å, respectively. In particular, the unit-cell dimensions are known to depend on the temperature of crystallization and/or annealing[5–8]. Two distinct melting endotherms observed in differential thermal analysis are of interest as a parallel phenomenon to the double-melting found for several other polymers, for which a variety of explanations have been proposed[4,6,9–13]. The kinetics of the crystallization of PEEK have also been well examined[9,14–18]. In recent years, there have been many publications dealing with blends based on PEEK with other high-performance thermoplastics such as polysulfone, poly(ether sulfone) (PES), poly(amide-imide), poly(ether imide), poly(phenylene sulfide), poly(ether ketone), etc.[19–25]. Incorporation of these polymers into PEEK may provide new means for modifying the properties of PEEK. Although some patents concerning copolymers including PEEK blocks have been reported recently[26–29], very few fundamental studies on the copolymers are found in the literature.

We have recently demonstrated an alternative synthetic route for the preparation of PEEK/PES multiblock copolymers through the reaction between PEEK and PES oligomers (oligomer–oligomer approach)[30,31]. The repeating units of this kind of copolymer can be represented by the formula shown.



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* To whom correspondence should be addressed

It was found that the relationship between the T_g's and the compositions (W) of the copolymers obeyed the following equation, $T_g = T_{g1}W_1 + T_{g2}W_2$, and that the PES content and the block length of the copolymers affected their crystallization behaviour. While the crystallinity of the copolymers decreased with an increase in PES content, the copolymers with PES contents of 25.7% or less showed obvious crystallization endotherms upon cooling from the melt. In particular, the copolymer with PES content of 22.4% exhibited the strongest exothermic peak. In this paper, we investigated further the crystallization and melting behaviours of this copolymer. A comparison of properties of the block copolymer with pure PEEK is also described.

EXPERIMENTAL

The PEEK/PES multiblock copolymer employed in this work was synthesized from the dihydroxyl-terminated PES oligomer and difluorine-terminated PEEK oligomer via a nucleophilic aromatic substitution reaction in diphenylsulfone at 260–310°C for 3 h according to the previously reported procedure[30–32]. The $\bar{M}_n$'s of PEEK and PES blocks in the copolymer are 10 000 and 2900, respectively, thus the PES content in the copolymer was fixed at 22.4 wt%. The copolymer had an inherent viscosity (η_{inh}) of 0.83 dl g^{-1} when measured in 0.1% H_2SO_4 solution at 25°C.

The copolymer samples were moulded into 0.5 mm film under a pressure of 10 MPa at 370–380°C for 10 min. To obtain amorphous film samples, the films were placed on an aluminium plate and immediately put into ice water for quenching. Crystalline film samples were prepared by annealing the amorphous film at various temperatures for a predetermined period of time, and cooled down to room temperature.

Wide-angle X-ray diffraction (WAXD) was measured on a Rigaku D/MAX-IIIA X-ray diffractometer with CuK_α radiation at 40 kV and 30 mA.

A Perkin-Elmer differential scanning calorimeter DSC-7 was used to detect thermal transitions and to monitor the rate of heat flow from the sample during isothermal crystallization from the melt. The samples (10 ± 2 mg) were placed in d.s.c. (differential scanning calorimeter) pans and quickly heated to 400°C for several minutes to destroy previous thermal and mechanical history, and then cooled very rapidly to crystallization temperature.

The heat generated during the development of the crystalline phase was recorded until no further heat evolution was observed, and analysed according to the usual procedure in order to obtain the relative degree of crystallinity. The relative degree of crystallinity as a function of time, was found from equation (1):

$$\chi_c(t)/\chi_c(\infty) = \int_{t_0}^{t} (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t \Big/ \int_{t_0}^{\infty} (\mathrm{d}H/\mathrm{d}t)\,\mathrm{d}t \qquad (1)$$

where t_0 is the time at which the sample attains isothermal conditions, as indicated by a flat baseline after the initial spike in the thermal curve, $\chi_c(t)$ the degree of crystallinity at time t, $\chi_c(\infty)$ the ultimate crystallinity at very long time, and $\mathrm{d}H/\mathrm{d}t$ the heat flow rate.

RESULTS AND DISCUSSION

WAXD curves of the pure PEEK and the PEEK/PES multiblock copolymer indicated that the values of 2θ for the major diffraction peaks of the copolymer were approximately the same as those of pure PEEK[31]; PEEK: $\eta_{inh} = 0.80$ (dl g^{-1}) in 0.1% H_2SO_4 at 25°C, $T_g = 143$°C. The crystalline structure of the copolymer has been found to belong to an orthorhombic system like pure PEEK, as evidenced from its WAXD curve. This indicates that the crystalline character of the copolymer originates from its PEEK segments, where the PES segments remain in an amorphous state.

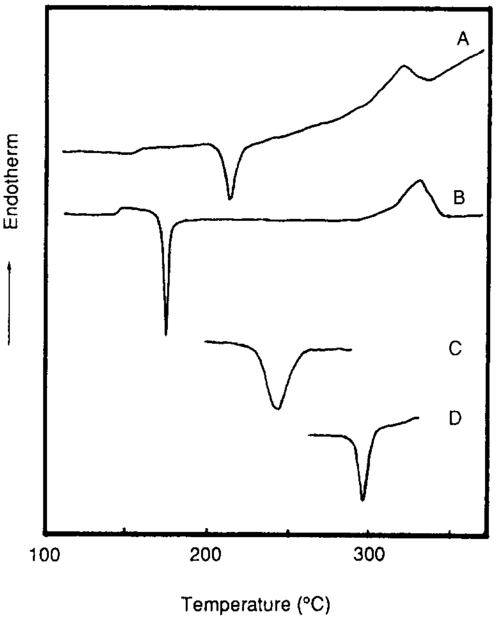

Figure 1 D.s.c. heating scans at 10°C min^{-1} for: (A) amorphous quenched PEEK/PES copolymer; (B) amorphous quenched PEEK, and d.s.c. cooling scans from the melt at −10°C min^{-1} for: (C) PEEK/PES copolymer; (D) pure PEEK. Taken from ref. 31

D.s.c. curves A and B in *Figure 1* were obtained by heating scans at a heating rate of 10°C min^{-1} for quenched amorphous PEEK/PES copolymer and PEEK, respectively[31]. The copolymer exhibits a thermal behaviour similar to the amorphous PEEK, a glass transition being observed at 160°C, followed by an exotherm at 214°C associated with cold-crystallization, and then an endotherm at 320°C associated with the melting of the crystals (T_m). The T_g and cold-crystallization temperature of the copolymer are about 17 and 39°C higher than those of the pure PEEK, respectively, while the T_m of the copolymer is about 14°C lower than that of the pure PEEK.

It has been reported that blends of PEEK and PES exhibited phase separation when the processing temperature was 350°C, although the samples moulded at 310°C were still compatible[23]. As even the copolymer sample moulded at 380°C shows a single T_g in the d.s.c. curve (*Figure 1A*), the PEEK and PES segments in the copolymer do not undergo phase separation but constitute a homogeneous phase. These results indicate that the compatibility of PEEK and PES segments in the copolymer is higher than that of PEEK and PES homopolymers. Therefore, crystallization of PEEK segments should occur under the influence of PES segment, and thus the use of the copolymer should give further information on the effect of PES segment on the crystallization behaviour of PEEK.

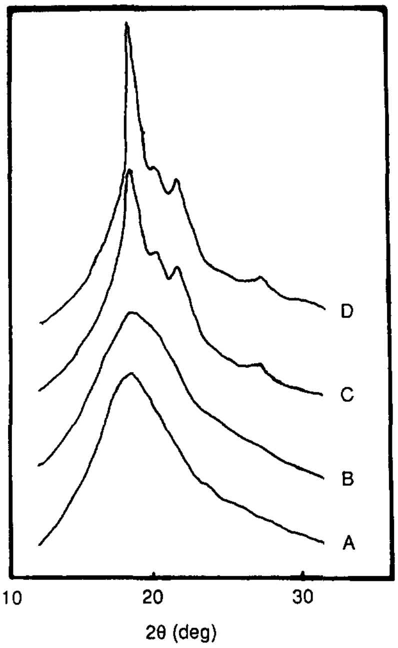

Figure 2 WAXD curves of the annealed PEEK/PES block copolymers; (A) annealed at 170°C, (B) at 180°C, (C) at 190°C and (D) at 210°C for 15 min

The crystallinity of the copolymer (χ_c) and the crystallinity with respect to the PEEK segments ($\chi_{c'\mathrm{PEEK}}$) that develop by crystallization during the heating scan, can be estimated from the heat of fusion ΔH determined by d.s.c. according to the following equations:

$$\chi_c = \Delta H / \Delta H_m^\circ \quad (2)$$

$$\chi_{c'\mathrm{PEEK}} = \chi_c / W_{\mathrm{PEEK}} \quad (3)$$

where ΔH_m° is the heat of fusion of 100% crystalline PEEK, $\Delta H_m^\circ = 130\,\mathrm{J\,g^{-1}}$ (ref. 4), and W_{PEEK} the weight fraction of PEEK segments in the copolymer. χ_c and $\chi_{c'\mathrm{PEEK}}$ of the copolymer are 14.4 and 18.3%, respectively, while the crystallinity of the pure PEEK is 32.6%. Curves C and D in *Figure 1* represent d.s.c. thermograms obtained by cooling scans at a cooling rate of $-10°\mathrm{C\,min^{-1}}$ for the samples once melted at 400°C for 2 min. The copolymer and the pure PEEK show crystallization exothermic peaks at 245 and 294°C, respectively. Crystallization temperature of the copolymer is about 50°C lower than that of the pure PEEK.

The amorphous copolymer samples were annealed for 15 min each at 170, 180, 190 and 210°C, and then subjected to X-ray diffraction analysis. The results are shown in *Figure 2*. As seen from the figure, the samples annealed at 170 and 180°C did not exhibit clear diffraction peaks corresponding to crystalline PEEK but showed a broad halo, while the diffraction peaks probably due to crystallization of the PEEK segments were observed for the samples annealed at 190 and 210°C. In the case of pure PEEK, obvious diffraction peaks were observed for the sample annealed even at 160°C for 15 min[33].

The present results of WAXD analysis as well as the previous results of d.s.c. analysis[31] suggest that the crystallization behaviour of the PEEK segments in the PEEK/PES copolymer is significantly affected by the existence of PES segments in the molecular chain, that is, crystallization of the PEEK segments in the copolymer is rather difficult as compared with that of pure PEEK.

Table 1 The two melting points (T_{m1} and T_{m2}) for the isothermally crystallized copolymer from the melt

T_c (°C)	T_{m1} (°C)	T_{m2} (°C)
246	260	319
248	261	319
252	265	319
256	269	319
258	272	320
291	311	331
294	316	332
297	317	333
300	318	334
302	320	335

T_c: Crystallization temperature

Isothermal crystallization of the copolymer from the melt produces a material which exhibits a double-melting endotherm upon heating scan in the DSC. A similar phenomenon has been observed for pure PEEK[4,6,9–12]. *Table 1* shows the two melting points for isothermally crystallized copolymer from the melt. The low-temperature melting peaks are 10–20°C higher than the crystallization temperatures (T_c's). The lower melting point (T_{m1}) increases as the T_c increases. In contrast, when the T_c is in the range of 246–258°C, the high-temperature melting peaks are almost constant regardless of T_c's. In contrast, when the T_c is higher than 290°C, the higher melting point (T_{m2}) increases slightly with increasing T_c.

Lee and Porter[11,12], and Blundell and Osborn[4] attributed the double-melting behaviour to partial melting and recrystallization of the lower melting lamellae during the d.s.c. scan. Bassett *et al.*[10] concluded from d.s.c. and electron microscopic experiments that the higher melting lamellae are formed prior to the formation of the lower melting crystallites that lay between the higher melting lamellae. Cheng *et al.*[13] found that the high melting crystallite portion crystallizes first. They also described that the lower melting crystallites reorganize to some extent during the d.s.c. scan and eventually can become a part of the higher melting crystallites at higher temperature. From the above observations, it is deduced that the high melting peak must be used in the Hoffman and Weeks procedure to evaluate the equilibrium melting point (T_m°).

Hoffman–Weeks equation is generally expressed by the following formula[34,35].

$$T_m = T_m^\circ(1 - 1/\gamma) + (1/\gamma)T_c \quad (4)$$

Equation (4) shows that T_m and the lamellar thickening factor γ can be determined from the intersection with the $T_m = T_c$ line and the slope, respectively, in a Hoffman–Weeks plot of T_m vs T_c. The T_{m2} values for melt-crystallized copolymer summarized in *Table 1* are plotted against T_c (*Figure 3*). When T_{m2} is considered to be T_m in equation (4), T_m° of the copolymer is calculated to be 357°C and γ is 2.49.

Blundell and Osborn[4] obtained a T_m for PEEK of about 395°C, and later Porter *et al.*[11,12] reported the value of 389 ± 4°C for a PEEK with $\bar{M}_n = 14\,100$ and $\bar{M}_w = 38\,600$.

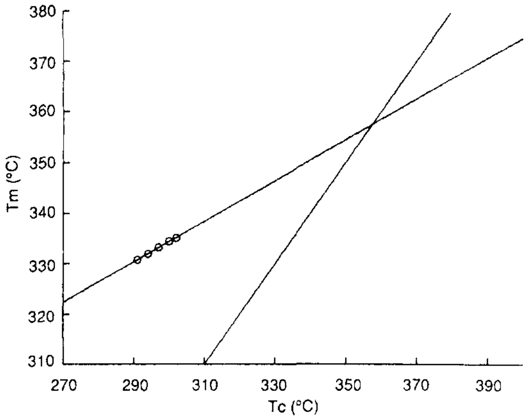

Figure 3 The high-melting peak temperature T_m of melt-crystallized copolymer vs crystallization temperatures

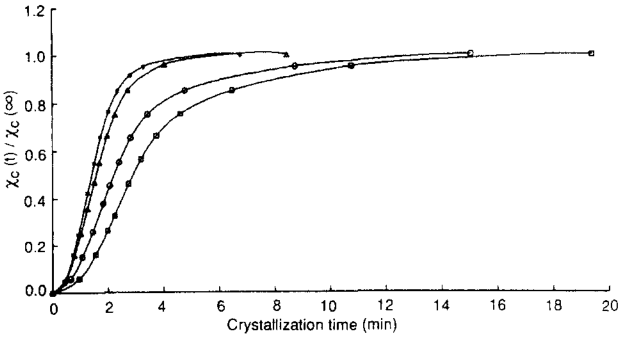

Figure 4 Development of relative crystallinity with time for isothermal crystallizations from the melt at 256°C (☆), 258°C (△), 261°C (○) and 263°C (□)

In the case of the copolymer, the PEEK crystallite growth is disturbed by the existence of the amorphous PES segment and thus the crystallite having an infinite thickness is not obtainable. Thus, the T_m^o obtained here may be regarded as the highest melting point that this particular copolymer can attain. Though the direct comparison of T_m^o of the copolymer with those reported for PEEK is difficult, the value for the copolymer is evidently smaller than the homopolymer. The lower T_m^o is ascribable to the incorporation of PES segments into the PEEK molecular chain in the copolymer. In the multiblock copolymer the thickness of the crystallite of PEEK segment cannot reach that of pure PEEK due to the disturbance of amorphous PES phase. We have prepared a series of PEEK/PES multiblock copolymers[31]. The effects of the composition and sequence length on the crystallization behaviour of block copolymers is particularly interesting and will be investigated.

The relative amount of crystallinity has been plotted in *Figure 4* for the four crystallization temperatures. Development of the relative crystallinity can be analysed by using the Avrami equation[36,37]:

$$\chi_c(t)/\chi_c(\infty) = 1 - \exp(-kt^n) \tag{5}$$

$$\ln[1 - \chi_c(t)/\chi_c(\infty)] = -kt^n \tag{6}$$

where n is a constant which depends upon the mechanism of nucleation and on the form of crystal growth, and k a constant containing the nucleation and growth parameters. Plots of $\log(-\ln[1 - \chi_c(t)/\chi_c(\infty)])$ vs $\log t$ are shown in *Figure 5*. Each curve has a linear portion followed by a gentle roll-off at longer times. The change to a secondary kinetic process is more evident for the high temperature crystallization than for the low temperature crystallization. The n and k values were determined from the plots of $\log(-\ln[1 - \chi_c(t)/\chi_c(\infty)])$ vs $\log t$ for times before the roll-off according to equation (6). The values are listed in *Table 2*. The values of exponent n, obtained from the Avrami analysis, are about 2.0; the rate constant k values decrease with increasing crystallization temperature. The crystallization half-times, $t_{1/2}$, the time at which the relative degree of crystallinity is 0.5, increase with increasing crystallization temperature.

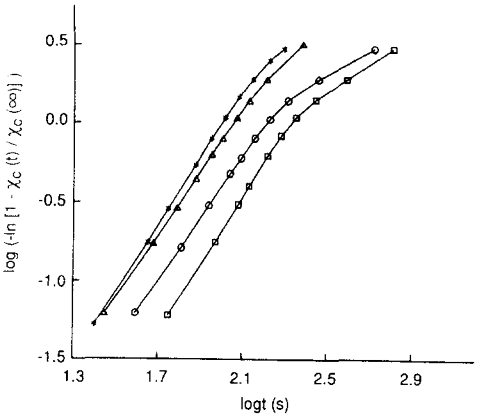

Figure 5 Plots of $\log(-\ln[1 - \chi_c(t)/\chi_c(\infty)])$ vs $\log t$ for isothermal crystallization at 256°C (☆), 258°C (△), 261°C (○) and 263°C (□)

Table 2 Parameters n and k from the Avrami analysis of isothermal crystallization

T_c (°C)	n	k	$t_{1/2}$ (min)
256	2.10	6.05×10^{-5}	1.43
258	2.06	5.86×10^{-5}	1.57
261	2.01	3.72×10^{-5}	2.20
263	2.14	1.06×10^{-5}	2.25

Kinetics of crystallization of commercial PEEK has led to variable values of n usually close to 3[9,14–17], indicating that the growth of crystals in these PEEK is probably spherulitic, though Day *et al.*[18] reported that using samples prepared in their laboratory, their analysis of the sigmoidal crystallization curves by means of the Avrami equation leads to $n \approx 2$.

The exponent ($n \approx 2$) obtained for the copolymer is not consistent with spherulitic growth ($n = 3$)[38] but rather disc-like spherulites as proposed by Lovinger and Davis[39]. The crystallization mechanism of PEEK segments in the copolymer can be explained as follows. The copolymer obtained from the melt comprises a homogeneous phase. Upon annealing, the phase separation of PEEK and PES segments should occur first, and the crystallization of PEEK segments follow in the next stage. The crystallite growth along the chain direction in PEEK crystallite stops when it reaches to the PES phase, i.e. the PEEK crystal can grow only along the PEEK layer. Such a two-dimensional growth should cause disc-like sperulites, leading to $n = 2$.

The rate constant k determined from the Avrami analysis is useful to gain further insight into the crystallization of PEEK/PES copolymer. The k value could be obtained in the temperature regime 256–263°C. We assume that in the homogeneous copolymer the degree of transformation could be satisfactorily described by the Avrami equation, and that all assumptions underlying the derivation of equation (5) hold also in copolymers. Calorimetric data obtained in isothermal conditions are useful for discussion of the overall crystallization behaviour according to nucleation theories[7]. In fact, it can be easily shown that, under isokinetic conditions for nucleation rate and linear growth rate G, k is related to G by the simple relation:

$$G \propto k^{1/n} \tag{7}$$

The theories of surface nucleation have been modified to account for the effect of non-crystallizable component on the linear growth rate of crystals developing in an undercooled homogeneous copolymer[40–43]. Because of lack of information on diffusion constants in copolymers, the equation commonly used to describe the linear growth kinetics reads:

$$\begin{aligned} G = {} & \Psi_2 G_0 \exp\{-U/R[C_2 + T_c - T_g(\Psi)]\} \\ & \times \exp\{-rb_0\sigma\sigma_e T_m^o(\Psi)/[kf\Delta H_m^o T\Delta T(\Psi)]\} \\ & \times \exp\{2\sigma T_m^o(\Psi)\ln\Psi_2/[b_0 f\Delta H_m^o \Delta T(\Psi)]\} \end{aligned} \tag{8}$$

where Ψ_2 is the volume fraction of the crystallizable polymer, U the activation energy for transport of crystallizable segments to the site of crystallization through the subcooled melt, $T_g(\Psi)$ the T_g of the copolymer, $T_m^o(\Psi)$ the T_m^o of the copolymer, ΔH_m^o the heat of fusion of 100% crystalline PEEK, C_2 is a constant usually assumed to be 51.6°C, f is a correction factor for the temperature dependence of the heat of fusion and can be expressed as $f = 2T_c/[T_m^o(\Psi) + T_c]$, σ and σ_e are the lateral and fold surface free energies of the developing crystals, respectively, and b_0 is the layer thickness. G_0 is a constant that depends on the regime of crystallization, and r is a parameter characteristic of the growth regime; $r = 4$ in Regimes I and III, $r = 2$ in Regime II[44]. It is expected that transitions from Regime I to III through II should be observed on increasing the ratio between the surface nucleation rate and the rate of spreading of the secondary nucleus on the substrate. $\Delta T(\Psi) = T_m^o(\Psi) - T$ is the actual undercooling experienced by the crystallizable chains in the copolymer.

Combining equations (7) and (8), followed by rearrangement, gives equation (9).

$$\begin{aligned} \alpha = {} & (\ln k)/n + U/R[C_2 + T_c - T_g(\Psi)] \\ & - [1 + 2\sigma T_m^o(\Psi)/b_0 f\Delta H_m^o \Delta T(\Psi)]\ln\Psi_2 \\ = {} & \ln G_0 - rb_0\sigma\sigma_e T_m^o(\Psi)/kf\Delta H_m^o T\Delta T(\Psi) \end{aligned} \tag{9}$$

Therefore, by plotting α as a function of $1/fT\Delta T(\Psi)$, straight lines with slopes related to the surface free energies of the lamellar crystals should be obtained.

The present data obtained from the copolymer are plotted in *Figure 6* according to equation (9). The n and k values have been evaluated from the preceding Avrami analysis; the values of $U = 8.38\,\mathrm{kJ\,mol^{-1}}$ and of $C_2 = 51.6$°C have been taken from the literature on crystallization kinetics of pure PEEK[4,8]. It should be noted that alternative reasonable choices of these values do not significantly affect the slopes of the lines in *Figure 6*, as can be expected for crystallizations at temperatures well above T_g. $T_g(\Psi)$ and $T_m^o(\Psi)$ are those discussed above, $b_0 = 0.2945\,\mathrm{nm}$ and $\sigma = 20.5\,\mathrm{erg\,cm^{-2}}$ has been taken from the literature[24]. *Figure 6* shows that experimental data obey equation (9) well. From the slopes of the plots, the fold surface free energy σ_e can be calculated readily if the growth regime is known. On the assumption that the regime III is operative at undercoolings of the order of 60°C, $\sigma_e = 73\,\mathrm{erg\,cm^{-2}}$ is obtained for the copolymer. The fold surface free energy of pure PEEK ($\sigma_e = 49\,\mathrm{erg\,cm^{-2}}$) was suggested by Blundell and Osborn[4]. This indicates that the fold surface free energy of PEEK segments is increased by incorporation of PES segments into its molecular chain.

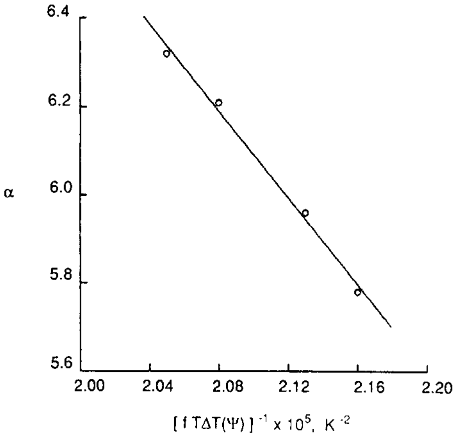

Figure 6 Plot of kinetic data according to equation (9)

CONCLUSION

The crystallization behaviour of a PEEK/PES multiblock copolymer was investigated. While the crystalline structure of the copolymer is similar to that of pure PEEK, the equilibrium melting point (T_m^o) of the copolymer was found to be 357°C, about 30°C lower than the commonly accepted value for pure PEEK. The crystallization of the copolymer follows an Avrami behaviour with the Avrami exponent n of about 2 during isothermal crystallization from the melt. The fold surface free energy (σ_e) for the copolymer crystallization from the melt was calculated to be $73\,\mathrm{erg\,cm^{-2}}$; the value is about $24\,\mathrm{erg\,cm^{-2}}$ higher than that of pure PEEK.

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