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Synthesis and properties of the block copolymers of poly(ether ether ketone) and the poly(aryl ether sulfone) containing biphenylene moiety

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The block copolymers of poly(ether ether ketone) (PEEK) and poly(aryl ether sulfone) containing biphenylene moiety (PEBS) were synthesized by a condensation reaction of fluorine-terminated PEEK oligomers and hydroxy-terminated PEBS oligomers. The content of PEBS in the copolymers was varied from 10 to 37 wt%, and the effect of the compositional variation on the properties was investigated. Microphase separation was not observed and the copolymer was a homogeneous system having good compatibility. The crystal structure of the copolymers is rhombic, equal to PEEK. Although the degree of crystallinity of the copolymers decreased with the increase of PEBS content, the glass transition temperature (T_g) rose greatly, and superior heat resistance and good mechanical properties at high temperature were obtained. Analyses of the isothermal crystallization kinetics of the copolymers provided an Avrami's exponent (n) of 2.0. © 1997 Elsevier Science Ltd.

(Keywords: PEEK; PEBS; block copolymer)

INTRODUCTION

Poly(ether ether ketone) (PEEK) is well known as a high-performance engineering thermoplastic possessing excellent mechanical properties, good environmental resistance, and high thermal and thermo-oxidative resistance. In recent years, several patents and papers have been published concerning the copolymerization of PEEK in order to improve its glass transition temperature (T_g), and processability at high temperatures, and to obtain low-cost materials[1–5]. It is already known that block copolymerization of PEEK and poly(ether sulfone) (PES) is an effective method to improve the T_g and mechanical properties at high temperature[1]. However, the improvement of T_g is not so marked in the copolymerization of PEEK and PES.

The poly(aryl ether sulfone) containing biphenylene moiety (PEBS) has a high T_g (260°C), which is 35°C higher than that of PES. In this paper, we report on the synthesis of PEEK/PEBS block copolymers and the investigation of their properties and crystallization behaviour.

EXPERIMENTAL

Materials

4,4′-Dihydroxydiphenylsulfone (m.p. 242°C, Yanbian Longjing Chemical factory), hydroquinone (Beijing North Suburb Chemical Factory) and 4,4′-difluorobenzophenone (m.p. 103–104°C, Yanbian Longjing Organic Chemical Factory) were used without further purification. 4,4′-Bis(4-chlorophenylsulfonyl)-biphenyl (m.p. 272–273°C) and diphenyl sulfone (m.p. 124–125°C) were prepared by the standard method[6].

Synthesis of PEEK/PEBS block copolymers

Hydroxy-terminated PEBS oligomer was synthesized by the reaction of 4,4′-bis(4-chlorophenylsulfonyl)-biphenyl and 4,4′-dihydroxydiphenylsulfone in the presence of sodium hydroxide in sulforane and subsequent protonation by hydrochloric acid[7] (*Scheme 1*).

Fluorine-terminated PEEK oligomers were synthesized by the reaction of 4,4′-difluorobenzophenone and hydroquinone in diphenyl sulfone in the presence of sodium carbonate and potassium carbonate according to a literature procedure (*Scheme 2*)[8,9].

Typical reaction conditions for the copolymer synthesis are as follows: fluorine-terminated PEEK oligomer was prepared first, but was not isolated from the reaction mixture. Hydroxy-terminated PEBS oligomer which had been isolated and characterized, potassium carbonate and diphenyl sulfone were added to the diphenyl sulfone solution of the PEEK oligomer at 250°C, and the two oligomers were reacted at 250–320°C for 3–4 h (*Scheme 3*)[6].

The copolymer solution was then poured into water, and, after cooling, the precipitate was crushed, washed repeatedly with acetone and water, 10 times in total, and finally dried *in vacuo* at 140°C for 24 h.

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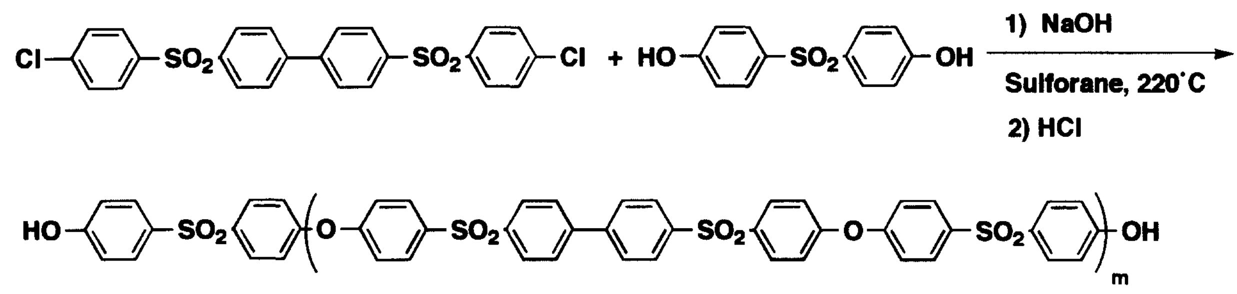
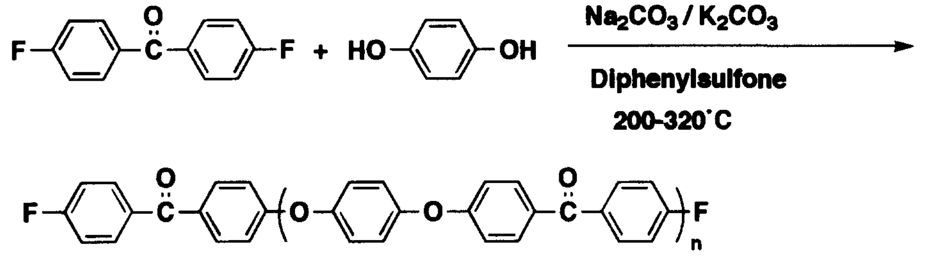
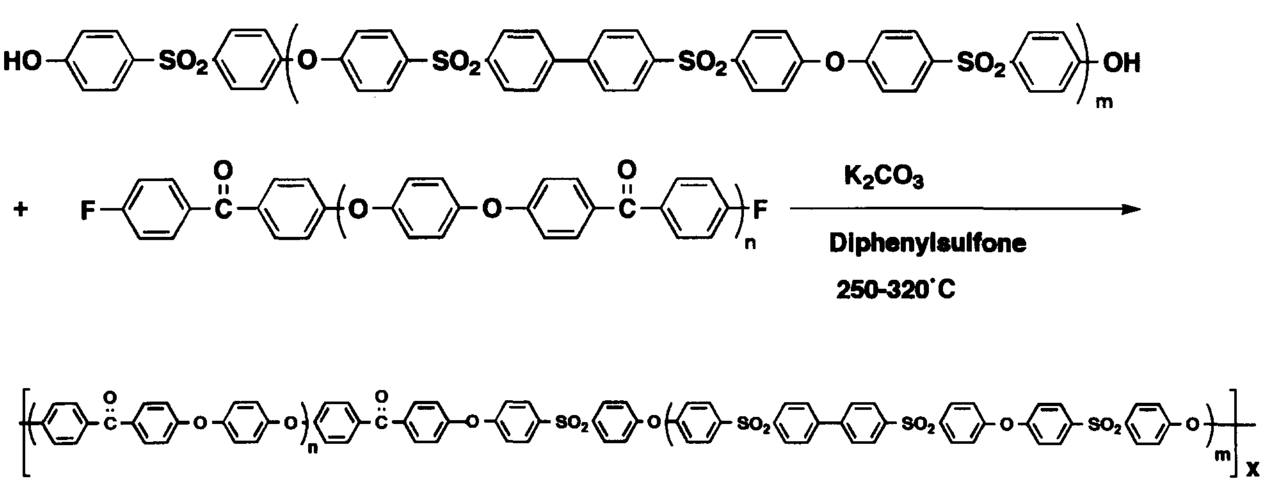


Scheme 1



Scheme 2



Scheme 3

Material preparation

The copolymer samples were moulded into films with a thickness of 0.5 mm at 10 MPa and 360–370°C for 5 min. To obtain amorphous film samples, the above films were quenched by immediately putting them into an ice/water mixture. Heat-treated samples were prepared by annealing the amorphous films at various temperatures for predetermined periods of time, and then cooling slowly to room temperature.

Measurements

The inherent viscosity (η_{inh}) of the copolymers was measured at a concentration of 0.1 wt% in H_2SO_4 at 25°C. I.r. spectra were measured on a Nicolet 5 DX-FT i.r. spectrometer (KBr method). D.s.c. was carried out with a DuPont TA-2000 thermoanalysis instrument, and thermogravimetric analysis (t.g.a.) was carried out on a Perkin Elmer TGS-2 thermogravimetric analyser at a heating rate of $10°\text{C}\,\text{min}^{-1}$ in a nitrogen atmosphere. Especially for the study on the isothermal crystallization kinetics, a Perkin Elmer DSC-IIC type instrument was used. The decomposition temperature (T_d) is defined as the temperature where the weight loss is 2.5%. Wide-angle X-ray diffraction (WAXD) was measured with a Rigaku D/MAX-IIA X-ray diffractometer, using CuK_α radiation, at 40 kV and 30 mA. Dynamic viscoelastic measurements were performed on a Rheovibron DDV-III EP dynamic mechanical analyser (Orientec Co. Ltd) using a heating rate of $2°\text{C}\,\text{min}^{-1}$ at 110 Hz.

RESULTS AND DISCUSSION

Characterization of the PEEK/PEBS block copolymers

In this study, oligomers with various molecular weights were synthesized by controlling the molar ratio of the two monomers, according to the modified Carothers equation, i.e. $X_n = (1+\gamma)/(1-\gamma)$, where X_n is the number-average degree of polymerization and γ is the molar ratio of the two monomers. The molecular weight of the PEBS oligomers was determined by the potentiometric titration method in non-aqueous media[10]. Although in the preparation of the PEEK/PEBS copolymers, the PEEK oligomers were used without isolation, the $\bar{M}_n$ of the PEEK oligomer which was

Table 1 Compositions and characterization data for the PEEK/PEBS copolymers

	$\bar{M}_n$ of oligomer								
No.	PEEK[a]	PEBS[b]	PEBS[c] (%)	η_{inh} (dl g^{-1})	T_g (°C)	T_m (°C)	T_c' (°C)	χ_c[d] (%)	χ_c (PEEK)[e] (%)
1	12 000	1330	10.0	0.95	153	330	201	21.8	24.2
2	12 000	3180	20.9	0.88	162	329	219	20.4	25.8
3	12 000	4200	25.9	0.92	167	326	238	15.3	20.7
4	12 000	5930	33.1	0.86	175	326	262	7.0	10.5
5	12 000	6790	37.2	0.84	183	328	271	6.1	9.8
PEEK				0.80	143	334	175	32.6	

[a] Estimated value from the feed ratio of 4,4′-difluorobenzophenone and hydroquinone

[b] Determined by potentiometric titration

[c] Calculated by $\{\bar{M}_n(\text{PEBS}) - [\bar{M}_n(\text{PEEK}) + \bar{M}_n(\text{PEBS})] \times \Delta\} \times 100\%/[\bar{M}_n(\text{PEEK}) + \bar{M}_n(\text{PEBS})](1 - \Delta)$, where Δ is the fraction of weight loss, and $\bar{M}_n$(PEEK) and $\bar{M}_n$(PEBS) are number-average molecular weights of the PEEK and PEBS oligomers, respectively

[d] Degree of crystallinity of the copolymers, calculated by d.s.c.

[e] Degree of crystallinity corresponding to the PEEK segments, calculated by d.s.c.

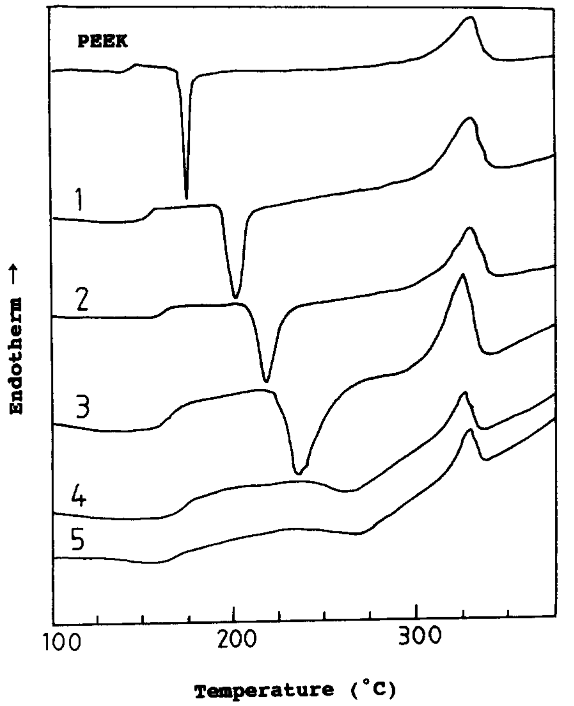


Figure 1 D.s.c. curves of the amorphous PEEK/PEBS copolymers and PEEK; compositions of the samples are given in *Table 1*

synthesized under the same conditions as in the preparation of PEEK/PEBS copolymer and isolated was identified by the ^{19}F n.m.r. method[1,11]. The value thus determined was 11 540, which was in fairly good agreement with the calculated value of 1.2×10^4. In the preparation of the PEEK/PEBS copolymers, the $\bar{M}_n$ was therefore assumed to be the same as that calculated from the molar ratio of 4,4′-difluorobenzophenone to hydroquinone.

In order to investigate the effect of composition on the properties of the PEEK/PEBS block copolymers, PEEK oligomers with a fixed $\bar{M}_n$ (1.2×10^4, calculated value) were first prepared, while the $\bar{M}_n$ values of the PEBS oligomers were changed over the range 1330–6790; in this way, the PEBS content in the copolymers varied from 10.0 to 37.2%. The composition of the copolymers and other characterization data are listed in *Table 1*. The powdered copolymers were extracted with *N,N*-dimethylformamide (DMF), which is a good solvent for PEBS. The weight loss after extraction was less than 0.5% when the PEBS content was less than 25.9%. The values were 1.5 and 2.8% for the copolymers with PEBS contents of 33.1 and 37.2% (samples 3 and 4), respectively. The i.r. spectra of the copolymers showed the stretching vibrational absorption of the ketone group at 1650 cm^{-1}, symmetrical stretching vibrational absorption of the sulfone groups at 1150 cm^{-1}, and characteristic absorptions of the *para*-substituted biphenylene moiety at 1011 and 1383 cm^{-1}. In addition, the inherent viscosities of 0.8–1.0 dl g^{-1} suggest that the samples have moderately high molecular weights. These facts indicate that samples prepared via the above methods should be the copolymers of the two oligomers, rather than blends of the two components, although the possibility that the residual polymers contain some PEEK oligomers cannot be ruled out completely.

Properties and compatibility of the PEEK/PEBS block copolymers

Figure 1 shows the d.s.c. results of the amorphous copolymer samples and pure PEEK. *Figure 2* shows plots of tan δ *versus* temperature of the copolymers, pure PEEK and pure PEBS. As is obvious from these figures, the copolymers showed single glass transitions, indicating that the copolymers formed a homogeneous system having good compatibility over the range of the compositions, or block lengths, discussed in this paper. Also, the T_g values of all the copolymer samples were higher than that of PEEK, and rose with the increase in PEBS content. The T_g of the copolymer with a PEBS content of 37.2% (sample 5) was 183°C, which is higher by 40°C than that of PEEK. As compared with the previously reported PEEK/PES block copolymer (T_g 180°C, PES content 48.3%)[1], the comparable T_g is obtained by the incorporation of much less of poly(aryl ether sulfone). Regarding the melting point (T_m), the value of the PEEK/PEBS copolymer (T_m 328°C, sample 5) was slightly shifted to lower temperature as the content of PEBS increased, in contrast to a considerable decrease in the case of the PEEK/PES block copolymer (T_m 316°C, PES content 35.1%)[1].

Figure 3 shows the typical t.g.a. curves in nitrogen for two of the PEEK/PEBS copolymers and of pure PEEK. T_d values at which the weight loss reached 2.5% of the original sample weight were 550, 550 and 529, for PEEK, samples 1 (PEBS content 10.0%) and 5 (PEBS content

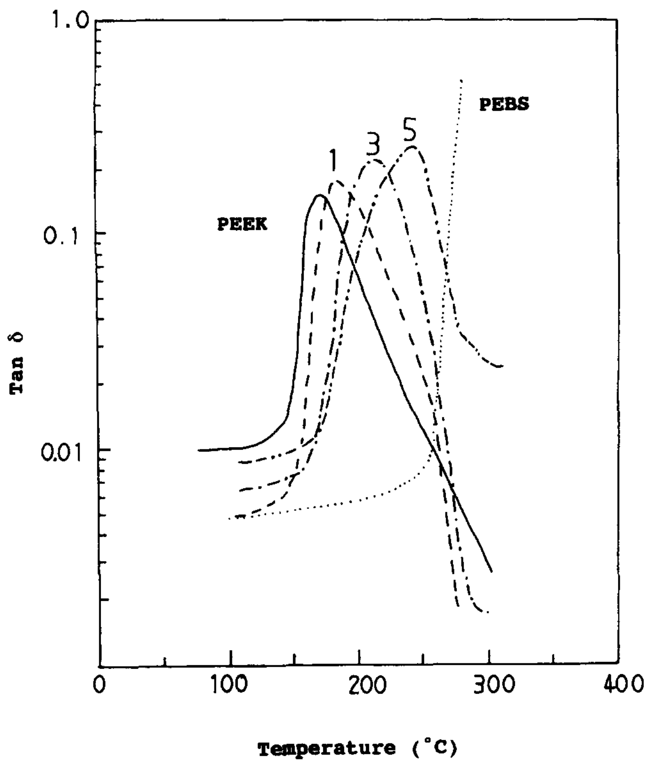


Figure 2 Loss factor curves obtained from dynamic viscoelastic measurements on the PEEK/PEBS copolymers, PEEK and PEBS; compositions of the samples are given in *Table 1*

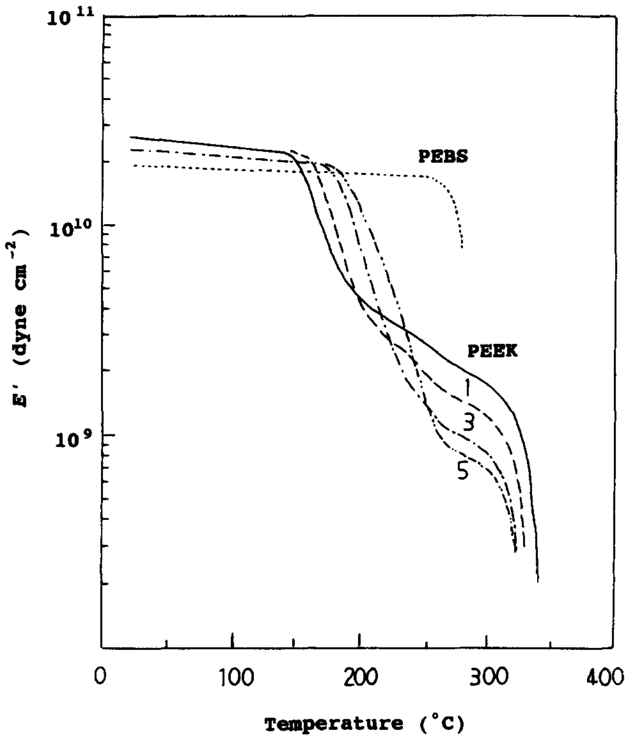


Figure 4 Storage modulus as a function of temperature for PEEK, PEBS, and the PEEK/PEBS copolymers; compositions of the samples are given in *Table 1*

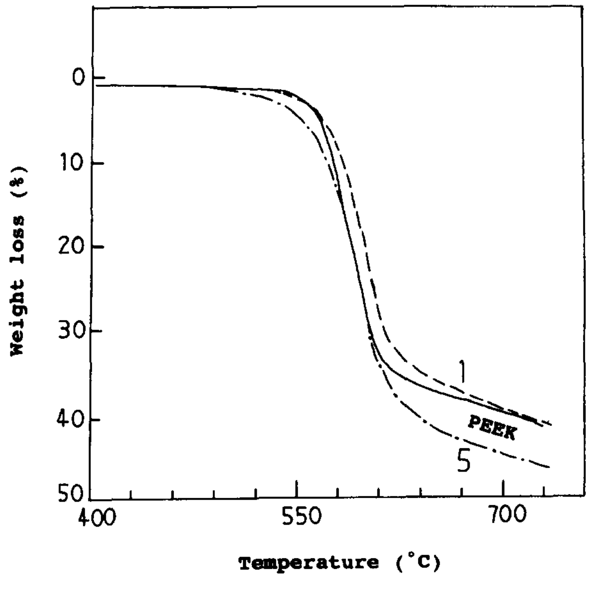


Figure 3 T.g.a. curves of the PEEK/PEBS copolymers and PEEK; compositions of the samples are given in *Table 1*

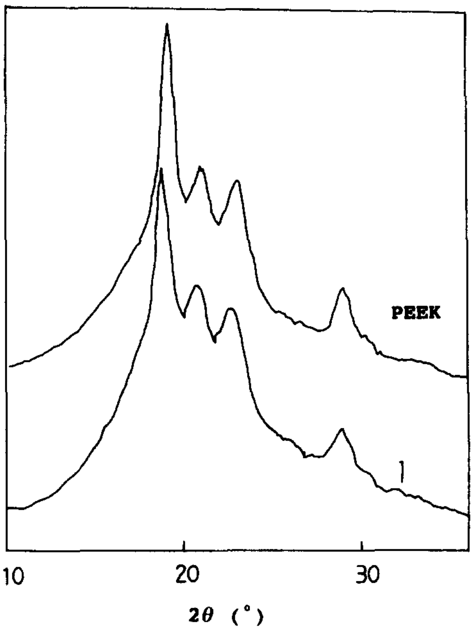


Figure 5 WAXD patterns of a crystalline PEEK/PEBS copolymer containing 10.0% PEBS and PEEK

37.2%), respectively. Although the T_d of sample 5 was somewhat reduced by the incorporation of PEBS, the value of sample 1 was still comparable to that of PEEK.

Figure 4 shows the temperature dependence of the storage modulus (E') for copolymer samples, pure PEEK and pure PEBS. The temperature where E' begins to decrease becomes higher as the content of PEBS increases. The values for the PEEK/PEBS copolymers were higher than those of PEEK/PES copolymers[1] having comparable PEEK contents, indicating that the copolymers have superior mechanical properties at higher temperature.

Crystallization behaviour of the PEEK/PEBS block copolymers

The results of WAXD measurements of PEEK and copolymer sample 1 are shown in *Figure 5*. The number of diffraction peaks and value of 2θ for each diffraction peak are the same as each other, suggesting that the crystal structure of the copolymer is a rhombic form system in the same manner as is PEEK[12]. It can therefore be presumed that the PEBS moiety is not in the crystal unit cell of the copolymer but in the non-crystalline phase between the crystalline lamellae. Crystal unit cell

Table 2 Parameters[a] of the crystalline unit cell of PEEK and PEEK/PEBS copolymer containing 20.9% PEBS

Sample	a (Å)	b (Å)	c (Å)	V (Å^3)	ρ_c (g cm^{-3})
PEEK[13]	7.75	5.86	10.00	454.15	1.400
PEEK	7.76	5.83	10.04	454.06	1.404
2	7.86	5.87	10.10	465.70	1.369

[a] The a axis and b axis were determined from the WAXD pattern of the powder, and the c axis was determined from the WAXD pattern of the fibre via reflections of $[00l]$[13]. ρ_c was calculated by the equation $\rho_c = zM/NV$, where z is the molecular chain number through the crystal unit cell (in this case 2), M is the molecular weight of molecular repeating unit in the crystal, V is the crystal unit cell volume and N is Avogadro's constant

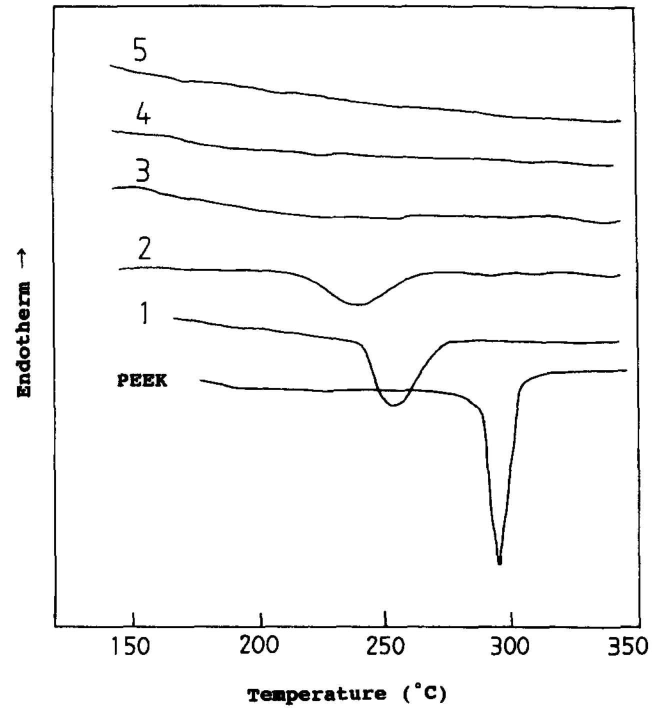


Figure 6 D.s.c. curves of the PEEK/PEBS copolymers and PEEK obtained after cooling from 400°C at a cooling rate of 10°C min^{-1}; compositions of the samples are given in *Table 1*

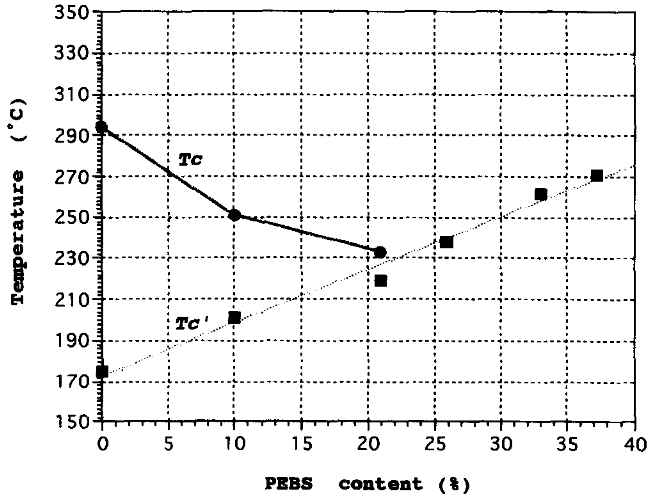


Figure 7 Effect of the PEBS content of the PEEK/PEBS copolymers on T_c' (■) and T_c (●)

parameters of PEEK and copolymer sample 2 obtained by the measurement of WAXD are listed in *Table 2*, where V is the volume of the unit cell, and ρ_c is the crystalline density. As compared with the parameters of PEEK, the a-axis is apparently large, and, therefore, V is also large for the copolymer. It is considered that the incorporation of the rigid PEBS segment affects the folded structure of the PEEK component. It can be seen from *Figure 1* that the quenched amorphous PEEK/PEBS copolymer samples show both a cold-crystallization temperature (T_c') and a T_m. The exothermic peak shows a strong shift towards higher temperatures with increasing PEBS content, and gradually becomes smaller and broader. In contrast, the endothermic peak is slightly shifted to lower temperature, and decreases in intensity with increasing PEBS content.

The degree of crystallinity of the copolymers (χ_c) and that which corresponds to the PEEK segments (χ_c(PEEK)) can be estimated from d.s.c. results by using the following equations:

$$\chi_c = \Delta H / \Delta H_c \tag{1}$$

$$\chi_c(\mathrm{PEEK}) = \chi_c / W_{\mathrm{PEEK}} \tag{2}$$

where ΔH is the heat of fusion of the copolymer determined by d.s.c., ΔH_c is the heat of fusion of 100% crystalline PEEK ($\Delta H_c = 130\,\mathrm{J\,g^{-1}}$)[12] and W_{PEEK} is the weight fraction of the PEEK segment in the copolymer. The crystallinity data are given in *Table 1*. Both the χ_c and χ_c(PEEK) values of the copolymers decrease with increasing PEBS content except for χ_c(PEEK) of 25.8% at a PEBS content of 20.9%.

Figure 6 shows the d.s.c. curves obtained for the above copolymers, after first melting at 400°C for 2 min, and then cooling, at a rate of 10°C min^{-1}, to room temperature. The copolymers with PEBS contents of less than 20.9% show an obvious crystallization exotherm temperature (T_c). The copolymers with PEBS content of 25.9% or above did not show any obvious crystallization exotherms. Plots of the T_c' and T_c values against the copolymer compositions are shown in *Figure 7*. These results suggest that crystallization of the copolymers becomes more difficult as the PEBS content increases.

Similarly to PEEK[14], when the PEEK/PES copolymer[1] was annealed at high temperature (290°C for 4 h), double melting peaks were observed in the d.s.c. curves (*Figure 8*). The peak maximum temperatures for the low-temperature melting peaks (T_{m1}) and those for the high-temperature melting peaks (T_{m2}), and the degree of crystallinity (χ_c and χ_c(PEEK)) of PEEK and PEEK/PEBS block copolymers, are summarized in *Table 3*. The low-temperature peaks were smaller, and remained almost constant, regardless of the PEBS content. T_{m1} was about 10°C higher than the annealing temperature. Although T_{m2} values for the PEEK/PEBS copolymers were lower than that of pure PEEK, those for the copolymers were almost constant regardless of the content of PEBS. Although χ_c of the copolymer samples became smaller with increasing PEBS content, χ_c(PEEK) did not change, remaining almost constant.

In this study on the crystallization kinetics of PEEK/PEBS, sample 2 (PEBS content 20.9%) was rapidly heated to 400°C under nitrogen at a heating rate of 320°C min^{-1}. After eradicating the thermal or mechanical memory effect by melting the sample for 5 min, it was

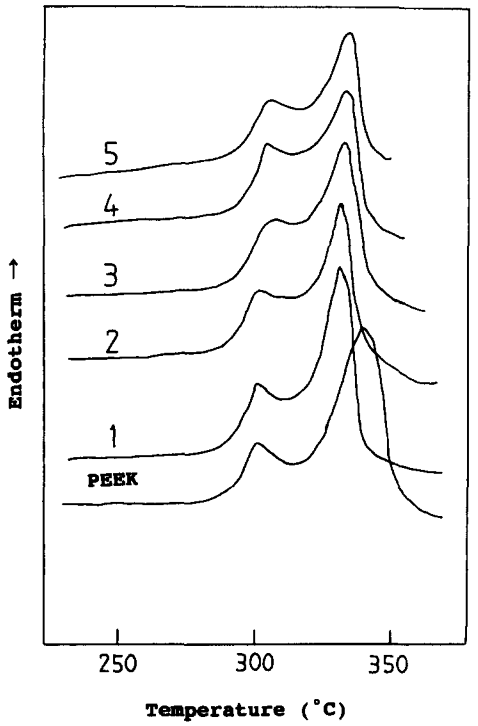


Figure 8 D.s.c. curves of the crystalline PEEK/PEBS copolymers and PEEK obtained after annealing at 290°C for 4 h; compositions of the samples are given in *Table 1*

Table 3 T_{m1}, T_{m2}, χ_c and χ_c(PEEK) of PEEK and PEEK/PEBS copolymers annealed at 290°C for 4 h; compositions of the samples are given in *Table 1*

	Sample					
	PEEK	1	2	3	4	5
T_{m1} (°C)	300	299	298	298	298	299
T_{m2} (°C)	340	331	331	330	328	330
χ_c (%)	29.5	26.7	23.4	22.6	20.5	18.7
χ_c(PEEK) (%)	29.5	29.6	29.7	30.5	30.6	29.8

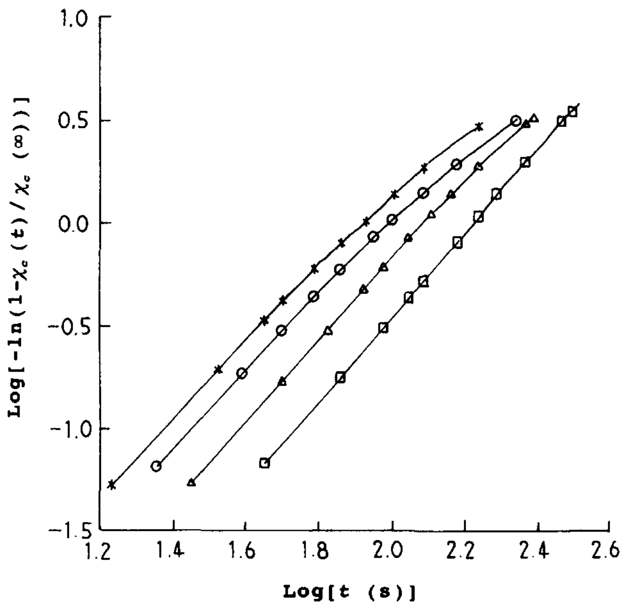


Figure 9 Plots of $\log[-\ln(1-\chi_c(t)/\chi_c(\infty))]$ versus $\log t$ for isothermal crystallization of the PEEK/PEBS copolymer containing 20.9% PEBS at 249°C (∗), 251°C (○), 257°C (△) and 261°C (□)

Table 4 n, K and $t_{1/2}$ of the PEEK/PEBS copolymer containing 20.9% PEBS

T_c (°C)	n	K	$t_{1/2}$ (min)[a]
249	1.87	2.69×10^{-4}	1.11
251	1.89	1.82×10^{-4}	1.31
257	2.00	6.92×10^{-5}	1.67
261	2.04	2.88×10^{-5}	2.34

[a] $t_{1/2}$ is the half-crystallization period, and is calculated by the equation $t_{1/2} = [(\ln 2)/K]^{1/n}$

cooled to a prescribed temperature at the cooling rate of $-80°\mathrm{C\,min^{-1}}$, and the enthalpy of isothermal crystallization was measured as a function of time and temperature. The isothermal crystallization kinetics of the molten polymer was studied by Avrami's equation[15]. The equation is expressed as follows:

$$\chi_c(t)/\chi_c(\infty) = 1 - \exp(-Kt^n) \qquad (3)$$

Equation (4) is derived from equation (3):

$$\log[-\ln(1-\chi_c(t)/\chi_c(\infty))] = \log K + n \log t \qquad (4)$$

where n is Avrami's exponent and K is the crystallization rate constant. Plots of $\log[-\ln(1-\chi_c(t)/\chi_c(\infty))]$ *versus* $\log t$ are shown in *Figure 9*. Avrami's exponent (n) and K calculated from the slope and intercept in the linear part of Avrami's equation, respectively, are listed in *Table 4*. As is obvious from *Table 4*, K decreases and $t_{1/2}$ increases as the isothermal crystallization temperature rises. Avrami's exponent (n) of the block copolymer is ~2.0, which is smaller than that of PEEK (~3.0) reported in the literature[16–18]. This result indicates that the mechanism of crystalline nucleation and crystalline growth in the crystallization of molten material is different for the PEEK/PEBS block copolymers and PEEK. The reason for the different crystallization mechanism is now under investigation.

ACKNOWLEDGEMENT

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