

Synthesis and Properties of Poly(ether ether ketone ketone)–Poly(ether sulfone) Block Copolymers

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SYNOPSIS

Poly(ether ether ketone ketone)–poly(ether sulfone) (PEEKK/PES) block copolymers were prepared from the corresponding oligomers via a nucleophilic aromatic substitution reaction, and the \bar{M}_n of the PEEKK segment was fixed at 12,000, while the \bar{M}_n 's of the PES segment ranged from 250 to 12,680. The different properties of the copolymers were investigated by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The results showed that the relationship between T_g and compositions of copolymers approximately followed the formula $1/T_g = W_1/T_{g1} + W_2/T_{g2}$. The PES content and the segment length of the copolymers had a significant influence on their melting points and crystallization behavior. The thermal properties and dynamic mechanical behavior of the copolymers were also studied. In the study of isothermal crystallization, the copolymers have the same nucleation mechanism and crystal growth as that of pure PEEKK. Owing to the introduction of the PES segment into the PEEKK main chain, it increases the free energy which forms the critical crystal nucleus and produces a resistant action to the whole crystallization process of the PEEKK segment. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In 1979, the ICI company first successfully synthesized poly(ether ether ketone) (PEEK).¹ Owing to its excellent mechanical properties, good environmental resistance, and high thermal and thermooxidative stability, it has been extensively used in electronics, nuclear, and chemical industries, etc. Poly(ether ether ketone ketone) (PEEKK)² is produced on the basis of PEEK. It has a higher glass transition temperature ($T_g = 160^\circ\text{C}$) and melting point ($T_m = 360^\circ\text{C}$) than those of PEEK ($T_g = 143^\circ\text{C}$, $T_m = 334^\circ\text{C}$). Unfortunately, these materials have a relatively low T_g , which results in a decrease of the modulus at elevated temperature. In addition, its price is comparatively high. This limits its widespread application.

Many works have been done to overcome these disadvantages, e.g., making blends with other high-performance thermoplastics such as polysulfone (PSF), poly(ether sulfone) (PES), poly(amide imide) (PAI), poly(ether imide) (PEI), and poly(phenylene sulfide) (PPS).^{3–9} However, most of these blends possess a phase-separated behavior which makes them unusable. Incorporation of the above-mentioned polymer blocks into poly(aryl ether ketone)s may afford new materials with improved properties and either homogeneous or microphase-separated morphologies should be possible. This could provide another means for modifying the properties of PEEKK. PES is an amorphous polymer, which possesses excellent properties, in particular, a high T_g (225°C) and a low price when compared with PEEKK. We have made the PEEKK/PES block copolymers with their corresponding oligomers and have published work on PEEK/PES block copolymers.^{10,11} In this article, we prepared PEEKK/PES block copolymers via the reaction of their relative oligomers. The miscibility, thermal properties, and crystallization behavior of the copolymers were studied.

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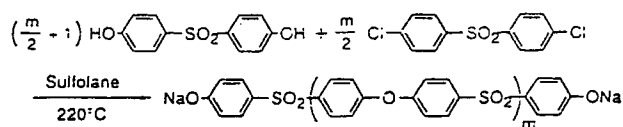
EXPERIMENTAL

Materials

4,4-Dichlorodiphenyl sulfone (mp 146°C) was obtained from Dalian Santang Chemical Factory, China, and 4,4-Dihydroxydiphenyl sulfone (mp 248°C), from Yan Bian Longjing Chemical Factory, China. Hydroquinone and other reagents for analysis (Beijing North Suburb Chemical Factory, China) were used without further purification, 1,4-Bis(4'-fluorobenzoyl)benzene (mp 219°C) and diphenyl sulfone (mp 124–125°C) were prepared in our laboratory.

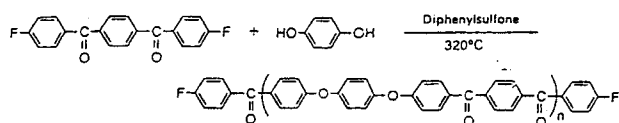
Synthesis of PES Oligomers

Dihydroxyl-terminated PES oligomers were prepared by a condensation reaction between 4,4'-dichlorodiphenyl sulfone and 4,4'-dihydroxydiphenyl sulfone in the presence of aqueous sodium hydroxide in sulfolane.¹² The reaction scheme is shown below:



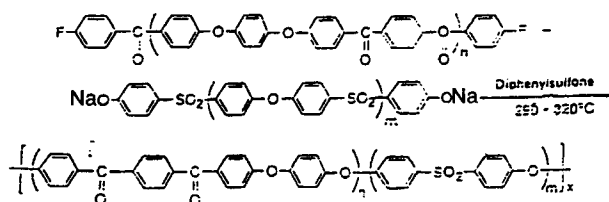
Synthesis of PEEKK Oligomers

Difluorine-terminated PEEKK oligomers were prepared by the reaction of 1,4-bis(4'-fluorobenzoyl)benzene with hydroquinone in diphenyl sulfone in the presence of Na₂CO₃ and K₂CO₃ according to the literature¹³:



Synthesis of PEEKK/PES Block Copolymers

PEEKK/PES block copolymers were prepared from the above two oligomers via a nucleophilic aromatic substitution reaction¹⁴:



Typical reaction conditions for the copolymer synthesis are as follows: PEEKK oligomer (0.2 mol) was prepared first, but not isolated from the reaction

mixture. PES oligomer (5.8 mmol) (solid powder), which had been isolated and characterized, was added to the diphenyl sulfone solution of the PEEKK oligomer and the two oligomers were reacted at 260–310°C for 2–4 h. The copolymer solution was then poured into water, and after cooling, the precipitate was crushed, repeatedly washed with acetone and water (for a total of 10 times), and, finally, dried.

Material Preparation

The powder samples were molded into films with a thickness of 0.5 mm by applying a pressure of 10 MPa at 400°C for 10 min:

1. The films were cooled to room temperature naturally and crystallization samples were obtained.
2. They were quenched by immediately putting them into an ice/water mixture, and amorphous samples were obtained. The isothermal crystallization samples can be prepared by annealing the amorphous films at various temperatures for predetermined periods of time and then they are put into the ice/water mixture.

Measurements

The number-averaged molecular weights (\bar{M}_n s) of the PES oligomers were determined by potentiometric titration in nonaqueous media by means of a glass calomel electrode system. *N,N*-dimethylformamide (DMF) and tetraethylammonium hydroxide were used as the solvent and titrant, respectively.

The \bar{M}_n of the PEEKK oligomers were determined by ¹⁹F-NMR spectroscopy. The spectra were obtained using a Varian FT-80A spectrometer operating at 74.8 MHz, at 25°C, with sodium trifluoroacetate used as the internal standard. The sample solution (–5 wt %) in H₂SO₄ was prepared at room temperature. The inherent viscosities (η_{inh}) of the copolymers were measured in 0.1% H₂SO₄ solution at 25°C. IR spectra were measured on a Nicolet 5PC infrared spectrometer.

The thermal analysis and the isothermal crystallization experiment were carried out with a DuPont thermal analyst 2000 instrument, and thermogravimetric analysis (TGA) of the copolymers was done on a Perkin-Elmer TGS-2 thermogravimetric analyzer, using a heating rate of 10°C/min in a nitrogen atmosphere.

Dynamic viscoelastic measurements were performed on a DDV-II-EA machine using a heating rate of $2^{\circ}\text{C min}^{-1}$, at 3.5 Hz. Wide-angle X-ray diffraction (WAXD) was measured on a Rigaku D/MAX-III A X-ray diffractometer, using $\text{CuK}\alpha$ radiation, at 40 kV and 30 mA.

RESULTS AND DISCUSSION

Characterization of the Block Copolymers

In this work, the oligomers with different molecular weights were prepared by changing the mol ratio of the two monomers according to the modified Carothers equation, $\bar{X}_n = (1 + r)/(1 - r)$, where \bar{X}_n is the number-average degree of polymerization and r is the molar ratio of the two monomers. The PES oligomers were isolated, and the number-averaged molecular weights were determined using the accurate method of potentiometric titration.¹⁵ Owing to the low solubility of PEEKK, this method used for the molecular characterization of PEEKK is limited. Devaux¹⁶ discussed two independent methods, i.e., gel permeation chromatography (GPC) and ^{19}F -NMR end-group analysis for the determination of PEEK and found the group analysis by ^{19}F -NMR spectroscopy to be a very reliable method.¹⁷ In the study of PES/PEEK block copolymers, we also found ^{19}F -NMR to be a very useful means of analysis. In the present study, ^{19}F -NMR measurements were first used to determine the \bar{M}_n of some of PEEKK oligomers which had been isolated before further reaction with the PES oligomers.

The \bar{M}_n values determined in this way are in fairly good agreement with calculated values for the oligomers. For example, the \bar{M}_n determined by ^{19}F -NMR for the PEEKK oligomer was 12,070, which was very close to the calculated value of 12,000. In the preparation of the PEEKK/PES copolymers, the PEEKK oligomers were used without isolation.

To investigate the effect of composition on the

properties of the PEEKK/PES block copolymers, PEEKK oligomers with a certain \bar{M}_n (12,000 calculated value) were first prepared. While the \bar{M}_n values of PES oligomers range from 250 to 12,680 (isolated and characterized) in this study, the PES content in the block copolymers varied from 2.06 to 51.38%. The detailed values are listed in Table I.

The block copolymers obtained were extracted with DMF, which is a good solvent for PES, but not for PEEKK. The results are shown in Table II. The fraction of the weight loss of the three samples after extraction are below 1.5%. The structures of the samples were also confirmed by means of IR spectroscopy. Spectra of the samples showed characteristic absorptions at 1314 cm^{-1} and 1145.9 cm^{-1} assigned to the sulfone group and at 1644.5 cm^{-1} assigned to the ketone group. In addition, the inherent viscosities of 0.7–1.03 suggest that the samples are high molecular weight. These facts indicate that samples prepared via the above methods should be copolymers of the two oligomers rather than blends of two components, although the possibility that the residual polymers contain some PEEKK oligomer cannot be ruled out completely.

Solubility experiments were also carried out for the copolymers. The results indicate that the copolymers did not dissolve in most of the common organic solvents at room temperature even in DMF or 1,2-dichloromethane, both of which are good solvents for PES and could only dissolve in concentrated sulfuric acid. Therefore, the PEEKK/PES block copolymers keep the chemical resistance properties of PEEKK.

Compatibility of the PEEKK/PES Block Copolymers

The DSC curves for the amorphous PEEKK and PEEKK/PES block copolymers are shown in Figure 1. It can be seen that the copolymers with various PES contents show a single T_g . The T_g values are

Table I Compositions and Partial Measured Data of PEEKK/PES Copolymers

No.	Oligomers \bar{M}_n		PES wt %	η_{iv} (dL/g)	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	T_d ($^{\circ}\text{C}$)
	PEEKK	PES						
1-1	12,000	252	2.06	1.02	161	357	194	528
1-2	12,000	2800	18.92	1.03	169	333	218	—
1-3	12,000	6060	33.55	0.96	179	326	253	526
1-4	12,000	12,680	51.38	0.70	189	—	—	—
PEEKK	—	—	0	1.22	161	362	187	540

Table II Extraction Experiment Data of PEEKK/PES Copolymers

No.	PES wt %	Weight Loss (%)
1-2	18.92	1.46
1-3	33.55	0.57
1-4	51.38	1.50

shifted to higher temperatures as the PES contents in the copolymers increase. For example, the T_g of the copolymer containing 33.55% of the PES segment is 179°C, 20°C higher than that of pure PEEKK. The plots of these T_g values against the copolymer compositions are shown in Figure 2, where the straight line indicates the calculated values according to the following equation:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (1)$$

where T_{g1} and T_{g2} stand for the T_g values of PEEKK and PES, respectively, and W_1 and W_2 denote the corresponding weight fractions of the PEEKK and PES segments in the copolymers. From Figure 2, we can see that the relationship between T_g and the compositions of PEEKK/PES block copolymers approximately follows that of eq. (1).

The samples prepared by compression molding at 400°C were also investigated by dynamic viscoelastic measurement. Plots of $\tan\delta$ vs. temperature (Fig. 3) show that each of the copolymers has only a single T_g . These results are consistent with the

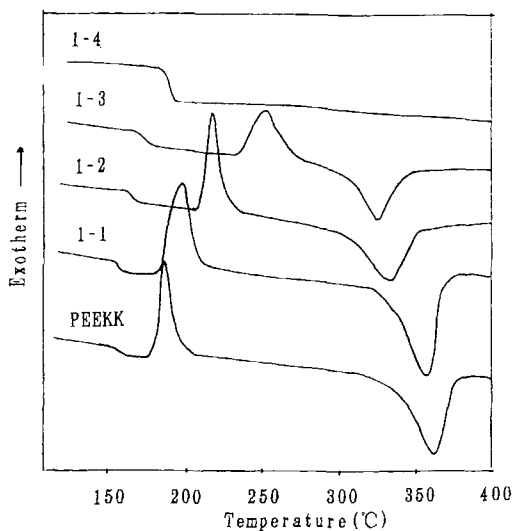


Figure 1 DSC curves of PEEKK and PEEKK/PES amorphous specimens.

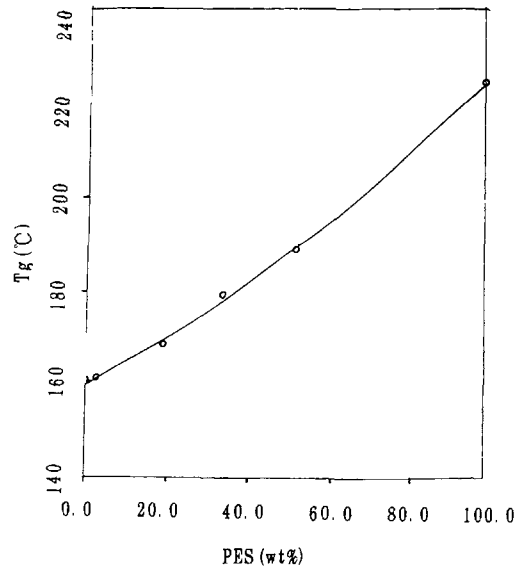


Figure 2 The relationship between T_g and PES content of PEEKK/PES block copolymers.

results from the above-mentioned DSC measurements and suggest that the PEEKK/PES block copolymers have homogeneous morphologies, over the range of compositions ($\leq 33.55\%$) or block lengths discussed in this article.

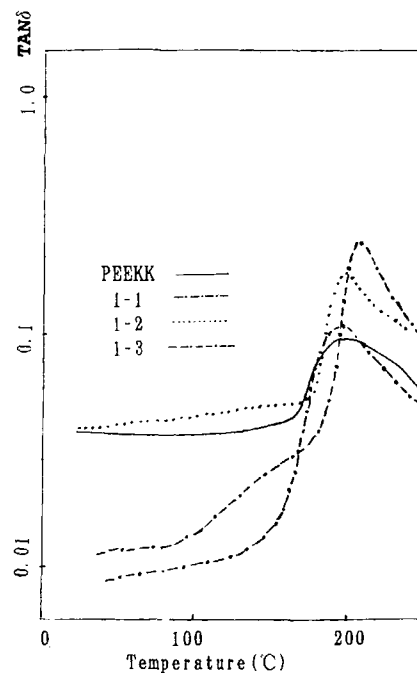


Figure 3 Loss factor curves obtained from dynamic viscoelastic measurements on the compositions of the samples given in Table I.

Thermal Stability and Dynamic Mechanical Behavior of the PEEKK/PES Block Copolymers

The thermal stability of the PEEKK/PES copolymers were measured by TGA. Figure 4 shows typical TGA traces in nitrogen for the two copolymers, together with that of pure PEEKK. The decomposition temperatures (T_d) at which weight loss reaches 2.5% of the original sample weight were 528, 526, and 540°C.

The decomposition temperature of the copolymer containing 33.55% PES segments (relative to pure PEEKK) was 526°C, only 14°C lower than that of pure PEEKK and 30°C higher than that of pure PES. Therefore, the thermal stability of the copolymers with a PES content less than 33.55% is still very good. Figure 5 shows the dependence of the storage modulus E' on temperature for copolymer samples obtained by compression molding at 400°C. The modulus of PEEKK starts to decrease at 170°C, then tends to reach a plateau, while the modulus of PES drops quickly at 230°C. For the PEEKK/PES block copolymers, the temperature at which the modulus begins to decrease is higher than that of the pure PEEKK. The temperature dependence of E' for the copolymers with the higher PEEKK contents resembles that of crystalline PEEKK, and the modulus decreases with increasing temperature and then forms a plateau. However, as the PES content increases, the modulus decreases more and more rapidly, becoming similar to the behavior shown by amorphous PES.

The extent of lowering of the storage modulus with increasing temperature can be expressed by the modulus-maintaining ratio. Figure 6 shows the storage modulus E' vs. temperature for PEEKK,

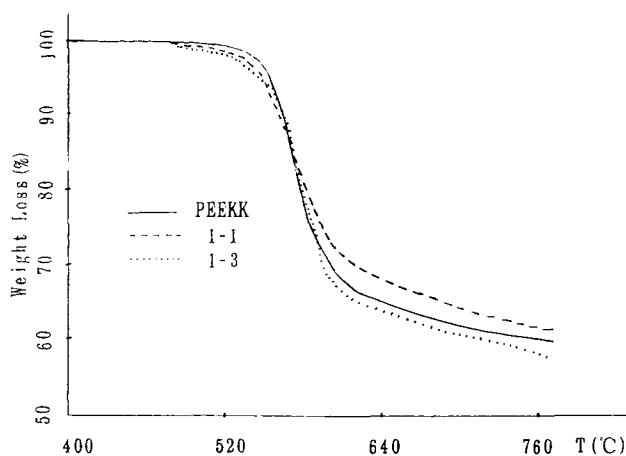


Figure 4 TGA curves for the PEEKK/PES copolymers and PEEKK.

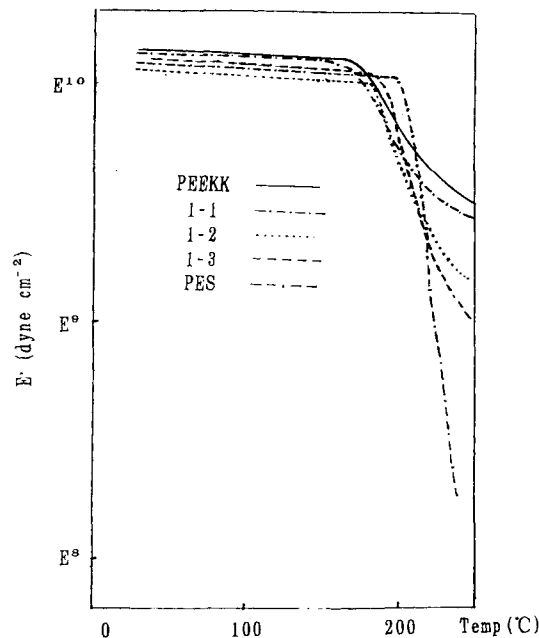


Figure 5 Storage modulus as a function of temperature for PEEKK/PES and PEEKK. Compositions of the samples are given in Table I.

PEKK/PES block copolymers, and PES. The modulus-maintaining ratio of the copolymers at 180, 190, and 240°C as a function of PES content is shown in Figure 6. At 180°C, the modulus-maintaining ratio increases with PES content and its value is more than 90% when the PES content is above 10%. Therefore, the copolymers with content above 10% can retain very good mechanical properties. At 190°C, the ratio increases significantly

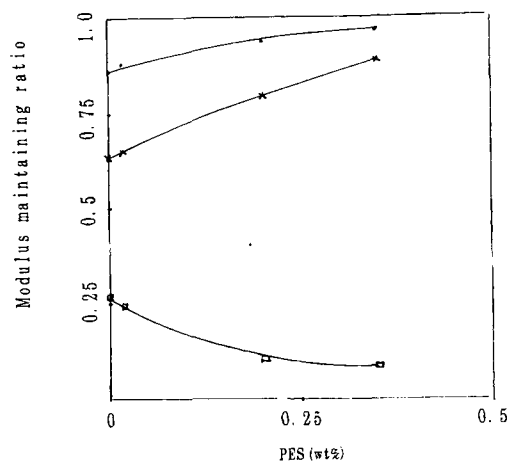


Figure 6 Effect of PES content of PEEKK/PES copolymers on the modulus-maintaining ratio at different temperatures: (●) 180°C; (X) 190°C; (□) 240°C.

with increasing PES content. However, at 240°C, the ratio decreases slowly with increasing PES content. This is because there are two phases present in the copolymers: One is the amorphous phase, containing PEEKK and PES components; the other is the PEEKK crystalline phase. The modulus of the copolymers is affected by the two phases: When the temperature is below the T_g of PES, this component in the copolymers can maintain very good mechanical properties. The miscible amorphous phase is a critical factor affecting the modulus of the copolymers because the T_g of this phase increases with PES content increasing. When the temperature is higher than the T_g of PES, the modulus of the amorphous phase shows a large decrease and, therefore, the presence of the PEEKK crystalline phase is the main factor affecting the modulus of the copolymers. Since the crystallinity of the copolymers decreases with the increasing of PES content, the modulus maintaining ratio also decreases.

Crystallization Behavior of PEEKK/PES Block Copolymers

Figure 7 shows the wide-angle X-ray diffraction curves for crystalline copolymers and pure PEEKK. The main diffraction peaks of the copolymers are very similar to those of PEEKK. The results suggest that the crystalline structure still belongs to the orthorhombic system. The PES segments do not penetrate into the crystalline PEEKK segment units. The crystallization of the copolymers is the contribution of PEEKK segments. The crystal parameters of PEEKK and the copolymer containing 18.92%

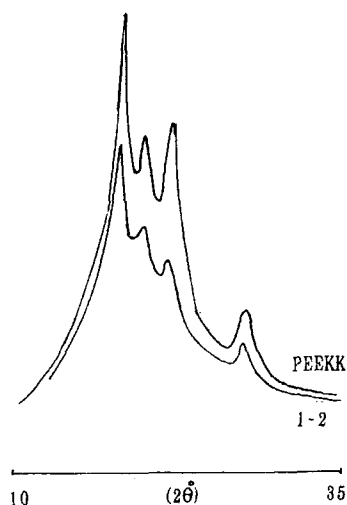


Figure 7 Wide-angle X-ray diffraction patterns of a crystalline PEEKK/PES copolymer 1-2 and PEEKK.

Table III Crystal Parameters of PEEKK and PEEKK/PES (Containing 18.92% PES)

Parameter	PEEKK	PEEKK/PES	PEEKK ¹⁹
a (Å)	7.71	7.91	7.75
b (Å)	5.83	6.08	6.00
c (Å)	10.13	10.16	10.10
Volume (Å ³)	455	488	470
Density	1.431	1.332	1.385

PES segments are listed in Table III. The crystal volume of copolymer is slightly larger than that of pure PEEKK, but it does not completely change the crystalline structure of the copolymer. Owing to the introduction of the PES segments, the a and b axes lengths become larger than that of pure PEEKK, whereas the density of complete crystallization becomes less than that of pure PEEKK. It can be seen from Figure 1 that the quenched amorphous samples with a PES content below 33.55% show both an exothermic peak (T_c) and a melting point (T_m). The exothermic peak (T_c) shifts toward higher temperature with increasing PES content and gradually becomes smaller and broader, whereas the endothermic peak is shifted to lower temperatures and decreases in intensity as PES content increases. For instance, the T_c for the copolymer with PES content of 33.55% is $\sim 66^\circ\text{C}$ higher than that of the pure PEEKK, while its T_m is 36°C lower than that of the pure component. The copolymer with a PES content of 51.38% did not show either a T_c or a T_m .

Figure 8 shows the DSC curves obtained for the block copolymers samples and PEEKK after annealing at 250°C for 6 h. These curves reveal that the copolymers mentioned above are all crystallizable polymers. These isothermally crystallized samples also exhibited a double-melting behavior just as observed for the pure PEEKK regardless of the PES content. The low-temperature melting peaks are small and remain almost constant, 10°C higher than the annealing temperature. The high-temperature melting peaks become smaller and lower with increasing PES content. The detailed values of T_{m1} and T_{m2} are listed in Table IV.

Table IV also shows absolute crystallinity X_c and relative crystallinity to pure PEEKK $X_{c(\text{PEEKK})}$, where X_c is

$$X_c = \frac{\Delta H}{\Delta H_f} \times 100\%$$

ΔH is the heat of fusion of the copolymer (determined by DSC), ΔH_f is the heat of fusion of 100%

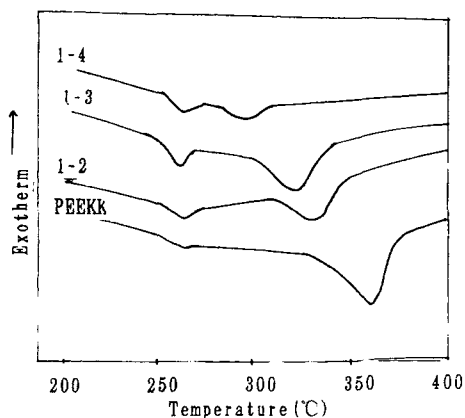


Figure 8 DSC curves of PEEKK and PEEKK/PES samples heat-treated at 250°C for 6 h.

crystalline PEEKK ($\Delta H_f = 124$ J/g),¹⁸ and $X_{c(\text{PEEKK})} = X_c/W_{\text{PEEKK}}$. W_{PEEKK} is the weight fraction of the PEEKK segment in the copolymer. In Table IV, both the X_c and $X_{c(\text{PEEKK})}$ values of the copolymers (in contrast to the pure PEEKK) decrease with increasing PES content. The decreasing of the $X_{c(\text{PEEKK})}$ further reveals that the PES segments deeply hinder the crystallization of PEEKK segments. The crystallization of the copolymer becomes slower and slower with increasing PES content and the length of the PES segments. From Table IV and Figure 1, we find that the amorphous copolymer with a PES content of 51.38% does not crystallize when scans are carried out at a 10°C/min heating rate. It crystallizes when annealing is kept at 250°C for a long time. This suggests that the samples with high PES content ($\leq 51.38\%$) copolymers can crystallize if the annealing time is long enough.

The above evidence shows that introduction of PES segments into the PEEKK molecular chain disturbs the close packing of the PEEKK repeat units, so that the crystallites become smaller and, thus, the melting points and the crystallinity of the copolymers are reduced.

Isothermal Crystallization Kinetics of the PEEKK/PES Block Copolymers

To choose the isothermal crystallization temperature, we first put the samples into the DSC stove and melt them at 400°C for 5 min, then cool them to room temperature at a 10°C/min rate. The DSC cooling curves are shown in Figure 9. The exothermic peak of the copolymer with a PES content of 18.92% is 261.75°C. It is 50°C lower than that of the pure PEEKK, whereas the exothermic peak for

Table IV T_{m_1} , T_{m_2} , X_c , and $X_{c(\text{PEEKK})}$ of Heat-treated Samples

No.	PEEKK	1-2	1-3	1-4
T_{m_1} (°C)	264.6	262.2	262.0	263.5
T_{m_2} (°C)	362.8	333.3	322.6	300.2
X_c (%)	20.19	12.14	8.72	2.28
$X_{c(\text{PEEKK})}$ (%)	20.19	14.97	13.12	4.68

the copolymer with a PES content of 33.55% disappear. Therefore, we chose the copolymer with a PES content of 18.92% for studying the isothermal crystallization kinetics. The isothermal temperatures changed from 259 to 269°C. A Du pont thermal analyzer was used to monitor the heat flow for the samples during crystallization. The samples were first heated to 400°C and kept for 5 min at that temperature and then were cooled quickly to the crystallization temperature.

Table V shows the results of crystallinity and time data for the isothermal crystallization from the melt, where t_{max} and $X_c(t_{\text{max}})$ are the time and crystallinity, respectively, at $dQ/dt = 0$, $Q(t)$ is the heat flow rate, and $X_c(\infty)$ is the final crystallinity. The relative amount of crystallinity is plotted in Figure 10 for the four crystallization temperatures. Development of the relative crystallinity can be analyzed using the Avrami equation:

$$X_c(t)/X_c(\infty) = 1 - \exp(-kt^n) \quad (2)$$

$$\ln[1 - X_c(t)/X_c(\infty)] = -kt^n \quad (3)$$

or

$$\log[-\ln(1 - X_c(t)/X_c(\infty))] = n \log t + \log k \quad (4)$$

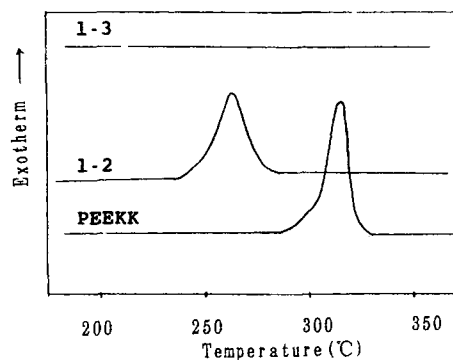


Figure 9 Exothermic curves of PEEKK, 1-2, and 1-3 copolymers.

Table V Relative and Absolute Crystallinity at t_{max}

Samples	T_c ($^{\circ}\text{C}$)	t_{max} (min)	$X_c(\infty)$	$X_c(t_{max})/X_c(\infty)$
1-2	259	1.07	20	0.28
	261	1.20	21	0.28
	265	1.91	17	0.30
	269	2.79	23	0.30

t_{max} and $X_c(t_{max})$ are the time and degree of crystallinity at $dQ/dt = 0$, respectively; Q is the heat flow rate.

where n is a constant whose value depends on the mechanism of nucleation and on the form of crystal growth, and k is a constant containing the nucleation and growth parameters. Plots of $\log[-\ln(1 - X_c(t)/X_c(\infty))]$ vs. $\log t$ are shown in Figure 11. Each curve has a linear portion followed by a gentle roll at a longer time. Fitting the initial linear portion of $\log[-\ln(1 - X_c(t)/X_c(\infty))]$ vs. $\log t$ allows us to determine n and k from eq. (4). The values are listed in Table VI. Since t_i is the solution of $d^2X/dt^2 = 0$, we can use eq. (2) to express t_i in terms of n and k , obtaining

$$t_i = \left(\frac{n-1}{nk} \right)^{1/n} \quad (5)$$

The calculated values of t_i listed in Table VI can be compared with t_{max} obtained directly from the plots of Q vs. t as listed in Table V. The agreement in t_i values suggests that the Avrami analysis works well in describing the initial process.

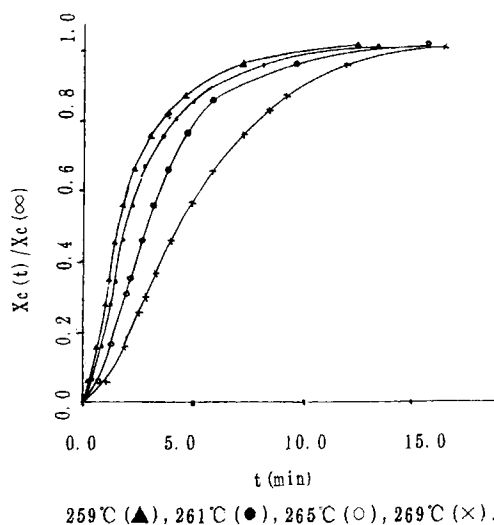


Figure 10 The relationship between crystallization time and crystallinity of PEEKK/PES copolymer for isothermal crystallization.

The values of n are from 1.77 to 1.88; this is very close to that of pure PEEKK.¹⁹ This suggests that the copolymer has the same nucleation mechanism and the form of crystal growth as that of pure PEEKK.

In addition, in the selected temperature range, the crystal rate constant k decreases. The crystal half-period increases with increasing of the isothermal temperature.

We scanned the samples which have just been subjected to the isothermal crystallization process. The thermograms show double peaks just as does PEEKK under different heating treatments. The low-temperature melting peaks are about 10°C higher than the isothermal crystallization temperature. The high-temperature melting peak increases with increasing of the isothermal crystallization temperature. By making use of the Hoffman-Weeks equation, we can approximately calculate the equilibrium melting point of the copolymer with a PES content of 18.93%. The value is 350°C , 37°C lower than that of pure PEEKK.¹⁹

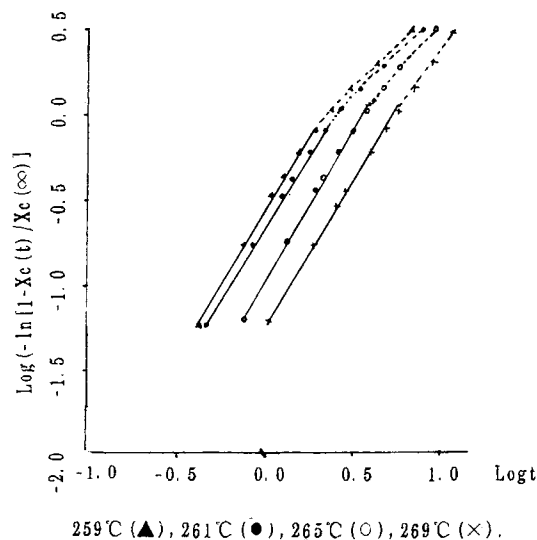


Figure 11 The relationship between $\log\{-\ln[1 - X_c(t)/X_c(\infty)]\}$ and $\log t$ of sample 1-2 for isothermal crystallization.

Table VI Avrami Parameter n , Rate Constant k , and $t_{0.5}$ of PEEKK/PES

Samples	T_c ($^{\circ}\text{C}$)	n	k	$t_{1/2}$ (min)	t_{\max} (min)	t_i (min)
1-2	259	1.86	0.2893	1.50	1.07	1.29
	261	1.81	0.2318	1.83	1.20	1.44
	265	1.88	0.1045	2.73	1.91	2.22
	269	1.77	0.0554	4.16	2.79	3.20

To obtain further insight into the crystallization process of the block copolymer, we may assume that the PEEKK/PES copolymer crystallization at high temperature follows the Hoffman-Lauritzen equation. We can write the growth equation as

$$G = G_0 \exp[-U/R(T - T_{\infty})] \exp[-Kg \cdot T_m^0 / T \Delta T \cdot f] \quad (6)$$

where U is the transport activation energy. We chose U to be equal to 2 kcal/mol. T_m^0 is the equilibrium melting point of the copolymer ($T_m^0 = 350 + 273 = 623$ K) and ΔT is the degree of undercooling. It may be written as $\Delta T = T_m^0 - T_c$. The factor f equals to $2T_c/T_c + T_m^0 T_{\infty}$ is chosen as $T_{\infty} = (T_g - 51.6)$, and Kg contains the surface free-energy product $\sigma \sigma_e$ and the heat of fusion of the perfect crystal. The relationship between the linear growth rate G and the Avrami parameter k can be written as

$$G \propto k^{1/n} \quad (7)$$

and according to the changing of eqs. (6) and (7), we can obtain

$$\ln G + \frac{U}{R(T - T_{\infty})} = \ln G_0 - Kg T_m^0 T \Delta T f \quad (8)$$

The graphs of $[\ln G + U/R(T - T_{\infty})]$ vs. $(f \cdot T \Delta T)^{-1}$ are shown in Figure 12; the slope of this curve is 1141.1 K. It is higher than that of pure PEEKK.¹⁹ ($Kg_{\text{PEEKK}} = 851.5$ K), indicating that the surface free energy ($\sigma \sigma_e$) of the copolymer is larger than that of pure PEEKK. Therefore, the introduction of PES segments into the PEEKK main chain increases the free energy of the critical crystal nucleus formation, producing resistance to crystallization.

CONCLUSIONS

1. The samples prepared via the reaction of two oligomers are copolymers rather than blends of the two components.

2. PEEKK/PES block copolymers keep the chemical resistance properties of PEEKK.
3. The T_g of the PEEKK/PES block copolymers approximately follow the equation $1/T_g = W_1/T_{g1} + W_2/T_{g2}$. The PEEKK/PES copolymers are a compatible system.
4. The crystalline structures of PEEKK/PES copolymers still belong to orthorhombic system; the crystalline character originates in the PEEKK segments of the copolymers.
5. Although the PES segments do not penetrate into the crystalline PEEKK segment units, the PES content and segment length have a significant influence on the crystallization behavior of the copolymers. As the PES content increases, the T_m and crystallization of the PEEKK segments in the copolymers becomes more difficult.
6. The PES content in the copolymers influence both the thermal stability and the dynamic mechanical behavior of the copolymers.
7. The copolymer has the same nucleation and crystal growth as that of pure PEEKK. Introduction of the PES segment into the

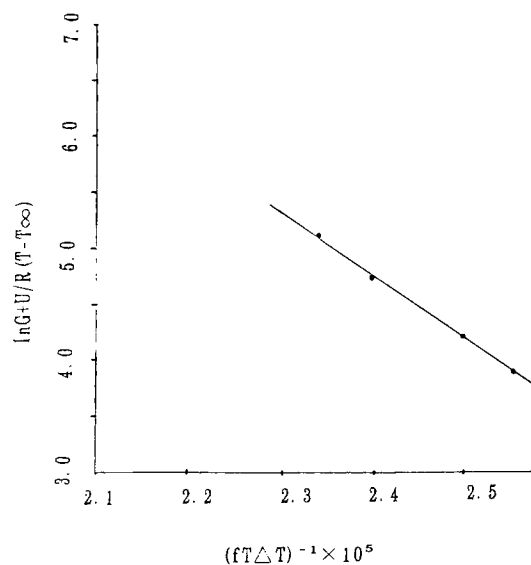


Figure 12 The relationship between $\ln G + U/R(T - T_{\infty})$ and $(fT\Delta T)^{-1}$.

PEEKK main chain raises the free energy of the critical crystal nucleus formation, inhibiting crystallization of PEEKK segments. Overall, the copolymers synthesized in this work have very good chemical resistance, high-temperature stability, and high-temperature mechanical properties.

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