

# Synthesis and Properties of Poly(aryl ether sulfone ether ketone ketone) (PESEKK)

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**ABSTRACT:** 4,4'-bis(Phenoxy)diphenyl sulfone (DPODPS) was synthesized by reaction of phenol with bis(4-chlorophenyl) sulfone in tetramethylene sulfone in the presence of NaOH. Two poly(aryl ether sulfone ether ketone ketone)s (PESEKKs) with high molecular weight were prepared by low temperature solution polycondensation of DPODPS and terephthaloyl chloride (TPC) or isophthaloyl chloride (IPC), respectively, in 1,2-dichloroethane and in the presence of aluminum chloride ( $\text{AlCl}_3$ ) and *N*-methylpyrrolidone (NMP). The resulting polymers were characterized by vari-

ous analytical techniques, such as FT-IR,  $^1\text{H-NMR}$ , DSC, TG, and WAXD. The results show that the  $T_g$  and  $T_d$  of PESEKKs are much higher, but its  $T_m$  is lower than those of PEKK. The other results indicate that PESEKKs exhibit excellent thermostabilities at  $300 \pm 10^\circ\text{C}$ . © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 489–493, 2005

**Key words:** 4,4'-bis(phenoxy)diphenyl sulfone; isophthaloyl chloride; terephthaloyl chloride; polymerization; poly(ether sulfone ether ketone ketone); structure and properties

## INTRODUCTION

Poly(aryl ether ketone)s are well-recognized higher performance engineering thermoplastics. These polymers have outstanding mechanical properties, long-term thermal stability, electrical insulation, and good chemical resistance, and find wide applications in other high technology fields,<sup>1</sup> and therefore, can be used as resin matrices of high-performance composites and superengineering plastics.<sup>2</sup> Poly(aryl ether ketone)s can be prepared via electrophilic or nucleophilic polycondensation. The electrophilic route has been the popular method to prepare various kinds of poly(aryl ether ketone)s because the monomers, which are used in the electrophilic route, have been more selective, cheaper, and easily attained. A series of new poly(aryl ether ketone)s has been reported in the literature. Stephen and Viktors<sup>3</sup> and Viktors and Heinich<sup>4</sup> synthesized the polymers through electrophilic polycondensation of terephthaloyl chloride (TPC) with 4,4'-bis(phenoxy) benzene, 4,4'-bis(phenoxy) diphenyl ether, or 4,4'-bis(phenoxy)diphenyl ketone, respectively. The crystallinity and the melting temperature ( $T_m$ ) of the polymers decreased in comparison with poly(aryl ether ketone ketone)s because of the increasing ratio of ether linkage. The poly(aryl ether ketone)s have excellent flexibility of the chain, good flame retardant resistance, and high caking power with metal, ceramic, and polar fiber if the highly polar sulfuryls are intro-

duced to the chain. Previously we have synthesized simple linear poly(aryl ether ketone ketone) and terpolymer with high molecular weight through electrophilic polycondensation in solution at low temperature.<sup>5,6</sup> In this contribution, we synthesized the poly(aryl ether sulfone ether ketone ketone)s. The crystallization behavior and the thermal properties were investigated by wide-angle X-ray diffraction (WAXD), differential scanning calorimeter (DSC), and thermal gravimetric analysis (TG). The results indicated that the polymers have a potentiality for industry.

## EXPERIMENTAL PROCEDURES

### Materials

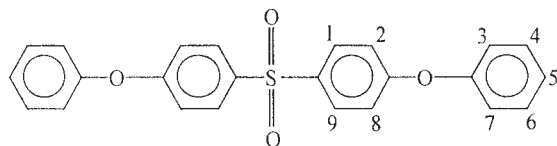
TPC and IPC (Shuanglin Chemical Co., China) were purified by distillation under vacuum to give m.p. 81.2–82.8°C and 43–44°C, respectively. Ethylene dichloride was purified by distillation and dried by 0.5 nm molecular sieve. NMP of C.P. was purified by distillation and dried by a 0.5 nm molecular sieve. Anhydrous aluminum chloride ( $\text{AlCl}_3$ ) of A.P. was used as received. Methylbenzene, tetramethylene sulfone, phenol and sodium hydroxide of A.P. were used without further treatment. Ethanol and methanol of industrial grade were used as received. Diphenyl ether was purified by distillation.

### Synthesis

#### Preparation of DPODPS

Phenol (47.0 g, 0.5 mol), sodium hydroxide (20.0 g, 0.5 mol) were stirred in methylbenzene (150 mL), tetram-

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**Scheme 1** Structure of DPODPS.

ethylene sulfone (150 mL) at 160°C to remove the water by refluxing to form sodium phenolate. Bis-(4-Chlorophenyl) sulfone (71.75 g, 0.25 mol) then was added to the salt and the mixture was stirred at 180–200°C for 4 h. Next, the reaction mixture was poured into ethanol (200 mL) to form the precipitation. The resulting solid material was filtered and washed with water several times. The crude product was recrystallized from methylbenzene and ethanol (*v/v* = 1/1) to effect 86 g of DPODPS. Yield: 85%; m.p.138–140°C.<sup>7</sup> The molecular structure was as follows in Scheme 1. FT-IR (KBr)*v* = 3065(w), 1578(s), 1485(s), 1236(s), 866(m), 836(m), 1318(m), 1160(m), 1145(s)cm<sup>-1</sup>; MS *m/z* = 403((M + 1)<sup>+</sup>, 16.33%), 402(M<sup>+</sup>, 54.17%), 217(45.63%), 185(44.25%), 51(37.88%), 115(35.91%), 141(22.72%), 129(20.04%), 77(100%); <sup>1</sup>H-NMR(CDCl<sub>3</sub>)δ = 6.99–7.04(s,8H,aromatic protons2,3,7,8),7.18–7.22(w,2H,aromatic protons5),7.33–7.39(m,4H,aromatic protons4,6),7.85–7.87(m,4H,aromatic protons1,9)ppm.

### Polymerization

PESEKK was prepared by using the procedure described by Song et al.<sup>5</sup> Anhydrous aluminum chloride (18 g) was stirred in ethylene dichloride (60 mL). The mixture of NMP (6 mL) and ethylene dichloride (60 mL) at 0°C was added dropwise. DPODPS (8.04 g, 0.02 mol) and TPC or IPC (4.06 g, 0.02 mol) then were added at -15°C. The reaction mixture was stirred at normal temperature for 8 h. Next, several drops of diphenyl ether were added to the mixture. Methanol (100 mL) was added dropwise into the reaction mixture after 2 h to terminate the reaction. The polymer structure was as shown in Scheme 2.

### Measurements

#### Differential scanning calorimeter (DSC)

A Perkin-Elmer Pyris 1, interfaced with a computer via analogue to a digital converter, was used to mon-

itor the rate of heat flow from the sample during fusion. Each sample was placed in a DSC pan and heated at a rate of 20°C/min under an atmosphere of circulating dry nitrogen. To detect the glass transition temperature of the sample, this treatment was followed by cooling at a rate of 40°C/min from 350°C to room temperature and heating at a rate of 40°C/min.

#### Wide-angle x-ray diffraction (WAXD)

WAXD data between 5.000 and 40.000° were recorded at 0.020°/s on a BRUKER AXS D8 ADVANCE diffractometer by using CuKα radiation at a generator voltage of 40 kV and a generator current of 40 mA at room temperature. Samples were powder.

#### <sup>1</sup>H-NMR

<sup>1</sup>H-NMR spectra were obtained at room temperature with a Bruker Avance operating at 400 MHz by using 5% (w/v) solutions in CDCl<sub>3</sub>. Chemical shifts were given in ppm using tetramethylsilane (TMS) as the internal reference.

#### Infrared spectra

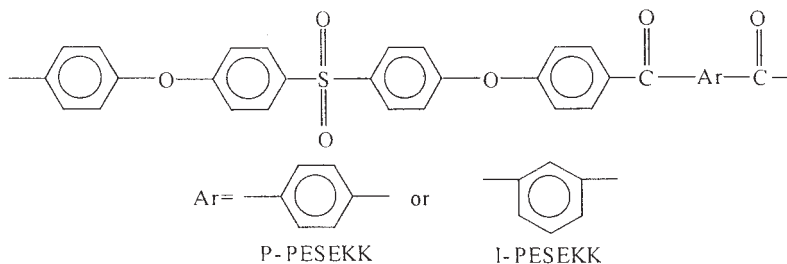
Infrared spectra were recorded on a Perkin-Elmer SP one FT-IR spectrometer. For each spectrum two scans with 4 cm<sup>-1</sup> resolution were co-added with air as the background.

#### Mass spectra

Mass spectra and purity of all the intermediates were recorded by using Hewlett-Packard 5989B mass detector.

#### Thermal gravimetric (TG) analysis

The TG curves were obtained with a Shimadzu DT-40 apparatus. Each sample was heated at a rate of 10°C/min in nitrogen flow.



**Scheme 2** structure of PESEKK.

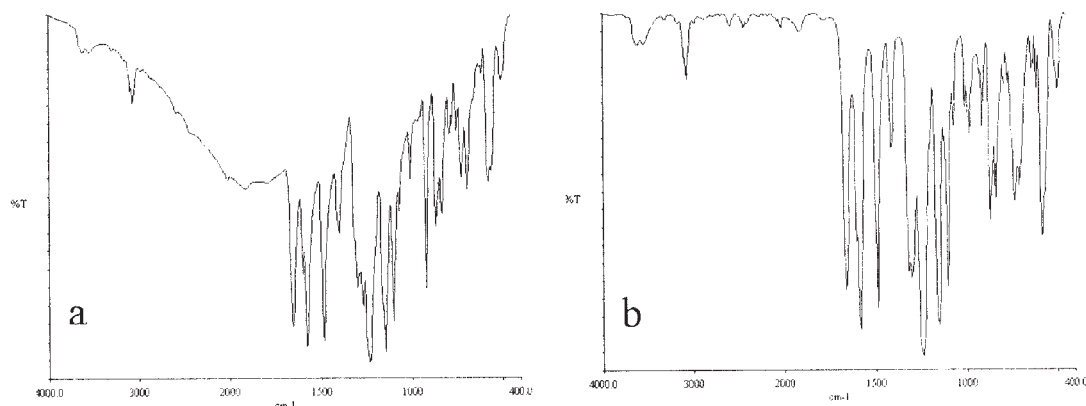


Figure 1 FT-IR spectra of (a) P-PESEKK and (b) I-PESEKK.

#### Ubbelodhe viscometer

Viscosities of the polymers were measured in 0.5 g/dL concentrated sulfuric acid solutions using an Ubbelodhe viscometer at 30°C. The inherent viscosity  $\eta_{inh}$  was calculated by the One-Point Method and expressed in dL/g:

$$\eta_{inh} = c^{-1} \ln t_1/t_0$$

#### Thermal stability Testing

The thermal stability of the polymers was carried out on a hot plate at  $300 \pm 10^\circ\text{C}$ . The polymers of P-PESEKK or I-PESEKK were each heated for 10, 20, 40, 60, 90, and 120 min. The change of  $\eta_{inh}$  values of the same polymer, which had been heated for different times were detected.

#### Induced crystallization procedure

The polymer of P-PESEKK was induced to crystallize. The procedure was carried out by legging at room temperature during fusion, or orienting in shearing order direction during fusion, or nonisothermal crystallization. In the case of nonisothermal crystallization, DSC was used to provide a constant rate of decreasing temperature (2, 5, or  $40^\circ\text{C}/\text{min}$ ) from the melt to monitor the heat flow as a function of temperature.

## RESULTS AND DISCUSSION

FT-IR spectra of P-PESEKK and I-PESEKK are presented in Figure 1 (a) and (b), respectively. The sample was quenched by immersion in the mixture of ice and water to make the material amorphous after heating to fusion. The characteristic transmittance for P-PESEKK is situated at 1638, 1600, 1500, 1150, 1320, 1237, and  $820, 720\text{cm}^{-1}$ . The first peak is attributed to arone. The next two peaks are attributed to the vibration of the

aromatic ring skeleton. The next two peaks at 1150,  $1320\text{cm}^{-1}$  are probably because of the symmetric and antisymmetric stretching vibration of the sulfonyl. The next peak at  $1237\text{cm}^{-1}$  is attributed to aryl oxide. The last two peaks are attributed to the 1,4-substitution of arone. In the spectrum shown in Figure 1(b), the first six peaks can be observed as well as the peaks of P-PESEKK; the other two peaks at 750,  $690\text{cm}^{-1}$  are attributed to 1,3-substitution of arone. The results above indicated that the polymers are anticipated.

The  $\eta_{inh}$  values of the polymers are indicated in Table I. The  $\eta_{inh}$  values of P-PESEKK and I-PESEKK are 1.20 and 0.98, respectively. It appears that the  $\eta_{inh}$  values of the polymers were much higher than the critical  $\eta_{inh}$  value of the macromolecule, respectively. Thus, the polycondensation route is appropriate.

The WAXD patterns of P-PESEKK and I-PESEKK are shown in Figure 2. The WAXD pattern of P-PESEKK fundamentally bore the same number and site of diffraction peak of every crystal facecrystal plane in comparison with that of PEKK,<sup>4</sup> but I-PESEKK only showed a diffuse diffraction peak. The result above indicated that P-PESEKK had the chain similar to that of PEKK to form the crystal that was included in the orthorhombic system with PEKK. But the crystallinity of P-PESEKK decreased greatly be-

TABLE I  
Thermal Properties of the polymers

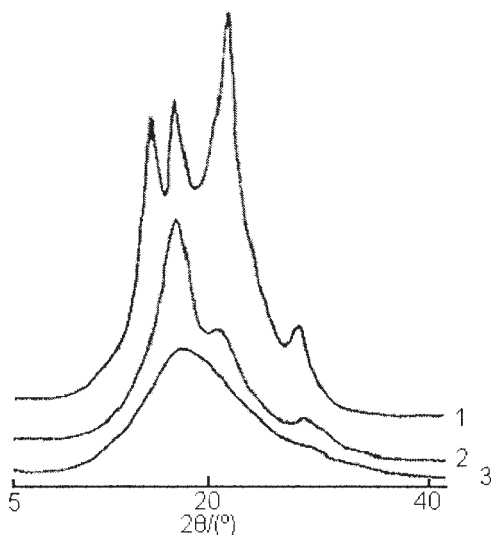
Polymer	$\eta_{inh}$ (dL/g) <sup>a</sup>	Tm(°C)	Tg(°C)	Td(°C) <sup>b</sup>
P-PESEKK	1.20	228,243	196	601
I-PESEKK	0.98	187 <sup>d</sup>	177	589
PEKK <sup>5, c</sup>	0.77	341	163	575

<sup>a</sup> Measured at a concentration of 0.5g/dL in concentrated sulfuric acid at 30°C

<sup>b</sup> 5% weight loss temperature observed by TG

<sup>c</sup> Containing 30% meta-substitution phenylene

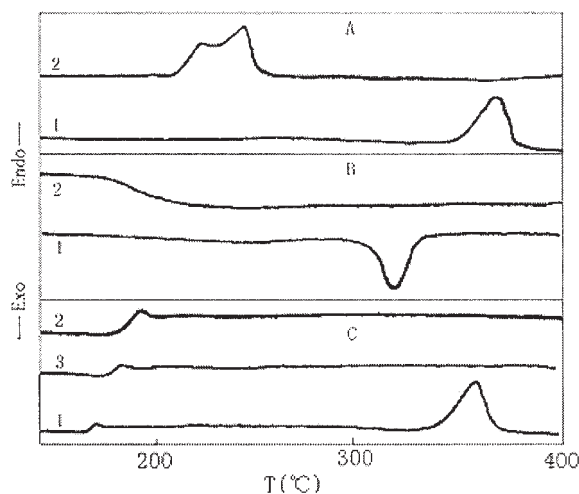
<sup>d</sup> Smelting temperature



**Figure 2** The WAXD patterns of the polymers 1:PEKK (containing 30% meta-substitution phenylene); 2:P-PESEKK; 3:I-PESEKK.

cause of the tetrahedral structure sulfuryl. I-PESEKK was amorphous, because the regularity of macromolecular chain decreased with the advent of the tetrahedral structure sulfuryl and meta-substitution phenylene with the meander configuration.

DSC and TG, as shown in Figure 3 and Table I, investigated the thermal properties of the polymers. DSC curves of the polymers are shown in Figure 3. In Figure 3, P-PESEKK both showed the glass transition and melting endothermic peak, but I-PESEKK only showed the glass transition. The results agreed with the WAXD results. In the case of P-PESEKK, it exhibited doubling melting peaks at 228 and 243°C. No crystallization was observed during the cooling in



**Figure 3** The DSC curves of the polymers 1:PEKK (containing 30% meta-substitution phenylene); 2:P-PESEKK; 3:I-PESEKK A: 1st heating; B: cooling; C: 2nd heating.

**TABLE II**  
 $\eta_{inh}^a$  values of the polymers at  $300 \pm 10^\circ\text{C}$

Heating time (min)	0	10	20	40	60	90	120
$\eta_{inh}$ (P-PESEKK)	0.63	0.62	0.62	0.62	0.64	0.63	0.63
$\eta_{inh}$ (I-PESEKK)	0.74	0.75	0.77	0.76	0.77	0.77	0.76

<sup>a</sup> Measured at a concentration of 0.5g/dL in concentrated sulfuric acid at  $30^\circ\text{C}$

DSC curves. In Table I the  $T_g$  and  $T_d$  of P-PESEKK or I-PESEKK were obviously higher than that of PEKK, and the temperature difference between  $T_m$  and  $T_d$  of P-PESEKK or I-PESEKK was large, thus the fusion processing can be accomplished. The results indicated that the polymers would have wide applications in thermosol fields.

The  $\eta_{inh}$  values of the polymers when heated at  $300 \pm 10^\circ\text{C}$  for different times are shown in Table II. We concluded that no significant change in the  $\eta_{inh}$  value took place compared with that of the original sample. Thus, no cross-linking took place when the polymers of P-PESEKK or I-PESEKK were heated for 2 h, respectively. The results showed that the polymers appeared to have good thermal stability and also to have potential for fusion processing.

P-PESEKK that has had crystallization induced was investigated by DSC and FT-IR, respectively. The polymers of P-PESEKK that was processed by legging, orientation in shearing order direction and nonisothermal crystallization were referred to P-PESEKK1, P-PESEKK2, and P-PESEKK3, respectively.

In the profile of DSC curves, P-PESEKK1 only showed a glass transition temperature with no melting temperature. The fact that no melting peak was observed during the first heating can be attributed to the P-PESEKK1 being amorphous after being processed by legging. P-PESEKK2 showed a  $T_g$  and a slight melting endotherm peak. The result above indicated that P-PESEKK2 may be slightly crystalline. Thus, it is very hard for P-PESEKK to recrystallize during fusion. But the polymer of P-PESEKK directly obtained by polycondensation had some degree of crystallization, because the crystallinity increased step by step in the polycondensation course, and crystallization rate decreased when the  $\eta_{inh}$  value of the polymer increased.

In the FT-IR spectra of P-PESEKK1 and P-PESEKK2 as shown in Figure 4, the obvious peaks can be observed between  $4000$  and  $1800\text{cm}^{-1}$  compared with those of Figure 1. This fact may be because the chain of P-PESEKK1 and P-PESEKK2 became a more ordered arrangement for processing by legging or orientation in shearing order direction. In comparison with P-PESEKK1 in Figure 4(a) and P-PESEKK in Figure 1, P-PESEKK2 exhibited a peak at  $1786\text{cm}^{-1}$  that was

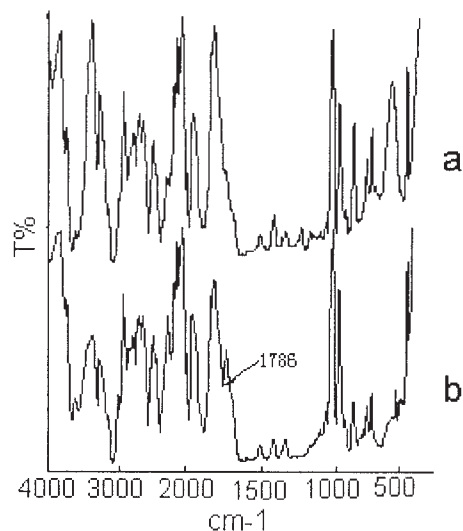


Figure 4 FT-IR spectra of (a)P-PESEKK1 (b)P-PESEKK2.

different from P-PESEKK1 and P-PESEKK. Here P-PESEKK1 and the sample used for Figure 1 were both amorphous. Thus, we concluded that the peak at  $1786\text{ cm}^{-1}$  may be because of the blue shift of the carbonyl group in the crystalline lattice of the polymer.

Nonisothermal crystallization was carried out on a Perkin-Elmer Pyris 1 apparatus. In the profile of DSC curves of P-PESEKK3, no crystallization peak was observed during the cooling in DSC curves at cooling rates of 2, 5, and  $40^\circ\text{C}/\text{min}$ , respectively.

Thus, from the results above, it is hard for P-PESEKK crystallization to be induced during fusion.

### CONCLUSION

1. The  $T_g$  and  $T_d$  of P-PESEKK or I-PESEKK were obviously higher than that of PEKK, and the

temperature difference between  $T_m$  and  $T_d$  of P-PESEKK or I-PESEKK was large, and the polymers of P-PESEKK and I-PESEKK have good stability at  $300 \pm 10^\circ\text{C}$ . Thus, the polymers have potential for fusion processing.

2. P-PESEKK fundamentally bore the same number and site of diffraction peak of every crystal face-crystal plane in comparison with that of PEKK, because P-PESEKK had a chain similar to that of PEKK in forming the crystal, which was included to orthorhombic system. A I-PESEKK was amorphous, because the regularity of the macromolecular chain decreased with the advent of the tetrahedral structure sulfuryl and *meta*-substitution phenylene with the meander configuration.
3. P-PESEKK both showed the glass transition and melting endothermic peak in the DSC profile, and I-PESEKK only showed the glass transition. This result agreed with the WAXD results.
4. Though the crystallinity increased step by step in the polycondensation course, it was very hard for P-PESEKK to recrystallize during fusion.

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### References

1. Park, S. K.; Kim, S. Y. *Macromolecules* 1998, 31, 3385.
2. Sun, Y. *Plastic Industry* 1990, 2, 25.
3. Stephen, M.; Viktors, J.; Klaus, D. WO 8601199, 1986.
4. Viktors, J.; Heinnch, G. WO 8403891, 1984.
5. Song, C.; Cai, M.; Zhou, L. *Acta Polym. Sinica* 1995, 1, 99.
6. Zhou, L.; Sheng, S.; Cai, M.; Song, C. *Chinese J of Appl Chemistry* 1998, 5, 6.
7. Hale, W. F.; Farnham, A. G.; Johnson, R. N. *J. Polym Sci A, Polym Chem* 1967, 5, 2399.