

Synthesis and Characterization of a Novel Phthalazinone Poly(Aryl Ether Sulfone Ketone) with Carboxyl Group

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ABSTRACT: Soluble, thermally stable phthalazinone poly(aryl ether sulfone ketone)s (PPESKs) containing a carboxyl group in its side chain have been synthesized by the nucleophilic displacement reaction of 4-(4-hydroxyphenyl)-1(2H)-phthalazinone with bis(4-chlorophenyl) sulfone, 4,4'-difluoro-benzophenone, and phenolphthalin. The polymerization reactions were conducted in sulfolane in the presence of K_2CO_3 to give high molecular weight polymers, which are soluble in solvent such as nitrobenzene and pyridine at room temperature and easily cast into flexible, yellow, and transparent film. The polymers are amorphous with high

glass transition temperature. The decomposition temperature of the polymers are $>400^\circ C$, which indicates high thermal stability. The crosslinking reaction of PPESK can occur by using dicyandiamide (Dicy) as curing agent. The apparent energy (ΔE) is 52.2 kJ/mol and reaction order (n) is close to 1.0. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1111–1114, 2003

Key words: poly(aryl ether sulfone ketone); crosslinking; active pendant group

INTRODUCTION

Poly(ether ketone)s (PEKs) and poly(ether sulfone)s (PES)s are the most important high performance engineering thermoplastics, widely used in the electronic, electric, aircraft, and aerospace industries.^{1–7} Initially, considerable effort was made to modify their chemical properties, essentially to improve their thermal properties.⁸ In the last few years, more attention has been paid to their functionalization.⁹ This can be achieved either by chemical modification of the polymer or by direct synthesis using functionalized monomers. In this study, a kind of novel phthalazinone PESK was synthesized by introducing a carboxyl group in the side chain based on phenolphthalin, a functionalized monomer. The crosslinking reaction of the PPESK by using diamine as curing reagent and the improvement of the thermal resistance of the PPESK after curing were discussed.

EXPERIMENTAL

Monomer synthesis

Phenolphthalein (50 g), sodium hydroxide (75 g), and zinc (32.5 g) were added to 1500 mL water, and the

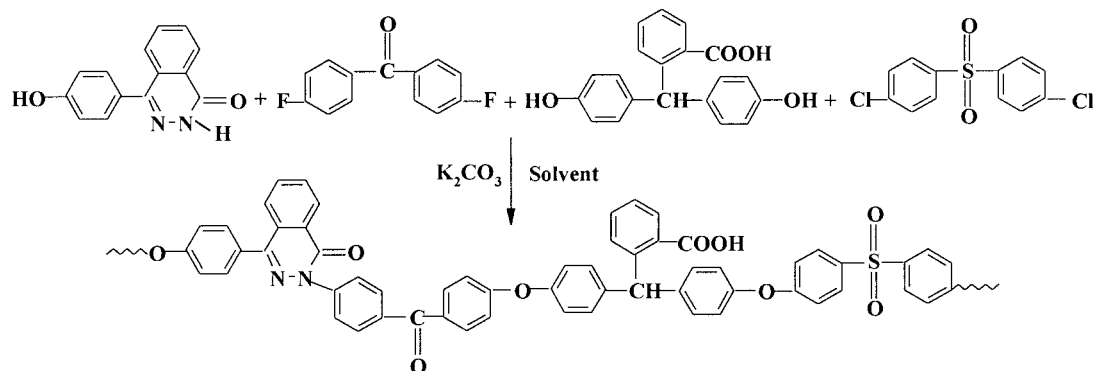
intensely red reaction mixture was heated at $70^\circ C$ under stirring until a greyish-white reaction mixture was resulted. The resulting product was filtered and excess conc. hydrochloric acid was added into the filtrate until sedimentation was completed. The semi-solid product was filtered off, washed with water to neutral, and was dried in a vacuum oven ($120^\circ C$) for 48 h and white powder phenolphthalin was obtained in almost quantitative yield. The mp is $243.5\text{--}244.5^\circ C$; 1H nuclear magnetic resonance (NMR) (200 MHz), δ (ppm) = 6.38 (s, 1H, CH), 6.66–6.78 (m, 8H, $2C_6H_4OH$), 6.98–7.72 (t, 4H, C_6H_4COOH), 9.23 (s, 2H, OH), 12.79 (s, 1H, COOH); Infrared (IR) part absorption bands ν (cm^{-1}) = 1684 (C=O), 1600, 1511, 1413 (phenyl), 2952 (CH), 3619 (OH); Anal. for $C_{20}H_{16}O_4$ (Calcd.: C, 74.99; H, 5.03; O, 19.98. Found: C, 74.88; H, 5.08; O, 20.04).

Polymer synthesis

Polymerization reaction was conducted in a three-neck flask, which was generally equipped with a nitrogen inlet, thermometer, Dean-Stark trap, and condenser. A typical synthesis of phthalazinone poly(ether sulfone ketone) (PPESK) is described as follows. The flask was charged with monomer phenolphthalin (10 mmol, 3.20 g), 4(4-hydroxyphenyl)-1(2H)-phthalazinone (DHPZ) (10 mmol, 2.38 g), bis(4-chlorophenyl) sulfone (DCS) (10 mmol, 2.85 g), 4,4'-difluorobenzophenone (DFB) (10 mmol, 2.18 g), and sulfolane (20

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Scheme 1 The synthesis of PPESK.

mL). After toluene (40 mL) was mixed in the system, anhydrous potassium carbonate (24 mmol, 3.31 g) was added. The reaction mixture was then heated until the toluene began to reflux. A reflux temperature range was maintained between 135 and 140°C until there was no water observed in the Dean-Stark trap. The temperature was gradually increased to 200°C during dehydration and slow removal of the toluene from the reaction mixture. The reaction mixture was cooled and diluted with sulfolane (10 mL) when the viscosity was increased dramatically. Several drops of weak acid (e.g., acetic acid) were then added to neutralize phenoxide end groups. The reaction product was coagulated in about 30 mL of water and filtered, redissolved in *N,N*-dimethylacetamide (DMAc), and filtered again. The DMAc solution was concentrated and then the reaction product was coagulated in ethanol. The white fibrous polymer was filtered and dried in a vacuum oven at 80°C for 48 h and the PPESK was obtained in almost quantitative yield.

Characterization of monomer and polymer

The ¹H-NMR spectra (200 MHz) was recorded on Varian Gemini 200 instrument using tetramethylsilane as the internal standard, in dimethylsulfoxide as the solvent. The chemical shift (δ) is quoted in ppm. The IR spectrum of PPESK was recorded with a Perkin-Elmer 1600 spectrophotometer with KBr disk. The inherent viscosity of the polymers was measured by Ubbelohde capillary viscometer at 25°C in *N*-methyl-

pyrrolidone as the solvent. The glass transition temperature (T_g) was determined by DuPont 2000 differential scanning calorimetry (DSC) at a heating rate of 10°C/min in an atmosphere of nitrogen. The thermooxidative stability was measured by thermogravimetric analysis (TGA) in an atmosphere of nitrogen at a heating rate of 10°C/min. Sulfolane was refluxed over sodium hydroxide and activated carbon for 2 h and was distilled in vacuum. Methylbenzene, phenolphthalein, sodium hydroxide, and zinc chloride were chemically pure reagents. Commercial DCS and DFB were used as received without further purification. DHPZ was synthesized according to the method of Jian et al.¹⁰

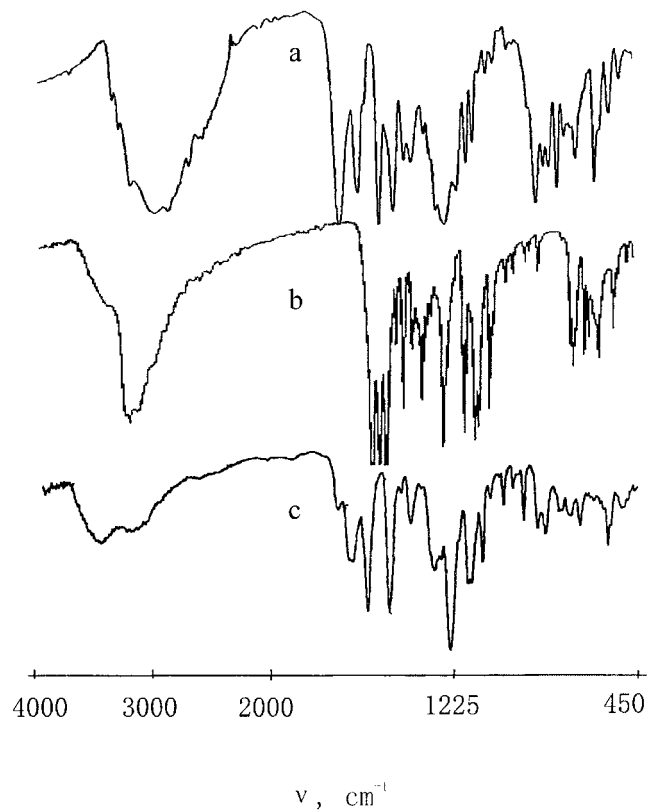


Figure 1 The FTIR of (a) phenolphthalein, (b) DHPZ, and (c) PPESK.

TABLE I
The Reactivity of Monomers and Thermal
Property of PPESK

$M_{\text{DHPZ}}:M_{\text{phenolphthalein}}$	$M_{\text{DCS}}:M_{\text{DFB}}$	η_{inh} (dL/g)	T_g (°C)
1:0	1:1	0.40	287
3:1	1:1	0.44	244
1:1	1:1	0.58	235
1:3	1:1	0.67	233
3:1	3:1	0.42	254
3:1	1:3	0.45	233

Key: reaction temperature is 200°C; reaction time is 4.5 h.

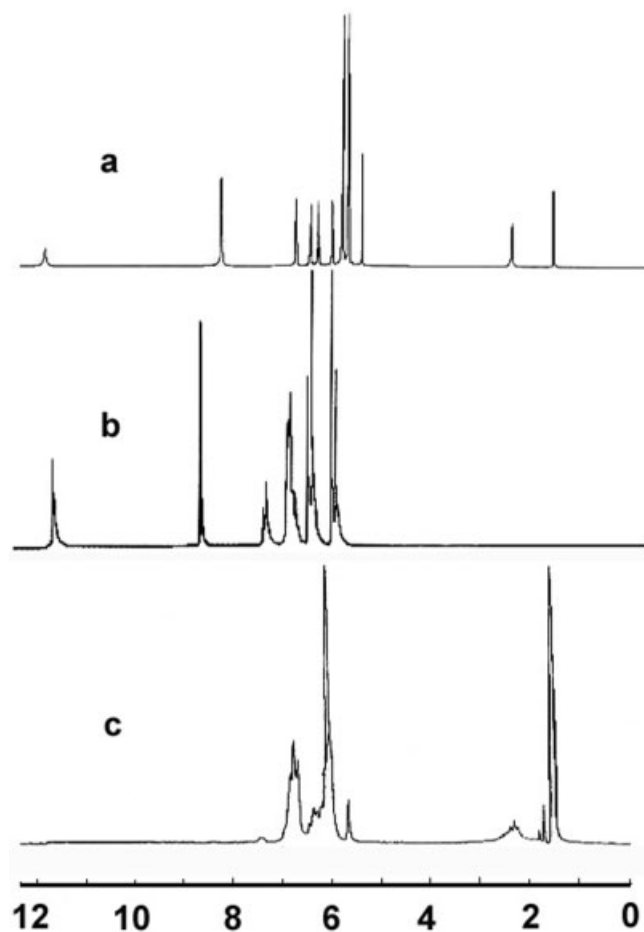


Figure 2 The $^1\text{H-NMR}$ spectra of (a) phenolphthalin, (b) DHPZ, and (c) PPESK.

RESULTS AND DISCUSSION

In the nucleophilic displacement polymerization reaction, an investigation of the reactivity of the monomer phenolphthalin vs DHPZ, a bisphenol-like compound, with DCS and DFB was carried out in the presence of potassium carbonate in a sulfolane/toluene (1/2) solvent mixture (Scheme I). For both reactions, the solid composition was maintained at 30 wt %, and any water present or generated during the bisphenoxide formation was removed as an azeotrope with toluene. The reactions were maintained at the reflux temperature of 135°C for 30 min, and upon completion of bisphenoxide formation and dehydration, the polymerization reaction was heated to 200°C to effect the displacement reaction. After 4 h, the reactions were

TABLE II
The Effects of Curing Reaction on Thermal Property of PPESK

		S:K	3:1	1:1	1:3
T_g ($^\circ\text{C}$)	Before curing		254	244	233
	After curing		280	262	260

DHPZ : phenolphthalin = 3:1

finished. The inherent viscosity of polymers was listed in Table I.

Fourier transform infrared (FTIR) and $^1\text{H-NMR}$ spectra of PPESK are shown in Figure 1 and Figure 2, respectively. From Figure 1 it can be found that the broad peak from 3000 to 3440 cm^{-1} is the typical absorption of hydroxyl group of carboxyl group. The strong peak that appears at 1242 cm^{-1} is assigned to the C—O—C absorption of the polymer, which does not exist in the spectra of the monomers. The apparent differences also can be found by comparing Figure 2(a) and (b) with (c). The peak appearing at 9.7 ppm of hydroxyl group and at 12.7 ppm of the NH— group in DHPZ disappears in PPESK. Moreover, the peak appearing at 9.3 ppm in phenolphthalin is unseen in PPESK. These imply that the reaction has taken place as expected.

It can be found, from Table I, that the inherent viscosity of the polymers is increased with increasing phenolphthalin units. It might be expected that DHPZ is a bisphenol-like and it has an —NH group on its side, which has low reactivity comparing to hydroxyl group. Therefore, the reactivity of phenolphthalin is higher than that of DHPZ. The addition of K_2CO_3 is also increased with increasing phenolphthalin units, because the carbonate group of phenolphthalin is neutral of K_2CO_3 during the reaction.

From Table I it can also be found that the T_g of PPESK is changed with the ratio of DHPZ and phenolphthalin, and it is decreased with increasing phenolphthalin units, which suggests that the flexibility is increased due to the introduction of the aliphatic chain in the backbone. The T_g of PPESK is also influenced by the content of the sulfone group and ketone group, and it is increased with increasing the content of the sulfone group, which implies that the polarity of the sulfone group is stronger than that of the ketone group. TGA shows that PPESK exhibits good thermal stability with 5% weight loss at $> 400^\circ\text{C}$.

The carboxyl group in the PPESK side chain is an active pendant group. It can be reacted with hydroxyl

TABLE III
The Solubility of PPESK

Solvent	DMAc	CHCl_3	DMF	DMSO	Py	NMP	NB	TCE*	THF*
PPESK	+	—	±	—	+	+	+	—	—

Key: +, fully soluble; ±, partially soluble; —, insoluble.

* TCE: 1,1,2,2-tetrachloroethane; THF: tetrahydrofuran.

and amide. In this experiment, the crosslinking reaction of PPESK occurs by using dicyandiamide (Dicy) as curing agent. The variation of the T_g is given in Table II, which indicates that the T_g of PPESK after curing is higher than that before curing. It might be expected that the movement of chain is limited by the formation of the mesh structure that is formed during curing.

The solubility of the PPESK (S/K = 1/1) in deneutralize polar solvents is listed in Table III. It can be found that the PPESK has good solubility and it can be dissolved in most deneutralized polar solvents such as *N*-methyl-pyrrolidone (NMP), *N,N*-dimethyl-acetylamide, pyridine (Py), and nitrobenzene (NB), and partially dissolved in *N,N*-dimethylformamide (DMF). The polarity of the PPESK is enhanced due to the introduction of a carboxyl group in the side chain.

The PPESK films can be prepared by casting the PPESK/DMAc solutions with the concentration of 8%–10%. The films with high strength and toughness are yellow and transparent. It can be used as high temperature special coating and impregnating varnish.

PPESK is amorphous polymer. The X-ray spectrum (Fig. 3) of PPESK shows a diffuse scattering peak with no crystallization peak due to the irregularity of the backbone structure.

The curing reaction of PPESK/Dicy systems with a heating cure procedure (β) at 5, 10, and 15°C/min is studied. The initial temperature (T_i), the peak temperature (T_p), and the final temperature (T_f) can be found from DSC curve (Table IV). T_i° , T_p° , and T_f° , which can be obtained from the curves of T_i , T_p , and T_f to $\beta = 0$, are 178, 198, and 262°C. That is, the curing reaction of PPESK/Dicy system occurs above 178°C, heat release is maximized at 198°C, and is finished at 262°C. The curing reaction is an exothermic reaction, the energy given off will cause system to rise in temperature.

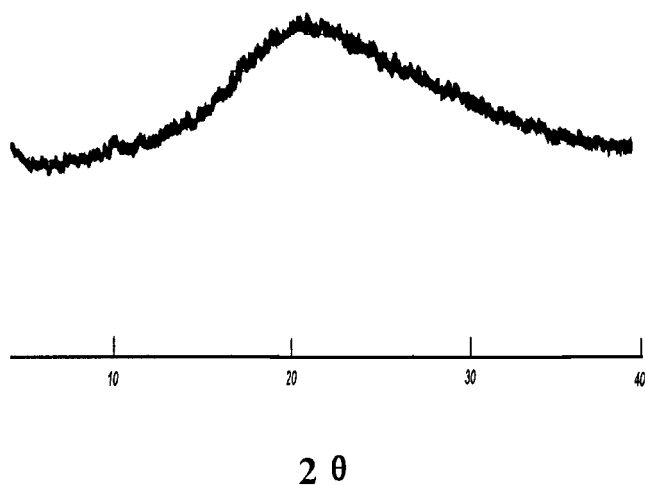


Figure 3 The XRD spectrum of PPESK (S/K = 1/3).

TABLE IV
The Effects of Heating Rates on Curing
Reaction of PPESK/Dicy

System	β (°C/min)	Exothermal peak temp. (°C)			ΔE (kJ/mol)	n
		T_i	T_p	T_f		
PPESK/Dicy	5	180	203	266	52.2	1.06
	10	184	206	275		
	15	186	209	281		

Therefore, the curing reaction temperature should control between T_i° and T_p° , the preference temperature should be close to T_p° .

The apparent activation energy (ΔE) and reaction order (n) of PPESK/Dicy are calculated according to the equation proposed by Kissinger and Crane.^{12,13} The result is listed in Table IV. ΔE of the crosslinking reaction is 52.2 kJ/mol and n is close to 1.0. Therefore, the crosslinking reaction is approximately seen as 1 grade reaction.

CONCLUSION

A kind of novel phthalazinone poly(ether sulfone ketone) containing carboxyl group has been synthesized. The polymerization reactions can be conducted in sulfolane in the presence of K_2CO_3 to produce high molecular weight polymers that can be dissolved in some deneutralize polar solvents. The decomposition temperature of the polymers is $>400^\circ C$, which indicates high thermal stability.

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References

- Lindfors, B. E.; Mani, R. S.; McGrath, J. E.; Mohanty, D. K. *Macromol Chem Rapid Commun* 1991, 12, 337.
- Wallace, T. J.; Schriesheim, A. *Tetrahedron Lett* 1963, 17, 1131.
- Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R.; Rose, J. B.; Staniland, P. A. *Polymer* 1981, 22, 1096.
- Bishop, M. T.; Karasz, F. E.; Russo, P. S.; Langley, K. H. *Macromolecules* 1985, 18, 86.
- Yang, H.; Sargent, J. R.; Hay, A. S. *J Polym Sci, Part A* 1995, 33, 989.
- Meng, Y.; Hill, A. R.; Hay, A. S. *J Polym Sci, Part A* 1999, 37, 1781.
- Xuan, Y. N.; Gao, Y.; Huang, Y.; Jian, X. G. *J Appl Polym Sci* 2001, 81, 1487.
- Mullines, M. J.; Woo, E. P. *JMS—Rev Macromol Chem Phys* 1987, c27(2), 313.
- Wang, F.; Roovers, J. *Macromolecules* 1993, 26, 5295.
- Jian, X. G.; Meng, Y. Z.; et al. CN Pat. ZL 93109179.9, 1993.
- Song, Y. G.; Pan, H. M. *China Adhesive* 1993, 2(1), 33.
- Kissinger, H. E.; Carroll, B. *J Phys Chem* 1958, 62, 394.
- Crane, L. W.; Dynes, P. J.; Knelble, D. H. *J Polym Sci, Polym Lett Ed* 1973, 11, 533.