

SYNTHESIS AND CHARACTERIZATION OF PHTHALAZINONE POLY(ARYL ETHER SULFONE KETONE) WITH CARBONYL GROUP*

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Abstract A kind of novel heat-resistant, high performance engineering thermoplastic phthalazinone poly(aryl ether sulfone ketone) (PPESK) containing a carboxyl group in its side chain was prepared by the nucleophilic displacement reaction of 4-(4-hydroxyphenyl)-1(2H)-phthalazinone with di(4-chlorophenyl) sulfone, 4,4'-difluoro-benzophenone and phenolphthalein in sulfolane in the presence of K_2CO_3 to produce high molecular weight polymers which can be dissolved in some polar solvents such as chloroform and nitrobenzene at room temperature and can be easily cast into flexible, yellowish and transparent films. PPESK is an amorphous polymer having a decomposition temperature above 400°C, which indicates that it has high thermal stability. At the same time, the thermal properties of PPESKs with dicyandiamide (DICY) as curing agent indicated that the heat-resistance properties of the PPESKs are improved after curing. The apparent activation energy (ΔE) of the cross-linking reaction and the reaction order (n) of PPESK/DICY were found to be 52.2 kJ/mol and ca.1.0, respectively. Therefore, the cross-linking reaction is approximately a first order reaction.

Keywords Poly(aryl ether sulfone ketone), Synthesis, Active pendant group

INTRODUCTION

Poly(aryl ether ketone)s (PPESKs) are one of the most important high performance engineering thermoplastics, widely used in electronic, electric, aircraft and aerospace industries. Initially, considerable effort was made to modify their chemical structures, essentially to improve their thermal properties^[1]. In the last few years, more attention was paid to their functionalization^[2]. This can be achieved easily by chemical modification of the polymer or by direct synthesis using functionalized monomers. In this paper, a novel PPESK was synthesized by introducing carboxyl group to the side chain based on phenolphthalein, a functionalized monomer. The cross-linking reaction of the PPESK by using diamine as curing reagent and the improvement of the heat-resistance of the PPESK after curing were also discussed.

EXPERIMENTAL

Materials

Sulfolane was refluxed over sodium hydroxide and activated carbon for 2 h and was distilled under vacuum. Methylbenzene, phenolphthalein, sodium hydroxide, zinc chloride were of chemically pure reagents. Commercial di(4-chlorophenyl) sulfone (DCS), 4,4'-difluorobenzophenone (DFB) were used as received without further purification. 4(4-hydroxyphenyl)-1(2H)-phthalazinone (DHPZ) was synthesized according to Ref. [3].

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Synthesis of Monomer

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°C under stirring until a greyish-white reaction mixture was obtained. The resulting product was filtered and excess concentrated hydrochloric acid was added to the filtrate until sedimentation was complete. The resulting semisolid was filtered, washed with water till neutral and was dried in a vacuum oven (120 °C) for 48 hours and white powder phenolphthalin was obtained in almost quantitative yield.

Synthesis of PPESK

Polymerization reaction was conducted in a three-necked flask, equipped with a nitrogen gas inlet, thermometer, Dean-Stark trap and condenser. A typical procedure for synthesizing PPESK (S/K = 1:1) is described as follows. The flask was charged with phenolphthalin monomer (10 mmol, 3.20 g), DHPZ (10 mmol, 2.38 g), DCS (10 mmol, 2.85 g), DFB (10 mmol, 2.18 g) and sulfolane (20 mL). Toluene (40 mL) and anhydrous potassium carbonate (24 mmol, 3.31 g) were then added. The reaction mixture was heated until toluene began to reflux. A reflux temperature range was maintained between 135°C and 140°C until no condensed water entered the Dean-Stark trap. The temperature was gradually raised 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) as the viscosity of the solution increased dramatically. Several drops of weak acid (e.g. acetic acid) were added to neutralize phenoxide end groups. The reaction product was then coagulated with 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 with ethanol. The white fibrous polymer was filtered and dried in a vacuum oven at 80°C for 48 hours to give an almost quantitative yield.

CHARACTERIZATION

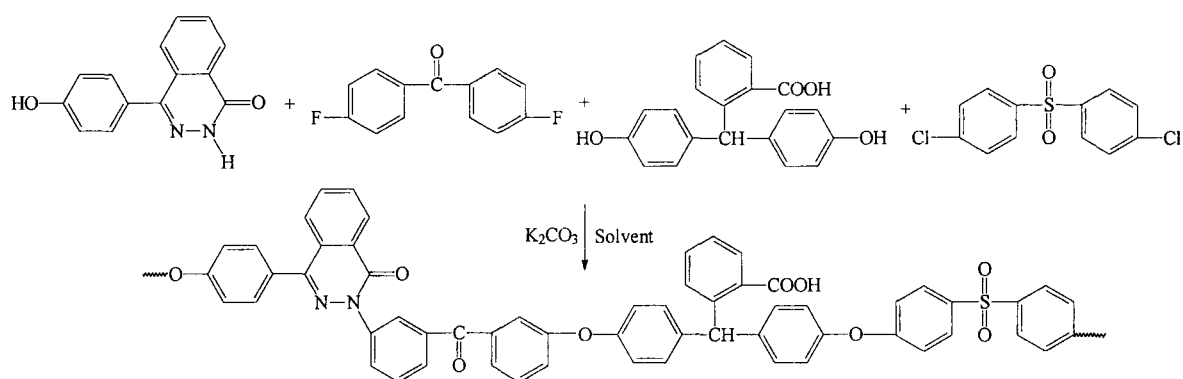
The ¹H-NMR spectra (200 MHz) were recorded on Varian Gemini 200 instrument using tetramethylsilane as the internal standard, with dimethylsulfone as the solvent. The chemical shift (δ) is quoted. The IR spectra were recorded with a Perkin-Elmer 1600 spectrometer with the sample as a KBr disk. The inherent viscosity of PPESKs was measured by a viscometer at 25°C with *N*-methyl-pyrrolidone as the solvent. The glass transition temperature (T_g) was determined using a DuPont 2000 differential scanning calorimeter (DSC) at a heating rate of 10 K/min in an atmosphere of nitrogen. The thermooxidative stability was measured by thermo gravimetric analysis (TGA) in an atmosphere of nitrogen and at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

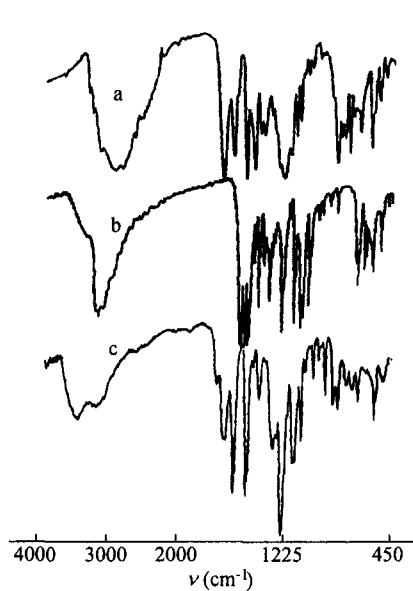
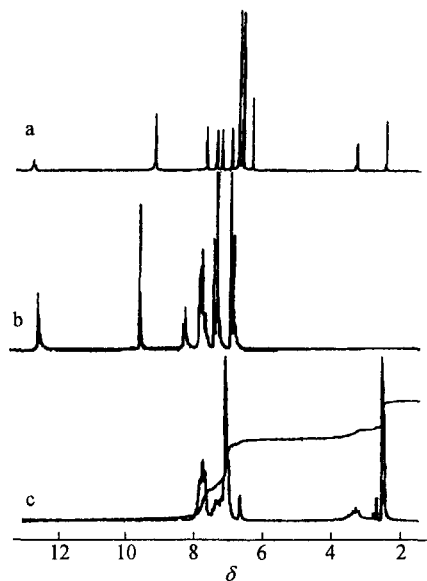
In the nucleophilic displacement polymerization reaction, an investigation of the reactivity of the phenolphthalin monomer towards DHPZ, a bisphenol-like compound, with DCS, DFB was carried out in the presence of potassium carbonate in a sulfolane/toluene (1/2) solvent mixture (Scheme 1).

For both reactions, the solid composition was maintained at 30 wt%, and any water present or generated during bisphenoxide formation was removed as an azeotrope with toluene. The reactions were maintained at the reflux temperature (135°C) for 30 min, and, upon the 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 complete. The inherent viscosity of the polymers is listed in Table 1.

It can be seen that the inherent viscosity of the polymers increases with increasing phenolphthalin units. It might be expected that DHPZ is a bisphenol-like compound and it has —NH group on its side, which has a lower reactivity comparing to that of hydroxyl group. Therefore, the reactivity of phenolphthalin is higher than that of DHPZ. At the meantime, the addition of K₂CO₃ is also increased with increasing phenolphthalin units, because the carbonate group of phenolphthalin can be neutralized by K₂CO₃ during the reaction.

**Scheme 1** The synthesis of PPESK**Table 1.** The reactivity of phenolphthalein and DHPZ

$M_{\text{DHPZ}}:M_{\text{phenolphthalein}}$	$M_{\text{K}_2\text{CO}_3}:M_{\text{bisphenols}}$	η_{inh} (dL/g)
1:0	140%	0.40
3:1	160%	0.44
1:3	180%	0.67
0:1	240%	0.77

Note: S:K = 1:1; $T = 200^\circ\text{C}$; $t = 4.5$ h**Fig. 1** The FT-IR spectra of (a) phenolphthalein, (b) DHPZ and (c) PPESK**Fig. 2** The ^1H -NMR spectra of (a) phenolphthalein, (b) DHPZ and (c) PPESK

FT-IR and ^1H -NMR spectra of PPESK are shown in Fig. 1 and Fig. 2 respectively. From Fig. 1(a) it can be seen that the broad peak from 3440 cm^{-1} to 3000 cm^{-1} is the typical absorption of the hydroxyl group in a carboxyl group. The strong peak at 1242 cm^{-1} in Fig. 1(a) is assigned to the C—O—C absorption of the polymer which is absent in the spectra of the monomers. Apparent differences between the ^1H -NMR spectra of the monomers and the polymer can also be found by comparing Fig. 2(a), (b) and (c). The peak appearing at $\delta = 9.7$ for hydroxyl group and at $\delta = 12.7$ for NH— group in DHPZ has disappeared in PPESK. Moreover, the peak appearing at $\delta = 9.3$ in phenolphthalein is absent in PPESK. These observations imply that the reaction has taken

place as expected.

From Table 2 it can be seen that the T_g of PPESK changes with the ratio of DHPZ and phenolphthalin and is decreased with increasing phenolphthalin units, suggesting that the flexibility of the polymer chains is increased due to the introduction of aliphatic chains into the backbone. The T_g of PPESK is also influenced by the content of sulfone group and ketone group (Table 3) and is increased with increasing content of sulfone group. This implies that the polarity of sulfone group is stronger than that of ketone group. Thermogravimetic analysis (TGA) shows that PPESK has good thermal stability with 5% weight loss above 400 °C.

Table 2. The properties of PPESK (S:K = 1:1)

$M_{DHPZ}:M_{phenolphthalin}$	3:1	1:1	1:3
η_{inh} (dL/g)	0.44	0.67	0.77
T_g (°C)	244	235	233

Table 3. The properties of PPESK (DHPZ:phenolphthalin = 3:1)

S:K	3:1	1:1	1:3
η_{inh} (dL/g)	0.42	0.44	0.45
T_g (°C)	254	244	233

The cross-linking reaction of PPESK can occur by using dicyanodiamide (DICY) as the curing agent. The variation of the T_g is given in Table 4, the T_g of PPESK after curing is increased and the greater the content of phenolphthalin, the larger is the alteration of T_g after curing. It might be expected that the movement of the chain is limited by the formation of a mesh structure during curing.

Table 4. The thermal property of PPESK (DHPZ:phenolphthalin = 3:1)

	S:K	3:1	1:1	1:3
T_g (°C)	Before curing	254	244	233
	After curing	280	262	260

The solubility of the PPESK (S/K = 1/1) in polar solvents is listed in Table 5. It can be seen that the PPESK has good solubility and it can be dissolved in most polar solvents. The polarity of the PPESK is enhanced due to the introduction of carboxyl group into the side chain.

Table 5. The solubility of PPESK

Solvent	DMAC	CHCl ₃	DMF	DMSO	Py	NMP	NB	TCE	THF
Solubility	+	–	±	–	+	+	+	–	–

Note: + completely soluble; ± partially soluble; – insoluble

The PPESK films can be prepared by casting a 8%–10% PEESK/DMAc solutions. The films with high strength and toughness are yellowish and transparent and can be used as high-temperature special coating and impregnating varnish.

PPESK is an amorphous polymer. The X-ray diffraction pattern of PPESK shows a diffuse scattering peak with no crystallization peak due to the irregularity of the backbone structure.

Figure 3 shows the DSC curves during the curing reaction of PPESK/DICY systems with heating rates (β) of 5 K/min, 10 K/min and 15 K/min in sequence. The initial temperature (T_i), the peak temperature (T_p) and the finished temperature (T_f) can be found from the DSC curve (Table 6). T_i° , T_p° and T_f° , which can be obtained from the curves of T_i , T_p , T_f to $\beta = 0$, are 178 °C, 198 °C 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 exothermal reaction, the energy given off will cause the temperature of the system to rise. Therefore, the curing reaction temperature should be controlled between T_i° and T_p° , the preferred temperature should lie close to $T_p^{[4]}$.

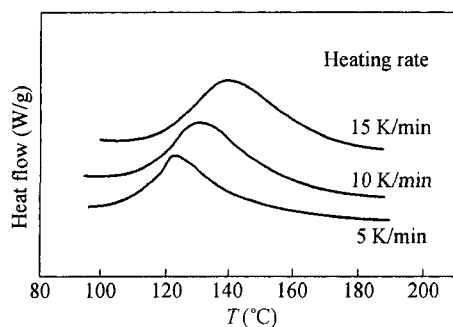


Fig. 3 The DSC curves of PPESK/DICY

The apparent activation energy (ΔE) and reaction order (n) of PPESK/DICY are calculated according to the equation proposed by Kissinger and Crane^[5, 6]. The result is listed in Table 6. ΔE of the cross-linking reaction is 52.2 kJ/mol and n is close to 1.0. Therefore, the cross-linking reaction is approximately a first order reaction.

Table 6. The effects of heating rates on curing reaction of PPESK/DICY

System	β (K/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		

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 which can be dissolved in some polar solvents and have a high decomposition temperature (400°C).

REFERENCES

- 1 Mullines, M.J. and Woo, E. P., JMS-Rev. Macromol. Chem. Phys., 1987, c27: 313
- 2 Wang, F. and Roovers, J., Macromolecules, 1993, 26: 5295
- 3 Jian, X.G., Meng, Y.Z., Zheng, H.B. and Zhu, X. L., 1993, CN Patent ZL 93109179.9
- 4 Song, Y.G. and Pan, H. M., China Adhesive, 1993, 2: 33
- 5 Kissinger H.A., J. Res Nat. Bur. Standards, 1956, 57: 217
- 6 Crane, L.W., Dynes, P.J. and Knelble, D.H., J. Polym. Sci. Polym. Letter Ed., 1973, 11: 533