

SYNTHESIS AND CHARACTERIZATION OF POLY(PHTHALAZINONE BIPHENYL ETHER SULFONE KETONE)S FROM 4,4'-DICHLOROBENZOPHENONE*

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Abstract A series of poly(aryl ether sulfone ketone)s containing phthalazinone and biphenyl moieties were synthesized by aromatic nucleophilic displacement polycondensation of 4-(4-hydroxyphenyl)(2H)-phthalazin-1-one (DHPZ), 4,4'-dichlorobenzophenone (DCB), 4,4'-dichlorodiphenyl sulfone (DCS) and 4,4'-biphenol (BP) in different molar ratios. The obtained copolymers were characterized by different instrumental techniques (FTIR, TGA, DSC, WAXD, etc.). The inherent viscosities of these polymers were in the range of 0.43–0.56 dL g⁻¹. They were amorphous and had good solubility in polar aprotic organic solvents. The copolymers exhibited high glass transition temperatures (T_g s) between 225°C and 256°C and excellent thermal stability up to 517–526°C (thermal decomposition temperatures for 5% weight loss, $T_{d,5\%}$) in nitrogen. The tensile strength and elongation at break of the polymers ranged from 63 MPa to 71 MPa and from 18% to 21%, respectively. The processability of the material was effectively improved by the introduction of biphenyl group into polymer backbone.

Keywords: Phthalazinone; Poly(aryl ether); Polycondensation; Processability; Thermal stability.

INTRODUCTION

Phthalazinone-based poly(aryl ether ketone sulfone) (PPESK) is a type of new thermoplastic high performance polymer, which has unique combination of chemical, physical, thermal and mechanical properties^[1–3]. The twisted and non-coplanar phthalazinone moiety in the polymer's main chain imparts it with excellent thermal properties (T_g s above 260°C and $T_{d,5\%}$ exceeding 450°C) as well as reasonable solubility in selected aprotic polar solvents, and make it a promising candidate in optical waveguide, membrane and composite materials^[4–10].

However, the special unsymmetrical, twisted and noncoplanar structure also induces entanglement among polymer chains, which leads to high melt viscosity and difficulties in injection molding, extrusion and blow molding processing. Therefore, improvement of their melt processability is of great industrial value. In previous reports^[11, 12], improvement of melt processability of PPESK was generally investigated by blending with oligomers, such as poly(aryl ether) (PAE) oligomer, or liquid crystalline polymers by physical method. From a thermodynamic point of view, however, polymer blends are almost immiscible in general^[13]. In this report, the biphenyl groups were incorporated into the PPESK main chain *via* copolymerization from 4,4'-biphenol (BP) by chemical route.

Currently, poly(aryl ether ketone)s are mainly synthesized from the more reactive difluoroaryketones, for

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example 4,4'-difluorobenzophenone, which results in corresponding expensive polymers. But high molecular weight polymers are not readily obtained from dichloroarylketone, for its low reactivity and side reactions during the polymerizations^[14, 15]. Compared with the corresponding fluorides, aromatic chlorides are much more inexpensive and so the preparation of high molecular weight aromatic poly(ether ketone) from dichlorobenzophenone is of industrial importance^[16, 17].

In this paper, we extended the effort on the synthesis of poly(phthalazinone ether sulfone ketone)s from 4,4'-dichlorobenzophenone (DCB) as the co-monomer. As a results, a series of poly(phthalazinone biphenyl ether sulfone ketone)s (PPBESKs) were synthesized from 4-(4-hydroxyphenyl)(2H)-phthalazin-1-one (DHPZ), DCB, 4,4'-dichlorodiphenyl sulfone (DCS) and 4,4'-biphenol (BP). The synthesis and characterization were discussed. In addition, their solubility, thermal properties, mechanical properties and the HAAKE rheological behavior were elaborated in details.

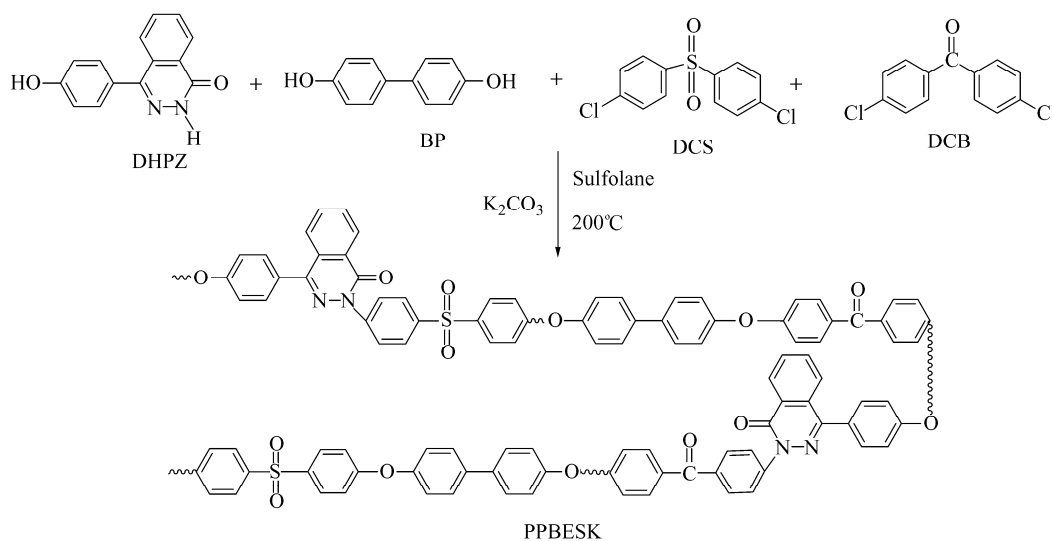
EXPERIMENTAL

Materials

4-(4-Hydroxyphenyl)(2H)-phthalazin-1-one (DHPZ) was gifted by Dalian Polymer New Material Company (China) and used after recrystallization from *N,N*-dimethylacetamide (DMAc); 4,4'-Dichlorobenzophenone (DCB) and 4,4'-dichlorodiphenyl sulfone (DCS) were recrystallized from toluene and isopropanol, respectively; Anhydrous K_2CO_3 was ground by mortar and pestle, and dried in vacuum at 130°C for 24 h before use. Other chemicals and solvents were commercially available and used as received.

Polymer Synthesis

This series of PPBESKs were synthesized by solution polycondensation reaction as shown in Scheme 1. In a typical procedure, with appropriate molar ratio, the monomers, BP, DHPZ, DCB and DCS, were placed into a 100 mL three-necked flask equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, a Dean-Stark trap and a condenser. Calculated amounts of K_2CO_3 , sulfolane and toluene were added into the reactor under a nitrogen atmosphere. The mixture was heated to reflux at 150°C and stirred for 2–3 h to promote phenolate formation. After the produced water was azeotroped off with toluene, the temperature was increased to 200°C and kept at this temperature for further 7–8 h until the viscosity of the solution did not increase obviously. The resultant solution was trickled into 800 mL of hot water with stirring to afford a fiber-like precipitate, and then the precipitate was washed thoroughly with hot water. The dried polymer was dissolved in chloroform for



Scheme 1 Preparation of PPBESK from DCB

further purification and then precipitated in ethanol. After being filtered, it was dried at 100°C under vacuum for 24 h to give final PPBESK.

Characterizations

IR spectra (films for polymers) were recorded on a Nicolet Magna 470 spectrometer. ^1H -NMR spectra were measured on a Bruker AM-300 MHz instrument with deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as internal standard. Inherent viscosities were measured at a concentration of 0.5 g dL $^{-1}$ in chloroform at 25°C with Ubbelohde viscometer. Glass transition temperatures (T_g s) were measured on a Mettler DSC822 differential scanning calorimeter (DSC) at a heating rate of 10 K min $^{-1}$ in N_2 , and the T_g values were taken at the inflection point of the step change. Thermal gravimetric analyses (TGA) of the polymers were measured on a Mettler TGA/SDTA851 instrument at a heating rate of 20 K min $^{-1}$ in N_2 . Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Rigaku D/max 2400 automatic X-ray diffractometer with Ni-filtered Cu K α radiation (40 V, 100 mA). The mechanical properties of synthesized polymers were measured on an Instron tensile tester (Model No. 5567) in the form of films with a crosshead speed of 2 mm min $^{-1}$ at 25°C. The rheological behaviors of the polymers were tested on a Thermo HAAKE PolyLab System with the rotor rate of 20 rad min $^{-1}$.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

The PPBESKs copolymers composed of different components are named as P1, P2, P3 and P4, respectively, as shown in Table 1. And they were prepared by tuning the molar ratio of the monomers, DHPZ, BP, BCS and DCB, *via* nucleophilic displacement polycondensation in the presence of K_2CO_3 catalyst. During the polymerization, the phthalazinone $-\text{NH}$ group behaved like phenolic $-\text{OH}$ group, thereby the polymers could be formed from a novel N–C coupling reaction through step growth polycondensation. Polymerizations of P1, P3 and P4 gave polymers with inherent viscosities of 0.56, 0.43 and 0.55 dL g $^{-1}$, respectively, indicating the reactivity of DCB was enough for these polymerizations. Moreover, the introduction of the crank, twist and noncoplanar phthalazinone moieties improved the solubility of the obtained polymers, which ensured the success of the polymerization. However, P2 had lower inherent viscosity than the others did and was precipitated from the solution during the reaction. This could be due to the poor solubility of the resultant polymer resulted from the more content of symmetrical biphenyl and benzophenone moieties.

Table 1. The characterization data of the copolymers

PPBESKs	Composition ^a	η_{inh} (dL g $^{-1}$) ^b	T_g^c (°C)	$T_{5\%}^d$ (°C)	C_y^e (%)
	DHPZ:BP:DCS:DCB				
P1	7:3:2:8	0.56	236	517	63
P2	3:7:2:8	< 0.2	—	—	—
P3	7:3:6:4	0.43	256	512	58
P4	3:7:6:4	0.55	225	526	53

^a The molar ratio of the monomer materials;

^b The inherent viscosities of the copolymers were measured in chloroform 0.5 g dL $^{-1}$ at 25°C;

^c Glass transition temperature was measured by DSC at a heating rate of 10 K min $^{-1}$ in nitrogen;

^d Decomposition temperatures at which a 5% weight loss was recorded by TGA at a heating rate of 20 K min $^{-1}$ in nitrogen;

^e Char yield calculated as the percentage of solid residue after heating from 75°C to 800°C

The formation of the PPBESKs was confirmed by FTIR and ^1H -NMR spectroscopic data. As shown in Fig. 1, the FTIR spectra of P1, P3 and P4 clearly exhibit the characteristic absorption at about 1668 (C=O), 1597 and 1496 (aromatic rings), 1240 (C–O–C), and 1308, 1151 cm $^{-1}$ (SO $_2$) respectively. There are no peaks in the range of 3100–3400 cm $^{-1}$ of the characteristic absorption for $-\text{NH}$ and $-\text{OH}$. Moreover, with the increase of the content of BP and DCS in the feeding materials, the relative absorption of the corresponding

bands of phenyl and sulfone groups increases. Figure 2 shows the ^1H -NMR spectra of P1, P3 and P4. As can be seen, the peak appears at $\delta = 8.6$ for all copolymers is ascribed to the typical hydrogen signal of the phthalazinone segment, owing to the deshielding ring current effect of adjacent lactam. The two sharp peaks at $\delta = 12.8$ and 9.6 corresponding to phthalazinone N—H and phenolic O—H protons are absent in polymer spectra. All the above results indicated that the polycondensation had occurred as expected.

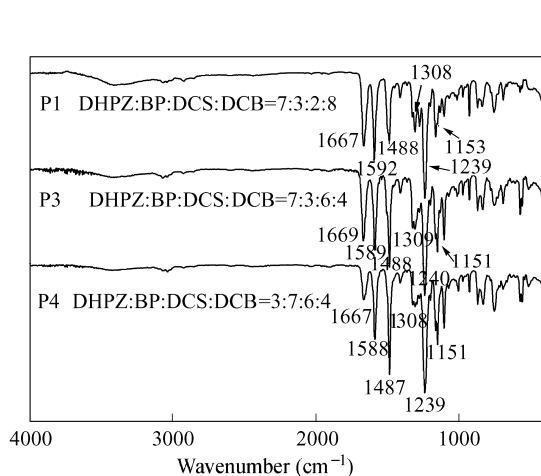


Fig. 1 FTIR spectra of PPBESKs

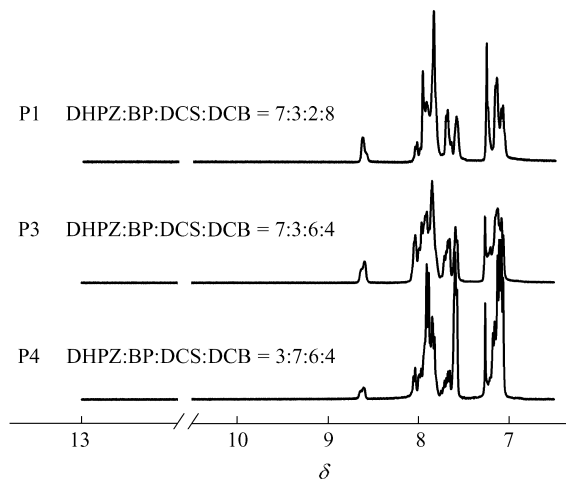


Fig. 2 ^1H -NMR spectra of PPBESKs

Thermal Properties

The thermal properties of the obtained PPBESKs were evaluated by DSC and TGA under nitrogen atmosphere at a heating rate of 10 K min^{-1} from 100°C to 400°C and 20 K min^{-1} from 75°C to 800°C , respectively, and the results are summarized in Table 1. As shown in Fig. 3, the obtained copolymers, P1, P3, and P4, exhibit outstanding thermal properties with glass transition temperature (T_g) in the range of 225 – 256°C . In details, The T_g value of P3 is higher than that of P1, which is due to the higher content of polar sulfone group in P3 as compared with that in P1. Moreover, although P4 has higher sulfone group content, the T_g value of P1 is higher than that of P4. It can be attributed to the higher content of aromatic heterocyclic phthalazinone moiety in P1 as compared with that in P4, which could not only restrict segmental mobility and hinder the chain rotation but also significantly enhance the entanglement of polymer backbone. These copolymers do not lose weight below 500°C obviously, as exhibited in Fig. 4. The temperatures for 5% weight loss are in the range of 517 – 526°C . The high glass transition temperatures and excellent thermal stability could be attributed to the rigid heterocyclic phthalazinone units in polymer backbone.

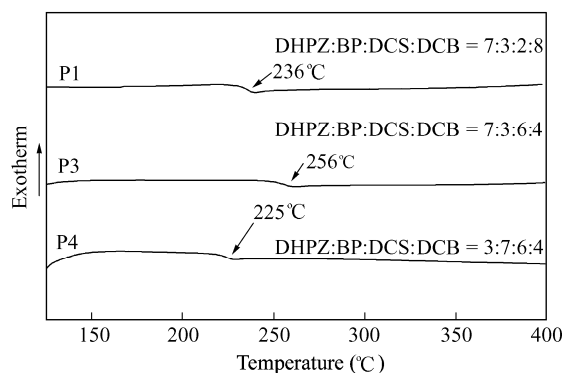


Fig. 3 DSC curves of PPBESKs

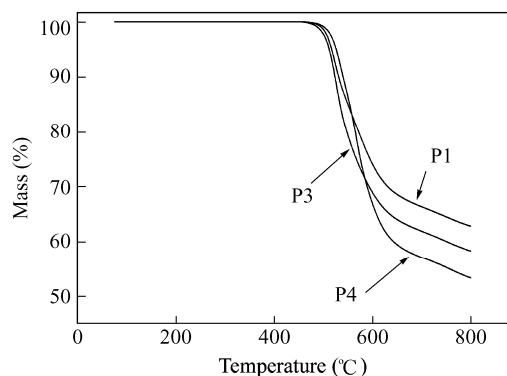


Fig. 4 TGA curves of the PPBESKs

Polymer Solubility

The solubility behavior of the resulting copolymers was studied in various organic solvents by dissolving 0.04 g of the polymers in 1 mL solvent (40 g/L) at room temperature. As summarized in Table 2, P1, P3 and P4 exhibit excellent solubility in common organic solvents such as chloroform, *N*-methyl-2-pyrrolidone (NMP), 1,1,2,2-tetrachloroethane (TCE), *N,N*-dimethylacetamide (DMAc) and nitrobenzene (NB). And P3 shows better solubility than P1 and P2 in tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), which might be attributed to more sulfone groups and phthalazinone moieties in its backbone. Probably, the improved solubility of these materials can be ascribed to that the polymer main chain is twisted by the kink noncoplanar phthalazinone architecture, which enlarges the free volume of these materials. As a result, this kind of materials could be processed by solution method.

Table 2. Solubility of PPBESKs

Polymer	CHCl ₃	NMP	TCE	DMAc	NB	THF	DMF	DMSO	Con. H ₂ SO ₄
P1	+	+	+	+	+	±	±	—	+
P3	+	+	+	+	+	+	±	±	+
P4	+	+	+	+	+	—	—	—	+

+: soluble; ±: partially soluble or swollen; —: insoluble

The Morphology of PPBESKs

Figure 5 is the WAXD patterns of obtained PPBESKs, which only show a very broad diffraction trace. Moreover, no melting peak was observed in the DSC curves shown in Fig. 3. Both of these imply that the polymers exhibit amorphous morphology. It could be attributed to the twisted and unsymmetrical phthalazinone units, which disrupt the symmetry of polymer chains.

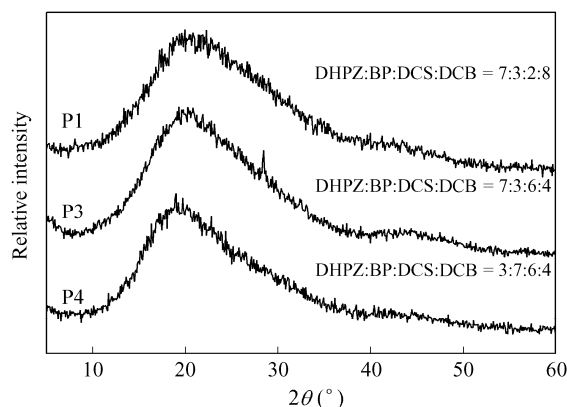


Fig. 5 WAXD diffractograms of PPBESKs

Mechanical Properties

The mechanical properties of the polymers were measured in the form of films. Tough and nearly transparent films of the polymers were cast from their NMP solution (100 g/L), and the mechanical properties of the PPESKs were determined at room temperature. As summarized in Table 3, all of these tested samples show high tensile strength of 63–72 MPa and elongation at break of 18%–21%. These results indicate the good mechanical properties of the synthesized polymers, which is one of the typical characteristics of high performance polymers. In details, the tensile strength of P1 is higher than that of P4, which maybe owe to the more phthalazinones moieties in P1. Generally, the naphthalene ring within the polymer backbone contributes more to the mechanical strength than the biphenylene ring does. P3 shows higher tensile strength and modulus than P1, which can be explained by the presence of polar sulfone groups that increase the chain interactions.

Table 3. Mechanical properties of the polymers

PPBESKs	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
P1	67	18	0.8
P3	72	21	0.9
P4	63	20	0.8

Polymer HAAKE Rheological Behaviors

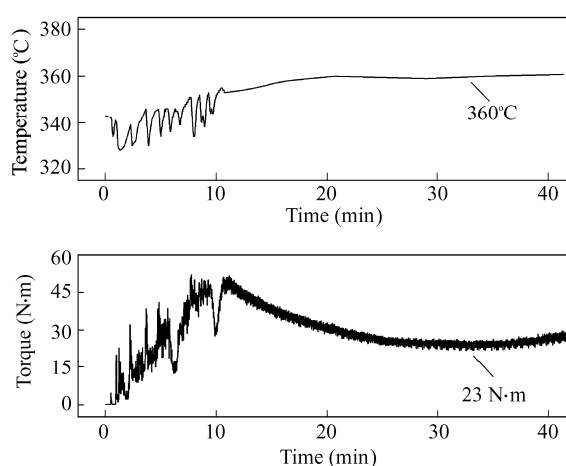
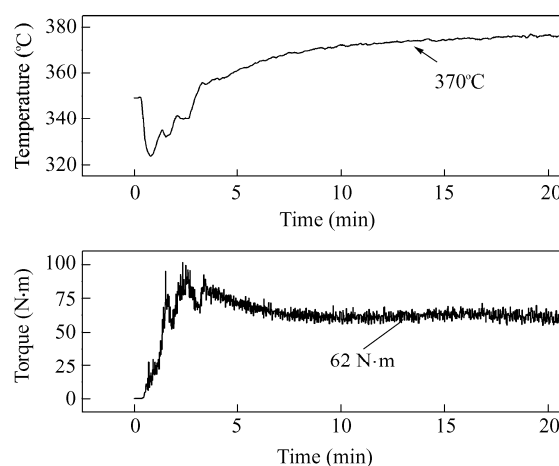
Generally, the torque of polymer on HAAKE behavior tests is greatly dependent on its melt viscosity when the designed measuring conditions are used. The larger torque, the higher the melt viscosity. Herein, the torque of the HAAKE Rheometer was used to determine the processability of PPBESKs. As unmodified polymers, PPESK28 and PPESK64 were synthesized and their HAAKE rheological behaviors were tested as comparison. The data are summarized in Table 4 and the HAAKE rheological curves of P3 and PPESK64 were taken for example as shown in Fig. 6 and Fig. 7, respectively.

It can be found that the torques of the polymers, such as P1, P3 and P4, reduced by more than half even at lower heating temperature, as compared with the corresponding PPESKs. When the molar ratio of DHPZ to BP is fixed, for instance 7:3, the torque of P1 and P3 were almost the same. However, the torque of P4 (DHPZ:BP = 3:7) is dramatically decreased to 6 N·m even at 330°C, indicating that the biphenyl segments in the polymer main chain reduce the melt viscosity of the materials. It may be attributed to the reduced entanglement between polymer chains by the biphenyl groups, and thus improve their melting processability. Moreover the linear segments containing biphenyl groups tend to act as plasticizers for the polymer.

Table 4. HAAKE rheological behaviors of the polymers

Polymers	Composite ^a	Test temperature (°C)	Torque (N·m)
PPESK28	DHPZ:DCS:DCB 10:2:8	370	58
P1	DHPZ:BP:DCS:DCB 7:3:2:8	360	26
PPESK64	DHPZ:BP:DCS:DCB 10:6:4	370	62
P3	DHPZ:BP:DCS:DCB 7:3:6:4	360	23
P4	DHPZ:BP:DCS:DCB 3:7:6:4	330	6

^a The molar ratio of the monomer materials

**Fig. 6** HAAKE rheological curves of P3**Fig. 7** HAAKE rheological curves of PPESK64

CONCLUSIONS

A series of poly(phthalazinone biphenyl ether sulfone ketone)s were successfully prepared from a cheaper monomer, 4,4'-dichlorobenzophenone, by nucleophilic solution polycondensation *via* a feasible and simple method. The obtained polymers show high T_g over 225°C and do not lose weight below 500°C obviously. They have good solubility in common organic solvents and could be cast into transparent, tough films. The introduction of biphenyl into the polymer backbone greatly improved the melt processability, and the utilization of cheaper monomer could lower the synthetic cost.

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