

Note

SYNTHESIS AND PROPERTIES OF SOLUBLE AROMATIC COPOLYAMIDES CONTAINING PHOSPHINE OXIDE MOIETY*

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Abstract Aromatic copolyamides were synthesized by the Yamazaki phosphorylation method starting from bis(4-carboxyphenyl) phenyl phosphine oxide, terephthalic acid and 4,4'-diaminodiphenyl methane. The copolymers with inherent viscosities of 0.52–0.99 dL/g were obtained. The structures of the copolyamides were characterized by elemental analysis, FTIR and NMR. The glass transition temperatures were measured by DSC and DMA, respectively, and the results showed that the T_g s of the polymers were higher than 287°C. Thermal decomposition temperatures of the copolyamides at 5% weight loss were found in the range of 423–469°C by TGA. Most of the copolymers were readily soluble in a variety of organic solvents such as NMP, DMAc, *m*-cresol and so on. The tensile experiments of the thin films showed that the polymers had good mechanical properties.

Keywords: Aromatic polyamide; Phosphorylation; BCPPO; Solubility; Thermal stability.

INTRODUCTION

Aromatic polyamides possess desirable properties such as excellent thermal stability, good mechanical and dielectric properties^[1]. However, the application of aromatic polyamides is restricted to some extent because of their difficulty in fabrication and processing. Commercial aromatic polyamide, for example, Kevlar® of DuPont, is insoluble in common organic solvents and infusible before decomposition because of their rigid, rod-like backbone and intramolecular hydrogen bonds^[2]. Therefore, many efforts have been concentrated on improving aromatic polyamides' solubility or melt processability without sacrificing their excellent properties. Several approaches were benefited to improving the solubility of polyamides^[3–9], including introduction of flexible bridging linkages, *meta*- or *ortho*-substituted phenylene rings, bulky pendant groups or bent non-coplanar units into the polymer backbone.

In this article, novel copolyamides were prepared by the Yamazaki-Higashi phosphorylation polyamidation procedure^[10] from bis(4-carboxyphenyl) phenyl phosphine oxide (BCPPO), terephthalic acid (TPA) and 4,4'-diaminodiphenyl methane (DDM). Insertion of phosphine oxide groups can lower the segmental rotational barrier and increase the degree of conformational freedom, while providing enhanced solubility because of decreased packing and crystallinity. The effects of phosphine oxide groups on various properties of copolyamides were investigated, including inherent viscosity, solubility, thermal properties and mechanical properties.

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EXPERIMENTAL

Materials

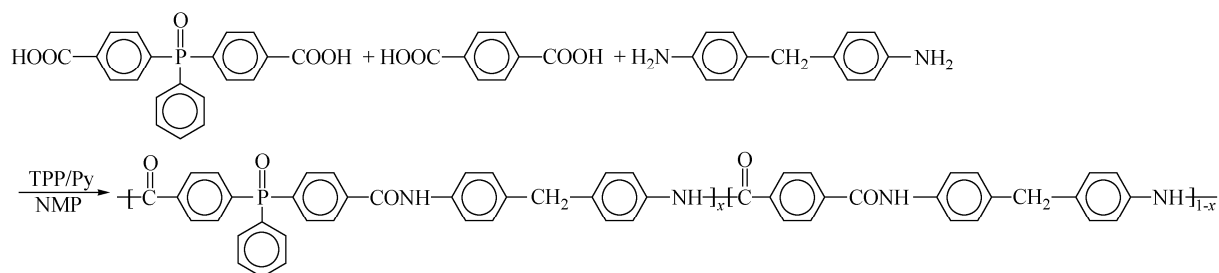
BCPPO was prepared as previously reported^[11]. TPA and DDM were reagent grade and used without further purification. *N*-methyl-2-pyrrolidone (NMP) and pyridine (Py) were dried on distillation under reduced pressure over calcium hydride and stored over 0.4 nm molecular sieves in a sealed bottle. Triphenyl phosphite (TPP) was purified by vacuum distillation. Anhydrous calcium chloride (CaCl₂) was dried under vacuum at 180°C for 3 h.

Characterization

The FT-IR spectra were recorded on a VECTOR 22 spectrometer. ¹H-NMR and ³¹P-NMR spectra were recorded using a Bruker AMX-400 NMR spectrometer with DMSO-d₆ as the solvent, tetramethylsilane and H₃PO₄ as the internal reference respectively. The elemental analyses of C and H were performed with a Carlo Erba 1106 elemental analyzer. P was measured with the Schoniger combustion flask method and detected by a UV spectrophotometer. The inherent viscosities of the polymers were measured at a concentration of 0.2 g/dL in NMP with an Ubbelohde capillary viscometer at 30°C. Differential scanning calorimetry (DSC) was measured on a Setaram DSC141 at a heating rate of 20 K/min under a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was conducted with a TA-DMA 2980 at a heating rate of 5 K/min and 1 Hz. The sample size was 6 mm width, 30 mm length and 0.06 mm thickness. Thermogravimetric analysis (TGA) was performed using a TGA-Q50 in nitrogen atmosphere (40 mL/min) at a heating rate of 20 K/min. Solubility was determined by dissolving 0.1 g of polymer in 10 mL of solvent. RGT-5 universal tester was used to measure the tensile property of the polymer films (10 mm width, 120 mm length, 0.06 mm thickness), and the crosshead speed was 5 mm/min.

Polymerization

The synthesis of copolyamide was illustrated in Scheme 1.



Scheme 1 Synthesis of copolyamides

A typical procedure was described as follows. In a three-necked flask equipped with a stirrer, reflux condenser, and N₂ inlet, BCPPO (1.098 g, 3 mmol), TPA (0.3323 g, 2 mmol) and DDM (0.9915 g, 5 mmol) were added. Then 2 g dried calcium chloride, 14 mL NMP, 2.8 mL pyridine and 2.8 mL TPP were charged. The resulting mixture was reacted at 120°C for 2 h under the nitrogen atmosphere. After the polymerization, the viscous mixture was poured into 200 mL methanol. The white precipitated polymer was filtered and washed by methanol and hot water, and then dried at 100°C for 12 h *in vacuo*. Other copolyamides were prepared *via* the analogous procedures.

RESULTS AND DISCUSSION

Polymerization and Characterization

Copolyamides with different monomer ratios were prepared by the Yamazaki phosphorylation method. The copolyamide with inherent viscosity of 0.99 dL/g could be obtained when the reaction temperature was 120°C, the reaction time 2 h and the concentration 0.7 mol/L. The results indicated that BCPPO was active enough to polymerize with aromatic diamide for the preparation of high molecular weight polymers.

The structures of the copolyamides were characterized by FTIR and NMR. The polymer displayed a broad single peak of secondary amine of polyamide at 3290 cm⁻¹. Stretching vibration absorption peak of C=O at

1667 cm^{-1} was observed. Peaks at 3055 cm^{-1} and 2964 cm^{-1} were characteristic absorption band corresponding to C—H bond in benzene ring and —CH₂—, respectively. The absorption peaks at 1437 cm^{-1} (P—Ar) and 1099 cm^{-1} (P=O) were also found. The ¹H-NMR and ³¹P-NMR spectra of P2 were shown in Fig. 1 and Fig. 2. $\delta = 7.21\text{--}8.07$ were resonance peak of protons in benzene ring. $\delta = 10.8$ was chemical shift for NHCO in polymer, and 3.89 was for —CH₂—. In ³¹P-NMR, there was a single peak around 27.0 which was corresponded to phosphorus of triphenylphosphine structure. The feed of monomers and the results of the elemental analysis of polymers are presented in Table 1, which indicated that the actual compositions were very close to those of the feed. The copolyamides obtained had inherent viscosities in the range of 0.52–0.99 dL/g.

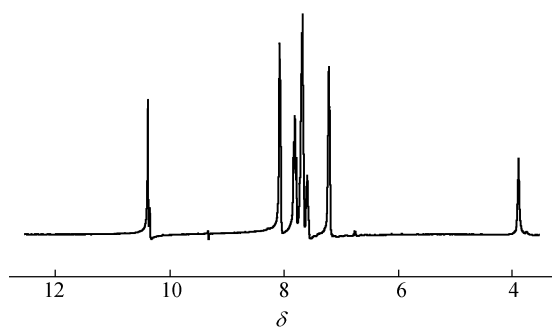


Fig. 1 ¹H-NMR spectrum of P2

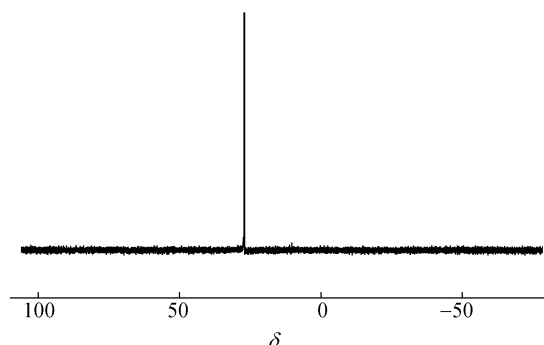


Fig. 2 ³¹P-NMR spectrum of P2

Table 1. Elemental analysis data for copolyamides

Sample	<i>n</i> BCPPO: <i>n</i> TPA: <i>n</i> DDM	Elemental analysis (wt%) ^a			η_{inh} (dL/g)
		P	C	H	
P1	1:0:1	5.82 (5.87)	75.2 (75.0)	4.71 (4.73)	0.52
P2	0.8:0.2:1	5.11 (5.08)	75.6 (75.2)	4.74 (4.75)	0.62
P3	0.6:0.4:1	4.13 (4.15)	75.3 (75.5)	4.81 (4.78)	0.99
P4	0.5:0.5:1	3.57 (3.62)	76.3 (75.7)	4.77 (4.79)	0.98
P5	0.4:0.6:1	3.08 (3.04)	76.4 (75.9)	4.82 (4.80)	0.90
P6	0.2:0.8:1	1.65 (1.68)	76.5 (76.3)	4.83 (4.84)	0.66

^aValues in parentheses represent calculated values which assumed that actual compositions were the same as those in feed.

Properties of the Phosphorous-Containing Copolyamides

The glass transition temperatures of polymers obtained from DSC and DMA are listed in Table 2, and Fig. 3 was the DMA curves of P2. The introduction of phosphine oxide improved the flexibility of the backbone, but pendant phenyl groups hindered the segmental motions. So the T_g values changed with the compositions of the copolyamides. The decomposition temperature of copolyamides in a nitrogen atmosphere was determined from the TGA thermograms. TGA curves of P2 were shown in Fig. 4. The T_d values at 5% weight loss were in the range of 423–469°C, and the char residues at 800°C were higher than 55%. The results showed that the phosphorous-containing copolyamides possessed good thermal stability.

Table 2. Thermal properties of copolyamides

Sample	T_g (°C) ^a	T_g (°C) ^b	T_d (°C) ^c	Char yield at 800°C (%)
P1	295	319	465	55
P2	292	313	463	62
P3	289	305	469	66
P4	287	302	463	63
P5	294	310	447	66
P6	302	—	423	69

^aValues from DSC; ^bValues from DMA; ^cTemperature at 5% weight loss

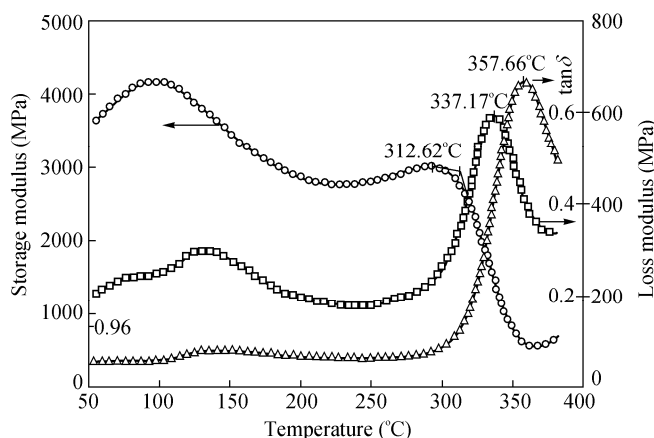


Fig. 3 DMA curves of P2

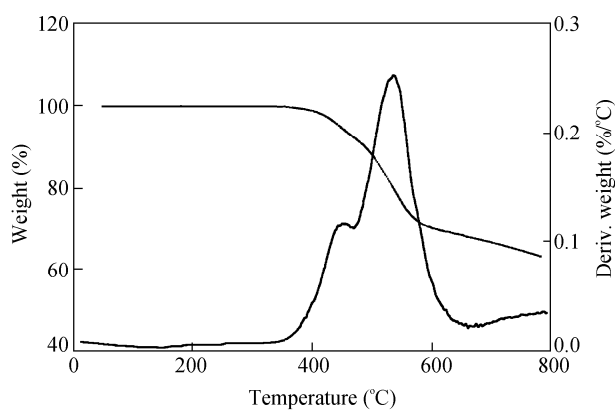


Fig. 4 TGA curves of P2

The solubility of copolyamides was shown in Table 3. All the polyamides, except for P5 and P6, were soluble in polar aprotic solvents at room temperature, such as NMP, DMAc, DMF, DMSO and *m*-cresol. P5 can be soluble in these solvent at elevated temperature. The results showed that the incorporation of BCPPO can improve the solubility of aromatic polyamides. The excellent solubility makes these polymers convenient for application in spin-in and casting processes.

Table 3. Solubility of copolyamides

Sample	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	Py	CHCl ₃	Toluene	THF
P1	+	+	+	+	+	—	—	—	—
P2	+	+	+	+	+	—	—	—	—
P3	+	+	+	+	+	—	—	—	—
P4	+	+	+	+	+	—	—	—	—
P5	+	+	±	±	±	—	—	—	—
P6	+	±	±	±	±	—	—	—	—

+ Soluble; ± Swelling at room temperature and soluble on heating; — Insoluble even on heating

Table 4 presents the tensile properties of the films prepared *via* solution casting. Tensile strengths were in the range of 45–95 MPa, elongations at break of 2%–9%, and initial moduli of 2.41–5.38 GPa. The films of polyamides showed a moderate extension to break, indicating strong and ductile materials.

Table 4. Tensile properties of copolyamide films

Sample	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation to break (%)
P1	3.57	48	2
P2	4.12	65	2
P3	2.41	78	6
P4	5.83	95	9
P5	3.82	87	9

CONCLUSIONS

Aromatic copolyamides were synthesized by the Yamazaki phosphorylation method starting from BCPPO, TPA and DDM. The copolymers obtained had high T_g s and good thermal stability. They were readily soluble in aprotic polar solvents such as NMP, DMAc, DMF and so forth. The copolyamide films were flexible and tough. This combination of properties qualifies them as potential high performance polymeric materials.

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