

Note

SYNTHESIS AND CHARACTERIZATION OF POLY(PHTHALAZINONE ETHER PHOSPHINE OXIDE)S BY N—C COUPLING REACTION*

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Abstract Based on several unsymmetrical, twist, noncoplanar phthalazinone-containing monomers **2a–2e** and an active bis(4-fluorophenyl)phenyl phosphine oxide (BFPPPO) monomer, a series of novel poly(phthalazinone ether phosphine oxide)s (PPEPO) was synthesized by anhydrous K_2CO_3 mediated N—C coupling reaction in DMAc. The polymers exhibited good thermal properties with T_g s ranging from 267°C to 306°C and 5% weight loss temperatures in nitrogen higher than 430°C, together with high char yield upon prolonged heating at 800°C (35%–56%). Moreover, the polymers were readily soluble in common organic solvents, such as *N*-methyl-2-pyrrolidone, chloroform and *m*-cresol. These polymers had inherent viscosities in the range of 0.45–0.72 dL/g and could be cast into flexible and colorless films by spin coating or casting approach.

Keywords: Phthalazinone; Poly(phthalazinone ether phosphine oxide)s; Synthesis.

INTRODUCTION

High performance polymers containing the phenylphosphine oxide moiety have received extensive attention recently, since the presence of the phenylphosphine oxide moiety in the polymers provides nonflammability and oxygen plasma resistance without sacrificing good thermooxidative stability and mechanical properties^[1–4]. The phenylphosphine oxide reacts with the atomic oxygen present in the oxygen plasma to form a phosphate layer which retards the erosion rate^[5]. These polymers have potential applications on spacecraft in low earth orbits (LEO). Moreover, introduction of the phosphine oxide group also increases the polarity of the polymers, which may improve the surface adhesion between the polymers and other materials, organic or inorganic, having hydroxyl groups, and probably serve as excellent proton acceptors^[6].

Previously, we reported a number of high performance poly(phthalazinone ether ketone)s which were synthesized by several methyl-substituted, phthalazinone-containing monomers with an active difluoro monomer based on a N—C coupling reaction^[7]. The introduction of an unsymmetrical, twist and noncoplanar phthalazinone architecture into the polymer backbone resulted in these polymers displaying high T_g s, good solubility and excellent thermal stability. Herein, we report the syntheses of novel poly(phthalazinone ether)s containing the phenylphosphine oxide moiety and investigate the effect of the bulky phthalazinone and the phenylphosphine oxide moieties on T_g s, solubility and thermal stability of the polymers.

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EXPERIMENTAL

Materials

N,N-dimethylacetamide (DMAc) was purchased from Shanghai Sinopharm Group and distilled under reduced pressure. Bis(4-fluorophenyl) phenyl phosphine oxide (**1**) was purchased from Aldrich chemical. 4-(4-Hydroxyphenyl)(2H)phthalazin-1-one (**2a**), 4-(2-methyl-4-hydroxyphenyl)(2H)phthalazin-1-one (**2b**), 4-(3-ethyl-4-hydroxyphenyl)(2H)phthalazin-1-one (**2c**), 4-(3-isopropyl-4-hydroxyphenyl)(2H)phthalazin-1-one (**2d**) and 4-(3-phenyl-4-hydroxyphenyl)(2H)phthalazin-1-one (**2e**) were synthesized according to the literature procedure^[7, 8]. All other chemicals were used without further purification.

Synthesis of Polymers 3a–3e

3d was used as an example (Scheme 1). A mixture of **1** (0.3143 g, 1 mmol), **2d** (0.2803 g, 1 mmol), K₂CO₃ (0.207 g, 1.5 mmol), 4 mL of DMAc and 4 mL of toluene was heated to 155°C for 5 h, then increased to 180°C for 16 h until the solution became very viscous. The solution was precipitated into 200 mL of 1:1 methanol/water containing 1 mL of acetic acid with stirring. The resultant polymer was washed with hot water, dissolved with chloroform and precipitated into methanol twice, then dried in vacuum to give the white, fibrous polymer **3d** (97% yield). The other polymers were synthesized by an analogous procedure described above.

3a: ¹H-NMR (400 MHz, CDCl₃, δ): 8.60 (m, 1H, 8-H), 7.95–7.13 (m, 20 H, ArH).

3b: 8.60 (m, 1H, 8-H), 7.91–7.00 (m, 19H, ArH), 2.35 (s, 3H, –CH₃).

3c: 8.60 (m, 1H, 8-H), 7.95–7.05 (m, 19H, ArH), 2.70 (q, 2H, –CH₂), 1.20–1.24 (t, 3H, –CH₃).

3d: 8.61 (m, 1H, 8-H), 7.95–7.07 (m, 19H, ArH), 3.29 (m, 1H, –CH), 1.25–1.26 (d, 6H, –(CH₃)₂).

3e: 8.61 (m, 1H, 8-H), 7.95–7.00 (m, 24H, ArH).

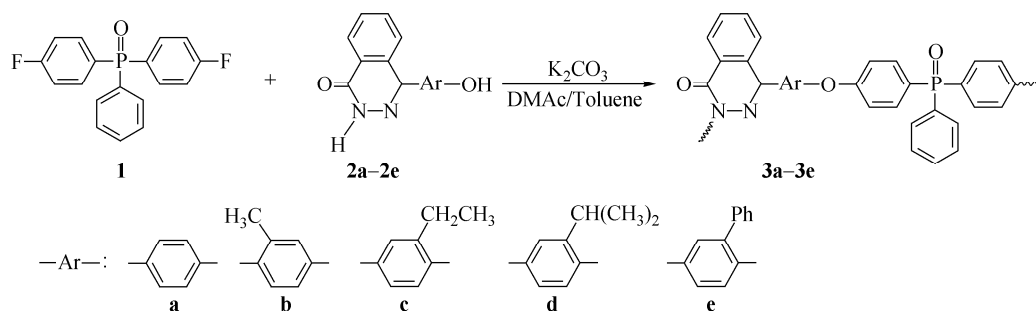
Measurements

FT-IR was recorded with KBr pellets on a Nicolet Nexus 670 FTIR spectrometer. ¹H-NMR spectra were measured on a Bruker DMX-400 instrument with chloroform (CDCl₃) as solvent and tetramethylsilane (TMS) as internal standard. DSC and TGA were performed on a Perkin Elmer DSC-7 and a TA instrument SDT-2960, respectively. Inherent viscosities of **3a–3e** were measured in CHCl₃ at 0.5 g/dL concentration with an Ubbelohde viscometer at 30°C.

RESULTS AND DISCUSSION

Polymer Synthesis

The synthesis of **3a–3e** is shown in Scheme 1. The phthalazinone –NH groups behaved like phenolic –OH groups during the polymerization, so **3a–3e** could be synthesized by a novel N–C coupling reaction^[9].



Scheme 1 Synthesis of **3a–3e**

The formation of **3a–3e** was confirmed by IR and ¹H-NMR spectra. The IR spectrum of **3d** exhibited an absorption at 1248 cm^{−1} corresponding to the ether linkage (C–O–C). There was no characteristic absorption in the range of 3100–3400 cm^{−1} for –NH and –OH. Moreover, two signals at δ = 12.72 and 9.71

corresponding to phthalazinone N–H and phenolic O–H protons of **2d** are absent in Fig. 1, and all other peaks shift to lower fields comparing to those of **2d**. The spectroscopic data of the other polymers gave results analogous to **3d**, which demonstrated that the structures were well matched with the assigned ones. A detailed assignment could not be made because of the strong overlap of aromatic proton peaks in ^1H -NMR.

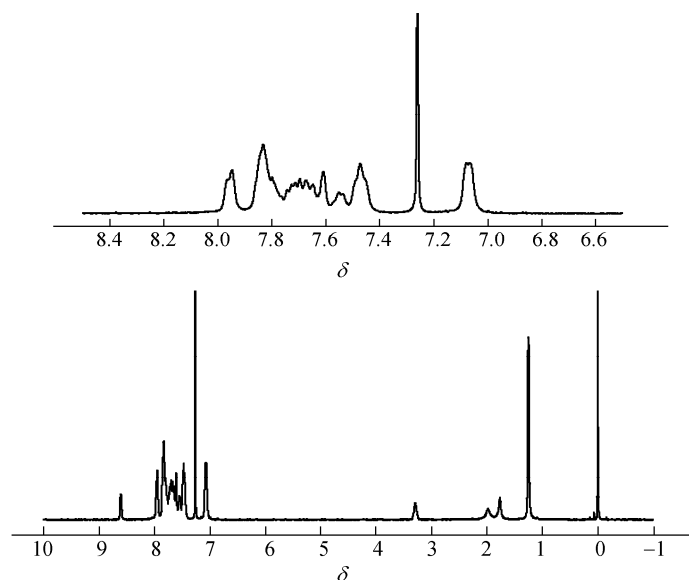


Fig. 1 ^1H -NMR spectra for **3d**

Solubility

As shown in Table 1, the good solubility could be attributed to the large free volume caused by twist, noncoplanar phthalazinone-containing moieties and phenylphosphine oxide architectures and the variation of the pendant substituted groups^[9, 10], which reduced the regularity of the main chain and led to the amorphous nature of **3a–3e**, so the polar solvent molecules could easily diffuse into the polymer containing strong polar moieties. The excellent solubility makes **3a–3e** potential candidates for practical applications in casting processes.

Table 1. Solubility of **3a–3e**

Polymer	CHCl_3	DMAc	DMF	NMP	THF	Pyridine	<i>m</i> -Cresol	Conc. H_2SO_4
3a	++	+	+	++	+-	++	+	++
3b	++	+	+	++	+-	++	+	++
3c	++	+	+	++	+-	++	+	++
3d	++	+	+	++	+	++	+	++
3e	++	+	+	++	+-	++	+	++

++ Fully soluble at room temperature; + Soluble; +- Partially soluble; - Insoluble

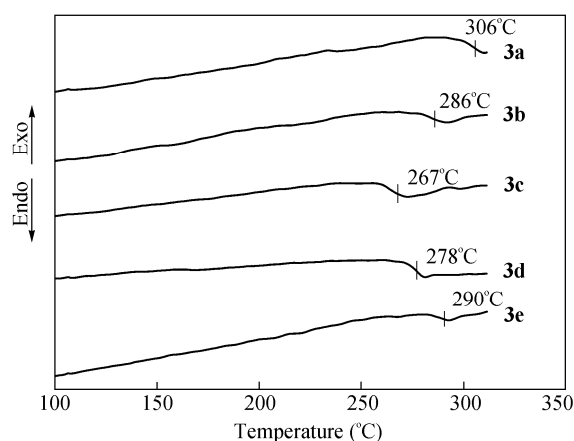
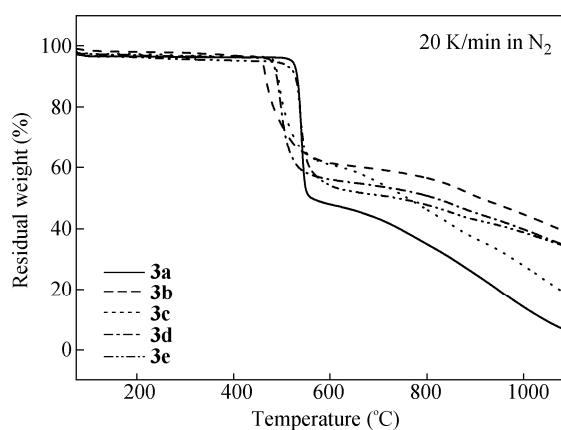
Thermal Properties

The thermal properties of **3a–3e** are listed in Table 2, and their corresponding DSC and TGA curves are shown in Fig. 2 and Fig. 3. The T_g s was in the range of 267–306°C. The introduction of various substituted groups increased probably the flexibility of the backbone, which led to **3b–3e** showing little lower T_g s than the nonsubstituted **3a**. The 5% weight loss temperatures were observed within the 434–521°C range. Moreover, **3a–3e** displayed high char yields of 35%–56% in nitrogen at 800°C. Obviously, the values demonstrated that incorporation of the phenylphosphine oxide caused an average decrease of 15% compared to our previously described non-phosphorus-containing polymers which displayed above 60% char yields^[7], but they were still considerably higher than those of the other phosphorus-containing thermoplastic^[11, 12]. The reason behind is still unknown, and is to be investigated in a future publication.

Table 2. Synthesis and properties of **3a–3e**

Polymer	Yield (%)	η_{inh}^a (dL/g)	T_g^b (°C)	T_d^c (°C)	T_d^d (°C)	Char yield ^e (%)
3a	96	0.45	306	521	532	35
3b	97	0.72	286	459	467	56
3c	91	0.58	267	483	492	46
3d	97	0.51	278	479	489	51
3e	91	0.57	290	434	528	48

^a Measured at a concentration of 0.5 g/dL in chloroform at 30°C; ^b From DSC measurements conducted at a rate of 10 K/min in nitrogen; ^c Temperature for 5% weight loss in nitrogen, heating rate of 20 K/min; ^d Temperature for 10% weight loss in nitrogen, heating rate of 20 K/min; ^e Residual weight when the samples were heated to 800°C in nitrogen

**Fig. 2** DSC curves of **3a–3e****Fig. 3** TGA curves of **3a–3e**

CONCLUSIONS

A series of novel poly(phthalazinone ether phosphine oxide)s **3a–3e** was synthesized by several unsymmetrical, twist, noncoplanar phthalazinone-containing monomers **2a–2e** and an active bis(4-fluorophenyl)phenyl phosphine oxide monomer **1** via an N–C coupling reaction. The polymers exhibited excellent thermooxidative stability, reasonable solubility and could be considered as good potential candidates for fire retardant materials and resistance to oxygen plasma. A further study of their application is in progress.

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