

Polyimides Possessing Bulky Phosphorus Groups: Synthesis and Characterization

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ABSTRACT: A series of polyimides with bulky pendent groups containing phosphorus were obtained from polymerization of various dianhydrides with a new diamine (2DOPO-A) bearing two bulky (9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl) (DOPO) substituents. The resulting polymers had inherent viscosities of 0.15–0.32 dL/g and glass transition temperatures of 260–283°C. The polyimides were soluble in some organic solvents due to the incorporation of bulky and polar DOPO groups. The non-coplanar cardo structure of 2DOPO-A also contributed to the improvement in the solubility of the polyimides. Incorporating DOPO groups into polyimides resulted in polymers with low

initial decomposition temperatures (IDT; 310–362°C) due to the independent decomposition of the DOPO groups. Thermogravimetric analysis showed that the DOPO-containing polyimides exhibited high integral procedural decomposed temperatures (IPDT) of 891–950°C. Incorporation of DOPO group into polyimides also improved their weight loss rate, thermal stability, thermal-oxidative stability, and heat insulating property in the high temperature region. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 791–796, 2003

Key words: polyimides; thermal properties; high performance copolymer

INTRODUCTION

In contrast to their excellent thermal and electrical properties, one of the main drawbacks of aromatic polyimides is their infusibility and poor solubility in organic solvents. Aromatic polyimides are therefore difficult to process by conventional methods. Among the methods utilized for improving the processing properties of aromatic polyimides, improvement of solubility has been the most attractive.^{1–4} Research efforts, including introduction of bulky substituents⁵ or flexible linkage,⁶ using fluoro-containing monomers,⁷ non-coplanar monomers,⁸ and nonsymmetrical monomers,⁹ have been investigated for synthesis of soluble polyimides in their fully imidized form.

Recently, phosphorus-containing monomers also showed their usefulness in the preparation of soluble polyimides.^{10–13} Introduction of the phenyl phosphine oxide group, which has a non-coplanar structure and highly polar P=O group, has significantly improved the solubility of polyimides. Utilization of monomers with another phosphorus group, 9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl (DOPO), which possesses a polar P=O group and a bulky structure, also resulted in polyimides with good solubility.¹³ Other attractive properties, such as flame retardancy, thermal-

oxidative stability, good adhesion, and low birefringence, were also observed for these phosphorus-containing polyimides.^{14,15} In the previous studies, a new diamine compound, 2DOPO-A, with two bulky pendent groups of DOPO, was prepared.^{16,17} 2DOPO-A possesses bulky and polar groups as well as a non-coplanar structure, which would contribute to the improvement of the solubility of the polymers. Incorporation of 2DOPO-A in aromatic polyamides has been shown to result in significant improvement in the solubility of the polymers.¹⁷

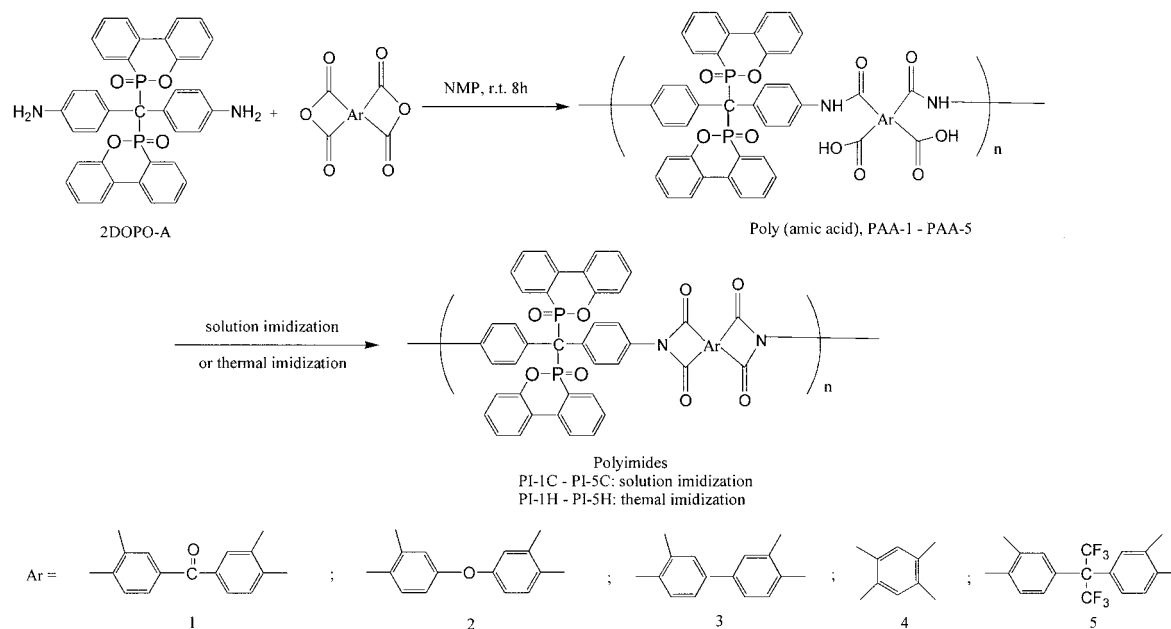
In the present work, 2DOPO-A was utilized in polyimide preparation by polymerizing with various dianhydrides. The resulting polymers, possessing bulky pendant groups, the polar phosphine oxide group, and a non-coplanar structure, were expected to show improved solubility in organic solvents. Both the conventional two-step method [preparation of poly(amic acid) followed by thermal imidization] and the one-pot method [preparation of poly(amic acid) and imidization in one solution] were performed to prepare polyimides. The chemical structure, solubility, inherent viscosity, and thermal properties of the resulting polyimides were characterized and are discussed.

EXPERIMENTAL

Materials

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) from ADD APT Chemical AG, the Nether-

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Scheme 1 Preparation of phosphorus-containing polyimides.

lands, was recrystallized from tetrahydrofuran prior to use. 4,4'-Diaminodiphenylbenzophenone (DABP) was obtained from Aldrich Chemical Company. 2DOPO-A (Scheme 1) was synthesized in the laboratory, according to the reported process.^{16,17} The dianhydrides of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic dianhydride (ODTA), 4,4'-bipthalic dianhydride (BPDA), pyromellitic dianhydride (PMDA), and 4,4'-(hexafluoroisopropylidene)diphthalic dianhydride (6FDA) were from Tokyo Kasei Kogyo Company and used as received.

Equipment

Infrared spectra were obtained with a Perkin-Elmer 2000 Fourier Transform Infrared Spectrophotometer (FTIR). The proton and phosphorus nuclear magnetic resonance spectra (¹H and ³¹P NMR, respectively) were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer. Elemental analysis was performed with an F002 Heraeus CHN-O rapid elemental analyzer employing 4-nitroaniline as a standard. The phosphorus contents of the synthesized monomer and polymers were determined by phosphorus elemental analysis with a Micro Digestion Apparatus with a spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded with a Thermal Analysis (TA) DSC-2900 differential scanning calorimeter at a heating rate of 20°C/min in nitrogen. Thermogravimetric analysis (TGA) was performed with a TA TGA-2950 thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen or air atmosphere. Wide-angle X-ray diffraction (WAXD) was performed

with a Rigaku X-ray diffractometer using Nickel filtered Cu-K α radiation.

Preparation of polyimides

Polyimides were synthesized by reacting stoichiometric amounts of diamine 2DOPO-A with aromatic dianhydrides at a concentration of 12% solids in *N*-methyl-2-pyrrolidinone (NMP). The formed poly(amic acid) was dehydrated to polyimide by a solution reaction or thermal treatment. A typical procedure for synthesizing PI-1 is given next as an example.

A 50-mL three-necked flask equipped with a nitrogen inlet and a stirrer was charged with 2.0 g (3.2 mmol) of 2DOPO-A and 22 g of NMP. After 2DOPO-A dissolved completely, the solution was cooled to 0°C with stirring. Then, 1.031 g (3.2 mmol) of BTDA was added to the solution in one portion. The solution was then warmed to room temperature and stirred for 8 h. Poly(amic acid) was obtained by precipitating poly(amic acid) solution from methanol. The precipitant was collected, washed with water and methanol, and dried *in vacuo* at 70°C for 12 h (PAA-1). Polyimide was obtained by reacting poly(amic acid) solution with acetic anhydride (2.6 g) and triethylamine (10 g). The mixed solution was allowed to react for another 24 h. The resulting solution was poured into methanol to give a white solid precipitant. The solid was collected and dried *in vacuo* at 100°C for 12 h (PI-1c, 93%). For thermal imidization, poly(amic acid) solution was cast on a glass plate. After being preheated *in vacuo* at 100°C for 12 h, the poly(amic acid) film was treated at 200°C for 2 h, 280°C for 1 h, and 280°C for 2 h. The film

TABLE I
Synthesis and Characterization of Polyimides

Sample	Elemental analysis Found % (calculated %)			FTIR absorption peak (cm ⁻¹)									
	C	H	P	N—H	C=O ^a	C—N ^b	C=O ^c	C=O ^d	C=O ^e	C—N ^f	P=O	P—O—Ph	P—Ph
PAA-1	68.01 (68.35)	3.44 (3.59)	6.2 (6.4)	3250	1650	1565	—	—	—	—	1216	932	1585
PAA-2	68.10 (67.95)	3.57 (3.63)	6.6 (6.6)	3452	1650	1565	—	—	—	—	1210	926	1585
PAA-3	69.32 (69.13)	3.78 (3.70)	6.6 (6.7)	3432	1655	1562	—	—	—	—	1209	932	1583
PAA-4	67.11 (66.82)	3.71 (3.55)	7.4 (7.3)	3428	1650	1560	—	—	—	—	1207	930	1580
PAA-5	62.54 (62.80)	3.44 (3.18)	5.7 (5.7)	3422	1650	1562	—	—	—	—	1195	922	1584
PI-1	70.71 (71.05)	3.14 (3.29)	6.4 (6.6)	—	—	—	1779	1725	716	1373	1212	925	1584
PI-2	71.02 (70.67)	3.24 (3.33)	6.7 (6.8)	—	—	—	1775	1717	712	1375	1197	919	1580
PI-3	72.21 (71.95)	3.55 (3.39)	6.8 (7.0)	—	—	—	1775	1717	712	1363	1200	919	1583
PI-4	70.10 (69.80)	3.36 (3.22)	7.7 (7.6)	—	—	—	1773	1719	720	1375	1204	922	1583
PI-5	64.47 (64.99)	3.02 (2.90)	5.9 (6.0)	—	—	—	1785	1719	714	1375	1194	924	1584

^a C=O stretching in amide.

^b C—N stretching in amide.

^c Asymmetric stretching of C=O in imide.

^d Symmetric stretching of C=O in imide.

^e C=O bending in imide.

^f C—N stretching in imide group.

was then washed with hot water and methanol, and dried *in vacuo* at 100°C for 12 h (PI-1h).

RESULTS AND DISCUSSION

The synthesis of the polyimides is shown in Scheme 1. After obtaining the poly(amic acid) solution, imidization was carried out in solution with acetic anhydride or by thermal treatment. The poly(amic acid) and polyimides thus formed were characterized with FTIR and elemental analysis (Table I). Characteristic absorption peaks in the FTIR spectra of poly(amic acid)s are found at 3250–3452 cm⁻¹ (—N—H), 1655–1650 cm⁻¹ (—C=O stretching of amide), and 1560–1565 cm⁻¹ (—C—N stretching of amide). After being cyclimidized, the polyimides show absorption bands corresponding to the characteristic imide bands at 1773–1779 cm⁻¹ (C=O asymmetric stretching), 1717–1725 cm⁻¹ (C=O symmetric stretching), 1363–1375 cm⁻¹ (C—N stretching), and 712–720 cm⁻¹ (C=O bending). Moreover, peaks are observed at 919–925

cm⁻¹ (P—O—Ph), 1194–1212 cm⁻¹ (P=O), and 1580–1584 cm⁻¹ (P—Ph) for all of the polyimides, denoting the maintenance of the cyclic DOPO groups in the fully-imidized polyimides.

The inherent viscosity of the polymers, measured in DMAc solution (0.5 g/dL) at 30°C, are in the range 0.15–0.32 dL/g (Table II). The inherent viscosities of the polyimides are not as high as other reported polyimides.^{5–9} However, the polyimides still have high enough molecular weights to permit the casting of films. Regardless of the anhydrides employed, all of the polyimides exhibit amorphous patterns in the WAXD analysis. The bulky pendent DOPO groups might increase the distance between chains, inhibit the chain packing, and decrease the interaction of the polymer chains, therefore resulting in an absence of crystallinity.¹³ The amorphous nature of the polyimides is also reflected by their transparency and improved solubility.

The solubility behavior of these polyimides was tested in various solvents, and the results are collected

TABLE II
Basic Property Data of Polyimides

Sample ^a	Inherent viscosity (dL/g)	T _g (°C)	T _d ^c		Char residue at 700°C (%)		Char residue at 800°C (%)	
			N ₂	Air	N ₂	Air	N ₂	Air
PI-1	0.15	263	387	408	61.9	50.8	58.5	25.5
PI-2	0.32	262	433	427	60.9	56.8	58.4	36.3
PI-3	— ^a	283	436	455	64.5	69.0	61.8	57.1
PI-4	0.21	257	425	395	62.3	54.5	58.3	17.6
PI-5	0.25	267	459	415	50.6	6.3	48.8	1.8
PI-6	— ^a	— ^b	565	562	64.0	3.6	61.3	0.7

^a Not soluble in DMAc.

^b Not found in the DSC scans.

^c Temperature at 10% weight loss.

TABLE III
Solubility of the Poly(amic acid)s and Polyimides in Organic Solvents^a

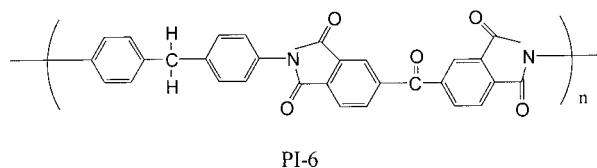
Polymer	Solvent ^b					
	NMP	DMAC	DMF	DMSO	Pyridine	THF
PI-1c	⊙	⊙	⊙	○	○	X
PI-2c	○	○	○	○	○	X
PI-3c	X	X	X	X	X	X
PI-4c	○	○	X	X	X	X
PI-5c	⊙	⊙	⊙	⊙	⊙	○
PI-6c ^c	X	X	X	X	X	X
PI-1h	X	X	X	X	X	X
PI-2h	○	○	○	○	○	X
PI-3h	X	X	X	X	X	X
PI-4h	X	X	X	X	X	X
PI-5h	○	○	○	○	○	○
PI-6h ^c	X	X	X	X	X	X

^a⊙: soluble at room temperature; ○: soluble in hot solvent; X: insoluble.

^bNMP: *N*-methyl-2-pyrrolidinone; DMAC: dimethyl acetamide; DMF: dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

^cDOPO-free polyimide.

in Table III. For evaluating the effect of DOPO on the solubility of the polyimide, poly(amic acid) (PAA-6) and polyimide (PI-6) based on 4,4'-diaminodiphenylmethane (DDM) and BTDA were prepared as reference samples (see structure).



The enhancement in solubility of the polymers by incorporating DOPO groups is first observed for PI-1c, which shows better solubility than its DOPO-free analogue PI-6c. Furthermore, except for PI-3c and PI-4c, the DOPO-containing polyamides are soluble in NMP, dimethyl acetamide (DMAC), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine at room temperature or on heating. PI-5c, being soluble in all the tested solvents, shows the best solubility. The excellent solubility of PI-5c can be attributed to the bulky, polar, and non-coplanar DOPO groups and the utilization of 6FDA.^{8b} However, the polyimides prepared by thermal imidization show decreased solubility in organic solvents compared with the polyimides prepared by solution imidization. Only PI-2h and PI-5h exhibit solubility in hot polar solvents. Solution imidization is known to promote isoimide formation to result in organosoluble polymers. On the other hand, thermal treatment might direct a chain ordering of polyimides to increase chain-to-chain interaction, thereby, reducing their solubility.^{9a}

The glass transition temperature (T_g) of the polyimides, obtained from the second heating scan of DSC measurements, are in the range 257–283°C. PI-3 exhib-

its the highest T_g among the polyimides because it possesses the rigid biphenyl group in the polymer backbone. The DOPO group might inhibit free rotation of the polymers and add rigidity to the polymer backbone, causing an increase in the T_g . However, the T_g of DOPO-containing polyimides is not as high as those of the other polyimides. The relatively low T_g of the polymers can be explained by the bulky DOPO groups, which significantly increase the free volume of the polymers and reduce their T_g .

Stress-strain tests indicate that PI-1c film has a tensile strength of 83 MPa. The tensile strength of the DOPO-containing polyimide (PI-1c) is comparable to that of the DOPO-free analogue PI-6h, which has a tensile strength of 105 MPa. The high tensile strength and film formability also suggest that the prepared DOPO-containing polyimides have high molecular weights. However, the low viscosity of the polyimide solution is unusual, and might be because DMAC is not a good solvent for the DOPO-containing PI.

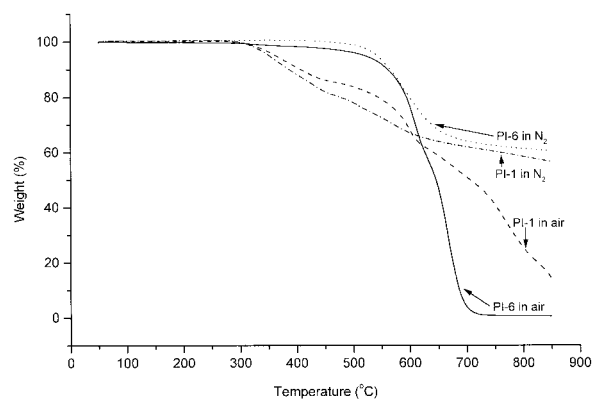


Figure 1 TGA thermograms of PI-1 and PI-6.

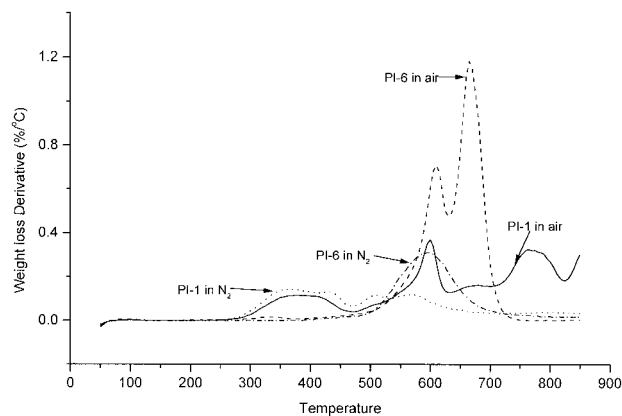


Figure 2 Differential TG (DTG) thermograms of PI-1 and PI-6.

The thermal decomposition behavior of the polyimides was investigated by TGA. The initial decomposition temperature and the weight loss behavior of the DOPO-containing polyimide PI-1 as well as that of the referenced sample PI-6 are shown in Figures 1 and 2. A weight loss at relatively low temperatures (~ 300 – 450°C at 5% weight loss), due to the decomposition of the DOPO pendent groups, is observed for PI-1 but not for PI-6. This weight loss at low temperature indicates that the DOPO-containing polyimides are not as thermally stable as the phosphorus-free polyimides. However, good thermal stability is observed for triphenylphosphine oxide-based polyamide and imide.¹¹ The low thermal stability of the prepared polymers might be due to the weak P—O bonds in the DOPO structure. On the other hand, low initial decomposition temperature is very commonly observed for phosphorus polymers.^{17,18} The phosphorus groups decomposing in the low temperature region result in char with extra thermal stability to retard the weight loss rates of the polymer residue and high char yields at high temperature region.¹⁸ This specific decomposition pattern has been determined to afford flame retardancy to the polymers.¹⁹ However, improving the

flame retardancy of polyimides is not critical because most polyimides exhibited good flame retardancy without modification. On the other hand, the thermal stability of the phosphorus-containing polyimides at high temperature under air atmosphere is noteworthy. As shown in Figure 1, the weight loss rate of PI-1 at temperatures $>600^\circ\text{C}$ is significantly lowered, especially when heated in air. The maximum weight loss temperature of polyimides heated in air is observed from 650°C (PI-6 in air) to 800°C (PI-1 in air). This result indicates that the incorporation of the DOPO group might enhance the thermal oxidative stability of polyimides.

The thermal stability of the DOPO-containing polyimides was probed further with another reliable degradation temperature, the integral procedural decomposition temperature (IPDT).^{20–22} Following Doyle's procedure,²⁰ the IPDTs of the polyimides were obtained from TGA analysis under nitrogen atmosphere (Table IV). The results clearly indicate that the IPDTs of the polyimides are significantly enhanced by incorporating the phosphorus DOPO group into the polymers. Therefore, it can be concluded that the thermal stability of the polyimides at high temperature is improved by the incorporation of DOPO groups, which retard the thermal degradation rates of the polymers and enhance the thermal stability of the residual polymer. Meanwhile, the formed phosphorus char is highly heat-resistant, which enhances the heat-insulating properties of the polyimides at high temperatures. These characteristics indicate that DOPO-containing polyimides are potentially useful for some heat-insulating materials.

The IPDTs of the polyimides in the temperature region 50 – 450°C were also measured. All DOPO-containing polyimides have an IPDT of $\sim 421^\circ\text{C}$. The unique IPDT implies that the degradation in this temperature region (50 – 450°C) is independent of the polyimide backbone structure. As already mentioned, this degradation is attributed to the DOPO group.

TABLE IV
Thermal Stability Parameters for Polyimides^a

Sample	1 st Stage weight loss		2 nd Stage weight loss		Thermal stability parameters for overall polymer degradation				Thermal stability parameters for degradation from DOPO groups			
	T_{\max} (°C)	R_{\max} (%/°C)	T_{\max} (°C)	R_{\max} (%/°C)	A^*	K^*	A^*K^*	IPDT (°C)	A^*	K^*	A^*K^*	IPDT (°C)
PI-1h	365	0.142	561	0.119	0.8189	1.3145	1.0764	911	0.9709	1.0352	1.0051	422
PI-2h	358	0.083	558	0.085	0.8187	1.3165	1.0778	912	0.9813	1.0214	1.0023	421
PI-3h	33	0.075	575	0.068	0.8261	1.2718	1.0506	891	0.9868	1.0149	1.0015	421
PI-4h	371	0.099	555	0.108	0.8186	1.3174	1.0783	913	0.9798	1.0235	1.0028	421
PI-5h	396	0.054	555	0.101	0.7918	1.4209	1.1251	950	0.9948	1.0055	1.0003	420
PI-6h	—	—	598	0.309	0.8851	1.1853	1.0491	889	—	—	—	—

^a Measured with TGA at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen.

CONCLUSIONS

Polyimides prepared from 2DOPO-A and commercially available dianhydrides show improved solubility in organic solvent. High glass transition temperatures, good thermal stability at high temperatures, and moderate mechanical properties are also observed for the polyimides.

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