Synthesis and Properties of Aromatic Poly(ester amide)s with Pendant Phosphorus Groups

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ABSTRACT: Two series of phosphorus-containing aromatic poly(ester amide)s with inherent viscosities of 0.46–3.20 dL/g were prepared by low-temperature solution polycondensation from 1,4-bis(3-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩-oxaphosphorin-6-yl)naphthalene and 1,4-bis(4-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)naphthalene with various aromatic diacid chlorides. All the poly(ester amide)s were amorphous and readily soluble in many organic solvents, such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP). Transparent, tough, and flexible films of these polymers were cast from DMAc and NMP solutions. Their casting films had tensile strengths of 71–214 MPa, elongations to break of 5–10%, and initial moduli of 2.3–6.0 GPa. These poly(ester amide)s had glass-transition temperatures of 209–239 °C (*m*-series) and 222–267 °C (*p*-series). The degradation temperatures at 10% weight loss in nitrogen for these polymers ranged from 462 to 489 °C, and the char yields at 800 °C were 55–63%. Most of the poly(ester amide)s also showed a high char yield of 35–45%, even at 800 °C under a flow of air. The limited oxygen indices of these poly(ester amide)s were 35–46. © 2002 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 40: 459–470, 2002; DOI 10.1002/pola.10129

Keywords: poly(ester amide)s; pendant phosphorus group; phosphorus-containing diesteramines; flame retardance; high-performance polymers; high-temperature materials

INTRODUCTION

Wholly aromatic polyamides (aramids) are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties.[1] However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms because of their high melting or glass-transition temperatures (T_g's) and their limited solubility in organic solvents.[2] Therefore, a great deal of effort has been expended to improve the processing characteristics of the relatively intractable polymers.[3–8] These studies include introducing flexible segments into the polymer chain; replacing symmetrical aromatic rings with unsymmetrical ones, which leads to a reduction in crystallinity; introducing bulky pendant groups to minimize crystallization; and forming a noncoplanar structure, thereby making crystallization impossible. Conventionally, it is convenient to synthesize

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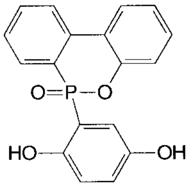
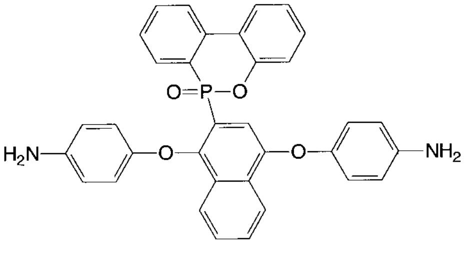
modified aramids via the incorporation of bulky pendant groups into diamine or dicarboxylic acid monomers, followed by polycondensation.[9–13] If the pendant groups are carefully chosen, it is possible to promote solubility without impairment of the thermal and mechanical properties to any great extent.

Phosphorus (P)-containing polymers have been known for many years to exhibit the primary advantage of flame retardancy, and they are increasingly gaining popularity over their halogen counterparts because they generally generate less toxic combustion products. The incorporation of organophosphorus functionality, either within the parent chain or as groups appended to it, has led to the production of inherently fire-retardant polymers. Several systems have been reported on poly(arylene ether)s, polyimides, polyamides, polyesters, and bismaleimide and epoxy networks.[14–39] Recently, Wang and coworkers[31–39] reported several P-containing polymer systems based on (6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)hydroquinone (DOPOHQ), a P-diol derived from the addition reaction of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) to *p*-benzoquinone. Most of the DOPOHQ-derived polymers showed several useful properties and were considered promising flame-retardant high-performance engineering plastics or thermosets. In connection with our interest in preparing easily processable high-performance polymers containing naphthyl units, this article deals with the synthesis and basic characterization of novel aromatic poly(ester amide)s having bulky lateral P-containing groups while maintaining high aromatic contents and symmetrical 1,4-naphthalene structures simultaneously in the main chain. This study was undertaken with the dual aim of enhancing solubility with the introduction of a bulky pendant P-containing group and endowing fire retardancy upon the polyamides because the fire-retardant nature of P-containing materials is well known. Our strategy was based on the low-temperature solution polycondensation of the P-diesteramines 1,4-bis(3-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)-naphthalene (*m*-**3**) and 1,4-bis(4-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)naphthalene (*p*-**3**) with various aromatic diacid chlorides. *m*-**3** and *p*-**3** were readily prepared by chain extension from 2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol (**1**; see Scheme 1) with *m*- or *p*-nitrobenzoyl chloride followed by the reduction of the intermediate dinitro compounds. The P-diol **1** was easily obtained from DOPO and 1,4-naphthaquinone according to a similar synthetic procedure for DOPOHQ. Before this study, we attempted to synthesize a P-containing dietheramine, 2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-bis(4-aminophenoxy)naphthalene (P-NDEA), through the aromatic nucleophilic displacement of *p*-chloronitrobenzene with the phenolate ion of **1** followed by reduction. However, the experiment failed because the side-chain P—Ar bond of **1** was cleaved by alkaline hydrolysis during the nucleophilic chloro-displacement reaction due to the presence of basic potassium carbonate. As described recently,[40] a similarly disappointing result was also obtained when the fluoro-displacement reaction of *p*-fluorobenzonitrile with **1** in a basic condition was carried out to attain an intermediate P-containing bis(ether nitrile) as a precursor to a P-containing bis(ether acid). Therefore, we adopted a strategy similar to that reported by Wang and Lin[34] to prepare the *P*-diesteramines *p*-**3** and *m*-**3** and from them a series of poly(ester amide)s with laterally attached P groups. The solubility, tensile properties, crystallinity, thermal properties, and flammability of the obtained polymers were also investigated. We also provide a comparison of the solubilities and T_g's of the prepared polymers and the analogous series based on DOPOHQ reported by Wang and Lin.[34]



DOPOHQ

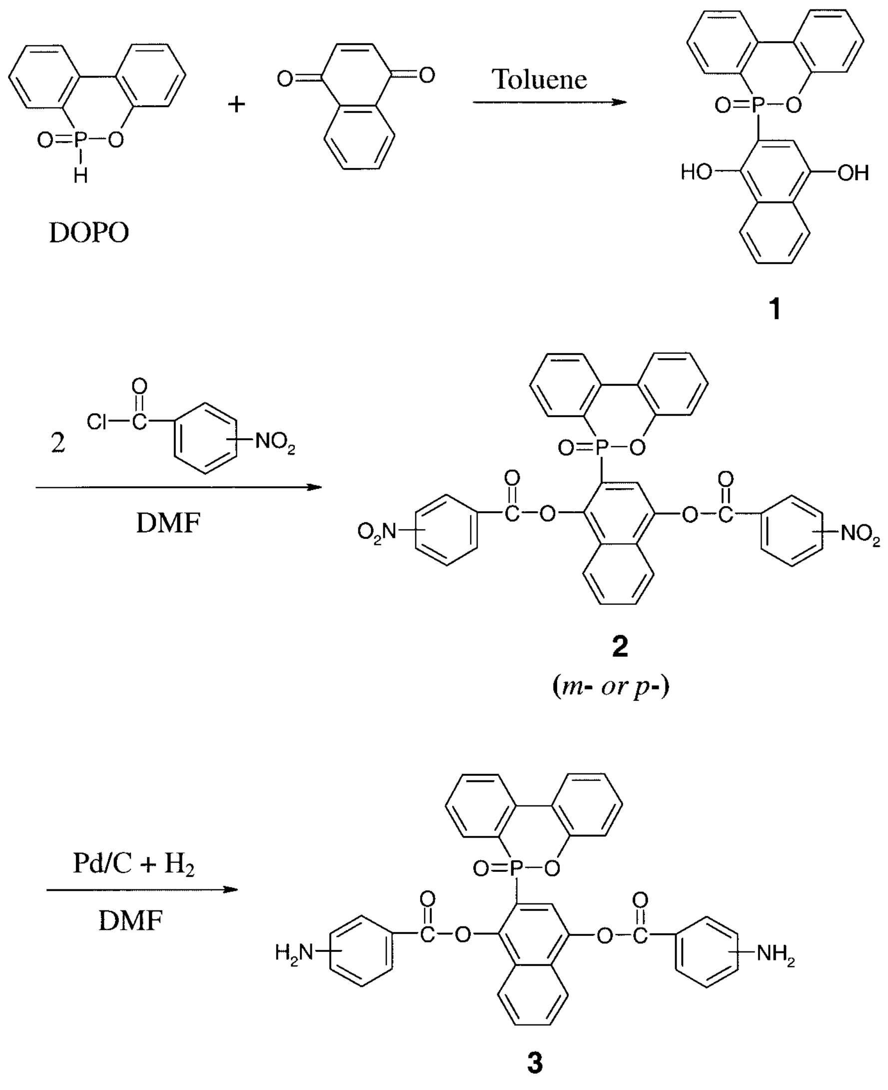


P-NDEA

EXPERIMENTAL

Materials

DOPO (from TCI), 1,4-naphthaquinone (from TCI), 3-nitrobenzoyl chloride, 4-nitrobenzoyl chlo-



Scheme 1

ride (from Fluka), and 10% Pd/C (from Lancaster) were used without further purification. According to a modification of the method reported by Endo et al.[41] and Wang and Lin,[35] the P-containing diol **1** (mp = 294–295 °C) was synthesized from the addition reaction of DOPO with 1,4-naphthaquinone. Details of the synthesis and characterization of **1** are described in another article.[40] As reported previously,[42] the P-diesteramines *m*-**3** (mp = 219–220 °C) and *p*-**3** (mp = 311–312 °C) were prepared by hydrogen Pd/C-catalyzed reduction of the dinitro compounds *m*-**2** and *p*-**2** resulting from the condensation reaction of **1** with 3-nitrobenzoyl chloride and 4-nitrobenzoyl chloride, respectively (Scheme 1). Terephthaloyl chloride (**4a**; mp = 83 °C) and isophthaloyl chloride (**4b**; mp = 45 °C; both from TCI) were purified by recrystallization before use. 4,4′-Sulfonyldibenzoyl chloride (**4c**; mp = 162 °C), 2,6-naphthalenedicarbonyl chloride (**4d**; mp = 191–192 °C), and 4,4′-oxydibenzoyl chloride (**4e**; mp = 90 °C) were prepared by chlorination of the corresponding dicarboxylic acids (all from TCI) with thionyl chloride in the presence of a few drops of *N,N*-dimethylformamide (DMF) as a catalyst[43] followed by recrystallization from toluene. 4,4′-(1,4-Phenylenedioxy)dibenzoyl chloride (**4f**; mp = 208–209 °C) was synthesized according to the published procedure.[44,45] DMF, *N,N*-dimethylacetamide (DMAc), and toluene were purified by distillation under reduced pressure over calcium hydride. Propylene oxide (PPO; from TCI) was used as received.

Synthesis of the Poly(ester amide)s

The synthesis of poly(ester amide) *p*-**5a** is described here as an example to illustrate the general synthetic route used to produce the poly(ester amide)s. A solution of 1.225 g (2.0 mmol) of diamine *p*-**3** in 10 mL of dried DMAc was cooled to −10 °C in an ice–acetone bath. After that, 0.7 mL of PPO was added to the solution, and then 0.407 g (2.0 mmol) of **4a** was added. The mixture was stirred at −10 °C for 1 h and then at 25 °C for 15 h under nitrogen. The reaction mixture was slowly poured into 300 mL of methanol. The precipitated polymer was collected by filtration, washed well with hot methanol, and dried *in vacuo* at 100 °C. The yield was quantitative. The inherent viscosity of the polymer (*p*-**5a**) was 3.20 dL/g, measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30 °C.

IR (film): 3300 (N—H stretch), 1681 (amide carbonyl), 1740 (ester carbonyl), 1250, 1075 (C—O stretch), 1170 (P═O stretch), 1039, 1010, 931 cm^{-1} (P—O stretch). ELEM. ANAL. Calcd. for $(C_{44}H_{27}N_2O_8P)_n$ $[(742.68)_n]$: C, 71.16%; H, 3.66%; N, 3.77%. Found: C, 69.83%; H, 3.92%; N, 3.94%.

Preparation of the Poly(ester amide) Films

A solution of polymer was made by the dissolution of about 1 g of the poly(ester amide) in 10 mL of hot DMAc or *N*-methyl-2-pyrrolidone (NMP) to afford an approximately 10 wt % solution. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven overnight to remove the most of the solvent. The semidried film was stripped off from the glass substrate and further dried *in vacuo* at 160 °C for 8 h. The obtained films were about 90–120 μm thick and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

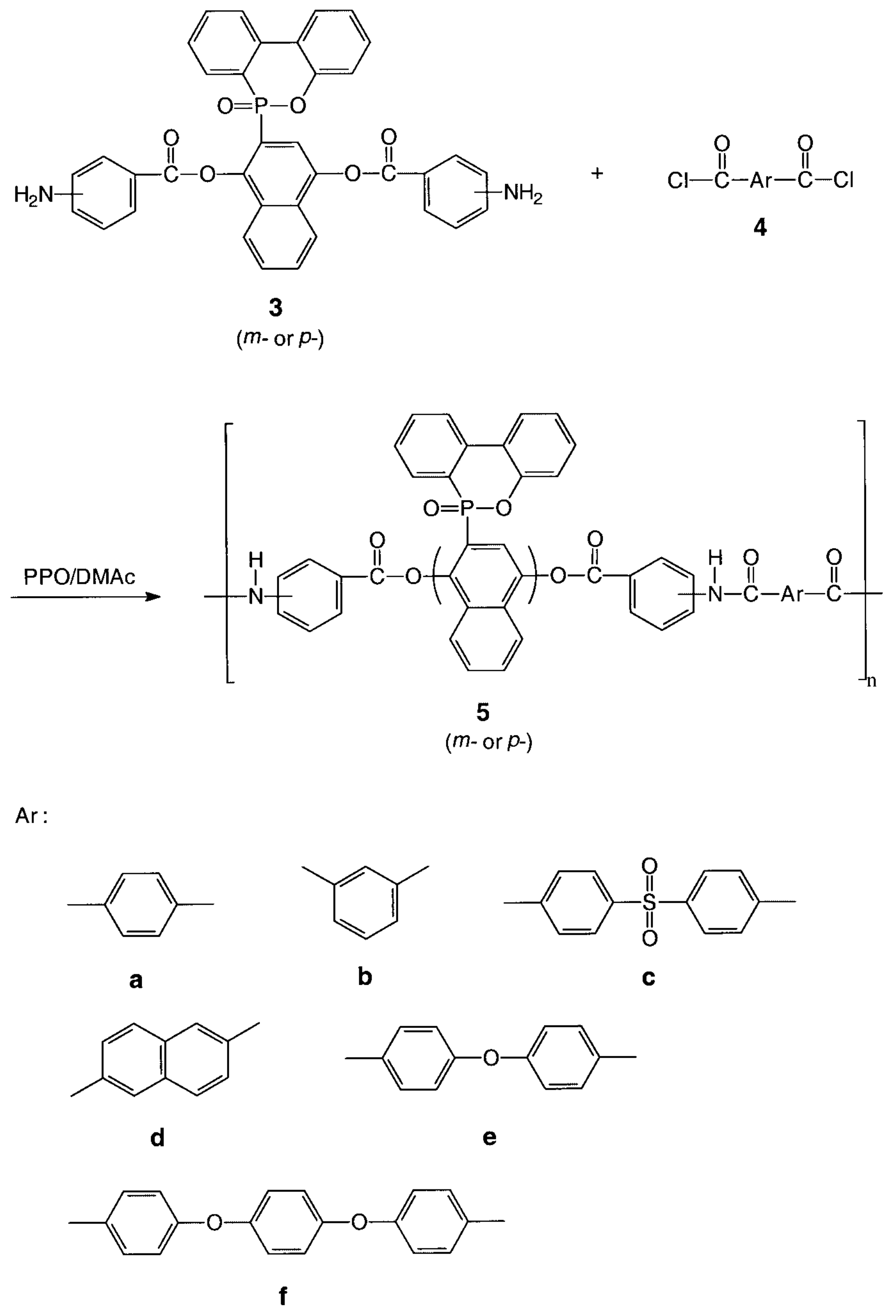
Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a PerkinElmer model 2400 CHN analyzer. ^1H NMR spectra were measured on a Varian Gemini 200 spectrometer with dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent and tetramethylsilane as the internal reference. The inherent viscosities were determined at a concentration of 0.5 g/dL in DMAc/5 wt % LiCl with a Cannon-Fenske viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on 3–5-mg samples heated in flowing nitrogen or air (30 cm^3/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) was performed on a PerkinElmer DSC 7 differential scanning calorimeter in flowing nitrogen (20 cm^3/min) at a heating rate of 20°C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 at a scan rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. The oxygen indices of the polymers were determined with a Suga ON-1 meter (made in Japan). The limited oxygen index (LOI) was defined as the minimum concentration of oxygen, expressed as a volume percentage, in a mixture of oxygen and nitrogen that was necessary to ignite and support a flame. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer with nickel-filtered Cu Kα radiation (40 kV, 15 mA), and the scanning rate was 2°/min. Measurements were performed with film specimens about 0.1 mm thick. An Instron model 1130 universal tester with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and ca. 90–120 μm thick), and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Polymer Synthesis

Two series of new P-containing poly(ester amide)s, *m*-**5a**–**5f** and *p*-**5a**–**5f**, were synthesized from diesteramines *m*-**3** and *p*-**3** with aromatic diacid chlorides (**4a**–**4f**) by low-temperature solution polycondensation in DMAc in the presence of PPO as an acid acceptor (Scheme 2). The parentheses in the formulas of these polymers indicate that the asymmetric moieties may appear in the polymer chain as shown or in the reverse orientation. All the reaction solutions were homogeneously transparent and became highly viscous, indicative of the formation of high molecular weights. Although the amino group in a position para to the carbonyl group of the diesteramine *p*-**3**



Scheme 2

is less basic than a normal aromatic diamine, such *p*-diamine was still sufficiently reactive to give high molecular weight polyamides when it was allowed to polymerize for a sufficient length of time. As shown in Table I, *m*-**5a–5f** and *p*-**5a–5f** were obtained with inherent viscosities of 0.46–0.89 and 0.52–3.20 dL/g, respectively. All the polymers had sufficiently high molecular weights to permit the casting of tough and flexible films.

The formation of poly(ester amide)s was confirmed with elemental analysis and IR and NMR spectroscopy. The FTIR spectra of the poly(ester amide)s showed characteristic absorptions of the amide group around 3300 (N—H stretch), 1670–1680 (carbonyl stretch), and 1530–1550 cm^{-1} (NH deformation). All the polymers also exhibited IR bands at 1740–1750 (carbonyl stretch) and 1250–1270 cm^{-1} (C—O stretch) due to the ester groups. The P=O stretching absorption occurred

Table I. Inherent Viscosities (η_{inh}) and Tensile Properties of the Poly(ester amide)s

		Tensile Properties of the Polymer Films[c]		
Polymer[a]	η_{inh} (dL/g)[b]	Tensile Strength (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
m-**5a**	0.63	95	5	4.0
m-**5b**	0.61	90	5	2.3
m-**5c**	0.71	93	6	2.6
m-**5d**	0.58	107	9	2.3
m-**5e**	0.46	71	5	2.3
m-**5f**	0.89	98	9	2.5
p-**5a**	3.20	214	9	6.0
p-**5b**	0.52	97	10	2.4
p-**5c**	1.06	110	8	3.2
p-**5d**	1.64	—[d]	—	—
p-**5e**	0.55	124	7	3.0
p-**5f**	0.63	116	8	3.0

[a] Polymerization was carried out with 2.0 mmol of each monomer and 0.7 mL of PPO in 10 mL of DMAc at −10 °C for 1 h and at 25 °C for 15 h.

[b] Measured at 0.5 g/dL in DMAc containing 5 wt % LiCl at 30 °C.

[c] Films were cast by slow evaporation of polymer solutions in DMAc.

[d] The polymer film puckered during solution casting from NMP.

in the region from 1160 to 1180 cm^{-1}. Two to three medium-intensity bands appeared from 900 to 1050 cm^{-1} (e.g., 931, 1010, and 1039 cm^{-1} for polymer *p*-**5a**), possibly because of coupled stretching and bending vibrations in the O═P—O groups. Figure 1 shows a typical set of FTIR spectra for poly(ester amide)s *p*-**5a** and *m*-**5a**, which had an isomeric repeat unit. Because almost all the polymers were soluble at room temperature or after heating in polar aprotic solvents, their NMR spectra could be recorded. The NMR spectra of the polymers were in agreement with the proposed structures. A typical ^{1}H NMR spectrum of poly(ester amide) *m*-**5a** (Fig. 2) in a DMSO-d_6 solution shows three singlets at 10.82, 10.56, and 10.50 ppm (amide H), a singlet at 8.85 ppm (aromatic H of terephthaloyl segments), and multiplets at 7.16–8.40 ppm (aromatic H of the other aromatic moieties). The multiple resonances for amide protons can be attributed to the constitutional disorder introduced by the asymmetrical diesteramine moieties, which gave rise to a random enchainment of the repeat units. In the ^{13}C NMR spectrum of polymer *m*-**5a**, the resonances in the downfield region (163–165 ppm) are ascribed to the carbonyl carbons of the ester and amide linkages. Similar to what was observed in a previous article,[42] the carbonyl carbon of the ester linkage ortho to the pendant P-containing group resonated as a doublet. The patterns appearing between 7.1 and 8.5 ppm in the ^{1}H NMR spectrum and between 120 and 150 ppm in the ^{13}C NMR spectrum peculiar to the aromatic units are more complex and so more difficult to interpret.

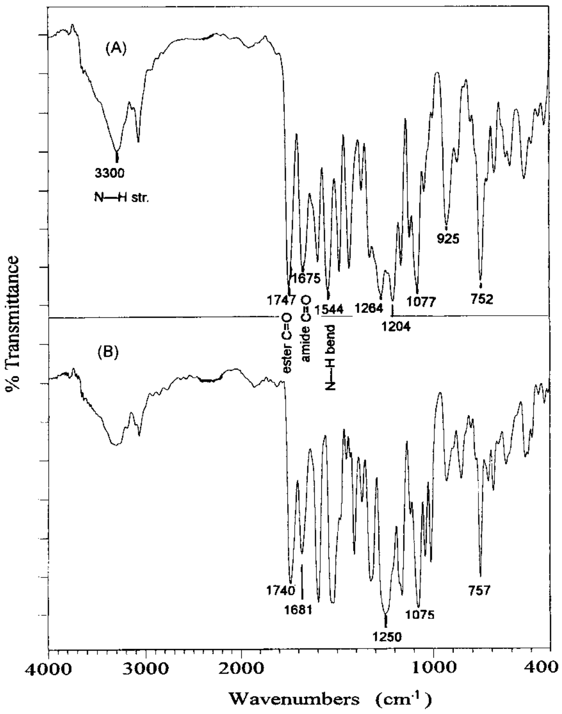


Figure 1. IR spectra of poly(ester amide)s (A) *m*-**5a** and (B) *p*-**5a**.

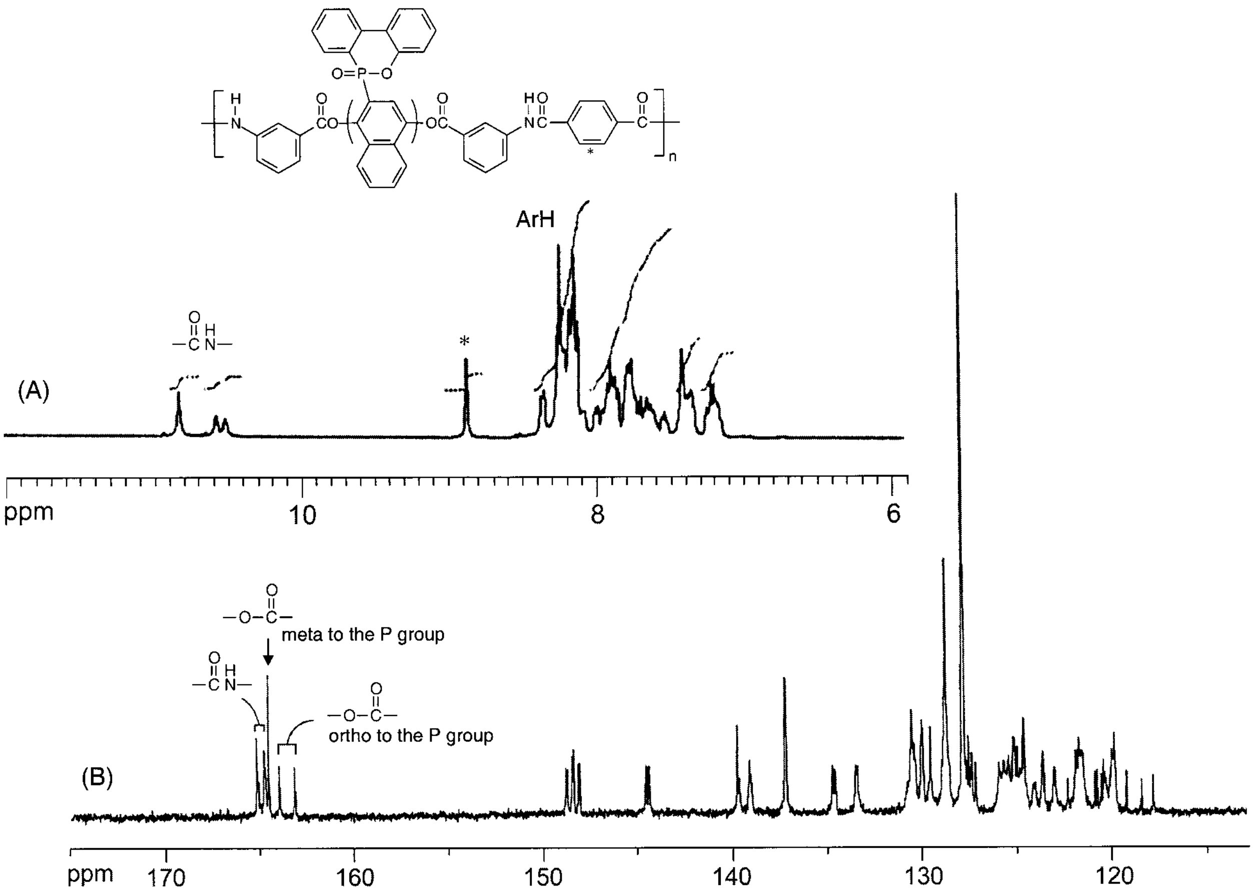


Figure 2. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of poly(ester amide) *m*-**5a** in DMSO-d_6.

Properties of the Polymers

As mentioned previously, except for polymer *p*-**5d**, all the poly(ester amide)s could be solution-cast into smooth, flexible, and tough films. These films were subjected to tensile testing, and the results are given in Table I. The tensile strengths, elongations to break, and initial moduli of these films were 71–214 MPa, 5–10%, and 2.3–6.0 GPa, respectively. Poly(ester amide) *p*-**5a**, derived from diamine *p*-**3** and **4a**, showed high tensile strength and modulus up to 214 MPa and 6.0 GPa, respectively. The relatively high strength and modulus of *p*-**5a** might have been caused by its high molecular weight and the high content of the *para*-phenylene unit in the main chain.

The solubility behavior of these poly(ester amide)s was tested in various solvents, and the results are summarized in Table II. Because of the introduction of a bulky lateral P-containing group and the 1,4-naphthalene structure of diamine **3**, all the poly(ester amide)s, except polymer *p*-**5d**, were readily soluble in polar solvents such as DMAc, NMP, DMF, and DMSO and even in less polar *m*-cresol. Polymer *p*-**5d** had poor solubility compared with other poly(ester amide)s due to the symmetrical and rigid backbone of the 2,6-naphthalene moiety in **4d**. Between these two series of isomeric poly(ester amide)s, the *m*-**5** series containing *meta*-phenylene rings showed higher solubility than the corresponding isomeric *p*-**5** series containing *para*-phenylene rings due to the more flexible backbones. The solubility studies also revealed that the *m*-**5** series exhibited better solubility than the corresponding analogues (the *m*-**5′** series; see the footnote in Table III) based on 1,4-bis(3-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)phenylene reported by Wang and Lin.[34] This could be attributed to the bulky effect of the 1,4-naphthyl units, which helped to prevent the close packing of chains in the *m*-**5** series. Therefore, the introduction of bulky side groups and 1,4-naphthyl units into the polymer backbone significantly improved the solubility of the poly(ester amide)s.

Table II. Solubility Behavior of the Poly(ester amide)s

	Solvent[a]					
Polymer	NMP	DMAc	DMF	DMSO	*m*-Cresol	Tetrahydrofuran
m-**5a**	+	+	+	+	+	−
m-**5b**	+	+	+	+	+h	−
m-**5c**	+	+	+	+	+	−
m-**5d**	+	+	+	+	−	−
m-**5e**	+	+	+	+	+	−
m-**5f**	+	+	+	+	+h	−
p-**5a**	+	+	+h	+	+h	−
p-**5b**	+	+	+	+	+h	−
p-**5c**	+	+	+	+	+	−
p-**5d**	+h	−	−	−	−	−
p-**5e**	+	+	+	+	+h	−
p-**5f**	+	+	+	+	+h	−

[a] The qualitative solubility was tested with 10-mg samples in 1 mL of solvent.
+ = soluble at room temperature; +h = soluble on heating at 100 °C; − = insoluble even on heating.

The good solubility makes these polymers potential candidates for practical applications in spin coating and casting processes.

The wide-angle X-ray diffraction studies of the polymers were performed with film specimens. The results indicated that all the polymers were completely amorphous. This could be attributed to the introduction of the packing-disruptive bulky biphenylenephosphonato lateral group and 1,4-naphthyl structure, which resulted in increased chain distances and decreased chain interactions. Therefore, the amorphous nature of these polymers was reflected in their excellent solubility.

The thermal stability of these poly(ester amide)s was studied with dynamic TGA. Typical TGA curves of a representative polymer (*p*-**5a**) in both air and nitrogen atmospheres are shown in Figure 3. Some thermal behavior data were determined from original thermograms and are tabulated in Table III. In general, all the polymers exhibited good thermal stability with insignificant weight loss up to 400 °C in air and up to 450 °C in nitrogen. The initial decomposition temperatures (T_d's; onset) were recorded from 454 to 478°C in nitrogen and from 431 to 476°C in air. The amount of carbonized residue (char yield) of these poly(ester amide)s in a nitrogen atmosphere was 55–63% at 800 °C. All poly(ester amide)s except those containing the sulfonyl group (*m*-**5c** and *p*-**5c**) also gave a high char yield (35–45%), even at 800 °C under a flow of air. The P-containing poly(ester amide)s self-extinguished as soon as the flame was removed. Apparently, these polymers are flame-resistant as well. As shown in Table III, the LOI values of the polymers ranged from 35 to 46%, indicating high intrinsic flame-retardant character. The flame retardancy of these polymers might be attributed to their high aromatic content and the effect of P.

IR spectra of the solid residues of the polymers after heat treatment were examined. Figure 4 shows IR spectra of a thin film of poly(ester amide) *p*-**5a** after being heated sequentially in air at 300, 350, 400, and 420 °C for 30 min each. The IR spectrum of polymer *p*-**5a** after heat treatment at 300 °C remained the same as before heat treatment. After 30 min of heating at 350 °C, a decrease in the relative intensities around 1740, 1250, and 1075 cm^{-1} indicated some loss of ester functionalities. After further heating at 400 °C for 30 min, an obvious decrease in the intensities of the ester absorption bands and C—H out-of-plane deformations of aromatics was observed. After further heat treatment at higher temperatures, such as 420 °C, the absorptions of the ester groups almost completely disappeared, whereas a high content of amide functionalities and aromatic skeletons was still detected. The characteristic P═O and P—O—Ph stretching was also detectable, which indicated an accumulation of P in the solid residue. This agreed with their high char yield at elevated temperatures. The aforementioned results show that these P-containing poly(ester amide)s seemed to start to decompose from the weaker ester linkages and could accumulate P in the condensed phase in the course of thermal decomposition.

Table III. Thermal Properties of LOIs of the Poly(ester amide)s

Polymer	T_g (°C)[a]	T_s (°C)[b]	T_d, Onset (°C)[c]		T_d, 10% (°C)[c]		Char Yield (wt %)[d]		LOI
			N_2	Air	N_2	Air	N_2	Air	
m-**5a**	231 (266)[e]	230	465	435	472	442	63	35	43
m-**5b**	214 (250)	208	459	435	467	442	62	35	43
m-**5c**	234 (261)	235	461	431	470	441	59	15	40
m-**5d**	239 (273)	237	458	467	469	475	55	39	45
m-**5e**	210 (250)	208	454	454	462	464	60	41	36
m-**5f**	209	202	468	467	483	478	60	43	35
p-**5a**	267	265	478	437	489	449	62	42	44
p-**5b**	247	235	456	455	464	468	57	42	41
p-**5c**	259	255	468	432	480	444	57	20	40
p-**5d**	263	252	463	476	474	487	61	45	46
p-**5e**	222	229	460	431	468	442	57	35	37
p-**5f**	227	224	464	441	475	452	56	41	35

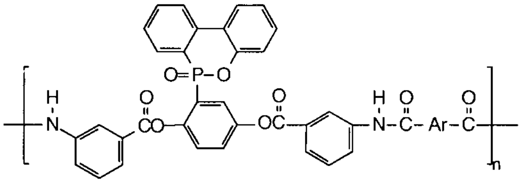
[a] The samples were heated from 30 to 400 °C at a scan rate of 20 °C/min; this was followed by rapid cooling to 30 °C at −100 °C/min in N_2. The midpoint temperature of the baseline shift on the subsequent DSC trace (from 30 to 400 °C at 20 °C/min) was defined as T_g.

[b] Taken as the onset temperature of the probe displacement on the TMA trace. The samples were heated at 250 °C for 30 min before the TMA test.

[c] Recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 30 cm^3/min.

[d] Residual weight percentage at 800 °C.

[e] Values in parentheses are the reported T_g's of analogous poly(ester amide)s (*m*-**5′**) with the corresponding —Ar— unit as in the *m*-**5** series (see ref. 34).



m-**5′**

DSC and TMA were used to evaluate the thermal transitions of the poly(ester amide)s. The influence of the residual solvent or the absorbed moisture and history of thermal annealing was sometimes observed in the first heating scan of DSC. The poly(ester amide)s were first heated to approximately 400 °C at 20 °C/min and then rapidly quenched to room temperature at a cooling rate of approximately −100 °C/min to form predominantly amorphous samples, so that T_g values of all the polymers could be easily measured in the DSC charts of the subsequent heating trace. The T_g values of the poly(ester amide)s *m*-**5** and *p*-**5** were observed at 209–239 and 222–267 °C, respectively, depending on the structure of the diacid chloride component, and decreased with the decreasing rigidity and symmetry of the polymer backbone. The T_g's of the *p*-**5** series poly(ester amide)s were about 12–36 °C higher than those of the corresponding *m*-**5** series counterparts because of the difference in symmetry between para and meta links. Compared with the corresponding poly(ester amide)s *m*-**5′** reported in the literature,[34] the *m*-**5** series of poly(ester amide)s showed T_g's decreased by 27–40 °C, possibly because of the increased polymer free volume caused by the naphthalene unit. None of the polymers showed clear melting endotherms from T_g to 400 °C on the DSC thermograms. This result supports the amorphous nature of these poly(ester amide)s. The softening temperatures (T_s's; also called the apparent T_g) of the polymer film samples were determined by the TMA method with a loaded penetration probe. They were obtained from the onset temperature of the probe displacement on the TMA trace. Typical TMA thermo-

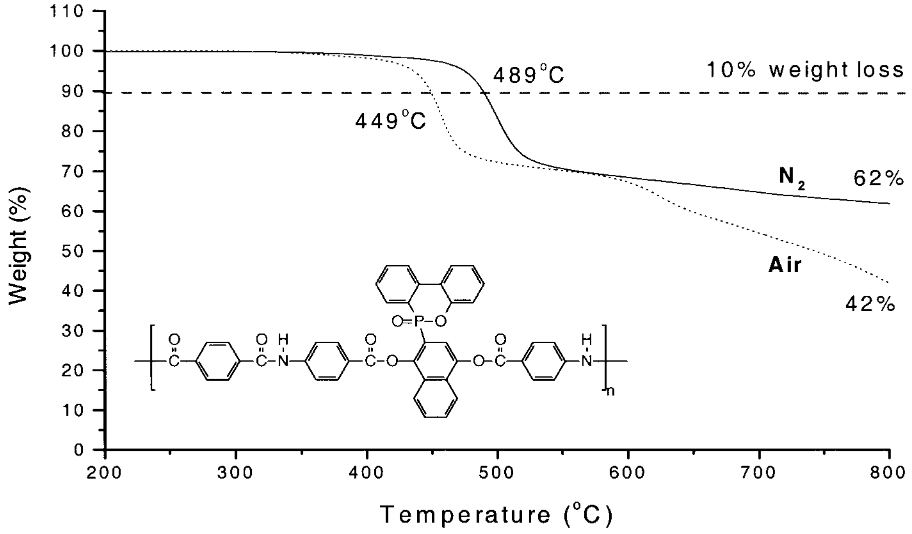


Figure 3. TGA thermograms of poly(ester amide) *p*-**5a** at a heating rate of 20 °C/min and a gas flow rate of 30 cm^3/min.

grams for polymers *p*-**5e** and *m*-**5e** are illustrated in Figure 5. The difference in the temperature dependence of the probe displacement of *p*-**5e** and *m*-**5e** clearly indicates the difference in their molecular mobility beyond T_g. Polymer *m*-**5e** showed a faster relaxation starting at about 208 °C that was attributable to a faster weakening of intermolecular interactions as the temperature increased. In most cases, the T_s values obtained by TMA were comparable to the T_g values measured by the DSC experiments. There was a large window between T_g or T_s and T_d of each polymer, which could be advantageous in the processing of these polymers by a thermoforming technique.

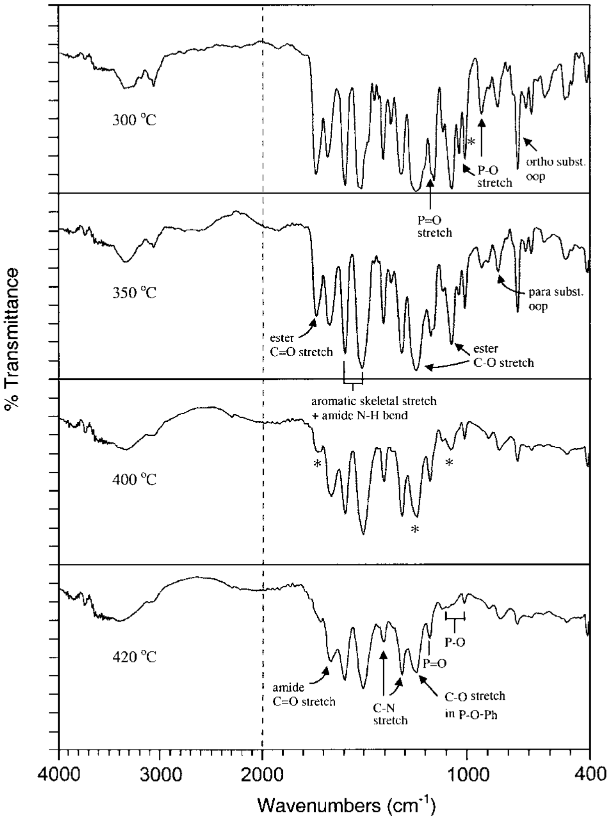


Figure 4. FTIR spectra (thin films) of poly(ester amide) *p*-**5a** after sequential heating in air at the indicated temperatures for 30 min each.

CONCLUSIONS

Two series of high molecular weight poly(ester amide)s were readily prepared from various combinations of P-diesteramine *m*-**3** and *p*-**3** with aromatic diacid chlorides (**4a–4f**) via a low-temperature solution polycondensation technique. Because of the presence of the bulky P-substituent and naphthalene unit, no crystallinity was observed for any of these polymers. Almost all the polymers had good solubility in many polar aprotic solvents and could be cast into transparent, tough, and flexible films. Good solubility, moderate T_g or T_s values suitable for molding, reasonable thermal stability, and good flame-retardant properties make these P-substituted poly(ester amide)s promising high-performance polymeric materials.

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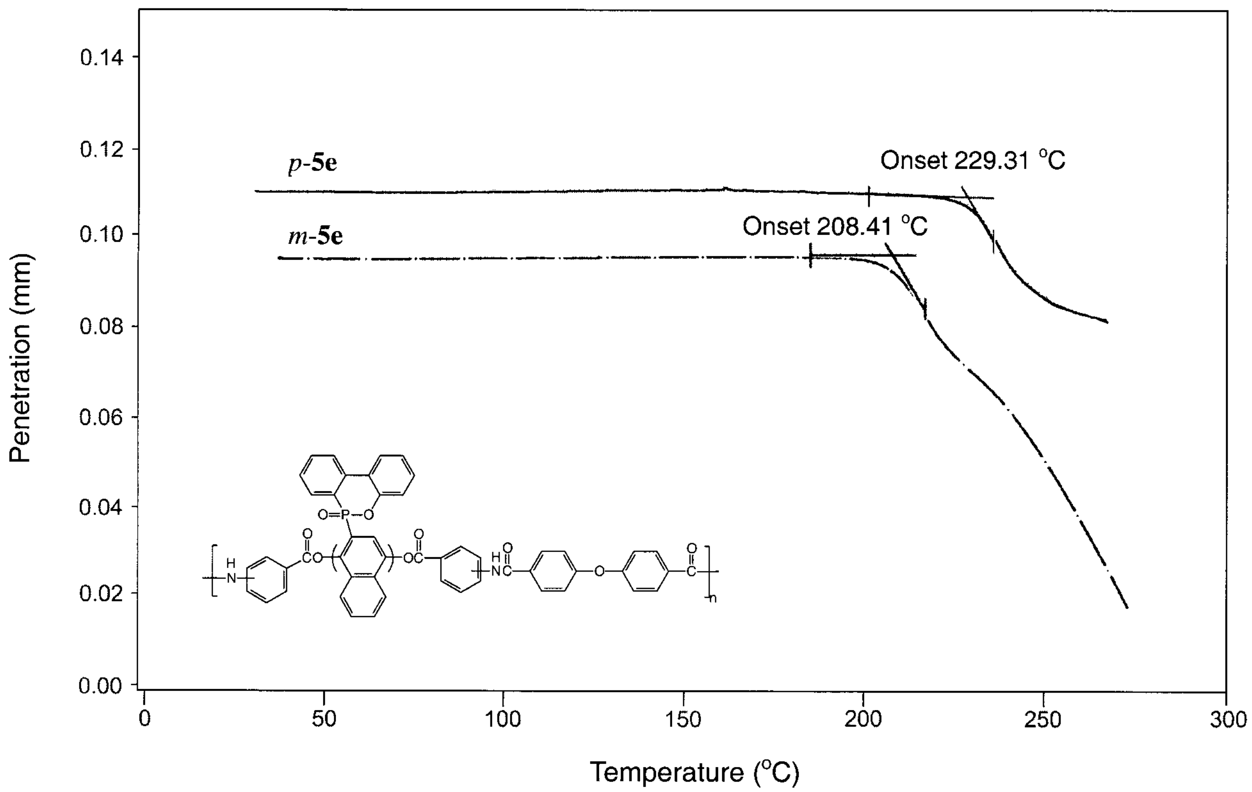

Figure 5. TMA thermograms of poly(ester amide)s *p*-**5e** and *m*-**5e** at a heating rate of 10 °C/min.

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