Synthesis and Properties of New Organosoluble and Alternating Aromatic Poly(ester-amide-imide)s with Pendant Phosphorus Groups

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ABSTRACT: New phosphorus-containing aromatic diesteramines, 1,4-bis(4-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)naphthalene (*p*-**3**) and 1,4-bis(3-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)naphthalene (*m*-**3**), were synthesized by the reaction of 2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol with 4-nitrobenzoyl chloride and 3-nitrobenzoyl chloride, respectively, followed by catalytic reduction. Two series of phosphorus-containing aromatic poly(ester-amide-imide)s with inherent viscosities of 0.94–2.00 and 0.41–0.56 dL/g were prepared via low-temperature solution polycondensation from *p*-**3** and *m*-**3**, respectively, with three imide ring-preformed diacid chlorides. All the poly(ester-amide-imide)s were amorphous and readily soluble in many organic solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP). Transparent, tough, and flexible films of these polymers were cast from DMAc or NMP solutions. Their casting films possessed a tensile strength range of 118–181 MPa, an elongation to break of 5–11%, and an initial modulus range of 2.41–4.46 GPa. They had useful levels of thermal stability associated with relatively high glass-transition temperatures (264–286 °C) and 10% weight-loss temperatures in excess of 450 °C in nitrogen or air. The limiting oxygen indices of these polymers were 41–46. © 2001 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 39: 1786–1799, 2001

Keywords: poly(ester-amide-imide)s; pendant phosphorus group; imide ring-preformed diacid chlorides; phosphorus-containing diesteramines

INTRODUCTION

Among the various heterocyclic polymers investigated for high-performance applications, aromatic polyimides are used widely in the semiconductor and electronic-packaging industries because of their outstanding thermal stability, good insulation properties with a low dielectric constant, good adhesion to common substrates, and superior chemical stability.[1,2] 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. Most conventional processing techniques involve the fabrication of polyamic acid precursors followed by thermal or chemical imidization. Problems can

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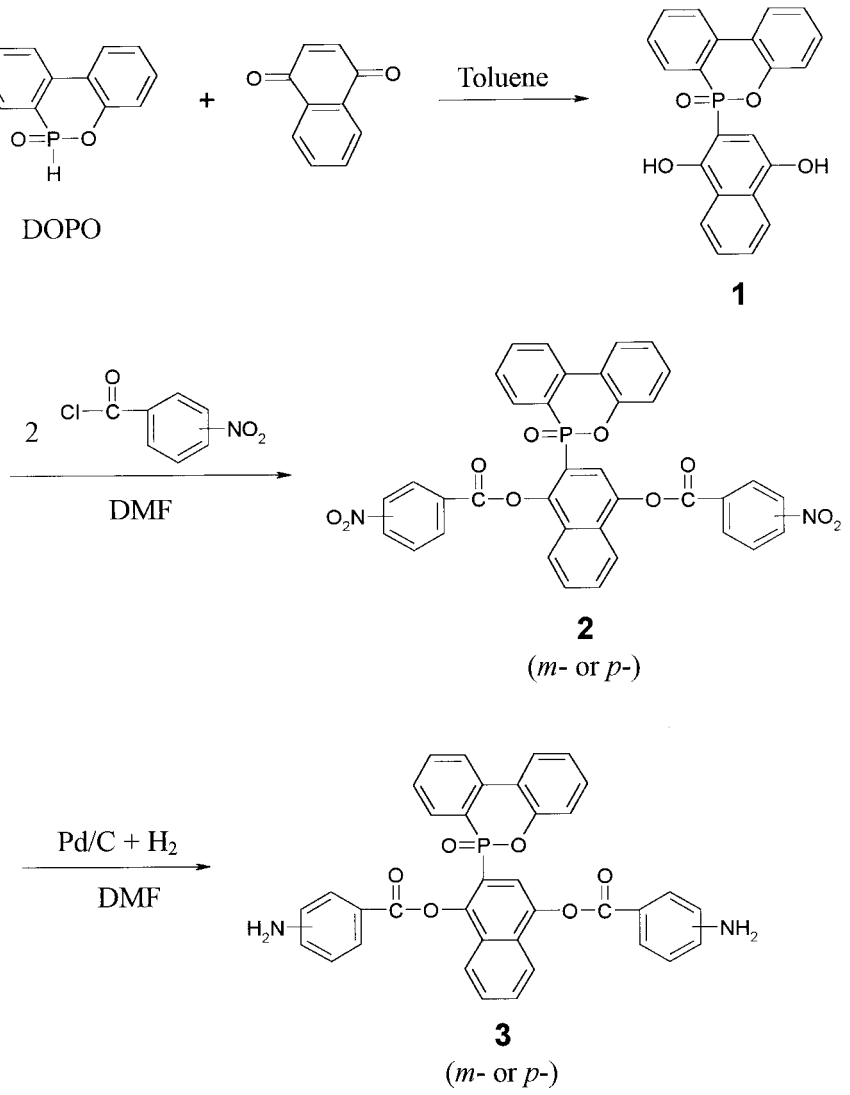
arise because polyamic acids are thermally and hydrolytically unstable. The water evolved from imidization can also form voids in bulk materials. Therefore, a great deal of effort has been expended to improve the processing characteristics of these relatively intractable polymers.[3–8] Attempts in this area 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. In addition, it is well known that the synthesis of poly(amide-imide)s can offer a compromise between excellent thermal stability and tractability.[9] On the other hand, the incorporation of a bulky aromatic pendant group onto a polymer macrochain is known to impart processability to the polymer with little reduction in thermal properties. Several polymer systems, such as poly(amide-imide)s,[10] poly(ester-imide)s,[11] poly(ether-imide)s,[12] and poly(benzoxazole-imide)s,[13,14] have been chemically modified by the polycondensation of monomers bearing bulky pendant groups.

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.[15–21] Kannan et al.[17] developed flame-retardant polyamide phosphate esters; however, their decomposition temperatures (T_d's), 250–300 °C, are not high enough. This phenomenon could be attributed to the polyphosphate amides having O═P—O bonds in the main chain. The polymers degrade rapidly during heating because the O═P—O bonds in the main chain cleave. Thus, to increase the thermal stability and maintain flame retardancy, one should covalently incorporate the O═P—O group into polymeric systems in side chains as pendant groups.[15,21] In this article, we report the synthesis of novel P-containing poly(ester-amide-imide)s with a bulky biphenylenephosphonato [O═P—O(Ph)$_2$] group in the side chain while a high aromatic content and symmetrical 1,4-naphthalene structure in the main chain were maintained simultaneously. This was undertaken with the dual aim of enhancing solubility due to the introduction of the bulky pendant biphenylenephosphonato groups and endowing fire retardancy upon the poly(ester-amide-imide)s because the fire-retardant nature of P-containing materials is well known. The additional introduction of ester linkages to the backbone was expected to bring about a reduction in the T_g values and a further increase in their solubility in organic solvents. These novel aromatic poly(ester-amide-imide)s were prepared by low-temperature solution polycondensation from the *P*-diesteramines 1,4-bis(4-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)naphthalene (*p*-**3**) and 1,4-bis(3-aminobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)naphthalene (*m*-**3**) with various imide ring-preformed aromatic diacid chlorides. The solubility, tensile properties, crystallinity, thermal properties, and flammability of the obtained polymers were also investigated.

EXPERIMENTAL

Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO; TCI), 1,4-naphthaquinone (TCI), 4-nitrobenzoyl chloride, 3-nitrobenzoyl chloride (Fluka), and 10% Pd/C (Lancaster) were used without further purification. According to reported procedures,[21(e),22] 2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)-1,4-naphthalenediol (**1**) [mp = 294–295 °C according to differential scanning calorimetry (DSC)] was prepared from the addition of DOPO to 1,4-naphthaquinone followed by a rearrangement reaction to a more stable aromatic structure. Details of the synthesis and characterization data of the P-containing diol **1** are described in another article.[23] As described in previous articles,[13,14] the imide ring-preformed diacid chlorides **4a**–**c** were prepared by the chlorination of the corresponding diimide-diacids 2,5-bis(trimilletimido)toluene, 1,4-bis(trimellitimido)-2,5-dimethylbenzene, and 1,4-bis(trimellitimido)-2,5-dichlorobenzene via thionyl chloride in the presence of trace amounts of *N,N*-dimethylformamide (DMF) as a catalyst. These diimide-diacids were prepared from the condensation reaction of the respective diamines with trimellitic anhydride.[9] DMF, *N,N*-dimethylacetamide (DMAc), and toluene were purified by distillation under re-



Scheme 1

duced pressure over calcium hydride. Triethylamine (from Aldrich) and propylene oxide (PPO; TCI) were used as received.

Synthesis of 1,4-Bis(4-nitrobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)naphthalene (*p*-2) and 1,4-Bis(3-nitrobenzoyloxy)-2-(6-oxido-6H-dibenz⟨*c,e*⟩⟨1,2⟩oxaphosphorin-6-yl)naphthalene (*m*-2)

Compound **1** (0.1 mol), which was dissolved in 300 mL of DMF, and triethylamine (0.22 mol) were introduced into a 500-mL flask equipped with a nitrogen inlet. After the reaction solution was cooled to 0–10 °C, 4-nitrobenzoyl chloride (0.22 mol) was added incrementally over 1 h, and the reaction mixture was maintained at room temperature for another 4 h. The precipitate was filtered, recrystallized from DMF twice, and then dried in a vacuum oven at 180 °C for 8 h to afford off-white crystals of *p*-**2** (70% yield).

mp: 332–333 °C (DSC). IR (KBr): 1348, 1539 (NO_2), 1240–1260 (C—O), 1739 cm^{-1} (C═O). ELEM. ANAL. Calcd. for $C_{36}H_{21}N_2O_{10}P$ (672.54): C, 64.29%; H, 3.15%; N, 4.16%. Found: C, 64.15%; H, 3.10%; N, 4.13%.

Dinitro compound *m*-**2** was synthesized from compound **1** and 3-nitrobenzoyl chloride according to the same procedure. Pure *m*-**2** (70% yield) was obtained as off-white crystals by two recrystallizations from DMF.

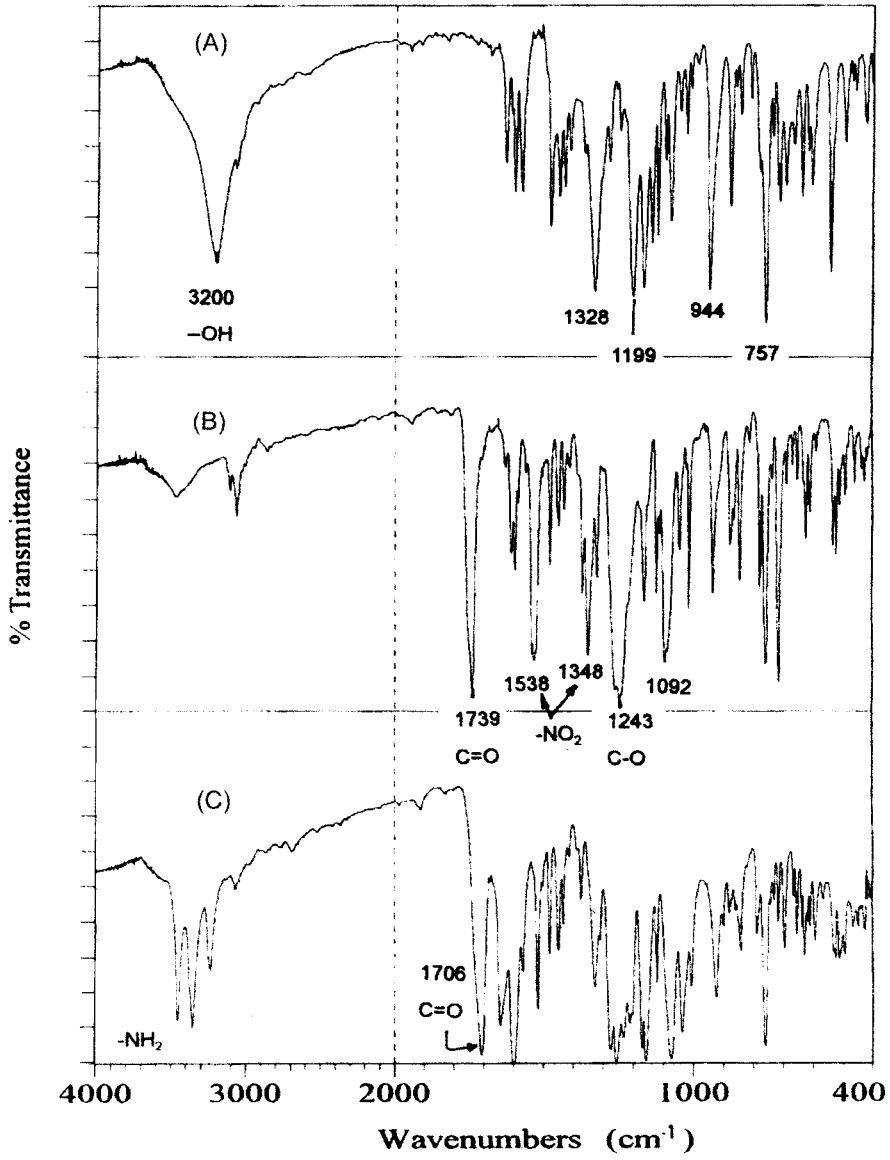


Figure 1. IR spectra of (A) P-containing diol **1**, (B) dinitro compound *p*-**2**, and (C) diamine *p*-**3**.

mp: 292–293 °C (DSC). IR (KBr): 1349, 1534 (NO_2), 1240–1260 (C—O), 1739 cm^{-1} (C═O). ELEM. ANAL. Calcd. for $C_{36}H_{21}N_2O_{10}P$ (672.54): C, 64.29%; H, 3.15%; N, 4.16%. Found: C, 63.92%; H, 3.12%; N, 4.14%.

Synthesis of *p*-3 and *m*-3

P-diesteramines *p*-**3** and *m*-**3** were synthesized according to a modification of Hert's method[24] by the hydrogen catalytic reduction of the dinitro compounds *p*-**2** and *m*-**2**, respectively. A mixture of 20.2 g (30 mmol) of *p*-**2** and 1.3 g of 10% palladium on carbon in 300 mL of DMF was stirred at 25 °C under a hydrogen atmosphere until the theoretical amount of hydrogen was consumed. The time taken to reach this stage was about 2 days. The solution was filtered, and the obtained filtrate was poured into 2 L of stirring water, giving rise to a precipitate that was isolated by filtration. White crystals of *p*-**3** were obtained (96% yield).

mp: 311–312 °C (DSC). IR (KBr): 3235, 3356, 3454 (NH_2), 1230–1260 (C—O), 1706 cm^{-1} (C═O). ^1H NMR [400 MHz, dimethyl sulfoxide (DMSO)-d_6, δ]: 6.14 (s, 2H, NH_2), 6.20 (s, 2H,

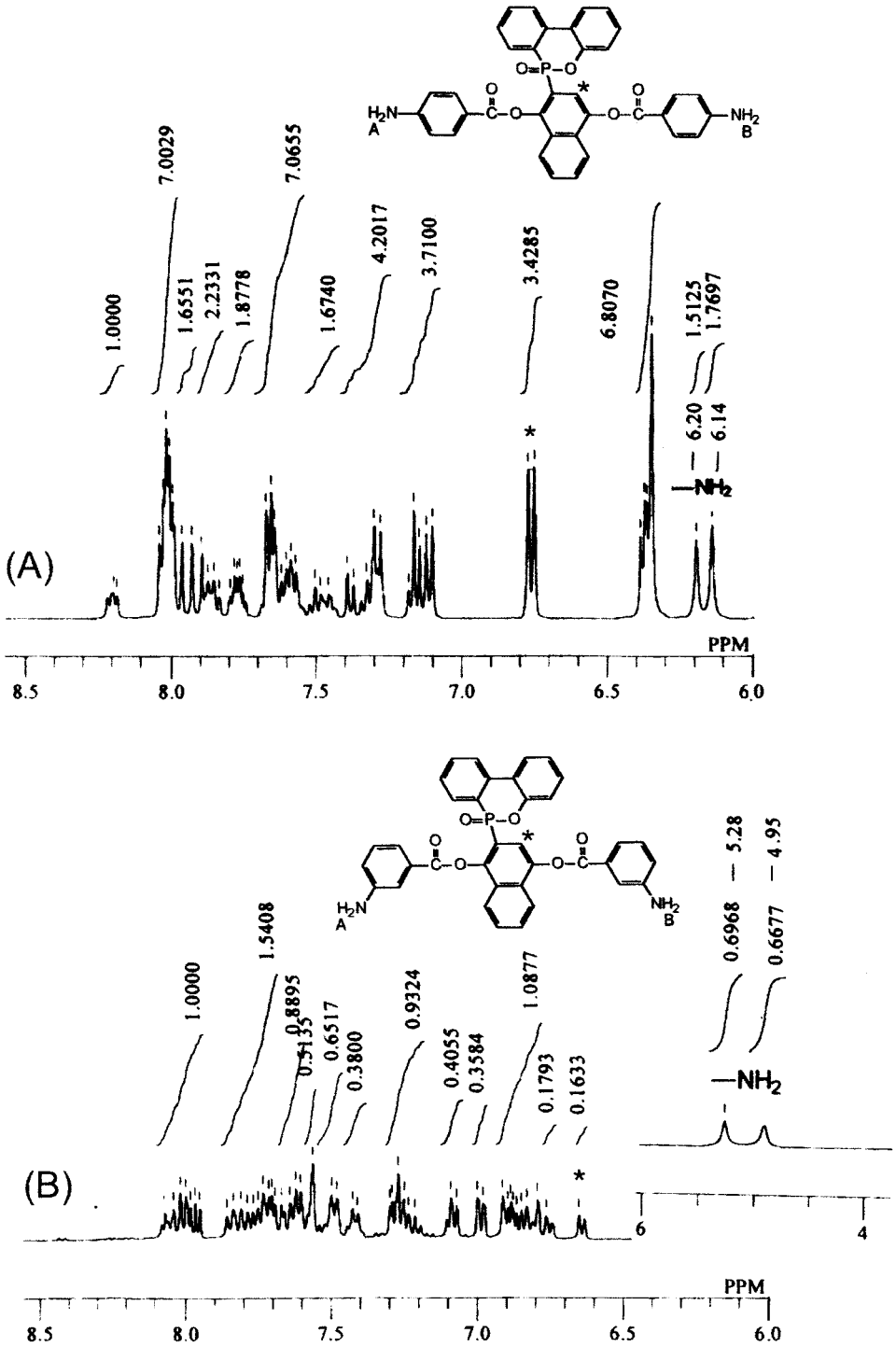


Figure 2. ^{1}H NMR spectra of (A) diamine *p*-**3** and (B) diamine *m*-**3** in DMSO-d_6.

NH_2), 6.35–8.20 (m, 21H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 166.67, 165.79, 165.13 (carbonyl carbons), 113.53–156.65 (m, aromatic carbons). ELEM. ANAL. Calcd. for $C_{36}H_{25}N_2O_6P$ (612.58): C, 70.59%; H, 4.11%; N, 4.57%. Found: C, 70.43%; H, 4.20%; N, 4.49%.

Diesteramine *m*-**3** was synthesized from dinitro compound *m*-**2** according to the same procedure. White crystals of *m*-**3** were obtained (95% yield).

mp: 219–220 °C (DSC). IR (KBr): 3363, 3467 (NH_2), 1211 (C—O), 1737 cm^{-1} (C═O). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 5.28 (s, 2H, NH_2), 4.76 (s,

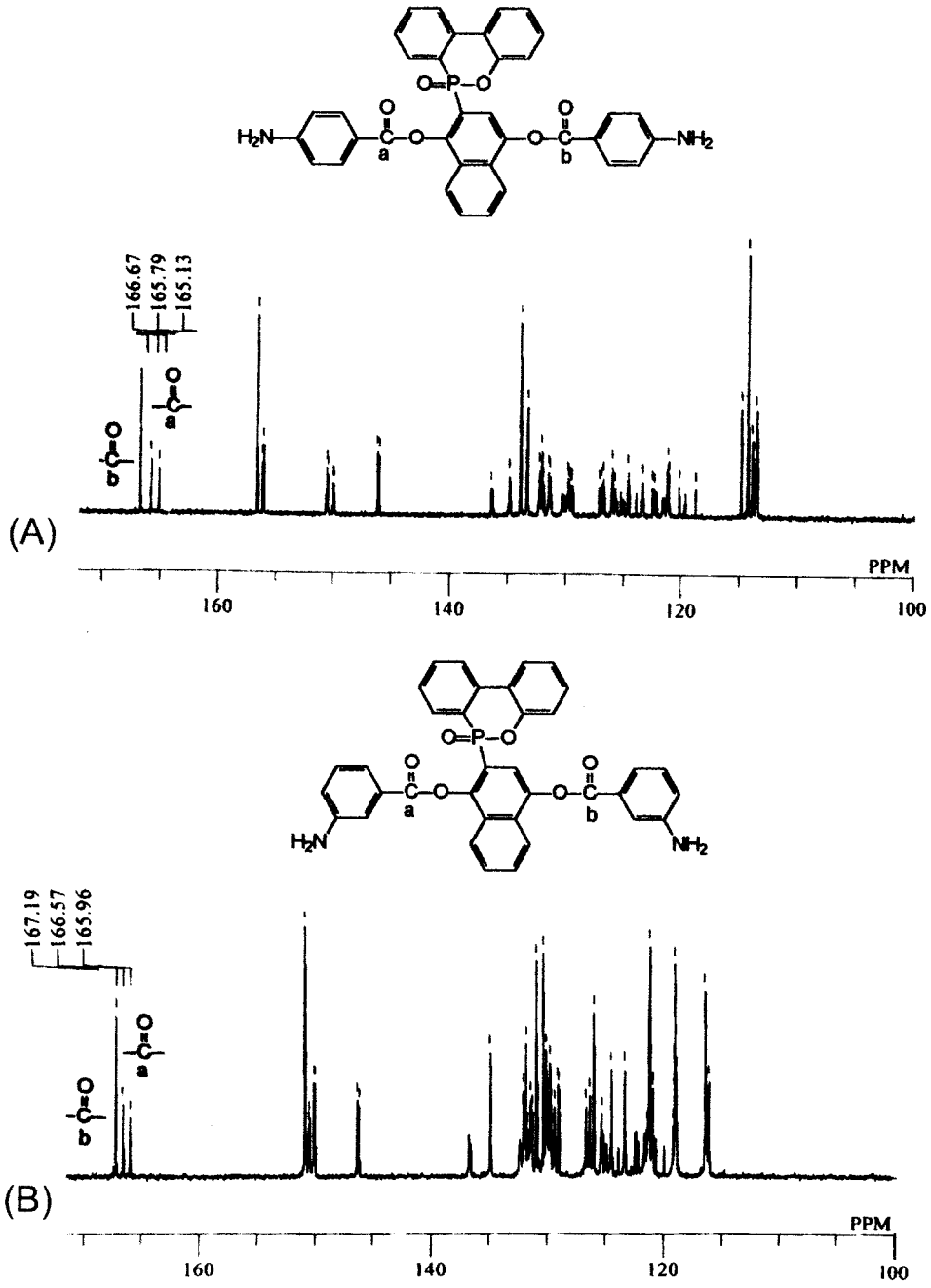
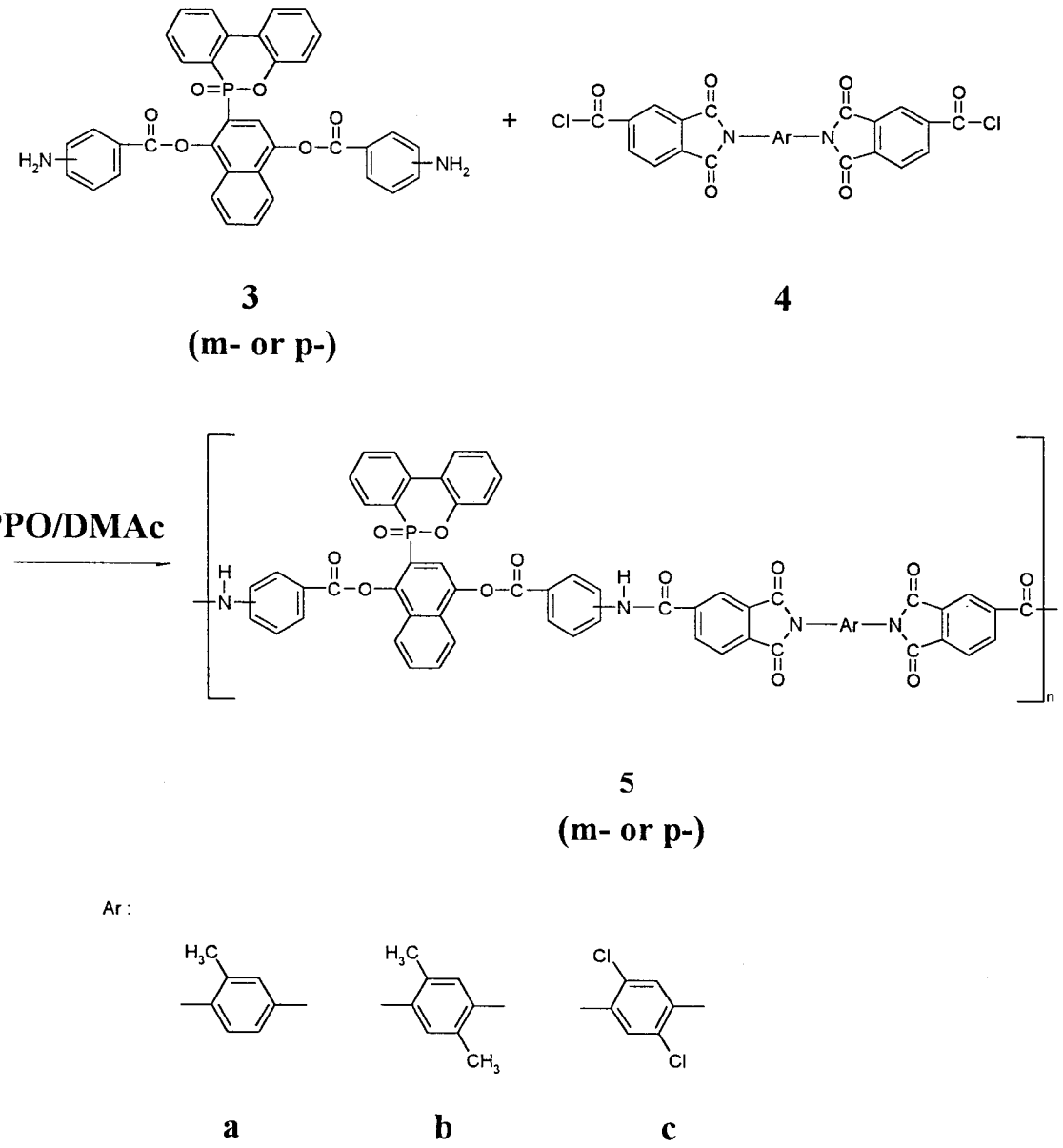


Figure 3. ^{13}C NMR spectra of (A) diamine *p*-**3** and (B) diamine *m*-**3** in DMSO-d_6.

2H, NH_2), 6.65–8.08 (m, 21H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 167.19, 166.57, 165.96 (carbonyl carbons), 116.19–150.96 (m, aromatic carbons). ELEM. ANAL. Calcd. for $C_{36}H_{25}N_2O_6P$ (612.58): C, 70.59%; H, 4.11%; N, 4.57%. Found: C, 70.26%; H, 4.02%; N, 4.47%.

Polymer Synthesis

The synthesis of poly(ester-amide-imide) *p*-**5a** is used as an example to illustrate the general synthetic route used to produce the poly(ester-amide-imide)s. A solution of 1.225 g (2.0 mmol) of diesteramine *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 diimide-diacid chloride **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 col-



Scheme 2

lected by filtration, washed well with hot methanol, and dried *in vacuo* at 100 °C. The yield was quantitative. The inherent viscosity of the polymer (**5a**) was 2.00 dL/g measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30 °C.

IR (film): 3340 (N—H), 1780 (imide carbonyl), 1720–1750 (imide plus ester carbonyls), 1680 (amide carbonyl), 1250 cm^{-1} (C—O). ELEM. ANAL. Calcd for $(C_{61}H_{35}N_4O_{12}P)_n$ $(1046.92)_n$: C, 69.98%; H, 3.37%; N, 5.36%. Found: C, 68.76%; H, 3.59%; N, 5.57%.

Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a PerkinElmer 2400 CHN analyzer. ^1H and ^{13}C NMR spectra were measured on a JEOL EX-400 spectrometer with 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

Table I. Inherent Viscosities and Tensile Properties of the Poly(ester-amide-imide)s

		Tensile Properties of the Polymer Films[c]		
Polymer[a]	η_{inh} (dL/g)[b]	Tensile Strength (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
p-**5a**	2.00	181	11	4.46
p-**5b**	0.94	149	5	3.84
p-**5c**	1.28	135	5	3.58
m-**5a**	0.41	127	9	2.68
m-**5b**	0.56	121	7	2.99
m-**5c**	0.41	118	7	2.41

[a] The polymerizations were 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 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 the slow evaporation of polymer solutions in DMAc. The cast films were dried *in vacuo* at 150 °C for 6 h prior to the tensile test.

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. 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 (Japan). The limiting oxygen index (LOI) is defined as the minimum concentration of oxygen, expressed as the volume percentage, in a mixture of oxygen and nitrogen that is 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 universal tester model 1130 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 about 0.1 mm thick), and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Monomer Synthesis

The P-containing aromatic diol **1** was successfully synthesized from the addition reaction of DOPO to 1,4-naphthaquinone (Scheme 1) according to a modification of the method reported by Endo et al.[22] and Wang and Lin.[21(e)] After the reaction, the distinctive absorption at 2384 cm^{-1} for P—H stretching in DOPO disappeared, but a broad absorption around 3200 cm^{-1} for phenolic OH appeared in **1** [Fig. 1(A)]. Consequently, this addition reaction could be monitored with these absorptions. The yield was satisfactory (70% after recrystallization). The molecular structure of **1** was also confirmed by elemental and NMR analysis, as described in another publication.[23]

The new polymer-forming *P*-diesteramines, *p*-**3** and *m*-**3**, were prepared by the hydrogen Pd/C-catalyzed reduction of the dinitro compounds *p*-**2** and *m*-**2** resulting from the condensation reaction of *P*-diol **1** with 4-nitrobenzoyl chloride or 3-nitrobenzoyl chloride, as shown in Scheme 1. IR, NMR, and elemental analysis identified the structures of all intermediates and monomers. The IR spectra of dinitro compound *p*-**2** and diesteramine *p*-**3** are illustrated in Figure 1(B,C), respectively. The nitro group of compound *p*-**2** gave two characteristic bands at 1538 and 1348 cm^{-1}. After the reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed a pair of N—H stretching bands at 3417 and 3363 cm^{-1}. In the IR spectrum of diesteramine *p*-**3**, the characteristic absorption appeared at 1706 cm^{-1} and was assigned to the ester carbonyl group, which is about 30 cm^{-1} lower than that of *m*-**3** (1737 cm^{-1}). Conjugation of the amino group substituted at the para-position caused the absorption shift. Figures 2 and 3 show the ^1H and ^{13}C NMR spectra of the diesteramines. The unsymmetrical molecular structure and spin coupling of ^{31}P to hydrogen and carbon nuclei resulted in a very complicated splitting pattern for these two diesteramines. No attempts were made to assign all the signals. Double resonance (spin decoupling) may be useful to simplify such a spectrum to the point where it can be assigned easily. However, it is interesting to note some characteristic peaks in the NMR spectra. As can be seen from ^1H NMR spectra (Fig. 2), each *P*-diesteramine (*p*-**3** or *m*-**3**) has two broad singlet peaks from their amino groups because of their chemical and magnetic nonequivalence. A downfield chemical

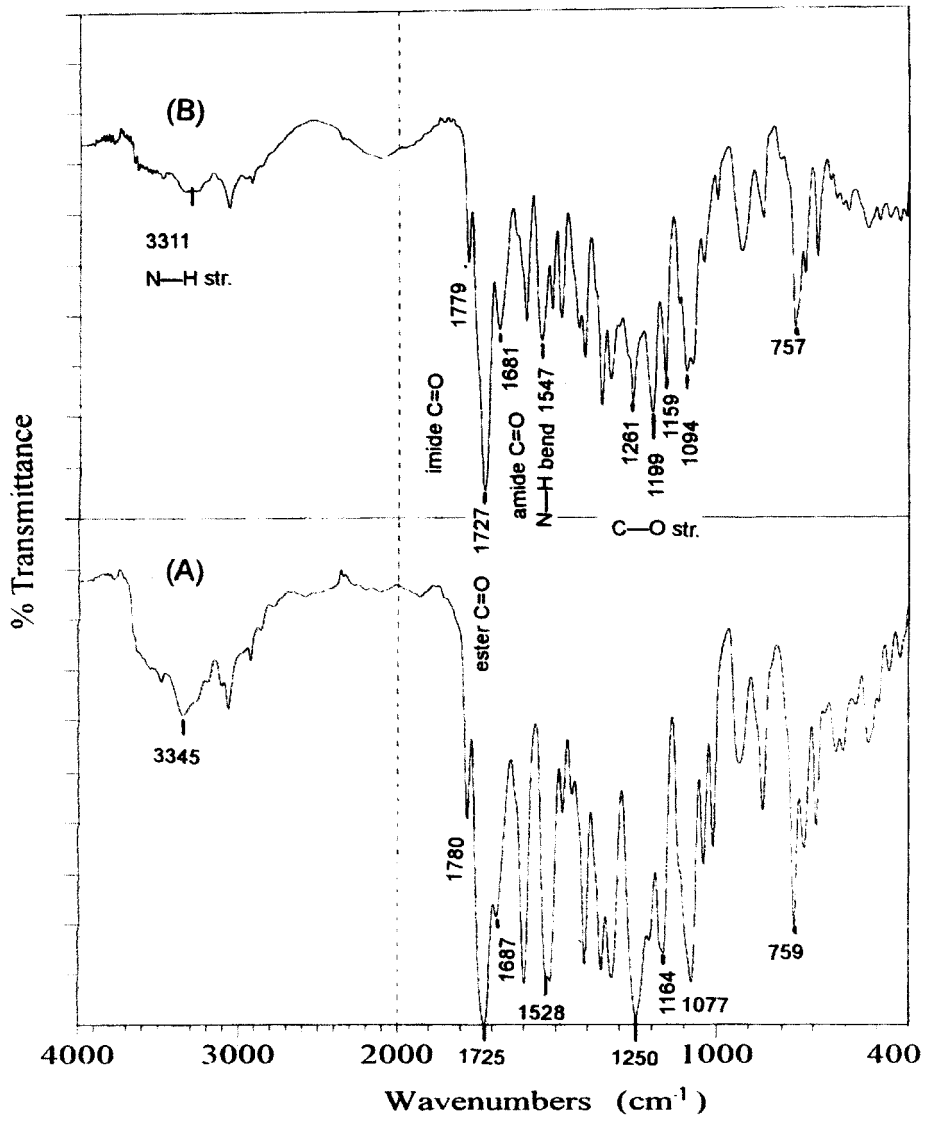


Figure 4. IR spectra of (A) poly(amide-ester-imide) *p*-**5b** and (B) poly(amide-ester-imide) *m*-**5b**.

shift (δ_H is increased) usually corresponds to the decrease in the electron-donating property of the amino group. The electron-withdrawing effect (by resonance) is stronger for the para-substituted carbonyl group than that substituted at the meta-position. Thus, the nucleophilicity for the amino groups of diesteramine *m*-**3** (δ_H = 4.95 and 5.28 ppm) was expected to be stronger than those of its para-isomer (*p*-**3**; δ_H = 6.14 and 6.20 ppm). In the ^{13}C NMR spectra of both diesteramines (Fig. 3), the carbonyl carbons labeled *a* showed a doublet probably due to ^{31}P coupling. The large coupling constant of 60–65 Hz seems to be caused by a one-bond coupling and suggests that the spin information may be transmitted through a special spatial arrangement of atoms.

Polymer Synthesis

Two series of new P-containing poly(ester-amide-imide)s, *p*-**5a–c** and *m*-**5a–c**, were synthesized from diesteramines *p*-**3** and *m*-**3** with diimide-diacid chlorides (**4a–c**) by low-temperature solution polycondensation in DMAc in the presence of PPO as an acid acceptor (Scheme 2). All the reaction solutions were homogeneously transparent and became highly viscous, indicative of the formation of high molecular weights. As shown in

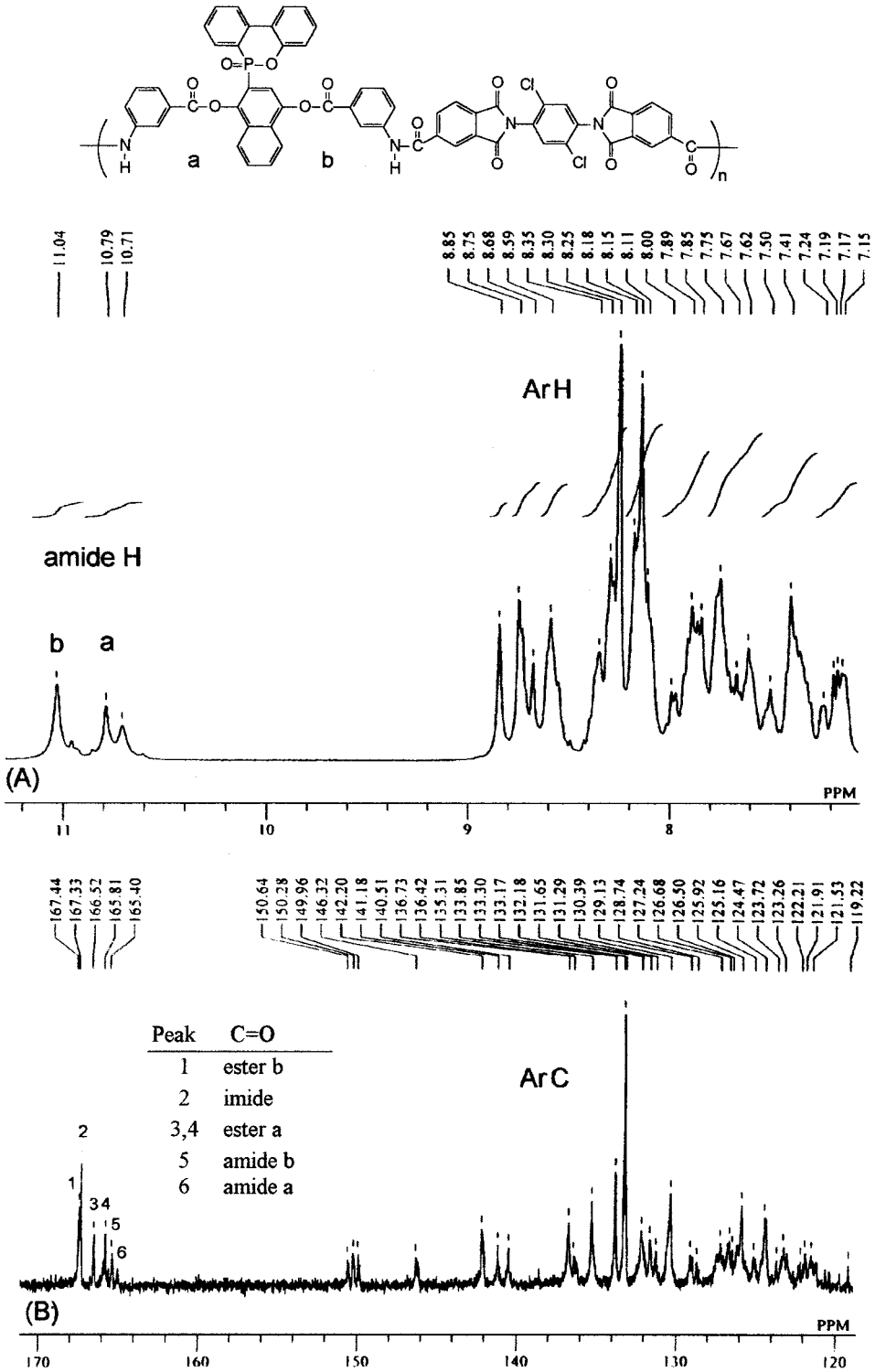


Figure 5. (A) ^{1}H and (B) ^{13}C NMR spectra of poly(ester-amide-imide) *m*-**5c** in DMSO-d_6.

Table I, poly(ester-amide-imide)s *p*-**5a**–**c** and *m*-**5a**–**c** were obtained with inherent viscosities of 0.94–2.00 and 0.41–0.56 dL/g, respectively. All the polymers had high enough molecular weights to permit the casting of tough and flexible films. The lower inherent viscosities of the *m*-series polymers, compared with those of the *p* series, may be attributed in part to their more flexible

Table II. Solubility of Poly(ester-amide-imide)s[a]

	Solvent					
Polymer	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF[b]
p-**5a**	+	+	+h	+h	+h	−
p-**5b**	+	+	−	−	+h	−
p-**5c**	+	+	+h	−	+h	−
m-**5a**	+	+	+	+	+h	−
m-**5b**	+	+	+	+	+h	−
m-**5c**	+	+	+	+	+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.
[b] THF = tetrahydrofuran.

structure. In interpreting the viscosity behavior, one must bear in mind that the inherent viscosity of a flexible polymer is much lower than that of a rigid polymer of a similar molecular weight.

The key structural features of the poly(ester-amide-imide)s were identified with IR and NMR spectra. Strong absorption bands around 1780 and 1720 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide rings. The absorption at 720 cm^{-1} is possibly due to imide ring deformation. Characteristic absorptions of the amide group appeared around 3300 (N—H stretching), 1670–1680 (carbonyl stretching), and 1530–1550 cm^{-1} (NH deformation). All the polymers also exhibited IR bands at 1740–1750 (carbonyl stretching) and 1250–1270 cm^{-1} (C—O stretching) due to the ester groups. Figure 4 shows a typical set of FTIR spectra for poly(ester-amide-imide)s *p*-**5b** and *m*-**5b**, which have an isomeric repeat unit. Typical ^1H and ^{13}C NMR spectra for the representative polymer *m*-**5c** are illustrated in Figure 5. Without additional information, we can only assign certain features of the spectra to particular carbon and hydrogen atoms of the polymer. In the ^1H NMR spectrum of *m*-**5c**, multiple resonances for the amide protons were observed between 10.6 and 11.1 ppm. This can be attributed to the constitutional disorder introduced by the unsymmetrical diesteramine moieties, which give rise to a random enchainment of the repeat units. In the ^{13}C NMR spectrum of *m*-**5c**, the resonances in the downfield region (165–168 ppm) are ascribed to the carbonyl carbons of the ester, amide, and imide linkages. Similar to what was observed in the spectra of the diesteramine monomers, the carbonyl carbons of the ester linkage ortho to the pendant P-containing group resonated as a doublet. The patterns appearing between 7 and 9 ppm in the ^1H NMR spectrum and 120 and 150 ppm in the ^{13}C NMR spectrum peculiar to the aromatic units are much more complex and thus more difficult to interpret.

Properties of the Polymers

As mentioned previously, all poly(ester-amide-imide)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 118–181 MPa, 5–11%, and 2.41–4.46 GPa, respectively. Poly(ester-amide-imide) *p*-**5a**, derived from diamine *p*-**3** and the diacid chloride of 2,5-bis(trimellitimido)toluene, showed high tensile strength and modulus up to 181 MPa and 4.46 GPa, respectively.

The solubility behavior of these poly(ester-amide-imide)s was tested in various solvents, and the results are summarized in Table II. Because of the introduction of the bulky biphenylenephosphonato side group and 1,4-naphthalene structure of diamine **3**, which help to prevent the close packing of chains in the polymer backbone, all the poly(ester-amide-imide)s were readily soluble in polar solvents such as *N*-methyl-2-pyrrolidone (NMP) and DMAc. Between these two series of isomeric poly(ester-amide-imide)s, the *m*-**5** series containing *meta*-phenylene rings showed higher solubility than the corresponding isomeric poly(ester-amide-imide)s *p*-**5** series containing *para*-phenylene rings due to the more flexible backbones. Good solubility makes these polymers potential candidates for practical applications in spin-coating and casting processes.

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 side group and 1,4-naphthyl units, which resulted in increased chain distances and decreased chain interactions. Thus, the amorphous nature of these polymers was reflected in their excellent solubility.

The thermal stability of these poly(ester-amide-imide)s was studied with TGA. Typical TGA curves of a representative polymer, *m*-**5a**, in both air and nitrogen atmospheres are shown in Figure 6. Some thermal behavior data were de-

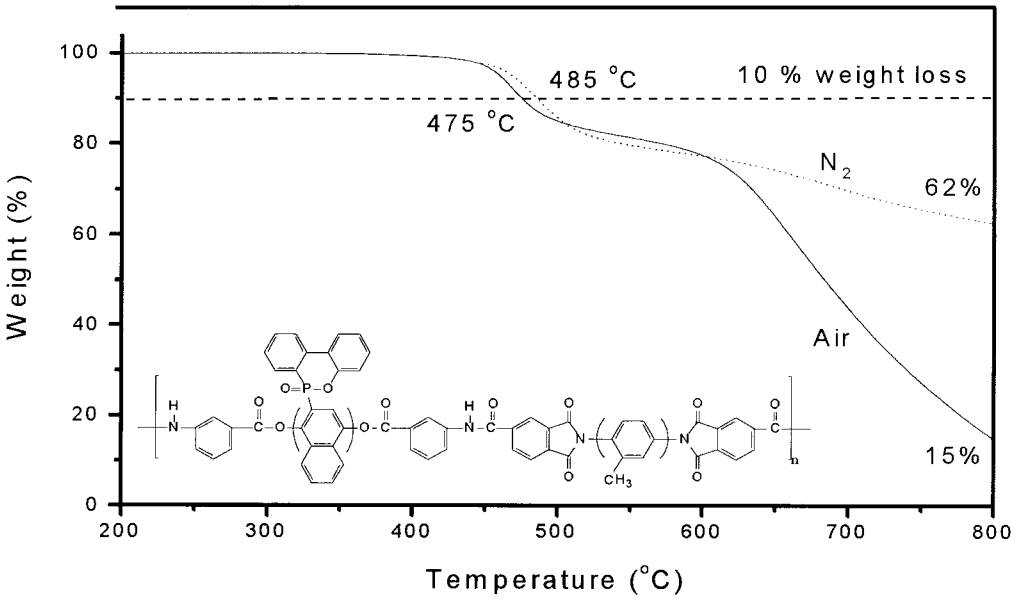


Figure 6. TGA thermograms of poly(ester-amide-imide) *m*-**5a** at a heating rate of 20 °C/min under a gas stream (flow rate = 30 cm^3/min).

termined 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 T_d's (T_d's at onset) were recorded at 442–467 °C in nitrogen and 434–461 °C in air. The amount of carbonized residue (char yield) of these poly(ester-amide-imide)s in a nitrogen atmosphere was 57–62% at 800 °C. The LOI values of the polymers ranged from 41 to 46%, indicating high flame-retardant characteristics.

DSC was used to evaluate the thermal transitions of the poly(ester-amide-imide)s. The influence of the residual solvent or the absorbed moisture and history of thermal annealing is sometimes observed in the first heating scan of DSC. The poly(ester-amide-imide)s were first heated to approximately 400 °C at 20 °C/min and then were rapidly quenched to room temperature at a cooling rate of approximately −100 °C/min to form predominantly amorphous samples; therefore, the T_g's of all the polymers could be easily mea-

Table III. Thermal Properties and LOIs of Poly(ester-amide-imide)s

Polymer	T_g (°C)[a]	T_s (°C)[b]	T_d at Onset (°C)[c]		T_d at 10% (°C)[c]		Char Yield (wt %)[d]		LOI
			N_2	Air	N_2	Air	N_2	Air	
p-**5a**	271	258	453	461	469	484	62	23	43
p-**5b**	286	278	467	456	482	492	60	25	43
p-**5c**	271	261	448	434	467	457	58	9	45
m-**5a**	264	249	458	447	484	474	62	15	44
m-**5b**	274	251	442	459	461	487	62	28	41
m-**5c**	265	257	443	444	457	458	57	5	46

[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 prior to the TMA test.

[c] Recorded via 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.

sured on the subsequent DSC heating traces. The T_g values of poly(ester-amide-imide)s *p*-**5** and *m*-**5** were observed to be 271–286 and 264–274 °C, respectively, depending on the structure of the diacid chloride components, and they decreased with the decreasing rigidity and symmetry of the polymer backbone. The T_g's of the *p*-**5** series poly(ester-amide-imide)s were slightly higher than those of the corresponding *m*-**5** series because of the difference in symmetry between para- and meta-links. None of the polymers showed clear melting endotherms from T_g to 400 °C on the DSC thermograms. This supports the amorphous nature of these poly(ester-amide-imide)s. The softening temperatures (T_s's) of the polymer film samples were also measured with TMA. In most cases, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments. There is a large window between T_g or T_s and T_d of each polymer; this could be advantageous in the processing of these polymers by a thermoforming technique.

CONCLUSIONS

New P and 1,4-naphthyl units containing aromatic diesteramines *p*-**3** and *m*-**3** were synthesized in high purity and high yields, starting from *P*-diol **1** and 4- or 3-nitrobenzoyl chloride. Two series of high molecular weight poly(ester-amide-imide)s were readily prepared from various combinations of *P*-diesteramines *p*-**3** and *m*-**3** with diimide-diacid chlorides (**4a–c**) via the low-temperature solution polyamidation technique. Because of the presence of the bulky P-substituent and 1,4-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. The *m*-series polymers revealed a slightly higher solubility and lower T_g value than the corresponding *p*-series polymers, whereas there was little difference in thermal stability and LOI values between isomeric polymers. 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-imide)s promising high-performance polymeric materials.

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