

# Thermally Stable and Organosoluble Cardo Binaphthylene Based Poly(amide imide)s and Poly(ester imide)s

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**ABSTRACT:** A new imide-containing dicarboxylic acid based on a twisted binaphthylene unit, 2,2'-bis(*N*-trimellityl)-1,1'-binaphthyl (**1**), was synthesized from 1,1'-binaphthyl-2,2'-diamine and trimellitic anhydride in glacial acetic acid. The structure of compound **1** was fully characterized with spectroscopic methods and elemental analysis. Series of thermally stable and organosoluble poly(amide imide)s (**4a–4d**) and poly(ester imide)s (**5a–5d**) with similar backbones were prepared by the triphenyl phosphite and diphenylchlorophosphate activated direct polycondensation of diimide dicarboxylic acid **1** with various aromatic diamines and diols, respectively. With due attention to the structural similarity of the resulting poly(amide imide)s and poly(ester imide)s, most of the differences between these two block copolyimides could be easily attributed to the presence of alternate amide or ester linkages accompanied by imide groups in the polymer backbone. The ultraviolet maximum wavelength values of the yellowish polymers were determined from their ultraviolet spectra. The crystallinity of

these copolyimides was estimated by means of wide-angle X-ray diffraction, and the resultant polymers exhibited a nearly amorphous nature, except for the polymers derived from benzidine and 4,4'-binaphthol. The poly(amide imide)s exhibited excellent solubility in a variety of highly polar aprotic solvents, whereas the poly(ester imide)s showed good solubility in less polar solvents. According to differential scanning calorimetry analyses, polymers **4a–4d** and **5a–5d** had glass-transition temperatures between 331 and 357°C and between 318 and 342°C, respectively. The thermal behaviors of the obtained polymers were characterized by thermogravimetric analysis, and the 10% weight loss temperatures of the poly(amide imide)s and poly(ester imide)s were between 579 and 604°C and between 566 and 577°C in nitrogen, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3203–3211, 2006

**Key words:** polycondensation; polyimides; thermal properties

## INTRODUCTION

Aromatic polyimides are well accepted as high-performance polymeric materials for their excellent heat and chemical resistance, favorable electrical insulating properties, and superior mechanical characteristics.<sup>1,2</sup> However, the major limitation of these polyimides for versatile applications is their insolubility in common organic solvents. In fact, unless carefully designed, polyimides are often insoluble in their fully imidized form. Thus, their applications are limited in some fields. Therefore, the preparation of soluble polyimides without a perceptible loss of favorable properties has been a major research interest. A great deal of effort has been expended to improve the processing characteristics of these intractable polymers.<sup>3–6</sup> One of the successful approaches to improving solubility is the incorporation of other functional groups, such as amide, ether, ester, and siloxane linkages, along the

polymer skeleton and, consequently, the preparation of the appropriate copolyimides.<sup>7–15</sup> On the other hand, the introduction of twisted bulky units such as cardo binaphthylene rings into the polymer backbone has been used to enhance the solubility in a variety of organic solvents.<sup>16–20</sup> The presence of cranked naphthalene rings in the macromolecular chains is expected to lead to a decrease in the linearity of the chains while maintaining comparable thermal stability in comparison with the phenyl rings. Thus, the combination of the two aforementioned effective factors may be proposed as a suitable choice for increasing the processability of rigid, aromatic polymers without an extreme loss of heat resistance. Moreover, cardo binaphthylene rings are very important chiral molecules and have been used in polymer systems. The chirality of binaphthyl compounds is derived from the restricted rotation along the carbon–carbon single bond of the two naphthalene rings, and the C<sub>2</sub> dissymmetric chiral configuration of binaphthyl is remarkably stable. Consequently, the synthesis of binaphthylene-based polymers should also be interesting for optical materials.<sup>21</sup>

Aromatic poly(amide imide)s and poly(ester imide)s can be successfully synthesized via the direct polycondensation of imide ring containing diacids

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and aromatic diamines or diols, respectively.<sup>22,23</sup> This direct method has previously been used by our group to prepare some families of wholly aromatic copolyimides.<sup>24–28</sup>

In a continuation of our previous studies, in this study, a new imide ring containing diacid, 2,2'-bis(*N*-trimellitoyl)-1,1'-binaphthyl (**1**), was synthesized and polymerized directly with various aromatic diamines and diols for the preparation of two series of block copolyimides, that is, poly(amide imide)s **4a–4d** and poly(ester imide)s **5a–5d**. The resulting polymers were thoroughly characterized by spectroscopic methods. Because of the structural similarity, the effects of amide and ester flexible groups on some properties of the obtained polymers, including the crystallinity, solubility, and thermal stability, could be easily clarified.

## EXPERIMENTAL

### Materials

All chemicals were purchased from either Merck (Lindenplatz, Germany) or Fluka Chemical Co. (Buchs, Switzerland) Trimellitic anhydride (**2**), pyridine (Py), and the condensing agents triphenyl phosphite (TPP) and diphenylchlorophosphate (DPCP) were used as obtained without further purification. 1,1'-Binaphthyl-2,2'-diamine (**2d**) was synthesized as described in the literature.<sup>29</sup> The diamines, including *m*-phenylene diamine (**2a**) and *p*-phenylene diamine (**2b**), were purified by vacuum distillation before use. Benzidine (**2c**) was of high purity when received and was used without any further purification. The aromatic diols, including resorcinol (**3a**), hydroquinone (**3b**), and 4,4'-biphenol (**3c**), were purified by recrystallization from ethanol. 1,1'-Binaphthyl-2,2'-diol (**3d**) was prepared from 2-naphthol with reference to the literature method.<sup>30</sup> *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. Tetrahydrofuran (THF), dichloromethane (DCM), and chloroform were dried over calcium hydride and distilled before use. Commercially obtained anhydrous CaCl<sub>2</sub> and LiCl were dried in vacuo at 150°C for 6 h and at 180°C for 10 h, respectively.

### Synthesis of diimide diacid **1**

**2d** (2.84 g, 10 mmol) and **2** (4.80 g, 25 mmol) were suspended in glacial acetic acid (40 mL) and heated at reflux for 24 h. The heterogeneous mixture was then filtered to yield a yellow solid, which was rinsed with ethanol to remove acetic acid. The obtained crude product was washed thoroughly with ethanol and was then reprecipitated from a DMF–methanol solu-

tion and dried at 100°C for 15 h in vacuo to give 5.44 g (86%) of a pale yellow, powdered product (**1**).

mp: >300°C. ANAL. Calcd. for C<sub>38</sub>H<sub>20</sub>N<sub>2</sub>O<sub>8</sub> (632.60): C, 72.14%; H, 3.19%; N, 4.43%. Found: C, 71.82%; H, 3.27%; N, 4.38%. The spectroscopic characteristics of the monomer are discussed in the Results and Discussion section.

### Preparation of the polymers

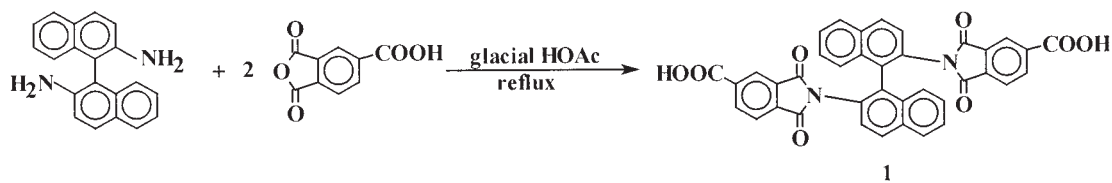
The general procedure for the synthesis of aromatic poly(amide imide)s **4a–4d** can be described as follows: A mixture of diimide diacid **1** (0.633 g, 1 mmol), **2a** (0.108 g, 1 mmol), calcium chloride (0.35 g), Py (1.2 mL), TPP (0.8 mL), and NMP (4.0 mL) was refluxed for 3 h with stirring. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring; this produced a precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100°C in vacuo. The inherent viscosity ( $\eta_{inh}$ ) of polymer **4a** in DMAc was 0.71 dL/g at a concentration of 0.5 g/dL at 30°C. All other poly(amide imide)s (**4b–4d**) were prepared in an analogous manner quantitatively.

A typical example of the synthesis of aromatic poly(ester imide)s **5a–5d** can be described as follows: A solution of DPCP (1 mL), lithium chloride (0.08 g), and Py (5.0 mL) was stirred at room temperature for 45 min and then added dropwise under a nitrogen atmosphere over a period of 1 h to a hot solution (preheated at 120°C) containing diimide diacid **1** (0.633 g, 1 mmol) and **3a** (0.110 g, 1 mmol) in Py (2.0 mL) at the reflux temperature with stirring. The final solution was stirred and heated at 120°C for 3 h under nitrogen. The obtained polymer solution was trickled into methanol (150 mL); this gave rise to a stringy precipitate, which was washed thoroughly with methanol and hot water, collected by filtration, and dried at 100°C under reduced pressure.  $\eta_{inh}$  of polymer **5a** was 0.82 dL/g at a concentration of 0.5 g/dL in DMAc at 30°C. This solution polycondensation was chosen as a procedure for the preparation of all other poly(ester imide)s (**5b–5d**) with compound **1** and appropriate aromatic dihydroxy compounds. The yield of these polymerizations was also almost quantitative.

The spectroscopic characteristics of all the polymers are discussed in the Results and Discussion section.

### Measurements

Melting points were determined with a Buchi 535 melting-point apparatus (Haverhill, MA). The  $\eta_{inh}$  values were measured by a standard procedure with a Cannon-Fenske routine viscometer (State College, PA) in DMAc at a concentration of 0.5 g/dL at 30°C. Elemental analyses were performed with a PerkinElmer



Scheme 1

2400 CHN analyzer (Wellesley, MA).  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded on a Bruker Advanced DPX-250 250-MHz spectrometer (Rheinstetten, Germany) in dimethyl sulfoxide- $d_6$  ( $\text{DMSO-}d_6$ ) at  $25^\circ\text{C}$  with frequencies of 250.13 and 62.89 MHz for the  $^1\text{H}$  and  $^{13}\text{C}$  spectra, respectively. Tetramethylsilane was used as an internal standard. Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer RX I FTIR spectrometer. The spectra of the solids were obtained with KBr pellets. Ultraviolet maximum wavelength ( $\lambda_{\text{max}}$ ) values were determined with a GBC model 916 ultraviolet-visible (UV-vis) instrument (GBC Scientific Equipment, Australia) in DMSO at a concentration of 0.1 mg/mL. Wide-angle X-ray diffraction patterns were performed at room temperatures with film specimens on a Bruker Advance D8 X-ray diffractometer with Ni-filtered  $\text{Cu K}\alpha$  radiation (30 kV, 25 mA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Mettler TA4000 system (Columbus, OH) under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . The DSC traces were obtained from heating, rapid cooling ( $-100^\circ\text{C}/\text{min}$ ), and reheating of samples in a range of  $50\text{--}400^\circ\text{C}$ . The range flow scan of 20 mW for DSC and 10 mG for TGA was used.

## RESULTS AND DISCUSSION

### Monomer synthesis

As shown in Scheme 1, the rigid-and-twisted-structure monomer, **1**, was synthesized by the condensation reaction of **2d** with 2 mol equiv of **2** in refluxing glacial acetic acid as a solvent. This reaction was carried out via a two-stage procedure including a ring-opening addition reaction between the amines and anhydride groups, as well as subsequent cyclodehydration, which progressed in a heterogeneous solution. The structure of the monomer was confirmed by FTIR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectroscopy, and elemental analysis. The FTIR spectrum of **1** showed absorption bands at 2400–3600  $[\text{C}(\text{O})\text{O}-\text{H}]$ , 1778 (symmetric imide  $\text{C}=\text{O}$  stretching), 1721 (asymmetric imide  $\text{C}=\text{O}$  stretching and acid  $\text{C}=\text{O}$  stretching), and  $1375\text{ cm}^{-1}$  (imide ring vibration), confirming the presence of an imide ring and carboxylic acid groups in the structures. The FTIR spectrum of **1** is presented in Figure 1. The  $^1\text{H-NMR}$  spectroscopy data of **1** are in the range of 7.18–8.34. The protons of the trimellitimidic aromatic ring create resonance signals around down-field regions ( $>8$  ppm). However, the proton for the

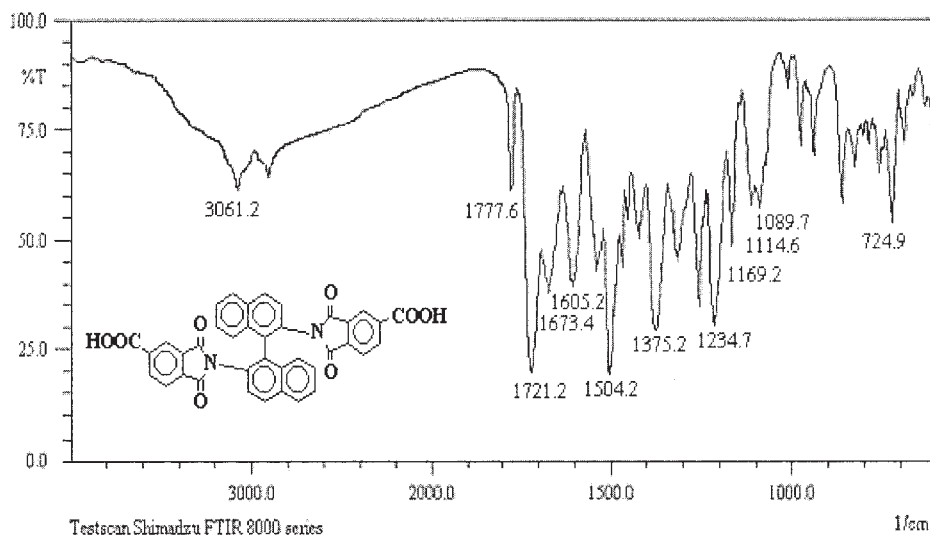


Figure 1 FTIR spectrum of new imide-containing diacid **1**.

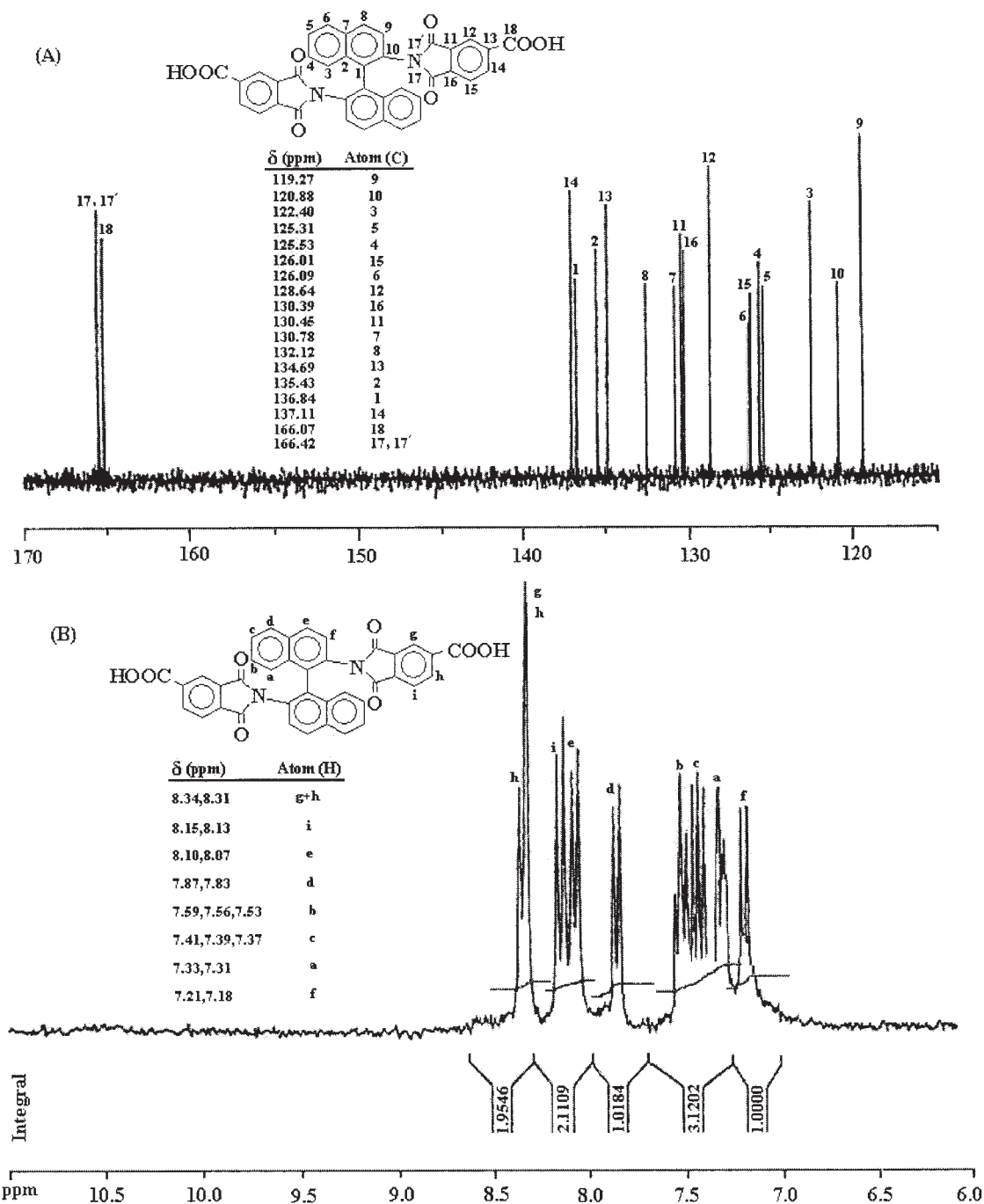
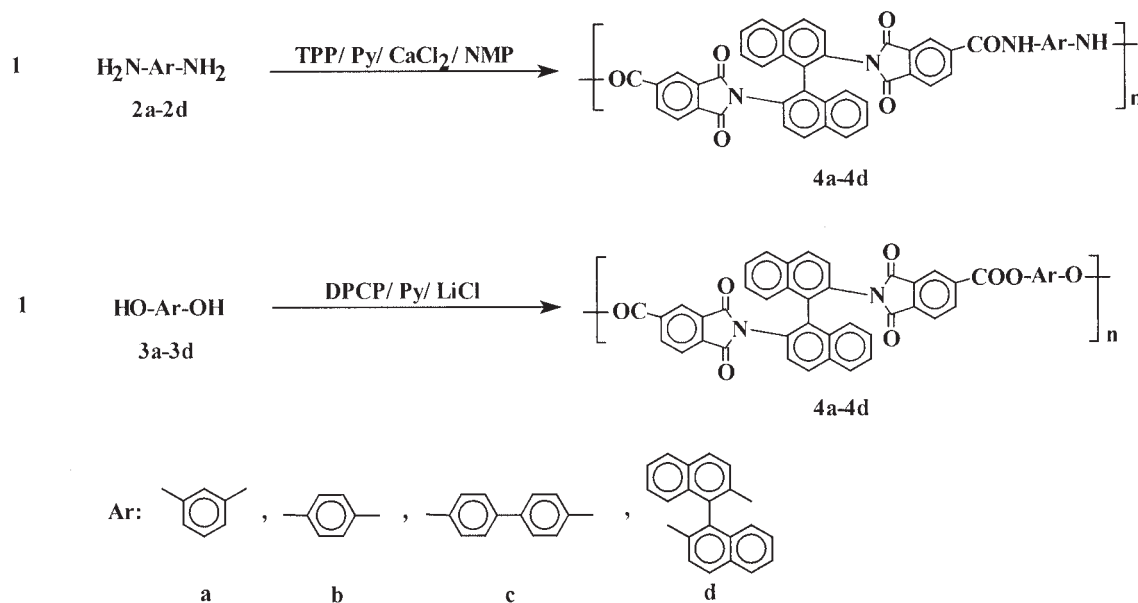


Figure 2 (A)  $^{13}\text{C}$ -NMR and (B)  $^1\text{H}$ -NMR spectra of **1** (solvent =  $\text{DMSO-}d_6$ ).

carboxylic acid group in the  $^1\text{H}$ -NMR spectrum was not observed. This was probably due to the fast exchange of this proton with a trace amount of moisture associated with the solvent. Furthermore, the  $^{13}\text{C}$ -NMR spectrum of **1** exhibited 16 peaks attributed to various absorptions of aromatic carbons. This revealed that the carbonyl carbon of carboxylic acid and imide groups resonated in the downfield at 166.07 and 166.42 ppm, respectively. The  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of **1** are given in Figure 2.

#### Poly(amide imide) and poly(ester imide) synthesis

The novel wholly aromatic poly(amide imide)s **4a–4d**, containing cardo groups, were prepared from diimide diacid **1** and various aromatic diamines, **2a–2d**, by a phosphorylation reaction with TPP as a promoter in NMP as a reaction solvent in the presence of Py and calcium chloride. Moreover, the new strictly alternating aromatic poly(ester imide)s **5a–5d**, containing binaphthylene units, were synthesized from diimide



diacid **1** and various dihydroxy compounds, **3a–3d**, with DPCP and lithium chloride as condensing agents in Py. The structures and codes of the resulting polymers are shown in Scheme 2.

All the polymerization reactions readily proceeded in a yellowish, homogeneous solution, except those of poly(amide imide) **4c** and poly(ester imide)s **5b** and **5c**, which were obtained from the polycondensation of imide-containing diacid **1** with **2c**, **3b**, and 4,4'-binaphthol, respectively. In fact, all the polymers except those mentioned previously remained soluble in the polymerization medium; this permitted an increase in their molecular weight. The polymers were prepared in almost quantitative yields after thorough washing with methanol and hot water.









As shown in Table I,  $\eta_{inh}$  values of 0.23–0.71 dL/g measured in DMAc at 30°C were observed for the poly(amide imide)s. Also, poly(ester imide)s **5a** and **5d** possessed  $\eta_{inh}$  values of 0.82 and 0.64 dL/g, respectively. Poly(ester imide)s **5b** and **5c** were not soluble in DMAc at 30°C. The solubility of the polymer solutions affected  $\eta_{inh}$  of the resulting polymers significantly. For example, the unsatisfactory viscosities obtained from monomers including **2b** and **2c** were probably due to the fact that the poor solubility of polymers **4b** and **4c** resulted in early precipitation during the course of the reaction, which retarded further polymerization. Moreover, poly(ester imide)s **5a** and **5d** had greater viscosities than those of poly(amide imide)s **4a** and **4d** with the same aromatic segments in the polymer backbone. Although this could be due to differences in the molecular weight of the polymers obtained with different preparation methods, it is likely that these higher viscosity values resulted from

polymers with extended conformations in solutions. Here it seems that the expansion of the poly(ester imide) macromolecular chains was greater than that of the poly(amide imide)s in their solutions. This might be attributed to the presence of susceptible hydrogens for intramolecular hydrogen bonding in the poly(amide imide)s, which interrupted chain spreading.

The obtained yellowish polymers absorbed visible and ultraviolet light in a broad range via their electron transitions because of their highly conjugated aromatic structures. The  $\lambda_{max}$  values for poly(amide imide)s **4a–4d** and poly(ester imide)s **5a–5d** were in the ranges of 287–294 and 274–277 nm, respectively, obtained from DMSO solutions at a concentration of 0.1 mg/mL. Generally, the highly conjugated aromatic structures of the obtained polymers led to various absorption bands in their UV–vis spectra as a number of broad and sharp peaks, which could be attributed to the various allowed ( $\pi-\pi^*$ ) and forbidden ( $n-\pi^*$ ) electron transitions.

Synthesized poly(amide imide)s **4a–4d** were characterized by their FTIR and  $^1\text{H-NMR}$  spectra. The resulting data are tabulated in Table II. As can be seen, the IR spectra exhibited characteristic absorption bands for the imide ring around 1780 and 1720 (asymmetric and symmetric C=O stretching vibration), 1380 (C–N stretching vibration), and 1090 and 725  $\text{cm}^{-1}$  (imide ring deformation). The absorption of amide groups appeared around 3420 (N–H stretch) and 1670  $\text{cm}^{-1}$  (C=O stretch). In general, the  $^1\text{H-NMR}$  spectra of the resulting poly(amide imide)s were divided into two parts: the first was due to amide group protons and appeared in the most downfield region, around 10.60 ppm, and the second was due to the

**TABLE I**  
Synthesis and Some Characteristics of the Copolyimides

Polymer code	Diamine or diol		$\eta_{inh}$ (dL/g) <sup>a</sup>	$\lambda_{max}$ (nm) <sup>b</sup>	Remark <sup>c</sup>
	Code	Ar			
4a	2a		0.71	287	S
4b	2b		0.39	289	S
4c	2c		0.23	294	P
4d	2d		0.51	288	S
5a	3a		0.82	274	S
5b	3b		– <sup>d</sup>	274	P
5c	3c		–	277	P
5d	3d		0.64	276	S

Polymerizations were carried out with 1.0 mmol of diacid and diamines with 0.8 mL of TPP, 0.35 g of CaCl<sub>2</sub>, and 1.2 mL of Py in 4.0 mL of NMP at a reflux temperature for poly(amide imide)s and with 1.0 mmol of diacid and diols with 1 mL of DPCP and 0.08 g of LiCl in 7.0 mL of Py at 120°C for poly(ester imide)s.

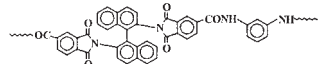
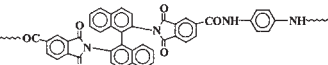
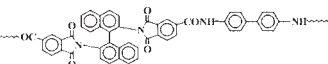
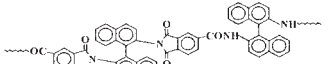
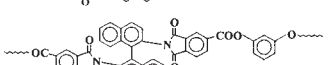
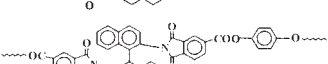
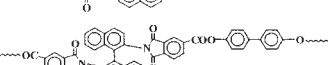
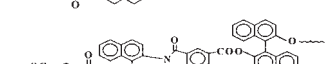
<sup>a</sup> Measured in DMAc at a concentration of 0.5 g/dL at 30°C.

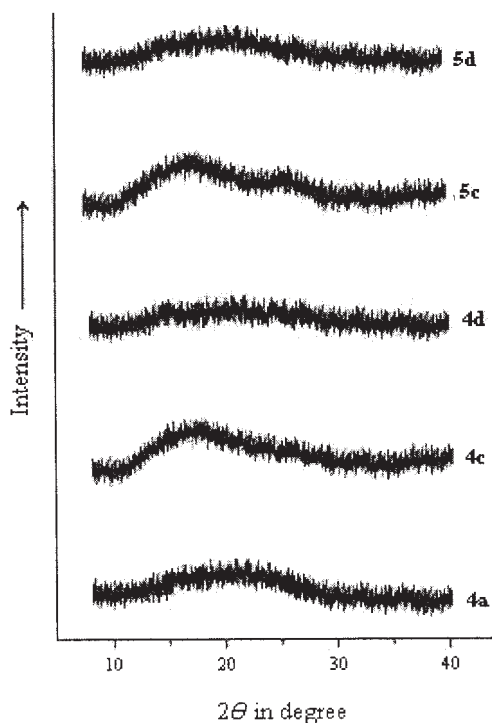
<sup>b</sup> Obtained in DMSO at a concentration of 0.1 mg/mL.

<sup>c</sup> S, solution through the reaction; P, precipitation during the reaction.

<sup>d</sup> Polymer was not soluble in DMAc at 30°C.

**TABLE II**  
IR and <sup>1</sup>H-NMR Spectroscopic Data of the Copolyimides

Polymer code	Polymer structure	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR (ppm)
4a		3421, 3043, 1780, 1721, 1671, 1501, 1375, 1090, 724	10.57 (amide H's), 8.44–7.09 (aromatic H's)
4b		3437, 3051, 1780, 1719, 1672, 1500, 1375, 1090, 724	10.61 (amide H's), 8.41–7.06 (aromatic H's)
4c		3422, 3049, 1780, 1721, 1665, 1502, 1372, 1091, 725	10.62 (amide H's), 8.40–7.01 (aromatic H's)
4d		3418, 3055, 1778, 1722, 1670, 1501, 1376, 1093, 724	10.60 (amide H's), 8.43–6.98 (aromatic H's)
5a		3045, 1778, 1722, 1673, 1504, 1374, 1091, 722	8.40–7.11 (aromatic H's)
5b		3045, 1778, 1721, 1674, 1504, 1372, 1090, 722	8.39–7.04 (aromatic H's)
5c		3044, 1777, 1721, 1671, 1505, 1373, 1090, 723	8.40–7.01 (aromatic H's)
5d		3045, 1778, 1718, 1675, 1500, 1374, 1089, 722	8.42–6.95 (aromatic H's)



**Figure 3** Wide-angle X-ray diffraction patterns of some of the polymers.

aromatic protons in the region of approximately 6.90–8.40 ppm. In the spectra, the hydrogens of the trimellitimido aromatic ring were also seen above 8 ppm.

The chemical structure of poly(ester imide)s **5a–5d** was also confirmed by FTIR and  $^1\text{H-NMR}$  spectra. All the IR spectra showed the characteristic absorptions of the imide group around 1780 and 1720  $\text{cm}^{-1}$ , peculiar to carbonyl stretching of imide and ester, respectively. The polymers exhibited absorption bands at about 1375 and 720  $\text{cm}^{-1}$ , which showed the presence of the imide heterocycle in these polymers. In general, the  $^1\text{H-NMR}$  spectra of all the poly(ester imide)s showed only a number of peaks in the region of approximately 6.95–8.40 ppm due to the aromatic protons. In these spectra, the hydrogens of the trimellitimido aromatic ring led to absorption peaks above 8 ppm, as predicted. In all cases, the chemical shifts and integral values of the peaks were conformable with the kind and number of attributed hydrogens.

### Polymer characterization

The crystallinity of the prepared polymers was measured with wide-angle X-ray diffraction scans at room temperature. Typical diffraction patterns for some representative polymers with  $2\theta$  ranging from 5 to 45° are presented in Figure 3. No crystal diffraction was detected for most of the polymers, except poly(amide imide) **4c** and poly(ester imide) **5c**, which bore biphe-

nylene moieties. Polymers **4c** and **5c** showed somewhat crystalline patterns because of the rigid, planar segments in their polymer backbones, which led to a better packing of the polymer chains. However, in general, a different diffuse diffraction pattern between the resulting polymers was revealed in the range of 15–25°, and the diffractions of the poly(ester imide)s were much stronger than those of the poly(amide imide)s. Therefore, the poly(ester imide)s might have possessed a certain imperfect long-distance order, and the poly(ester imide)s had a better ordered structure than the poly(amide imide)s. Moreover, highly binaphthylated chains of polymers **4d** and **5d** showed a significant decrease in the crystallinity behavior, which was reasonable because the presence of cranked bulky binaphthylene rings induced looser chain packing. Consequently, the aforementioned polymers showed almost amorphous diffraction patterns. In comparison with the poly(amide imide)s and poly(ester imide)s with *p*-phenylene units (polymers **4b** and **5b**), the incorporation of *m*-phenylene units into the backbones of polymers **4a** and **5a** also led to a large decrease in the crystallinity. Generally, the crystallinity nature of all the polymers was reflected in their solubility behavior, and this was in agreement with the general rule that the solubility decreased with increasing crystallinity.

The solubility behavior of the polymers in common organic solvents was studied. The results are summarized in Table III. All the obtained poly(amide imide)s could be easily dissolved in polar aprotic solvents such as DMAc, DMF, DMSO, NMP, and Py, and most of them were partially soluble in weakly polar solvents such as chloroform, DCM, and THF. On the other hand, all the poly(ester imide)s were almost soluble in both polar aprotic solvents such as DMAc, DMF, DMSO, NMP, and Py and weakly polar solvents such as chloroform, DCM, and THF, except poly(ester imide) **5c** based on 4,4'-binaphthol. The obtained poly(amide imide)s could be more readily dissolved in highly polar solvents than those less polar, whereas the poly(ester imide)s were almost more soluble in weakly polar solvents than those highly polar. A similar solubility behavior of binaphthalene-based polymers was also observed in our previous works.<sup>24,28</sup> In general, the flexible amide, ester, and ether groups affected the solubility of the copolyimides to a great extent because of a solvation effect. The high solubility of the poly(amide imide)s in highly polar solvents and the high solubility of the poly(ester imide)s with the same structure in weakly polar solvents showed that the strong solvation of the amide and imide groups by polar aprotic solvents improved the solubility of the poly(amide imide)s in NMP, DMAc, DMF, and DMSO, whereas the strong solvation of the ester linkage by DCM, THF, Py, and *m*-cresol caused the better solubility of the poly(ester imide)s in weakly polar

TABLE III  
Solubility of the Various Poly(amide imide)s and Poly(ester imide)s<sup>a</sup>

Polymer code	DMAc	DMF	DMSO	NMP	Py	Cloroform	DCM	THF	Acetone
4a	++	++	++	++	++	±	±	±	-
4b	++	++	+	++	+	±	±	±	-
4c	++	++	+	++	-	±	-	-	-
4d	++	++	++	++	++	+	+	±	-
5a	++	++	+	++	+	++	++	++	-
5b	±	±	±	±	±	+	+	+	-
5c	-	-	-	-	-	±	±	±	-
5d	++	++	++	++	++	++	++	++	-

Solubility: ++ = soluble at room temperature; + = soluble on heating; ± = partially soluble on heating; - = insoluble.  
<sup>a</sup> Concentration = 5 mg/mL.

solvents than in those highly polar. Besides the solvation effects related to the enthalpy factor, the good solubility of these polymers was also caused mainly by the entropy advantage resulting from cranked cardo binaphthylene rings in the polymer structures, which led to the expansion of the macromolecular chains in their solution state. This means that the organosoluble behavior of the obtained polymers could also be attributed to the introduction of bulky and twisted binaphthylene units, which inhibited the close packing of the polymer chains. Polymers 4c and 5c, having symmetrical and rigid biphenylene moieties, were insoluble in some tested solvents. This could be due to an incorporation of the units into the polymer backbone that could not cause an interruption in the chain packing, thus leading to poor solubility. Moreover, the solubility of the obtained polymers was greatly improved by the introduction of bulky and cranked 1,1'-binaphthyl-2,2'-diyl units into the polymer backbone, particularly for polymers 4d and 5d.

The thermal behavior of the obtained polymers was evaluated both by DSC and by TGA/differential thermogravimetry (DTG). The thermal property data are summarized in Table IV.

High glass-transition temperatures ( $T_g$ 's) were found for both poly(amide imide)s 4a–4d and poly(ester imide)s 5a–5d because of their intractable, wholly aromatic chains. The DSC investigations were achieved at a heating rate of 20°C/min in a nitrogen atmosphere. The influence of residual water or a reaction solvent was observed in the first scanning of the DSC measurements. However, the study of these first heating traces in DSC curves did not show obvious peaks indicating phase transitions because of their amorphous nature, which could have easily resulted from wide-angle X-ray diffractograms. Moreover, a rapid quenching from the elevated temperatures to room temperature (-100°C/min) yielded predominantly amorphous samples, so discernible baseline shifts could be easily measured in the DSC charts of

the second-heating trace. Generally, the DSC thermograms of the resulting poly(amide imide)s and poly(ester imide)s showed  $T_g$ 's between 331 and 357°C and 318–342°C, respectively, depending on the structures of the diamine and dihydroxy components. Among poly(amide imide)s 4a–4d and poly(ester imide)s 5a–5d, polymer 4d and polymer 5d showed higher  $T_g$  values than those of the other polymers. This could be attributed to the high incorporation of bulky and rigid binaphthylene segments along the polymer backbone, which restricted the free rotation of the macromolecular chains, leading to an enhanced  $T_g$  value. In comparison, the poly(amide imide)s had some higher  $T_g$ 's than the poly(ester imide)s, and this could be related to the higher rigidity of the amide-functional groups than those of the ester linkages.

The TGA/DTG measurements were performed at a heating rate of 10°C/min in a nitrogen atmosphere. Both the poly(amide imide)s and the poly(ester imide)s were stable up to 550°C and lost 10% of their total weight between 579 and 604°C and 566 and 577°C,

TABLE IV  
Thermal Properties of the Copolyimides

Polymer code	$T_g$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>	Char yield (%) <sup>c</sup>
4a	339	579	65
4b	331	594	63
4c	335	596	66
4d	357	604	63
5a	328	566	61
5b	318	575	59
5c	321	573	60
5d	342	577	58

<sup>a</sup> From the second heating traces of DSC measurements with a heating rate of 10°C/min in nitrogen.

<sup>b</sup> Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min in nitrogen.

<sup>c</sup> Percentage weight of material left undecomposed after TGA analysis at a maximum temperature of 800°C in nitrogen.



respectively. The high thermal stability of the resulting polymers was ascribed to their wholly aromatic structures. All TGA/DTG curves of polymers **4a–4d** and **5a–5d** were almost similar. In fact, all the copolyimides, particularly the poly(ester imide)s, showed an obvious two-stage decomposition at elevated temperatures. Assuming a different stability of the amide or ester units and the imide units, the first stage of weight losses might be attributed to the early degradation of the amide and ester groups.<sup>31,32</sup> Therefore, the 10% weight loss temperatures were mainly caused by the decomposition of amide and ester linkages. Generally, poly(amide imide)s **4a–4d** exhibited more thermal stability than poly(ester imide)s **5a–5d**. This higher heat resistance might be attributed to the later degradation of the amide linkages than those of the ester groups against high temperatures.

### CONCLUSIONS

Series of new poly(amide imide)s (**4a–4d**) and poly(ester imide)s (**5a–5d**) derived from imide-containing diacid **1** were synthesized by TPP- and DPCP-activated direct polycondensation with various aromatic diamines and dihydroxy compounds, respectively, in the presence of Py and an inorganic salt. Most of the resultant polymers exhibited a nearly amorphous nature because of their disorderly, twisted structures. Moreover, because of the presence of the cranked cardo binaphthylene units in the polymer backbones, the synthesized polymers showed good solubility in common organic solvents. Of course, the poly(amide imide)s were more soluble than the poly(ester imide)s in highly polar aprotic solvents, and the poly(ester imide)s were more soluble than the poly(amide imide)s in weakly polar solvents. Because of the wholly aromatic structure, the resulting polymers, particularly the poly(amide imide)s, exhibited excellent thermal stability by means of their TGA curves. Consequently, diimide dicarboxylic acid **1** can be considered a candidate for the synthesis of soluble and high-temperature-resistant copolyimides. On the other hand, these binaphthylene-based polymers should be interesting for optical materials because of their chiral character.

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