

# Synthesis and Characterization of New Soluble Poly(ester-imide)s Containing Noncoplanar 2,2'-Dimethyl-4,4'-biphenylene Unit

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Received 16 January 2003; accepted 26 November 2003

**ABSTRACT:** A new diimide–diacid chloride (**3**) containing a noncoplanar 2,2'-dimethyl-4,4'-biphenylene unit was synthesized by treating 2,2'-dimethyl-4,4'-diamino-biphenylene with trimellitic anhydride followed by refluxing with thionyl chloride. Various new poly(ester-imide)s were prepared from **3** with different bisphenols by solution polycondensation in nitrobenzene using pyridine as hydrogen chloride quencher at 170°C. Inherent viscosities of the poly(ester-imide)s were found to range between 0.31 and 0.35 dL g<sup>-1</sup>. All of the poly(ester-imide)s, except the one containing pendent adamantyl group **5e**, exhibited excellent solubility in the following solvents: *N,N*-dimethylformamide, tetrahy-

drofuran, tetrachloroethane, dimethyl sulfoxide, *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidinone, *m*-cresol, *o*-chlorophenol, and chloroform. The polymers showed glass-transition temperatures between 166 and 226°C. The 10% weight loss temperatures of the poly(ester-imide)s, measured by TGA, were found to be in the range between 415 and 456°C in nitrogen. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2486–2493, 2004

**Key words:** conformational analysis; diimide–diacid chloride; poly(ester-imide); polycondensation; pendent group

## INTRODUCTION

Wholly aromatic polyimides and poly(ester-imide)s have high thermal stabilities, and are used as high-strength and high-modulus fibers, as well as high-performance engineering resins.<sup>1</sup> However, processing of such polymers is cumbersome because their softening temperatures are high and they are insoluble in most of the common organic solvents. Copolymerization has been regarded as an effective method for modifying the chemical structure of polyimides to improve their processability.<sup>2,3</sup> Two different functionalities are combined into a single polymer to take advantage of individual properties.<sup>4</sup>

In this article we present the preparation of a series of new poly(ester-imide)s containing a 2,2'-dimethyl-4,4'-biphenylene unit. The incorporation of 2,2'-disubstituted biphenylene in a *para*-linked polymer chain reduces the interactions of polymer chains. The phenyl rings are forced by the 2,2'-disubstitution into a noncoplanar conformation, decreasing the intermolecular forces between the polymer chains.<sup>5–7</sup> The crystallization tendency is significantly lowered and solu-

bility is substantially enhanced. Harris et al.<sup>8</sup> investigated the influence of introducing pendent groups (CH<sub>3</sub>, I, Br, and Cl) in the 2- and 2'-positions of 4,4'-diaminobiphenyl on the solubility and mechanical properties of resulting polyimides, respectively, and they observed improvement in the solubility of the polymers, which they attributed to a noncoplanar structure for improvement in the solubility. Improvement in the solubility of methyl or aryl disubstituted polymer is attributed not only to side groups but also to noncoplanar structure. Solubilities of two different polyimides containing methyl side groups derived from 2,2'-dimethyl-4,4'-diaminobiphenyl and 3,3'-dimethyl-4,4'-diaminobiphenyl were investigated. As expected, 2,2'-disubstituted polyimide (noncoplanar) exhibited better solubility than that of the 3,3'-disubstituted polyimide.<sup>8</sup> Significant improvement in the solubility of 2,2'-disubstituted polyimide was attributed to possession of noncoplanar structure resulting from steric hindrance in the presence of groups at the 2,2'-positions. Contrary to this, introduction of methyl groups at the 3,3'-positions does not alter the polymer structure attributed to the absence of steric hindrance and the improvement of the solubility is ascribed only to the side group effect. These studies clearly demonstrated the position of substitution (which induces noncoplanar structure) is more prominent than the side group effect in improving the solubility.<sup>8</sup> It was also observed that the polymers with the 2,2'-dimeth-

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Contract grant sponsor: National Science Council of the Republic of China.

yl-4,4'-biphenylene unit showed good thermal and mechanical properties because of the presence of the *para*-linked biphenylene unit.<sup>7,9–12</sup> Therefore, the incorporation of the noncoplanar 2,2'-dimethyl-4,4'-biphenylene unit in the polymer backbone is expected to increase processability, as well as thermal and mechanical properties of the poly(ester-imide)s.

A few synthetic routes to poly(ester-imide)s were previously described: (1) melt transesterification from carboxylic acid (or hydroxy) group of a monomer containing a built-in imide ring with a hydroxy (or carboxylic acid) group of another, or (2) solution polycondensation from a dianhydride containing a preformed ester group with a diamine.<sup>13–16</sup> In this study, a new diacid chloride containing a preformed imide group was synthesized and reacted with various bisphenols by solution polycondensation in nitrobenzene using pyridine as hydrogen chloride quencher at 170°C. The general properties such as crystallinity, solubility, and thermal properties of the poly(ester-imide)s were investigated.

## EXPERIMENTAL

### Materials

2,2'-Dimethyl-4,4'-diamino-biphenylene (**1**) kindly supplied by Wakayama Seika Kogyo Co. (Japan), was purified by recrystallization from ethanol. Trimellitic anhydride (TCI) was purified by sublimation under vacuum. The solvents used for polymerization were purified according to standard methods.

### Synthesis of diimide–diacid chloride

Dimethyl-4,4'-diamino-biphenylene (**1**) and trimellitic anhydride were reacted in refluxing glacial acetic acid to give diimide–dicarboxylic acid (**2**) as a white product, which was filtered, washed with ethanol, and recrystallized from DMF/water (v/v 7:1). Compound **2** was then refluxed with an excess of thionyl chloride, using DMF as a catalyst, to give diimide–diacid chloride **3**, which was recrystallized twice from toluene to provide white crystals (m.p. 316–317°C) in 75% yield.

IR (KBr): 1765 and 1711  $\text{cm}^{-1}$  (C=O). ANAL. calcd for  $\text{C}_{32}\text{H}_{18}\text{O}_6\text{N}_2\text{Cl}_2$  (597.41): C, 64.34%; H, 3.04%; N, 4.69%. Found: C, 64.45%; H, 3.23%; N, 4.44%.

### Preparation of polymer

A typical polymerization process was as follows: bisphenol A (**4a**, 0.2283 g, 1.0 mmol), diimide–diacid chloride **3** (0.5974 g, 1.0 mmol), pyridine (0.3 mL), and nitrobenzene (3.5 mL) were homogenized at room temperature and subjected to a temperature of 170°C for 10 h. The resulting viscous polymer solution was

poured into methanol to precipitate the polymer. The white polymer was washed with hot methanol, collected on a filter, and dried *in vacuo* at 70°C for 24 h. The yield of the polymer was 83%. The inherent viscosity of the polymer (**5a**) in DMAc was 0.31  $\text{dL g}^{-1}$ , measured at a concentration of 0.5  $\text{g dL}^{-1}$  at 30°C.

IR spectra (KBr disk): 1770, 1716  $\text{cm}^{-1}$  (C=O). ANAL. calcd for  $\text{C}_{47}\text{H}_{32}\text{O}_8\text{N}_2$ : C, 74.99%; H, 4.28%; N, 3.72%. Found: C, 74.68%; H, 4.35%; N, 3.68%.

All other poly(ester-imide)s (**5b–5h**) were prepared using a similar procedure.

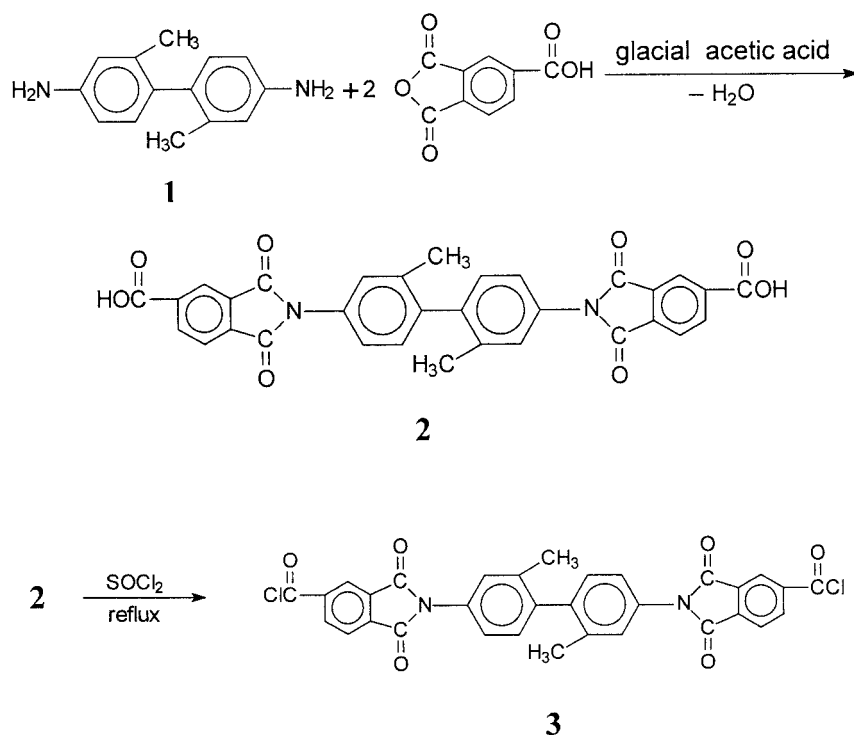
### Measurements

Inherent viscosities of the polymers were measured in DMAc at a concentration of 0.5  $\text{g dL}^{-1}$  at 30°C using an Ubbelohde viscometer (Cannon–Ubbelohde, State College, PA). Elemental analysis was performed on a Perkin–Elmer 2400 instrument (Perkin Elmer Cetus Instruments, Norwalk, CT).  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectra were obtained using a JEOL EX-400 (JEOL, Tokyo, Japan) operating at 399.65 MHz for proton and 100.40 MHz for carbon. Thermogravimetric analysis (4 mg) was performed on a DuPont 2200 thermogravimetric analyzer (DuPont, Boston, MA), heated under nitrogen (100  $\text{cm}^3/\text{min}$ ) at a heating rate of 20°C/min. Differential scanning calorimetry (DSC, 2 mg) analysis was performed on a DuPont 2100 differential scanning calorimeter at a heating rate of 20°C/min. IR spectra were recorded on a Jasco IR-700 spectrometer (Jasco, Tokyo, Japan) using KBr pellets. Wide-angle X-ray diffraction patterns were performed at room temperature with film specimens on an X-ray diffractometer (model PW 1710, Philips, The Netherlands) with Ni-filtered  $\text{Cu-K}_\alpha$  radiation (30 kV, 25 mA).

## RESULTS AND DISCUSSION

### Monomer synthesis

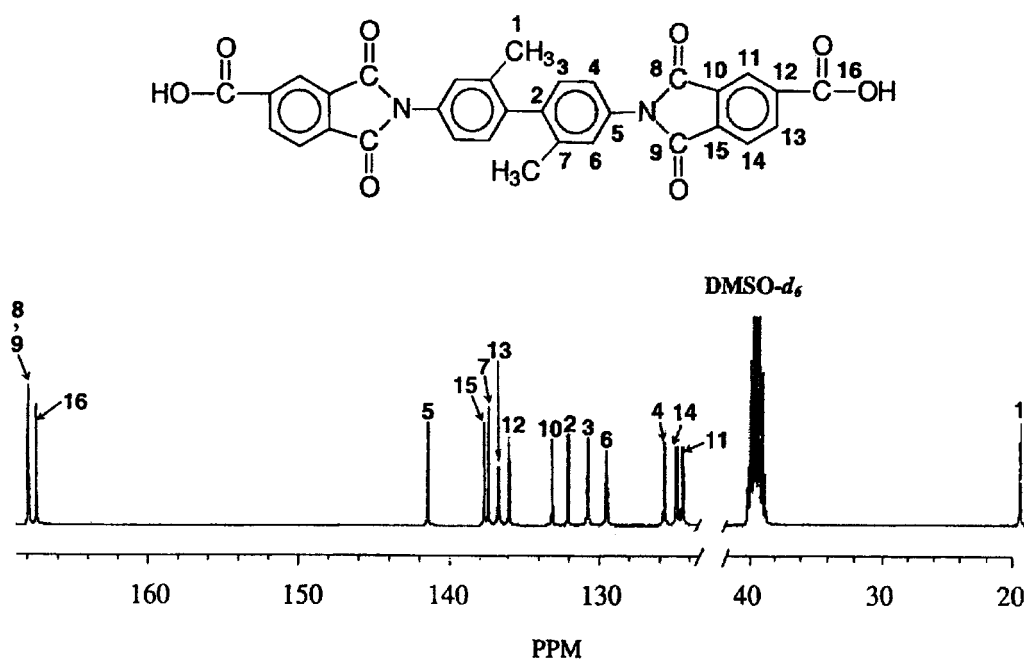
**Scheme 1** outlines the synthetic route to the synthesis of the new diimide–diacid chloride **3**. 2,2'-Dimethyl-4,4'-diamino-biphenylene (**1**) was purified by recrystallization from ethanol. The pure diamine (**1**) was reacted with trimellitic anhydride in refluxing glacial acetic acid. It was a convenient method for preparing the diimide–diacid compound with high purity. The diimide–diacid compound could also be purified by recrystallization in a DMF/water mixture (v/v 7:1). The structure and purity of the diimide–diacid compound were confirmed by IR and NMR spectra. In the IR spectra of the compound, a broad C(O)O—H absorption band appeared in the region of 2500–3400  $\text{cm}^{-1}$  and a C=O stretching absorption band appeared at 1671  $\text{cm}^{-1}$ . Figures 1 and 2 show the  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectra of compound **2**. As can be seen,



**Scheme 1** Synthesis of new diimide–diacid chloride 3.

the spectra of compound 2 were consistent with its structure. The diimide–diacid chloride 3 was obtained by refluxing the diimide–dicarboxylic acid 2 with excess thionyl chloride. It could be purified by recrystallization in toluene. The structure of the diimide–diacid chloride 3 was confirmed by elemental analysis,

IR, and NMR spectroscopy. In the IR spectrum of the diimide–diacid chloride, the absorption band around  $2500\text{--}3400\text{ cm}^{-1}$ , attributed to the absorption of carboxylic acid, disappeared. The  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectra of compound 3 are presented in Figures 3 and 4, respectively. No significant difference in the resonance



**Figure 1**  $^{13}\text{C}$ -NMR spectrum of diimide–dicarboxylic acid 2 (solvent  $\text{DMSO-}d_6$ ).

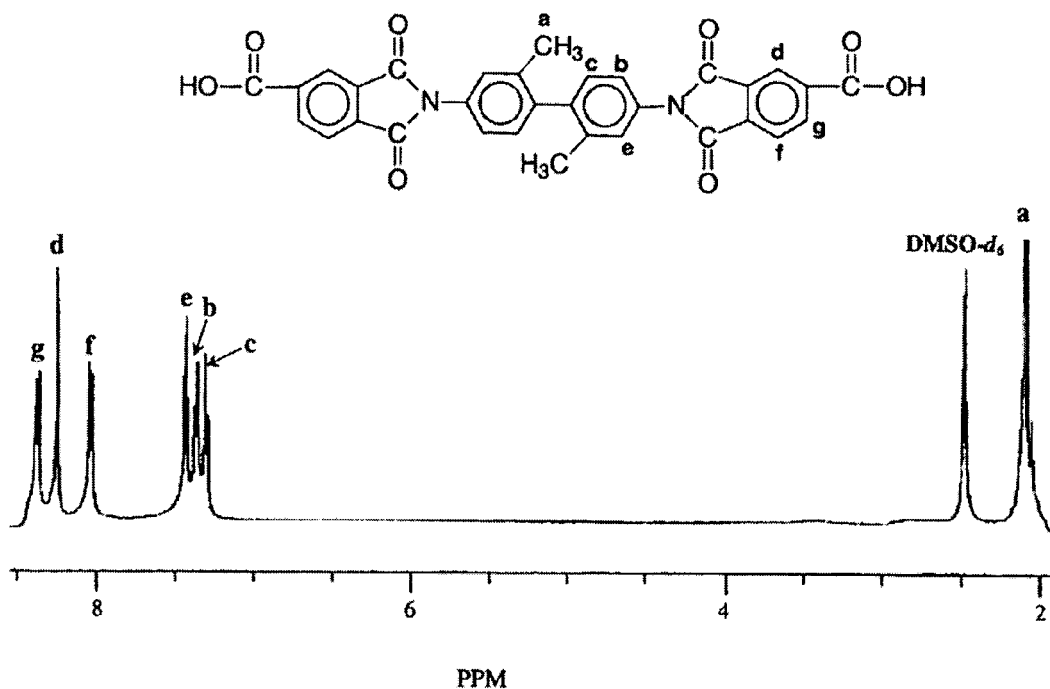


Figure 2  $^1\text{H-NMR}$  spectrum of diimide-dicarboxylic acid 2 (solvent  $\text{DMSO-}d_6$ ).

of the  $^{13}\text{C-NMR}$  between the diimide-dicarboxylic acid (2) and diimide-diacid chloride (3) was observed.

### Polymer synthesis

A series of noncoplanar poly(ester-imide)s (5a–5h) was prepared by solution polycondensation of the

diimide-diacid chloride 3 with various bisphenols including the following: (4a) bisphenol A, a common bisphenol used widely in the industry; (4b) containing isopropylidene and tetramethyl substituent on the phenylene unit; (4c) containing a noncoplanar 2,2'-dimethyl-4,4'-biphenylene unit, (4d) containing an adamantyl substituent; and (4e–4h)

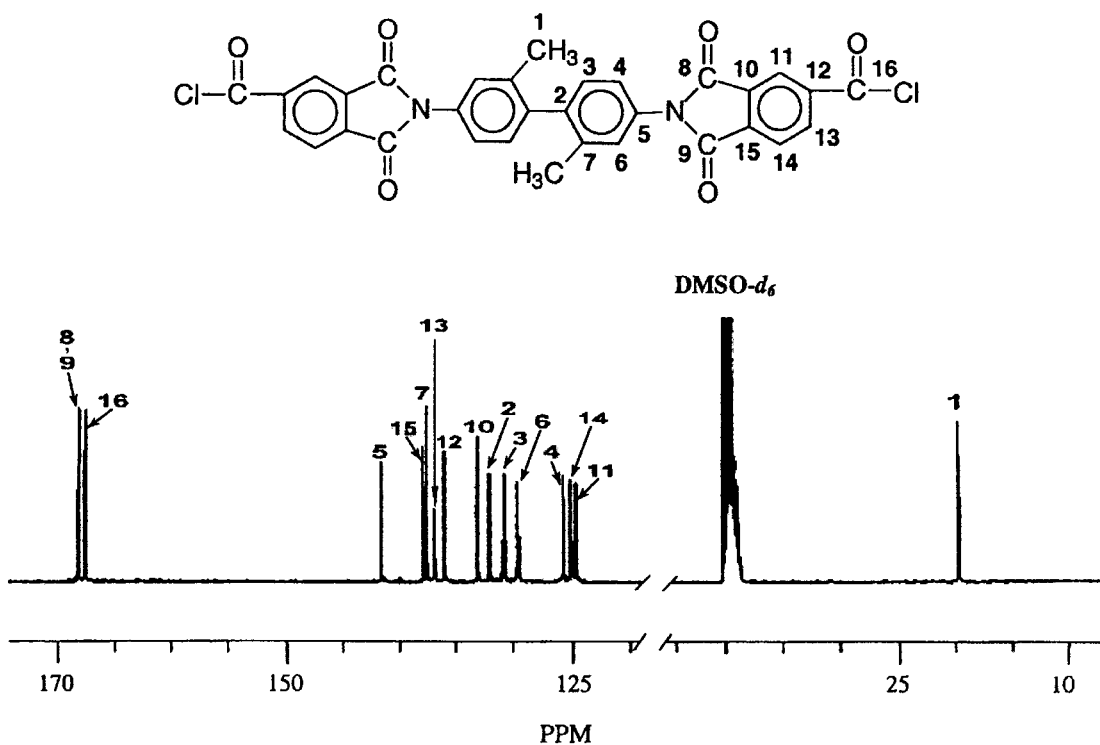


Figure 3  $^{13}\text{C-NMR}$  spectrum of diimide-diacid chloride 3 (solvent  $\text{DMSO-}d_6$ ).

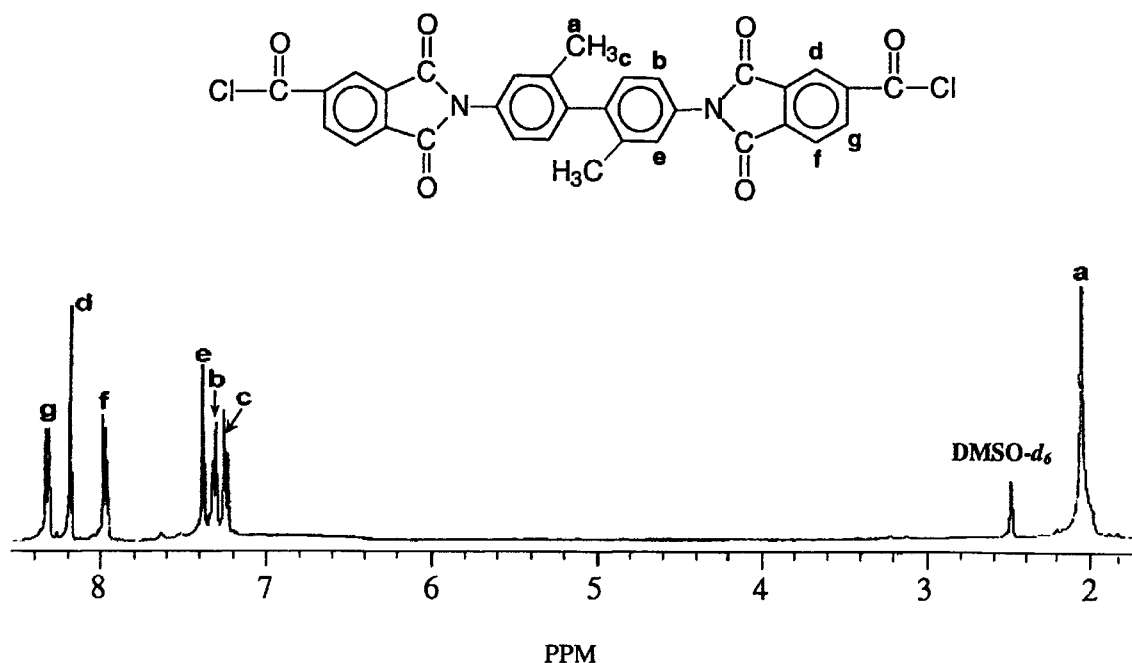


Figure 4  $^1\text{H-NMR}$  spectrum of diimide-diacid chloride **3** (solvent  $\text{DMSO-}d_6$ ).

containing cardo groups. The polymerization was carried out by solution polycondensation in nitrobenzene using pyridine as hydrogen chloride quencher at  $170^\circ\text{C}$  (Scheme 2).

In this study, bisphenol A (**4a**) was used to obtain the bisphenol A-based poly(ester-imide)s for comparison. All of the poly(ester-imide)s, except polymer **5e**, remained soluble in the polymerization medium, thus permitting an increase in their molecular weight. The poly(ester-imide)s were produced in high yield above 82%. They possessed inherent viscosities ranging between  $0.31$  and  $0.35 \text{ dL g}^{-1}$  (Table I). The structure of the polymer was confirmed by IR spectra and elemental analysis. The IR spectra of these polymers showed characteristic imide absorption ( $\text{C=O}$ ) around  $1770$  and  $1716 \text{ cm}^{-1}$ . The elemental analysis data of the poly(ester-imide)s as listed in Table I were in good agreement with the respective structures.

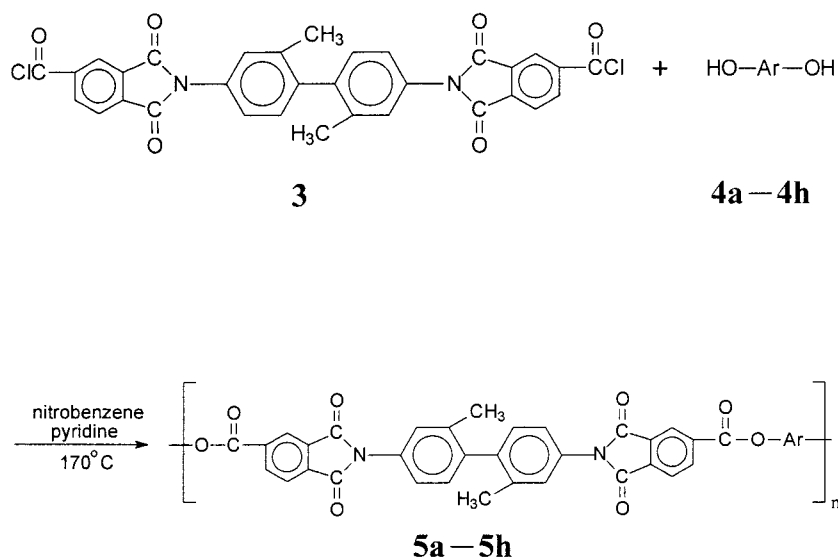
### Polymer characterization

Crystallinity of the new poly(ester-imide)s was estimated by means of wide-angle X-ray diffractograms, shown in Figure 5. As can be seen, all the polymers, except polymer **5e**, presented amorphous patterns. Polymer **5e** containing the pendent adamantyl group showed a fair degree of crystallinity. The crystalline nature of the polymer may be attributable to the presence of the rigid and pendent adamantyl group. It should be noted that the polymers with a 4,4'-biphenylene unit always show a high crystallinity, attrib-

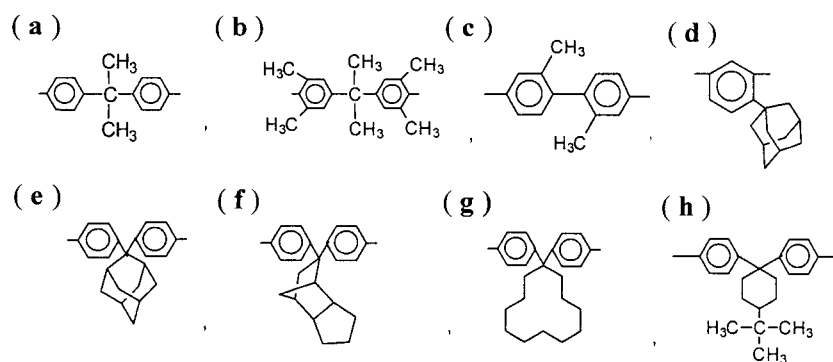
uted to the presence of the rigid and symmetric biphenylene unit. In this study, however, the presence of 2,2'-dimethyl substituent on the 4,4'-biphenylene unit led to a noncoplanar conformation of the biphenylene,<sup>5-7</sup> which decreased the intermolecular forces between the polymer chains and reduced the crystallinity of the polymers. The incorporation of the rigid adamantyl pendent group (**5e**) enhanced the rigidity of the polymer backbone and resulted in high crystallinity, whereas the other pendent groups (**5f-5h**) showed an amorphous nature. It is interesting to note that the polymer (**5d**) bearing the adamantyl group as substituent on the phenylene unit was amorphous in nature. Obviously, the pendent adamantyl group (**5e**) enhanced the order along the chain, whereas the adamantyl substituent (**5d**) decreased the order of the polymer chain arising from a random arrangement of the substituent.<sup>17,18</sup>

The solubility of the poly(ester-imide)s in several organic solvents at 3.0% (w/v) is summarized in Table II.

All the poly(ester-imide)s, except polymer **5e**, exhibited good solubility in a variety of solvents such as *N,N*-dimethylformamide, tetrahydrofuran, tetrachloroethane, dimethyl sulfoxide, *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidinone, *m*-cresol, *o*-chlorophenol, and chloroform at room temperature or upon heating at  $70^\circ\text{C}$ . In contrast, the polyesters derived from terephthaloyl (or isophthaloyl) chloride with various cardo bisphenols in our previous study<sup>19</sup> showed less solubility compared with that of the poly(ester-imide)s in this study. For example, the polyester **Ref-1** derived from terephthaloyl chloride



Ar:



Scheme 2 Preparation of various new poly(ester-imide)s.

with *tert*-butylcyclohexane biphenol showed a solubility that was inferior to that of polymer **5h** (Table II). It was also observed that poly(ester-imide)s showed better solubility than that of the polyimides

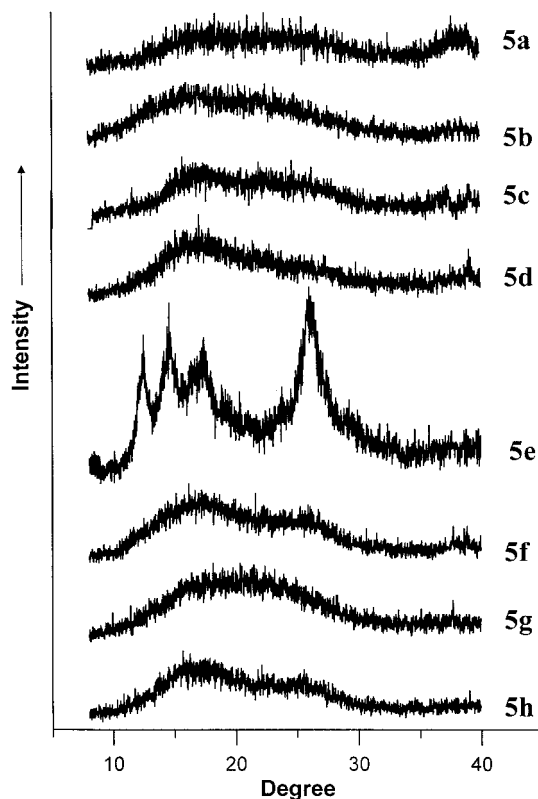
reported in our earlier studies.<sup>20,21</sup> This indicated that the copolymers with both imides and esters groups have better solubility than that of polyimides and polyesters.

**TABLE I**  
Polymerization Result, IR Spectra, and Elemental Analysis of Various Poly(ester-imide)s

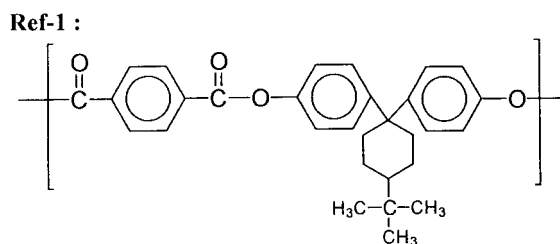
Polymer code	Yield (%)	$\eta_{inh}^a$ (dL g <sup>-1</sup> )	IR (C=O) (cm <sup>-1</sup> )		Elemental analysis (%)		
					Calcd	Found	C
<b>5a</b>	83	0.31	1770	1716	Calcd (Found)	74.99 (74.68)	4.28 (4.38)
<b>5b</b>	84	0.32	1772	1718	Calcd (Found)	75.73 (75.60)	4.98 (5.11)
<b>5c</b>	82	0.34	1771	1716	Calcd (Found)	74.99 (74.60)	4.72 (4.66)
<b>5d</b>	88	0.31	1768	1717	Calcd (Found)	74.99 (74.46)	4.72 (4.64)
<b>5e</b>	86	— <sup>b</sup>	1780	1718	Calcd (Found)	76.76 (76.94)	7.77 (7.82)
<b>5f</b>	84	0.32	1770	1716	Calcd (Found)	76.76 (76.63)	4.77 (4.69)
<b>5g</b>	85	0.35	1766	1716	Calcd (Found)	76.69 (76.58)	5.52 (5.68)
<b>5h</b>	89	0.33	1780	1714	Calcd (Found)	76.40 (76.31)	5.22 (5.16)

<sup>a</sup> Inherent viscosity measured in DMAC at a concentration of 0.5 g dL<sup>-1</sup> at 30°C.

<sup>b</sup> Polymer could not be dissolved in DMAC.



**Figure 5** Wide-angle X-ray diffractogram of poly(ester-imide)s.



The thermal behavior of the poly(ester-imide)s was evaluated both by differential scanning calorimetry (DSC) and by thermogravimetric analysis (TGA). The thermal properties are summarized in Table II. The DSC thermograms of the poly(ester-imide)s obtained from the second-heating traces showed glass-transition temperatures ( $T_g$ 's) in the range between 166 and 226°C. This order was comparable to the decreasing order of stiffness of the polymer backbones. Among the poly(ester-imide)s, polymers **5d** and **5e** containing adamantyl groups showed higher  $T_g$  values. In general, the chain rigidity was increased because of the pendent cardo group, which restricted the free rotation of the polymer backbone.<sup>22</sup> Hence, the polymers showed high glass-transition temperature. Poly(ester-imide)s derived from bisphenol A showed the lowest  $T_g$  value among the poly(ester-imide)s, attributed to the presence of isopropylidene, a kink unit, in the polymer backbone. The incorporation of the kink unit into the polymer backbone lowered the rigidity of the polymer backbone and reduced the  $T_g$  value of the polymers. In contrast, polymer **5b** containing both kink isopropylidene and methyl-substituted phenylene exhibited a higher  $T_g$  value than that of **5g**, which may be attributed to the fact that the methyl group on the phenylene unit inhibits the free rotation of the polymer chains leading to an enhanced  $T_g$  value.

The 10% weight loss temperatures ( $T_{d10}$ ) of the poly(ester-imide)s in nitrogen, measured by TGA, are also summarized in Table II. All the poly(ester-imide)s exhibited good thermal stability. They were stable up to 350°C and lost 10% of their total weight between 415 and 456°C in nitrogen atmosphere. Among these polymers, poly(ester-imide) **5d**, derived from the adamantane-containing bisphenol, exhibited the highest  $T_{d10}$  value, showing a higher thermal stability than

**TABLE II**  
Solubility and Thermal Properties of Various Poly(ester-imide)s<sup>a</sup>

Polymer code	DMF	THF	TCE	DMSO	DMAc	NMP	<i>m</i> -Cresol	Chloroform	<i>o</i> -Chlorophenol	$T_g^b$ (°C)	$T_{d10}^c$ (°C)
<b>5a</b>	++	++	++	+–	++	++	+	++	++	166	441
<b>5b</b>	++	++	++	+	++	++	++	++	++	182	437
<b>5c</b>	++	++	++	+	++	++	+	++	++	177	451
<b>5d</b>	++	++	++	+–	++	++	+	++	++	225	456
<b>5e</b>	–	–	–	–	–	–	–	–	–	222	452
<b>5f</b>	++	++	++	++	++	++	+	++	++	226	433
<b>5g</b>	++	++	++	++	++	++	+	++	++	204	415
<b>5h</b>	++	++	++	+	++	++	++	++	++	217	451
<b>Ref-1</b>	+–	+–	++	–	+–	+	+–	–	++	210	411

<sup>a</sup> Solubility: ++, soluble at room temperature; +, soluble on heating at 70°C; +–, partially soluble at 70°C; –, insoluble. Abbreviations: DMF, *N,N*-dimethylacetamide; THF, tetrahydrofuran; TCE, tetrachloroethane; DMSO, dimethylsulfoxide; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidinone.

<sup>b</sup> Glass-transition temperature was measured by DSC at a heating rate of 20°C min<sup>–1</sup>.

<sup>c</sup> Temperature at 10% weight loss recorded on TGA at a heating rate of 20°C min<sup>–1</sup> in nitrogen.

that of the other poly(ester-imide)s. As expected, polymer **5g** containing the alicyclic dodecyl group showed the lowest  $T_{d10}$  value. However, polymer **5h** also showed a higher  $T_g$  value and 10% weight loss temperatures ( $T_{d10}$ ) than those of the polyester **Ref-1**.

### CONCLUSIONS

The successful preparation of a series of new poly(ester-imide)s containing the noncoplanar 2,2'-dimethyl-4,4'-biphenylene unit was reported. The incorporation of such unit in the polymer backbone effectively reduced the crystallinity and enhanced the solubility of poly(ester-imide)s. All the poly(ester-imide)s, except the polymer with the pendent adamantyl group, showed excellent solubility and even dissolved in chloroform at room temperature. By use of bisphenol containing isopropylidene and tetramethyl substituent on the phenylene unit, noncoplanar 2,2'-dimethyl-4,4'-biphenylene unit, and adamantyl substituent as well as cardo groups higher glass-transition temperatures than those derived from conventional bisphenol A were exhibited. Results presented herein also clearly demonstrate that poly(ester-imide)s with unsymmetric adamantyl substituent (**5d**) led to lower crystallinity and better solubility than those with pendent adamantyl groups (**5e**).

The authors thank the National Science Council of the Republic of China for the financial support, and B. Y. Liaw for his technical assistance.

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