

# Synthesis and Properties of Poly(amide-imide)s Based on 1,5-Bis(4-trimellitimido)naphthalene

Chin-Ping Yang\*, Sheng-Huei Hsiao and Ming-Ru Tsai

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd. Sec. 3, Taipei 10451, Taiwan, ROC

**Abstract:** 1,5-Bis(4-trimellitimido)naphthalene (**II**) was prepared by the condensation reaction of 1,5-naphthalenediamine and trimellitic anhydride. A series of aromatic poly(amide-imide)s (**IV<sub>a-o</sub>**) was synthesized by the direct polycondensation of the diimide-diacid (**II**) and various aromatic diamines (**III<sub>a-o</sub>**). The reaction utilized triphenyl phosphite and pyridine as condensing agents in the presence of calcium chloride in *N*-methyl-2-pyrrolidone (NMP). The inherent viscosities of the resulting poly(amide-imide)s were in the range of 0.55~1.39 dL/g. These polymers were generally soluble in polar solvents, such as *N,N*-dimethylacetamide (DMAc), NMP, *N,N*-dimethylformamide (DMF). Flexible and tough poly(amide-imide) films were obtained by casting from a DMAc solution and had tensile strengths of 90~145 MPa, elongations to break of 5~13 %, and initial moduli of 2.29~3.73 GPa. The glass transition temperatures of some poly(amide-imide)s were recorded in the range of 206~218 °C, and most of the polymers did not show discernible glass transition on their DSC traces. The 10% weight loss temperatures were above 522 °C in nitrogen and above 474 °C in air atmosphere.

**Keywords:** Poly(amide-imide)s, 1,5-Naphthalenediamine, Trimellitic anhydride.

## Introduction

Aromatic polyimides are of industrial interest because they exhibit high thermal stability with good mechanical and electrical performance over a wide temperature range as well as excellent solvent resistance [1,2]. However, their applications have been limited owing to their poor solubility and intractable characteristics. To overcome these drawbacks, some copolymers have been proposed, poly(amide-imide)s, in particular. Because they contain both amide and imide groups in polymer repeating units, poly(amide-imide)s have properties between polyamides and polyimides; accordingly, this class of polymers offers a good compromise between optimal thermal stability and processability.

In the past, aromatic poly(amide-imide)s were usually prepared from trimellitic anhydride (TMA) or its acyl chloride with aromatic diamines or diisocyanates [3-16]. In the last decade, we have successfully applied the phosphorylation reaction [17] to the direct synthesis of high-molecular-weight poly(amide-imide)s from the TMA-based imide ring-containing dicarboxylic acids and aromatic diamines

using triphenyl phosphite and pyridine as condensing agents [18-25]. This method provides significant advantages in manufacturing operations compared with conventional methods. Thus, many new series of poly(amide-imide)s have been readily prepared by this convenient technique in our laboratory. Recently, we have become interested in the potential usefulness of a naphthyl-containing structure as a bulky unit in the main polymer chain. As a continuation of our efforts in this area, we describe here the preparation and characterization of a new series of poly(amide-imide)s based on the diimide-diacid prepared from 1,5-naphthalenediamine and trimellitic anhydride.

## Experimental

### 1. Materials

Bis[4-(4-aminophenoxy)phenyl]ether (**III<sub>k</sub>**) was prepared according to previous reports [26,27]. *p*-Phenylenediamine (**III<sub>a</sub>**) and *m*-phenylenediamine (**III<sub>b</sub>**) were purified by vacuum distillation before use. All other diamines had a high purity when

\*To whom all correspondence should be addressed.

received from manufacturers and were used without any further purification, including 1,5-naphthalenediamine (from TCI), 4,4'-oxydianiline (**III<sub>c</sub>**, from TCI), 3,4'-oxydianiline (**III<sub>d</sub>**, from Teijin Ltd., Tokyo), 4,4'-diaminodiphenyl sulfide (**III<sub>e</sub>**, from TCI), 4,4'-diaminodiphenylmethane (**III<sub>f</sub>**, from TCI), 1,4-bis(4-aminophenoxy)benzene (**III<sub>g</sub>**, from TCI), 1,3-bis(4-aminophenoxy)benzene (**III<sub>h</sub>**, from Chriskev), 2,2-bis(4-aminophenoxy)hexafluoropropane (**III<sub>i</sub>**, from TCI), 4,4'-bis(4-aminophenoxy)biphenyl (**III<sub>j</sub>**, from TCI), 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (**III<sub>l</sub>**, from Chriskev), 2,2'-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**III<sub>m</sub>**, from TCI), 2,2'-bis[4-(4-aminophenoxy)phenyl]sulfone (**III<sub>n</sub>**, from TCI). According to the reported method [28], 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (**III<sub>o</sub>**) was synthesized starting from tetraphenylthiophene, which was easily prepared by the reaction of benzyl chloride with powdered sulfur at an elevated temperature. Trimellitic anhydride (from Wako) was used without previous purification. Commercially available calcium chloride (CaCl<sub>2</sub>) was dried under a vacuum at 180 °C for 10 hrs. *N,N*-Dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethyl-formamide (DMF) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure.

## 2. Synthesis of diimide-diacid (II)

A mixture of 4.746 g (0.03 mol) of 1,5-naphthalenediamine, 11.4 g (0.06 mol) of trimellitic anhydride, 20 mL of toluene, and 120 mL of dry DMF was charged into a 250 mL flask equipped with a Dean-Stark trap, a condenser, and a stirrer. The mixture was heated at a reflux temperature of about 140 °C and water that was formed during the reaction was collected in the Dean-Stark trap. After 4 hrs, the residual toluene was removed by distillation; the resulting solution was cooled to precipitate the diimide-diacid monomer (**II**). The precipitate was filtered and dried under a vacuum to give 12.6 g of yellow powder (yield: 83%, mp. 170~171 °C). Anal. calcd. for C<sub>28</sub>H<sub>14</sub>N<sub>2</sub>O<sub>8</sub>: C, 66.41; H, 2.79; N, 5.53%; Found: C, 66.43; H, 2.90; N, 5.41%.

## 3. Polymerization

Poly(amide-imide)s **IV<sub>a-o</sub>** were synthesized by direct polycondensation from diimide-diacid **II** and various aromatic diamines. A typical example of polymerization is described as follows: A 50-mL flask was charged with 0.633 g (1.25 mmol) of 1,5-bis(trimellitimidido)naphthalene (**II**), 0.523 g (1.25 mmol) of 2,5-bis(4-aminophenyl)-3,4-di-

phenylthiophene (**III<sub>o</sub>**), 0.8 g of calcium chloride, 8 mL of NMP, 1.5 mL of pyridine, and 0.8 mL of triphenyl phosphite (TPP). The mixture was heated at 100 °C while being stirred for 3 hrs under nitrogen. The obtained polymer solution was poured slowly into 400 mL stirring methanol giving rise to a fiber-like precipitate, which was washed thoroughly with methanol and hot water, collected by filtration and finally dried under a vacuum. The inherent viscosity of the polymer on a concentration of 0.5 g/dL in DMAc was 1.39 dL/g at 30 °C. Anal. calcd. for (C<sub>56</sub>H<sub>32</sub>N<sub>4</sub>O<sub>6</sub>S)<sub>n</sub>: C, 75.66; H, 3.63; N, 6.30%; Found: C, 75.29; H, 3.85; N, 5.92%.

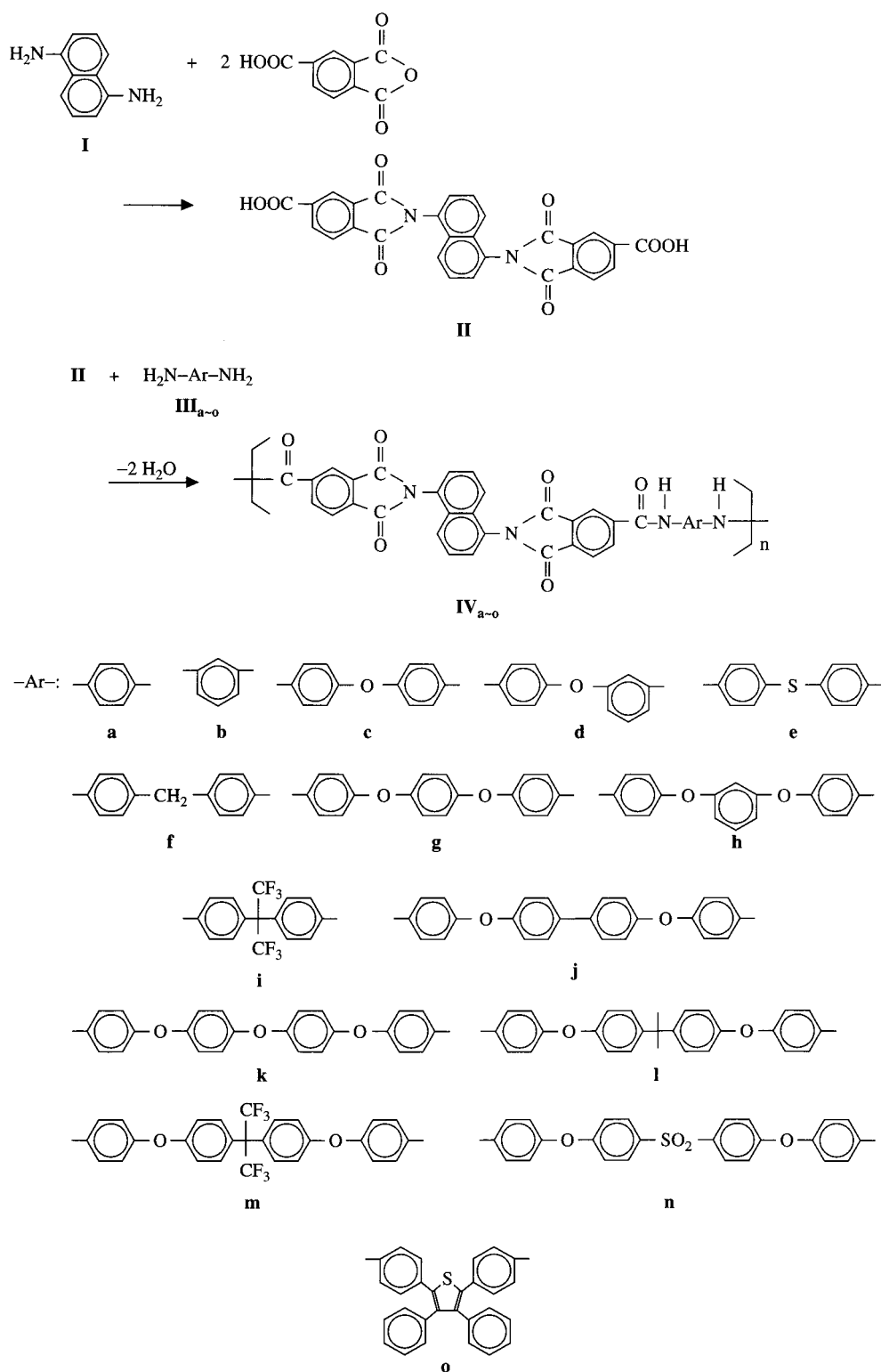
## 4. Measurements

Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform Infrared Spectrometer. The inherent viscosities were determined at 0.5 g/dL concentration using a Cannon-Fenske viscometer at 30 °C. Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller in flowing nitrogen (50 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. Thermogravimetric analysis (TGA) was done on a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Measurements were performed with 10 ± 2 mg samples in flowing nitrogen (50 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. Wide-angle X-ray measurements were conducted at room temperature with film specimens, which were about 0.3 mm thick, or with powder samples, on a Rigaku Geiger Flex D-Max **III<sub>a</sub>** X-ray diffractometer, using Ni-filtered CuK<sub>α</sub> radiation (40 kV, 15 mA). The scanning rate was 2 °/min. An Instron Universal Tester Model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the sample. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.3 mm thick), and an average of at least five individual determinations was reported.

## Results and Discussion

### 1. Synthesis of diimide-diacid (II)

As shown in Scheme 1, 1,5-bis(trimellitimidido)naphthalene (**II**) was synthesized from the condensation of 1,5-naphthalenediamine and two equivalent amounts of trimellitic anhydride in a polar solvent such as DMF. The intermediate amic acid obtained during the reaction was cyclodehydrated to



Scheme 1

imidodicarboxylic acid (**II**) and was purified by means of toluene-water azeotropic distillation. The elemental analysis of the diimide-diacid obtained was in good agreement with the calculated values for the

proposed structure. The infrared spectrum (KBr) exhibits characteristic absorptions at 3502 cm<sup>-1</sup> (-OH carboxylic acid), 1778 and 1725 cm<sup>-1</sup> (C=O symmetrical stretching and asymmetrical stretching),

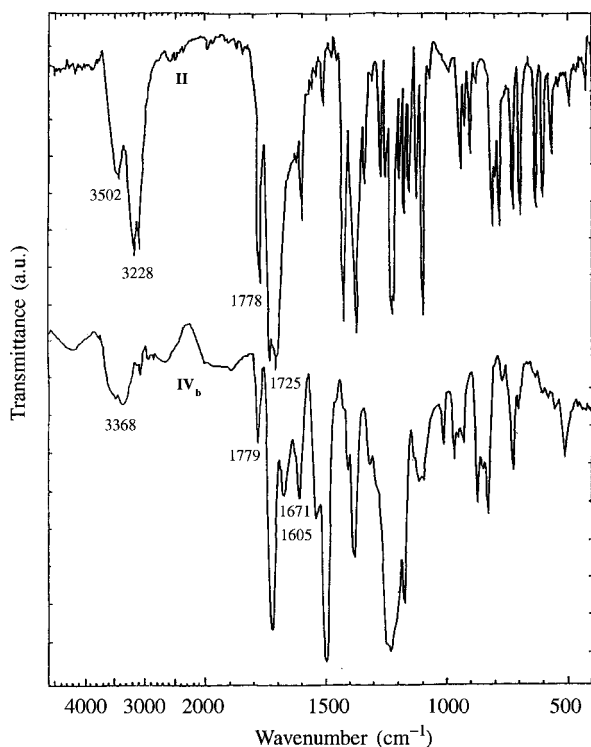


Figure 1. IR spectra of diimide-diacid **II** and representative poly(amide-imide) **IV<sub>b</sub>**.

which is shown in Figure 1.

## 2. Synthesis of poly(amide-imide)s

A series of novel poly(amide-imide)s containing the 1,5-naphthyl group were synthesized by direct polycondensation from diimide-diacid (**II**) and various aromatic diamines (**III<sub>a-o</sub>**) in NMP in the presence of calcium chloride using triphenyl phosphite and pyridine as condensing agents. The inherent viscosities of the yellowish stringy poly(amide-imide) precipitates were in the range of 0.55–1.39 dL/g (Table I). The yields were usually quantitative. All the polycondensations proceeded homogeneously throughout the reaction except in the case of polymer **IV<sub>a</sub>**. Homogeneity of the reaction medium favors the polycondensation reaction. A sufficient amount of metal salts, such as calcium chloride dissolved in the reaction solvent, is necessary to prevent an early precipitation that may hinder the polycondensation reaction. Using a higher initial reactant concentration and adding a supplemental solvent before a swollen gel formed or precipitation occurred usually could produce polymers with a higher inherent viscosity. For example, poly(amide-imide)s **IV<sub>m</sub>** and **IV<sub>o</sub>** were obtained with inherent viscosity higher than 1.0 dL/g. The structures and compositions of these polymers were confirmed by IR spectroscopy and elemental analysis. A representative IR spectrum is reproduced in Fig-

Table I. Preparation of poly(amide-imide)s<sup>(a)</sup> from diimide-diacid (**II**) and diamine (**III<sub>a-o</sub>**).

Polymer	Diamine	Additional amount of NMP (mL)	Yield (%)	$\eta_{inh}^{(b)}$ (dL/g)	Appearance
<b>IV<sub>a</sub></b>	<b>III<sub>a</sub></b>	3	97	0.69 <sup>(c)</sup>	Powder
<b>IV<sub>b</sub></b>	<b>III<sub>b</sub></b>	0	99	0.65	Stringy
<b>IV<sub>c</sub></b>	<b>III<sub>c</sub></b>	0	100	0.82	Stringy
<b>IV<sub>d</sub></b>	<b>III<sub>d</sub></b>	0	99	0.55	Stringy
<b>IV<sub>e</sub></b>	<b>III<sub>e</sub></b>	0	99	0.66	Stringy
<b>IV<sub>f</sub></b>	<b>III<sub>f</sub></b>	0	99	0.58	Stringy
<b>IV<sub>g</sub></b>	<b>III<sub>g</sub></b>	0	99	0.90	Stringy
<b>IV<sub>h</sub></b>	<b>III<sub>h</sub></b>	0	100	0.60	Stringy
<b>IV<sub>i</sub></b>	<b>III<sub>i</sub></b>	0	99	0.88	Stringy
<b>IV<sub>j</sub></b>	<b>III<sub>j</sub></b>	0	100	0.65	Stringy
<b>IV<sub>k</sub></b>	<b>III<sub>k</sub></b>	0	99	0.65	Stringy
<b>IV<sub>l</sub></b>	<b>III<sub>l</sub></b>	0	99	0.70	Stringy
<b>IV<sub>m</sub></b>	<b>III<sub>m</sub></b>	1	100	1.06	Stringy
<b>IV<sub>n</sub></b>	<b>III<sub>n</sub></b>	0	99	0.65	Stringy
<b>IV<sub>o</sub></b>	<b>III<sub>o</sub></b>	3	99	1.39	Stringy

(a) Polymerization was carried out with 1.25 mmol of each monomer, 8.0 mL of NMP, 0.8 mL of TPP, 1.5 mL of pyridine, and 0.8 g of CaCl<sub>2</sub> at 100 °C for 3 hrs.

(b) Measured in DMAc at a concentration of 0.5 g/dL at 30 °C.

(c) Measured in conc. H<sub>2</sub>SO<sub>4</sub> at a concentration of 0.5 g/dL at 30 °C.

Table II. Elemental analysis of poly(amide-imide)s.

Polymer	Formula (Mol. weight)		Elemental analysis (%)		
			C	H	N
<b>IV<sub>a</sub></b>	(C <sub>34</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (578.54) <sub>n</sub>	Calcd	70.59	3.14	9.68
		Found	70.38	3.22	9.52
<b>IV<sub>b</sub></b>	(C <sub>34</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (578.54) <sub>n</sub>	Calcd	70.59	3.14	9.68
		Found	70.45	3.25	9.56
<b>IV<sub>c</sub></b>	(C <sub>40</sub> H <sub>22</sub> N <sub>4</sub> O <sub>7</sub> ) <sub>n</sub> (670.64) <sub>n</sub>	Calcd	71.64	3.31	8.35
		Found	71.22	3.44	8.24
<b>IV<sub>d</sub></b>	(C <sub>40</sub> H <sub>22</sub> N <sub>4</sub> O <sub>7</sub> ) <sub>n</sub> (670.64) <sub>n</sub>	Calcd	71.64	3.31	8.35
		Found	71.31	3.46	8.21
<b>IV<sub>e</sub></b>	(C <sub>40</sub> H <sub>22</sub> N <sub>4</sub> O <sub>6</sub> S) <sub>n</sub> (686.70) <sub>n</sub>	Calcd	69.96	3.23	8.16
		Found	69.78	3.35	8.07
<b>IV<sub>f</sub></b>	(C <sub>41</sub> H <sub>24</sub> N <sub>4</sub> O <sub>6</sub> ) <sub>n</sub> (668.66) <sub>n</sub>	Calcd	73.65	3.62	8.38
		Found	73.55	3.81	8.29
<b>IV<sub>g</sub></b>	(C <sub>46</sub> H <sub>26</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (762.73) <sub>n</sub>	Calcd	72.44	3.44	7.35
		Found	72.33	3.56	7.25
<b>IV<sub>h</sub></b>	(C <sub>46</sub> H <sub>26</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (762.73) <sub>n</sub>	Calcd	72.44	3.44	7.35
		Found	72.28	3.58	7.23
<b>IV<sub>i</sub></b>	(C <sub>43</sub> H <sub>22</sub> N <sub>4</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub> (804.66) <sub>n</sub>	Calcd	64.19	2.76	6.96
		Found	64.08	2.88	6.75
<b>IV<sub>j</sub></b>	(C <sub>52</sub> H <sub>30</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (838.83) <sub>n</sub>	Calcd	74.46	3.60	6.68
		Found	74.35	3.78	6.55
<b>IV<sub>k</sub></b>	(C <sub>52</sub> H <sub>30</sub> N <sub>4</sub> O <sub>9</sub> ) <sub>n</sub> (854.83) <sub>n</sub>	Calcd	73.06	3.54	6.55
		Found	72.89	3.67	6.41
<b>IV<sub>l</sub></b>	(C <sub>55</sub> H <sub>36</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (880.91) <sub>n</sub>	Calcd	74.99	4.12	6.36
		Found	74.77	4.24	6.27
<b>IV<sub>m</sub></b>	(C <sub>52</sub> H <sub>30</sub> N <sub>4</sub> O <sub>8</sub> F <sub>6</sub> ) <sub>n</sub> (952.82) <sub>n</sub>	Calcd	65.55	3.17	5.88
		Found	65.38	3.28	5.70
<b>IV<sub>n</sub></b>	(C <sub>52</sub> H <sub>30</sub> N <sub>4</sub> O <sub>10</sub> S) <sub>n</sub> (902.89) <sub>n</sub>	Calcd	69.17	3.35	6.21
		Found	69.02	3.42	6.09
<b>IV<sub>o</sub></b>	(C <sub>56</sub> H <sub>32</sub> N <sub>4</sub> O <sub>6</sub> S) <sub>n</sub> (888.95) <sub>n</sub>	Calcd	75.66	3.63	6.30
		Found	75.50	3.81	6.18

**Table III.** Solubility<sup>(a)</sup> of poly(amide-imide)s.

Polymer	Solvent <sup>(b)</sup>							
	DMF	DMAc	DMSO	NMP	<i>m</i> -cresol	<i>o</i> -ch	Py	conc. H <sub>2</sub> SO <sub>4</sub>
IV <sub>a</sub>	-	-	-	-	-	-	-	+
IV <sub>b</sub>	+	+	+	+	+	+	+	+
IV <sub>c</sub>	+	+	+	+	+-	-	+	+
IV <sub>d</sub>	+	+	+	+	+-	+	+	+
IV <sub>e</sub>	+	+	-	+	-	+	-	+
IV <sub>f</sub>	+	+	+	+	+-	-	-	+
IV <sub>g</sub>	+	+	+	+	-	-	+	+
IV <sub>h</sub>	+	+	+	+	-	+-	+	+
IV <sub>i</sub>	+	+	+	+	+	+	+	+
IV <sub>j</sub>	+	+	+	+	+	+	+	+
IV <sub>k</sub>	+	+	+	+	+-	+-	+	+
IV <sub>l</sub>	+	+	+	+	-	-	+	+
IV <sub>m</sub>	-	+	-	+	-	-	-	+
IV <sub>n</sub>	+	+	+	+	+	+	+	+
IV <sub>o</sub>	+	+	+	+	-	+	+	+

(a) Solubility: +, soluble at room temperature; +-, partially soluble; -: insoluble.

(b) DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; Py: pyridine; *o*-ch: *o*-chlorophenol.**Table IV.** Tensile properties of poly(amide-imide)s films<sup>(a)</sup>.

Polymer	Strength at yield (MPa)	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
IV <sub>b</sub>	84	100	5	2.81
IV <sub>d</sub>	100	114	13	2.92
IV <sub>e</sub>	-	98	8	2.42
IV <sub>h</sub>	-	118	9	2.71
IV <sub>i</sub>	113	111	13	3.56
IV <sub>j</sub>	-	106	9	3.44
IV <sub>k</sub>	-	118	10	2.29
IV <sub>l</sub>	-	117	7	3.12
IV <sub>n</sub>	94	90	8	2.31
IV <sub>o</sub>	148	145	12	3.73

(a) Films were cast from polymer solutions of DMAc.

ure 1. The IR spectrum of IV<sub>b</sub> exhibited characteristic absorptions at 1779 and 1725 cm<sup>-1</sup> (imide) and 3368 and 1671 cm<sup>-1</sup> (amide) and the results of elemental analysis (Table II) of the polymers are in good agreement with the calculated values for the proposed structures.

### 3. Properties of polymers

The qualitative solubilities of all the poly(amide-imide)s in various polar solvents are listed in Table III. Almost all of poly(amide-imide)s, except for IV<sub>a</sub> and IV<sub>m</sub>, were soluble in amide-type solvents, such as DMF, DMAc, DMSO, and NMP. The poor solubility of IV<sub>a</sub> may be caused by the rigid structure of *p*-phenylenediamine moiety. The solubilities of the polymers bearing flexible, pendent or large bulky bridging groups, such as *m*-phe-

nylene, ether, hexafluoroisopropylidene, sulfone and tetraphenylthiophene (IV<sub>b</sub>, IV<sub>i</sub>, IV<sub>k</sub>, IV<sub>n</sub>, and IV<sub>o</sub>), revealed high solubility. These polymers were also soluble in less polar solvents, such as *m*-cresol, *o*-chlorophenol and pyridine. The high solubility can be partly due to the presence of the bulky 1,5-naphthyl unit. The crystallinity of the prepared poly(amide-imide)s was evaluated by wide-angle X-ray diffraction measurements. It was found that almost all the polymers showed an amorphous diffraction pattern due to the reason cited above.

Transparent, tough and flexible films of most poly(amide-imide)s could be cast from the DMAc solutions. Polymer IV<sub>a</sub> was insoluble in DMAc, and the films of polymers IV<sub>c</sub>, IV<sub>f</sub>, IV<sub>g</sub>, and IV<sub>m</sub> were noncreasable. The tensile properties of the flexible films were determined by an Instron machine. Table IV summarizes the results. The tensile strength, elongation to break, and initial modulus of the poly(amide-imide) films were in the range of 90~145 MPa, 5~13 %, and 2.29~3.73 GPa, respectively.

The thermal stability and glass transition temperatures (T<sub>g</sub>s) of these polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. Table V summarizes the thermal behavior data of all the poly(amide-imide)s, including T<sub>g</sub>s, the temperatures at various weight loss %, and the char yield at 800 °C. The TGA curves (Figure 2) of these polymers indicated that none of the polymers lost significantly weight under 400 °C in nitrogen or air atmosphere. The T<sub>10</sub>s were recorded in the range of 522~575 °C

**Table V.** Thermal properties of poly(amide-imide)s.

Polymer	$T_g^{(a)}$ (°C)	Decomposition temperature (°C) <sup>(c)</sup> at various weight loss %				Char <sup>(d)</sup> yield (%)
		$T_5$	$T_{10}$	$T_{15}$	$T_{20}$	
<b>IV<sub>a</sub></b>	— <sup>(b)</sup>	501 (403)	554 (480)	602 (540)	701 (616)	66
<b>IV<sub>b</sub></b>	—	462 (464)	548 (516)	618 (552)	670 (568)	60
<b>IV<sub>c</sub></b>	—	462 (464)	549 (516)	606 (553)	656 (568)	59
<b>IV<sub>d</sub></b>	—	459 (445)	549 (492)	613 (533)	668 (549)	61
<b>IV<sub>e</sub></b>	—	449 (436)	534 (507)	612 (571)	691 (584)	65
<b>IV<sub>f</sub></b>	—	429 (419)	522 (474)	596 (523)	653 (537)	61
<b>IV<sub>g</sub></b>	208	490 (463)	552 (515)	604 (559)	661 (577)	62
<b>IV<sub>h</sub></b>	218	471 (455)	550 (500)	610 (540)	666 (565)	61
<b>IV<sub>i</sub></b>	—	456 (479)	575 (526)	629 (561)	716 (577)	68
<b>IV<sub>j</sub></b>	—	460 (446)	550 (494)	545 (536)	598 (552)	60
<b>IV<sub>k</sub></b>	214	473 (461)	523 (523)	579 (577)	622 (599)	62
<b>IV<sub>l</sub></b>	212	479 (465)	544 (521)	593 (565)	657 (582)	63
<b>IV<sub>m</sub></b>	—	465 (464)	545 (514)	573 (553)	681 (584)	60
<b>IV<sub>n</sub></b>	206	465 (464)	531 (504)	590 (582)	642 (602)	61
<b>IV<sub>o</sub></b>	—	478 (476)	556 (523)	610 (583)	634 (598)	61

(a) From the second heating traces of DSC measurements conducted at a heating rate of 20 °C/min in nitrogen.

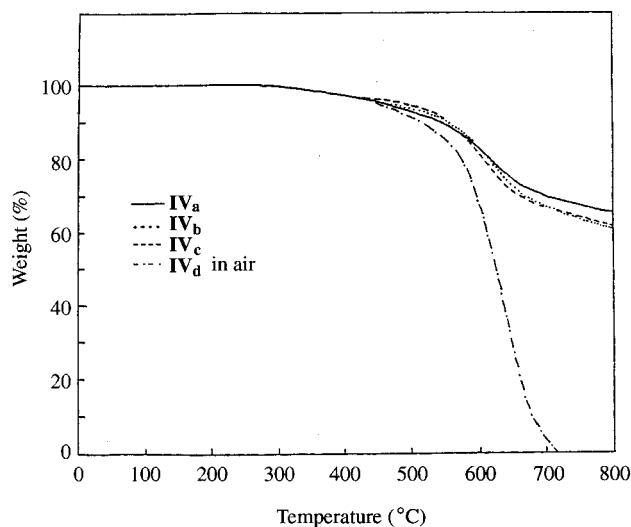
(b) No  $T_g$  was observed in DSC traces.

(c) Thermogravimetry was conducted at a heating rate of 20 °C/min in nitrogen (or in air).

(d) Residual weight percentage at 800 °C in nitrogen.

in nitrogen and 474~526 °C in air, respectively. The char yields of all polymers were above 59% in nitrogen atmosphere when heated to 800 °C. Quenching from elevated temperatures to room temperature produced predominantly amorphous samples so that  $T_g$  of polymers could easily be detected in the second heating. However, in most cases, no discernible glass transition was observed in the DSC traces. As shown in Table V, only five polymers (**IV<sub>g</sub>**, **IV<sub>h</sub>**, **IV<sub>k</sub>**, **IV<sub>l</sub>**, and **IV<sub>n</sub>**) revealed a clear glass transition between 206 and 218 °C. The difficulty encountered in determining their  $T_g$  values by DSC may be attributed to the rigid nature of their macromolecular backbones due to the presence of the bulky rigid 1,5-bis(phthalimido)naphthalene unit.

## References



**Figure 2.** TGA curves of poly(amide-imide)s **IV<sub>a</sub>**, **IV<sub>b</sub>** and **IV<sub>c</sub>** with a heating rate of 20 °C/min in nitrogen and **IV<sub>d</sub>** in air atmosphere.

1. D. Wilson, H. D. Stenzenberger and P. H. Hergenrother Eds., *Polyimides*, Blackie & Son, Glasgow and London, 1990.
2. M. K. Ghosh and K. L. Mittal Eds., *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, 1996.
3. Standard Oil Co., U. S. Pat. 3,920,612 (1975).
4. Standard Oil Co., U. S. Pat. 4,048,114 (1977).
5. B. A. Zhubanov, S. A. Mashkevich and S. R. Rafikov, *Vysokomol. Soedin., Ser. A*, **14**, 2201 (1972).
6. J. de Abajo, J. P. Gabarda and J. Fontan, *Angew. Makromol. Chem.*, **71**, 143 (1972).
7. S. Maiti and A. Ray, *J. Appl. Polym. Sci.*, **27**, 4345 (1982).
8. S. Maiti and A. Ray, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 999 (1983).
9. H. Shigeyoshi, Y. Tsunemasa, I. Masao and U. Moriya, *Jpn. Pat. 72-30,312* (1972).
10. G. Bellmann and A. Groult, *Fr. Demande 2,399,452* (1979).
11. M. Ghosh, *Angew. Makromol. Chem.*, **172**, 165 (1989).
12. T. Nishioka, I. Ishibashi, Y. Suzuki and Y. Hamada, *Jpn. Pat. 70-35,072* (1970).
13. K. Tanaka, *Jpn. Pat. 71-413* (1971).
14. J. de Abajo, A. G. Brunet, S. G. Babe and J. Fontan, *An. Quim.*, **70**, 908 (1974).
15. J. L. Nieto, J. G. de la Campa and J. de Abajo, *Makromol. Chem.*, **183**, 557 (1982).
16. Y. Segui, H. Benalla and J. Farenc, *Proc. Int. Conf. Conduct. Breakdown Solid Dielectr., 1st*, 124 (1989).
17. N. Yamazaki, M. Matsumoto and F. Higashi, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1373 (1975).
18. C. P. Yang and S. H. Hsiao, *Makromol. Chem.*, **190**, 2119 (1989).
19. S. H. Hsiao and C. P. Yang, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 1449 (1990).
20. S. H. Hsiao and C. P. Yang, *Makromol. Chem.*, **191**, 155 (1990).
21. S. H. Hsiao and C. P. Yang, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 447 (1991).
22. C. P. Yang, S. H. Hsiao and J. H. Lin, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 1175 (1991).

23. C. P. Yang, S. H. Hsiao and Y. Y. Yen, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1885 (1992).
24. C. P. Yang, S. H. Hsiao and J. H. Lin, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1865 (1993).
25. C. P. Yang, J. M. Cheng and S. H. Hsiao, *Makromol. Chem.*, **193**, 455 (1992).
26. N. A. Adrova, M. M. Koton, A. M. Dubnova and N. P. Kuznetsov, *Vysokomol. Soedin. B*, **16**, 504 (1974).
27. R. B. Stackman and A. B. Conciatori, U. S. Pat. 4,064,107 (1978).
28. Y. Imai, N. N. Malder and M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2189 (1984).