

Synthesis and Properties of Poly(amide imide)s Based on 2,2'- or 4,4'-Bis(4-aminophenoxy)biphenyl and Various Bis(trimellitimide)s

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ABSTRACT: Three series of isomeric poly(amide imide)s (series III, IV, and V) were synthesized by the direct polycondensation of 2,2'-bis(4-aminophenoxy)biphenyl (2,2'-BAPB), 4,4'-bis(4-aminophenoxy)biphenyl (4,4'-BAPB), or their equimolar mixture (2,2'-BAPB/4,4'-BAPB = 1/1) with 12 diimide diacids and with triphenyl phosphite and pyridine as condensing agents. A comparison of the physical properties of these three series was also made. The inherent viscosities of series III, IV, and V were 0.25–0.84, 0.25–1.52, and 0.43–1.30 dL g⁻¹, respectively. Most of the series III polymers showed better solubility because of the non-para structure, with the solubility order found to be III > V > IV. According to X-ray diffraction patterns, the amorphous poly(amide imide)s had excellent solubility, whereas the

crystalline polymers were less soluble. All the soluble polymers afforded transparent, flexible, and tough films, which had tensile strengths of 57–104 MPa, elongations at break of 3–20%, and initial moduli of 2.05–2.86 GPa. The glass-transition temperatures (measured by differential scanning calorimetry) were highest for series IV, which contained the rigid 4,4'-biphenyl units (254–299°C); copolymer series V ranked second (237–277°C), and series III, with crank 2,2'-biphenyl structures, had the lowest values (227–268°C). The 10% weight-loss temperatures (measured by thermogravimetric analysis) were close to one another, ranging from 527 to 574°C in nitrogen and from 472 to 543°C in air. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2763–2774, 2002

INTRODUCTION

Aromatic polyimides have excellent physical properties and thermal stability, but their applications are limited because of their poor solubility and difficult processing. To solve these problems, amide groups may be introduced into polyimides to form poly(amide imide)s with improved solubility. Aromatic poly(amide imide)s possess desirable characteristics with merits of both polyamides and polyimides, such as high thermal stability and good mechanical properties as well as easy processability. There are many methods for synthesizing poly(amide imide)s,^{1–8} and in recent years, Yamazaki et al.'s⁹ phosphorylation–polyamidation technique has been successfully applied in our laboratory. With this technique, imide-containing dicarboxylic acids are reacted with aromatic diamines by direct polycondensation with triphenyl phosphite (TPP) and pyridine (Py) as con-

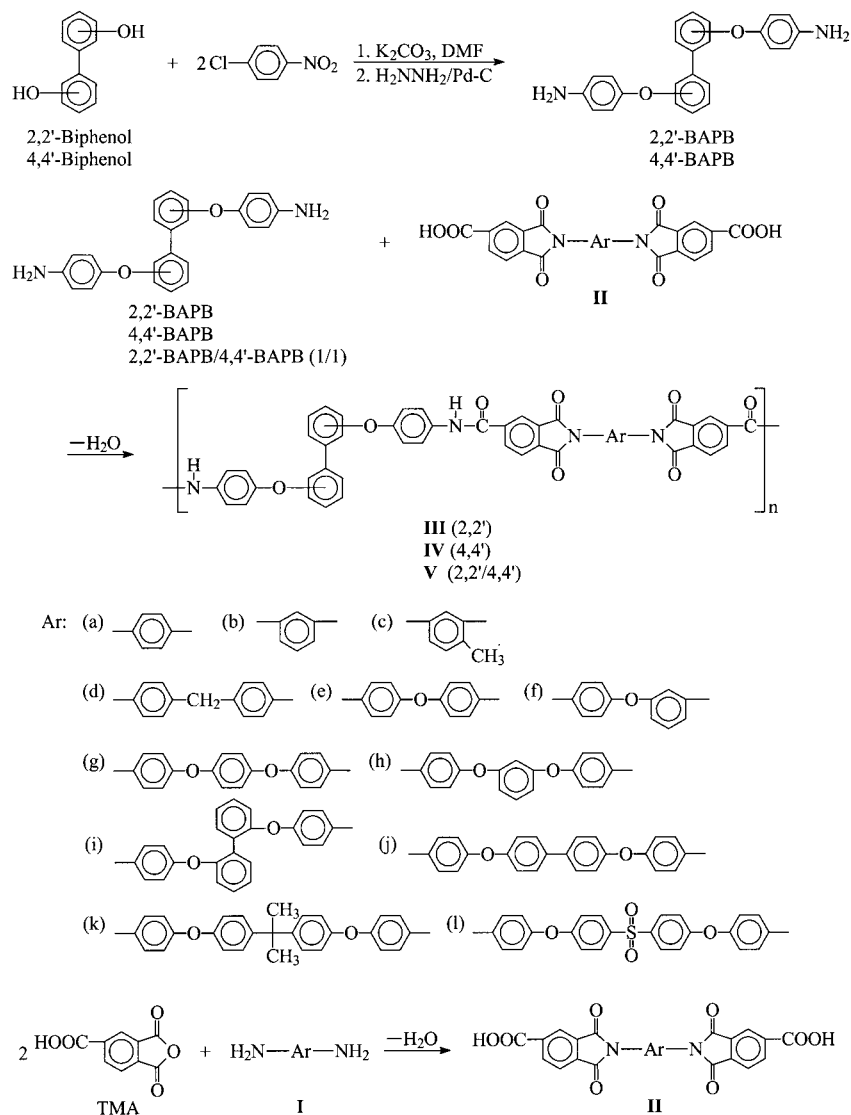
densing agents. The molecular structure of the poly(amide imide)s that form has alternating imide–imide–amide–amide units in the backbone.^{10–21}

In high-performance polymer materials, the molecular chain containing 2,2'- or 4,4'-biphenylene may effectively change certain properties of the polymers, leading to high crystallinity and poor solubility. However, phenoxy groups introduced into the aromatic diamines can effectively improve solubility and processability.^{22–24} For the study of polymers containing ether and biphenylene structures such as 2,2'- or 4,4'-bis(4-aminophenoxy)biphenyl (4,4'-BAPB), although 2,2'-bis(4-aminophenoxy)biphenyl (2,2'-BAPB) containing crank structures has been used to prepare polyamides²⁵ and polyimides,²⁶ and several polyamides,^{27–31} polyimides,³² and poly(amide imide)s^{17,19,21,33,34} have been synthesized from the more rigid 4,4'-BAPB, a systematic investigation into the effects of these monomers on the characteristics of poly(amide imide)s is lacking.

In this study, three series of poly(amide imide)s were synthesized by direct polycondensation from 2,2'-BAPB and 4,4'-BAPB or from a mixture of the two diamines (2,2'-BAPB/4,4'-BAPB = 1/1) with a series of diimide dicarboxylic acids [II_{a–l}], which were prepared from trimellitic anhydride (TMA) and 12 kinds

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Scheme 1

of aromatic diamines]. The properties of these three series were also investigated and compared.

EXPERIMENTAL

Materials

p-Phenylenediamine (**I_a**; Wako) and *m*-phenylenediamine (**I_b**; TCI) were vacuum-distilled before use. Other diamines, including 2,4-diaminotoluene (**I_c**; TCI), 4,4'-methylenedianiline (**I_d**; TCI), 4,4'-oxydianiline (**I_e**; TCI), 3,4'-oxydianiline (**I_f**; Chriskev), 1,4-bis(4-aminophenoxy)benzene (**I_g**; TCI), 1,3-bis(4-aminophenoxy)benzene (**I_h**; Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**I_k**; Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone (**I_l**; Chriskev), were used as received. The diimide dicarboxylic acids **II_{a-1}** were prepared according to the reported method.^{35,36} TMA (Wako) and TPP (TCI) were used without fur-

ther purification. The calcium dichloride (CaCl₂; Wako) was dried under vacuum at 180°C for 10 h. *N,N*-Dimethylacetamide (DMAc; Fluka), *N*-methyl-2-pyrrolidone (NMP; Fluka), *N,N*-dimethylformamide (DMF; Fluka), and Py (Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Synthesis of 2,2'-BAPB and 4,4'-BAPB

2,2'-BAPB is described as a representative example. 2,2'-Biphenol (50 g, 0.27 mol) and *p*-chloronitrobenzene (92.63 g, 0.59 mol) were dissolved in 180 mL of DMF in a 250-mL, round-bottom flask connected to a reflux condenser. Anhydrous K₂CO₃ (85.56 g, 0.62 mol) was added to this solution, and the mixture was heated to reflux and stirred for 8 h. After cooling to room temperature, the product was poured into 300

TABLE I
Synthesis of Poly(amide imide)s^a

Polymer	Initial amount of NMP (mL)	Additional amount of NMP (mL)	CaCl ₂ (g)	Appearance of reaction mixture	Polymer appearance	η_{inh}^b (dL/g)
III _a	3.5	5	0.28	ppt	pdr	0.41 ^c
III _b	3	0	0.25	clr	stg ^d	0.43
III _c	2.5	0	0.20	clr	stg ^d	0.44
III _d	4	0	0.30	ppt → clr	stg ^d	0.55
III _e	3	2.5	0.26	clr	stg ^d	0.59
III _f	3	3	0.26	clr	stg	0.84
III _g	4	0	0.30	clr → ppt	pdr	0.32 ^c
III _h	2	0	0.25	clr	pdr	0.25
III _i	3	0	0.25	clr	stg ^d	0.40
III _j	4	0	0.30	ppt	pdr	0.34 ^c
III _k	2.5	0	0.25	clr	stg	0.76
III _l	3	0	0.25	clr	stg ^d	0.44
IV _a	4	0	0.42	ppt	pdr	0.25 ^c
IV _b	4	2.5	0.40	clr	stg	0.68
IV _c	3	1	0.30	clr	stg	0.80 ^c
IV _d	4	0	0.40	ppt	stg ^d	0.48 ^e
IV _e	4	2	0.40	clr (viscous)	stg	1.52
IV _f	4	0	0.40	ppt	pdr	0.44 ^c
IV _g	4	0	0.40	ppt	pdr	0.35 ^c
IV _h	4	0	0.40	ppt	pdr	0.33 ^c
IV _i	3.5	0	0.35	ppt	pdr	0.56 ^c
IV _j	4	0	0.40	ppt	pdr	0.27 ^c
IV _k	3.5	3	0.38	ppt (viscous)	stg ^d	1.47 ^e
IV _l	3.5	0	0.30	clr	stg ^d	0.60
V _a	4	0	0.42	ppt	pdr	0.46 ^c
V _b	3	1.5	0.30	clr	stg	0.63
V _c	2.5	0	0.27	clr	stg	0.81
V _d	3	0	0.30	clr	stg	0.68
V _e	3	2.0	0.30	clr	stg	0.96
V _f	3	1.0	0.27	clr (viscous)	stg	1.28
V _g	3	2.5	0.30	ppt	stg	0.52 ^c
V _h	3.5	0	0.35	clr → ppt	pdr	0.43 ^c
V _i	2.5	0	0.25	ppt	stg ^d	0.88 ^c
V _j	3	0	0.30	ppt	pdr	0.48 ^c
V _k	3	3.0	0.27	clr	stg ^d	1.30 ^e
V _l	3	0	0.30	clr	stg ^d	0.67

ppt = precipitated; clr = clear; pdr = powder; stg = stringy.

^a Polymerization was carried out with 0.625 mmol of each monomer, 0.4 mL of TPP, 0.8 mL of Py, and calcium chloride in NMP at 100°C for 3 h.

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

^c Measured at a concentration of 0.5 g/dL in H₂SO₄ at 30°C.

^d Stringy product was brittle.

^e Measured at a concentration of 0.5 g/dL in NMP at 30°C.

mL of ethanol/water (1:1 v/v). The precipitate was filtered, recrystallized from DMF, and then dried in a vacuum oven at 100°C for 8 h to afford 85.68 g (82% yield) of off-white crystals of dinitro compound (mp = 158–160°C).

The dinitro compound (60 g, 0.14 mol), 0.42 g of 10% Pd-C, and 480 mL of ethanol were introduced into a three-necked flask, and the mixture was heated and refluxed at 85°C in an oil bath, while 50 mL of hydrazine monohydrate was added dropwise with a dropping funnel. The reaction mixture was maintained at 85°C for 8 h after the complete addition of hydrazine monohydrate. Appropriate amounts of tetrahydrofuran were added to the flask until the reaction mixture

became clear. The resulting hot, clear solution was filtered for the removal of Pd-C. When the solution cooled, white crystals precipitated, and they were isolated by filtration and dried to afford 2,2'-BAPB.

Yield: 42 g (81%). mp: 158–160°C (lit.²⁵ 158–159°C). IR (KBr): 3456, 3370 (N—H), 1224 cm⁻¹ (C—O). ELEM. ANAL. Calcd. for C₂₄H₂₀N₂O₂ (368.43): C, 78.24%; H, 5.47%; N, 7.60%. Found: C, 78.18%; H, 5.53%; N, 7.60%.

4,4'-BAPB was prepared with a similar method.

Yield: 95%. mp: 198–200°C. IR (KBr): 3454, 3374 (N—H), 1228 cm⁻¹ (C—O). ELEM. ANAL. Calcd. for C₂₄H₂₀N₂O₂ (368.43): C, 78.24%; H, 5.47%; N, 7.60%. Found: 78.18%; H, 5.55%; N, 7.59%.

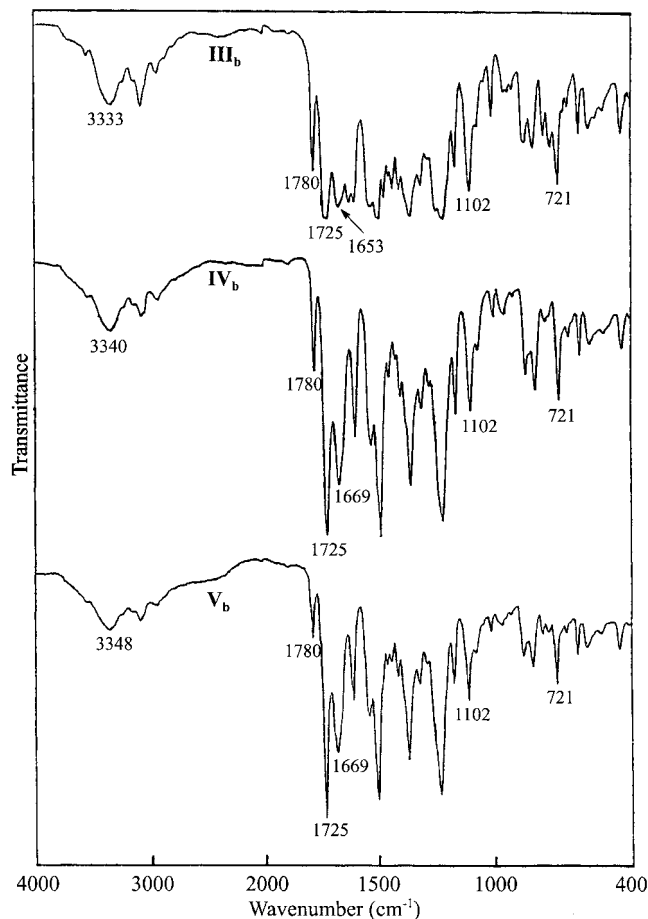


Figure 1 Fourier transform infrared spectra of representative poly(amide imide)s: **III_b**, **IV_b**, and **V_b**.

Synthesis of diimide dicarboxylic acids

II_g is described as a representative example. A mixture of diamine **I_g** (4.38 g, 0.015 mol) and TMA (5.76 g, 0.03 mol) was dissolved in 40 mL of dry DMF. About 10 mL of toluene was added, and the mixture was heated with reflux for 4 h until about 0.55 mL of water was distilled off azeotropically. The residual toluene was then distilled off under reduced pressure. After the mixture cooled, a yellow precipitate was collected by filtration, recrystallized from DMF, and then dried in vacuum to produce 9.4 g of diimide dicarboxylic acid **II_g**.

Yield: 98%. mp: 398–399°C. ELEM. ANAL. Calcd. for C₃₆H₂₀N₂O₁₀ (640.54): C, 67.50%; H, 3.15%; N, 4.37%. Found: C, 67.40%; H, 3.19%; N, 4.32%.

Other diimide dicarboxylic acids (**II_{a-1}**) were prepared with an analogous procedure as described.

Polymerization of poly(amide imide)s

A typical example of polycondensation is described as follows. A mixture of diimide diacid **II_e** (0.3425 g, 0.625 mmol), 4,4'-BAPB (0.230 g, 0.625 mmol), 0.4 g of

CaCl₂, 0.8 mL of Py, 0.4 mL of TPP, and 4 mL of NMP was heated with stirring at 100°C for 3 h. The viscosity of the reaction solution increased after 1 h, and an additional 2 mL of NMP was added to the reaction mixture. At the end of the reaction, the obtained polymer solution was trickled into 300 mL of stirred methanol. The stringy polymer was washed thoroughly with hot water and methanol, collected by filtration, and dried at 100°C under reduced pressure. The yield was quantitative. The inherent viscosity of the polymer in DMAc at a 0.5 g dL⁻¹ concentration at 30°C was 1.52 dL g⁻¹. Other poly(amide imide)s were prepared in an analogous manner.

Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. Elemental analyses were performed with a PerkinElmer model 2400 CHN analyzer. The inherent viscosities of all polymers were measured with a Cannon-Fenske viscometer at 30°C. Solubilities were determined at a 1% (w/w) concentration. Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with samples (10 ± 2 mg) heated in flowing nitrogen or air (50 cm³ min⁻¹) at a heating rate of 20°C min⁻¹. The measurements were taken after an initial 250°C drying step for 5 min. 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 (30 cm³ min⁻¹) at a heating rate of 20°C min⁻¹. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa, with Ni-filtered Cu Kα radiation (40 kV, 15 mA) at a scanning rate of 2° min⁻¹. The measurements were performed with film specimens 0.1 mm thick. An Instron model 1130 universal tester with a load cell of 5 kg was used to study the stress-strain behavior of the sample. A gauge of 2 cm and a strain rate of 5 cm min⁻¹ were used for this study. Measurements were performed at room temperature (0.5 cm wide, 6 cm long, and ca. 0.1 mm thick), and an average of at least six individual determinations was used.

RESULTS AND DISCUSSION

Polymer synthesis

Two kinds of bis(4-aminophenoxy)biphenyl (2,2'-BAPB and 4,4'-BAPB) were prepared from the condensation of corresponding biphenols with *p*-chloronitrobenzene, followed by the hydrogenation reduction of the intermediate dinitro compounds. Two

TABLE II
Elemental Analysis of Poly(amide imide)s

Polymer	Formula (weight-average molecular weight)	Elemental analysis ^a (%)				Moisture uptake ^b (%)
		C	H	N		
III _a	(C ₄₈ H ₂₈ O ₈ N ₄) _n (788.744) _n	Calcd.	73.09	3.58	7.10	2.51
		Found	71.32	3.69	6.86	
		Corrected	73.11	3.60	7.03	
III _b	(C ₄₈ H ₂₈ O ₈ N ₄) _n (788.744) _n	Calcd.	73.09	3.58	7.10	3.60
		Found	70.53	3.72	6.81	
		Corrected	73.07	3.59	7.06	
III _c	(C ₄₉ H ₃₀ O ₈ N ₄) _n (802.770) _n	Calcd.	73.31	3.77	6.98	4.31
		Found	70.29	3.93	6.64	
		Corrected	73.32	3.76	6.93	
III _d	(C ₅₅ H ₃₄ O ₈ N ₄) _n (878.862) _n	Calcd.	75.16	3.90	6.38	3.91
		Found	72.32	3.80	6.15	
		Corrected	75.15	3.65	6.39	
III _e	(C ₅₄ H ₃₂ O ₉ N ₄) _n (880.836) _n	Calcd.	73.63	3.66	6.36	2.21
		Found	72.00	3.91	6.21	
		Corrected	73.59	3.82	6.35	
III _f	(C ₅₄ H ₃₂ O ₉ N ₄) _n (880.836) _n	Calcd.	73.63	3.66	6.36	4.04
		Found	70.80	3.78	6.09	
		Corrected	73.66	3.63	6.34	
III _g	(C ₆₀ H ₃₆ O ₁₀ N ₄) _n (972.928) _n	Calcd.	74.06	3.73	5.76	1.85
		Found	72.69	3.81	5.64	
		Corrected	74.03	3.71	5.74	
III _h	(C ₆₀ H ₃₆ O ₁₀ N ₄) _n (972.928) _n	Calcd.	74.06	3.73	5.76	1.60
		Found	72.85	3.83	5.66	
		Corrected	74.02	3.77	5.75	
III _i	(C ₆₆ H ₄₀ O ₁₀ N ₄) _n (1049.020) _n	Calcd.	75.56	3.84	5.34	3.73
		Found	72.79	4.04	5.17	
		Corrected	75.51	3.89	5.34	
III _j	(C ₆₆ H ₄₀ O ₁₀ N ₄) _n (1049.020) _n	Calcd.	75.56	3.84	5.34	1.92
		Found	74.11	3.91	5.30	
		Corrected	75.53	3.83	5.40	
III _k	(C ₆₉ H ₄₆ O ₁₀ N ₄) _n (1091.098) _n	Calcd.	75.95	4.25	5.14	1.67
		Found	74.57	4.18	5.12	
		Corrected	75.82	4.11	5.23	
III _l	(C ₆₆ H ₄₀ O ₁₂ N ₄ S) _n (1113.090) _n	Calcd.	71.21	3.62	5.03	3.12
		Found	69.04	3.77	4.95	
		Corrected	71.19	3.65	5.10	
IV _a	(C ₄₈ H ₂₈ O ₈ N ₄) _n (788.744) _n	Calcd.	73.09	3.58	7.10	4.54
		Found	69.91	3.87	6.79	
		Corrected	73.08	3.69	7.10	
IV _b	(C ₄₈ H ₂₈ O ₈ N ₄) _n (788.744) _n	Calcd.	73.09	3.58	7.10	4.57
		Found	69.89	3.76	6.73	
		Corrected	73.08	3.59	7.04	
IV _c	(C ₄₉ H ₃₀ O ₈ N ₄) _n (802.770) _n	Calcd.	73.31	3.77	6.98	3.47
		Found	70.82	3.98	6.80	
		Corrected	73.28	3.84	7.04	
IV _d	(C ₅₅ H ₃₄ O ₈ N ₄) _n (878.862) _n	Calcd.	75.16	3.90	6.38	3.93
		Found	72.30	4.08	6.18	
		Corrected	75.14	3.92	6.42	
IV _e	(C ₅₄ H ₃₂ O ₉ N ₄) _n (880.836) _n	Calcd.	73.63	3.66	6.36	3.29
		Found	71.25	3.82	6.13	
		Corrected	73.59	3.69	6.33	
IV _f	(C ₅₄ H ₃₂ O ₉ N ₄) _n (880.836) _n	Calcd.	73.63	3.66	6.36	2.83
		Found	71.59	3.80	6.19	
		Corrected	73.62	3.69	6.37	
IV _g	(C ₆₀ H ₃₆ O ₁₀ N ₄) _n (972.928) _n	Calcd.	74.06	3.73	5.76	2.98
		Found	71.93	3.86	5.64	
		Corrected	74.07	3.74	5.81	
IV _h	(C ₆₀ H ₃₆ O ₁₀ N ₄) _n (972.928) _n	Calcd.	74.06	3.73	5.76	2.25
		Found	72.41	3.85	5.70	
		Corrected	74.04	3.76	5.83	

TABLE II Continued

Polymer	Formula (weight-average molecular weight)	Elemental analysis ^a (%)			Moisture uptake ^b (%)
		C	H	N	
IV _i	(C ₆₆ H ₄₀ O ₁₀ N ₄) _n (1049.020) _n	Calcd.	75.56	3.84	1.65
		Found	74.36	3.94	
		Corrected	75.59	3.83	
IV _j	(C ₆₆ H ₄₀ O ₁₀ N ₄) _n (1049.020) _n	Calcd.	75.56	3.84	1.65
		Found	74.36	3.89	
		Corrected	75.58	3.88	
IV _k	(C ₆₉ H ₄₆ O ₁₀ N ₄) _n (1091.098) _n	Calcd.	75.95	4.25	1.95
		Found	74.49	4.33	
		Corrected	75.94	4.25	
IV _l	(C ₆₆ H ₄₀ O ₁₂ N ₄ S) _n (1113.090) _n	Calcd.	71.21	3.62	3.45
		Found	68.83	3.77	
		Corrected	71.20	3.64	
V _a	(C ₄₈ H ₂₈ O ₈ N ₄) _n (788.744) _n	Calcd.	73.09	3.58	3.78
		Found	70.42	4.09	
		Corrected	73.08	3.94	
V _b	(C ₄₈ H ₂₈ O ₈ N ₄) _n (788.744) _n	Calcd.	73.09	3.58	4.53
		Found	69.89	3.94	
		Corrected	73.06	3.76	
V _c	(C ₄₉ H ₃₀ O ₈ N ₄) _n (802.770) _n	Calcd.	73.31	3.77	2.95
		Found	71.23	4.15	
		Corrected	73.32	4.03	
V _d	(C ₅₅ H ₃₄ O ₈ N ₄) _n (878.862) _n	Calcd.	75.16	3.90	3.49
		Found	72.62	4.18	
		Corrected	75.15	4.03	
V _e	(C ₅₄ H ₃₂ O ₉ N ₄) _n (880.836) _n	Calcd.	73.63	3.66	2.69
		Found	71.72	4.00	
		Corrected	73.65	3.89	
V _f	(C ₅₄ H ₃₂ O ₉ N ₄) _n (880.836) _n	Calcd.	73.63	3.66	2.35
		Found	71.93	3.91	
		Corrected	73.62	3.82	
V _g	(C ₆₀ H ₃₆ O ₁₀ N ₄) _n (972.928) _n	Calcd.	74.06	3.73	2.32
		Found	72.41	3.97	
		Corrected	74.09	3.88	
V _h	(C ₆₀ H ₃₆ O ₁₀ N ₄) _n (972.928) _n	Calcd.	74.06	3.73	1.52
		Found	72.99	3.94	
		Corrected	74.10	3.88	
V _i	(C ₆₆ H ₄₀ O ₁₀ N ₄) _n (1049.020) _n	Calcd.	75.56	3.84	2.03
		Found	74.03	4.04	
		Corrected	75.53	3.96	
V _j	(C ₆₆ H ₄₀ O ₁₀ N ₄) _n (1049.020) _n	Calcd.	75.56	3.84	2.48
		Found	73.75	3.99	
		Corrected	75.58	3.89	
V _k	(C ₆₉ H ₄₆ O ₁₀ N ₄) _n (1091.098) _n	Calcd.	75.95	4.25	1.99
		Found	74.49	4.42	
		Corrected	5.97	4.33	
V _l	(C ₆₆ H ₄₀ O ₁₂ N ₄ S) _n (1113.090) _n	Calcd.	71.21	3.62	2.08
		Found	69.76	3.84	
		Corrected	71.20	3.76	

^a For C and N, corrected value = found value × (100% + moisture uptake %). For H, corrected value = found value × (100% - moisture uptake %).

^b Moisture uptake (%) = (W - W₀)/W₀ × 100%, where W is the weight of polymer sample after standing at room temperature and W₀ is the weight of polymer sample after being dried in a vacuum at 100°C for 10 h.

series of poly(amide imide)s (series III and IV) were synthesized by the direct polycondensation of these diamines with 12 diimide dicarboxylic acids, as shown in Scheme 1. The results of the polycondensations are shown in Table I. When 2,2'-BAPB was reacted with various diimide diacids, most of the reactions proceeded smoothly in homogeneous solutions, except

the solutions of polymers III_{a,g,j}, which exhibited a milky, nonhomogeneous phase. However, the inherent viscosities of this series were not high, and III_f had the highest value (0.84 dL g⁻¹). On the contrary, when 4,4'-BAPB was used to synthesize series IV, except for IV_{b,c,e,l}, most of the polymers precipitated during the polymerization and had low degrees of polymeriza-

TABLE III
Solubility of Poly(amide imide)s

Polymer	Solvent							
	DMAc	NMP	DMF	DMSO	Py	<i>o</i> -Chlorophenol	<i>m</i> -Cresol	Concentrated H ₂ SO ₄
III _a	-	-	-	-	-	-	-	+
IV _a	-	-	-	-	-	-	-	+
V _a	-	-	-	-	-	-	-	+
III _b	+	+	+	+	+	+	+	+
IV _b	+	+	+	+	+	+	+	+
V _b	+	+	+	+	+	+	+	+
III _c	+	+	+	+	+	+	+	+
IV _c	+	+	+	+	+	+	+	+
V _c	+	+	+	+	+	+	+	+
III _d	+	+	+	+	+	+	+	+
IV _d	+	+	-	-	-	-	+	+
V _d	+	+	+	±	-	+	-	+
III _e	+	+	+	+	+	+	+	+
IV _e	-	+	-	-	-	-	-	+
V _e	+	+	-	-	-	-	-	+
III _f	+	+	+	+	+	+	+	+
IV _f	-	-	-	-	-	-	-	+
V _f	+	+	-	-	-	-	-	+
III _g	-	-	-	-	-	-	-	+
IV _g	-	-	-	-	-	-	-	+
V _g	-	±	-	-	-	-	-	+
III _h	+	+	+	-	-	-	-	+
IV _h	-	-	-	-	-	-	-	+
V _h	-	±	-	-	-	-	-	+
III _i	+	+	+	+	+	+	+	+
IV _i	-	-	-	-	-	-	-	+
V _i	-	+	-	-	-	-	-	+
III _j	-	-	-	-	-	-	-	+
IV _j	-	-	-	-	-	-	-	+
V _j	-	-	-	-	-	-	-	+
III _k	+	+	+	+	+	+	+	+
IV _k	-	+	-	-	-	-	-	+
V _k	-	+	-	-	-	-	-	+
III _l	+	+	+	+	+	+	+	+
IV _l	-	+	-	-	-	-	-	+
V _l	+	+	+	+	-	+	+	+

Measured at a concentration of 1 wt %: + = soluble at room temperature; ± = partially soluble; - = insoluble.

tion. However, IV_k still had a high degree of polymerization because the precipitation occurred in the later period.

Because the stereostructure and solubility of the isomeric diamines (2,2'-BAPB and 4,4'-BAPB) might affect the polycondensation, copolymers (series V) based on mixed diamines in a 1:1 ratio were synthesized to improve the previously cited phenomenon by the compensation principle. From the results (Table I), it was found that homogeneous phase copolymerizations were much better than those of series IV, and the inherent viscosities of the copolymers were higher than those of series III. Although some series V copolymers also precipitated during the polymerization, their inherent viscosities were higher than those of the two homopolymer series. This was probably because the copolymers with random arrangements had better solubility during the polymerization, so larger molec-

ular weight copolymers were produced before the precipitation occurred.

Typical IR spectra of these polymers are shown in Figure 1, and the characteristic absorptions are almost identical. The IR spectra of the polymers exhibit characteristic absorptions for the imide ring at 1780 and 1725 cm⁻¹ that are peculiar to the symmetrical and asymmetrical carbonyl stretching vibration and at 1102 and 721 cm⁻¹ due to ring deformation. The absorptions of amide groups appear at 3333–3348 (N—H stretch) and 1653–1669 cm⁻¹ (C=O stretch). The elemental analysis data of all the poly(amide imide)s are listed in Table II. The uptakes of water were 1.52–4.57%, which could be calculated from the weight change of the vacuum-dried polymer samples after exposure to air at room temperature. When the found values were corrected by the elimination of the amount of absorbed water, the cor-

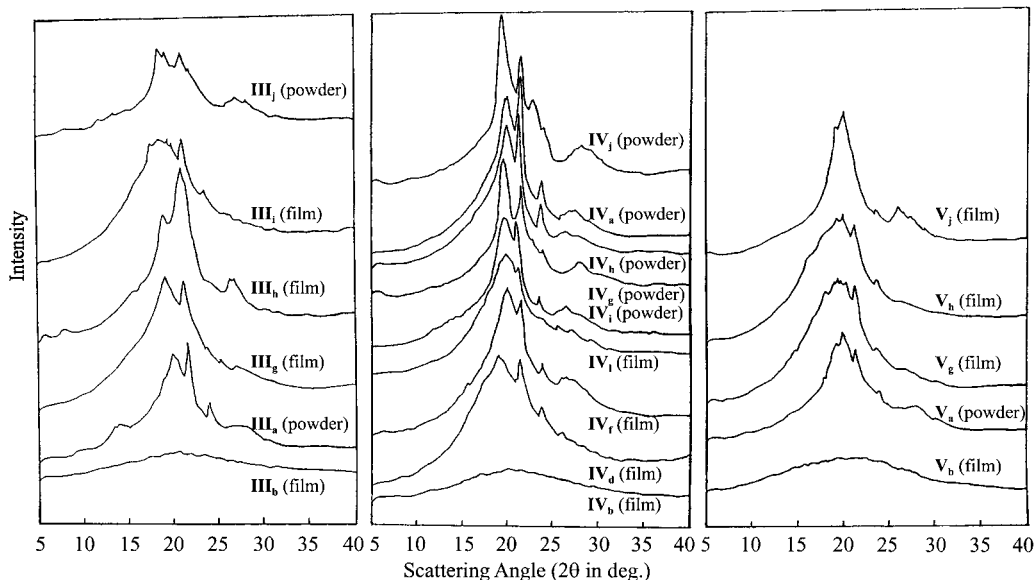


Figure 2 X-ray diffraction patterns of some poly(amide imide)s.

rected values were in good agreement with the calculated values.

Properties of the polymers

The solubilities of all the poly(amide imide)s were tested qualitatively in various solvents, and the results are listed in Table III. The concentration for the solubility tests was 1 wt %. Most of the series III polymers were soluble in amide-type polar solvents such as DMAc, DMF, and NMP. However, the polymers II-

I_{a,g,j'} containing more rigid structures, could only be dissolved in H₂SO₄. The solubility of series IV polymers, based on all para-linked 4,4'-BAPB, was even poorer. Only IV_{b,c} were soluble in various testing solvents, IV_{d,e,k,l} could be dissolved in NMP, and the rest of the IV polymers were soluble only in H₂SO₄. The solubility of random V copolymers was between those of series III and IV, depending on the rigidity of the dicarboxylic acids. From the aforementioned results, it was known that the solubility of series III, containing crank 2,2'-biphenyl structures, was better

TABLE IV
Mechanical Properties of Poly(amide imide) Films

Polymer	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
III _b	—	61	3	2.56
IV _b	99	87	11	2.33
V _b	—	104	8	2.41
III _c	—	81	4	2.53
IV _c	86	80	20	2.18
V _c	—	105	8	2.33
III _d	—	84	6	2.05
V _d	—	79	5	2.44
III _e	—	95	6	2.42
IV _e	—	96	16	2.41
V _e	98	90	8	2.50
III _f	—	89	5	2.48
V _f	96	80	10	2.86
V _i ^a	—	57	3	2.39
III _k	—	102	6	2.45
IV _k ^a	—	77	9	2.07
V _k	—	74	5	2.36
III _l ^a	—	66	3	2.50
V _l ^a	—	99	7	2.44

Films were cast from a polymer solution of DMAc.

^a Films were cast from a polymer solution of NMP.

TABLE V
Thermal Properties of Poly(amide imide)s

Polymer	DSC		TGA		Char yield ^c (%)
	T_g^a (°C)	T_m^a (°C)	Decomposition temperature ^b (°C)		
			In air	In N ₂	
III _a	268	— ^d	521	551	62
IV _a	—	—	505	559	58
V _a	—	392	513	567	60
III _b	237	—	516	556	60
IV _b	292	—	520	557	59
V _b	270	—	536	565	64
III _c	266	—	472	540	60
IV _c	299	—	495	554	61
V _c	277	—	483	547	64
III _d	240	—	507	541	60
IV _d	—	—	504	545	55
V _d	257	—	499	552	67
III _e	244	—	528	561	62
IV _e	286	—	522	574	58
V _e	253	—	523	570	61
III _f	239	—	503	552	57
IV _f	262	—	518	562	53
V _f	247	—	517	558	62
III _g	238	363	527	539	61
IV _g	—	—	506	561	58
V _g	255	—	510	551	56
III _h	229	317	527	556	62
IV _h	—	—	514	569	58
V _h	243	—	532	557	62
III _i	227	338	515	554	57
IV _i	254	401	512	569	61
V _i	237	—	543	560	62
III _j	239	382	538	557	63
IV _j	—	—	514	568	60
V _j	—	—	537	558	65
III _k	229	—	522	527	60
IV _k	283	349	509	532	58
V _k	257	318	489	531	61
III _l	236	—	528	531	59
IV _l	267	381	542	543	59
V _l	262	—	531	541	62

^a From the first (T_m) or second (T_g) heating traces of DSC measurements conducted with a heating rate of 20°C min⁻¹ in nitrogen.

^b Temperature at which a 10% weight loss was recorded by TG at a heating rate of 20°C min⁻¹.

^c Char yield at 800°C in nitrogen.

^d No T_g or T_m was observed in the DSC trace.

than that of series IV and V, containing rigid 4,4'-biphenyl structures or mixed diamines. Moreover, although the random arrangements of polymer molecules could decrease the crystallinity, the solubility improvement of series V was not significant.

All the polymers were structurally characterized with X-ray diffraction studies. The diffraction patterns of series III, IV, and V are illustrated in Figure 2. Some polymers of series III, such as III_{a,g,h,i,j,l}, having regular arrangements and more rigid structures, revealed higher degrees of crystallinity, whereas most of the series IV polymers showed a fair degree of crystallinity and exhibited sharp X-ray diffraction peaks due to the rigid, para-symmetric, and straight-chain structure

of this series. With the exception of the partial crystallinity of V_{a,g,h,j,l}, almost all the series V copolymers displayed a nearly completely amorphous pattern. In this study, the degree of crystallinity seemed to depend on two factors: (1) polymers with regular arrangements had higher crystallinity than those with random arrangements, and (2) polymers with pararigid structures in the backbone, such as 4,4'-biphenylene, *p*-phenylene, or 1,4-bis(4-oxyphenylene)benzene, showed higher crystallinity.

Seven polymers of series III, four polymers of series IV, and eight copolymers of series V could be cast into transparent, tough, and flexible films from their DMAc or NMP solutions. Table IV shows the mechan-

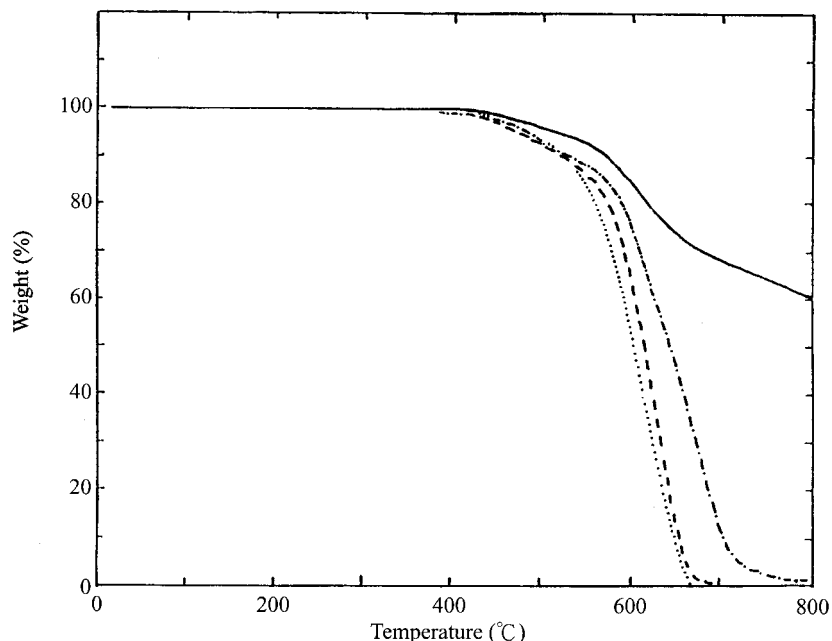


Figure 3 TGA curves of poly(amide imide)s III_e , IV_e , and V_e at a heating rate of $20^\circ\text{C min}^{-1}$: (—) V_e in nitrogen and (- - -) III_e , (· · ·) IV_e , and (—) V_e in air.

ical properties of these solution-casting films. Among the three series, polymers containing rigid Ar linkages ($\text{II}_{a,g,h,j}$) could not be cast into films because of the insolubility. However, polymers containing the Ar linkages of *m*-phenylene ($\text{II}_{b,c}$), 4,4'-oxydiphenylene (II_e), and 2,2'-bis[4-(4-oxyphenylene)phenyl]propane (II_k) possessed excellent film-forming properties. Furthermore, poly(amide imide)s $\text{IV}_{b,c}$ and copolymers $\text{V}_{e,f}$ showed clear yield points, which implied that they belonged to strong and tough materials. In a comparison of the mechanical properties of the series V copolymers and series III polymers, the former showed larger elongation and smaller initial modulus than the latter, and some of the former also showed obvious yield points. All the poly(amide imide) films had tensile strengths at break of 57–104 MPa, elongations at break of 3–20%, and initial moduli of 2.05–2.86 GPa.

The thermal properties of all the poly(amide imide)s were evaluated with TG and DSC. The thermal behavior data of all the polymers are given in Table V. The thermogravimetric traces indicated that all the polymers possessed high thermal stability in nitrogen and had 10% weight-loss temperatures (T_{10} 's) greater than 530°C . A comparison of various Ar linkages was made, and the T_{10} orders of three series of polymers were obtained, as shown in Table V: $\text{III}_e > \text{III}_{b,h,j} > \text{III}_{a,f,i} > \text{III}_{c,d,g} > \text{III}_{k,l}$, $\text{IV}_e > \text{IV}_{h,i,j} > \text{IV}_{a,b,c,f,g} > \text{IV}_{d,l} > \text{IV}_k$, and $\text{V}_e > \text{V}_{a,b} > \text{V}_{f,h,i,j} > \text{V}_{c,d,g} > \text{V}_{k,l}$. Poly(amide imide)s containing 4,4'-oxydiphenylene groups (II_e) showed the best thermal resistance in the three series. Polymers containing aryl ether groups

also exhibited excellent thermal stability, but polymers with aliphatic or sulfonyl groups, such as $\text{II}_{k,l}$, had lower thermal resistance because of the ready degradation during the heating process and the weak bonding of the C—S bond.

For polymers with the same Ar linkage in three series, almost all the series III polymers showed lower thermal resistance, whereas isomeric series IV polymers exhibited higher thermal stability. The copolymers of series V possessed excellent thermal stability, just as the homopolymers did. Moreover, copolymers $\text{V}_{a,b,d}$ had higher thermal stability than their corresponding poly(amide imide)s. The T_{10} values of most of these polymers were greater than 500°C in air and were lower than those in nitrogen within the temperature range 10 – 70°C . The lowest T_{10} value of a II_c -containing polymer in air was probably due to the ready oxidation of pendent methyl structures. Polymers with sulfone units (II_i) showed the least difference between their T_{10} 's in nitrogen and in air, and this might be due to the antioxidating actions of sulfonyl groups. Typical thermogravimetric analysis (TGA) curves are shown in Figure 3. The polymers III and V had higher char yields and better thermal stability than series IV did.

DSC measurements were conducted at a heating rate of $20^\circ\text{C min}^{-1}$ in nitrogen. Quenching from the elevated temperatures (ca. 400°C) to room temperature in air gave predominantly amorphous samples, so the glass-transition temperatures (T_g 's) of most poly(amide imide)s could be easily measured in the second DSC heating traces. The T_g values of

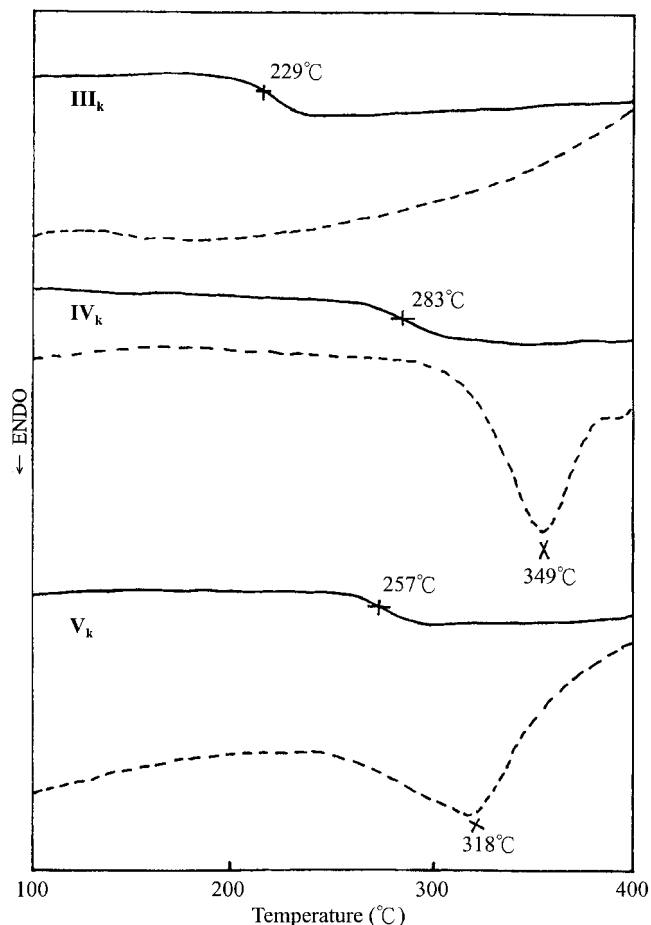


Figure 4 DSC curves of poly(amide imide)s III_k , IV_k , and V_k at a heating rate of $20^\circ\text{C min}^{-1}$ in nitrogen: (—) first heating and (---) second heating.

all series **III** polymers containing crank 2,2'-biphenylene could be obtained, and III_a containing the *para*-phenylene in diamine, which had higher rigidity, exhibited the highest T_g value (268°C). On the contrary, no discernible T_g values of polymers $\text{IV}_{a,d,g,h,j}$ with the rigid and symmetric 4,4'-biphenylene were detected with DSC, and the T_g values of the other **IV** polymers were high (254 – 299°C). Series **V** copolymers synthesized from equimolar amounts of 2,2'-BAPB and 4,4'-BAPB exhibited T_g values ranging from 237 to 277°C . In a comparison of the three isomeric series, series **IV** had the highest T_g values, whereas series **III** had the lowest, and series **V** showed intermediate T_g values. In addition, the melting temperatures (T_m 's) of some poly(amide imide)s could be observed in the first DSC heating traces, and typical DSC curves are shown in Figure 4. There were four kinds of series **III** polymers (III_{g-j}), three kinds of series **IV** polymers ($\text{IV}_{i,k,l}$), and two kinds of series **V** polymers ($\text{V}_{a,k}$) with T_m values within 317 – 401°C .

CONCLUSIONS

Three series of biphenylene-containing poly(amide imide)s were successfully synthesized in this study. Most polymerizations of series **III** polymers with crank 2,2'-biphenyl units proceeded smoothly in homogeneous solutions, whereas most series **IV** polymers with rigid 4,4'-biphenyl groups precipitated during the reaction. The series **V** copolymers possessed higher inherent viscosities because of the increasing solubility of the reaction system. Series **III** showed better solubility than series **IV**, and the solubility of series **V** was intermediate between those of the corresponding series. These polymers were characterized by excellent thermal stability and high transition temperatures.

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