

Preparation of Polyimides Derived from Biphenyltetracarboxylic Dianhydrides and Aromatic Diamines Bearing Alkylene Spacers

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ABSTRACT: Four series of aromatic polyimides (PIs V–VIII) composed of biphenyltetracarboxylic dianhydrides (BPDA) and aromatic diamines bearing alkylene spacers were prepared by two methods. Most polymers could be readily prepared in a one-step method for the combination of *a*-BPDA with α,ω -bis(3-aminophenoxy)alkanes, *a*-BPDA with α,ω -bis(4-aminophenoxy)alkanes, and *s*-BPDA with α,ω -bis(3-aminophenoxy)alkanes. However, the polymerization of *s*-BPDA with α,ω -bis(4-aminophenoxy)alkanes gave powders. On the other hand, all four monomer combinations afforded the desired polyamic acid solution in a two-step method. These polymer solutions could be cast into tough and flexible films, which were characterized by their inherent viscosity, differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical spectrometry measurements. The glass transition temperatures (T_g s) of the polymers were in the range of 110–240°C, but they were not clearly defined for PIs VIII and VI. The 5% weight loss temperatures were around 450°C for all prepared PIs. For PI VIII an “odd–even” behavior of the tensile properties of the films was detected, corresponding to the reported behavior of the melting temperatures. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2404–2413, 1999

Key words: polyimides; 3,3',4,4'-biphenyltetracarboxylic dianhydride; 2,3,3',4'-biphenyltetracarboxylic dianhydride; α,ω -bis(3-aminophenoxy)alkanes; α,ω -bis(4-aminophenoxy)alkanes; polycondensation

INTRODUCTION

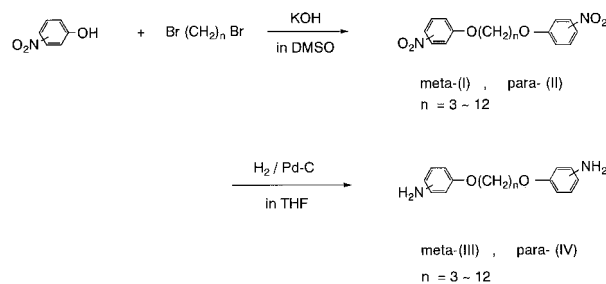
Aromatic polyimides (PIs) are well known as high-temperature resistant materials, and they are widely used in the aerospace and microelectronics industries.^{1–3} Kapton® [poly(4,4'-oxydiphenylene pyromellitimide)] was commercialized by DuPont in the 1960s. We developed a method of production for biphenyltetracarboxylic dianhydride (BPDA)^{4,5} and put a new PI (Upilex®)⁶ on

the market in 1982. These wholly aromatic PIs are absolutely infusible; thus, the two-step process is generally utilized for the production of PI films, which are indeed indispensable in a wide range of electronics industries. On the other hand, soluble materials should be better suited for applications in dielectric coatings, adhesives, matrices, alignment layer films for the liquid crystal display, and other similar uses.⁷ A number of strategies were employed to improve the processability and, in particular, the solubility of these rigid rodlike PIs.^{8–17}

PIs composed of α,ω -bis(4-aminophenoxy)alkanes and aromatic tetracarboxylic dianhydrides

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Scheme 1 Synthesis of diamines.

were also prepared. However, these polymers were less soluble due to semicrystalline or liquid crystalline properties.^{18–20}

In this contribution we report on the preparation of new soluble PIs derived from *a*- and *s*-BPDA and a number of α,ω -bis(3- and 4-amino-phenoxy)alkanes.

EXPERIMENTAL

Materials

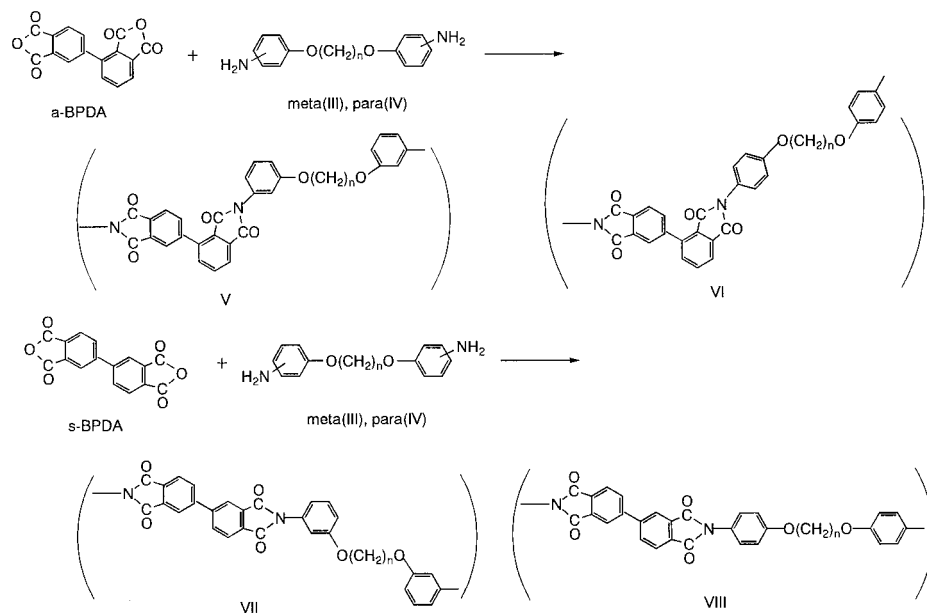
3,3',4,4'-BPDA (*s*-BPDA) and 2,3,3',4'-BPDA (*a*-BPDA) are products of UBE Industries Ltd. Other chemicals were commercially available. *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure.

Monomer Synthesis

α,ω -Bis(3-nitrophenoxy)Hexane (16)

The reaction vessel was a 500-mL three-necked round flask equipped with a mechanical stirrer, a water separating trap topped by a condenser, and a nitrogen inlet.

In a typical experiment *m*-nitrophenol (31.31 g, 0.225 mol), KOH (12.64 g, 0.225 mol) in 60 mL of DMSO, and 60 mL of toluene were placed in the vessel. The reaction mixture was heated to 100°C to afford a homogeneous solution, then heated to 180°C within 1 h and kept at this temperature for 15 min, after which water (ca. 4.8 mL) was removed azeotropically with toluene; finally, all toluene was distilled off. After cooling the reaction mixture to room temperature, 1,6-dibromohexane (25.43 g, 0.104 mol) was added through a dropping funnel into the reaction mixture at room temperature within 1 h. The reaction temperature was raised to 60°C and maintained at 60°C for 2 h, heated to 150°C within 1 h, then kept at 150°C for 1 h. After cooling to room temperature, the reaction mixture was poured into 1 L of water and the precipitated product was collected by filtration, washed thoroughly with water, and washed with 200 mL of methanol. The products were recrystallized two times from DMSO (45 mL) with active charcoal and dried in a vacuum at 120°C for 3 h. The yield of yellow needles was 22.43 g (60%).



Scheme 2 Polymerization of polyimides.

Table I Preparation of α,ω -Bis(nitrophenoxy)Alkanes (I, II)

Nitro Deriv.	<i>n</i>	Yield (%)	mp (°C)	Elemental Analysis				¹ H-NMR ^a								
				Calcd.	Found	C	H	N	Ph	OCH ₂	OCH ₂ CH ₂	(CH ₂) _n				
I	3	41	123	Calcd.	56.6	4.4	8.8									
II	3	72	131 (170–171) ^b	Found	57.1	4.6	8.9									
				Found	56.9	4.6	8.8									
				Calcd.	57.8	4.9	8.4									
I	4	38	136	Found	58.0	4.9	8.5									
II	4	69	146 (98–99) ^b	Found	58.1	5.0	8.6									
				Calcd.	59.0	5.2	8.1									
I	5	52	93	Found	59.3	5.4	8.2									
II	5	53	102	Found	59.1	5.4	8.1									
				Calcd.	60.0	5.6	7.8									
I	6	60	138	Found	60.3	5.7	7.8									
II	6	73	108	Found	59.7	5.6	7.7									
				Calcd.	61.9	6.2	7.2									
I	8	58	84	Found	61.5	6.1	7.4									
II	8	59	122 (119–120) ^c	Found	61.4	6.2	7.2									
				Calcd.	62.7	6.5	7.0									
I	9	53	72	Found	62.2	6.4	7.0									
II	9	64	94 (89–90) ^c	Found	62.6	6.5	7.0									
				Calcd.	63.5	6.8	6.7									
I	10	59	85 (79–80) ^c	Found	63.5	6.6	6.9									
II	10	57	90 (81–82) ^c	Found	63.5	6.8	6.8									
				Calcd.	64.9	7.3	6.3									
I	12	62	86	Found	64.2	7.1	6.6									
II	12	52	83 (77–78) ^c	Found	64.4	7.2	6.4									

^a I and II3 to I and II5 and II6 were measured in CDCl₃ at room temperature; I6 and I and II8 to I and II12 were measured in DMSO-*d*₆ at 80°C.^b Reference 19.^c Reference 18.

Table II Preparation of α, ω -Bis(aminophenoxy)Alkanes (III, IV)

Amino Deriv.	<i>n</i>	Yield (%)	mp (°C)	Elemental Analysis					¹ H-NMR (DMSO- <i>d</i> ₆ at Room Temperature)							
				C	H	N	Ph	OCH ₂	OCH ₂ CH ₂	(CH ₂) _n	NH ₂					
III	3	78	152	Calcd.	69.7	7.0	10.8									
IV	3	76	107 (63–64) ^a	Found	69.8	7.1	10.7	6.06–6.92 (m, 8H)	4.02 (t, 4H)	2.08 (quin, 2H)			5.00 (s, 4H)			
				Found	69.8	7.1	10.7	6.47–6.62 (m, 8H)	3.94 (t, 4H)	2.01 (quin, 2H)			4.59 (s, 4H)			
				Calcd.	70.6	7.4	10.3									
III	4	67	131	Found	70.5	7.5	10.2	6.06–6.92 (m, 8H)	3.90 (m, 4H)	1.80 (m, 4H)			5.00 (s, 4H)			
IV	4	67	138 (124–125) ^a	Found	70.5	7.5	10.1	6.47–6.66 (m, 8H)	3.85 (m, 4H)	1.76 (m, 4H)			4.57 (s, 4H)			
				Calcd.	71.3	7.7	9.8									
III	5	92	122	Found	71.5	7.7	9.7	6.04–6.91 (m, 8H)	3.86 (t, 4H)	1.72 (m, 4H)	1.52 (m, 2H)		4.99 (s, 4H)			
IV	5	94	79	Found	71.3	7.8	9.8	6.47–6.66 (m, 8H)	3.81 (t, 4H)	1.68 (m, 4H)	1.52 (m, 2H)		4.57 (s, 4H)			
				Calcd.	72.0	8.1	9.3									
III	6	89	97	Found	71.7	8.0	9.2	6.04–6.91 (m, 8H)	3.84 (t, 4H)	1.69 (m, 4H)	1.43 (m, 4H)		4.99 (s, 4H)			
IV	6	84	144	Found	71.7	8.0	9.1	6.46–6.65 (m, 8H)	3.80 (t, 4H)	1.65 (m, 4H)	1.42 (m, 4H)		4.56 (s, 4H)			
				Calcd.	73.1	8.6	8.5									
III	8	94	108	Found	73.2	8.7	8.5	6.03–6.91 (m, 8H)	3.83 (t, 4H)	1.66 (m, 4H)	1.34 (m, 8H)		5.01 (s, 4H)			
IV	8	80	134 (130–132) ^b	Found	72.8	8.5	8.3	6.46–6.65 (m, 8H)	3.79 (t, 4H)	1.63 (m, 4H)	1.33 (m, 8H)		4.57 (s, 4H)			
				Calcd.	73.7	8.8	8.2									
III	9	82	112	Found	73.5	8.8	8.0	6.03–6.91 (m, 8H)	3.82 (t, 4H)	1.66 (m, 4H)	1.32 (m, 10H)		5.01 (s, 4H)			
IV	9	94	75 (80–82) ^b	Found	73.5	8.9	7.9	6.46–6.65 (m, 8H)	3.79 (t, 4H)	1.63 (m, 4H)	1.31 (m, 10H)		4.58 (s, 4H)			
				Calcd.	74.1	9.1	7.9									
III	10	94	105 (100–102) ^b	Found	74.1	9.2	7.9	6.03–6.91 (m, 8H)	3.82 (t, 4H)	1.65 (m, 4H)	1.29 (m, 12H)		5.01 (s, 4H)			
IV	10	83	121 (111–112) ^b	Found	73.9	8.9	7.6	6.46–6.64 (m, 8H)	3.78 (t, 4H)	1.62 (m, 4H)	1.28 (m, 12H)		4.58 (s, 4H)			
				Calcd.	75.0	9.4	7.3									
III	12	92	95	Found	74.9	9.5	7.3	6.03–6.90 (m, 8H)	3.82 (t, 4H)	1.65 (m, 4H)	1.27 (m, 16H)		5.01 (s, 4H)			
IV	12	79	116 (111–113) ^b	Found	75.0	9.5	7.3	6.46–6.64 (m, 8H)	3.78 (t, 4H)	1.62 (m, 4H)	1.26 (m, 16H)		4.57 (s, 4H)			

^a Reference 19.^b Reference 18.

α,ω -Bis(3-aminophenoxy)Hexane (III6)

In an autoclave (300 mL) were charged 20.95 g (55.6 mmol) of I6 prepared as described above, 2.4 g of 5% Pd/C, and 50 mL of tetrahydrofuran under a 70 kg/cm² pressure of hydrogen. The hydrogenation was conducted at 100°C for 4 h. After cooling to room temperature, the Pd catalyst was filtered off and the filtrate was evaporated to dryness. The product was recrystallized from ethanol (40 mL) and dried in a vacuum at 60°C for 6 h. The yield of yellow needles was 14.91 g (89%).

Polymer Synthesis***One-Step Method***

As a typical experiment the polycondensation of *α*-BPDA with III6 under nitrogen was conducted as follows: III6 (1.613 g, 5.37 mmol), *m*-cresol (15 mL), and *α*-BPDA (1.580 g, 5.37 mmol) were combined in a 100-mL four-necked round flask equipped with a mechanical stirrer, a water separating trap topped by a condenser, and a nitrogen inlet. The mixture was heated in an oil bath to 200°C for 6 h to afford a viscous PI solution that resulted after removing the water. The viscous solution was poured into 1 L of methanol under rapid stirring and the precipitate was pulverized with a cooking mixer, filtered, and dried in a vacuum at 120°C for 3 h. The yield was 2.83 g (94%).

Two-Step Method

The typical experiment of the polycondensation of *s*-BPDA with III6 under nitrogen was conducted as follows: In a 100-mL four-necked round flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet were combined III6 (1.076 g, 3.58 mmol), DMAc (10 mL), and *s*-BPDA (1.053 g, 3.58 mmol). The mixture was stirred at room temperature for 2 h to afford a viscous polyamic acid solution.

Measurements

The films used for the thermal measurements were prepared by casting PI NMP solutions containing 20% polymer by weight (one-step method) or by direct casting polyamic acid DMAc solutions containing 18% polymer by weight (two-step method) onto a glass plate and drying them at 60°C for 30 min, then heating to 200°C within 45 min and 200°C for 30 min. Differential scanning

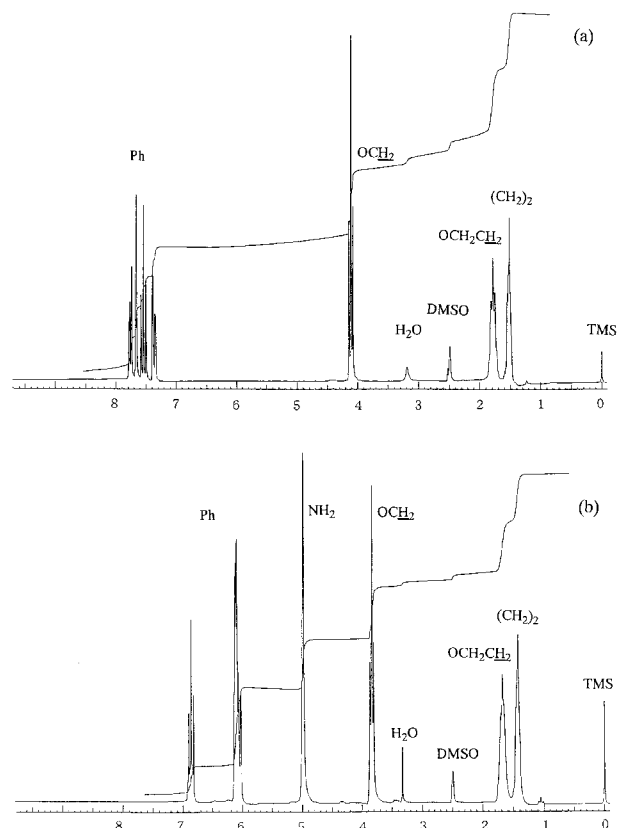


Figure 1 ¹H-NMR spectra of (a) *α,ω*-bis(3-nitrophenoxy)hexane and (b) *α,ω*-bis(3-aminophenoxy)hexane.

calorimetry (DSC) measurements were conducted on a Seiko–Denshi DS2000 instrument in aluminum pans at a heating rate of 10°C/min under nitrogen.

Glass transition temperatures (T_g s) were determined from the endothermic peak in the second heating run of the DSC curves. The T_g s of polymers VIII and most of polymers VI could not be unambiguously determined from the DSC measurements.

Thermogravimetric analysis (TGA) measurements were conducted at a heating rate of 10°C/min under nitrogen. The 5% weight loss temperatures (T_d^5 s) were determined from the TGA curve.

Inherent viscosities were measured with a Cannon Fenske viscosimeter in PI NMP solution (0.5 g/dL, 30°C) for the one-step method and in polyamic acid DMAc solution (0.5 g/dL, 30°C) for the two-step method.

The melting points of the monomers were determined from the top endothermic peak of the DSC measurements.

Table III One-Step Polymerization of PI

Polymer	Monomer			Yield (%)	η_{inh}^a (dL/g)	DSC ^b
	Dianhydride	Diamine	<i>n</i>			
V	<i>a</i> -BPDA	III	3	88	0.47	
		III	4	95	0.58	
		III	5	97	0.96	
		III	6	94	0.70	
		III	8	94	0.67	
		III	9	95	0.87	
		III	10	93	0.67	
VI	<i>a</i> -BPDA	III	12	94	0.99	
		IV	3	91	0.73	
		IV	4	94	Precip	419
		IV	5	92	0.83	
		IV	6	91	Precip	338, 364
		IV	8	94	0.80	
		IV	9	96	1.35	
VII	<i>s</i> -BPDA	IV	10	93	0.79	
		IV	12	93	0.80	
		III	3	91	Precip	
		III	4	86	Precip	303, 319
		III	5	91	2.05	
		III	6	88	1.22	
		III	8	93	1.36	
VIII	<i>s</i> -BPDA	III	9	94	1.81	
		III	10	93	1.42	
		III	12	93	2.24	
		IV	6	90	Precip	451
		IV	8	94	Precip	388, 427, 445 (426, 440)
		IV	9	93	Precip	386, 437 (388, 436)
		IV	10	91	Precip	364, 392, 429 (394, 430)
IV	12	95	Precip	322, 366, 415 (374, 420)		

A mixture of an equimolar amount of BPDA and diamine in *m*-cresol (solid content 18%) was polymerized at 200°C for 6 h. Precip, the precipitations took place.

^a The η_{inh} was measured in a polyimide NMP solution (0.5 g/dL, 30°C).

^b The top endothermic peaks of DSC measurements were detected and the literature data¹⁸ are in parentheses.

Dynamic mechanical spectrometry (DMS) measurements were performed on a Rheometrics RSA-II mechanical spectrometer in the plate geometry using 0.03-mm plates at 10 Hz (62.8 rad/s). Dynamic data were recorded at a step of 3°C in the range of strain of 0.05%.

¹H-NMR spectra were recorded on a Nihon-Denshi FX-200 instrument in CDCl₃ or dimethylsulfoxide-*d*₆ using tetramethylsilane as an internal standard.

Test pieces (6 cm long, 0.4 mm wide, and 0.02 mm thick) for mechanical measurements were prepared by a casting method as described above, and the tensile data were obtained according to the ASTM D882 standard.

RESULTS AND DISCUSSION

Diamine Synthesis

Two series of α,ω -bis(3- and 4-aminophenoxy)alkanes (III and IV) were prepared. The condensation of *meta*- or *para*-nitrophenol with α,ω -dibromoalkanes was carried out in DMSO in the presence of potassium hydroxide to give the corresponding α,ω -bis(3- and 4-nitrophenoxy)alkanes (I and II). The bis(nitro) derivatives were then hydrogenated in tetrahydrofuran by means of a Pd/charcoal catalyst to afford the desired diamines. The molecular structures of the diamines are shown in Scheme 1. The yields, elemen-

Table IV Two-Step Polymerization of PI

Polymer	Monomer			η_{inh}^a (dL/g)			
	Dianhydride	Diamine	n				
VI	α -BPDA	IV	3	1.00			
			4	1.00			
			5	1.14			
			6	0.97			
			8	1.14			
			9	1.43			
			10	1.07			
			12	1.12			
			VII	s -BPDA	III	3	0.84
						4	1.03
5	0.81						
6	0.87						
8	1.11						
9	0.82						
10	0.96						
12	0.89						
VIII	s -BPDA	IV	3	1.72			
			4	2.02			
			5	1.72			
			6	1.13			
			8	1.37			
			9	2.04			
			10	2.27			
			12	2.48			

A mixture of an equimolar amount of BPDA and diamine in DMAc (solid content 18%) was polymerized at room temperature for 2 h.

^a The η_{inh} was measured in a polyamic acid DMAc solution (0.5 g/dL, 30°C).

tal analyses, and melting points of the nitro derivatives and diamines are summarized in Tables I and II, respectively. The elemental analyses were in good agreement with the calculated ones, but the melting points measured by DSC indicated some deviations from the reported values.^{18,19} However, the ¹H-NMR spectra confirmed the molecular structures proposed; the ¹H-NMR spectra of the typical momers α,ω -bis(3-nitrophenoxy)hexane (I6) and α,ω -bis(3-aminophenoxy)hexane (III6) are shown in Figure 1.

Polymer Synthesis

A series of new PIs was prepared by two methods.

One-Step Method

α -BPDA was polymerized with α,ω -bis(3-aminophenoxy)alkanes (III) in *meta*-cresol at 200°C, at

which the polymerizations were carried out with 18% solid contents. The reaction mixtures became homogeneous solutions within a few minutes, affording viscous polymer solutions from which polymer powders were collected by precipitation in methanol. All diamines with methylene spacers C3–C12 readily gave the desired PIs (V). PIs V all revealed absolutely amorphous properties and nicely cast into flexible films.

The polymerizations of α -BPDA with α,ω -bis(4-aminophenoxy)alkanes (IV) and s -BPDA with α,ω -bis(3-aminophenoxy)alkanes (III) proceeded smoothly, but in several cases (VI4, VI6, VII3, and VII4) precipitations were observed (Table III).

PIs VIII were obtained as powders only, according to what was recently described.¹⁸

Two-Step Method

s -BPDA was polymerized with α,ω -bis(4-aminophenoxy)alkanes (IV) in DMAc at room temperature in a conventional method to readily give a polyamic acid solution. At variance with the results described above in the one-step method, we met with no problems in performing the polycondensations of s -BPDA and IV for all diamines with methylene spacers C3–C12.

The polymerizations of α -BPDA with α,ω -bis(4-aminophenoxy)alkanes (IV) and s -BPDA with α,ω -bis(3-aminophenoxy)alkanes (III) also proceeded smoothly (Table IV). PIs V could all be easily prepared in a one-step method and could be obtained in a two-step method, too. However, sys-

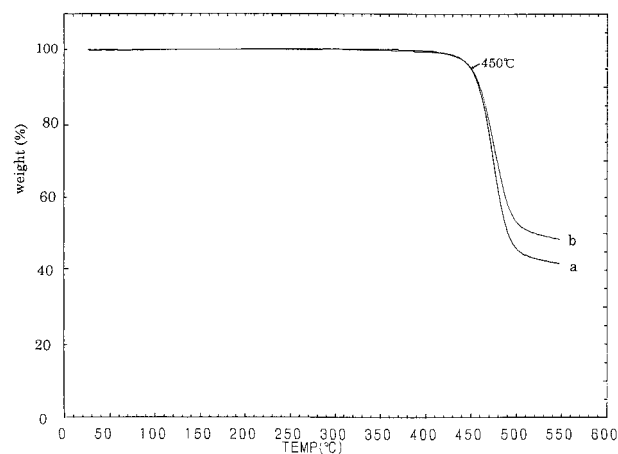


Figure 2 Thermogravimetric analyses of polymers (a) V6 in the one-step method and (b) VII6 in the two-step method.

Table V Properties of PI

Polymer	<i>n</i>	T_g (°C)	T_d^5 (°C)	Strength at Yield (kg/cm ²)	Strength at Break (kg/cm ²)	Initial Modulus (kg/cm ²)	Elongation at Break (%)	
V ^a	3	178	455	YP	950	27,900	6	
	4	178	454	YP	940	23,700	7	
	5	168	454	870	730	21,700	13	
	6	157	450	770	630	20,100	38	
	8	142	449	730	620	19,800	70	
	9	134	451	650	570	17,500	122	
	10	127	448	670	560	17,800	133	
	12	116	448	590	520	16,400	156	
	VI ^b	3	232	454	970	830	21,000	23
		5	208	454	770	700	16,700	71
9		NC	451	730	650	16,100	105	
10		NC	447	820	710	17,000	12	
12		NC	448	731	620	15,600	29	
VII ^b	3	184	455	980	900	26,500	22	
	4	175	448	870	760	23,200	58	
	5	165	452	850	760	21,000	78	
	6	153	451	830	790	21,700	96	
	8	138	450	770	730	18,800	109	
	9	132	448	680	710	18,500	116	
	10	125	447	640	730	17,500	136	
	12	116	449	580	700	16,000	145	
VIII ^b	3	NC	464	1,060	1,000	27,900	56	
	4	NC	458	YP	800	30,200	7	
	5	NC	457	880	850	22,300	77	
	8	NC	452	YP	700	20,300	10	
	9	NC	456	700	730	16,800	127	
	10	NC	450	780	830	19,000	60	
	12	NC	451	700	780	16,400	73	

T_g , the glass transition temperature from DSC measurements at a heating rate of 10°C/min; T_d^5 , 5% weight loss temperature from TGA measurements at a heating rate of 10°C/min; NC, not clearly defined; YP, yield point was not observed.

^a Films were prepared by casting of polyimide NMP solutions.

^b Films were prepared by casting of polyamic acid DMAc solutions.

tematic polymerizations were not attempted in these systems.

Properties of Polymers

Most polymers except the series of PIs VIII and some cases of PIs VI and VII (VI4, VI6, VII3, and VII4) exhibited good solubility in *meta*-cresol. The polymerizations could be easily conducted in the one-step method to afford viscous solutions.

The DSC curves showed the endothermic peaks for the powders PIs VIII, which are almost identical to the reported ones (Table III), indicating that the polymers should be semicrystalline or liquid crystalline. In the DSC curves of powders of PIs VI4, VI6, and VII4, endothermic peaks were

observed, suggesting the higher rigidity of these materials.

On the other hand, the two-step method could be applied to all monomer combinations, even the PIs VIII, which were obtained as powders in the one-step method because of low solubilities. The polyamic acid solutions were cast on a glass plate and after curing yellow transparent films were obtained. Only the films of PIs VIII showed some turbidity due to the crystalline properties.

In the case of polymer VIII6, a pulverization took place during the thermal imidization process for the cast film of the polyamic acid solution. This finding may have been due to high crystallinity in which

packing of molecular chains is supposed to be eminently suitable for this polymer.

From the relationship between the molecular structure and the solubility of the polymer it is known that the chain flexibility of the polymer backbone provides few interchain interactions and prevents efficient packing of polymer chains.²¹

The bent units of the α -BPDA components and *meta*-aminophenoxy units of α,ω -bis(3-aminophenoxy)alkanes caused an effective alteration of the molecular structures. Thus, the solubilities of the prepared polymers were found to be in the order V > VI, VII \gg VIII. A similar enhanced solubility by the α -BPDA unit was observed in the poly(amide-imides) system.²² Inherent viscosities ranged at ca. 0.5–2.3 dL/g for PI powders (Table III) and ca. 0.8–2.5 dL/g for polyamic acids (Table IV).

The molecular weights of the prepared polymers were high enough to give tough and flexible films when cast on glass plates, followed by curing up to 200°C. The TGA charts for the typical polymers V6 and VII6 are shown in Figure 2. The T_d^5 s and T_g s were obtained from measurements on the films, which were prepared by direct casting of polyamic acid solutions of VI, VII, and VIII or a PI solution of V dissolved in NMP.

The T_d^5 s and T_g s are summarized in Table V. The T_d^5 s of the polymers were found at around 450°C, indicating good thermal stabilities at elevated temperatures. The T_g s were in the range of 110–240°C. However, the T_g s are not clearly defined for PIs VIII and VI in the DSC charts (Table V). We conducted the DMS measurements for the PIs VIII. However, the DMS curves did not indicate a clear transition for all PIs VIII. Figure 3(b) shows the temperature dependence of the dynamic storage modulus (E') and the loss modulus (E'') for a typical example (PI VIII 10) in which a broad maximum of the quantity E'' was recognized at around 153°C. On the other hand, a clear transition is detected for PI VI3 [Fig. 3(a)]. The quantity E'' displays a clear maximum value at 243°C, which roughly coincides with the T_g (232°C) by the DSC measurement.

The transition temperatures at the E'' maximum value were supposed to be a glass transition and $E''(\text{max})$ corresponds to T_g .^{23–25}

Tensile properties of typical PIs are given in Table V. Typically found were tensile strengths at break of ca. 500–1,000 kgf/cm², elongation at break of 5–160%, and initial moduli of ca. 15,000–30,000 kgf/cm². With a longer alkylene chain the

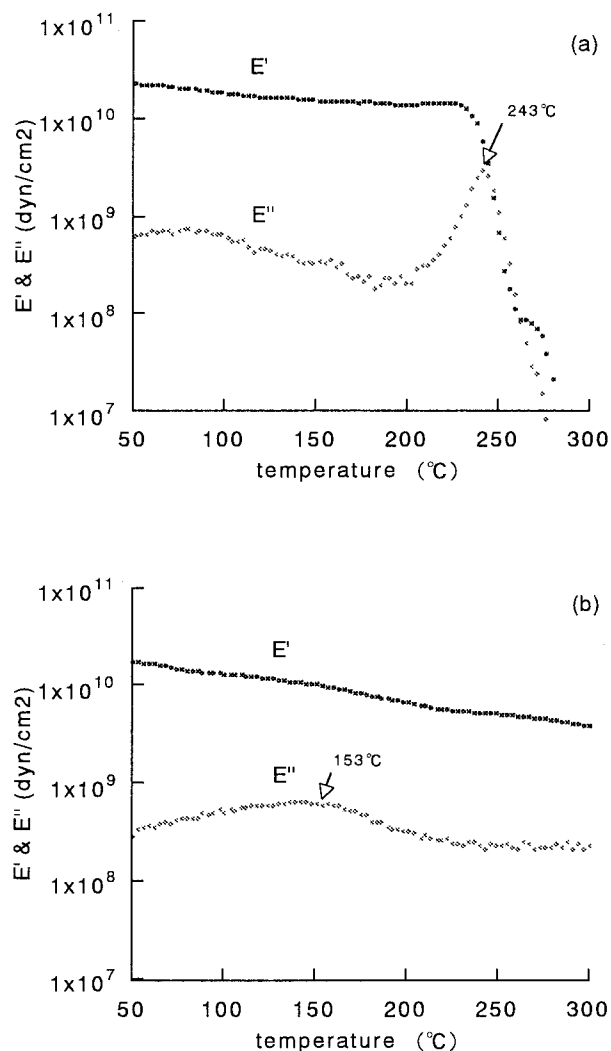


Figure 3 Temperature dependence of moduli E' and E'' for polymers (a) VI3 and (b) VIII10.

tensile strengths at break and initial moduli decreased due to the flexibility of the alkylene chain.

It is interesting to note the “odd–even” behavior of the tensile properties of polymer VIII films similar to the reported behavior of the melting temperatures for these polymers¹⁸ and for analogous aliphatic PIs^{26,27} and as reported in the behavior of the tilt bias angle for aliphatic PIs.²⁸

Thus, tensile strengths at break and initial moduli of polymers with an even number of methylene spacers have larger values than those of polymers with an odd number of methylene spacers.

CONCLUSION

Four series of aromatic polyimides (V–VIII) composed of BPDAs and aromatic diamines bearing

alkylene spacers were prepared by two methods. Most polymers could be readily prepared in a one-step method for the combination of α -BPDA with α,ω -bis(3-aminophenoxy)alkanes, α -BPDA with α,ω -bis(4-aminophenoxy)alkanes, and s -BPDA with α,ω -bis(3-aminophenoxy)alkanes. However, polymerization of s -BPDA with α,ω -bis(4-aminophenoxy)alkanes gave powders. On the other hand, all four monomer combinations afforded the desired polyamic acid solution in a two-step method. The polymers were characterized by inherent viscosity, DSC, TGA, and DMS measurements. The tensile properties of the films were discussed.

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