Synthesis and Characterization of Soluble Polyimides from 1,1-Bis(4-aminophenyl)cyclohexane Derivatives

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ABSTRACT: A series of novel aromatic diamines (**1**−**3**) containing kinked cyclohexylidene moieties was synthesized by a reaction of excess aniline and corresponding methyl-substituted cyclohexanone derivatives. The structures of (**1**−**3**) were identifield by ^{1}H NMR, ^{13}C NMR, and FT-IR. The polymers were synthesized from the obtained diamines and various aromatic dianhydrides by the conventional polycondensation reaction followed by chemical imidization as well as high-temperature one-step polymerization. The inherent viscosities and weight-average molecular weights of the resulting polyimides were in the ranges of 0.55−1.58 dL/g and (7.4−15.2) × 10^4 g/mol, respectively. The prepared polyimides showed excellent thermal stabilities and good solubility. All polymers were readily soluble in common organic solvents such as tetrahydrofuran, chloroform, tetrachloroethane, etc., and the glass transition temperatures were observed at 290−372 °C.

Introduction

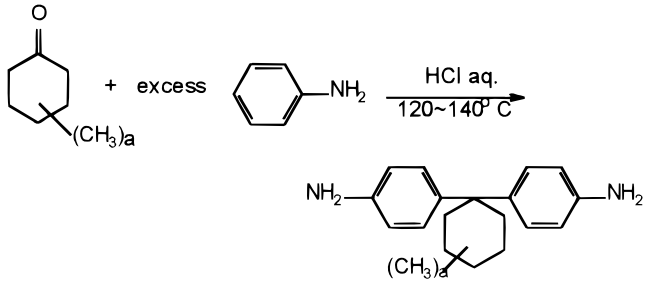
Aromaic polyimides have been noted for their excellent characteristics. But their processability is poor, which limits their application areas.[1,2] Therefore, various efforts have focused on the synthesis of soluble polyimides without sacrifice of their excellent properties. Typical approaches were to introduce the alicyclic structures into a polymer backbone and incorporate their pendant bulky groups.[3,4] According to these research trends, we previously reported the synthesis of poly(amidimides) with good solubility as well as thermal stability by introduction of an alicyclic diamine containing the 3,3,5-trimethylcyclohexane structure.[5,6] From the results of this work, it was known that the inter-chain interaction of the resulting polymers was decreased by the introduction of trimethylsubstituents, which resulted in good solubility of the polymers. Furthermore, the chain rigidity of the polymer was also increased due to the substituted alicyclic structure, which restricted the free rotation of the polymer backbone. Hence, the obtained polymers showed good thermal stability as well as solubility. On the basis of this idea, the present work was undertaken to synthesize novel aromatic diamines containing alicyclic structures such as 1,1-bis(4-aminophenyl)cyclohexane [BACH (**1**)], 1,1-bis(4-aminophenyl)-4-methylcyclohexane [BAME (**2**)], and 1,1-bis(4-aminophenyl)-3,3,5-trimethylcyclohexane [BATM (**3**)].

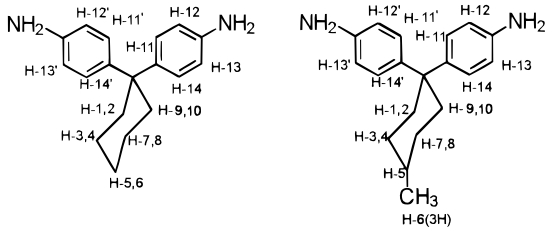
This paper also relates the synthesis and characterization of new soluble polyimides derived from the above three diamines (**1**−**3**) and conventional aromatic dianhydrides.

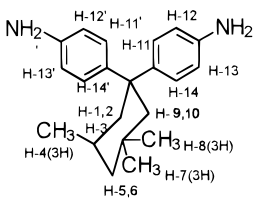
Results and Discussions

Monomer Synthesis. The synthetic route of the monomers is shown in Scheme 1. Several aromatic diamines were prepared by the reaction of the corresponding cyclohexanone derivatives with excess aniline in an autoclave at temperatures of 120−140 °C for 24 h. Aromatic diamines **1** and **2** prepared from cyclohexanone or 4-methylcyclohexanone were obtained with comparably high yields above 70%. However, the yield of compound **3** was only 40%. As shown in Scheme 2, it can be expained by the steric hindrance of 3,3,5-trimethylcyclohexanone. The addition reaction of aniline a proceded from the less hindered direction, which resulted in the hydroxonium intermediate (**4**). However, one of the two methyl groups at the 3,3-positioned in the cyclohexane ring retarded the substitution reaction of the second aniline (b).

Scheme 1







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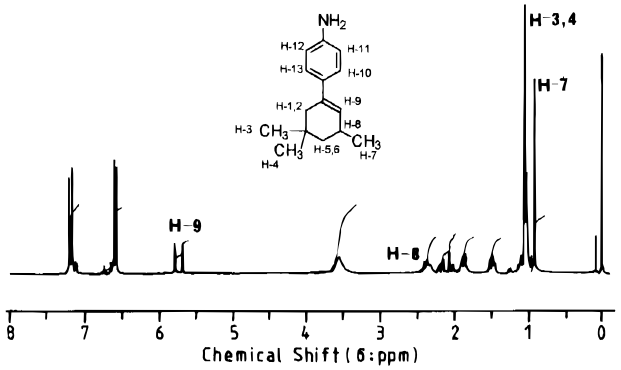
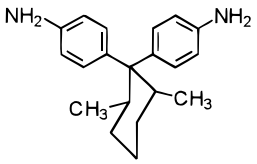


Figure 1. ^{1}H NMR (300-MHz) spectrum of compound **5** in $CDCl_3$.

This mechanism was confirmed by the structural identification of a major byproduct (**5**), which was the dehydration product of compound **4**, of whose ^{1}H NMR spectrum is shown in Figure 1.

This showed that the dehydration reaction occurred faster than the substitution reaction of aniline b in the sterically hindered cyclohexanone derivatives like 3,3,5-trimethylcyclohexanone. Furthermore, we tried to synthesize the aromatic diamine **6** containing the 2,6-dimethylcyclohexylidene group. However, we could not obtain the desired dianiline compound (**6**) at all.



(6)

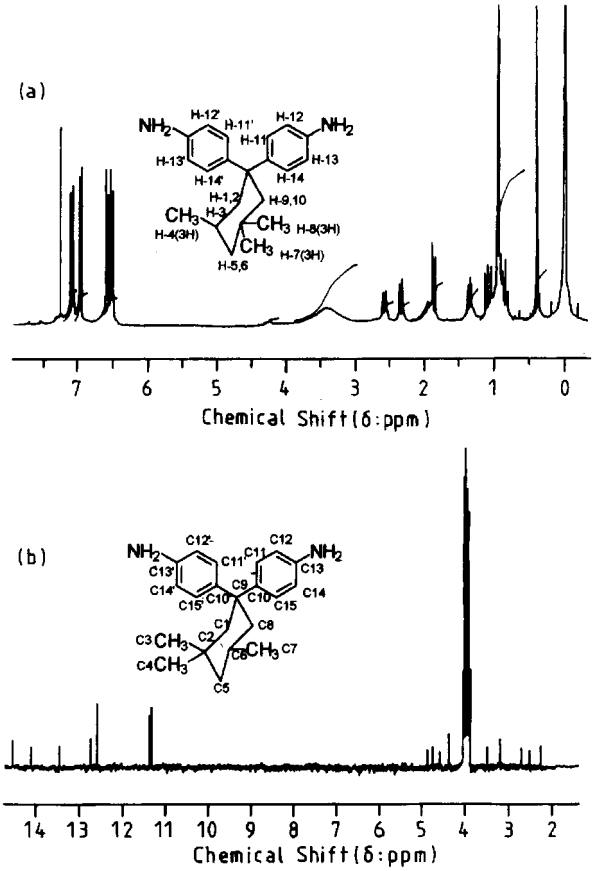
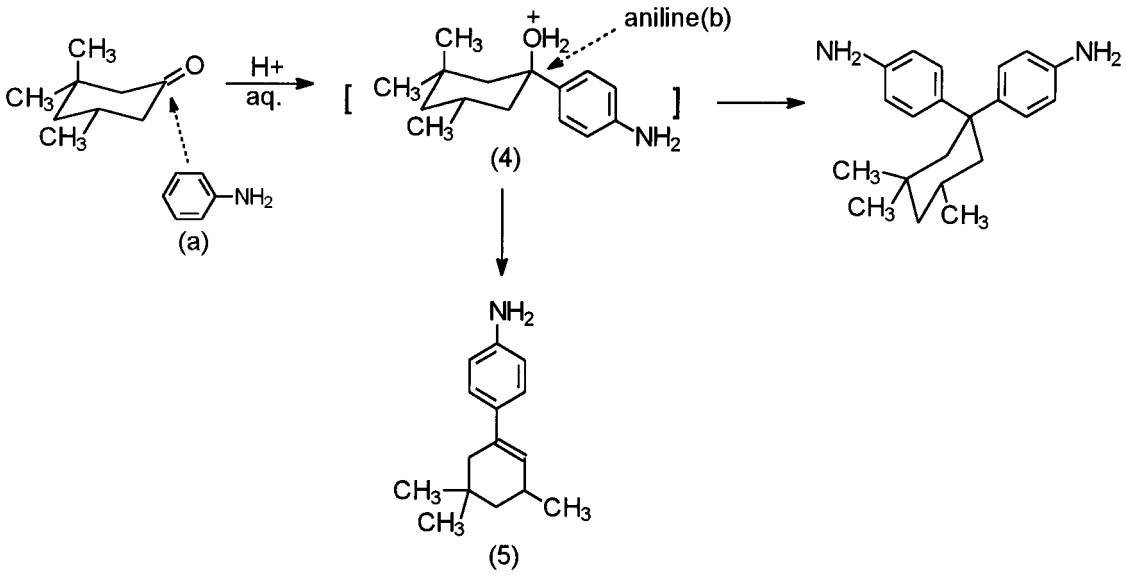


Figure 2. (a) ^{1}H NMR (300-MHz) and (b) ^{13}C NMR (125-MHz) spectra of compound **3** in $CDCl_3$. The atom labelings used here are the same as those of compound **3** in the Experimental Section.

The ^{1}H NMR and ^{13}C NMR spectra of compound **3** in $CDCl_3$ are shown in Figure 2. The structure assignment is described in the Experimental Section in detail.

Polymer Synthesis. For the synthesis of polyimides, two different synthetic routes were applied as shown in Scheme 3. At first, we had prepared the polyimides from BATM with aromatic dianhydrides by a conventional polycondensation reaction followed by chemical imidization using acetic anhydride and pyridine according to synthetic route a. The inherent viscosities of the obtained polyimides were in the range of 0.55−0.68 dL/g, which might be due to the bended structure of BATM. However, one-step polymerization at high temperature, as shown in synthetic route b, provided enough energy even for the monomer with a highly bended structure like BATM, which resulted in high viscosity as well as high molecular weight. The results of the polymerization are summarized in Table 1. The inherent viscosities of the polyimides obtained by one-step polymerization were in the range of 0.57−

Scheme 2



Scheme 3. Synthesis of Soluble Polyimides

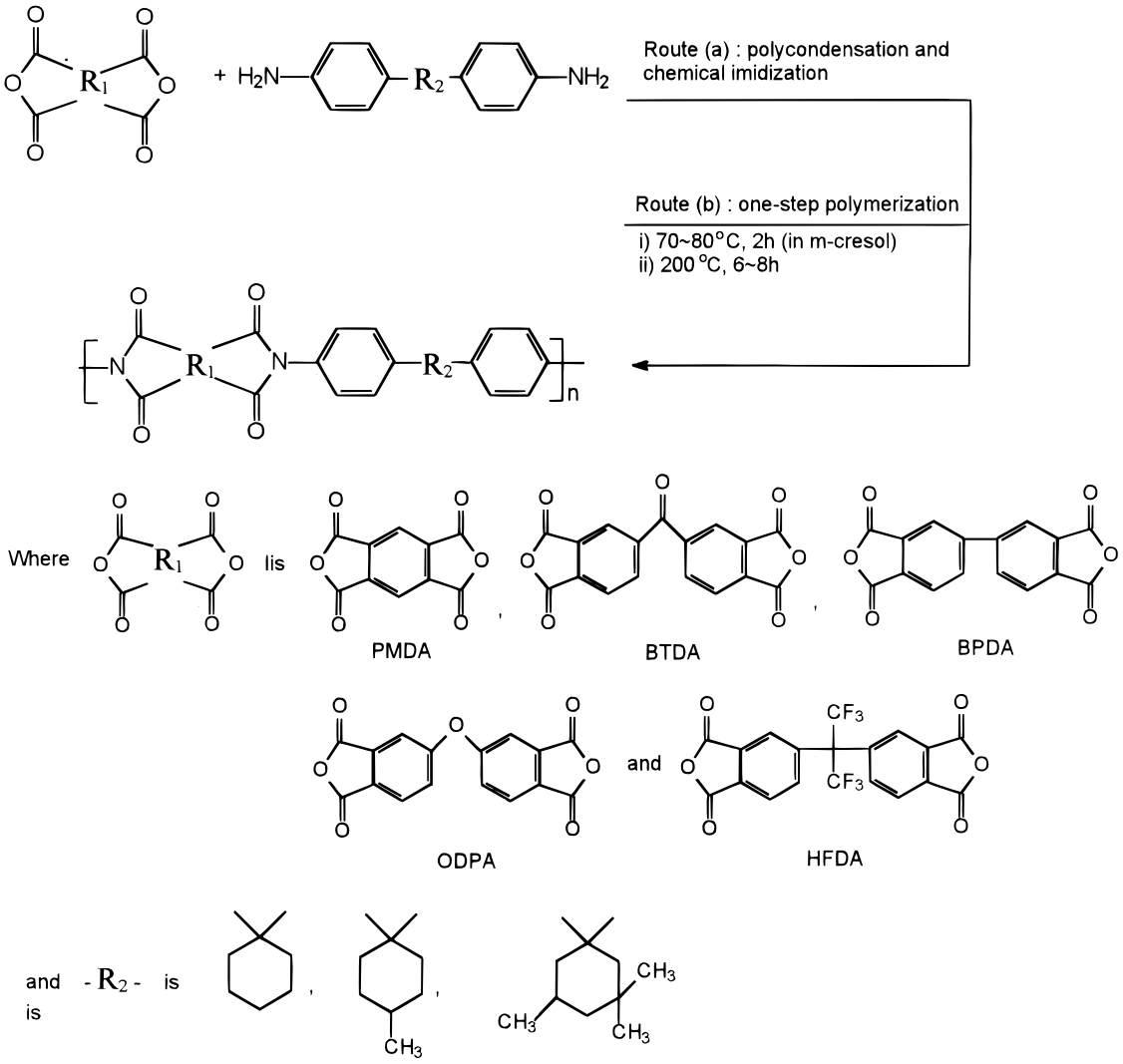


Table 1. Synthesis of New Soluble Polyimides

					GPC		
polymer	diamines[a]	dianhydrides[b]	polymerization	η_{inh}, dL/g	M_n, g/mol	M_w, g/mol	PDI
C-1	BACH	PMDA	one-step[c]		*e*		
C-2	BACH	BTDA	one-step[c]	1.03			
C-3	BACH	BPDA	one-step[c]	0.93			
C-4	BACH	ODPA	one-step[c]	0.66			
C-5	BACH	HFDA	one-step[c]	0.57			
M-1	BAME	PMDA	one-step[c]	1.18	86 000[f]	119 000	1.38
M-2	BAME	BTDA	one-step[c]	1.58	104 000	152 000	1.47
M-3	BAME	BPDA	one-step[c]	1.31			
M-4	BAME	ODPA	one-step[c]	1.02	92 000	138 000	1.50
M-5	BAME	HFDA	one-step[c]	0.89	117 000	177 000	1.51
T-1	BATM	PMDA	one-step[c]	1.04	76 000[g]	129 000	1.70
T-2	BATM	BTDA	one-step[c]	1.21	87 000	133 000	1.53
T-3	BATM	BPDA	one-step[c]	1.25	74 000	132 000	1.78
T-4	BATM	ODPA	one-step[c]	1.26	92 000	159 000	1.97
T-5	BATM	HFDA	one-step[c]	0.84	91 000	142 000	1.46
T-(1)	BATM	PMDA	two-step[d]	0.68	60 000[g]	109 000	1.82
T-(2)	BATM	BTDA	two-step[d]	0.66	38 800	89 000	2.31
T-(3)	BATM	BPDA	two-step[d]	0.56	40 000	94 000	2.32
T-(4)	BATM	ODPA	two-step[d]	0.55	44 000	74 000	1.68
T-(5)	BATM	HFDA	two-step[d]	0.55	60 000	102 000	1.70

[a] Abbreviations: BACH,1,1-bis(4-aminophenyl)cyclohexane; BAME, 1, 1-bis(4-aminophenyl)-4-methylcyclohexane; BATM, 1,1-bis(4-aminophenyl)-3,3,5-trimethylcyclohexane. [b] Abbreviations: PMDA, pyromellitic dianhydride; BTDA, 3,3′4,4′-benzophenonetetracarboxylic dianhydride, BPDA, 3,3′4,4′-biphenyltetracarboxylic dianhydride; ODPA, 3,3′,4,4′-tetracarboxydiphenyl oxide dianhydride; HFDA, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride. [c] 5.0 mmol of diamine and dianhydride were reacted in 19.0 mL of *m*-cresol at 70−80 °C for 2 h and at 200 °C for 6−8 h under nitrogen atmosphere in the presence of isoquinoline as a catalyst. [d] Polymerization was performed with 5.0 mmol each of diamine and dianhydride in 10.5 mL of NMP at 20−25 °C for 24 h and followed by chemical imidization using Ac_2O/pyridine under nitrogen atmosphrene. [e] Insoluble. [f] Measured in DMF solution at 80 with μ-Styragel column HT6E5E3. [g] Measured in chloroform solution at 40 with μ-Styragel column HT6E5E3.

Table 2. Solubility of Polyimides Based on BATM and Various Dianhydrides

		solvents							
polymer	dianhydrides	NMP[b]	DMF	TCE	γ-butyrolactone	*m*-cresol	THF	$CHCl_3$	acetone
T-1	PMDA[a]	++	++	++	++	++	++	++	−−
T-2	BTDA	++	++	++	++	++	++	++	−−
T-3	BPDA	++	+−	++	+−	+−	+−	++	−−
T-4	ODPA	++	++	++	++	++	++	++	−−
T-5	HFDA	++	++	++	++	++	++	++	−−

[a] Abbreviations: PMDA, pyromellitic dianhydride; BTDA, 3,3′4,4′-benzophenonetetracarboxylic dianhydride; BPDA, 3,3′4,4′-biphenyltetracarboxylic dianhydride; ODPA, 3,3′,4,4′-tetracarboxydiphenyl oxide dianhydride; HFDA, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride. [b] Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMF, dimethylformamide; TCE, 1,1,2,2-tetrachloroethane; THF, tetrahydrofuran. [c] Key: ++, soluble; +−, partially soluble; −−, insoluble.

Table 3. Solubility of Polyimides Derived from PMDA and Various Diamines

		solvents						
polymer	dianhydride	NMP[b]	DMF	TCE	*m*-cresol	THF	$CHCl_3$	acetone
C-1	BACH[a]	−−	−−	++	−−	−−	−−	−−
M-1	BAME	++	++	++	++	−−	−−	−−
T-1	BATM	++	++	++	++	++	++	−−

[a] Abbreviations: BACH, 1,1-bis(4-aminophenyl)cyclohexane; BAME, 1,1-bis(4-aminophenyl)-4-methylcyclohexane; BATM, 1,1-bis(4-aminophenyl)-3,3,5-trimethylcyclohexane. [b] Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMF, dimethylfomamide; TCE, 1,1,2,2-tetrachloroethane. [c] Key: ++, soluble; +−, partially soluble; −−, insoluble.

1.58 dL/g, which was remarkably increased as compared to those of polyimides prepared by chemically imidized two step polycondensation. On the other hand, the relatively lower molecular weights of the polyimides based on BACH resulted from their poor solubility to reaction medium. For example, the polyimide (C-1) derived from BACH and PMDA was not soluble in *m*-cresol even at a high temperature of 200 °C, which was precipitated out during polymerization without increasing the molecular weight.

The molecular weights of the obtained polyimides were estimated by gel permeation chromatography (GPC) in chloroform at 40 °C after calibration with polystyrene standard. The polyimides had weight-average molecular weights (M_w's) in the range of (7.4−15.2) × 10^4 g/mol and gave tough/flexible films. The tensile strengths of polyimide films (T-1−T-5) were measured, which were in the range of 840−1160 kg/cm^2. The structures of all the polyimides were identified by FT-IR and ^{1}H NMR spectroscopy. The typical ^{1}H NMR spectra of poly(amic acid) and polyimide (T-2) are shown in Figure 3. The amide proton peaks of poly(amic acid) at 10.0−10.5 ppm were not detected.

Solubility. The solubilities of the polyimides based on BATM toward various kinds of organic solvents are summarized in Table 2. All of these polymers were soluble in typical aprotic dipolar solvents such as *N*-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), and dimethylformamide (DMF). Moreover, these polymers were soluble in less hydrophilic solvents like γ-butyrolactone and exhibited good solubility to common organic solvents with low boiling points such as chloroform, tetrahydrofuran, etc. This property can be contributed to widening the application fields of polyimides. The preimidized polymer solution can be used in the liquid-crystal alignment layer for full color TFT−LCD (thin-film transistor−liquid-crystal display), which requires lower processing temperatures. Table 3 also summarizes the solublility of the polyimides based on PMDA and various aromatic diamines prepared in this study. Most of the polyimides derived from BACH which has no methyl substituent were not soluble in common organic solvents. On the other hand, polyimides obtained from BATM having three methyl substituents showed the best solubility. The three methyl substitutions might decrease the inter-chain interaction of rigid aromatic repeating units, resulting in improved solubility.

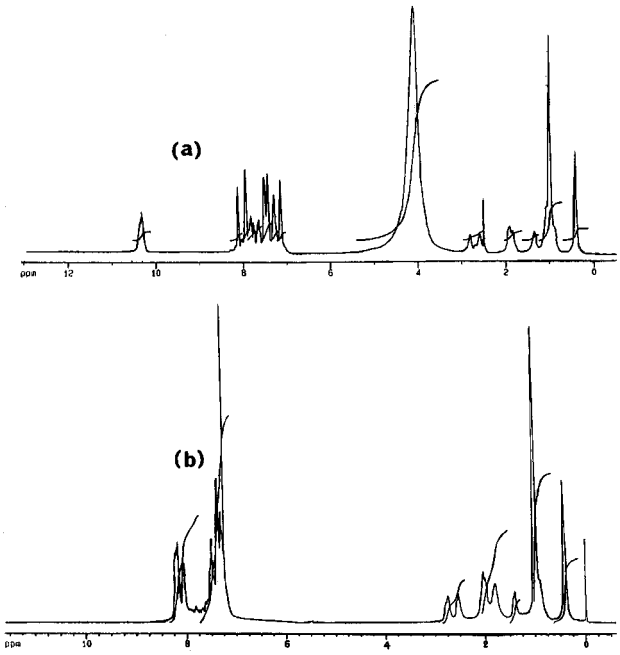


Figure 3. ^{1}H NMR (500-MHz) spectra of polymers based on BATM and BTDA: (a) poly(amic acid) in DMSO-d_6; (b) polyimide (T-2) in $CDCl_3$.

Thermal Stability. The thermal stabilities of the polyimides were evaluated by thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC) under nitrogen atmosphere, and typical TGA curves are represented in Figure 4. The polyimides exhibited excellent thermal stability. They are stable up to 500 °C, and the residual weights at 800 °C were above 30%, which is comparable to the typical soluble polyimides derived from diaminophenylindane (DAPI) produced by Ciba Geigy. The glass transition temperatures (T_g's) measured by differential scanning calorimetry (DSC) ranged from 290 to 372 °C. The polyimides prepared from BPDA had relatively high T_g's, because of their rigid structure. As shown in Table 4, the T_g's of the polymer were decreased with an increase

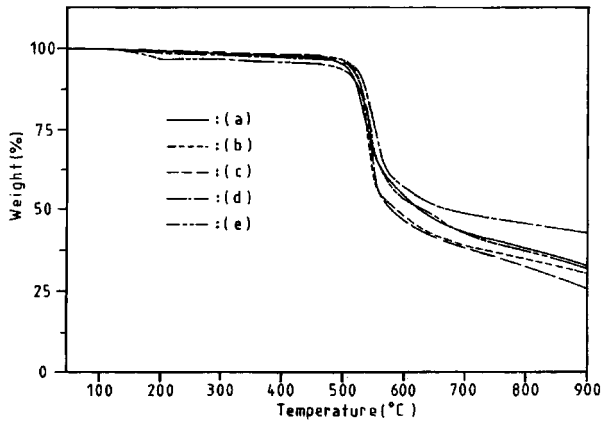


Figure 4. Typical TGA curves of polyimides based on BATM under nitrogen atmosphere with a heating rate of 20 °C/min. (a) T-1, (b) T-2, (c) T-3, (d) T-4, (e) T-5.

Table 4. Glass Transition Temperature of Polyimides

	glass transition temp[b] for dianhydride				
diamine	PMDA	BPDA	BTDA	6FDA	ODPA
BACH[a]	*c*		305	293	290
BAME	349	355	346	306	300
BATM		~370(372)[d]	336(347)	323(332)	330(316)

[a] Abbreviations: BACH, 1,1-bis(4-aminophenyl)cyclohexane; BAME, 1,1-bis(4-aminophenyl)-4-methylcyclohexane; BATM, 1,1-bis(4-aminophenyl)-3,3,5-trimethylcyclohexane. [b] From the second heating traces of DSC measurements conducted with a heating rate 10 °C/min in nitrogen atmosphere. [c] Not detected. [d] T_g's of polyimides prepared by two-step chemical imidization.

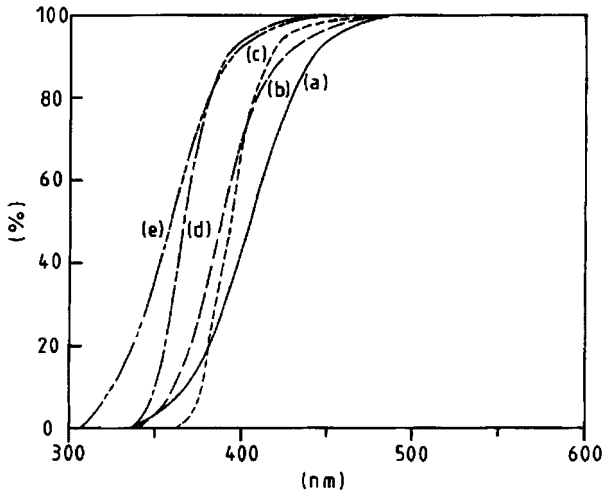


Figure 5. Typical UV−Vis spectra of polyimide solutions in NMP at a concentration of 5×10^{-3} mol/L. (a) T-1, (b) T-2, (c) T-3, (d) T-4, (e) T-5.

of the flexibility of dianhydrides according to the following series; ODPA < HFDA < BTDA < PMDA < BPDA. It was also found that the T_g's were increased with the number of methyl substituents because of the increasing restriction on the main-chain rotational motion.

Transmittance. UV−Visible spectra of polymers obtained from BATM and various aromatic dianhydrides with a concentration of 5×10^{-3}mol/L in NMP solution are shown in Figure 5. All the polymers showed high transmission above 90% in the wavelength range of 450−600 nm. That is, the trimethylcyclohexylidene moiety increased the intermolecular chain distance and decreased with the intramolecular interaction, which resulted in good optical transparency. Especially, polyimides based on HFDA exhibited better transparency than those of other polymer series. It can be seen that the electron conjugation of the HFDA moiety was also prohibited by the bulky trifluoromethyl structure. On the other hand, the polyimides derived from PMDA showed strong absorption with a cut-off between 330 and 450 nm, which was due to the electronic conjugation structure of PMDA.

Experimental Section

Materials. *N*-Methyl-2-pyrrolidone (NMP) was dried over calcium hydride for 12 h and distilled under reduced pressure. Pyromellitic dianhydride (PMDA, 99.2%, Daicel Chemical Industry, Ltd.), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, 98.6%, Daicel Chemical Industry, Ltd.), and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA, 99.6%, Mitsubishi Kasei) were used without further purification, because they were of highly purified grade for polyimide synthesis. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (HFDA, Tokyo Chemical Industry Co., Ltd., >98%) and 3,3′,4,4′-tetracarboxydiphenyl oxide dianhydride (ODPA, Tokyo Chemical Industry Co., Ltd., >98%) were used as received. *m*-Cresol was freshly distilled under reduced pressure. Aniline (Aldrich Chemical Co., Inc., 99%, bp 184 °C), cyclohexanone (Tokyo Chemical Industry Co., Ltd., >98%, bp 157 °C), 4-methylcyclohexanone (Tokyo Chemical Industry Co., Ltd., >97%, bp 171 °C) and 3,3,5-trimethylcyclohexanone-(Tokyo Chemical Industry Co., Ltd., >98%, bp 190 °C) were used as received.

Measurements. All NMR spectra were taken on a Bruker AMX 500 using $CDCl_3$ or dimethyl-d_6 sulfoxide (DMSO-d_6) as a solvents. Infrared spectra were obtained with a Bio-Rad Digilab Division FTS-165 FT-IR spectrophotometer. UV−Visible spectra were recorded on a Shimadzu UV 2100 UV−visible spectrotometer. Mass spectra and elemental analysis were measured with a Jeol JMS-DX 303 mass spectrometer and a FISONS Instruments EA-1108, respectively. The inherent viscosities of the polymers were measured with a Ubbelohde viscometer at a concentration of 0.5 g/dL in *m*-cresol or NMP at 30 °C. The molecular weights of polymers were measured by Waters Model 150C ALC/GPC equipped with Styragel columns in chloroform solution at 40 °C or dimethylformamide solution at 80 °C. The melting points of the prepared monomers were determined by DSC. Thermogravimetric analysis (TGA) was done with a Perkin-Elmer TGA 7 at a heating rate of 20 °C/min under nitrogen atmosphere. Differential scanning calorimeter (DSC) analysis was performed on a Du Pont Model 910.

Monomer Synthesis. 1,1-Bis(4-aminophenyl)cyclohexane (BACH) (1). Compound **1** was prepared by the condensation of cyclohexanone and excess aniline as follows.[7,8] To a solution of cyclohexanone (40.0 g, 0.41 mol) in 145 mL of 35% HCl aqueous solution in a 1-L autoclave equipped with a mechanical stirrer was added excess aniline (156.3 g, 1.68 mol), and the mixture was stirred at 120 °C for 20 h. After cooling, the solution was made basic with NaOH aqueous solution to pH 10, and the oily layer was separated and distilled to remove the unreacted excess aniline. The residual crude product was recrystallized from benzene to afford 86.4 g (79.4% yield) of light-yellow crystal: mp 112 °C; MS *m*/*e* 266 (M^+); ^{1}H NMR δ ($CDCl_3$) 1.40 (6 H, br s, H-3−8), 2.06 (4 H, br s, H-1,2,9,10), 3.20−3.70 (4 H, br s, amine protons), 6.55−6.60 (4 H, d, H-12,-12′,13,13′), 7.00−7.03 (4 H, d, H-11,11′,14,14′); ^{13}C NMR δ ($CDCl_3$) 22.6 (C-2,4), 26.0 (C-3), 36.6 (C-1,5), 43.8 (C-6), 113.7 (C-9,11), 127.0 (C-8,12), 136.4 (C-7), 145.5 (C-10); FT-IR (KBr pellet) 3343, 2932, 1627, 1513, 1469, 1362, 1279, 1189 cm^{-1}. Elemental Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.09; H, 8.26; N,-10.51. Found: C, 80.91; H,8.50; N, 10.24.

1,1-Bis(4-aminophenyl)-4-methylcyclohexane (BAME) (2). Compound **2** was prepared in a similar manner to that of compound **1** with 4-methylcyclohexanone instead of cyclohexanone. A light-yellow crystal was obtained after recrystallization from isopropyl alcohol: Yield, 70%; mp 158.8 °C; MS *m*/*e* 280 (M^+); ^{1}H NMR δ ($CDCl_3$) 0.75 (3 H, d, $J_{4,5} = 6.3$ Hz, H-5), 1.00 (2 H, dd, H-1,2), 1.40 (1 H, m, H-6), 1.51 (2 H,

d, H-9,10), 1.68 (2 H, m, H-3,4), 1.68, 2.49 (4 H, m, H-3,4,7,8), 3.50 (4 H, br s, amine protons), 6.49−6.60 (2 H, d, H-12′,13′), 6.60−6.65 (2 H, d, H-12,13), 6.92−6.97 (2 H, d, H-11′,14′), 7.09−7.14 (2 H, d, H-11,14); ^{13}C NMR δ ($CDCl_3$) 22.2 (C-4), 28.8 (C-2,5), 29.4 (C-5), 39.7 (C-1,6), 44.0 (C-7), 115.2, 114.8 (C-11,12), 127.1, 128.7 (C-9,13), 136.1, 142.5 (C-8,8′), 143.4, 143.5 (C-11,11′); IR (KBr pellet) 3447, 3360, 3032, 2940, 1614, 1514, 1464 cm^{-1}. Elemental Anal. Calcd for C_{19} $H_{24}N_2$: C, 81.3; H, 8.56; N,.9.98. Found: C, 81.14; H,8.82; N, 9.79.

1,1-Bis(4-aminophenyl)-3,3,5-trimethylcyclohexane (BATM) (3). As described above, compound **3** was prepared in a similar procedure to that of compound **1** with 3,3,5-trimethylcyclohexanone instead of cyclohexanone. A pure pale-yellow powder was obtained by recrystallization from isopropyl alcohol in 40% yield: mp 46 °C; MS *m*/*e* 308 (M^+); ^{1}H NMR δ ($CDCl_3$) 0.38 (3 H, s, H-4), 0.91, 1.07 (6 H, s, H-7,8), 0.85, 1.05 (2 H, dd, H-5,6), 1.33 and 1.85 (2 H, d, $J_{9,10}$=10.0 Hz,H-9,10),1.94 (1 H, m, H-3), 2.30 and 2.56 (2 H, dd, $J_{1,2}$ = 11−14, $J_{1,3}$ = $J_{2,3}$ = 2.0 Hz, H-1,2), 2.50−3.0 (4 H, br s, amine protons), 6.50−6.54 (2 H, d, H-12′, 13′), 6.60−6.61 (2 H, d, H-12,13), 6.94−6.99 (2 H,d, H-11′,14′), 7.06−7.10 (2 H, d, H-11,14); ^{13}C NMR δ ($CDCl_3$) 22.8 (C-5), 25.6 (C-2), 26.9 (C-3), 32.2 (C-6), 34.9 (C-7), 44.5 (C-9), 46.4 (C-1), 48.0 (C-4), 49.0 (C-8), 114.5 (C-14,14′), 114.9 (C-12,12′), 126.7 (C-15,15′) 128.3 (C-11,11′), 137.5 and 143.3 (C-10,10′), 143.4 and 143.8 (C-13,-13′); IR (KBr pellet) 3394, 2946, 1620, 1513, 1459, 1362, 1272, 1187, 1119 cm^{-1}. Elemental Anal. Calcd for C_{21} $H_{28}N_2$: C, 81.8; H, 9.08; N, 9.08. Found: C, 79.7; H, 9.09; N, 8.45.

Polymer Synthesis. Preparation of Polyimides by Synthetic Route a. To a solution of **3** (5 mmol, 1.54 g) in 17.9 mL of NMP, BTDA (5 mmol, 1.61 g) was added with a solid content of 15 wt %. The solution was continuously stirred at room temperature for 24 h. To the reaction mixture were added 1.5 mL of acetic anhydride and 2.0 mL of pyridine, and then the temperature was raised to 120 °C. After the reaction mixture was kept at 120 °C for 3 h, the resulting viscous solution was poured into excess methanol and filtered. The precipitated polymer was washed several times with water and methanol, and then the polymer was dried at 100 °C for 12 h in vacuo. The polymerization yield was almost quantitative. ^{1}H NMR δ ($CDCl_3$) 0.38 (3 H, s, H-4), 1.05 (6 H, s, H-7,8), 0.8−1.10 (2 H, m, H-5,6), 1.35 (1 H, m, H-10), 1.8−2.0 (2 H, m, H-3,9), 2.6−2.7 and 2.9−3.0 (2 H, m, H-1,2), 7.2−7.7 (8 H, m, phenyl ring protons of BATM moiety), 8.0−8.10 (4 H, s, H-16,-17), 8.2−8.3 (2 H, s, H-15); IR (KBr pellet) 3061, 2949, 1780 and 1726 (C═O), 1370 (C═O) cm^{-1}. Elemental Anal. Calcd for $C_{38}H_{30}N_2$: C, 76.77; H, 5.05; N, 4.71. Found: C, 75.24; H, 5.13; N, 4.67.

Preparation of Polyimides by One-Step Polymerization.[9] To a solution of BATM (5 mmol, 1.54 g) in 19 mL of freshly distilled *m*-cresol, BTDA (5 mmol, 1.61 g) and isoquinoline (0.95 mL) as a catalyst were added at room temperature under nitrogen atmosphere. The reaction mixture was heated to 70−80 °C over 2 h and kept at that temperature for 2 h, and then the solution temperature was slowly raised to 200 °C over 2 h and refluxed for 6−8 h. The polymerization was performed under a gentle nitrogen stream to remove the water produced during imidization. The work-up process was the same as for synthetic route a.

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