

Synthesis and Characterization of Novel Aromatic Polyimides from Aromatic Diamine and 3,3''',4,4'''-*p*-Sexiphenyltetracarboxylic Dianhydride

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ABSTRACT: A new rigid tetracarboxylic dianhydride, 3,3''', 4,4'''-*p*-sexiphenyltetracarboxylic dianhydride, was synthesized in seven steps starting from diethyl 4-bromophthalate. New aromatic polyimides containing a *p*-sexiphenyl unit were synthesized from this tetracarboxylic dianhydride and various aromatic diamines by the conventional two-step procedure of ring-opening polyaddition in a polar amide-type solvent and subsequent thermal cyclic dehydration. These polyimides had inherent viscosities of 1.20–1.69 dL g⁻¹, and were insoluble in organic solvents. The polyimides were characterized by differential scanning calorimetry (DSC), thermogravimetry (TG), wide-angle X-Ray diffraction measurements, and dynamic mechanical analysis (DMA). Typical polyimides were noncrystalline and showed excellent thermal stability, and had glass transition temperatures (*T*_g) at about 250°C. Decrease in the modulus at the glass transition temperature was less than corresponding polyimides having no *p*-sexiphenyl unit due to the presence of the rigid *p*-sexiphenyl unit.

KEY WORDS 3,3''', 4,4'''-*p*-Sexiphenyltetracarboxylic Dianhydride / Aromatic Polyimides / Glass Transition Temperature / Dynamic Mechanical Analysis /

Aromatic polyimides are characterized by high glass transition temperature (*T*_g) along with high decomposition temperature and good mechanical properties.¹ In recent years, interest has been focused on the synthesis of soluble polyimides by introduction bulky pendant phenyl group, and a number of organic soluble polyimides having high *T*_gs have been prepared.^{2–11}

However, it is also interesting to prepare very rigid polyimides which have no bulky pendant group and examine their properties. For such the rigid structure was expected to cause higher chain packing and increase transition temperature of these polymers. Recently, we synthesized very rigid polyimides from 3,3''', 4,4'''-*p*-quarterphenyltetracarboxylic dianhydride and various aromatic diamines.¹² The polyimides were crystallized at about 300°C, which had been hardly observed as almost wholly aromatic polyimides, and had high thermal stability. Therefore, it is of interest to prepare more rigid polyimides and examine the properties of these polymers. We conducted the synthesis of a new rigid tetracarboxylic dianhydride, 3,3''', 4,4'''-*p*-sexiphenyltetracarboxylic dianhydride, which has two more phenylene unit than 3,3''', 4,4'''-*p*-quarterphenyltetracarboxylic dianhydride and has not been prepared, and aromatic polyimides were derived from it. This article is the first to report the synthesis and characterization of novel aromatic polyimides from tetracarboxylic dianhydride and aromatic diamines. The properties of polyimide, especially thermal behavior, are discussed.

EXPERIMENTAL

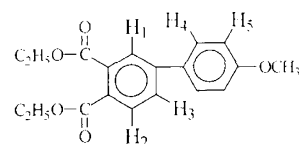
Materials

4,4'-Diaminodiphenyl ether (**XIa**), 4,4'-diaminodiphenyl methane (**XIb**), *m*-phenylenediamine (**XIc**), and *p*-phenylenediamine (**XId**) were obtained commercially

and purified by distillation under reduced pressure. 4,4'-bis(4-aminophenoxy)biphenyl (**XIe**) and 2,2-bis(4-(4-aminophenoxy)phenyl)propane (**XIf**) were obtained commercially and used without purification. *N*-methyl-2-pyrrolidone (NMP) was purified by vacuum distillation over calcium hydride. Diethyl 4-bromophthalate (**I**),¹² (4-methoxyphenyl)boronic acid (**II**),¹³ and bis(trimethylene)-4,4'-biphenylenediboronate (**VII**)¹⁴ were prepared as previously reported.

Monomer Synthesis

Diethyl 4-(4-methoxyphenyl)Phthalate (III). 22.58 g (75 mmol) of **I**, 15.20 g (0.10 mol) of **II**, 13.80 g (0.1 mmol) of potassium carbonate, and 150 mL of deoxygenated toluene were added to a flask equipped with a reflux condenser. The system was flushed with nitrogen, and 0.8 g of tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) was added to the reaction mixture. After the mixture was stirred at 90°C for 8 h, salts were removed by filtration, and solvent was evaporated. The residue was distilled under reduced pressure (glass tube oven) to give pure **III**. Yield: 18.90 g (77%). Bp: 235–240°C (1 torr). Mp: 45.0–46.0°C. The IR spectrum (NaCl) exhibited absorption bands at 2990 cm⁻¹ (C–H), and 1720 cm⁻¹ (C=O).



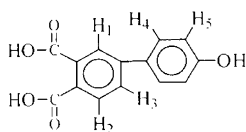
¹H Nuclear magnetic resonance (NMR) spectrum [δ in CDCl₃] showed signals at 1.35 (t, 3H, *J* = 7.0 Hz, -CH₂-CH₃), 1.37 (t, 3H, *J* = 7.0 Hz, -CH₂CH₃), 3.86 (s, 3H, OCH₃), 4.36 (q, 2H, *J* = 7.0 Hz, -CH₂CH₃), 4.38 (q, 2H, *J* = 7.0 Hz, -CH₂CH₃), 6.99 (d, 2H, *J* = 8.8 Hz, H5), 7.56 (d, 2H, *J* = 8.8 Hz, H4), 7.67–7.70 (dd, 1H, *J* = 8.1 Hz, *J* =

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2.2 Hz, $J=8.1$ Hz, H3), 7.82 (d, 1H, $J=8.1$ Hz, H2) and 7.83 (d, 1H, $J=2.2$ Hz, H1). ^{13}C NMR spectrum [δ in CDCl_3] exhibited peaks at 14.14, 55.43, 61.55, 61.78, 115.93, 126.78, 128.59, 128.65, 129.43, 129.99, 131.68, 133.80, 145.80, 160.12, 167.25, and 168.23 ppm.

Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_5$: C, 69.50%; H, 6.14%. Found: C, 69.38%; H, 5.99%.

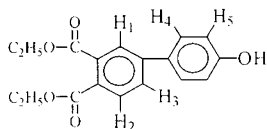
4-(4-Hydroxyphenyl)phthalic Acid (IV). 18.06 g (55 mmol) of **III** was heated together with 70 g of pyridine hydrochloride at reflux temperature for 30 min. After the reaction mixture became homogeneous, it was poured into water (1000 mL). The precipitated solid was collected by filtration, washed thoroughly with water, and dried under vacuum. The crude product was used in next reaction without further purification. Yield: 13.63 g (96%). The IR spectrum (KBr) exhibited absorption bands at 3400–3000 cm^{-1} (OH), and 1700 cm^{-1} (C=O).



^1H NMR spectrum [δ in dimethyl sulfoxide ($\text{DMSO}-d_6$)] showed signals at 6.88 (d, 2H, $J=8.8$ Hz, H5), 7.57 (d, 2H, $J=8.8$ Hz, H4) and 7.72–7.79 (m, 3H, H1, H2, and H3). ^{13}C NMR spectrum [δ in $\text{DMSO}-d_6$] exhibited peaks at 115.11, 126.23, 128.10, 128.74, 129.81, 130.09, 131.55, 133.71, 144.80, 157.61, 167.30, and 167.41 ppm.

Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_5$: C, 65.12%; H, 3.90%. Found: C, 64.98%; H, 3.85%.

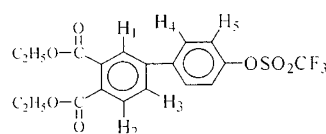
Diethyl 4-(4-hydroxyphenyl)phthalate (V). 12.91 g (50 mmol) of **IV**, 200 mL of absolute ethanol, and 0.3 mL of sulfuric acid were added to a flask, and heated at reflux for about 60 h. After the mixture was washed twice with 100 mL 10 wt% sodium carbonate solution, the organic layer was collected, and the aqueous layer was extracted twice with 50 mL dichloromethane. The combined extract was dried over anhydrous magnesium sulfate. After the evaporation of the solvent, the residue was purified by silica gel column chromatography eluted by dichloromethane. Yield: 12.89 g (82%). Mp: 84.0–85.0°C. The IR spectrum (KBr) exhibited absorption bands at 3400–3000 cm^{-1} (OH), 2980 cm^{-1} (C-H), and 1730 cm^{-1} (C=O).



^1H NMR spectrum [δ in CDCl_3] showed signals 1.39 (t, 3H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 1.40 (t, 3H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 4.38 (q, 2H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 4.40 (q, 2H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 6.93 (d, 2H, $J=8.8$ Hz, H5), 7.49 (d, 2H, $J=8.8$ Hz, H4), 7.66–7.69 (dd, 1H, $J=2.2$ Hz, 8.1 Hz, H3), 7.81 (d, 1H, $J=8.1$ Hz, H2), and 7.83 (d, 1H, 2.2 Hz, H1). ^{13}C NMR spectrum [δ in CDCl_3] exhibited peaks at 14.14, 61.58, 61.77, 115.94, 126.71, 128.51, 128.58, 129.37, 129.75, 131.68, 133.50, 143.84, 156.15, 167.25, and 168.23 ppm.

Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_5$: C, 68.78%; H, 5.77%. Found: C, 68.51%; H, 5.71%.

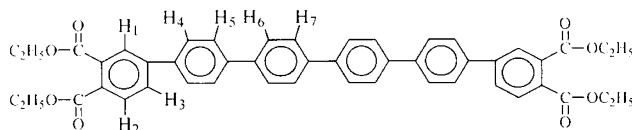
3',4'-Di(ethoxycarbonyl)biphenyl Triflate (VI). A solution of 14.11 g (50 mmol) of trifluoromethanesulfonyl anhydride in 70 mL of dichloromethane was added dropwise to a solution of 12.57 g (40 mmol) of **V** and 10 mL of pyridine in 150 mL of dichloromethane at 0°C. After stirring at 20°C for 2 h, the mixture was poured into ice-water. The organic layer was collected and the aqueous layer was extracted twice with 50 mL of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by silica gel chromatography eluted by dichloromethane. Yield: 16.25 g (91%). Mp: 80.0–81.0°C. The IR spectrum (KBr) exhibited absorption bands at 2990 cm^{-1} (C-H), 1730 cm^{-1} (C=O), 1420 (S=O), and 1215 (C-F).



^1H NMR spectrum [δ in CDCl_3] showed signals 1.39 (t, 3H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 1.40 (t, 3H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 4.38 (q, 2H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 4.40 (q, 2H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 7.39 (d, 2H, $J=8.8$ Hz, H5), 7.68 (d, 2H, $J=8.8$ Hz, H4), 7.69–7.72 (dd, 1H, $J=2.2$ Hz, 8.1 Hz, H3), 7.85 (d, 1H, $J=8.1$ Hz, H2), and 7.87 (d, 1H, $J=2.2$ Hz, H1). ^{13}C NMR spectrum [δ in CDCl_3] exhibited peaks at 14.09, 61.74, 61.87, 118.7 (q, $J=320$ Hz), 121.97, 127.49, 129.10, 129.27, 129.83, 131.25, 133.43, 139.60, 142.08, 149.58, 167.02, and 167.48 ppm.

Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{O}_7\text{F}_3\text{S}$: C, 51.12%; H, 3.84%. Found: C, 50.96%; H, 3.67%.

Tetraethyl 3,3',4,4'-*p*-Sexiphenyltetracarboxylate (VIII). 5.15 g (16 mmol) of **VII**, 15.62 g (35 mmol) of **VI**, 4.83 (35 mmol) of potassium carbonate, and 100 mL of deoxygenated *N,N*-dimethylformamide were added to a flask equipped with a reflux condenser. The flask was flushed with nitrogen, and 1.0 g tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$) were added to the reaction mixture. The mixture was stirred at 90°C for 8 h, and cooled to room temperature. The precipitated product was collected by filtration, washed with water to remove salts, dried under vacuum, and twice recrystallized from NMP to give pure **VIII**. Mp 331–332°C. Yield: 8.48 g (71%). The IR spectrum (KBr) exhibited absorption bands at 2980 cm^{-1} (C-H), and 1725 cm^{-1} (C=O).

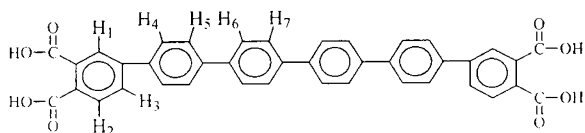


^1H NMR spectrum [δ in CDCl_3] showed signals 1.39 (t, 6H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 1.40 (t, 6H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 4.38 (q, 4H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 4.40 (q, 4H, $J=7.0$ Hz, $-\text{CH}_2\text{CH}_3$), 7.73 (d, 4H, $J=8.8$ Hz, H5), 7.76–7.78 (m, 8H, H6 and H7), 7.78 (d, 4H, $J=8.8$ Hz, H4), 7.77–7.82 (dd, 2H, $J=2.2$ Hz, 8.1 Hz, H3), 7.87 (d, 2H, J

= 8.1 Hz, H2), and 7.96 (d, 2H, $J=2.2$ Hz, H1). ^{13}C NMR spectrum [δ in CDCl_3] exhibited peaks at 14.17, 61.65, 61.81, 127.22, 127.51, 127.53, 127.62, 127.71, 129.10, 129.80, 130.30, 133.51, 138.10, 139.39, 139.87, 140.74, 143.66, 167.21, and 167.97 ppm.

Anal. Calcd for $\text{C}_{48}\text{H}_{42}\text{O}_8$: C, 77.19%; H, 5.67%. Found: C, 77.00%; H, 5.62%.

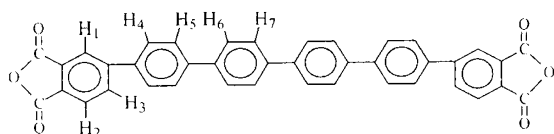
3,3''''', 4,4'''''-p-Sexiphenyltetracarboxylic Acid (IX). In a flask, 2.24 g (3 mmol) of VIII were dissolved in 800 mL of 2-(2-methoxyethoxy)ethanol at 190°C. A solution of 0.96 g (24 mmol) of sodium hydroxide in 10 mL of water was added, and the mixture was heated at this temperature for two hours to give a white precipitate. The reaction mixture was concentrated under reduced pressure, and a solution of 0.96 g (24 mmol) of sodium hydroxide in 2000 mL of water was added. The system was then heated at reflux for 2 h. After being cooled to room temperature, the solution was acidified by 6 M hydrochloric acid. The precipitated IX was collected and dried *in vacuo*. This compound was used without purification for the subsequent reaction. The yield: 1.68 g (88%). The IR spectrum (KBr) exhibited absorption bands at 3400–3000 cm^{-1} (OH), and 1705 cm^{-1} (C=O).



^1H NMR spectrum [δ in $\text{DMSO}-d_6$ at 120°C] showed signals 7.82 (d, 2H, $J=8.1$ Hz, H2), 7.85 (d, 4H, $J=8.8$ Hz, H5), 7.86–7.88 (m, 8H, H6, and H7), 7.89 (d, 4H, $J=8.8$ Hz, H4), 7.91–7.95 (dd, 2H, $J=2.2$ Hz, 8.1 Hz, H3) and 7.97 (d, 2H, $J=2.2$ Hz, H1). ^{13}C NMR spectrum [δ in $\text{DMSO}-d_6$ at 120°C] exhibited peaks at 125.69, 126.59, 126.62, 126.67, 126.91, 127.78, 130.37, 130.89, 133.75, 137.06, 138.13, 139.18, 141.53, 146.72, 167.35, and 167.76 ppm.

Anal. Calcd for $\text{C}_{40}\text{H}_{26}\text{O}_8$: C, 75.70%; H, 4.13%. Found: C, 75.50%; H, 3.96%.

3,3''''', 4,4'''''-p-Sexiphenyltetracarboxylic Dianhydride (X). 2.22 g (3.5 mmol) of IX were heated together with 350 mL of diphenyl ether at reflux temperature for about one hour. The reaction mixture became homogeneous, and was cooled to give yellow crystalline. Pure X was obtained by recrystallization from diphenyl ether. Mp 290–291°C. The yield: 1.89 g (90%). Mp: 336.0–337.0°C. The IR spectrum (KBr) exhibited absorption bands at 1850 cm^{-1} and 1780 cm^{-1} (C=O).



^1H NMR spectrum [δ in $\text{DMSO}-d_6$ at 120°C] showed signals at 7.93 (d, 4H, $J=8.8$ Hz, H5), 7.95–7.98 (m, 8H, H6, and H7), 8.00 (d, 4H, $J=8.8$ Hz, H4), 8.15 (2H, d, $J=8.1$ Hz, H2), 8.34–8.37 (dd, 2H, $J=2.2$ Hz, 8.1 Hz, H3), and 8.38 (d, 2H, $J=2.2$ Hz, H1). ^{13}C NMR spectrum [δ in $\text{DMSO}-d_6$ at 120°C] exhibited peaks at 122.75, 125.74,

126.58, 126.95, 127.27, 127.92, 129.48, 132.12, 134.02, 136.69, 138.15, 139.70, 141.58, 147.13, 162.67, and 162.81 ppm.

Anal. Calcd for $\text{C}_{40}\text{H}_{22}\text{O}_6$: C, 80.26%; H, 3.70%. Found: C, 80.11%; H, 3.66%.

Polymerization

Polyimide XIIIa from X and XIa. In a three necked flask, 0.75 g (1.25 mmol) of solid X were added to a solution of 0.25 g (1.25 mmol) of diamine XIa in 30 mL of NMP in one portion. The mixture was stirred at 30°C for 24 h under nitrogen. A part of the resulting viscous solution was diluted with NMP. Inherent viscosity of the polyamic acid (XIIa) in NMP was 1.69 dL g^{-1} , measured at a concentration of 0.5 g dL^{-1} at 30°C. Remaining NMP solution was cast onto a glass plate and the solvent was removed at 80°C. Thermal cyclodehydration of the polyamic acid was performed by heating at 100°C for 1 h, 200°C for 1 h and finally 300°C for 1 h under vacuum. The IR spectrum (film) exhibited absorption band at 1780 and 1720 cm^{-1} (C=O) and 1360 cm^{-1} (C-N).

Anal. Calcd for $(\text{C}_{52}\text{H}_{30}\text{N}_2\text{O}_5)_n$: C, 81.88%; H, 3.96%; N, 3.67%. Found: C, 81.66%; H, 3.82%; N, 3.52%.

Other polymers were synthesized by similar procedure.

Measurement

^1H and ^{13}C NMR spectra and IR spectra were recorded on a JNM-GSX-400 FT-NMR spectrometer and SHIMADZU Spectro Photometer IR 435, respectively. X-Ray diffraction was performed with a Rigaku RAD-B System. For differential scanning calorimetry (DSC) and thermogravimetry (TG) a Shimadzu DSC-60 and Rigaku Thermal Analysis Station TG 8110 were used, respectively, and measurement was made at a heating rate of 10°C min^{-1} in air or nitrogen. Dynamic mechanical analysis (DMA) was performed with the Advanced Rheometric Expansion System at 1.0 Hz at 5°C min^{-1} . Polyimide films were annealed at 400°C for 10 min in a vacuum oven.

RESULTS AND DISCUSSION

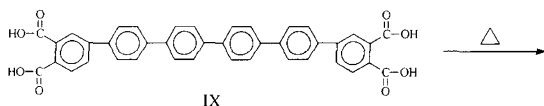
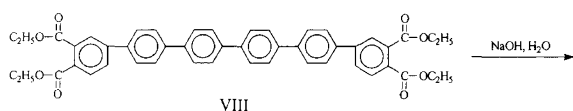
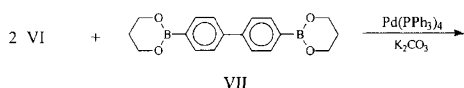
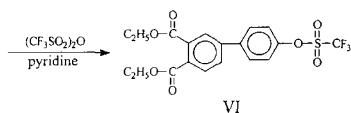
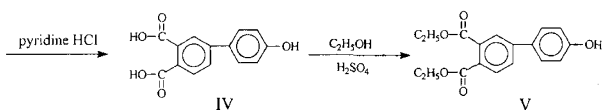
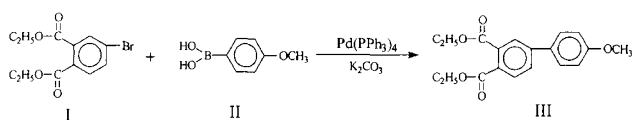
Monomer Synthesis

p-Sexiphenyltetracarboxylic dianhydride was synthesized by reactions involving the extension of phenylene unit using *p*-methoxyphenyl boronic acid, as previously reported (eq 1).¹⁵ Cross-coupling^{16,17} of I with (*p*-methoxyphenyl)boronic acid, II, using tetrakis(triphenylphosphine)paladium ($\text{Pd}(\text{PPh}_3)_4$) as catalyst, yielded diethyl 4-(4-methoxyphenyl)phthalate, III. III was treated with pyridine hydrochloride to give 4-(4-hydroxyphenyl)phthalic acid, IV and converted to diethylester V. After V was converted to the triflate VI, which was reactive, using trifluoromethanesulfonic anhydride, cross-coupling of VI with VII gave tetraethyl *p*-sexiphenyltetracarboxylate VIII. Hydrolysis of VIII afforded tetracarboxylic acid IX, and IX was converted to tetracarboxylic dianhydride, X, by heating in diphenyl ether.

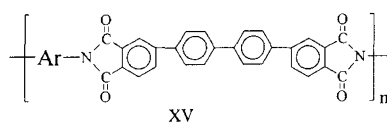
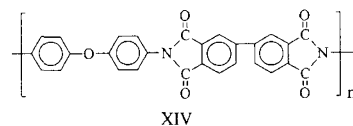
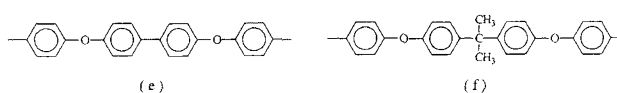
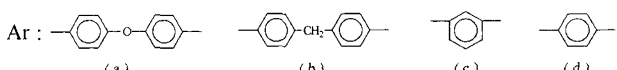
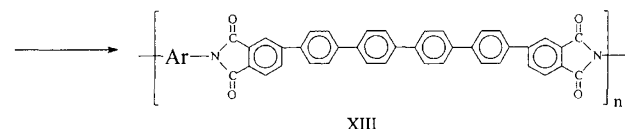
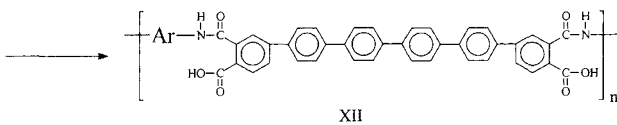
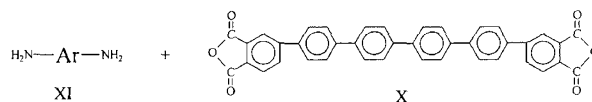
Chemical structures were confirmed by IR and NMR spectra and elemental analysis.

Compound X showed IR absorption at 1850 and 1780 cm^{-1} characteristic of carboxylic anhydride. The ^{13}C

Polyimides from *p*-Sexiphenyltetracarboxylic Dianhydride



(1)



(2)

Table I. Synthesis of polyamic acids

Diamine	Polyamic acid ^a	Yield/%	$\eta_{\text{inh}}^{\text{b}}$ /dL g ⁻¹
XIa	XIIa	97	1.69
XIb	XIIb	98	1.62
XIc	XIIc	97	1.20
XId	XIId	95	— ^c
XIe	XIIe	94	1.54
XIf	XIIIf	97	1.49

^a Polymerization was carried out with 1.25 mmol each monomer in 30 mL NMP at 30°C for 24 h under nitrogen. ^b Measured at 0.5 g dL⁻¹ in DMAc at 30°C. ^c Insoluble in organic solvents.

NMR spectrum of **X** exhibited 16 peaks due to symmetry, indicating the formation of postulated tetracarboxylic dianhydride. Elemental analysis of all compounds was in good agreement with calculated results for proposed structures.

Polymer Synthesis

Aromatic polyimides **XIIIa–XIIIf** were synthesized by the ring-opening polyaddition of aromatic diamine **XIa–XIIf** to **X** and thermal cyclodehydration as shown in eq 2.

In the first step, ring-opening polyadditions was carried out in NMP at 30°C, leading to the formation of polyamic acids. The solubility of **X** in NMP was very low and thus the polymerization was carried out at a low concentration (3.1 wt%) and the reaction mixture was stirred for 24 h. The reaction mixture was homogeneous except for polymerization with *p*-phenylene diamine, **XId**. All polyamic acids, which were once reprecipitated, were insoluble in organic solvent and even in NMP. We determined inherent viscosity from diluted reaction solution. The polyamic acids had rather high inherent viscosities of 1.20–1.69 dL g⁻¹ (Table I). Polyamic acid **XIId**, from **XId**, was precipitated during polymerization due to low solubility, as that inherent viscosity of **XIId** could not be measured.

In the second step, thermal conversion of the polyamic acids to polyimides was performed by heating precursor

polymers in the form of film at 100°C for 1 h, 200°C for 1 h and 300°C for 1 h under vacuum. The polyimides except **XIIIId** gave tough films in spite of rigid backbones. Polyimide **XIIIId** was not obtained as film due to low solubility of polyamic acid, **XIId**.

The formation of polyimides was confirmed by absorption bands at around 1780 cm⁻¹ and 1720 cm⁻¹ (C=O) and at 1360 cm⁻¹ (C–N) characteristic of the imide group in IR spectra. Elemental analysis values data in close agreement with those calculated, thus supporting polyimide formation.

Polymer Properties

Crystallinity of as-made polymers was estimated by X-Ray diffraction. All polymers were amorphous despite rigid structures, while **XIIIId** was crystalline.

Thermal behavior of the polyimides was evaluated by

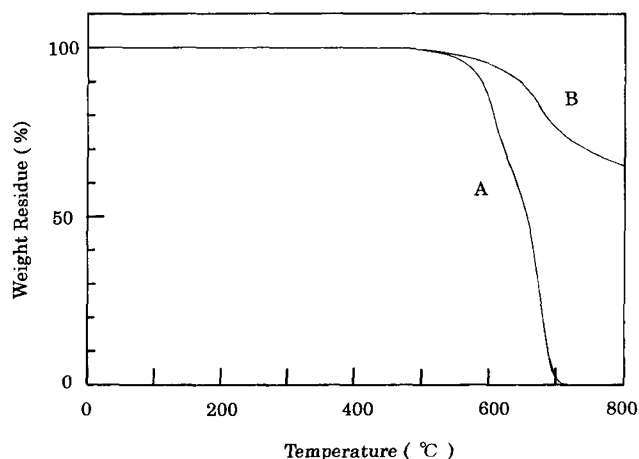


Figure 1. TG curves for polyimide XIIIa at heating rate of $10^{\circ}\text{C min}^{-1}$ in (A) air and (B) nitrogen.

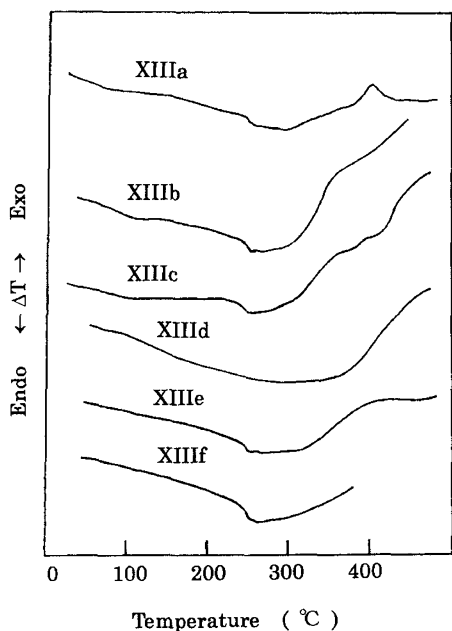


Figure 2. DSC curves for polyimides XIII (first heating) at heating rate of $10^{\circ}\text{C min}^{-1}$ in nitrogen.

TG and DSC. Figures 1 and 2 show TG curves of Polyimide, XIIIa, and DSC curves of all polyimides (first heating), and transition temperatures and 10% weight loss temperatures (T_{10}) are summarized in Table II. No polyimides (XIIIa, XIIIc, XIIId, and XIIIe) without aliphatic groups lost weight below 490°C in air or nitrogen, and T_{10} in air and nitrogen was from 580 – 595°C and 600 – 645°C respectively. More than 65% weight was retained even at 800°C in nitrogen for the polyimides. These results indicated high thermal stability of the present polyimides. On the basis of T_{10} , the polyimides have thermal stability as much as polyimide from *p*-phenylene diamine and 3,3',4,4'-biphenyltetracarboxylic dianhydride, the most thermally stable polymer in the aromatic polyimides.¹⁸ The thermal stability of the polymers having aliphatic groups was reduced.

DSC curves of polyimides XIIIa, XIIIb, XIIIc, and VI-IIe showed glass transition temperatures (T_g) around

Table II. Thermal behavior of aromatic polyimides

Polyimide	$T_g/^{\circ}\text{C}^a$	$T_f/^{\circ}\text{C}^a$	$T_m/^{\circ}\text{C}^a$	$T_{10}/^{\circ}\text{C}^b$	$T_{10}/^{\circ}\text{C}^c$
XIIIa	244	377–421	>470	585	640
XIIIb	244	330–385	>470	580	637
XIIIc	237	335–380	385–425	590	600
XIII d				595	645
XIIIe	232	325–455	>470	580	635
XIII f	236			540	608

^a Determined by DSC in nitrogen at a heating rate of $10^{\circ}\text{C min}^{-1}$. ^b Temperature at which 10% weight loss was recorded by TG at heating rate of $10^{\circ}\text{C min}^{-1}$ in air. ^c Temperature at which 10% weight loss was recorded by TG at heating rate of $10^{\circ}\text{C min}^{-1}$ in nitrogen.

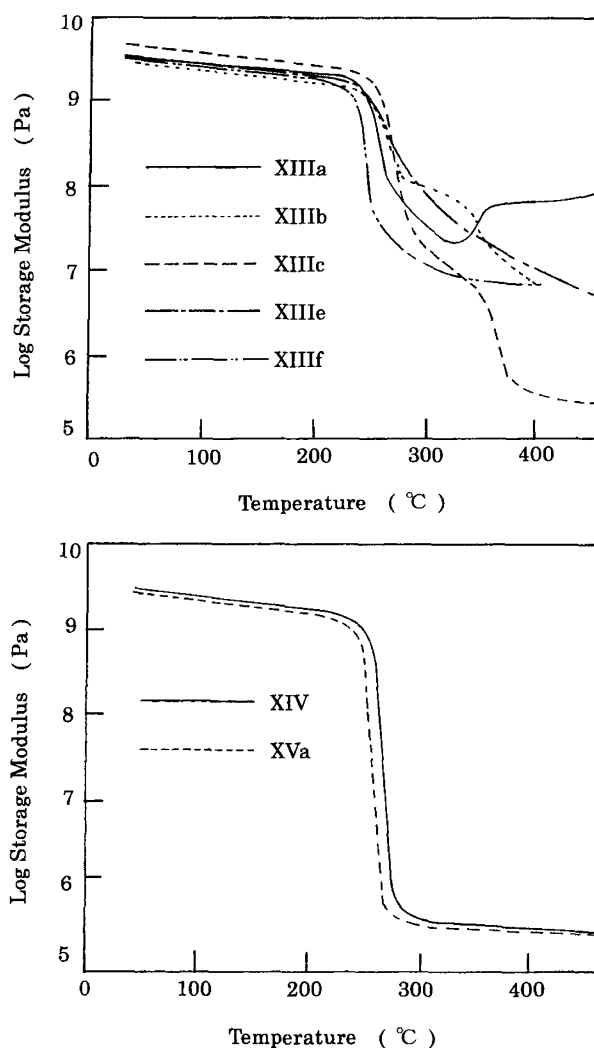


Figure 3. Storage modulus of polyimides XIII, XIV, and XVa.

237 – 244°C followed by broad exothermic peaks around 320 – 420°C above their T_g s, and only polyimide XIIIc exhibited broad endothermic peaks (390 – 420°C) prior to decomposition. T_g was almost comparable to that of the previously reported polyimides, XV, prepared from 3,3',4,4'-*p*-quarterphenyltetracarboxylic dianhydride,¹² but crystallization temperatures (T_c s) were higher than those of XV. Polyimide XIIIf having the most flexible connecting groups exhibited only T_g at 236°C , and polyimide XIIId with the most rigid symmetric structure did not undergo obvious transition due to crystallinity.

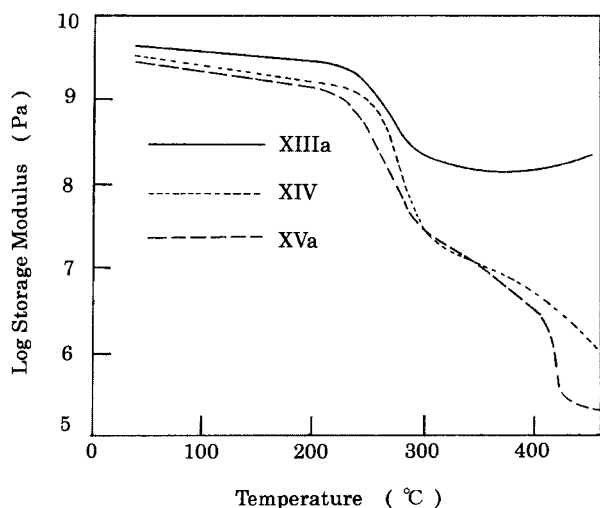


Figure 4. Storage modulus of annealed polyimides **XIII**, **XIV**, and **XVa**.

Figure 3 shows the temperature dependence of the dynamic storage modulus for polyimides **XIII**, **XIV**, and **XV**.¹² **XIV** was prepared from **IXa** and biphenyltetracarboxylic dianhydride. We could not determine the storage modulus of **XIIIc** because this polyimide was not obtained as film. A high modulus glassy region was followed by sudden decrease of modulus in the glass transition region. The modulus decreased rapidly around 250°C to a very low level for **XIV** and **XV**, which did not have a rigid *p*-sexiphenyl structure, without showing a plateau region. The present polyimides **XIII** showed a plateau region with modulus above 10 MPa around 300°C. The modulus of **XIIIa** increased at about 360°C and constant above this temperature, thus possibly corresponding to the exothermic peak around 390°C observed in DSC. In contrast to **XIIIa**, the modulus of **XIIIc** decreased rapidly above 360°C, corresponding to a broad endothermic peak around 400°C.

Polyimides **XIII** may thus form an ordered *paracrystalline* structure above glass transition possibly due to strong intermolecular interaction between rigid *p*-sexiphenyl backbones of the polymers, although we could not detect X-Ray diffraction patterns. The ordered structure develops above 300°C to form temporary networks and prevents further drop in the storage modulus. In **XIIIa**, the ordered structure develops with increasing temperature, while in **XIIIc** the structure disappears with drop in modulus at high temperature.

To confirm the effects of structure ordering, we annealed polyimide **XIIIa** at 400°C for 10 min. Temperature dependence of the storage modulus of annealed **XIIIa** is shown in Figure 4. The modulus of **XIV** and **XVa**

is shown in the figure for comparison. The modulus above glass transition for **XIIIa** further increased to as high as 300 MPa even at 450°C. This was due to the development of structure ordering by annealing, although we could not detect crystalline order by X-Ray diffraction. This is in contrast to the behavior observed in **XVa**,¹² where annealed **XVa** showed an ordered crystalline pattern. The longer *p*-sexiphenyl unit may cause less movement of polymer backbone and thus less order in chains.

All polyimides were insoluble in organic solvents and sulfuric acid even on heating.

CONCLUSION

The authors synthesized a new rigid tetracarboxylic dianhydride, 3,3',4,4'-*p*-sexiphenyltetracarboxylic dianhydride, which was used for polycondensation with aromatic diamines to obtain aromatic polyimides. The present polyimides were insoluble in organic solvents, but decrease in modulus at the glass transition was less than for polyimides, without the *p*-sexiphenyl structure, and effects of *p*-sexiphenyl structure was conspicuous in DMA spectra above glass transition.

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