

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

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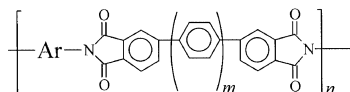
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ABSTRACT: A new rigid tetracarboxylic dianhydride, 3,3''',4,4'''-*p*-quinquephenyltetracarboxylic dianhydride, was synthesized in seven steps starting from diethyl 4-bromophthalate. New aromatic polyimides containing a *p*-quinquephenyl unit were synthesized 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 0.20–1.20 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 had glass transition temperatures (*T*_g) at about 250°C, and crystallized above *T*_gs. The effects of *p*-quinquephenyl structure were reflected in the high storage modulus above the glass transition temperature.

KEY WORDS 3,3''',4,4'''-*p*-Quinquephenyltetracarboxylic Dianhydride / Aromatic Polyimides / Glass Transition Temperature / Dynamic Storage Modulus /

Aromatic polyimides are characterized by high glass transition temperature (*T*_g) along with high decomposition temperature and good mechanical properties,^{1,2} and are used in various fields including aerospace and electronics industries. The properties of the polyimides originate from unique aromatic heteroaromatic rings. Because of the rigidity of the ring, polyimides do not dissolve into organic solvents and melt without degradation. However, polyimides having rather rigid chemical structure between aromatic polyimide units exhibit high modulus and strength,^{3,4} and may be used to introduce highly rigid structure into polyimides and examine the properties of the polymers.

Recently, we reported aromatic polyimides **PI-Ar-*m*** containing *p*-quarterphenyl (*m* = 2)⁵ and *p*-sexiphenyl (*m* = 4)⁶ unit, which were very rigid, and compared the properties of these polyimides with those of polyimides from 3,3'',4,4''-*p*-terphenyltetracarboxylic dianhydride (*m* = 1) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (*m* = 0), which have been previously prepared.⁷



*T*_gs were independent on the number of phenylene units (*m*) of the dianhydrides, while moduli were higher and decrement of moduli at the glass transition decreased with increasing *m*.

We conducted the synthesis of a new rigid tetracarboxylic dianhydride, 3,3''',4,4'''-*p*-quinquephenyltetracarboxylic dianhydride, and aromatic polyimides

(*m* = 3) 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

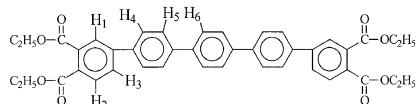
Materials

4,4'-Diaminodiphenyl ether (**VIa**), 3,4'-diaminodiphenyl ether (**VIb**), 4,4'-diaminodiphenyl methane (**VIc**), *m*-phenylenediamine (**VIId**), and *p*-phenylenediamine (**VIe**) were obtained commercially and purified by distillation under reduced pressure. 4,4'-bis(4-aminophenoxy)biphenyl (**VIIf**) were obtained commercially and used without purification. *N*-Methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF) was purified by vacuum distillation over calcium hydride. 3',4'-Di(ethoxycarbonyl)biphenyl triflate (**I**) were prepared as previously reported. 1,4-Phenylene diboronic acid (**II**) was obtained from Tokyo Kasei Kogyo Co., Japan and used without purification. Tetrakis(triphenylphosphine)paladium (Pd(PPh₃)₄) was obtained from Kanto Kagaku Co., Japan.

Monomer Synthesis

Tetraethyl 3,3''',4,4'''-p-Quinquephenyltetracarboxylate (III). To a flask equipped with a reflux condenser, 11.82 g (26.6 mmol) of **I**, 2.0 g (12.1 mmol) of **II**, 3.837 g (27.8 mmol) of potassium carbonate, and 60 mL deoxygenated DMF were added.

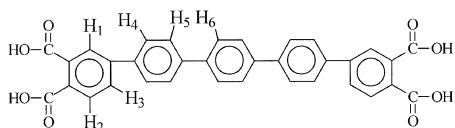
The flask was flushed with nitrogen, and 1.3 g tetrakis(triphenylphosphine)paladium (Pd(PPh₃)₄) were added to the reaction mixture. After the mixture was stirred at 90°C for 8 h, precipitated salts were removed by filtration, and the solvent was removed by distillation under reduced pressure. The residue was washed with methanol, and recrystallized from DMF to give pure **III**. Mp 273–275°C. Yield: 5.1 g (63%). The IR spectrum (KBr) exhibited absorption bands at 2980 cm⁻¹ (C–H), and 1725 cm⁻¹ (C=O).



The ¹H NMR spectrum [δ in CDCl₃] showed signals at 1.39 (t, 6H, *J* = 7.0 Hz, –CH₂CH₃), 1.40 (t, 6H, *J* = 7.0 Hz, –CH₂CH₃), 4.38 (q, 4H, *J* = 7.0 Hz, –CH₂CH₃), 4.40 (q, 4H, *J* = 7.0 Hz, –CH₂CH₃), 7.73 (d, 4H, *J* = 8.8 Hz, H5), 7.76 (s, 4H, H6), 7.77 (d, 4H, *J* = 8.8 Hz, H4), 7.78–7.82 (dd, 2H, *J* = 2.2 Hz, 8.1 Hz, H3), 7.87 (d, 2H, *J* = 8.1 Hz, H2), and 7.97 (d, 2H, *J* = 2.2 Hz, H1). ¹³C NMR spectrum [δ in CDCl₃] exhibited peaks at 14.18, 14.26, 61.67, 61.81, 127.06, 127.19, 127.49, 127.59, 128.92, 129.71, 130.20, 133.40, 138.05, 139.49, 140.55, 143.53, 167.08, and 167.84 ppm.

Anal. Calcd for C₄₂H₃₈O₈: C, 75.21%; H, 5.71%. Found: C, 74.99%; H, 5.52%.

3,3''',4,4''''-p-Quinquephenyltetracarboxylic Acid (IV). In a flask, 2.66 g (3.966 mmol) **III** were dissolved in 200 mL 2-(2-methoxyethoxy)ethanol at 140°C. A solution of 1.78 g (31.72 mmol) potassium hydroxide in 10 mL water was added, and the mixture was heated at this temperature for 2 h to give a white precipitate. The reaction mixture was concentrated under reduced pressure, and 350 mL water were added. The system was then heated at reflux for 4 h. After being cooled to room temperature, the solution was acidified by 6 M hydrochloric acid. The precipitated **IV** was collected and dried *in vacuo*. This compound was used without purification for subsequent reactions. Yield: 2.0 g (92%). The IR spectrum (KBr) exhibited absorption bands at 3400–3000 cm⁻¹ (OH), and 1705 cm⁻¹ (C=O).

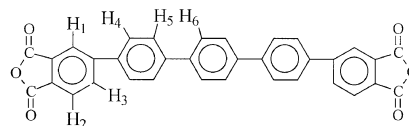


The ¹H NMR spectrum [δ in DMSO-*d*₆ at 120°C] showed signals at 7.82 (d, 2H, *J* = 8.1 Hz, H2), 7.86 (d, 4H, *J* = 8.8 Hz, H5), 7.87 (s, 4H, H6), 7.89 (d, 4H, *J* =

8.8 Hz, H4), 7.92–7.96 (dd, 2H, *J* = 2.2 Hz, 8.1 Hz, H3) and 7.98 (d, 2H, *J* = 2.2 Hz, H1). ¹³C NMR spectrum [δ in DMSO-*d*₆ at 120°C] exhibited peaks at 125.53, 126.44, 126.50, 126.74, 127.59, 128.70, 130.37, 130.78, 133.60, 137.98, 138.29, 139.02, 141.34, 167.15, and 167.54 ppm.

Anal. Calcd for C₃₄H₂₂O₈: C, 73.11%; H, 3.97%. Found: C, 72.95%; H, 3.91%.

3,3''',4,4''''-p-Quinquephenyltetracarboxylic Dianhydride (V). 1.000 g (1.790 mmol) of **IV** were heated together with 150 mL diphenyl ether at reflux temperature for about 2 h. The reaction mixture became homogeneous, and was cooled to give yellow crystal. Pure **V** was obtained by recrystallization from diphenyl ether. Mp: 322–324°C. Yield: 0.78 g (84%). The IR spectrum (KBr) exhibited absorption bands at 1850 cm⁻¹ and 1780 cm⁻¹ (C=O).



¹H NMR spectrum [δ in DMSO-*d*₆ at 120°C] showed signals at 7.88 (s, 4H, H6), 7.92 (d, 4H, *J* = 8.8 Hz, H5), 8.00 (d, 4H, *J* = 8.8 Hz, H4), 8.15 (d, 2H, *J* = 8.1 Hz, H2), 8.34–8.37 (dd, 2H, *J* = 2.2 Hz, 8.1 Hz, H3) and 8.41 (d, 2H, *J* = 2.2 Hz, H1). ¹³C NMR spectrum [δ in DMSO-*d*₆ at 120°C] exhibited peaks at 125.87, 127.09, 127.17, 128.02, 129.62, 130.88, 132.32, 134.20, 139.26, 140.12, 147.11, 168.03, and 168.61 ppm.

Anal. Calcd for C₃₄H₁₈O₆: C, 78.16%; H, 3.47%. Found: C, 78.05%; H, 3.41%.

Polymerization

Polyimide **VIIIa** from **V** and **VIa**. In a three necked flask, 0.52 g (1.0 mmol) solid **V** was added to a solution of 0.20 g (1.0 mmol) of diamine **VIa** in 10 mL of NMP in one portion. The mixture was stirred at room temperature for 5 h under nitrogen. A part of the resulting viscous solution was poured into 200 mL methanol. The precipitated polymer was filtered, washed with methanol and dried under vacuum. The inherent viscosity of the polyamic acid **VIIa** in *N,N*-dimethylacetamide (DMAc) was 1.19 dL g⁻¹ at 30°C. The 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 successive 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 $(C_{46}H_{26}N_2O_5)_n$: C, 80.46%; H, 3.82%; N, 4.08%. Found: C, 80.15%; H, 3.62%; N, 3.89%.

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 $10^\circ C \text{ min}^{-1}$ in air or nitrogen. Dynamic mechanical analysis (DMA) was performed with the Advanced Rheometric Expansion System at 1.0 Hz at $5^\circ C \text{ min}^{-1}$. Polyimide films were annealed at $350^\circ C$ for 1 h in a vacuum oven.

RESULTS AND DISCUSSION

Monomer Synthesis

New aromatic tetracarboxylic dianhydride having the quinquephenyl structure, *p*-quinquephenyl-tetracarboxylic dianhydride **V** was synthesized in three steps starting from 3',4'-di(ethoxycarbonyl)biphenyl triflate **I** according to eq 1. **I** was previously prepared by reactions involving the extension of phenylene unit using *p*-methoxyphenyl boronic acid.⁶

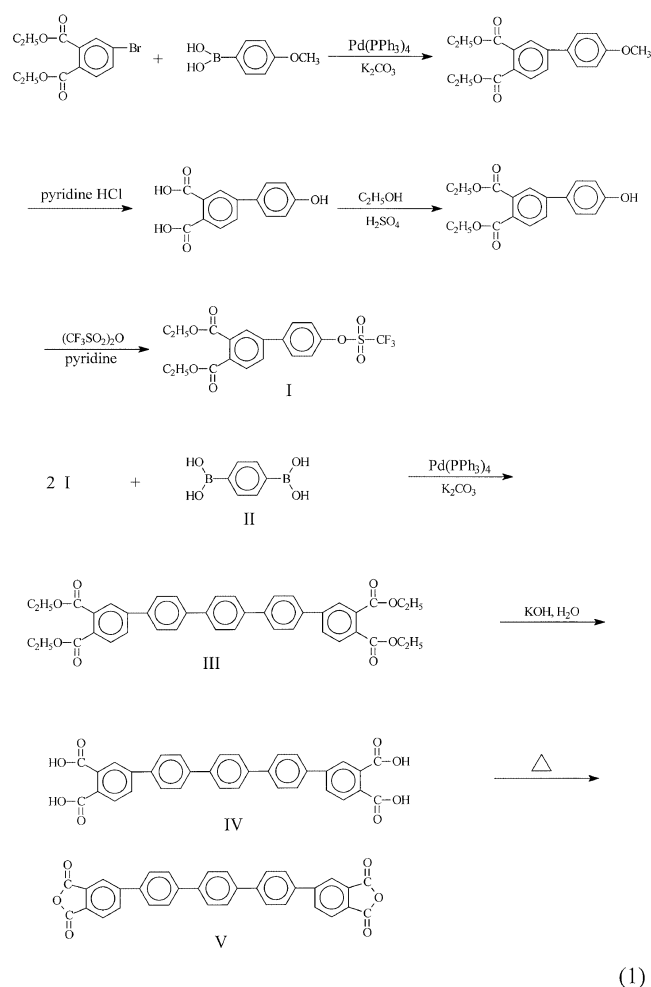
Cross-coupling^{8,9} of **I** with **II**, using $Pd(PPh_3)_4$ as catalyst, yielded tetraethyl 3,3''',4,4'''-*p*-quinquephenyltetracarboxylate **III** in 63%. Subsequent hydrolysis of **III** afforded quinquephenyltetracarboxylic acid **IV** in 92%, and **IV** was converted to tetracarboxylic dianhydride **V** by heating in diphenyl ether (84%).

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

Compound **V** showed IR absorption at 1850 and 1780 cm^{-1} characteristic of carboxylic anhydride. The ^{13}C NMR spectrum of **V** exhibited 14 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 **VIIIa-VIIIf** were synthesized by the usual two-step procedure which involved ring-opening polyaddition of aromatic diamine **VIa-VI f** to **V** and subsequent thermal cyclodehydration as shown



(1)

Table I. Synthesis of polyamic acids

Diamine	Polyamic acid ^a	Yield	η_{inh}^b
		%	dL g ⁻¹
VIa	VIIa	96	1.19
VIb	VIIb	94	0.61
VIc	VIIc	95	0.59
VI d	VII d	89	0.21
VI e	VII e	94	1.12
VI f	VII f	96	0.95

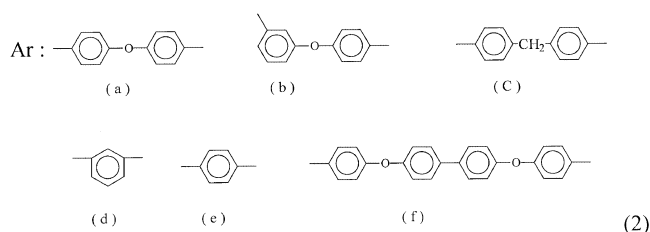
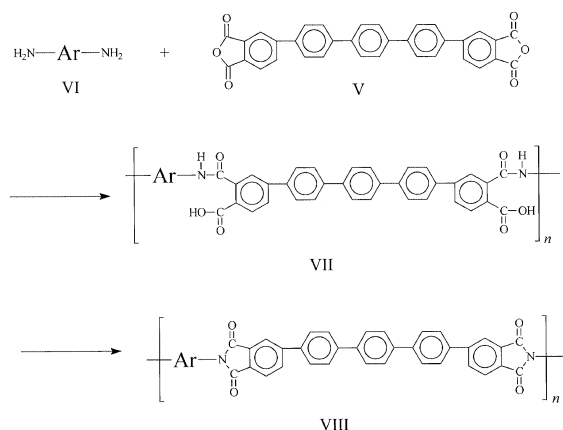
^aPolymerization carried out with 1.0 mmol each monomer in 10 mL NMP at room temperature for 5 h under nitrogen.

^bMeasured at 0.5 g dL^{-1} in DMAc at $30^\circ C$.

in eq 2.

In the first step, ring-opening polyadditions were carried out in NMP at room temperature, leading to the formation of polyamic acids having inherent viscosities of $0.20\text{--}1.20 \text{ dL g}^{-1}$ in DMAc (Table I). The polymerization proceeded in homogeneous solution in reaction media (NMP), and viscosity of the polyamic acids was rather high except for the polymer **VII d**, possibly due to the steric hindrance of diamine **VI d** with V-shaped narrow angle between two amino groups.

In the second step, thermal conversion of the polyamic acids to polyimides was performed by heat-

**Table II.** Thermal behavior of aromatic polyimides

Polyimide	$T_g/^\circ\text{C}^a$	$T_c/^\circ\text{C}^a$	$T_{10}/^\circ\text{C}^b$	$T_{10}/^\circ\text{C}^c$
VIIIa	243	326–341	575	635
VIIIb	235		570	632
VIIIc	260	326–363	560	605
VIIId	260	345–453	570	610
VIIIe	263	332–371	565	637
VIIIf	233		550	610

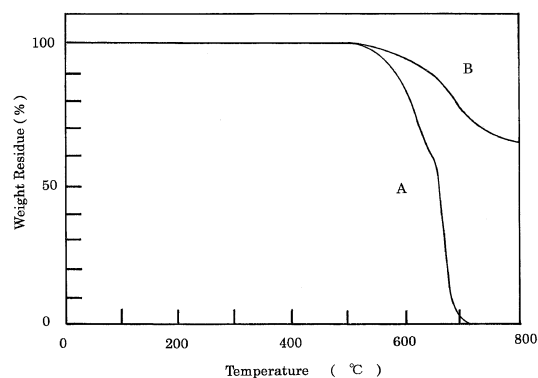
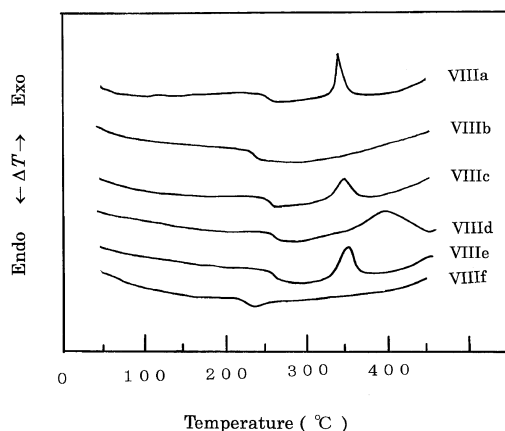
^aDetermined by DSC in nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$. ^bTemperature at which 10% weight loss was recorded by TG at heating rate of $10^\circ\text{C min}^{-1}$ in air. ^cTemperature at which 10% weight loss was recorded by TG at heating rate of $10^\circ\text{C min}^{-1}$ in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

ing precursor polymers in the form of film successively at 100°C for 1 h, 200°C for 1 h, and 300°C for 1 h under vacuum. The polyimides except **VIII**d gave tough films in spite of having rigid backbone. Polyimide **VI**-**II**d was not obtained as film probably due to the low inherent viscosity of polyamic acid **VII**d.

The formation of polyimides was confirmed by the appearance of absorption bands at around 1770 cm^{-1} and 1720 cm^{-1} (C=O) and at about 1360 cm^{-1} (C–N) characteristic of imide group in the IR spectra. Elemental analysis values were in close agreement with those calculated supporting polyimide formation.

Polymer Properties

Thermal behavior of the polyimides was evaluated by TG and DSC. Figures 1 and 2 show TG curves of polyimide **VIII**a and DSC curves of all the polyimides, respectively, and transition temperatures and 10% weight

**Figure 1.** TG curves for polyimide **VIII**a at heating rate of $10^\circ\text{C min}^{-1}$ in (A) air and (B) nitrogen.**Figure 2.** DSC curves for polyimides at heating rate of $10^\circ\text{C min}^{-1}$ in nitrogen.

loss temperatures (T_{10}) are summarized in Table II. No polyimides lost weight below 470°C in air or nitrogen, and T_{10} in air and nitrogen were in the range of 550 – 570°C and 610 – 640°C , respectively. More than 65% weight was retained even at 800°C in nitrogen for these polyimides. These results indicate high thermal stability of the present polyimides. On the basis of T_{10} , the polyimides had as high thermal stability as the polyimide from *p*-phenylene diamine and 3,3',4,4'-biphenyltetracarboxylic dianhydride, which was one of the most thermally stable polymer in the aromatic polyimides.¹⁰

DSC curves of polyimides **VIII**a, **VIII**c, **VIII**d, and **VIII**e showed glass transition temperature (T_g) around 230 – 265°C followed by exothermic peaks (T_c) around 325 – 450°C , above T_g s. T_g was essentially comparable to that of the previously reported polyimides prepared from 3,3''',4,4'''-*p*-quarterphenyltetracarboxylic dianhydride ($m = 2$) and 3,3''',4,4''',4,4''''-*p*-sexiphenyltetracarboxylic dianhydride ($m = 4$),⁶ but crystallization temperatures (T_c s) increased in the order of $m = 2 < m = 3 < m = 4$. Increase in phenylene units may have effect on the segment movement. Polyimide **VIII**b and **VIII**f exhibited only T_g

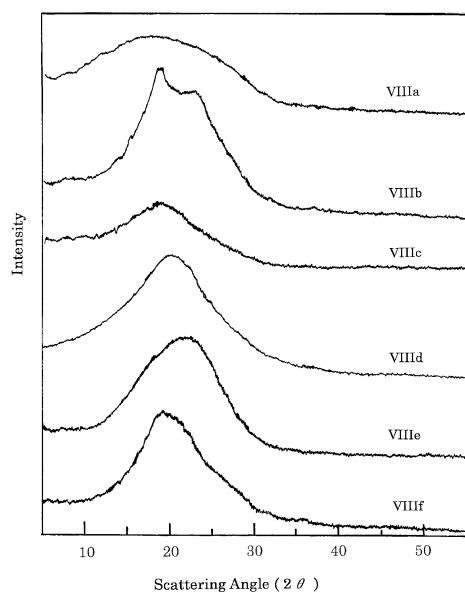


Figure 3. X-Ray diffraction patterns of as-prepared polyimides.

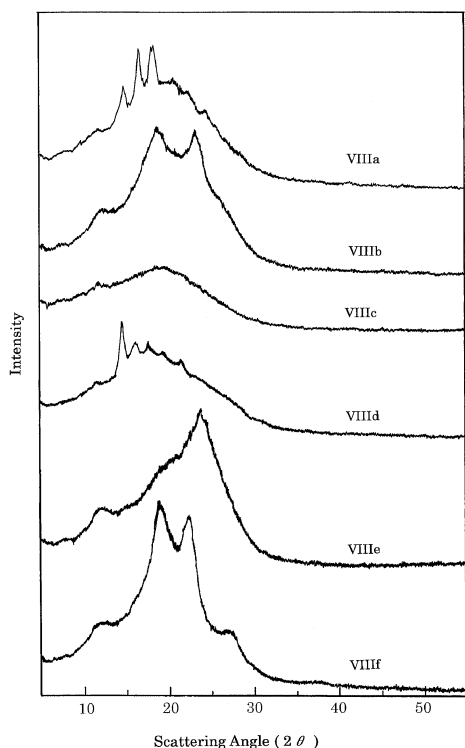


Figure 4. X-Ray diffraction patterns of annealed polyimides at 350°C for 1 h.

at 235°C and 233°C, respectively, and did not undergo obvious transition due to crystallinity. This may be explained by the low rotational energy barrier around the ether linkages. No polyimides exhibited endothermic melting peaks prior to decomposition.

In X-Ray diffraction studies, all polymers were amorphous, while **VIIIb** was slightly crystalline, which was thought to be crystallized during imidation, (Figure 3). However, polyimides **VIIIa**, **VIId**, **VIIIe**, and **VIIf** could be crystallized by annealing (Fig-

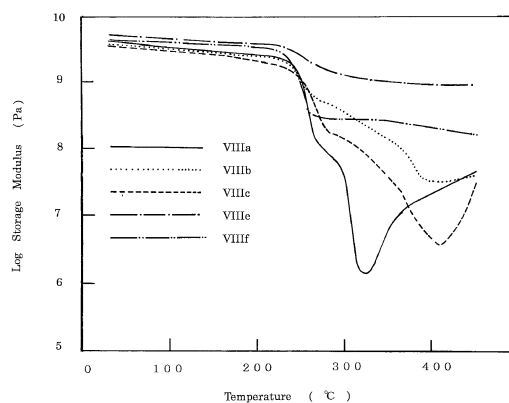


Figure 5. Storage modulus of polyimides.

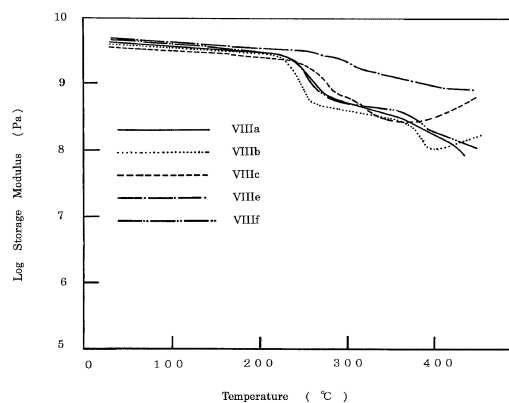


Figure 6. Storage modulus of annealed polyimides at 350°C for 1 h.

ure 4). This result was consistent with the DSC measurement. However, the annealed polyimide **VIIIc** did not show any crystalline pattern in spite of the presence of exothermic peak in DSC measurement.

Figure 5 shows the temperature dependence of dynamic storage moduli for polyimides **VIIIa**, **VIIIb**, **VIIIc**, **VIIIe**, and **VIIf**. We could not determine the storage modulus of **VIId** 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. Polyimides showed quite high moduli (above 10 MPa) even at temperatures higher than 350°C due to the crystallization. The modulus at the higher temperature increased by annealing, and polyimide **VIIIa**, and **VIIIe** were as high as 0.1 GPa and 1.0 GPa at 400°C, respectively (Figure 6).

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*-quinquephenyl-tetracarboxylic dianhydride, which was used for polycondensation with aromatic diamines to obtain aro-

matic polyimides. The polyimides crystallized above 300°C, and had high thermal stability. The effects of rigid *p*-quinquepheny structure in DMA spectra above glass transition.

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