

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

Atsushi MORIKAWA

Department of Materials Science, Faculty of Engineering, Ibaraki University,
4-12-1, Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan

(Received August 30, 1999)

ABSTRACT: A new rigid tetracarboxylic dianhydride, 3,3',4,4'-*p*-quarterphenyltetracarboxylic dianhydride, was synthesized in three steps starting from diethyl 4-bromophthalate. New aromatic polyimides containing a *p*-quarterphenyl unit were synthesized from this tetracarboxylic dianhydride and various aromatic diamines by the conventional two-step procedure that included ring-opening polyaddition in a polar amide-type solvent and subsequent thermal cyclic dehydration. These polyimides had inherent viscosities of 0.41–0.83 dl g⁻¹, and were insoluble in organic solvents. The glass transition temperatures (T_g) of the polyimides were 220–260°C, and exothermic crystallization was observed on heating above its T_g . Almost all the polyimides underwent melting prior to its decomposition.

KEY WORDS 3,3',4,4'-*p*-Quarterphenyltetracarboxylic Dianhydride / Aromatic Polyimides / Glass Transition Temperature / Exothermic Crystallization / Melting /

Aromatic polyimides have attracted much interest because of their high-temperature resistance and mechanical strength.¹ Generally, aromatic polyimides are prepared through a two-step procedure by the ring-opening polyaddition of aromatic diamines to aromatic tetracarboxylic dianhydrides, followed by thermal cyclodehydration, and many polyimides have been prepared.¹ In recent years, interest has been focused on the synthesis of rigid-rod polyimides by incorporating aromatic rings into the polymer backbone.^{2–11} The increased number of conjugated aromatic rings enhances the rigidity of the polymer backbone, and their polarizable π -electrons lead to strong intermolecular interactions to increase the transition temperatures of these polymers.

However, recently almost all such rigid-rod polyimides have been prepared by reactions of newly prepared diamines having many conjugated aromatic rings with commercially available tetracarboxylic dianhydrides, and therefore only limited tetracarboxylic dianhydrides have been used, for example, pyromellitic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-terphenyltetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, and 4,4'-oxydiphtalic anhydride.^{2–11} 3,3',4,4'-terphenyltetracarboxylic dianhydride has the most conjugated aromatic rings in these tetracarboxylic dianhydrides, but the number is only three. There have been only a few polyimides from tetracarboxylic dianhydrides having more than four conjugated aromatic rings, and the properties of the polyimides have not been described.^{12,13} Therefore, it is of interest to prepare polyimides from new tetracarboxylic dianhydrides, which have more than four aromatic rings, and examine the properties of the polyimides.

I conduct the synthesis of a new rigid-rod tetracarboxylic dianhydride, 3,3',4,4'-*p*-quarterphenyltetracarboxylic dianhydride, which has one more phenylene unit than 3,3',4,4'-terphenyltetracarboxylic dianhydride and has not been prepared, and aromatic polyimides derived from it. This article is the first to report the synthesis and characterization of novel aromatic polyimides from this tetracarboxylic dianhydride and aromatic diamines.

Such a rigid structure was not expected to improve solubility of the polyimides due to the high rigidity,¹⁴ but expected to cause higher chain packing.

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 (**VIff**) and 5-bromophthalic anhydride were obtained commercially and used without purification. *N,N*-Dimethylacetamide (DMAc) was purified by vacuum distillation over calcium hydride. Bis(trimethylene)-4,4'-biphenylenediboronate (**II**) were prepared as previously reported.¹⁵

Monomer Synthesis

Diethyl 4-bromophthalate (I). 45.4 g (0.20 mol) of 5-bromophthalic anhydride, 40 mL of absolute ethanol, 40 mL of toluene, and 0.3 g of *p*-toluenesulfonic acid monohydrate were added to a flask equipped with a reflux condenser in a flask, and heated at 95–105°C for 2 h. The condenser was changed for distillation, and an azeotropic mixture of ethanol, toluene and water was distilled at 75–78°C. When the temperature began to drop, 80 mL absolute ethanol were added, and the mixture was again heated under reflux for 12 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 evaporation of the solvent, the residue was distilled under reduced pressure to give **I**. Bp 138–141°C (1 torr). The yield was 51.4 g (85%). The IR spectrum (NaCl) exhibited absorption bands at 2920 cm⁻¹ (C–H), and 1720 cm⁻¹ (C=O). ¹H NMR spectrum [δ in CDCl₃] showed signals at 1.35 (t, 3H, $J = 7$ Hz), 1.37 (t, 3H, $J = 7$ Hz), 4.35 (q, 2H, $J = 7$ Hz), 4.37 (q, 2

H, $J = 7$ Hz), 7.59–7.67 (m, 2H), and 7.82 (d, 1H, $J = 2.2$ Hz). ^{13}C NMR spectrum [δ in CDCl_3] exhibited peaks at 13.91, 61.68, 61.85, 125.40, 130.41, 130.49, 131.60, 133.70, 134.17, 166.18, and 166.41 ppm.

Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{O}_4\text{Br}$: C, 47.86%; H, 4.35%; Br, 26.53%. Found: C, 47.81%; H, 4.36%; Br, 26.48%.

Tetraethyl 3,3''', 4,4'''-p-quarterphenyltetracarboxylate (III). 15.46 g (48 mmol) of **II**, 36.1 g (120 mmol) of **I**, potassium carbonate (16.58 g, 120 mmol), 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 1.5 g tetrakis(triphenylphosphine)paladium ($\text{Pd}(\text{PPh}_3)_4$) were added to the reaction mixture. After the mixture was stirred at 90°C for 8 h, salts were removed by filtration, and the solvent was removed by distillation under reduced pressure. The residue was washed with methanol, and twice recrystallized from toluene to give pure **III**. Mp $188\text{--}189^\circ\text{C}$. The yield was 21.2 g (74%). The IR spectrum (KBr) exhibited absorption bands at 2920 cm^{-1} (C–H), and 1720 cm^{-1} (C=O). ^1H NMR spectrum [δ in CDCl_3] showed signals 1.39 (t, 6H, $J = 7.0$ Hz), 1.40 (t, 6H, $J = 7.0$ Hz), 4.38 (q, 4H, $J = 7.0$ Hz), 4.40 (q, 4H, $J = 7.0$ Hz), 7.73 (d, 4H, $J = 8.8$ Hz), 7.76 (d, 4H, $J = 8.8$ Hz), 7.78–7.82 (q, 2H, $J = 2.2$ Hz, 8.1 Hz), 7.87 (d, 2H, $J = 8.1$ Hz), and 7.96 (d, 2H, 2.2 Hz). ^{13}C NMR spectrum [δ in CDCl_3] exhibited peaks at 14.12, 61.63, 61.79, 127.17, 127.63, 127.71, 128.99, 129.76, 130.30, 133.45, 138.29, 140.33, 143.52, 167.16, and 167.92 ppm.

Anal. Calcd for $\text{C}_{36}\text{H}_{34}\text{O}_8$: C, 72.71%; H, 5.76%. Found: C, 72.55%; H, 5.69%.

3,3''',4,4'''-p-quarterphenyltetracarboxylic acid (IV). In a flask, 20.81 g (35 mmol) of **III** were dissolved in 350 mL 2-(2-methoxyethoxy)ethanol at 140°C . A solution of 15.71 g (0.28 mol) of potassium hydroxide in 50 mL of water was added to the solution, and the mixture was heated at this temperature for about 2 h, resulting in the formation of a white precipitate. The reaction mixture was then concentrated under reduced pressure, and 300 mL water were added to the resulting mixture, which was then heated at reflux for 5 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 the further reaction. The yield was 14.3 g (85%). The IR spectrum (KBr) exhibited absorption bands at $3400\text{--}3000\text{ cm}^{-1}$ (OH), and 1710 cm^{-1} (C=O). ^1H NMR spectrum [δ in dimethyl sulfoxide ($\text{DMSO}-d_6$)] showed signals at 7.82 (d, 2H, $J = 8.1$ Hz), 7.85 (d, 4H, $J = 8.8$ Hz), 7.88 (d, 4H, $J = 8.8$ Hz), 7.91–7.94 (q, 2H, 2.2 Hz, 8.1 Hz) and 7.98 ppm (d, 2H, 2.2 Hz). ^{13}C NMR spectrum [δ in CDCl_3] exhibited peaks at 125.74, 126.81, 127.00, 127.87, 128.94, 130.95, 133.82, 137.25, 138.97, 141.53, 167.45, and 167.86 ppm.

Anal. Calcd for $\text{C}_{28}\text{H}_{18}\text{O}_8$: C, 69.71%; H, 3.76%. Found: C, 69.82%; H, 3.72%.

3,3''',4,4'''-p-Quarterphenyltetracarboxylic dianhydride (V). 4.82 g (10 mmol) of **IV** was heated together with 400 mL acetic anhydride at reflux temperature for about 2 h. The reaction mixture became homogeneous, and was cooled to give yellow crystalline of **V**. Mp $290\text{--}291^\circ\text{C}$. The yield was 3.81 g (85%). The IR spectrum (KBr) exhibited absorption bands at 1860 cm^{-1} and 1770

cm^{-1} (C=O). ^1H NMR spectrum [δ in $\text{DMSO}-d_6$] showed signals at 7.93 (d, 4H, $J = 8.8$ Hz), 8.00 (d, 4H, $J = 8.8$ Hz), 8.15 (2H, d, 8.1 Hz), 8.34–8.37 (q, 2H, 2.2 Hz, 8.1 Hz), and 8.38 (d, 2H, 2.2 Hz). ^{13}C NMR spectrum [δ in CDCl_3] exhibited peaks at 122.80, 125.80, 127.30, 127.97, 129.55, 132.19, 134.05, 136.71, 139.70, 147.11, 162.67, and 162.81 ppm.

Anal. Calcd for $\text{C}_{28}\text{H}_{14}\text{O}_6$: C, 75.34%; H, 3.16%. Found: C, 75.11%; H, 3.14%.

Polymerization

Polyimide VIIa from V and VIa. In a three necked flask, 1.116 g (2.5 mmol) of solid **V** were added to a solution of 0.500 g (2.5 mmol) of diamine **VIa** in 15 mL of DMAc 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 hot methanol and dried under vacuum. The inherent viscosity of the polyamic acid (**IIIa**) in DMAc was 0.83 dl g^{-1} , measured at a concentration of 0.5 g dl^{-1} at 30°C . The rest of the DMAc 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 280°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 $(\text{C}_{40}\text{H}_{22}\text{N}_2\text{O}_5)_n$: C, 78.68%; H, 3.63%; N, 4.59%. Found: C, 78.49%; H, 3.66%; N, 4.45%.

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. UV/Vis spectra were recorded on a Shimadzu UV-3101 PC spectrometer. X-ray diffraction was performed with a Rigaku RAD-B System. Differential scanning calorimetry (DSC) and thermogravimetry (TG) used a Shimadzu DSC-60 and a Rigaku Thermal Analysis Station TG 8110, respectively, and measurements were made at a heating rate of $10^\circ\text{C min}^{-1}$ in air or nitrogen.

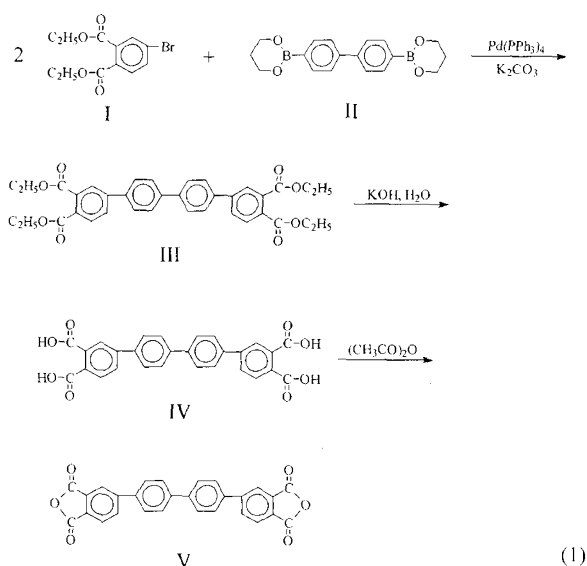
RESULTS AND DISCUSSION

Monomer Synthesis

A new aromatic tetracarboxylic dianhydride having the quarterphenyl structure, 3,3''',4,4'''-p-quarterphenyltetracarboxylic dianhydride (**V**), was synthesized in three steps starting from diethyl 4-bromophthalate (**I**) according to eq 1.

The cross-coupling^{16,17} of **I** with **II**, using tetrakis(triphenylphosphine)paladium ($\text{Pd}(\text{PPh}_3)_4$) as catalyst, yielded tetraethyl 3,3''',4,4'''-p-quarterphenyltetracarboxylate (**III**) in 74%. Subsequent hydrolysis of **III** afforded quarterphenyltetracarboxylic acid (**IV**) in 85%, and **IV** was converted to tetracarboxylic dianhydride (**V**) using acetic anhydride (85%).

Chemical structures were confirmed by IR and NMR spectra, and elemental analysis. Compound **V** showed IR absorption at 1860 and 1770 cm^{-1} characteristic of carboxylic anhydride. The ^{13}C NMR spectrum of **V** exhib-



ited 12 peaks due to symmetry, indicating the formation of the postulated tetracarboxylic dianhydride. Elemental analysis of all the compounds was also in good agreement with calculated results for the proposed structures. The absorption spectrum of **V** showed maxima at 345 nm, and the value compared with that of 3,3'-4,4'-biphenyltetracarboxylic dianhydride strongly blue-shifted by 47 nm, indicating longer conjugation.

Polymer Synthesis

Aromatic polyimides **VIIIa**–**VIIIf** were synthesized by the usual two-step procedure involving the ring-opening polyaddition of aromatic diamine **VIa**–**VI f** to **V** and subsequent thermal cyclodehydration as shown in eq 2.

In the first step, ring-opening polyadditions were carried out in DMAc at room temperature, leading to the formation of polyamic acids having inherent viscosities of 0.41–0.83 dl g⁻¹ in DMAc (Table I). The polymerization proceeded in homogeneous solution in the reaction media (DMAc), and viscosity of the polyamic acids was rather high.

In the second step, the thermal conversion of the polyamic acids to polyimides was performed by heating precursor polymers in the form of film successively at 100°C for 1 h, 200°C for 1 h and 280°C for 1 h under vacuum. These polyimides gave tough films in spite of having rigid backbone.

The formation of polyimides was confirmed by 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, thus also 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 and DSC curves of all the polyimides, respectively, and transition temperatures and 10% weight loss temperatures (*T*₁₀) are summarized in Table II. None of the present polyimides lost weight below 470°C in air or ni-

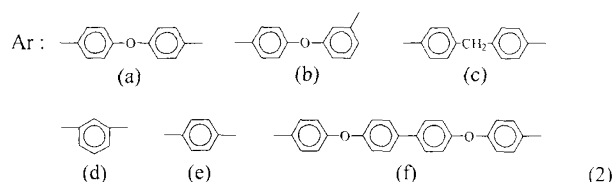
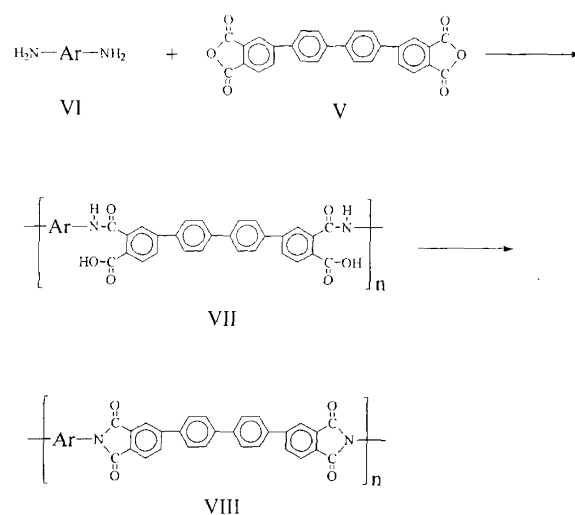


Table I. Synthesis of polyamic acids

Diamine	Polyamic acid ^a	Yield/%	η_{inh}^b /dl g ⁻¹
VIa	VIIa	98	0.83
VIb	VIIb	97	0.83
VIc	VIIc	97	0.53
VId	VII d	95	0.41
VIe	VIIe	93	0.68
VI f	VIII f	96	0.71

^a Polymerization was carried out with 1.5 mmol each monomer in 7.0 mL DMAc at room temperature for 5 h under nitrogen.

^b Measured at 0.5 g dl⁻¹ in DMAc at 30°C.

trogen, and *T*₁₀ in air and nitrogen were from of 575–600°C and 600–645°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, these polyimides have as high thermal stability as the polyimide from *p*-phenylene diamine and 3,3',4,4'-biphenyltetracarboxylic dianhydride, the most thermally stable polymer in the aromatic polyimides.¹⁸

DSC curves of the present polyimides showed the glass transition temperatures (*T*_g) around 234–251°C followed by exothermic crystallization around 280–380°C, above their *T*_gs. The rigid *p*-quarterpheny structure may cause high order in the chains and therefore such crystallization. Such crystallization has not been observed in almost wholly aromatic polyimide, and thus this finding is very interesting. The polyimides, except **VIIIe**, exhibited broad exothermic melting peaks prior to their 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, these polyimides could be crystallized by annealing at 350°C for 1 h (Figure 4). This is consistent

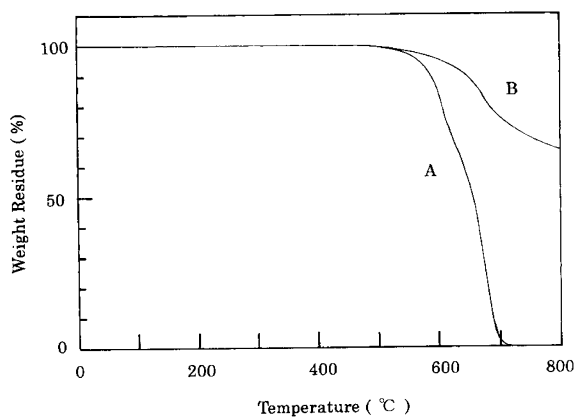


Figure 1. TG curves for polyimide **VIIIa** at heating rate of $10^{\circ}\text{C min}^{-1}$ in (A) air and (B) nitrogen.

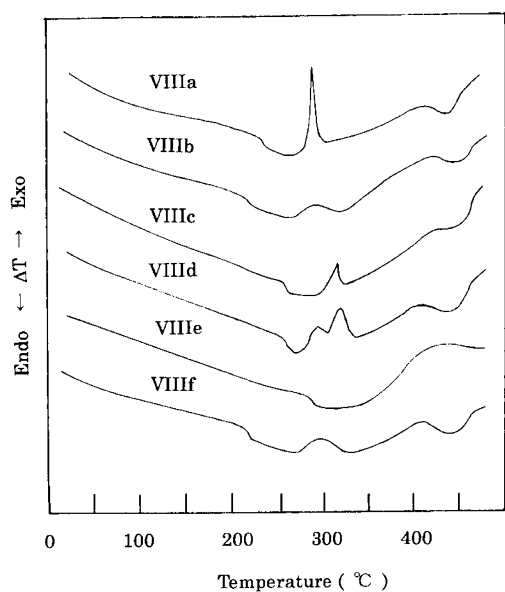


Figure 2. DSC curves for polyimides at heating rate of $10^{\circ}\text{C min}^{-1}$ in nitrogen.

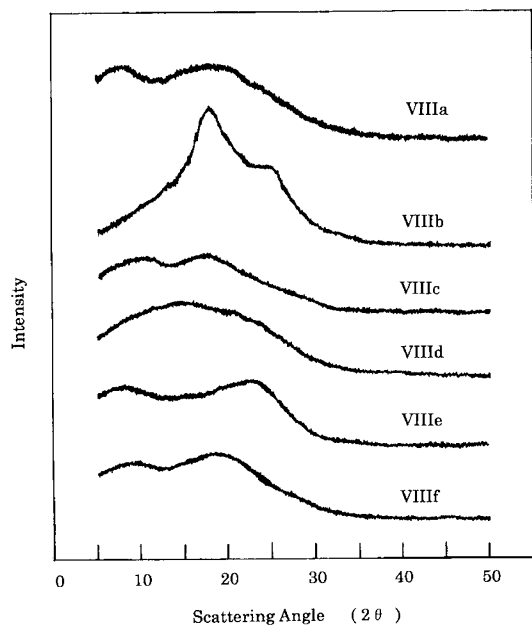


Figure 3. X-ray diffraction patterns of the prepared polyimides.

Polyimide	$T_g/^{\circ}\text{C}^a$	$T_f/^{\circ}\text{C}^a$	$T_m/^{\circ}\text{C}^a$	$T_{10}/^{\circ}\text{C}^a$	$T_{10}/^{\circ}\text{C}^c$
VIIIa	236	275–297	415–453	585	638
VIIIb	226	265–302	430–460	585	635
VIIIc	252	300–322	420–462	570	600
VIIId	253	277–328	417–458	585	625
VIIIe	282	345–470	>470	600	645
VIIIf	220	276–322	413–465	575	612

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

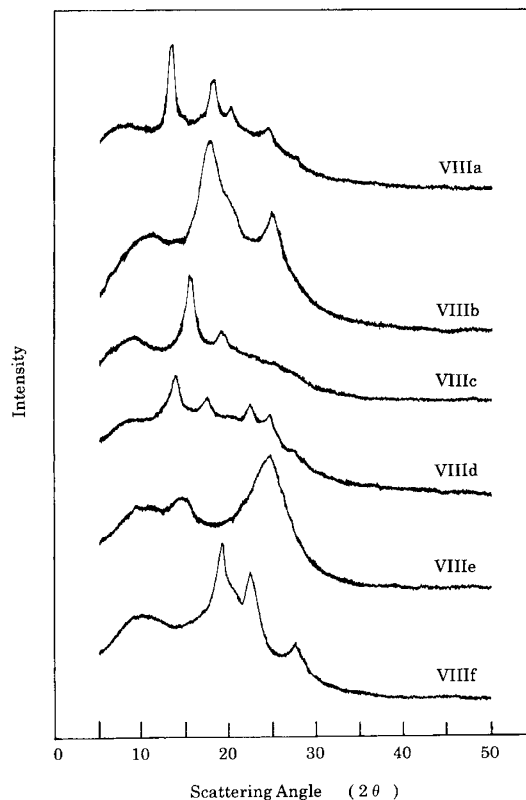


Figure 4. X-ray diffraction patterns of annealed polyimides at 350°C for 1 h.

with the DSC measurement. The annealed polyimide **VIIIe** showed a more disordered crystalline pattern in spite of the very rigid structure, and suggests that the annealing at the higher temperature is necessary for higher crystallinity of **VIIIe**.

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

CONCLUSION

The author synthesized a new rigid tetracarboxylic dianhydride, 3,3''',4,4'''-*p*-quarterphenyltetracarboxylic dianhydride, which was used for polycondensation with aromatic diamines to obtain aromatic polyimides. The polyimides were crystallized above 300°C , and had high thermal stability.

REFERENCE

1. P. E. Cassidy, "Thermally Stable Polymer", Marcel Dekker, New York, N.Y., 1980, Chapter 4.
2. I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules*, **29**, 5313 (1996).
3. I. K. Spiliopoulos and J. A. Mikroyannidis, *Polymer*, **38**, 2733 (1997).
4. I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules*, **31**, 1236 (1998).
5. I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules*, **31**, 515 (1998).
6. Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2189 (1984).
7. H.-J. Jeong, A. Kobayashi, M. Kakimoto, and Y. Imai, *Polym. J.*, **26**, 373 (1994).
8. H.-J. Jeong, Y. Ohishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 39 (1991).
9. H.-J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 1691 (1991).
10. Y. Oishi, M. Ishida, M. Kakimoto, Y. Imai, and T. Kurosaki, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1027 (1992).
11. A. Morikawa and T. Hatakeyama, *Polym. J.*, **31**, 76 (1999).
12. A. A. Berlin, B. I. Liogon'kii, B. L. Zapazinskii, E. A. Kazantseva, and A. O. Stankevich, *J. Macromol. Sci., Chem.*, **A11**, 1 (1977).
13. F. W. Harris, W. A. Feld, and L. H. Lanier, *J. Polym. Sci., Polym. Polym. Lett. Ed.*, **13**, 283 (1975).
14. Y. Imai, *High Perform. Polym.*, **7**, 337 (1995).
15. G. C. Coutts, H. R. Goldschmid, and O. C. Musgrave, *J. Chem. Soc., C*, 488 (1970).
16. T. Oh-e, N. Miyaura, and A. Suzuki, *Synlett*, 221 (1990).
17. W.C. Shieh and J. A. Carlson, *J. Org. Chem.*, **57**, 379 (1992).
18. I. Mita, T. Hisano, and K. Horie, *Macromol.*, **21**, 3003 (1988).