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A facile solid-state synthesis of crystalline oxydianiline-based polypyromellitimides via salt monomers

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Two isomeric oxydianiline-based polypyromellitimides, P-44PM and P-34PM, were readily synthesized by the thermal solid-state polycondensation of the corresponding salt monomers, 44PME and 34PME, composed of 4,4′-oxydianiline and 3,4′-oxydianiline, respectively, and 2,5-di(ethoxycarbonyl)terephthalic acid derived from pyromellitic dianhydride. The thermal polycondensations of the salt monomers were conducted under reduced pressure or under high pressure, yielding highly crystalline polyimide oligomers. The P-44PM and P-34PM oligomers were subjected to solid-state post-polymerization at a high temperature up to 400°C, leading to the formation of higher molecular weight polyimides. The P-44PM polymer post-polymerized at 400°C had a high inherent viscosity of 1.11 dl g^{-1}. During the thermal post-polymerization, the crystal structure of P-44PM markedly changed.

(Keywords: solid-state polycondensation; thermal post-polycondensation; high pressure polycondensation)

INTRODUCTION

Aromatic polyimides have been commercially available since the early 1960s, and used in a variety of fields including aerospace and microelectronics industries due to their excellent properties such as high thermal stability, good mechanical properties, low dielectric constant and high chemical resistance[1–3]. In general, aromatic polyimides have been prepared by a two-step procedure using a polar solvent. The first step involves the synthesis of a soluble poly(amic acid) precursor, which has easy processability to form film, fibre and coating. The second step involves the conversion of a poly(amic acid) precursor to polyimide by either thermal or chemical means.

Aliphatic polyimides were also prepared in 1955 by the melt or thermal solid-state polycondensation of the salt monomers composed of aliphatic diamines and aromatic tetracarboxylic acids or their diester-dicarboxylic acids[4,5]. Bell reported in the mid 1960s that the aromatic polyimide could be obtained by the thermal polycondensation of the salt monomer derived from 4,4′-oxydianiline (4,4′-ODA) and the diisopropyl ester of pyromellitic acid[6]. However, no detailed studies on the synthesis of aromatic polyimides via the salt monomers have been disclosed so far.

Recently we have investigated the thermal polycondensation of the 1 : 1 salt monomer derived from octamethylenediamine and 4,4′-oxydiphthalic acid under high pressure, affording the highly crystalline aliphatic polyimide (P-8-ODP) with high molecular weight[7]. When the polycondensation was conducted under reduced pressure, however, the resulting polyimide was amorphous and quite insoluble in any solvents including concentrated sulfuric acid, indicating that the polyimide had crosslinked through some side reactions. In addition, we have examined the thermal polycondensation of the salt monomers consisting of a series of aliphatic diamines and 2,5-di(ethoxycarbonyl)terephthalic acid (PME) derived from pyromellitic dianhydride both under reduced pressure and under high pressure conditions[8]. The solubility behaviour of the resulting aliphatic polypyromellitimides was similar to that observed for P-8-ODP. The aliphatic polypyromellitimides obtained by both polymerization conditions were highly crystalline and these polymers had a tendency to show layered structures similar to smectic liquid crystalline polymers. In addition, the polyimides polymerized under high pressure had a more developed crystalline structure. These results suggested that the application of high pressure inhibited the crosslinking reaction and induced simultaneous crystallization during the polymerization.

We have applied this methodology to the polycondensation of the salt monomers comprised of PME and aromatic diamines, 4,4′-ODA and 3,4′-ODA, and succeeded in the preparation of the aromatic polyimides with high crystallinity (*Scheme 1*). This paper deals with a facile solid-state synthesis of crystalline oxydianiline-based polypyromellitimides via the salt monomers[9].

EXPERIMENTAL

Apparatus

The polymerization under high pressure was carried

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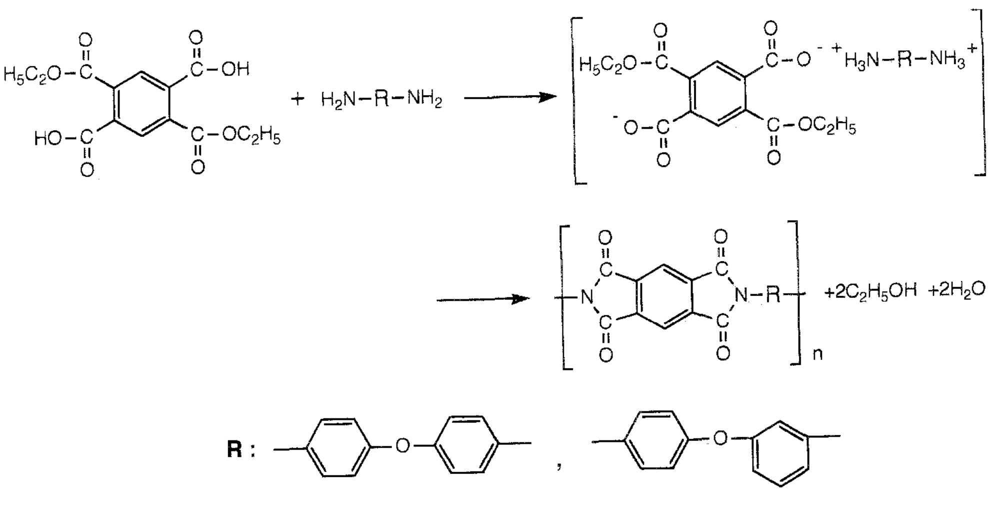


Scheme 1

out by using a piston-cylinder type hot pressing apparatus as described previously[10]. The pressure was generated by a hydraulic press, and the temperature could be varied between room temperature and 330°C. The polymerization under reduced pressure and the thermal post-polymerization were conducted by using a glass tube oven equipped with a heat control unit.

Materials

Pyromellitic dianhydride (PMDA) and 4,4′-ODA were purified by sublimation. 3,4′-ODA was purified by distillation under reduced pressure. Ethanol was dried with magnesium and iodine, and distilled before use. 1,4-Diethyl ester of pyromellitic acid, i.e. 2,5-di(ethoxycarbonyl)terephthalic acid (PME), was synthesized according to a modification of the method of Nishizaki and Moriwaki[11] and that of Bell[6] by the reaction of PMDA with absolute ethanol. The separation of PME from a mixture of the two isomeric *para*- and *meta*-diester-diacids was achieved by fractional recrystallization from chlorobenzene, followed by washing with hot benzene to remove impurities. The yield of PME was 45%; m.p.: 216–218°C (lit.[12] m.p. 201–203°C). I.r. (KBr): 1732 (ester C=O) and 1703 cm^{-1} (carboxylic acid C=O). ^1H n.m.r. (δ in DMSO-d_6): 7.99 (s, 2H, aromatic H); 4.31 (q, 4H, CH_2); 1.29 ppm (t, 6H, CH_3). Analysis: calculated for $C_{14}H_{14}O_8$: C, 54.20; H, 4.55%. Found: C, 54.19; H, 4.44%.

Preparation of salt monomers

Salt 44PME from 4,4′-ODA and PME. To a solution of 4,4′-ODA (2.00 g, 10 mmol) in ethanol (50 ml) and distilled water (10 ml) was added PME (3.10 g, 10 mmol) with stirring at 60°C. The resulting solution was allowed to stand at 0°C for 24 h, and the beige-coloured salt precipitated. The precipitate was collected by filtration and dried under vacuum at room temperature. The yield of the salt was 4.37 g (86%); m.p.: 161 and 169°C (by d.t.a. at a heating rate of 10°C min^{-1}). I.r. (KBr): 1721 (ester C=O), 1628 (NH_3^+), and 1593 cm^{-1} (COO^-). Analysis: calculated for $C_{26}H_{26}N_2O_9$: C, 61.17; H, 5.13; N, 5.49%. Found: C, 60.69; H, 5.22; N, 5.47%.

Salt 34PME from 3,4′-ODA and PME. Salt 34PME was synthesized virtually by the same procedure as that described above, except that 3,4′-ODA was used instead. The yield of the salt was 85%; m.p. 174°C (by d.t.a.). I.r. (KBr): 1725 (ester C=O), 1630 (NH_3^+), and 1592 cm^{-1} (COO^-). Analysis: calculated for $C_{26}H_{26}N_2O_9$: C, 61.17; H, 5.13; N, 5.49%. Found: C, 61.11; H, 5.08; N, 5.49%.

Polymerization of salts under high pressure

Polymer P-44PM. The polymerization under high pressure was carried out by using a piston-cylinder type hot pressing apparatus. About 0.5 g of salt 44PME was placed into a Teflon capsule (15 mm i.d.) and then the capsule was loaded into the cylinder. The piston-cylinder was set in the furnace and pressure was applied at room temperature to the capsule, followed by raising the temperature. The polymerization was carried out at 280°C under 220 MPa for 5 h. The reaction time was recorded from the point where the temperature reached 280°C, which required ~ 2 h. After the polymerization, the temperature was lowered to room temperature, followed by releasing the pressure to 1 atm. The polymer in the form of a flat cylindrical pellet (15 mm diameter, ~ 3 mm thick) was removed from the Teflon capsule. This pellet was dark-brown in colour and very brittle. The pellet was then dried under vacuum at room temperature for 24 h for the complete removal of water and ethanol generated during the polymerization. The inherent viscosity of the polymer was 0.19 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} in concentrated sulfuric acid at 30°C. I.r. (KBr): 1777 and 1725 (imide C=O), 1379 (C–N) and 725 cm^{-1} (imide ring). Analysis: calculated for $(C_{22}H_{10}N_2O_5)_n$: C, 69.11; H, 2.64; N, 7.33%. Found: C, 67.14; H, 3.21; N, 6.87%.

Polymer P-34PM. The polymerization of salt 34PME was conducted at 240°C under 260 MPa for 5 h essentially by the same procedure as that described above. The polymer formed had an inherent viscosity of 0.11 dl g^{-1} in concentrated sulfuric acid. I.r. (KBr): 1779 and 1725 (imide C=O), 1379 (C–N) and 725 cm^{-1} (imide ring). Analysis: calculated for $(C_{22}H_{10}N_2O_5)_n$: C, 69.11; H, 2.64; N, 7.33%. Found: C, 66.73; H, 3.35; N, 6.69%.

Table 1 Post-polymerization of as-polymerized polyimide oligomers

As-polymerized polymer		Post-polymerization conditions[a]		Post-polymerized polymer
Type	η_{inh}[b] (dl g^{-1})	Temp. (°C)	Time (h)	η_{inh}[b] (dl g^{-1})
P-44PM[c]	0.19	250	1	0.24
		300	1	0.31
		350	1	0.40
		400	1	1.11
P-34PM[d]	0.11	350	1	0.15
		400	1	0.27
		465	5 (min)	0.24

[a] The post-polymerization was carried out under a slow stream of nitrogen

[b] Measured at a concentration of 0.5 g dl^{-1} in concentrated sulfuric acid at 30°C

[c] Obtained by polymerization at 280°C under 220 MPa for 5 h

[d] Obtained by polymerization at 240°C under 260 MPa for 5 h

Polymerization of salts under reduced pressure

Polymer P-44PM. The polymerization of ~ 0.5 g of salt 44PME was carried out by using a glass tube oven in a test tube at 170°C under 2.6 kPa (20 torr) for 1.5 h. The inherent viscosity of the polymer was 0.14 dl g^{-1} in concentrated sulfuric acid. The i.r. spectrum was the same as that of polymer P-44PM obtained by polymerization under high pressure.

Polymer P-34PM. The polymerization of salt 34PME was conducted at 170°C under 2.6 kPa for 1.5 h. The polymer formed had an inherent viscosity of 0.11 dl g^{-1} in concentrated sulfuric acid. The i.r. spectrum was the same as that of polymer P-34PM described above.

Thermal post-polymerization

Polymer P-44PM. The as-polymerized polymer P-44PM obtained by the high pressure polymerization was heated by using a glass tube oven in a test tube separately at 250, 300, 350 or 400°C for 1 h each under a slow stream of nitrogen. The results are listed in *Table 1.* The polymer post-polymerized at 400°C had an inherent viscosity of 1.11 dl g^{-1} in concentrated sulfuric acid. The characteristic absorption bands for the i.r. spectrum were the same as those described above. Analysis: calculated for $(C_{22}H_{10}N_2O_5)_n$: C, 69.11; H, 2.64; N, 7.33%. Found: C, 69.14; H, 2.50; N, 7.23%.

Polymer P-34PM. The as-polymerized polymer P-34PM described above was allowed to post-polymerize separately at 350 or 400°C for 1 h each, or at 465°C for 5 min. The results are summarized in *Table 1.* The inherent viscosity of the polymer post-reacted at 400°C for 1 h was 0.27 dl g^{-1} in concentrated sulfuric acid. Analysis: calculated for $(C_{22}H_{10}N_2O_5)_n$: C, 69.11; H, 2.64; N, 7.33%. Found: C, 69.48; H, 2.63; N, 7.39%.

Measurements

I.r. spectra were recorded on a Shimadzu FT/IR-8100 spectrophotometer. ^{1}H n.m.r. spectra were obtained on a JEOL FX90Q spectrometer operating at 90 MHz in DMSO-d_6. Differential thermal analysis (d.t.a.) and thermogravimetry (t.g.) were performed with Shimadzu thermal analyzers DTA-40 and TGA-40, respectively, both at a heating rate of 10°C min^{-1} in nitrogen. Wide angle X-ray diffraction (WAXD) patterns were recorded with a Rigakudenki RU-200 diffractometer with Ni-filtered CuKα radiation by scintillation counters at 50 kV and 180 mA. The scanning region of the diffraction angle (2θ) ranged from 3 to 40°. Samples for the WAXD measurements were prepared by compressing the polymers under pressure to form pellets (~ 1 mm thick).

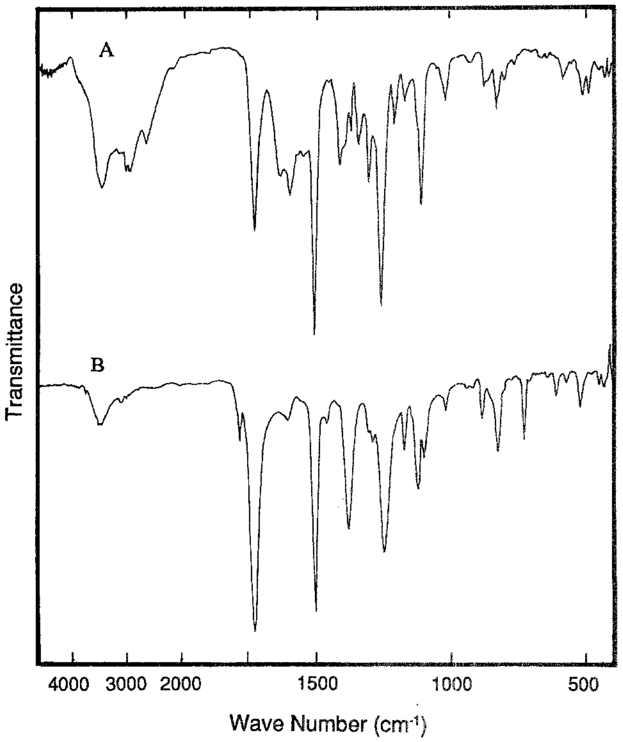


Figure 1 I.r. spectra of (A) salt monomer 44PME and (B) P-44PM oligomer prepared at 280°C and 220 MPa for 5 h

RESULTS AND DISCUSSION

Salt monomers

1,4-Diethyl ester of pyromellitic acid, i.e. 2,5-di-(ethoxycarbonyl)terephthalic acid (PME) was prepared by reacting PMDA with absolute ethanol, followed by fractional recrystallization from chlorobenzene. PME was characterized by means of i.r. and ^{1}H n.m.r. spectroscopy and shown to have the expected chemical structure. The i.r. spectrum exhibited absorption bands at 1732 and 1703 cm^{-1} due to ester carbonyl stretching and carboxylic acid function, respectively. The ^{1}H n.m.r. spectrum showed a strong singlet at 7.99 ppm (δ) attributed to the two equivalent aromatic protons of the 1,4-diethyl ester of pyromellitic acid[11].

The two polyimide-forming salt monomers, 44PME and 34PME, were then prepared by the reaction of PME with two isomeric oxydianilines, 4,4′-ODA and 3,4′-ODA, respectively, in essentially the same manner as that reported by Bell[6]. As shown in *Figure 1A*, the formation of salt 44PME was confirmed by means of i.r. spectroscopy, with the disappearance of the absorption bands due to carboxylic (1703 cm^{-1}) and amino (around

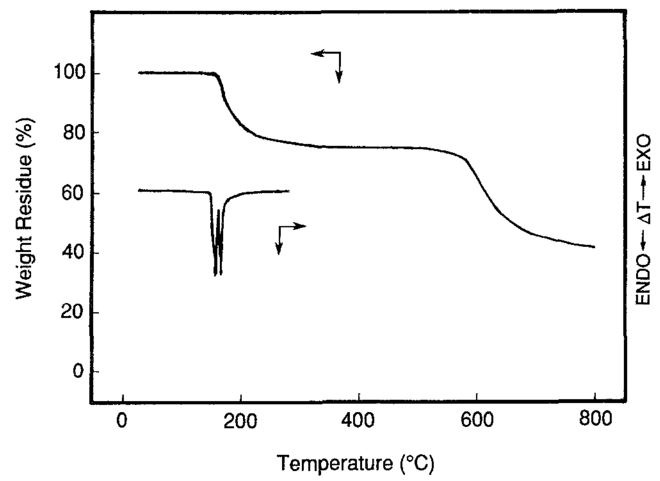


Figure 2 D.t.a. and t.g. curves of salt monomer 44PME, both at a heating rate of 10°C min^{-1} in nitrogen

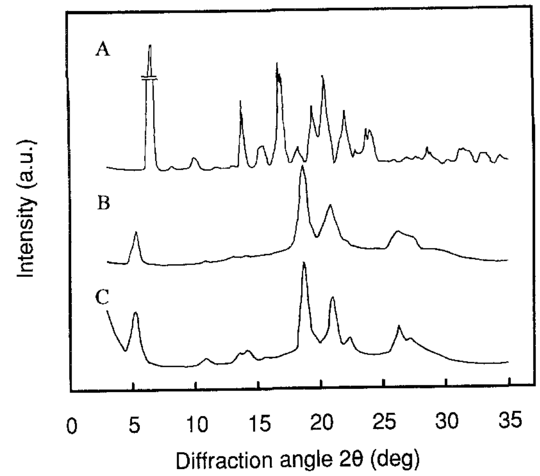


Figure 3 Wide angle X-ray diffraction patterns of (A) salt monomer 44PME, (B) polyimide P-44PM obtained under reduced pressure (170°C, 2.6 kPa, 1.5 h) and (C) polyimide P-44PM obtained under high pressure (280°C, 220 MPa, 5 h)

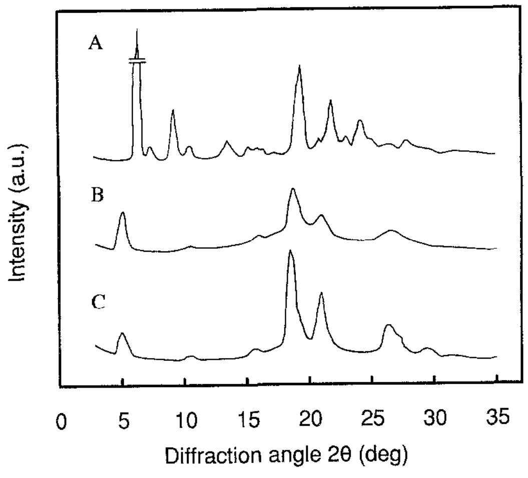


Figure 4 Wide angle X-ray diffraction patterns of (A) salt monomer 34PME, (B) polyimide P-34PM obtained under reduced pressure (170°C, 2.6 kPa, 1.5 h) and (C) polyimide P-34PM obtained under high pressure (240°C, 260 MPa, 5 h)

3400 cm^{-1}) functions of the two starting materials, but with the retention of an ester absorption (1721 cm^{-1}) and the appearance of ammonium carboxylate bands (1628 and 1593 cm^{-1}) in the salt. The elemental analysis also supported the proposed transformation. The chemical structure of salt 34PME was also confirmed by i.r. spectroscopy and elemental analysis.

Figure 2 shows the d.t.a. and t.g. curves of salt 44PME. The d.t.a. curve of the salt showed sharp endothermic peaks at 161 and 169°C, which were accompanied by rapid weight loss probably due to the evolution of ethanol and water leading to the formation of polyimide as shown in the t.g. curve. This supposition was supported by the fact that the weight loss value of 25% between the temperatures of 160°C and 400°C agreed quite well with the calculated value of 25.1% based on the loss of two molecules each of both ethanol and water from one molecule of the salt. Though the occurrence of the double endothermic peaks in the d.t.a. curve during heating of the salt is unexpected and not fully understood, it may be a consequence of crystal transformation (melting–recrystallization–melting) during heating, which is accompanied by the reaction of the salt.

The thermal behaviour of salt 34PME was also followed by d.t.a. and t.g. measurements. The t.g. curve of 34PME was very similar to that of 44PME, whereas the d.t.a. diagram of 34PME showed only a single endothermic peak at 174°C.

The WAXD patterns of salts 44PME and 34PME are shown in *Figures 3A* and *4A*, respectively. The WAXD patterns of the salts are typical of crystalline solids. The strong low-angle peaks at 6.7° (2*θ*) for salt 44PME and 6.3° (2*θ*) for 34PME corresponded to *d*-spacings of 1.32 and 1.40 nm, respectively, presumably arising from the periodicity of the repeat distance along the chain axis of the salt monomers.

Polymerization of salt monomers

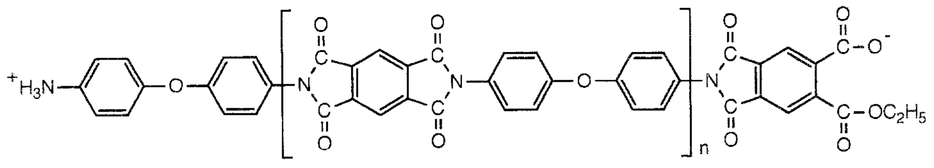
The polycondensations of the two salt monomers, 44PME and 34PME, were carried out by using a glass tube oven at 170°C for 1.5 h under reduced pressure of 2.6 kPa (20 torr). The polymerization proceeded rapidly along with colour change of the solids from beige to dark brown, the characteristic colour of most polyimides, while retaining the solid form with non-melting behaviour. The polyimides obtained, P-44PM and P-34PM, were readily soluble in concentrated sulfuric acid, and had low inherent viscosities of 0.14 and 0.11 dl g^{-1}, respectively, in the solvent.

Next, the high pressure polycondensation of the two salt monomers was conducted in a sealed Teflon capsule by using a piston-cylinder type hot pressing apparatus[10]. In this process, the by-products of ethanol and water eliminated by the polycondensation of the salt monomers were retained in the reaction capsule.

In the case of salt 44PME, the polyimide was obtained by the reaction at 280°C under 220 MPa for 5 h. However, the polymer had low inherent viscosity of 0.19 dl g^{-1} just like the polyimide obtained under reduced pressure, indicative of low molecular weight. The high pressure polymerization of 44PME under more severe conditions at 320°C under 260 MPa for 15 h also afforded the polyimide with the same viscosity value as above. When

34PME was subjected to polycondensation at 240°C under 260 MPa for 5 h, the polyimide with low inherent viscosity of 0.11 dl g^{-1} was produced.

The formation of polyimides P-44PM and P-34PM under these high pressure conditions was confirmed by means of i.r. spectroscopy. The i.r. spectrum of P-44PM is shown in *Figure 1B*. The characteristic absorption bands due to imide ring were observed at 1777–1779, 1725, 1379 and 725 cm^{-1}, with the disappearance of the characteristic bands of the salt monomers mentioned above. However, the elemental analysis values of the polyimides differed from the calculated values, suggesting the formation of low molecular weight polyimides that had unreacted end groups, to some extent. The chemical structure of low molecular weight polyimide P-44PM (P-44PM oligomer) is:



On the basis of the elemental analysis data and the postulated chemical structure, the degree of polymerization (n) of P-44PM oligomer ($\eta_{inh} = 0.19$ dl g^{-1}) could be estimated to be ~ 1.5 corresponding to a molecular weight (*MW*) of 1020, and P-34PM oligomer ($\eta_{inh} = 0.11$ dl g^{-1}) to have n of ~ 1.0 ($MW = \sim 830$). Thus, the polycondensations of the salt monomers under the above conditions proceeded incompletely, producing polyimide oligomers.

There is a marked difference between the melting points of the salt monomers (around 170°C) and the glass transition temperatures (T_g) of the resulting polyimides. The T_g of polyimides P-44PM and P-34PM were reported to be around 400–420°C[13–15] and 475°C[15], respectively, and the melting temperatures of these polyimides should be much higher. The molecular motion of the growing polymers associated with conformational changes was, indeed, reduced sharply as the polycondensation proceeded, and hence the polymerization virtually stopped at an early stage and remained incomplete, even after a long reaction period.

Figure 3 shows the WAXD patterns of salt monomer 44PME and the corresponding polyimides P-44PM formed under both reduced pressure and high pressure conditions. As shown in *Figures 3B* and *C*, the strong low-angle peak at 6.7°C (2θ) in the WAXD pattern of salt 44PME (*Figure 3A*) shifted to lower angle at 5.5° (2θ) after the polymerization, and the other diffraction peaks of the salt disappeared, indicative of the transformation of the salt into the corresponding polyimides with low molecular weights. It is to be noted that the polyimides formed both under high pressure and under reduced pressure had sharp diffraction peaks, indicating that a high degree of crystallinity was maintained during the reaction.

Figure 4 shows the WAXD patterns of salt 34PME and the corresponding polyimide P-34PM formed under both reduced pressure and high pressure conditions. Polyimide P-34PM contains the unsymmetrical 3,4′-oxydiphenylene unit that may introduce head-to-head and head-to-tail structures into the polymer backbone. Nevertheless, the WAXD patterns indicated that salt 34PME was transformed into the corresponding polyimides with high degree of crystallinity. In addition, it is interesting to note that the WAXD patterns of polyimide P-44PM oligomer shown in *Figures 3B* and *C* resembled those of polyimide P-34PM oligomer shown in *Figures 4B* and *C*.

As mentioned above, the thermal polycondensation of the salt monomers afforded highly crystalline polyimide oligomers. It may be assumed that the rigidity of the polymer chain and the strong interaction of the pyromellitimide moiety such as dipole–dipole interaction and/or charge transfer interaction[16,17] can minimize the disorder of the molecular packing during the thermal polymerization of the salt monomers. Hence the polycondensation of the salt monomers is presumably accompanied by simultaneous crystallization of the growing polyimide molecule probably giving extended chain crystals under both reduced pressure and high pressure conditions.

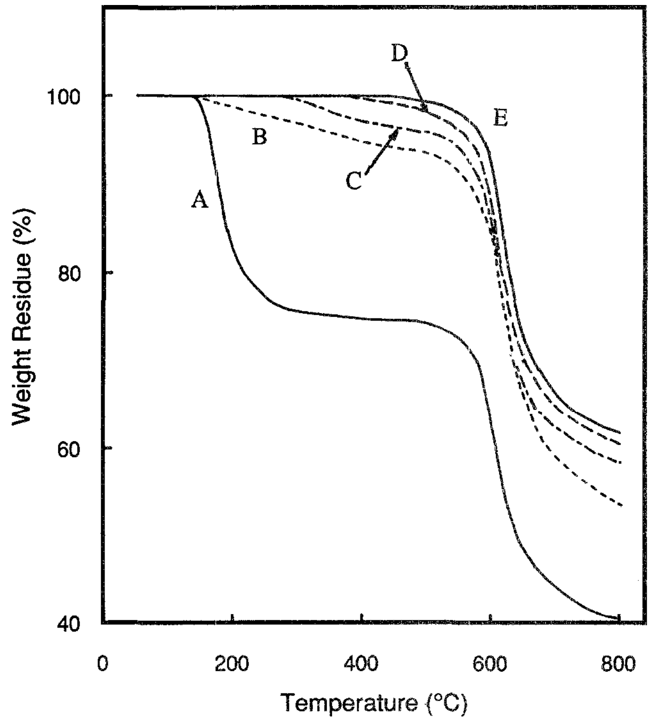


Figure 5 T.g. curves of (A) salt monomer 44PME, (B) the as-polymerized P-44PM obtained under high pressure (280°C, 220 MPa, 5 h), and the post-polymerized P-44PM (C) at 250°C, (D) at 350°C and (E) at 400°C for 1 h each

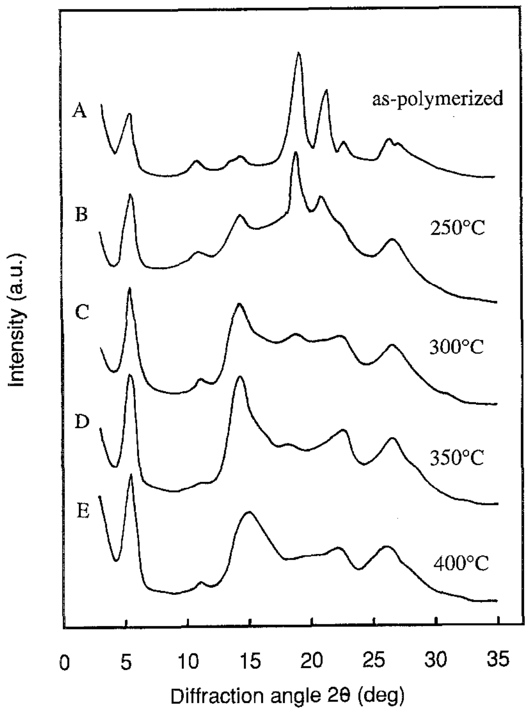


Figure 6 Wide angle X-ray diffraction patterns of (A) the as-polymerized P-44PM obtained under high pressure (280°C, 220 MPa, 5 h), and the post-polymerized P-44PM (B) at 250°C, (C) at 300°C, (D) at 350°C and (E) at 400°C for 1 h each

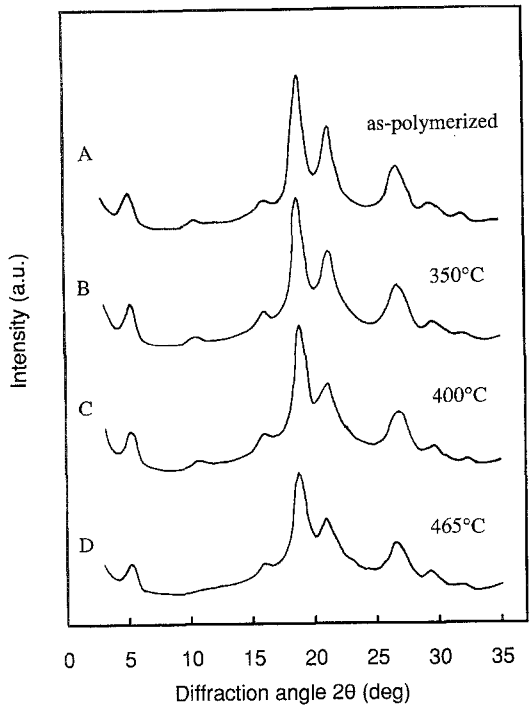


Figure 7 Wide angle X-ray diffraction patterns of (A) the as-polymerized P-34PM obtained under high pressure (240°C, 260 MPa, 5 h), and the post-polymerized P-34PM (B) at 350°C for 1 h, (C) at 400°C for 1 h and (D) at 465°C for 5 min

Thermal post-polymerization

It was found that the polycondensations of the salt monomers under the above conditions were incomplete, affording polyimides with only low inherent viscosity values. Therefore, to complete the polycondensation, the as-polymerized P-44PM oligomer was subjected to thermal post-polymerization, which was carried out in a glass tube oven separately at 250, 300, 350 or 400°C for 1 h each under a slow stream of nitrogen. The results are summarized in *Table 1*. The inherent viscosity of P-44PM gradually increased from 0.19 dl g^{-1} with increasing reaction temperature, finally reaching 1.11 dl g^{-1}, indicative of high molecular weight, after post-polymerization at 400°C for 1 h. The elemental analysis values were in good agreement with the calculated values for the proposed chemical structure. Since the T_g of polyimide P-44PM was reported to be around 400–420°C[13–15], these results indicated that a temperature of 400°C was essential to enhance the mobility of the polymer chain ends of the growing polymer molecule necessary for further progress of polymerization, thereby giving a high molecular weight polyimide. In the case of thermal post-polymerization of P-34PM oligomer with inherent viscosity of 0.11 dl g^{-1}, post-polymerization at 400°C for 1 h was insufficient, as judged from the inherent viscosity value of 0.27 dl g^{-1} (*Table 1*). Post-polymerization at 465°C for 5 min also afforded polyimide with a low inherent viscosity of 0.24 dl g^{-1}, whereas longer reaction time caused decomposition of the polymer.

Figure 5 shows the t.g. curves of polyimide P-44PM obtained at various post-polymerization temperatures (250, 350 and 400°C) as well as those of salt monomer 44PME and the as-polymerized P-44PM oligomer. The incomplete polycondensation of the as-polymerized oligomer was again evidenced by the t.g. curves (curve B), where the weight loss was observed due to further reaction in the temperature range of 150–450°C in nitrogen. The weight loss value of P-44PM decreased with increasing post-polymerization temperature (curves C and D), indicating that the as-polymerized P-44PM oligomer underwent thermal post-polymerization in the solid state. The polymer post-polymerized at 400°C showed no weight loss below 450°C (curve E), which was identical to typical polyimide P-44PM.

We have further investigated the evolution of the structure of polyimide P-44PM during the thermal post-polymerization. *Figure 6* shows the WAXD patterns of polymer P-44PM prepared by heating the as-polymerized P-44PM oligomer separately at 250, 300, 350 or 400°C for 1 h each under nitrogen. No appreciable change of the low-angle peak at 5.5° (2*θ*) was observed for the polymers at each heating temperature, that is, the periodicity of the repeat distance along the chain axis was retained during the thermal post-polymerization. However, for the polymers heated between 250°C and 300°C, major changes occurred at the higher diffraction angle, which caused decreases in intensity of the two strong peaks at 19.1 and 21.4° (2*θ*) and intensity increase of the three peaks at about 14.8, 22.2 and 26.2° (2*θ*).

The WAXD pattern of high molecular weight polyimide P-44PM shown in *Figure 6E* was virtually identical to that of a typical polyimide P-44PM moulding (du Pont's Vespel®). Though the shape of the main three peaks at higher diffraction angle was broader than the low-angle peaks, polyimide P-44PM post-polymerized at 400°C for 1 h had a relatively high degree of crystallinity. In the case of a conventional two-step procedure, the poly(amic acid) precursor derived from PMDA and 4,4′-ODA exhibited smectic-like ordering and the molecular ordering was virtually retained when the thermal imidization of the precursor was conducted at the relatively low temperature of 200°C[18,19]. To develop crystalline ordering, high temperature imidization[13,19] or high temperature annealing[14,18] was necessary because of the high T_g of polyimide P-44PM.

Figure 7 shows the WAXD patterns of polymer P-34PM post-polymerized separately at 350 or 400°C for 1 h each or at 465°C for 5 min. In contrast to marked changes in the WAXD patterns of polyimide P-44PM in *Figure 6*, the WAXD patterns of polymer P-34PM remained almost unchanged after the thermal post-polymerization.

CONCLUSIONS

Highly crystalline P-44PM and P-34PM oligomers could be obtained by the thermal solid-state polycondensation of the corresponding salt monomers 44PME and 34PME, respectively, both under high pressure and under reduced pressure conditions. High molecular weight polyimide P-44PM having inherent viscosity of $1.11\,\mathrm{dl\,g^{-1}}$ could be prepared by the thermal post-polymerization of P-44PM oligomer at a high temperature of 400°C, indicating that the polymer chain ends of the polyimide oligomer possessed a considerable degree of mobility in the solid state at such a high temperature to continue further polymerization. It is interesting to note that the WAXD pattern of the as-polymerized P-44PM oligomer is quite different from those of previously reported polyimide P-44PM and changed markedly after the thermal post-polymerization. Recently Liu *et al.*[20] reported the existence of a new orthorhombic unit cell of the polyimide oligomer synthesized from PMDA and 4,4′-ODA in the melt state. The WAXD pattern of the new unit cell reported is similar to that of our P-44PM oligomer sample except that the intense (0 0 1) reflection was not observed in our WAXD experiment using a flat-plate camera. A detailed study of this subject will be reported subsequently.

One of the principal advantages of this salt method is that the salt monomers could be prepared with exact molar balance of the two starting monomers. A second advantage is that the polycondensation was carried out without use of any solvent. Furthermore, the polymerization proceeded readily, because the two reactive functional groups are likely to be adjacently arranged in the salt monomer crystals and the growing polymer chain ends.

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