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Melt processible polyimides and their chemical structures

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A series of aromatic ether diamines having different numbers of benzene rings, different amino-substituted positions and different moieties in their structures was synthesized. By using these synthesized ether diamines and commercially available tetracarboxylic dianhydrides, various kinds of polyimides having almost the same molecular weights were synthesized. The glass transition temperature (T_g) values and thermoplasticity were studied by focusing on the chemical structures of their repeating structure units. It was shown that T_g and melt-processibility of polyimide depended on the chain length and *meta*-linkage contents of ether diamine, and the difference of amino substituted position in ether diamine. Copyright © 1996 Elsevier Science Ltd.

(Keywords: melt processible; polyimides; ether diamine)

INTRODUCTION

Aromatic polyimides[1] have marked thermal stability; and excellent mechanical, electrical and solvent-resistance properties. Therefore, they are being used in such applications as automobile and aircraft parts and packaging in printed electronic circuitry. Aromatic polyimides synthesized from aromatic monomers generally possess excellent thermal stability and mechanical properties[2]. However, many of these polymers are insoluble and infusible, rendering them impossible to process by conventional methods, i.e. their processibility was one of their drawbacks. Therefore, much effort has been expended on synthesizing tractable polyimides that maintain reasonably high strength and thermal stability[3,4]. Mainly, there are two methods to improving the processibility of polyimides. One is the improvement of their solubility, worked on by Harris and Lanier[5] and other scientists[6]. They successfully produced several organo-soluble polyimides[7] by using aromatic monomers with bulky side-groups. The other method is the improvement of their thermoplasticity. This method was chosen by the National Aeronautics and Space Administration (NASA) and Mitsui Toatsu Chemicals, Inc., and the melt-processable polyimide, LARC #1500[8,9] was produced. In order to improve thermoplasticity of polyimides, Yamaguchi and Ohta[10] investigated the relationship between chemical structures of polyimides and their T_g values by using bis(aminophenoxy)benzene (APB) isomers and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) as aromatic monomers, and reported that T_g values of obtained polyimides depended strongly on the amino-substituted position of the diamine monomers used. Kumar and Gupta[11] also studied the processability of aromatic thermoplastic polyimide obtained from bis(aminophenoxy)benzophenone (BAPB). However, systematic study of the relationship between chemical structure of a polyimide and its thermoplasticity was not carried out. In this research work, the improvement of melt-processability of aromatic polyimides was investigated in order to establish the relationship between chemical structures and their thermoplasticity.

EXPERIMENTAL

Starting materials

4-Chloronitrobenzene, 1,3-dinitrobenzene, 1,3-diaminobenzene [1b], 1,4-diaminobenzene [1a] are products of Mitsui Toatsu Chemicals, Inc. 4,4′-Diaminodiphenylether [2a] was received from Wakayama Seika Co., Ltd. 3-Aminophenol and 4-aminophenol were obtained from Tokyo Kasei Kogyo Co., Ltd. and used as received. 1,3,5-Trichlorobenzene, 4,4′-dichlorodiphenylsulfone, 4,4′-dichlorobenzophenone, resorcinol, and hydroquinone were obtained from Aldrich Chemical Co. and used as received. Diphenol compounds which were used as starting materials for diamene synthesis, 2,2-bis(4-hydroxyphenyl)propane, 4,4′-dihydroxybiphenyl, 4,4′-dihydroxydiphenylether, 4,4′-dihydroxydiphenylsulfide, 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane were obtained from commercial sources and used as received. Pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) were obtained from Daicel Chemical Co. Ltd. 3,3′,4,4′-biphenyl tetracarboxylic dianhydride (BPDA)

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was obtained from Mitsubishi Kasei Kogyo Co., Ltd. 3,3′,4,4′-Diphenylether tetracarboxylic dianhydride (ODPA), and 1,4-bis(3,4-dicarboxyphenoxy)benzene-dianhydride (HQDA) were obtained from Occidental Chemicals, Inc. 2,2-Bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) was obtained from Hoechst Chemikalien Co. Ltd., and 3,3′,4,4′-diphenylsulfone tetracarboxylic dianhydride (SODA) was obtained from New Japan Chemical Co., Ltd., and used as received.

Monomer synthesis

Typical procedures for synthesizing ether diamines in this research work and melting points (m.p.) of obtained diamines are reported.

Synthesis of ether diamines having two benzene rings

3,3′-Diaminodiphenylether (3,3′-ODA) and, 3,4′-diaminodiphenylether (3,4′-ODA) were synthesized according to the method of previous work[12]. 3,3′-ODA [2c]; m.p. 81–82°C. 3,4′-ODA [2b]; m.p. 74–75°C.

Synthesis of ether diamines having three benzene rings

A typical procedure for preparing ether diamine having three benzene rings, 1,3-bis(3-aminophenoxy)-benzene [3d], was as follows. In a 2-litre flask equipped with a stirrer and a water-separator were fed 120 g (1.1 mol) 3-aminophenol, 75 g (1.15 mol) granular potassium hydroxide, 500 ml 1,3-dimethyl-2-imidazolidinone (DMI) and 50 ml xylene. The temperature was raised while passing nitrogen over with stirring, to remove the water content in the reaction system by azeotropical removal with xylene. The amount of water removed was 20.5 ml. A solution obtained from 250 ml of DMI and 91 g (0.5 mol) of 1,3,5-trichlorobenzene was added over 1 h, and then the mixture was kept at 145–150°C for 5 h with removal of xylene from the system. The temperature was then raised to 170–180°C, to carry out the reaction, for 18 h. After completion of the reaction, DMI solvent was distilled off under a reduced pressure of 50–70 mmHg. The amount of recovered DMI was 690 ml. The distillation residue was fed into 1.5 l, with vigorous stirring, to separate a brown oily substance as a lower layer. This brown oily substance was raw 1,3-bis(3-aminophenoxy)-5-chlorobenzene. To the separated brown oily substance by decantation was added 520 g (2.5 mol) of 6 N HCl aqueous solution, and the substance was dissolved by heating. The solution was allowed to cool to precipitate out 1,3-bis(3-aminophenoxy) 5-chlorobenzene hydrochloride, which was then filtered out and dried. 174.4 g (0.436 mol) of 1,3-bis(3-aminophenoxy)-5-chlorobenzene hydrochloride was then fed into a closed glass vessel with 54.5 g (1.31 mol) of granular sodium hydroxide, 3.5 g of 5% Pd-C catalyst and 870 ml of methanol. Hydrogen was introduced with vigorous stirring. Reaction was carried out at ambient temperature for 3 h to absorb 9.6 l of hydrogen. No more absorption was observed, showing that the reaction was completed. The reaction mixture was successively filtered to remove insoluble residue, and then 870 ml of conc. HCl was added to the filtrate to precipitate white crystals of 1,3-bis(3-aminophenoxy)benzene hydrochloride. The crystal was filtered, washed with isopropanol and dried. This 1,3-bis(3-aminophenoxy)benzene hydrochloride was dissolved in water and neutralized with dilute aqueous ammonia to precipitate white crystal, followed by filtering, washing with water and drying to yield 102 g (70% based on 1,3,5-trichlorobenzene) of 1,3-bis(3-aminophenoxy)benzene; m.p. 105–107°C.

Elemental analysis: Calculated for $C_{18}H_{16}N_2O_2$: C 73.95%, H 5.52%, N 9.58%. Found: C 73.88%, H 5.70%, N 9.51%.

The other ether diamines with three benzene rings were synthesized from 1,3-dinitrobenzene or 4-chloronitrobenzene with diphenol compounds according to the previous method. 1,4-Bis(3-aminophenoxy)benzene [3c] (m.p. 98–100°C) was synthesized from hydroquinone and 1,3-dinitrobenzene followed by reduction. 1,4-Bis(4-aminophenoxy)benzene [3a] (m.p. 172–173°C) was synthesized from hydroquinone and 4-chloronitrobenzene followed by reduction. 1,3-Bis(4-aminophenoxy)-benzene [3b] (m.p. 115–117°C) was synthesized from resorcinol and 4-chloronitrobenzene followed by reduction.

Synthesis of ether diamines having four benzene rings

A typical procedure for preparing *meta*-amino-substituted ether diamine with four benzene rings (4,4′-bis(3-aminophenoxy)diphenylether [4a-m]) was as follows: A 2-litre five-necked round bottom flask containing 258.9 g (1.54 mol) 1,3-dinitrobenzene, 141.6 g (0.70 mol) 4,4′-dihydroxydiphenylether, 232.2 g (1.68 mol) potassium carbonate, 120 ml toluene and 1.3 l of *N*,*N*-dimethylformamide (DMF) were fitted with a mechanical stirrer, condenser with a Dean-Stark trap, nitrogen pad and a thermometer. This mixture was heated to 140°C with stirring. After the heating of this mixture at 150°C for 17 h under nitrogen atmosphere, it was cooled down to ambient temperature. An insoluble inorganic residue was filtered off and filtrate was obtained. 1.2 l DMF was removed using a rotary evaporator, and then concentrated filtrate was poured into 700 ml of methanol. The precipitated brown powder was collected by filtration, followed by through-washing with 200 ml of methanol. It was dried at 60°C. The yield was 241.5 g (77.6%). A 2-l five-necked round bottom flask containing 241.5 g (0.543 mol) 4,4′-bis(3-nitrophenoxy)diphenylether, 0.433 g (0.0016 mol) ferric chloride, 12.1 g active carbon and 800 ml ethyleneglycol monomethyl ether was fitted with a mechanical stirrer, condenser, nitrogen pad and a thermometer. This mixture was heated to 90°C with stirring and 136.0 g (2.17 mol) of hydrazine hydrate (80%) was dropped into the mixture during 4 h. Then this mixture was heated to 110°C for 2 h with stirring, and then an insoluble residue was filtered off and the filtrate was obtained. Ethyleneglycol monomethyl ether was removed using a rotary evaporator, and the oil obtained was recrystallized from a mixture of conc. HCl, water and NaCl. The precipitated powder was filtered out and dissolved in 665 ml of ethyleneglycol monomethyl ether, and then neutralized using aqueous ammonia (28%). The powder was collected by filtration. A mixture of this powder, 14.3 g of active carbon, 600 ml of ethyleneglycol monomethyl ether and 400 ml of water were heated to 60°C for 30 min, and then the active carbon was filtered off under hot conditions and the filtrate was cooled down to ambient temperature. The white precipitated powder was collected by filtration, followed by thorough washing with 200 ml of mixed solvent (ethyleneglycol monomethyl ether/water = 60/40 wt/wt). It was dried at 60°C. The yield of 4,4′-bis(3-aminophenoxy)diphenylether was 111.2 g (53.3%); m.p. 114–115°C.

Elemental analysis: Calculated for $C_{24}H_{20}N_2O_3$: C 75.00%, H 5.47%, N 7.29%. Found: C 74.98%, H 5.63%, N 7.13%.

The other *meta*-amino-substituted ether diamines were synthesized by almost the same method as mentioned above. Synthesized *meta*-amino-substituted diamines were: 4,4′-bis(3-aminophenoxy)diphenyl [4b-m] (m.p. 144.5–145.5°C); 4,4′-bis(3-aminophenoxy)diphenylsulfone [4c-m] (m.p. 134.5–135.5°C); 4,4′-bis(3-aminophenoxy)diphenylsulfide [4d-m] (m.p. 112.8–114.4°C); 4,4′-bis(3-aminophenoxy)benzophenone [4e-m] (m.p. 143.0–144.5°C); 2,2-bis[4-(3-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane [4g-m]; (m.p. 134.9–137.5°C), 2,2-bis[4-(3-aminophenoxy)phenyl]propane [4f-m]; (m.p. 106–108°C).

A typical procedure[13] for preparing *para*-amino-substituted ether diamine with four benzene rings (4,4′-bis(4-aminophenoxy)benzophenone [4e-p] was as follows: A 2-litre five-necked round bottom flask containing 160.2 g (1.46 mol) 4-aminophenol, 176.4 g (0.70 mol) 4,4′-dichlorobenzophenone, 84 g KOH (96%), and 1050 g *N*-methyl-2-pyrrolidinone (NMP) was fitted with a mechanical stirrer, a condenser with a Dean-Stark trap, a nitrogen pad and a thermometer. This mixture was heated to 170–175°C with stirring. After heating this mixture at 170–175°C for 3 h under nitrogen atmosphere, it was cooled down to ambient temperature. This mixture was poured into 5.6 l of water, and then precipitated powder was collected by filtration. A mixture of the obtained powder, 2.7 l of water, 150 g of conc. HCl, 14 g of active carbon and 1250 ml of isopropanol was heated to 65°C for 30 min and the insoluble residue was filtered off under hot conditions. The obtained filtrate, i.e. the solution of 4,4′-bis(4-aminophenoxy)benzophenone hydrochloride, was neutralized with dilute aqueous ammonia to precipitate white crystals. The precipitated white crystals were filtered out, washed with water; and dried to yield 196 g (68%) of 4,4′-bis(4-aminophenoxy)benzophenone; m.p. 154–156°C.

Elemental analysis: Calculated for $C_{25}H_{20}N_2O_3$: C 75.76%, H 5.05%, N 7.07%. Found: C 75.28%, H 5.18%, N 7.03%.

The other *para*-amino-substituted ether diamines were synthesized by almost the same method as mentioned above. Synthesized *para*-amino-substituted diamines were: 4,4′-bis(4-aminophenoxy)biphenyl [4b-p] (m.p. 197.0–198.0°C); 4,4′-bis(4-aminophenoxy)diphenylsulfone [4c-p] (m.p. 194.5–196.5°C); 4,4′-bis(4-aminophenoxy)diphenylether [4a-p] (m.p. 125.9–127.9°C); 4,4′-bis(4-aminophenoxy)diphenylsulfide [4d-p] (m.p. 124.0–125.6°C); 2,2-bis[4-(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane [4g-p] (m.p. 159.0–161.0°C); 2,2-bis[4-(4-aminophenoxy)phenyl]propane [4f-p] (m.p. 124.8–126.8°C).

Polymer synthesis

A typical procedure for polyimide synthesis was as follows: A mixture of 18.05 g (0.0582 mol) of ODPA, 12.02 g (0.0600 mol) of 3,3′-ODA, 0.53 g (0.0036 mol) of phthalic anhydride which was a termination of a polymer chain end, 0.84 g (0.009 mol) of γ-picoline in 123 g of *m*-cresol was stirred at 150°C for 4 h, and then after cooling down, the reaction mixture was poured into methanol. The precipitated polyimide was collected by filtration, followed by thorough washing with methanol and dried in a forced air oven to a temperature around the T_g of the polyimide. The other polyimide powders were prepared by the same method as mentioned above.

MEASUREMENTS

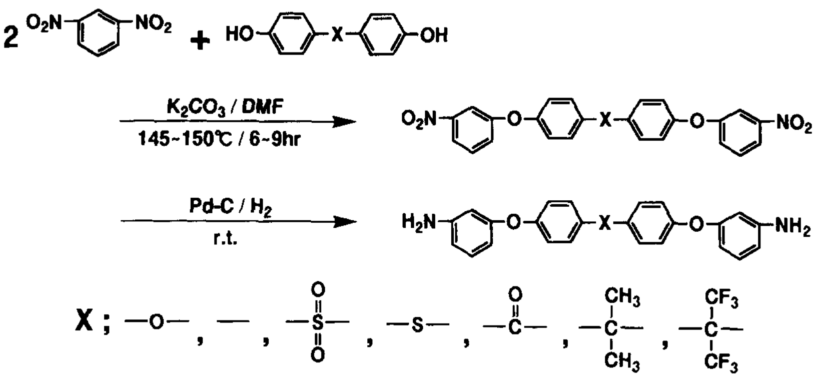
The inherent viscosities (ηs) of polyimides were obtained at a concentration of 0.5% in a solvent (*p*-chlorophenol/phenol = 9/1 wt/wt) at 35°C. Glass transition temperatures (T_gs) and melting temperatures (T_ms) of polyimides were determined using a Shimadzu 40 type differential scanning calorimeter (d.s.c.) with a 16°C min^{-1} heating rate in N_2. T_g values were taken at the inflection point of the ΔT *versus* temperature curve, and T_m values were taken at endothermic peak temperatures from the d.s.c. curve. Thermo-oxidative stability of polyimide were estimated by 5% weight reduction temperature in air (T_{d5}), using a Shimadzu 40 type thermogravimetric analyser (t.g.a.) with a 10°C min^{-1} heating rate. Melt-flow start temperature was determined by using a Flow-Tester (Shimadzu Flowtester CFT-500) setting an orifice with 1 mm diameter and 10 mm length, under 100 kg cm^{-2} load with a 5°C min^{-1} heating rate. Melt-flow viscosities of polyimides at 420°C were also determined by using a Flow-Tester under a 100 kg cm^{-2} load.

RESULTS AND DISCUSSION

Synthesis procedure of *meta*-amino-substituted ether diamine having four benzene rings are shown in *Scheme 1*. Basically, *meta*-amino-substituted diamines are synthesized from 1,3-dinitrobenzene and corresponding dihydroxy compounds by nitro-displacement reaction[14,15] followed by reduction. Yields of diamines based on dihydroxy compounds were around 55–80%. *Para*-amino-substituted diamines are synthesized from 4-aminophenol and corresponding dichloro compounds or 4-chloronitrobenzene and corresponding dihydroxy compounds followed by reduction. In the case of *para*-amino-substituted diamines, their yields were normally around 75–95%. Structures of diamines used in this research work and their entry numbers are summarized in *Figure 1*.

Polyimides were synthesized from ether diamines summarized in *Figure 1* and tetracarboxylic dianhydrides, according to *Scheme 2*. Inherent viscosities of synthesized polyimide powders were controlled to around 0.5 dl g^{-1} by selecting the optimum mole ratio between diamine and tetracarboxylic dianhydride. The polymer chain ends were terminated using phthalic anhydride as an end-capper[9].

The effect of chain length of ether diamine monomer on T_gs of obtained polyimides was studied by using polyimides synthesized from ether diamines having a different number of benzene rings and ODPA, and the result is summarized in *Table 1*. Inherent viscosities (ηs) of the polyimides [P2–P8] were controlled to 0.45–0.54 dl g^{-1}. P1–P4 were obtained by using *para*-amino-substituted diamines [1a–4a-p], and P5–P8 were obtained by using *meta*-amino-substituted diamines



Scheme 1

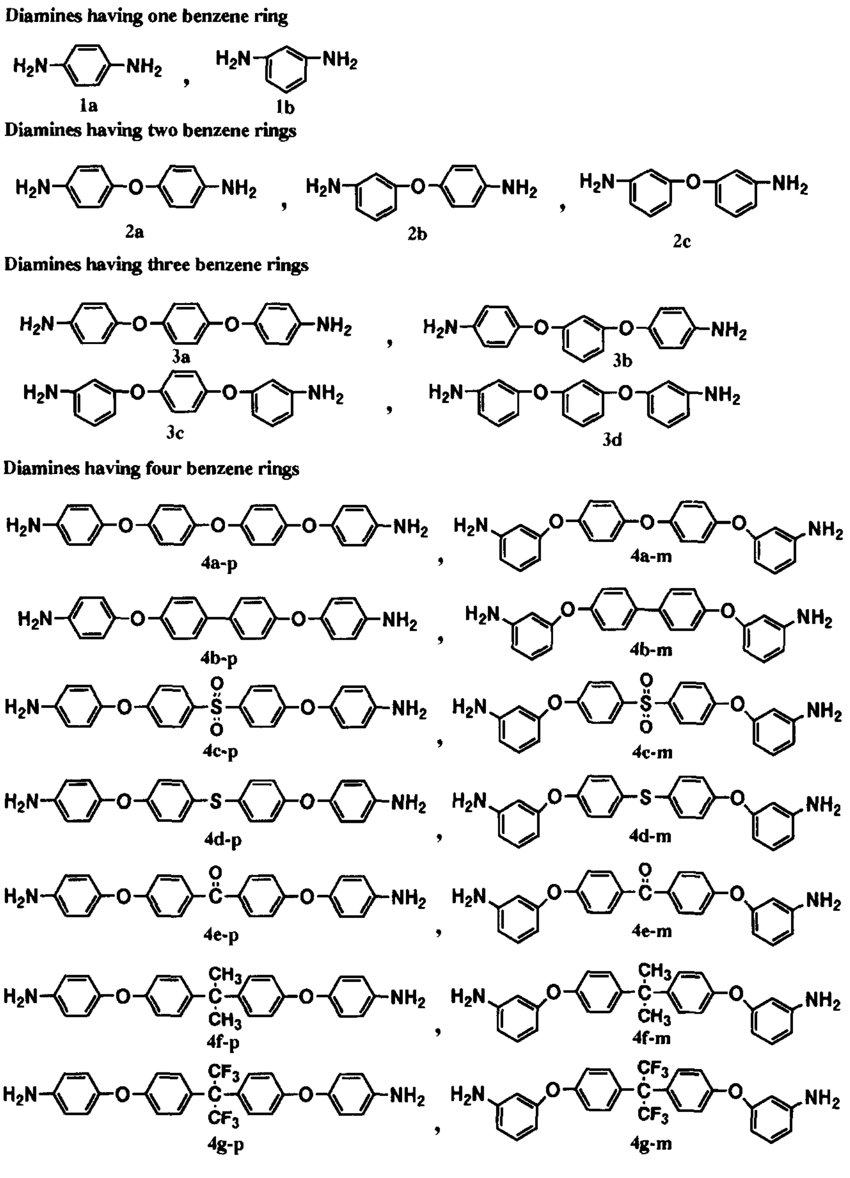
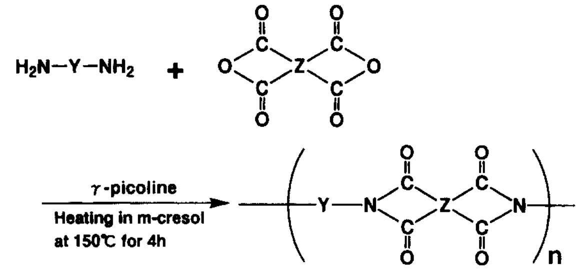


Figure 1 Diamines used for polyimides synthesis.

[1b, 2c, 3c, 4a-m]. T_g values of polyimides [P1–P4] decrease with increasing chain length of diamines [1a–4a-p], and those of polyimides [P5–P8] decrease according to increase of chain length of diamines [1b, 2c, 3c, 4a–m]. In contrast their T_ms ranged from 318 to 491°C and showed no clear relationship between chain length of used diamines. These results suggest that T_g value of polyimide can be controlled from 181 to 326°C by selecting ether diamine having suitable chain length.

The effect of chain length of ether diamines used as monomers for polyimides synthesis on the T_g value of obtained polyimides is summarized in *Figure 2*. From the result, it can be seen that T_g values of polyimides [P1–P4] from *para*-amino-substituted diamines [1a–4a-p] are



Scheme 2

higher than those of polyimides [P5–P8] from *meta*-amino-substituted diamines [1b, 2c, 3c, 4a–m], at the same time, the difference in T_g values between polyimides [P1–P4] and polyimides [P5–P8] decreases according to the increase in the number of benzene rings in ether diamines used.

The effect of the amino-substituted position of the ether diamine on the T_g of obtained polyimides was studied by using ether diamine isomers. T_gs and T_ms of polyimides synthesized from various ether diamine isomers having two or three benzene rings and ODPA were summarized in *Table 2*. Polyimides [P2, P9, P10] were obtained from ODPA and ether diamines having two benzene rings, and then polyimides [P8, P11–P13] were obtained from ODPA and ether diamines with three benzene rings. Inherent viscosities of these polyimides summarized in *Table 2* were controlled to 0.45–0.53 dl g^{-1}. Polyimides except for P10 and P13, showed T_ms. P10 and P13 were synthesized from 2c to 3d ether diamines, respectively. 2c and 3d diamines are *meta*-amino-substituted diamines having *meta*-ether linkage as shown in *Figure 1*. Therefore, the polyimides [P10, P13] obtained from these diamines are more flexible than the other polyimides. Because of these flexible structures of the crystalline phase in polymer was not observed in the case of P10 and P13.

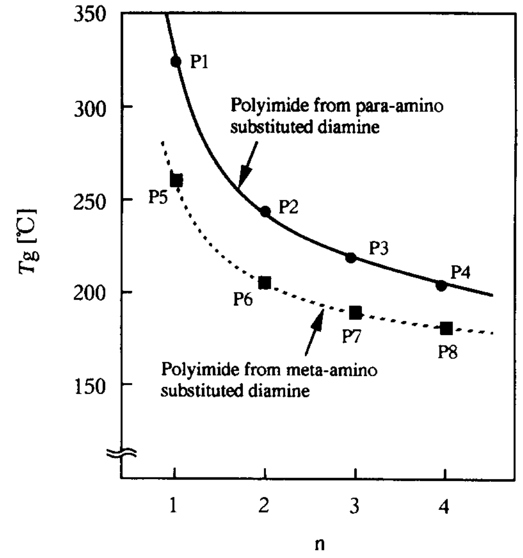


Figure 2 Effect of chain length of ether diamine on T_g of polyimide

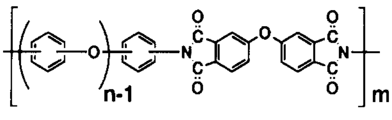
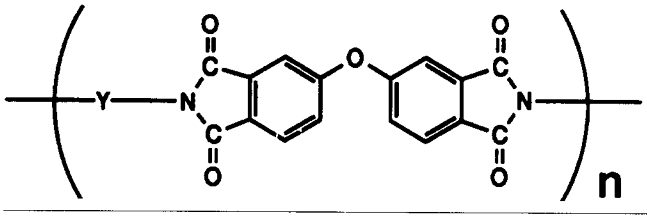
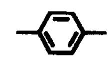
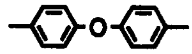
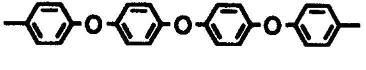
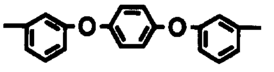
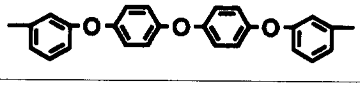


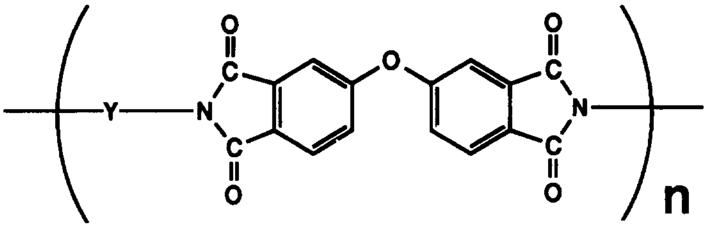
Table 1 Characterization of polyimides obtained from ether diamines having different chain length

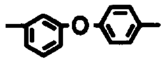
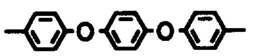


Polyimide	Dianhydride	Diamine	Y	η (dl g^{-1})[a]	T_g (°C)[b]	T_m (°C)[b]
P1	ODPA	1a		I.S.[c]	326	N.D.[d]
P2	ODPA	2a		0.52	242	374
P3	ODPA	3a		0.50	222	428
P4	ODPA	4a-p		0.45	204	332
P5	ODPA	1b		0.47	261	491
P6	ODPA	2c		0.49	205	N.D.
P7	ODPA	3c		0.45	189	318
P8	ODPA	4a-m		0.54	181	N.D.

[a] Inherent viscosity (η) determined on 0.5% solutions in a solvent (*p*-chlorophenol/phenol = 9/1 wt/wt) at 35°C
[b] D.s.c. at a heating rate of 16°C min^{-1}
[c] Insoluble in a solvent for η measurement
[d] Not detected

Table 2 Characterization of polyimides obtained from ether diamine isomers having two or three benzene rings



Polyimide	Dianhydride	Diamine	Y	η (dl g^{-1})^a	T_g (°C)^b	T_m (°C)^b
P2	ODPA	2a		0.52	242	374
P9	ODPA	2b		0.50	219	325
P10	ODPA	2c		0.49	205	N.D.^{c}
P11	ODPA	3a		0.50	222	428
P12	ODPA	3b		0.50	201	341
P8	ODPA	3c		0.45	189	318
P13	ODPA	3d		0.53	168	N.D.

^{a} Inherent viscosity (η) determined on 0.5% solutions in a solvent (p-chlorophenol/phenol = 9/1 wt/wt) at 35°C

^{b} D.s.c. at a heating rate of 16°C min^{-1}

^{c} Not detected

From the comparison of T_g values of P2, P9 and P10, it was found that T_g values were decreasing from 242 to 205°C according to the increase of *meta*-linkage contents in ether diamine structure as shown in *Table 2*. This trend was also observed in the case of polyimides [P8, P11–P13] which were obtained from ODPA and ether diamines having three benzene rings. P8 and P11–P13 were structural isomer polyimides. T_g values of these structural isomer polyimides ranged from 222 to 168°C. T_g values of P11 and P12, which were obtained from *para*-amino-substituted ether diamines [3a, 3b] were higher than those of P8 and P13 which were obtained from *meta*-amino-substituted ether diamines [3c, 3d]. The difference in the T_g values between P11 and P12 was only 21°C, while the difference in the T_g values between P11 and P8 was 38°C. This result suggests that the difference in the amino-substituted position in ether diamine has a greater effect than the difference in the ether linkage position among the benzene rings of ether diamine on the T_g value difference of the polyimides obtained. A similar trend was observed in the case of polyimides from PDMA and ether diamines having four benzene rings and various kinds of moieties (*Table 3*).

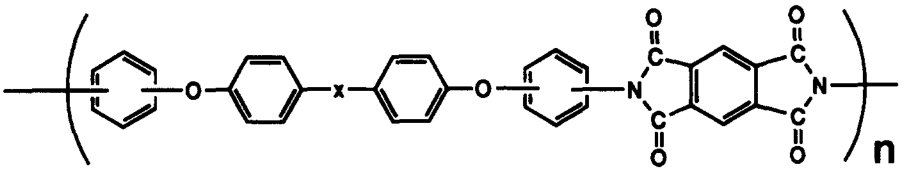
Table 3 indicates that the amino substituted position in ether diamine markedly affected T_g of the polyimide [P14–P25]. Inherent viscosities (ηs) of these polyimides, summarized in this table, were controlled to around 0.46–0.54 dl g^{-1}. On account of this, the different T_g values of these polyimides were attributed to chemical structures of repeating structure units.

T_gs of polyimides from *meta*-amino-substituted ether diamines (having $-m$ diamines) ranged from 208 to 254°C, and those from *para*-amino-substituted ether diamines (having $-p$ diamines) ranged from 288 to 320°C. It is assumed that the above T_g difference is caused by the different moiety in ether diamine, having an amino substituent at the same position. The difference in T_g values was only 32–46°C among polyimides obtained from ether diamine having an amino substituent at the same position. At the same time, as shown in Table 3, it was found that the differences in amino-substituted position in ether diamine had a greater effect than differences in the moiety in ether diamine on T_g of the obtained polyimide, from the comparison of T_g values of structural isomer polyimides. The differences in T_g values among structural isomer polyimides were 59–92°C.

T_gs of various kinds of polyimides from *meta*-amino-substituted diamines with four benzene rings, and tetracarboxylic dianhydrides received from commercial sources, are summarized in *Table 4*. Inherent viscosities (ηs) of all polyimides summarized in this table were controlled to around 0.5 dl g^{-1}. This result indicated that T_gs of polyimides could be controlled from 169 to 254°C by selecting suitable structures of polyimides, i.e. by suitable selection of monomer combination. It was also found that T_g values of polyimides were decreasing according to the increase of structural flexibility of selected monomers.

The relationship between melt-flowability of polyimide and its structure was studied. Melt-flowability was estimated from the melt-flow start temperature determined by using a Flow-Tester, setting an orifice with 1 mm diameter and 10 mm length size, under 100 kg cm^{-2} load with a 5°C min^{-1} heating rate. Melt-flow start temperatures of various kinds of polyimides and their structures are summarized in *Table 5*. As it is known that organic compounds are unstable at temperatures higher than

Table 3 Effect of amino substituted position in ether diamine having four benzene rings on T_g of polyimide



Polyimide	Dianhydride	Diamine	X	η (dl g^{-1})^a	T_g (°C)^b
P14	PMDA	4d-p	–S–	0.49	288
P15	PMDA	4d-m		0.48	2.08
P16	PMDA	4f-p	$-\overset{CH_3}{\underset{CH_3}{C}}-$	0.51	304
P17	PMDA	4f-m		0.54	218
P18	PMDA	4g-p	$-\overset{CF_3}{\underset{CF_3}{C}}-$	0.53	310
P19	PMDA	4g-m		0.49	218
P20	PMDA	4e-p	$-\overset{O}{\overset{\parallel}{C}}-$	0.46	289
P21	PMDA	4e-m		0.51	230
P22	PMDA	4b-p	——	I.S.^{c}	310
P23	PMDA	4b-m		0.49	250
P24	PMDA	4c-p	$-\overset{O}{\underset{O}{S}}-$	0.47	320
P25	PMDA	4c-m		0.49	254

[a] Inherent viscosity (η) determined on 0.5% solutions in a solvent (p-chlorophenol/phenol = 9/1 wt/wt) at 35°C

[b] D.s.c. at a heating rate of 16°C min^{-1}

[c] Insoluble in a solvent for η measurement

500°C, this was selected as the maximum test temperature. To summarize, melt-flow start temperatures measured at a temperature lower than 500°C are summarized in *Table 5*, so N.F. in this table means that melt flow was not observed at a temperature lower than 500°C.

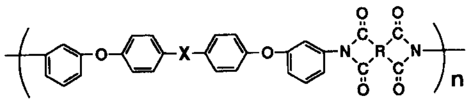
As shown in *Table 5*, in the case of *para*-amino-substituted diamines, melt-flowable polyimides were obtained from diamines having more than two benzene rings and tetracarboxylic dianhydrides having flexible moiety in monomer structures, such as BPDA, BTDA, ODPA and HQDA. Melt-flowable polyimide was not obtained from PMDA, while, in the case of *meta*-amino-substituted diamines, melt-flowable polyimide was obtained from 1,3-diaminobenzene [1b] having only one benzene ring and HQDA. Its melt-flow start temperature was 290°C. Polyimides from PMDA and *meta*-amino-substituted diamines with more than three benzene rings showed melt-flow start temperatures ranging from 260 to 385°C. In the case of polyimides from 3d diamine and dianhydride monomers such as PMDA, BPDA, BTDA and ODPA, flexibility in the dianhydride monomer increases in the order PMDA, BPDA, BTDA and ODPA. Melt-flow start temperatures of these polyimides reduce from 315 to 220°C, according to the order of flexibility in the dianhydride monomer. The tendency of the melt-flow start temperature to reduce with increase in flexibility in monomer structures is observed.

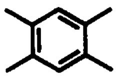
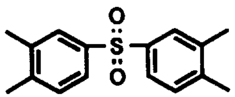
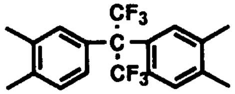
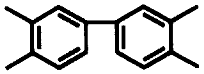
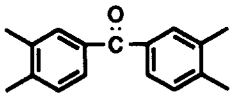
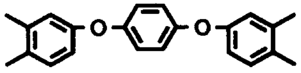
Two kinds of polyimides having high T_g values in *Table 3*, polyimide A [from 4,4′-bis(3-aminophenoxy-phenyl)sulfone [4c-m] and PMDA] and polyimide B [from 4,4′-bis(3-aminophenoxy)biphenyl [4b-m] and PMDA], were selected, and their basic thermal property, and melt processability were studied (*Table 6*). As shown in this table, melt viscosities of these polyimides were 4100–4500 Pa s at 420°C. The low melt-viscosity values suggested that the melt-processable properties of polyimides A and B are outstanding, even though they showed high T_g values, 254°C and 250°C, respectively. T_d5 values of polyimide A and B were 539°C and 550°C respectively. T_d5 values showed the temperature of 5% weight loss in air, therefore these high T_d5 values of these polyimides show excellent thermo-oxidative stability. These results suggest that the two polyimides A and B have excellent heat-resistant properties as super engineering plastics, at the same time showing melt-processibility for a wide variety of mouldings, which is clearly different from any type of currently available thermoset or semi-thermoplastic polyimides.

SUMMARY AND CONCLUSIONS

A series of aromatic ether diamines having different numbers of benzene rings, different amino-substituted positions and different moieties in their structures was synthesized. By using these synthesized ether diamines and commercially available tetracarboxylic dianhydrides, various kinds of polyimides having almost the same molecular weights were synthesized. Polymer chain ends of synthesized polyimides were terminated by using phthalic anhydride as an end-capper. T_g values of polyimides and their thermoplasticity were obtained, and related with their chemical structures of repeating structure units. It was found that the T_g of a polyimide depended on the chain-length and *meta*-linkage contents

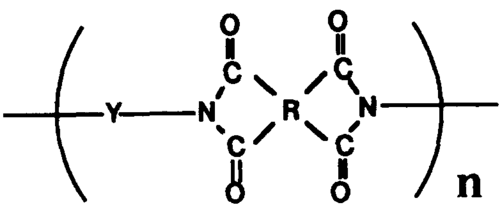
Table 4 T_gs of polyimides and their chemical structures



X	R, T_g (°C)[a]						
	 PMDA	 DSDA	 6FDA	 BPDA	 BTDA	 ODPA	 HQDA
$-\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}-$	254	237	236	235	224	211	200
—	250	232	228	221	216	199	195
$-\overset{\mathrm{O}}{\mathrm{C}}-$	230	222	214	211	205	193	183
$-\overset{\mathrm{CF_3}}{\underset{\mathrm{CF_3}}{\mathrm{C}}}-$	218	215	209	208	201	189	182
$-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-$	218	212	202	202	195	184	178
$-\mathrm{O}-$	212	208	200	199	192	181	171
$-\mathrm{S}-$	208	207	200	195	186	175	169

[a] D.s.c. at a heating rate of 16°C min^{-1}

Table 5 Melt-flow start temperature of polyimide and its structure



Diamine (Y)			Melt flow start temperature (°C) Dianhydride (R)				
Amino-substituted position	Number of benzene rings	Structure	PMDA	BPDA	BTDA	ODPA	HQDA
para	1	1a	N.F.[a]	N.F.	N.F.	N.F.	N.F.
	2	2a	N.F.	N.F.	440	360	350
		3a	N.F.	N.F.	N.F.	430	–
	3	3b	N.F.	N.F.	445	345	–
	4	4a–p	N.F.	–	–	335	–
		4b–p	N.F.	430	–	–	–
meta	1	1b	N.F.	N.F.	N.F.	N.F.	290
	2	2c	N.F.	310	355	280	290
	3	3c	–	390	–	320	–
		3d	315	285	260	220	–
	4	4a–m	260	270	260	245	235
		4b–m	385	300	325	270	–
		4c–m	330	300	285	275	265
		4d–m	265	255	260	235	230
		4e–m	280	275	270	250	265
		4f–m	345	–	–	–	–
		4g–m	380	265	265	255	240

[a] Melt flow was not observed at a temperature lower than 500°C
[b] Did not measure

Table 6 Basic properties of melt processible polyimides

Items	Test method	Unit	Polyimide A	Polyimide B
η	–	$\mathrm{dl\,g^{-1}}$	0.48	0.50
T_g	d.s.c.	°C	254	250
T_m	d.s.c.	°C	N.D.	388
T_d5^a	t.g.a.	°C	539	550
Melt viscosity (at 420°C under 100 kg load)	Flow Tester	Pa • sec	4520	4100

[a] 5% weight reduction temperature in air

of ether diamine used, and the difference in amino-substituted positions in the ether diamine. Polyimides whose η values were controlled to around 0.5 $\mathrm{dl\,g^{-1}}$ were synthesized from *meta*-amino-substituted ether diamines having four benzene rings and various kinds of tetracarboxylic dianhydrides, and their T_g values were studied. It was then found that T_g values could be controlled by a suitable selection of monomer combinations. By using molecular weight-controlled polyimides, their melt-flowability was also studied, and it was indicated that polyimides from *meta*-amino-substituted diamines showed good melt-flowability. Finally two kinds of polyimides having high T_g values, polyimide A [4,4′-bis(3-aminophenoxyphenyl)sulfone/PMDA] and polyimide B [4,4′-bis(3-aminophenoxy)biphenyl/PMDA] were selected and characterized, i.e. high T_g values and excellent melt-processibility were obtained.

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