

Preparation and characterization of novel aromatic polyimides having 4,5-di(1,3-phenylene)imidazole structure

Fumihiko Akutsu*, Mari Inoki, Mamoru Sawano, Yoshio Kasashima, Kiyoshi Naruchi and Masatoshi Miura

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba-shi 263, Japan

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Novel diamines 4,5-di(3-aminophenyl)imidazole (**1**), 4,5-di(3-aminophenyl)-2-methylimidazole (**2**), and 4,5-di(3-aminophenyl)-2-phenylimidazole (**3**) were prepared, and novel aromatic polyimides were synthesized by ring-opening polyaddition of aromatic tetracarboxylic dianhydrides to the diamines, followed by thermal cyclodehydration. The inherent viscosities of the polyamic acids ranged from 0.37 to 0.98 dl g⁻¹. Glass transition temperatures (T_g s) of the polyimides were found in the range from 279 to 353°C, and weight residues at 600°C were above 82%. Interestingly, although polyimide **10c** derived from **3** and 3,3',4,4'-biphenyltetracarboxylic dianhydride (**4c**) has a side pendant phenyl group, the T_g of **10c** was approximately 30°C higher than that of the corresponding polyimide derived from **1** and **4c**, which do not have the side pendant. Some polyimides exhibited good solubility. Particularly, **10c** was soluble in pyridine at room temperature and *m*-cresol at 80°C at 2.0% (w/v) as well as possessing high thermal resistance supported by the T_g of 346°C and the weight residue at 600°C of 87%. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: aromatic polyimides; solubility; thermal properties)

INTRODUCTION

Aromatic polyimides, which show high thermal resistance and excellent mechanical properties, are used as films and adhesives in various fields^{1,2}. However, aromatic polyimides cannot be easily processed because they possess high glass transition temperatures (T_g s) and melting points as well as poor solubility in organic solvents. In order to overcome these problems, several attempts at improving the solubility have been investigated. However, in many cases, this improvement is accompanied by reducing thermal resistance. Recent research has suggested that the introduction of a rigid, polar and bulky unit to polyimide structure can effectively improve the solubility without lowering high thermal resistance^{3–8}. We previously reported that polyimides derived from 2,3-di(4-aminophenyl)quinoxaline⁹ (4-DAPQ) and those derived from 4,5-di(4-aminophenyl)-2-phenylimidazole¹⁰ (4-DAPI), of which the structures are rigid, polar, and bulky, possessed high thermal resistance and good solubility. Similarly, polyimides synthesized from 2,3-di(3-aminophenyl)quinoxaline (3-DAPQ), which has two 1,3-phenylene units instead of 1,4-phenylene units in 4-DAPQ, showed better solubility than the corresponding polyimides derived from 4-DAPQ. However, their thermal resistance lowered somewhat¹¹. In the present study, novel diamines 4,5-di(3-aminophenyl)imidazole (**1**), 4,5-di(3-aminophenyl)-2-methylimidazole (**2**), and 4,5-di(3-aminophenyl)-2-phenylimidazole (**3**) were prepared as the monomer. Novel polyimides were synthesized from the diamines as shown in Scheme 1, and their solubility and thermal properties were studied. Since the imidazole unit

has higher polarity than the quinoxaline unit, the introduction of the 4,5-di(1,3-phenylene)imidazole unit to the main chain of polyimides was expected to maintain high thermal resistance and to improve solubility. In addition, the properties of the polyimides derived from **3** were compared to those of the corresponding polyimides derived from 4-DAPI or those derived from 3-DAPQ in order to determine the relationship between the structures of polyimides and their properties.

RESULTS AND DISCUSSION

Syntheses of monomers

Novel diamines **1**, **2** and **3** were synthesized from 3,3'-dinitrobenzil¹² (**11**) as the starting material, as shown in Scheme 2. **11** was prepared by nitration of benzil¹², but it was reported that the nitration of benzil was accompanied by the formation of isomers^{11,12}, and that the isolation led to a remarkable decrease in the yield¹¹. Accordingly, crude 3,3'-dinitrobenzil was used, and purification was carried out after the formation of the imidazole ring. The formation of the imidazole ring was performed according to the method reported by van Es *et al.*^{13,14} Reactions of **11** with hexamethylenetetramine or aldehydes yielded 2,3-di(3-nitrophenyl)imidazoles **12**, **13** and **14**. Reductions of 2,3-di(3-nitrophenyl)imidazoles using tin dichloride and hydrochloric acid afforded the diamines. The products were identified as diamines **1**, **2** and **3** by elemental analysis and spectroscopic data, respectively.

Syntheses of polyimides

Polyimides **8**, **9** and **10** were synthesized by the two-step

* To whom correspondence should be addressed

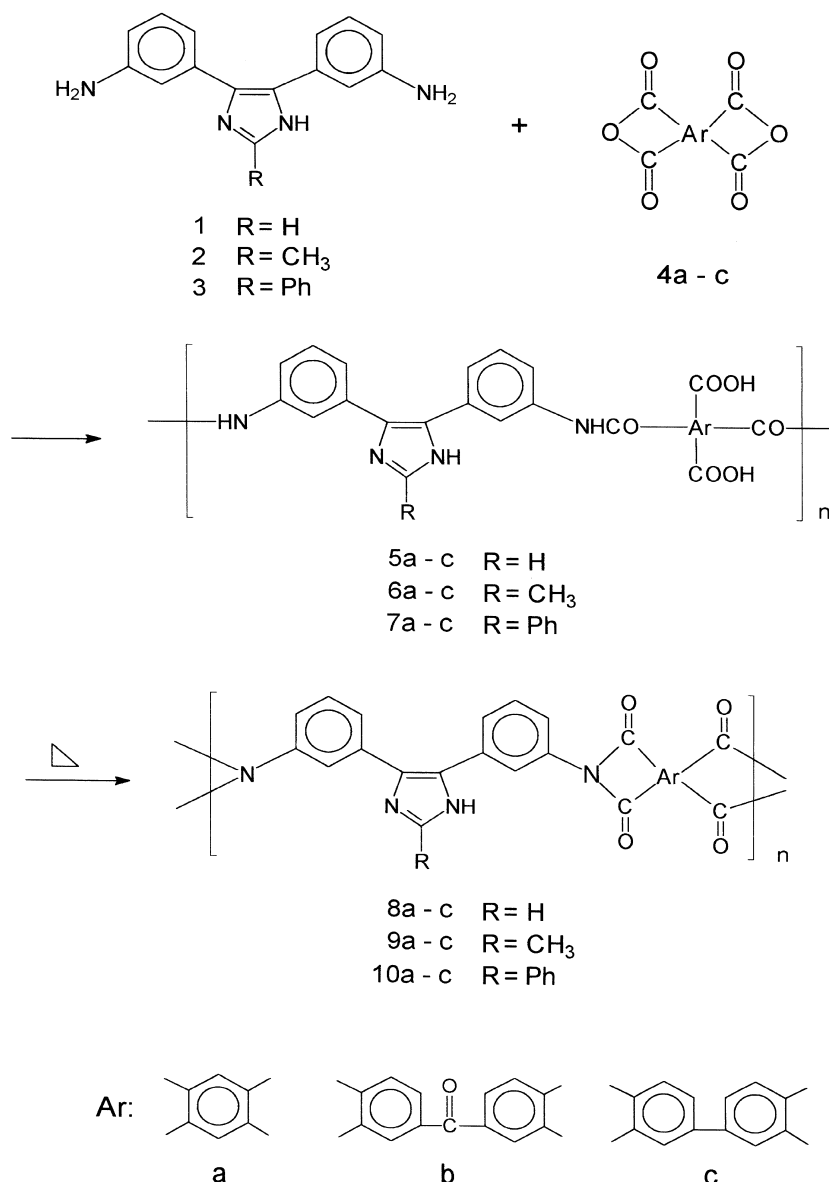
procedure¹⁵ as follows: polyamic acids **5**, **6** and **7** were prepared by ring-opening polyaddition of aromatic tetracarboxylic dianhydrides **4** to the diamines, followed by thermal cyclodehydration under reduced pressure, as shown in Scheme 1. Pyromellitic dianhydride (**4a**), 4,4'-carbonyldiphthalic anhydride (**4b**), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (**4c**) were used as the aromatic tetracarboxylic dianhydride monomers. The results of ring-opening polyaddition are listed in Table 1. When *N,N*-dimethylacetamide (DMAc) was used as the solvent, a precipitate formed during the polymerization of **6a** (run 7), but the other polyadditions proceeded in a homogeneous system. When the monomer concentration was decreased from 0.17 mol l⁻¹ to 0.040 mol l⁻¹ (run 8), the precipitation occurred. Even when the solvent was changed from DMAc to dimethyl sulfoxide (DMSO) (run 9), precipitation occurred. Therefore, the inherent viscosity of **6a** could not be measured. Polyadditions of **5a**, **5b**, **5c** and **7a** were carried out as the conditions of the second step were changed from 3 h at room temperature to 6 h at 60°C (runs 2, 4, 6 and 13). The inherent viscosities of the polyamic acids were improved in runs 2 and 4, but no improvement of the

inherent viscosities showed in runs 6 and 13. Thus, the inherent viscosities of the obtained polyamic acids ranged from 0.37 to 0.98 dl g⁻¹.

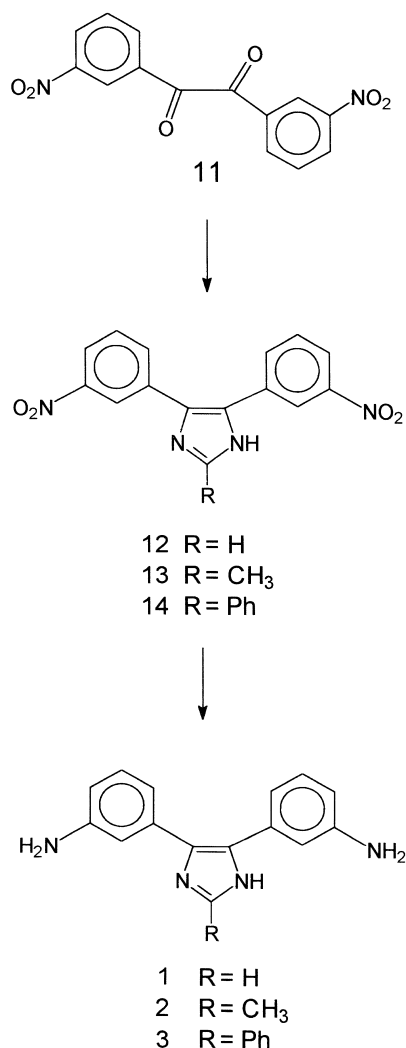
Thermal cyclodehydration of the polyamic acids was conducted in an electric furnace at 170°C for 2 h, and at 300°C for 1 h under reduced pressure. After heating, the colour of the obtained films darkened. Completion of cyclodehydration was confirmed by the presence of the characteristic imide absorptions near 1380, 1710 and 1780 cm⁻¹ in the infra-red (i.r.) spectrum, respectively.

Thermal properties of polyimides

*T*_gs were determined by differential scanning calorimetry (d.s.c.). The temperatures at 10% weight loss (*T*_{d10s}) and weight residues at 600°C were determined by thermogravimetric analysis (t.g.a.) under a nitrogen atmosphere. Thermal properties of polyimides are tabulated in Table 2. The thermogram of **8b**, obtained by d.s.c., showed no clear endotherm corresponding to the glass transition. *T*_gs of the other polyimides ranged from 279°C to 353°C. *T*_gs of **8a**, **9a**, **10a** and **10c** were particularly high, above 345°C, despite the unsymmetrical and zigzag structures. These high *T*_gs



Scheme 1.



Scheme 2.

result from high polarity and rigidity of the 4,5-di(1,3-phenylene)imidazole unit. Although **10c** contains a side pendant phenyl group, the T_g was approximately 30°C higher than those of **8c** and **9c**. The reason is not clear. In contrast, little difference was observed in the T_g s of **8**, **9** and **10** with respect to polyimides **a** or **b**. This may be due to the large influence of the 4,5-di(1,3-phenylene)imidazole unit which masks the effects of the side pendants.

T_{d10S} of the polyimides ranged from 567°C to 610°C, and weight residues at 600°C were above 82%. In particular, those of **8a**, **8c** and **9c** were above 90%. The polyimides exhibited excellent thermal stability, due to the highly phenylated structure and the thermally stable imidazole unit.

Solubility of polyimides

The solubility of the polyimides at 2.0% (w/v) in various organic solvents was examined at room temperature and at 80°C. The results are summarized in Table 3. Polyimides **8** exhibited poor solubility, whereas **9** and **10** indicated good solubility for aromatic polyimides. **9b**, **9c** and **10b** were soluble in formic acid at room temperature, and 1-methyl-2-pyrrolidone (NMP) and *m*-cresol at 80°C. In particular, **10c** was soluble in pyridine at room temperature and *m*-cresol at 80°C although showing the high T_g of 346°C.

The solubility of **9** and **10** was better than that of corresponding **8**. But, the T_g s of **9** and **10** did not differ from those of corresponding **8**. Since the side pendant phenyl group in **10** is not coplanar to the imidazole ring slightly, the resonance effect is considered little. Thus, it seems that these pendant groups play a role in an electron-donating group to the imidazole unit and increase electron density of nitrogen atoms in the imidazole unit, leading to an increase in polarity. This higher polarity may cause a stronger intermolecular dipole-dipole interaction between the molecular chain and molecules of the aprotic polar solvent.

X-ray diffraction patterns of **8**, **9** and **10** indicate that the

Table 1 Results of the preparations of polyamic acids^a

Run	Polyamic acid	First step	Second step	$\frac{\eta_{inh}^b}{dl\ g^{-1}}$	Appearance ^c
1	5a	1 h at -17°C	3 h at r.t. ^d	0.30	H
2	5a	1 h at -17°C	6 h at 60°C	0.60	H
3	5b	1 h at -17°C	3 h at r.t.	0.33	H
4	5b	1 h at -17°C	6 h at 60°C	0.50	H
5	5c	1 h at -17°C	3 h at r.t.	0.98	H
6	5c	1 h at -17°C	6 h at 60°C	0.76	H
7	6a	1 h at -17°C	3 h at r.t.	—	P
8 ^e	6a	1 h at -17°C	3 h at r.t.	—	P
9 ^f	6a	1 h at -17°C	3 h at r.t.	—	P
10	6b	1 h at -17°C	3 h at r.t.	0.40	H
11	6c	1 h at -17°C	3 h at r.t.	0.43	H
12	7a	1 h at -17°C	3 h at r.t.	0.94	H
13	7a	1 h at -17°C	6 h at 60°C	0.51	H
14	7b	1 h at -17°C	3 h at r.t.	0.67	H
15	7c	1 h at -17°C	3 h at r.t.	0.37	H

^aPolymerization was carried out with 1.0 mmol of each monomer and 6.0 ml of DMAc. Obtained polyamic acids were all pale yellow

^bInherent viscosity, measured at a concentration of 0.66 g dl⁻¹ in DMAc at 30°C

^cH, Homogeneous system; P, precipitation

^dr.t.; Room temperature

^ePolymerization was carried out with 1.0 mmol of each monomer and 25.0 ml of DMAc

^fDMSO was used as a solvent instead of DMAc

Table 2 Thermal properties of polyimides

Run ^a	Polymer	T _g ^b °C	T _{d10} ^c °C	Weight residue ^d at 600°C %
2	8a	353	602	91
4	8b	— ^e	592	88
5	8c	317	606	91
7	9a	351	568	82
10	9b	291	576	85
11	9c	317	610	92
12	10a	351	589	87
14	10b	279	567	84
15	10c	346	585	87

^aSample run numbers appear in Table 1^bMeasured by d.s.c. in a nitrogen atmosphere; heating rate, 10 K min⁻¹^cTemperature at 10% weight loss, observed with t.g.a. in a nitrogen atmosphere^dObserved with t.g.a^eNot observed**Table 3** Solubilities of polyimides^a

Run ^b	Polymer	Py	<i>m</i> -Cre	DMAc	NMP	HCOOH	DMSO	H ₂ SO ₄
2	8a	—	—	—	—	(+)	—	+
4	8b	—	(±)	(SW)	(±)	(+)	—	+
5	8c	—	(±)	—	(±)	SW	—	+
7	9a	—	±	—	±	+	—	+
10	9b	(SW)	(+)	±	(+)	+	(±)	+
11	9c	(±)	(+)	(±)	(+)	+	(±)	+
12	10a	—	—	—	±	+	—	+
14	10b	—	(+)	+	(+)	+	(±)	+
15	10c	+	(+)	±	±	±	(±)	+

^aMeasured at 2.0% (w/v). Data in parentheses were obtained during heating. The symbols have the following meanings: +, soluble; ±, partially soluble; SW, swelling; —, insoluble; Py, pyridine; *m*-Cre, *m*-cresol; DMAc, *N,N*-dimethylacetamide; NMP, 1-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide^bSample run numbers appear in Table 1

polyimides were all amorphous. The introduction of a zigzag and unsymmetrical structure to the main chains of polyimides led to the amorphous nature, contributing to the improved solubility.

Comparison of the properties of **10** with those of **15**

The solubility and T_g s of polyimides **10** were compared with those of polyimides **15** derived from 4-DAPI¹⁰, as shown in Scheme 3. The inherent viscosities of samples of **15** were almost as high as those of corresponding **10**. The solubility of **10** was lower than that of corresponding **15**. T_g s of **10** were also lower than those of corresponding **15**. We previously demonstrated that a polyimide with higher polarity has the higher T_g and better solubility¹⁶. The introduction of two 1,3-phenylene units instead of two 1,4-phenylene units appears to decrease the interaction between the electron-withdrawing imidazole group at the 1 position and the electron-withdrawing imide group at the 3 position, which may reduce the overall polarity of **10**. Thus, it is considered that this reduced polarity led to the lower T_g and lower solubility in aprotic polar solvents.

Comparison of the properties of **10** with those of **16**

The solubility and T_g s of polyimides **10** were compared with those of **16** derived from 3-DAPQ¹¹. The solubility of **10** was similar to that of **16**, whereas the T_g s of **10** were higher than those of **16**. The quinoxaline structure is as bulky as the 2-phenylimidazole unit, but more symmetrical.

Further, the resonance effect of the quinoxaline structure is much larger than the 2-phenylimidazole unit. Therefore, the polarity of the quinoxaline unit is lower than that of the 2-phenylimidazole unit. Thus, the higher T_g s of polyimides **10** are attributed to the higher polarity of the 2-phenylimidazole unit.

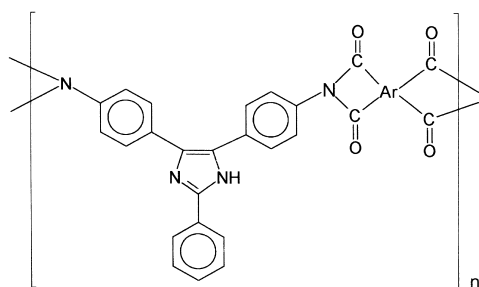
Conclusion

It is concluded that the introduction of the 2-methyl-4,5-di(1,3-phenylene)imidazole unit or the 2-phenyl-4,5-di(1,3-phenylene)imidazole unit into the main chains of aromatic polyimides improves solubility maintaining high thermal resistance.

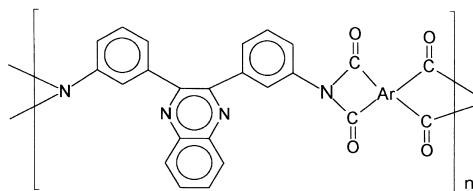
EXPERIMENTAL

4,5-Di(3-nitrophenyl)imidazoles

4,5-Di(3-nitrophenyl)imidazole **12** was synthesized as follows. Acetic acid (950 ml), ammonium nitrate (113 g, 1.4 mol), hexamethylenetetramine (12.2 g, 87 mmol), and crude **11**¹¹ (45.0 g, 0.15 mol) were placed in a flask, and the mixture was refluxed for 5 h. After cooling to room temperature, the reaction mixture was filtrated, poured into water (2 l), and made basic with aqueous ammonia solution for precipitation. The collected yellow precipitate was washed with ethanol. The product was recrystallized from acetone to give yellow needles (16% yield from benzil), melting point (m.p.), 253.0–254.5°C. I.r. (KBr,



15



16

Scheme 3.

cm^{-1}): 1524 and 1348 (NO_2). Analysis calculated for $\text{C}_{15}\text{H}_{10}\text{N}_4\text{O}_4$ (310.3): C, 58.06; H, 3.25; N, 18.06. Found: C, 58.05; H, 3.29; N, 18.06.

2-Methyl-4,5-di(3-nitrophenyl)imidazole **13** was prepared from ammonium acetate (90.21 g, 1.17 mol), paraldehyde (9.6 ml), acetic acid (810 ml), and crude **11** (46.6 g, 0.16 mol) by the similar procedure. The crude product was recrystallized from methanol to obtain yellow powders (yield from benzil 20%), m.p. 263.0–263.0°C. I.r. (KBr , cm^{-1}): 1524 and 1348 (NO_2). Analysis calculated for $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_4$ (324.3): C, 59.26; H, 3.73; N, 17.28. Found: C, 59.31; H, 3.77; N, 17.20.

4,5-Di(3-nitrophenyl)-2-phenylimidazole **14** was prepared as follows. Ammonium acetate (100.5 g, 1.30 mol), benzaldehyde (49.5 ml), acetic acid (550 ml), and crude **11** (40.1 g, 0.13 mol) were placed in a flask. The mixture was refluxed for 1 h, and cooled to room temperature to form precipitate. The product was washed with water, with ethanol, and recrystallized from acetone to obtain yellow powders (yield from benzil 21%), m.p. 290.4–291.3°C. I.r. (KBr , cm^{-1}): 1524 and 1348 (NO_2). Analysis calculated for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_4$ (386.4): C, 65.28; H, 3.65; N, 14.50. Found: C, 65.14; H, 3.60; N, 14.59.

4,5-Di(3-aminophenyl)imidazoles

A typical procedure, giving 4,5-di(3-aminophenyl)imidazole **1**, is as follows: Into a four-necked flask equipped with a nitrogen inlet, a reflux condenser, a magnetic stirrer bar and a thermometer, hydrochloric acid (280 ml) and tin dichloride dihydrate (157.7 g, 0.70 mol) were added, and the mixture was dissolved on heating. The solution was cooled with an ice bath, and **12** (23.82 g, 76.8 mmol) were added. The mixture was stirred at 70°C for 4 h under a nitrogen atmosphere. The precipitating product was collected by filtration, and dissolved in water (100 ml). The solution was poured into sodium hydroxide aqueous solution (20 wt%, 500 ml) for precipitation. The product was washed with sodium hydroxide aqueous solution (10 wt%), and with water, and recrystallized from water

with an activated charcoal under a nitrogen atmosphere to afford pale brown needles (yield 67%), m.p. 200.5–200.8°C. I.r. (KBr , cm^{-1}): 3440 and 3356 (N-H). ^1H n.m.r. (DMSO-d_6 , ppm): 4.92 (s, 4H, $-\text{NH}_2$), 6.60–7.00 (m, 8H, Ar-H) 7.60 (m, 1H, imidazole $\text{C}^2\text{-H}$), and 12.11 (s, 1H, imidazole N-H). ^{13}C n.m.r. (DMSO-d_6 , ppm): 112.67, 113.39, 115.76 (Ar C^2 , C^4 and C^6), 128.50 (imidazole C^4), 133.85, 134.41 (Ar C^1 and C^5), 136.14 (imidazole C^2), and 148.21 (Ar C^3). Analysis calculated for $\text{C}_{15}\text{H}_{14}\text{N}_4$ (250.3): C, 71.97; H, 5.64; N, 22.39. Found: C, 71.77; H, 5.61; N, 22.44.

Other diamines were obtained by a similar procedure.

4,5-Di(3-aminophenyl)-2-methylimidazole **2**: recrystallization from water gave pale brown needles, m.p. 212.8–213.5°C. I.r. (KBr , cm^{-1}): 3440 and 3348 (N-H). ^1H n.m.r. (CDCl_3 : $\text{DMSO-d}_6 = 1:1$ by volume, ppm): 2.30 (s, 3H, $-\text{CH}_3$), 4.84 (s, 4H, $-\text{NH}_2$), and 6.40–7.00 (m, 8H, Ar-H) 11.77 (s, 1H, imidazole N-H). ^{13}C n.m.r. (DMSO-d_6 , ppm): 13.67 ($-\text{CH}_3$), 112.52, 113.29, 115.65 (Ar C^2 , C^4 and C^6), 128.47 (imidazole C^4), 133.87, 134.15 (Ar C^1 and C^5), 143.09 (imidazole C^2), and 148.27 (Ar C^3). Analysis calculated for $\text{C}_{16}\text{H}_{16}\text{N}_4$ (264.3): C, 72.70; H, 6.10; N, 21.20. Found: C, 72.75; H, 6.34; N, 20.99.

4,5-Di(3-aminophenyl)-2-phenylimidazole **3**: recrystallization from methanol-water afforded pale brown needles, m.p. 242.5–243.5°C. I.r. (KBr , cm^{-1}): 3440 and 3382 (N-H). ^1H n.m.r. (DMSO-d_6 , ppm): 4.94 (s, 4H, $-\text{NH}_2$), and 6.40–8.10 (m, 13H, Ar-H), and 12.48 (s, 1H, imidazole N-H). ^{13}C n.m.r. (DMSO-d_6 , ppm): 112.31, 113.45, 115.27, 128.33, 128.68, 129.01, 130.64, 132.04, 135.91, 137.31, 148.39 and 148.72. Analysis calculated for $\text{C}_{21}\text{H}_{18}\text{N}_4$ (326.4): C, 77.27; H, 5.56; N, 17.17. Found: C, 77.20; H, 5.50; N, 17.21.

Ring-opening polyaddition and cyclodehydration of the polyimide

Aromatic tetracarboxylic dianhydrides **4a**, **4b** and **4c** were obtained commercially, recrystallized from acetic anhydride, and sublimed under reduced pressure just before polymerization.

A typical procedure (run 2) is as follows. In a four-necked 10 ml reaction tube equipped with a mechanical stirrer and a nitrogen inlet having a calcium chloride tube, diamine **1** (0.250 g, 1.0 mmol) and DMAc (4.0 ml) were placed. The mixture was chilled to -20°C , and **4a** (0.218 g, 1.0 mmol) and DMAc (2.0 ml) were added. It was stirred at -18°C for 1 h, and then at 60°C for 6 h. The reaction mixture was allowed to stand overnight at room temperature. A 1.0 ml portion of the reaction mixture was removed for viscosity measurement. The remaining mixture was spread on a glass plate and the solvent was removed at 50°C for 2.5 h, and at 70°C for 1 h. The obtained film was dried under reduced pressure at 70°C . Inherent viscosity of polyamic acid **5a** was 0.60 dl g^{-1} (0.66 g dl^{-1} in DMAc at 30°C). I.r. (film, cm^{-1}): 3500–2800 (O-H), 1720 (C=O), 1610 and 1564 (amide I, II).

Thermal cyclodehydration of polyamic acid **5a** was performed by heating at 180°C for 2 h and then 300°C for 1 h in an electric furnace under reduced pressure. As soon as heating was over, the product was taken out of an electric furnace and cooled to room temperature. A colour of the obtained film darkened after the thermal treatment. I.r. (film, cm^{-1}): 1776, 1714 (imide C=O), 1380 (imide C-N). Analysis calculated for $(\text{C}_{25}\text{H}_{12}\text{N}_4\text{O}_4)_n$ (432.4): C, 69.44; H, 2.80; N, 12.96. Found: C, 69.43; H, 3.22; N, 10.41.

Other polyimides were synthesized by a similar procedure.

Measurements

T_{d10} s and weight residues at 600°C were obtained by t.g.a. (MAC science TG-DTA 4100). T_g s were determined by d.s.c. (Rigaku DSC 8055D1). These thermoanalytical measurements were performed under the following conditions: heating rate = 10 K min⁻¹; nitrogen atmosphere. T_g s were determined by second scannings. I.r. spectra were recorded on a Hitachi 270-30 spectrophotometer. ¹H n.m.r. spectra were recorded at a 400 MHz JEOL LA-400 FT-NMR spectrometer. ¹³C n.m.r. spectra were recorded at a 100 MHz JEOL LA-400 FT-NMR spectrometer. Wide angle X-ray diffraction patterns were obtained for specimens on a Rigaku KG X-ray diffraction apparatus with Cu-K_α radiation (25 kv, 10 mA) using virgin samples.

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