

Synthesis and Characterization of Novel Aromatic Polyamides and Polyimides Derived from 2,3-Di(3-aminophenyl)quinoxaline

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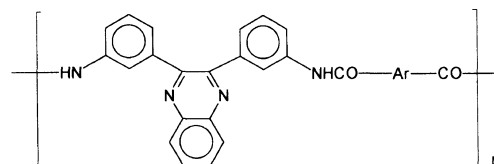
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ABSTRACT: A novel aromatic diamine 2,3-di(3-aminophenyl)quinoxaline (DAPQ) was prepared from benzil through three steps. New aromatic polyamides were synthesized by the direct polycondensation of DAPQ and several aromatic dicarboxylic acids. The polyamides were obtained almost quantitatively. The inherent viscosities ranged from 0.49 to 0.56 dl g⁻¹. The glass transition temperatures (*T*_gs) of the polyamides ranged from 258 to 291°C, and the temperatures at 10% weight loss (*T*_{d10}s) ranged between 515 and 546°C. Novel aromatic polyimides were synthesized by the ring-opening polyaddition of several aromatic tetracarboxylic dianhydrides to DAPQ, followed by thermal cyclodehydration. The polyamic acids indicated the inherent viscosities of 0.28–1.13 dl g⁻¹. *T*_gs of the polyimides ranged between 263 and 298°C, and *T*_{d10}s were above 550°C. The polyamides and polyimides were soluble in several organic solvents such as *m*-cresol.

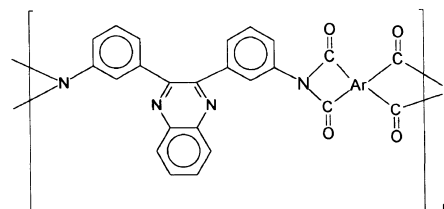
KEY WORDS Aromatic Polyamides / Aromatic Polyimides / Solubility / Thermal Properties /

Aromatic polyamides and polyimides have high thermal resistance and excellent mechanical properties. Therefore, these polymers are applied in various fields as high-performance engineering plastics.^{1,2} However, an important industrial problem is their low processability, which is caused by the poor solubility in many organic solvents and by the high melting points and glass-transition temperatures. The improvement of their solubility is consequently accompanied by lowering high thermal properties largely. One of the effective method without lowering high thermal properties is known to be the introduction of rigid and zigzag structures to main chains of polymers.^{3–12} We previously reported the polyamides and polyimides containing rigid and zigzag structures, such as the combination of 1,4-phenylene unit with 1,2-heteroarylene units, possessed high thermal behavior as well as good solubility.^{13–20}

In this article, novel aromatic polyamides **1** and polyimides **2** containing 2,3-di(1,3-phenylene)quinoxaline structure, as shown in Scheme 1, were synthesized and their properties were examined. Aromatic polyamides and polyimides introduced 2,3-di(1,4-phenylene)quinoxaline structure were found to indicate the high thermal properties and good solubility.^{14,17,20} The introduction of 1,3-phenylene unit, instead of 1,4-phenylene unit, to the polymer backbone is known to be effective against the improvement of the solubility of polymers. As the monomer, a new aromatic diamine having 2,3-quinoxalinediyl structure as well as 1,3-phenylene unit, 2,3-di(3-aminophenyl)quinoxaline (DAPQ) was prepared, and the polyamides and polyimides were synthesized from DAPQ. In addition, these properties were compared with those of polymers containing 2,3-di(1,4-phenylene)quinoxalinediyl structure^{14,20} in order to investigate a structural effect on properties of polyamides and polyimides.



1



2

Scheme 1.

EXPERIMENTAL

2,3-Di(3-nitrophenyl)quinoxaline **5**

In a flask equipped with a condenser was added 53 ml of fuming nitric acid (*d* = 1.52), and then 40.4 g (0.19 mol) of benzil **3** (Tokyo Kasei Kogyo Co., Ltd.) was added little by little during cooling with an ice bath. The mixture was refluxed for 5 h. After cooling to room temperature, the reaction mixture was poured into an ice water for precipitation. The precipitate was washed with water, and dried under reduced pressure. Crude yield 82%. IR (KBr, disk) 1680 (C=O), 1510 and 1350 cm⁻¹ (N–O).

In a flask were added 720 ml of acetic acid, 112.5 g (0.38 mol) of the crude nitration product, and 41.6 g (0.39 mol) of *o*-phenylenediamine. The mixture was refluxed for 5 h. After cooling to room temperature, the

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formed precipitate was collected by filtration, recrystallized from acetic acid three times to give pale brown needles; mp 213–214°C. Yield from **3** 51%. IR (KBr, disk) 1480 cm⁻¹ (C=N).

Anal. Calcd for C₂₀H₁₂N₄O₄ (372.3): C, 64.51%; H, 3.25%; N, 15.05%. Found: C, 64.56%; H, 3.35%; N, 14.98%.

DAPQ

In a 50-ml four-necked flask equipped with a nitrogen inlet, a reflux condenser, a magnetic stirrer bar and a thermometer were placed 200 ml of conc. hydrochloric acid and 101.2 g (0.45 mol) of stannous chloride, and dissolved on heating. The solution was cooled with an ice bath, and 20.84 g of **5** (56.0 mmol) was added. The mixture was stirred for 2 h during chilling, then for 1 day at room temperature under a nitrogen atmosphere. The reaction mixture was filtrated, and added to 900 ml of a 15-wt% aqueous solution of sodium hydroxide to obtain a yellow precipitate. The product was collected by filtration, and washed with an aqueous solution of sodium hydroxide, and with water. The product was dissolved in 50 ml of 3 M HCl, filtrated on heating, poured into a 5-wt% aqueous solution of sodium hydroxide for precipitation. The product was washed with water, and dried under reduced pressure. The crude product was recrystallized from aqueous methanol to afford yellow needles; mp 232–233°C. Yield 81%.

IR (KBr, disk) 3432, 3320 cm⁻¹ (N-H).

¹H NMR (400 MHz, DMSO-*d*₆): δ = 5.19 (s; 4H, -NH₂), 6.48 (m; 2H, Ar-H), 6.58 (m; 2H, Ar-H), 6.94 (m; 4H, Ar-H), 7.85 (m; 2H, quinoxaline-H), 8.10 (m; 2H, quinoxaline-H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 114.29 (Ar-C₂), 114.68 (Ar-C₄), 117.36 (Ar-C₆), 128.18 (quinoxaline-C₆), 128.63 (quinoxaline-C₅), 130.02 (Ar-C₅), 139.64 (Ar-C₁), 140.21 (quinoxaline-C₉), 148.49 (Ar-C₃), 153.73 (quinoxaline-C₂).

Anal. Calcd for C₂₀H₁₆N₄ (312.4): C, 76.90%; H, 5.16%; N, 17.94%. Found: C, 76.63%; H, 5.09%; N, 17.92%.

Other Monomers

Aromatic dicarboxylic acids, such as terephthalic acid (**6a**), isophthalic acid (**6b**), 4,4'-biphenyldicarboxylic acid (**6c**), were obtained commercially, and used after recrystallization (**6a** and **6b**, from methanol/water; **6c**, from benzene). Pyromellitic dianhydride (**9d**), 3,3',4,4'-biphenyltetracarboxylic dianhydride (**9e**), and 4,4'-carbonyldiphthalic anhydride (**9f**) were obtained commercially, recrystallized from acetic anhydride, and sublimated under reduced pressure just before polymerization.

Direct Polycondensation of Polyamides

A typical procedure is as follows. Into a four-necked 10-ml reaction tube equipped with a reflux condenser, a mechanical stirrer, and a nitrogen gas inlet having a calcium-chloride tube were placed 0.075 g lithium chloride, 0.225 g of calcium chloride, and 3.75 ml of 1-methyl-2-pyrrolidone (NMP). The mixture was heated with stirring under a nitrogen atmosphere until the salts were dissolved. After the mixture was cooled to room temperature, 0.249 g of isophthalic acid (1.50 mmol), 0.788 ml of

triphenyl phosphite (3.00 mmol), and 0.75 ml of pyridine were added. The mixture was stirred for 10 min, and 0.469 g of DAPQ (1.50 mmol) were added. The reaction mixture was heated at 115°C for 5 h with stirring. It was then cooled and poured into aqueous methanol (1 : 1 by volume). The precipitate was collected on a glass filter, washed with methanol in reflux and dried under reduced pressure. Yield 97%.

$\eta_{inh} = 0.56 \text{ dl g}^{-1}$ (0.5 g dl⁻¹ in conc. sulfuric acid at 30°C). IR (KBr, disk) 1664, 1536 cm⁻¹ (amide I, II).

Anal. Calcd for (C₂₈H₁₈N₂O₄)_n (442.5)_n: C, 76.00%; H, 4.10%; N, 12.67%. Found: C, 74.67%; H, 4.06%; N, 12.18%.

Other polyamides were synthesized by a similar procedure.

Ring-Opening Polyaddition and Cyclodehydration of Polyimides

A typical procedure 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, were placed 0.469 g of DAPQ (1.5 mmol) and 3.0 ml of *N,N*-dimethylacetamide (DMAc). The mixture was chilled to -18°C, to which were added 0.483 g of **9f** (1.5 mmol) and 2.0 ml of DMAc. It was stirred for 5 h, and then was allowed to stand over night at room temperature. A 0.40-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 90°C. The obtained film was dried under reduced pressure at 60°C. The inherent viscosity of the polyamic acid **10f** was 0.89 dl g⁻¹ (0.5 g dl⁻¹ in DMAc at 30°C). IR (film) 3500–2800 (O-H, N-H), 1720 (C=O), 1622, 1554 (amide I, II) cm⁻¹.

Thermal cyclodehydration of polyamic acid **10f** was performed by heating at 250°C for 2 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. IR (film) 1776, 1710 (imide C=O), 1370 (imide C-N) cm⁻¹.

Anal. Calcd for (C₃₇H₁₈N₄O₅)_n (598.6)_n: C, 74.24%; H, 3.03%; N, 9.36%. Found: C, 73.14%; H, 3.19%; N, 9.00%.

Other polyimides were synthesized by a similar procedure.

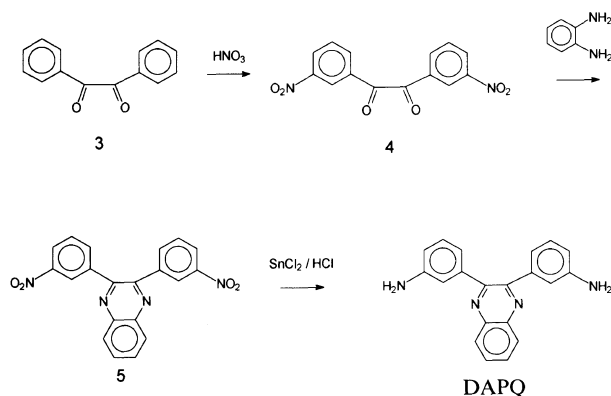
Measurements

Glass-transition temperatures (*T*_gs), temperatures at 10% weight loss (*T*_{410s}) and weight residues at 600°C were obtained by thermogravimetry (TG)-differential scanning calorimetry (DSC) (Rigaku TG-DSC 8055D1) under the following conditions: heating rate, 10 K min⁻¹; in a nitrogen atmosphere. *T*_gs were determined by second scanings. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. Wide angle X-ray diffraction patterns were obtained for specimens on a Rigaku XG X-ray diffraction apparatus with Cu-*K*_α radiation (25 kV, 10 mA) using virgin samples. NMR spectra were obtained with FT-NMR spectrometer (JEOL JNM-GSX400).

RESULTS AND DISCUSSION

Monomer Synthesis

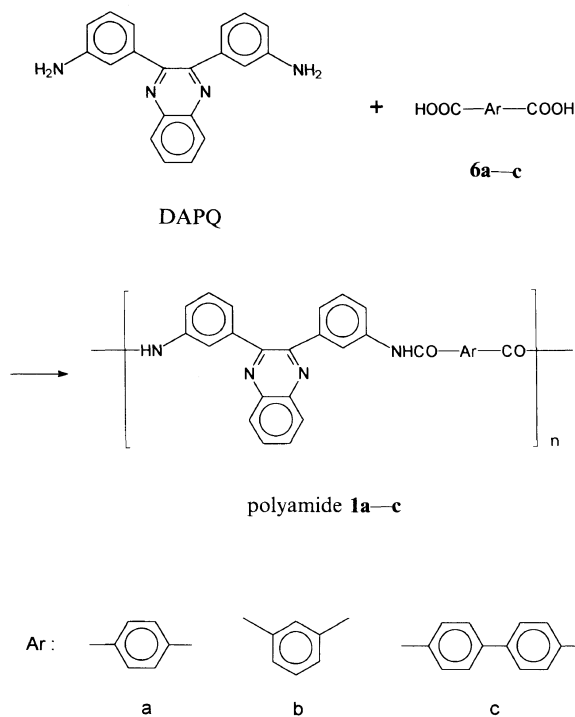
Novel diamine DAPQ was synthesized from benzil (**3**) through three steps, as shown in Scheme 2. 3,3'-Dinitrobenzil (**4**) was not isolated because nitration of **3** gave the isomeric mixture²¹ and the purification by recrystallization was accompanied by lowering the yield largely. 2,3-Di(3-nitrophenyl)quinoxaline (**5**) was prepared by the reaction of the crude nitration product with *o*-phenylenediamine for the formation of a quinoxaline ring.²² DAPQ was obtained by the reduction of **5** using stannous chloride and hydrochloric acid. The product was identified by elemental analysis and spectroscopic data as DAPQ.



Scheme 2.

Polyamide Synthesis

Polyamides **1** were prepared by direct polycondensation of DAPQ with several aromatic dicarboxylic acids, such as terephthalic acid (**6a**), isophthalic acid (**6b**), and 4,4'-biphenyldicarboxylic acid (**6c**), using triphenyl phosphite, pyridine, lithium chloride, and calcium chlo-



Scheme 3.

Table I. Results of polycondensations^a and thermal properties of polyamides

Polymer	Yield %	η_{inh}^b dl g ⁻¹	T_g^c °C	T_{d10}^d °C	Weight residue at 600°C/% ^e
1a	98	0.49	268	546	85
1b	97	0.56	258	528	85
1c	95	0.54	291	515	76

^a Polymerization was carried out with 1.50 mmol of each monomer, 75 mg of lithium chloride, 225 mg of calcium chloride, 0.788 ml of triphenyl phosphite, 0.75 ml of pyridine, and 3.75 ml of NMP at 115°C for 5 h. The polymerizations proceeded in a homogeneous system. The obtained polyamides were pale yellow. ^b Inherent viscosity, measured in conc. sulfuric acid (0.50 dl⁻¹) at 30°C. ^c Glass transition temperature, measured by DSC. ^d Temperature at 10% weight loss, determined by TG in a nitrogen atmosphere. ^e Determined by TG in a nitrogen atmosphere.

ride as condensation agents,²³⁻²⁵ as shown in Scheme 3. All polycondensations proceeded in a homogeneous system. The obtained polymers were identified by elemental analysis and IR spectra. The IR spectra of the polymers showed characteristic amide absorptions near 1660 and 1540 cm⁻¹. All polyamides were obtained almost quantitatively. The inherent viscosities of polyamides **1** ranged from 0.49 to 0.56 dl g⁻¹. The results are shown in Table I.

Thermal Properties and Solubility of Polyamides

T_g s were determined by differential scanning calorimetry (DSC). The temperatures at 10% weight loss (T_{d10} s) and weight residues at 600°C were determined by thermogravimetry (TG). Thermal behavior of polyamides is summarized in Table I. T_g s of polyamides **1** ranged from 258 to 291°C. T_{d10} s ranged between 515 and 546°C, and weight residues at 600°C was above 76%. The high thermal stability was due to the high ratio of aromatic rings in the polyamide structure and a thermally stable quinoxaline ring.

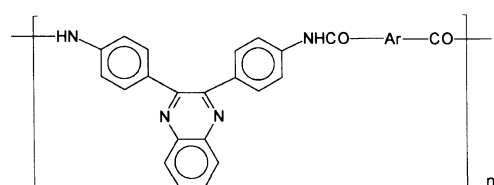
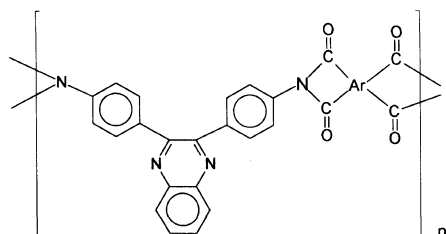
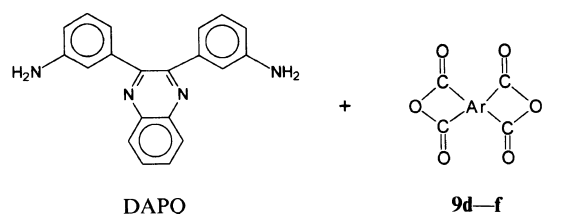
Solubilities in several organic solvents at 2.0% (w/v) are tabulated in Table II. Polyamides **1** showed high solubility. In particular, polyamide **1b** was soluble in conc. sulfuric acid, dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), hexamethylphosphoric triamide (HMPA), 1-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *m*-cresol, and pyridine at room temperature. X-Ray diffraction patterns showed that polyamides **1** were all amorphous. It was considered that the high solubility of **1** was due to the amorphous nature, induced by the introduction of zigzag and unsymmetrical 2,3-di(1,3-phenylene)quinoxaline structure to the polyamide backbone.

The solubility and T_g s of **1** were compared with those of corresponding polyamides **7** having 2,3-di(1,4-phenylene)quinoxaline structure¹⁴ as shown in Scheme 4, respectively. T_g s of polyamides **1** were lower than those of corresponding polyamides **7**, while having the almost equal values of the inherent viscosity. The solubility of **1** was higher than that of corresponding **7**. The lower T_g s and higher solubility of **1** were attributed to the more zigzag main-chain shape of polyamides **1** produced by the combination of 1,3-phenylene moiety and 2,3-quinoxalinediyl unit.

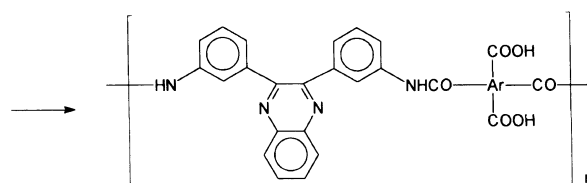
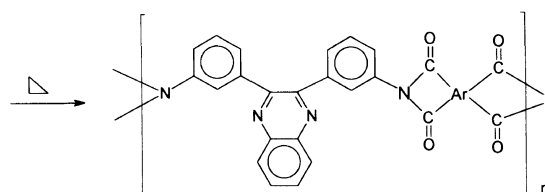
Table II. Solubilities^a of polyamides and polyimides

Polymer	Py	<i>m</i> -Cre	DMAc	NMP	HMPA	HCOOH	DMSO	H ₂ SO ₄
1a	±	+	+	+	+	±	+	+
1b	+	+	+	+	+	+	+	+
1c	—	±	±	±	±	±	±	+
2d	±	+	±	+	±	+	—	+
2e	±	+	—	±	—	—	—	+
2f	—	+	±	+	±	—	—	+

^a Measured at 2.0% (w/v). The symbols have the following meanings: +, soluble; ±, partially soluble; —, insoluble. Py, pyridine; *m*-Cre, *m*-cresol; DMAc, *N,N*-dimethylacetamide; NMP, 1-methyl-2-pyrrolidone; HMPA, hexamethylphosphoric triamide; DMSO, dimethylsulfoxide.

polyamide **7**polyimide **8****Scheme 4.**

DAPQ

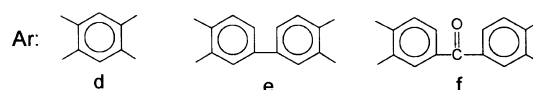
9d-f**10d-f**polyimide **2d-f****Table III.** Results of ring-opening polyadditions^a and thermal properties of polyimides

Polyimide	η_{inh}^b dl g ⁻¹	T_g^c °C	T_{d10}^d °C	Weight residue at 600°C/% ^e
2d	0.28	298	550	77
2e	1.13	286	579	86
2f	0.89	263	566	84

^a Polymerization was carried out with 1.5 mmol of each monomer and 5.0 ml of DMAc at -18°C for 5 h. The obtained polyamic acids were yellow. ^b Inherent viscosity of the corresponding polyamic acid, measured in DMAc (0.50 g dl⁻¹) at 30°C. ^c Glass transition temperature, measured by DSC. ^d Temperature at 10% weight loss, determined by TG in a nitrogen atmosphere. ^e Determined by TG in a nitrogen atmosphere.

Polyimide Synthesis

Polyimides **2** were synthesized by the two-step procedure²⁶ as shown in Scheme 5. Polyamic acids **10** were prepared by the ring-opening polyaddition of aromatic tetracarboxylic dianhydrides to DAPQ, followed by thermal cyclodehydration under reduced pressure. Pyromellitic dianhydride (**9d**), 3,3',4,4'-biphenyltetracarboxylic dianhydride (**9e**), and 4,4'-carbonyldiphthalic anhydride (**9f**) were used as the aromatic tetracarboxylic dianhydride monomers. The results of the ring-opening polyaddition were tabulated in Table

**Scheme 5.**

III. All polyadditions proceeded in a homogeneous system. The inherent viscosities of polyamic acids **10** ranged from 0.28 to 1.13 dl g⁻¹. The reason for the irregular low inherent viscosity of **10d** is not clear, which may be due to the lower reactivity of oligoamic acid caused by some steric effects.

The thermal cyclodehydrations of polyamic acids **10** were performed in an electric furnace at 250°C for 2 h under reduced pressure. The products were identified as polyimides **2** by IR spectroscopy and elemental analysis.

Thermal Properties and Solubility of Polyimides

Thermal properties of polyimides **2** are shown in Table III. T_g s of polyimides **2** ranged from 263 to 298°C. T_{d10} s of **2** was observed above 550°C, and weight residues at 600°C of **2** ranged between 77 and 86%. The solubility of polyimides **2** at 2.0% (w/v) are indicated in Table II. Polyimides **2** showed good solubility. **2e** was soluble in *m*-cresol and conc. sulfuric acid at room temperature.

2d and **2f** were further soluble in NMP. The introduction of zigzag and unsymmetrical 2,3-di(1,3-phenylene)quinoxaline structure was effective against the improvement of the solubility of aromatic polyimides. X-Ray diffraction patterns of **2** indicated the polyimides are all amorphous. The introduction of the zigzag and unsymmetrical structure to the polyimides caused the amorphous nature, which contributed to the improvement of the solubility.

Except for **2d**, the properties of **2** were compared with those of corresponding polyimides **8** containing 2,3-di(1,4-phenylene)quinoxaline structure,²⁰ as shown in Scheme 4, of which the values of inherent viscosity were almost equal. The solubility of **2** was better than that of **8**. T_g s of **2** were lower than those of **8**. These facts were attributed to the sparser molecular-chain packings of **2**, induced by the introduction of more unsymmetrical and zigzag 2,3-di(1,3-phenylene)quinoxaline structure.

CONCLUSION

Novel aromatic polyamides and polyimides having 2,3-di(1,3-phenylene)quinoxaline structure in the main chain possessed the high solubility and high thermal stability, respectively.

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