Synthesis and Properties of Aromatic Polyamides and Polyimides from 9,10-Dihydro-9,10-*o*-benzoanthracene-1,4-diamine

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ABSTRACT: Aromatic polyamides and polyimides were synthesized from 9,10-dihydro-9,10-*o*-benzoanthracene-1,4-diamine (2,5-triptycenediamine). Aromatic polyamides were synthesized by the low-temperature solution polycondensation, whose inherent viscosities were 0.67–1.68 dl g⁻¹. The polyamide from isophthaloyl dichloride was soluble in dimethylacetamide (DMAc), 1-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), dimethylsulfoxide (DMSO), and conc. sulfuric acid. The solubility was lower than that of corresponding polyamides from 2,7-triptycenediamine. This lowering was attributed to the more linear and symmetrical structure of the diamine component. The glass transition temperatures (*T*_gs) of the polyamides were 339–370°C and temperatures at 5% weight loss (*T*_d) were 442–482°C, which indicate that this polyamide has high thermal stability. These thermal properties were as high as those of polyamide from 2,7-triptycenediamine. The aromatic polyimides were synthesized by thermal cyclodehydration from polyamic acids prepared from the diamine with tetracarboxylic dianhydride by ring-opening polyaddition. The inherent viscosities of the polyamic acids were 0.65–0.87 dl g⁻¹. Polyimide from the diamine with 3,3',4,4'-sulfonyldiphenyltetracarboxylic dianhydride was soluble in DMAc, DMF, DMSO, and conc. sulfuric acid. *T*_gs of polyimides were 391–411°C and *T*_ds were up to 521°C, which were showed high values.

KEY WORDS 9,10-Dihydro-9,10-*o*-benzoanthracene-1,4-diamine / Aromatic Polyamide / Aromatic Polyimide / Solubility / Thermal Property /

Aromatic polyamides and polyimides are well known as thermal resistant materials. But, their rigid structures cause high softening temperature and poor solubility to many organic solvents, and thus they are costly and difficult to apply to industry.¹ Therefore, investigations concerned with the improvement of solubility have proceeded extensively. We regard the introduction of the rigid and three-dimensionally bulky triptycene structure to polyamide backbone as the effectiveness in the improvement of solubility and reported² preparations and properties of aromatic polyamides from 9,10-dihydro-9,10-*o*-benzoanthracene-1,5-diamine (2,7-triptycene-

diamine) **1** having high thermal properties and good solubility. In this report, the syntheses and properties of polyamides and polyimides from 9,10-dihydro-9,10-*o*-benzoanthracene-1,5-diamine (2,5-triptycenediamine) **3** are investigated. The structure of polyamide backbone introduced 2,5-triptycenediyl unit is more linear and symmetrical than those introduced 2,7-triptycenediyl unit. Accordingly, it is considered that these factors influence the properties of polyamides. It is interesting and important to clear these influence from the view point of the design of new aromatic polyamides having good solubility and thermal properties. Mikitaev *et al.*

already reported³ polyamides, polyimides, and polymeric Schiff base from 2,5-triptycenediamine. However, their inherent viscosities were not very high (0.40–0.50 dl g⁻¹). In addition, concerning thermal properties, only the temperature at 10% weight loss was reported, and other thermal properties such as glass transition temperature were not investigated. Moreover, the solubility of polymers to organic solvents was not examined. It is impossible to discuss the relation between the modification of polyamide structure and characterization by the comparison of the report³ of Mikitaev *et al.* with our study. Therefore, we synthesized polyamides and polyimides polycondensated diamine **3** with several aromatic dicarbonyl dichlorides or tetracarboxylic dianhydride having higher inherent viscosities, and examined thermal properties as well as the solubility in many organic solvents of those polymers obtained.

RESULTS AND DISCUSSION

9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-diamine **3** (2,5-triptycenediamine) was prepared by the method⁴ of Bartlett *et al.* from anthracene. Total yield from the starting material was 27.4%.

Model reactions for polyamide and poly-

imide syntheses were performed by the use of benzoyl chloride or phthalic anhydride. The structures of obtained products were confirmed by spectroscopic data as well as by elemental analysis. IR spectra of model compounds showed characteristic amide or imide absorptions.

Poly(imino-9,10-dihydro-9,10-*o*-benzenoanthracene-1,4-diyliminocarbonylarylene-carbonyl)s (**4a–d**) were prepared by the low-temperature solution polycondensation⁵ of diamine **3** with aromatic dicarbonyl dichlorides, *e.g.*, terephthaloyl dichloride (**a**), isophthaloyl dichloride (**b**), 4,4'-biphenyldicarbonyl dichloride (**c**), 4,4'-sulfonyldibenzoyl dichloride (**d**). Lithium carbonate or propylene oxide was used as hydrogen chloride acceptor. The results are shown in Table I. All polycondensations proceeded in quantitative yields. The IR spectra of the polymers showed characteristic amide absorptions near 1660 and 1510 cm⁻¹. The inherent viscosities of polyamides synthesized by propylene oxide were higher than those by lithium carbonate.

Solubility in several organic solvents is indicated in Table II. Polyamide **4a** and **4c** were soluble in conc. sulfuric acid only. But polyamide **4b** was soluble in dimethylsulfoxide (DMSO), dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP), dimethylacetamide

(DMAc), and pyridine. Polyamide **4d** was soluble in hexamethylphosphoric triamide (HMPA) in addition to these solvents except pyridine. Compared with the solubility of polyamides **2**, that of polyamides **4** was lower. In particular, while polyamide **2a** was soluble in many organic solvents, corresponding polyamide **4a** was slightly soluble. Polyamide **4b** was not soluble in *m*-cresol and cyclohex-

anone in which polyamide **2b** was soluble on heating. Polyamide **4d** was also partially soluble in DMF and pyridine in which polyamide **2d** was soluble at room temperature. This tendency was attributed to the shape and degree of the symmetry of the polyamide backbone. The structure of 2,7-triptycenediyl unit is more asymmetrical than that of 2,5-triptycenediyl unit, while both are rigid.

Thermal properties of polyamides **4** are shown in Table III. The glass transition temperatures (T_g s) of polyamides **4a** and **4c** were not observed by differential scanning calorimetry (DSC), and their films were too brittle to be analyzed by dynamic mechanical thermal analysis (DMA). T_g of polyamide **4b** was 339°C and that of **4d** was 370°C, both high values. The temperatures at 5% weight loss (T_d s) and weight residues at 600°C were observed by thermogravimetry (TG). T_d s of polyamides **4** were 442–482°C and weight residues at 600°C were 57–68%, which are high values. Compared with thermal properties between polyamides **2** and **4**, those of polyamides **4** were as high as those of the corresponding polyamides **2**. T_g s of **2b** was 337°C, that of **4b** was 339°C, and T_g s of **2d** and **4d** were 370°C. T_d s of polyamides **2** also showed values as high as those of corresponding polyamides **4**. These were due to the same

Table I. Results of preparation of polyamides

Polymer	Method ^a	Yield		η_{inh}^b dl g ⁻¹	Appearance ^c	Color
		(%)				
4a	PO	97.0	0.67	S	S	White
	LC	101.1	0.44	S	S	White
4b	PO	101.2	1.00	S	S	Pale yellow
	LC	101.0	0.48	P	P	Pale yellow
4c	PO	99.9	1.68	P	P	Pale yellow
	LC	102.1	0.97	P	P	Pale yellow
4d	PO	96.5	0.84	S	S	White
	LC	96.3	0.69	S	S	White

^a PO, low-temperature solution polycondensation used propylene oxide as acid acceptor; LC, low-temperature solution polycondensation used lithium carbonate as acid acceptor.

^b Measured at a concentration of 0.50% in conc. H₂SO₄ at 30°C.

^c S, homogeneous system; P, heterogeneous system.

Table II. Solubility of polyamides^a

Polymer	CHO	Py	<i>m</i> -Cre	DMAc	NMP	HMPA	DMF	DMSO	H ₂ SO ₄
a	(±)	(±)	(±)	+	(+)	(+)	(±)	+	+
2³b	(+)	+	(+)	+	+	(+)	+	+	+
c	(±)	(±)	—	—	(+)	(±)	—	—	(+)
d	(±)	+	(±)	+	+	(+)	+	+	+
a	—	—	—	—	(±) ^b	—	—	—	+
4b	—	(+)	—	+	+	±	+	+	+
c	(±)	±	(±)	(±)	(±) ^b	(±)	±	±	+
d	SW	±	SW	+	+	(+)	±	+	+

^a Measured at a concentration of 0.020 g ml⁻¹.

CHO, cyclohexanone; Py, pyridine; *m*-Cre, *m*-cresol; DMAc, dimethylacetamide; NMP, 1-methyl-2-pyrrolidone; DMF, dimethylformamide; DMSO, dimethylsulfoxide; HMPA, hexamethylphosphoric triamide.

+, soluble; ±, partially soluble; —, insoluble; SW, swelling; (), on heating.

^b It was soluble when lithium chloride was added at room temperature.

Table III. Thermal properties of polyamides

Polymer	$T_g/^\circ\text{C}$		T_d^c °C	Weight residue/% at 600°C ^d
	DSC ^a	DMA ^b		
a	— ^e	— ^f	486	59
2³b	337	309	446	58
c	368	380	467	50
d	370	364	456	68
a	— ^e	— ^g	482	59
4³b	339	336	442	68
c	— ^e	— ^g	466	64
d	370	377	455	57

^a Measured by differential scanning calorimetry (DSC) (heating rate 10 K min⁻¹ in nitrogen atmosphere).

^b Measured by dynamic mechanical thermal analysis (DMA) (heating rate 1 K min⁻¹ in nitrogen atmosphere at 0.025 Hz).

^c Temperature at 5% weight loss was determined by thermogravimetry (TG) (heating rate 10 K min⁻¹ in nitrogen atmosphere).

^d Determined by TG.

^e Not observed.

^f No data.

^g The film was too brittle to be analyzed by DMA.

bulkiness and similar rigidity and shape of the main chains of polyamides **2** and **4**. The main chain of polyamide **2** is more linear and symmetrical than that of polyamide **4**. However, the structure of the diamine **3** component was not asymmetrical to lower the thermal properties because of the rigid structure, but enough to improve solubility in organic solvents.

Polyimides **6** were prepared by a two-step procedure⁶: polyamic acids **5**, prepared by ring-opening polyaddition of diamine **3** to tetracarboxylic dianhydrides, were cyclodehydrated by heating. Pyromellitic dianhydride (PMDA) (**a'**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPDA) (**b'**), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BTDA) (**c'**), and 3,3',4,4'-biphenylsulfonetetracarboxylic dianhydride (BSDA) (**d'**) were used as tetracarboxylic dianhydrides. The results of polymerization of diamine **3** with tetracarboxylic dianhydrides are summarized in

Table IV. Results of preparations of polyamic acids **5**

Polyamic acid	η_{inh}^a dl g ⁻¹	Color
a'	0.87	yellow
5³b'	0.68	yellow
c'	0.65	yellow
d'	0.79	yellow

^a Inherent viscosity measured in NMP (0.50 g dl⁻¹) at 30°C.

Table IV. The inherent viscosities of polyamic acids **5** were 0.65–0.87 (dl g⁻¹). The color of all polyamic acids was yellow. Thermal cyclodehydrations of polyamic acids **5** were performed on a hot plate at 180°C for 2 h and then at 350°C for 1 h under nitrogen. Completion of cyclodehydration was confirmed as follows. The IR spectra of polyimides showed absorptions at 1780, 1720 (imide C=O), 1360 (imide C–N) cm⁻¹.

As shown in Table V, the solubility of polyimides **6** was rather poor. Polyimide **6a'** and **6b'** were soluble only in concentrated sulfuric acid on heating. The solubility of **6c'** was partially soluble in DMF and conc. sulfuric acid. However, that of polyimide **6d'** was

Table V. Solubility of polyimides^a

Polymer	CHO	Py	<i>m</i> -Cre	DMAc	NMP	HMPA	DMF	DMSO	H ₂ SO ₄
a'	—	—	—	SW	(±)	—	(±)	—	(+)
b'	—	—	—	—	—	—	—	—	(+)
c'	—	—	—	(SW)	—	—	(±)	(SW)	(±)
d'	—	—	—	+	(±)	(±)	+	+	+

^a Measured at 0.020 g ml⁻¹.CHO, cyclohexanone; Py, pyridine; *m*-Cre, *m*-cresol; DMAc, dimethylacetamide; NMP, 1-methyl-2-pyrrolidone; DMF, dimethylformamide; DMSO, dimethylsulfoxide; HMPA, hexamethylphosphoric triamide.

+, soluble; ±, partially soluble; —, insoluble. SW, swelling; (), on heating.

good for aromatic polyimide, which was soluble in DMAc, DMF, DMSO, and conc. sulfuric acid.

The thermal properties of polyimides **6** are summarized in Table VI. T_g s of polyimides were determined by DMA. T_g s of polyimides **6** were observed in the 389–418°C range due to the rigidity and symmetry of the diamine component. The temperatures at 5% weight loss of polyimides **6** were up to 521°C and the weight residue at 600°C was above 82%, and even at 800°C was above 64%, which gave indication of highly thermally stable polymer. Especially, polyimide **6d'** had good solubility in several organic solvents and highly thermal properties (T_g = 404°C, T_d = 521°C).

EXPERIMENTAL

9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-diamine (2,5-triptycenediamine) **3**: The diamine was synthesized from anthracene and *p*-quinone, as starting materials through five steps by the method⁴ of Bartlett *et al.* The total yield from starting materials was 27.4%. mp 310°C (DTA) (lit.⁴ 307°C), light gray powder. IR (KBr) 3464, 3384 cm⁻¹ (N–H).

Anal. Calcd for C₂₀H₁₄N₂ (284.4): C, 84.48%; H, 5.67%; N, 9.85%. Found: C, 84.72%; H, 5.59%; N, 9.75%.

Monomer

4,4'-Sulfonyldibenzoic acid and 3,3',4,4'-biphenylsulfonetetracarboxylic dianhydride

Table VI. Thermal properties of polyimides

Polymer	T_g^a	T_d^b	Weight residue/% ^c	
	°C	°C	at 600°C	at 800°C
a'	—	563	83	64
b'	399	592	93	68
c'	391	570	85	67
d'	411	521	82	65

^a Measured by dynamic mechanical thermal analysis (DMA) (heating rate 1 K min⁻¹ in nitrogen atmosphere at 0.025 Hz).^b Temperature at 5% weight loss was determined by thermogravimetry (TG) (heating rate 10 K min⁻¹ in nitrogen atmosphere).^c Determined by TG.

were obtained from New Japan Chemical Co., Ltd., and used as received. Aromatic dicarbonyl dichlorides were synthesized from the aromatic dicarboxylic acid with thionyl chloride and DMF. Terephthaloyl dichloride was recrystallized from dry *n*-hexane. Isophthaloyl dichloride was recrystallized from dry ligroin. 4,4'-Biphenyldicarbonyl chloride and 4,4'-sulfonyldibenzoyl chloride were recrystallized from dry benzene. Pyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride, and 3,3',4,4'-biphenyltetracarboxylic dianhydride were obtained commercially, recrystallized from acetic anhydride, and sublimated under vacuum just before polymerization.

1,4-Dibenzamide-9,10-dihydro-9,10-o-benzoanthracene (Polyamide Model)

In a 50-ml four-necked flask equipped with a reflux condenser and a nitrogen gas inlet were placed 1.49 g of diamine **3**, 7.83 ml of DMAc, 1.86 ml of benzoyl chloride, and a magnetic stirrer bar. The mixture was cooled to -18°C and stirred until all the ingredients were dissolved. Then, 5.92 ml of propylene oxide were added. The reaction mixture was stirred for 1 h. The mixture was stirred at room temperature for 2 h and then poured into 400 ml of water. The precipitates were filtrated, washed with 380 ml of 10% sodium carbonate solution and 500 ml of water, and dried *in vacuo*. Crude products were recrystallized from acetone. Yield 91%. mp $321\text{--}322^{\circ}\text{C}$ (DTA). IR (KBr) $1654, 1514\text{ cm}^{-1}$ (amide I, II).

Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{N}_2\text{O}_2$ (492.6): C, 82.91%; H, 4.91%; N, 5.69%. Found: C, 82.70%; H, 4.72%; N, 5.42%.

N,N'-(9,10-Dihydro-9,10-o-benzoanthracene-1,4-diyl)-diphthalimide (Polyimide Model)

In a four-necked 10-ml reaction tube equipped with a mechanical stirrer and nitrogen inlet with a calcium chloride tube were placed 0.568 g of diamine **3** and 3.0 ml of NMP. After the mixture was cooled to -15°C , 0.604 g of phthalic anhydride was added. It was stirred at that temperature for 1 h and then at room temperature for 4 h. The resulting solution was spread on a glass plate and the solvent was removed at 60°C for 1.5 h and then at 70°C for 1 h. The film thus obtained was dried *in vacuo* at 60°C . Thermal cyclodehydration was performed at 150°C for 2 h in a nitrogen atmosphere and then at 300°C . Crude yield was 85.5%. The products were recrystallized from cyclohexanone. Yield 40.2%. mp 460°C (DTA, white powder). IR (KBr) $1720 (\text{C}=\text{O}), 1372 (\text{C}-\text{N})\text{ cm}^{-1}$.

Anal. Calcd for $\text{C}_{36}\text{H}_{20}\text{N}_2\text{O}_4$ (544.5): C, 79.40%; H, 3.70%; N, 5.14%. Found: C,

79.18%; H, 3.56%; N, 4.94%.

Low-Temperature Solution Polycondensation of Polyamide

A typical procedure is as follows. In a 10-ml reaction tube equipped with a nitrogen gas inlet having a calcium chloride tube were placed 0.1287 g of lithium chloride, 0.2843 g of diamine **3**, and 1.80 ml of NMP. The mixture was dissolved, cooled to -18°C , to which were added 0.3431 g of 4,4'-sulfonyldibenzoyl chloride and 0.70 ml of propylene oxide. It was stirred at -18°C for 1 h, subsequently at -10°C for 1 h, and at room temperature for 5 h. The reaction mixture was poured into aqueous methanol ($\text{MeOH}:\text{H}_2\text{O}=1:1$ in volume). The precipitates were collected with a glass filter (3G) and then dried in reduced pressure at 70°C . Yield 96.5%. $\eta_{\text{inh}}=0.84\text{ dl g}^{-1}$ (0.5 g dl^{-1} conc. H_2SO_4 at 30°C). IR (KBr) $1656, 1514\text{ cm}^{-1}$ (amide I, II).

Anal. Calcd for $(\text{C}_{34}\text{H}_{22}\text{N}_2\text{O}_4\text{S})_n$ (554.6) $_n$: C, 73.63%; H, 4.00%; N, 5.05%. Found: C, 71.62%; H, 3.98%; N, 4.86%. Other polyamides were synthesized by similar procedure.

Ring-Opening Polyaddition and Cyclodehydration of Polyimide 6

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 0.2844 g of diamine **3** and 1.0 ml of NMP. The mixture was chilled to -15°C , and to which were added 0.2180 g of pyromellitic anhydride and 1.0 ml of NMP. It was stirred at room temperature for 4 h and then was allowed to stand over night. A 0.50-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 70°C . The obtained film was dried under reduced pressure. Thermal cyclodehydration of the polyamic acid **7** was performed by heating at 180°C for 2 h and then at 350°C for 1 h. As soon as heating was over, the product was

taken out of an electric furnace and cooled to room temperature. The inherent viscosity of the polyamic acid was 0.47 dl g^{-1} (0.5 g dl^{-1} NMP at 30°C).

Anal. Calcd for $(\text{C}_{30}\text{H}_{14}\text{N}_2\text{O}_4)_n$ (466.4) $_n$: C, 77.25%; H, 3.03%; N, 6.01%. Found: C, 74.22%; H, 3.33%; N, 5.45%. Other polyimides were synthesized by similar procedure.

MEASUREMENTS

T_g s were obtained by DSC (Rigakudenki Thermal Analysis 8055D1), and determined on dynamic mechanical thermal analysis (DMA) (Mac Science TMA 4000). DMA measurement was made at a frequency of 0.025 Hz at a heating rate of 1 K min^{-1} . The sample was about 0.02 mm thick, 5 mm wide, and 20 mm gauge length. T_d s and weight residues were obtained by TG-DTA (Mac Science TG-DTA 2000). IR spectra were recorded on a Hitachi 270-30 spectrophotometer (KBr tablet).

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