

Synthesis and Characterization of Soluble Aromatic Polyamides Derived from Diamines with the 4,5-Imidazolediyl Structure

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The introductions of the rigid, zigzag, bulky, and polar units to the backbone of aromatic polyamides improves solubility while maintaining high thermal resistance,^{1–7} but improvement is not satisfactory. We previously demonstrated that the introduction of the rigid, zigzag, bulky, and polar 2-methyl-4,5-di(1,3-phenylene)imidazole unit or 2-phenyl-4,5-di(1,3-phenylene)imidazole unit to the backbone of aromatic polyimides improves solubility without decreasing high thermal resistance.⁸ In the present study, novel aromatic polyamides with their structures were investigated. As shown in Scheme 1, polyamides **I**, **II**, and **III** were synthesized from the diamines such as 4,5-di(3-aminophenyl)imidazole (**1**), 4,5-di(3-aminophenyl)-2-methylimidazole (**2**), and 4,5-di(3-aminophenyl)-2-phenylimidazole (**3**), which were prepared as the monomer for the polyimide synthesis,⁸ and their solubility and thermal properties were examined. Introductions of the 4,5-di(1,3-phenylene)imidazole units increase polarity and bulkiness, and make the backbone of polyamide zigzag maintaining rigidity. As shown in Scheme 2, aromatic polyamides **II'**, the isomers of polyamides **II**, were prepared from novel diamine 4,5-di(4-aminophenyl)-2-methylimidazole (**5**), and their properties were compared with those of polyamides **II**.

RESULTS AND DISCUSSION

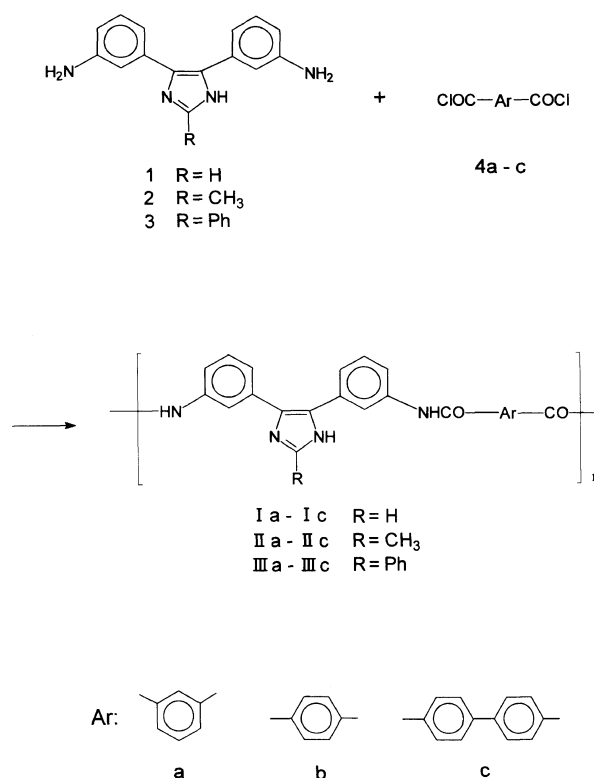
Polyamide Synthesis

Polyamides **I**, **II**, and **III** were synthesized by low-temperature solution polycondensation⁹ of diamines **1**, **2**, and **3** with several aromatic diacyl chlorides, such as isophthaloyl dichloride (**4a**), terephthaloyl dichloride (**4b**), and 4,4'-biphenyldicarbonyl dichloride (**4c**), respectively. The results are summarized in Table I (runs 1–14). The effect of acid acceptor was investigated on the polymerization of **Ia**, **Ib**, **Ic**, **IIa**, and **IIIa**. Except for the polymerization of **IIa** (run 7), lithium carbonate as the acid acceptor afforded better results than methyl oxirane. Thus, other polymerizations were carried out using lithium carbonate. All polyamides were obtained in the yield above 88%, and inherent viscosity ranged from 0.26 to 1.24 dl g⁻¹.

5 was prepared by the reduction of 2-methyl-4,5-di(4-nitrophenyl)imidazole¹⁰ (**6**). A characteristic chemical

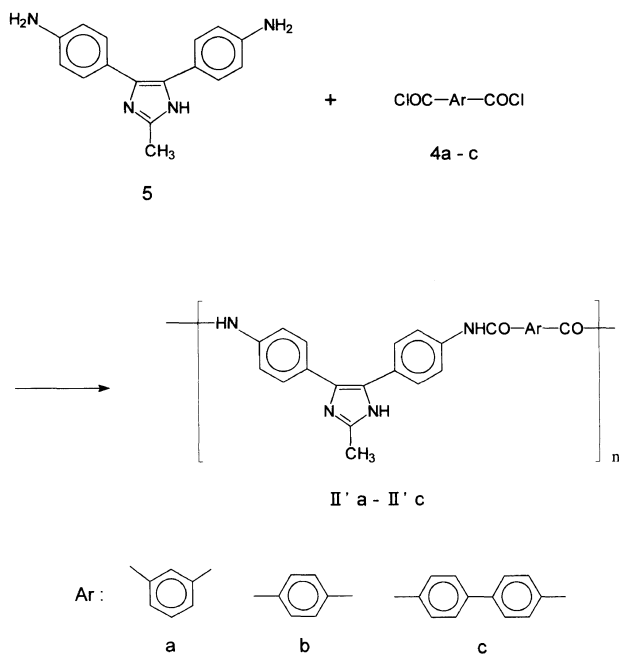
shift near 12 ppm resulting from imidazole N–H was not observed in the ¹H NMR spectrum of the product in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆). ¹H NMR spectrum of 2-methylimidazole was also measured in DMSO-*d*₆. Similarly, no chemical shift near 12 ppm was observed in the ¹H NMR spectrum. Therefore, the product was identified as diamine **5** by elemental analysis and other spectroscopic data such as ¹³C NMR and IR spectroscopy.

Polyamides **II'** were prepared by low-temperature solution polycondensation, and the results are summarized in Table I (runs 15–20). When methyl oxirane was used as the acid acceptor (runs 15, 17, 19), the inherent viscosity of the obtained polyamide was higher than that of the polyamide synthesized by the corresponding polymerization using lithium carbonate (runs 16, 18, 20). These results were different from those of the polymerizations of **I**, **II**, and **III**, but the reason is not clear. Thus, polyamides **II'** were afforded in the yield above



Scheme 1.

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Scheme 2.

Table I. Results of polyamide preparations^a

Run	Polymer	Acid acceptor ^b	Yield	η_{inh}^c
			%	dl g ⁻¹
1	Ia	MO	96	0.42
2	Ia	Li ₂ CO ₃	97	1.24
3	Ib	MO	96	0.15
4	Ib	Li ₂ CO ₃	97	0.45
5	Ic	MO	94	0.16
6	Ic	Li ₂ CO ₃	95	0.93
7	IIa	MO	90	0.69
8	IIa	Li ₂ CO ₃	98	0.37
9	IIb	Li ₂ CO ₃	94	0.26
10	IIc	Li ₂ CO ₃	100	0.69
11	IIIa	MO	88	0.39
12	IIIa	Li ₂ CO ₃	97	0.40
13	IIIb	Li ₂ CO ₃	98	0.49
14	IIIc	Li ₂ CO ₃	97	0.52
15	II'a	MO	93	0.30
16	II'a	Li ₂ CO ₃	98	0.28
17	II'b	MO	92	0.47
18	II'b	Li ₂ CO ₃	79	0.24
19	II'c	MO	94	1.00
20	II'c	Li ₂ CO ₃	98	0.53

^aAll polycondensations proceeded in a homogeneous system. ^bMO, methyl oxirane; Li₂CO₃, lithium carbonate. ^cInherent viscosity, measured in conc. sulfuric acid (0.50 g dl⁻¹) at 30°C.

92%, and inherent viscosity ranged between 0.30 and 1.00 dl g⁻¹.

Thermal Properties of Polyamides

The thermal properties of the polyamides are summarized in Table II. Polyamides **I**, **II**, and **III** showed high T_g s ranging from 275 to 304°C although having the zigzag and bulky structures. In each series of the polyamides, T_g decreased in the following order: **c** > **b** > **a**, depending on symmetry and rigidity of the carboxylic acid unit of the polyamides. There was little difference between T_g s of **I**, **II**, and **III**. T_g of the polyamide derived from bis(4-aminophenyl)ether and isophthaloyl dichloride

Table II. Thermal properties of polyamides

Run ^a	Polymer	T_g^b	T_d^c	T_{d10}^d	Weight residue ^e at 600°C/%
		°C	°C	°C	
2	Ia	275	387	511	81
4	Ib	284	394	498	71
6	Ic	287	408	514	73
7	IIa	288	413	470	72
9	IIb	293	389	473	77
10	IIc	304	433	487	75
12	IIIa	284	412	480	69
13	IIIb	298	439	489	62
14	IIIc	303	456	494	63
15	II'a	329	396	473	67
17	II'b	337	413	483	66
19	II'c	337	433	501	72

^aSample run numbers appear in Table I. ^bGlass transition temperature, observed by DSC in a nitrogen atmosphere; heating rate, 10 K min⁻¹. ^cThermal decomposition temperature, observed by TGA in a nitrogen atmosphere. ^dTemperature at 10% weight loss, observed by TGA in a nitrogen atmosphere. ^eObserved by TGA.

ride (polyamide **IV**) is known to be 260°C.¹ T_g s of **Ia**, **IIa**, and **IIIa** were *ca.* 15–25°C higher than that of **IV**, respectively. Thus, the introduction of the 4,5-di(1,3-phenylene)imidazole unit to the main chain of polyamide increased T_g . This is attributed to the dipole–dipole interaction between the polar imidazole units introduced.

T_d s ranged from 387 to 456°C, and T_{d10} s from 470 to 514°C. Weight residues at 600°C were above 62%. Thus, polyamides **I**, **II**, and **III** exhibited high thermal stability. The thermal stability of **III** was expected to be higher than that of corresponding **I** because of the more highly phenylated structure of **III**. However, the T_{d10} s of **I** were higher than those of corresponding **III**, and the weight residues of **I** were also higher than those of corresponding **III**. Probably, scission of the bonding between the imidazole ring and the pendant phenyl group may be somewhat easy, since the imidazole ring is not coplanar to the pendant phenyl group.

T_g s of **II'** were quite high, *ca.* 330°C. T_d s ranged from 396 to 433°C, T_{d10} s were above 473°C, and weight residues at 600°C were above 66%.

Solubility of Polyamides

Solubility in several organic solvents at 2.0% (w/v) was examined at room temperature and at 80°C. The results are listed in Table III. Some polyamides indicated good solubility for wholly aromatic polyamides. In particular, **IIa** was soluble in DMSO, formic acid, *N,N*-dimethylacetamide (DMAc) at room temperature, and *m*-cresol at 80°C. It is known that polyamide **IV** is soluble in conc. sulfuric acid, DMAc, and pyridine at room temperature, but insoluble in *m*-cresol.¹ The solubility of polyamides **Ia**, **IIa**, and **IIIa** was higher than that of **IV**, respectively. Thus, the introduction of the 4,5-di(1,3-phenylene)imidazole units to the polyamide backbone has effect on improvement of the solubility without sacrificing high thermal resistance. The solubility of **I** did not differ from that of **II** and **III**, respectively.

X-Ray diffraction patterns showed that polyamides **I**, **II**, and **III** are all amorphous. It is considered that the introduction of the rigid and zigzag 4,5-di(1,3-phenylene)imidazole structure led to the amorphous nature.

Table III. Solubilities^a of polyamides

Run ^b	Polymer	<i>m</i> -Cre	DMAc	NMP	DMF	HCOOH	DMSO	H ₂ SO ₄
2	Ia	(+)	(+)	+	(+)	(+)	(+)	+
4	Ib	(±)	±	±	(±)	+	(±)	+
6	Ic	(±)	SW	(±)	SW	(+)	SW	+
7	IIa	(+)	+	+	+	+	+	+
9	IIb	±	(±)	SW	SW	+	SW	+
10	IIc	(±)	SW	(+)	SW	(+)	(±)	+
12	IIIa	(±)	+	+	±	+	(+)	+
13	IIIb	(±)	±	±	±	(+)	+	+
14	IIIc	(±)	SW	±	SW	SW	SW	+
15	II'a	±	+	+	+	+	+	+
17	II'b	+	+	+	+	+	+	+
19	II'c	(±)	+	+	+	+	+	+

^a Measured at 2.0% (w/v). Data in parentheses were obtained during heating. The symbols have the following meanings: +, soluble; ±, partially soluble; −, insoluble; SW, swelling. ^b Sample run numbers appear in Table I. *m*-Cre, *m*-cresol; DMAc, *N,N*-dimethylacetamide; NMP, 1-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; HCOOH, formic acid; DMSO, dimethyl sulfoxide.

One factor for improved solubility is the amorphous nature of the polyamides.

Polyamides II'a and II'c were soluble in DMSO, formic acid, *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP), and DMAc at room temperature. II'b was soluble in *m*-cresol as well. Thus, polyamides II' also possessed high thermal resistance and excellent solubility. The properties of II' were compared with those of isomeric II. Each T_g of II' was *ca.* 30°C higher than that of corresponding II. The solubility of II' in all cases was also much higher than that of corresponding II. Thus, the introduction of 2-methyl-4,5-di(1,4-phenylene)imidazole structure to the polyamide backbone was more effective not only in improving solubility but also in maintaining T_g than the introduction of 2-methyl-4,5-di(1,3-phenylene)imidazole structure. Similar tendency was observed in case of aromatic polyimides. The polyimides derived from 4,5-di(4-aminophenyl)-2-phenylimidazole possessed higher T_g s and better solubility than the corresponding polyimides derived from 3.^{8,11} The introduction of 1,4-phenylene moiety between an electron-withdrawing amide linkage and an electron-withdrawing imidazole ring may thus lead these two groups to attract electron each other, resulting in increasing polarity of the polyamide structure over all. Therefore, the higher polarity of polyamides II' may induce higher T_g and further improve solubility in aprotic polar solvents.

Conclusions

The introduction of the rigid, zigzag, bulky, and polar 4,5-di(1,3-phenylene)imidazole units to the polyamide backbone improves solubility while maintaining high thermal resistance. Polyamides II' possess higher T_g s as well as better solubility in aprotic polar solvents than isomeric polyamides II.

EXPERIMENTAL

Monomers

Diamines 1, 2, and 3 were prepared according to the method previously reported.⁸ Aromatic diacyl dichlorides 4a, 4b, and 4c were prepared by chlorination of the corresponding dicarboxylic acids using thionyl chloride and DMF, and recrystallized from dry ligroin or dry

benzene. Diamine 5 was prepared by the reduction of 6 as follows.

Stannous chloride dihydrate (21.0 g, 93 mmol) was dissolved in hydrochloric acid (40 ml) on heating, and the solution was chilled to −5°C. 6 (5.11 g, 15.8 mmol) was added gradually, and the mixture was stirred at room temperature for 1 h, and at 50°C for 5 h. The reaction mixture was chilled to −20°C to precipitate. The product was collected by filtration, and dissolved in water (100 ml). The solution was filtrated, poured into aqueous sodium hydroxide solution (20 wt%, 400 ml), and stirred overnight. The product was collected by filtration again, washed with NaOH solution, and with water. The crude product was recrystallized from water adding activated charcoal to give pale brown needles. Yield 34%. mp 230.1–231.0°C. IR (KBr, disk) 3452, 3384 cm^{−1} (Ar–NH₂). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.24 (s; 3H, −CH₃), 5.01 (s; broad, 4H, −NH₂), 6.47 (d; *J* = 8.2 Hz, 4H, Ar–H), 7.08 (d; *J* = 8.3 Hz, 4H, Ar–H). ¹³C NMR (100 MHz, DMSO-*d*₆): 13.8 (−CH₃), 113.7 (Ar C³), 121.7 (imidazole C⁴), 127.9, 128.1 (Ar C¹, C²), 142.2 (imidazole C²), 147.1 (Ar C⁴). *Anal.* Calcd for C₁₆H₁₆N₄ (264.3): C, 72.70%; H, 6.10%; N, 21.20%. Found: C, 72.56%; H, 6.16%; N, 21.20%.

Low-Temperature Solution Polycondensation

A typical procedure (run 2) is as follows. 1 (1.001 g, 4.00 mmol) and 13.5 ml of NMP were placed into a four-necked reaction tube equipped with a mechanical stirrer and a nitrogen gas inlet having a calcium chloride tube. After the mixture was chilled to −20°C, isophthaloyl dichloride (0.812 g, 4.00 mmol) and 2.5 ml of NMP were added. The reaction was carried out at −20°C for 1 h. Lithium carbonate (0.296 g, 4.01 mmol) was added, and the reaction mixture was stirred at room temperature for 5 h, diluted with NMP, and poured into aqueous methanol (1:1 by volume) for precipitation. The product was washed with hot water, and with hot methanol, and dried under reduced pressure at 200°C. Yield 97%. $\eta_{inh} = 1.24$ dl g^{−1} (0.50 g dl^{−1} in conc. sulfuric acid at 30°C). IR (KBr) 1656, 1532 cm^{−1} (amide I, II). *Anal.* Calcd for (C₂₃H₁₆N₄O₂)_{*n*} (380.4)_{*n*}: C, 72.62%; H, 4.24%; N, 14.73%. Found: C, 71.02%; H, 4.16%; N, 14.40%.

Other polyamides were synthesized by a similar

procedure.

Measurements

T_{d5} , T_{d10} s, and weight residues at 600°C were obtained by thermogravimetric analysis (TGA). (MAC Science TG-DTA 2000). T_g s were determined by differential scanning calorimetry (DSC) (Rigaku DSC 8055D1). These thermoanalytical measurements were carried out under the following conditions: heating rate, 10 K min⁻¹; in a nitrogen atmosphere. T_g s were determined by second scannings. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. 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. ¹H NMR spectra (400 MHz) and ¹³C NMR spectra (100 MHz) were recorded on a 400 MHz JEOL JNM-LA 400 spectrometer.

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