Preparation and Properties of Aromatic Polyamides from 2,2′-Bibenzoic Acid and Aromatic Diamines

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SYNOPSIS

Aromatic polyamides having inherent viscosities up to 1.8 dL/g were synthesized either by the direct polycondensation of 2,2′-bibenzoic acid with various aromatic diamines or by the low temperature solution polycondensation of 2,2′-bibenzoyl chloride with aromatic diamines. All the aromatic polyamides were amorphous and soluble in a variety of organic solvents including *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone, dimethyl sulfoxide, *m*-cresol, and pyridine. Transparent and flexible films of these polymers could be cast from the DMAc solutions. These aromatic polyamides had glass transition temperatures in the range of 226–306°C and began to lose weight around 350°C in air.

INTRODUCTION

It is well known that wholly aromatic polyamides (aramids) possess high thermal stability and excellent mechanical properties. Fabrication of most aramids, however, was extremely difficult because of their high melting temperatures or softening temperatures and their limited solubility in organic solvents.[1] Recently, new processable engineering plastics possessing moderately high glass transition temperatures and good solubility in some organic solvents have been required in practical use. One of the approaches to improve their processability would be the introduction of bulky and rigid 2,2′-biphenylylene unit into the polymer backbone. However, only a limited number of 2,2′-biphenylylene-containing polyamides derived from 2,2′-diaminobiphenyl and dicarboxylic acid chlorides have been reported earlier by Russian researchers,[2,3] and the polyamides from 2,2-bibenzoic acid (diphenic acid) and aromatic diamides have not been investigated in detail.

This article deals with the preparation and characterization of high molecular weight aromatic polyamides from 2,2′-bibenzoic acid (or diacid chloride) and various aromatic diamines by either direct polycondensation or low temperature solution polycondensation (Scheme 1).

EXPERIMENTAL

Materials

2,2′-Bibenzoic acid (**Ia**) was obtained commercially and purified by recrystallization from distilled water.

2,2′-Bibenzoyl chloride (**Ib**) was prepared by reacting the diacid with thionyl chloride and was purified by distillation twice before use. The yield was 76%; mp 92–93°C (lit.[4] mp 92–94°C). The infrared (IR) spectrum (KBr) exhibited a characteristic carbonyl absorption at 1775 cm^{-1}.

ANAL. Calcd for $C_{14}H_8O_2Cl_2$: C, 60.24%; H, 2.83%; Cl, 25.40%. Found: C, 60.36%; H, 2.88%; Cl, 25.14%.

Reagent-grade aromatic diamines such as *m*-phenylenediamine (**IIa**) and *p*-phenylenediamine (**IIb**) were purified by distillation under reduced pressure. Bis(4-aminophenyl)methane (**IIc**) was recrystallized from benzene, and both bis(4-aminophenyl) ether (**IId**) and bis(4-aminophenyl) sulfone (**IIf**) were recrystallized from ethanol. The other diamines (**IIe, IIg–IIl**) were used as received.

N-methyl-2-pyrrolidone (NMP), pyridine, triphenyl phosphite, and triethylamine were purified

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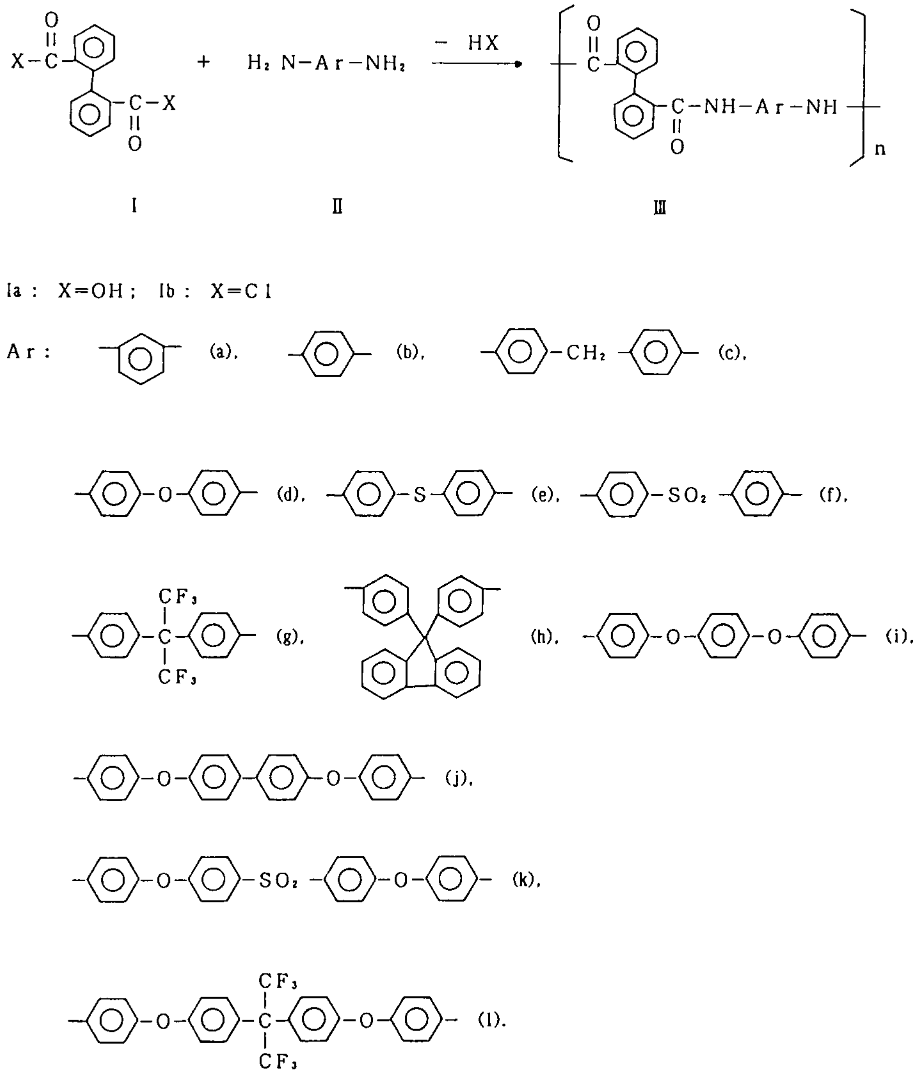

Scheme 1.

by distillation before use. Calcium chloride was dried at 150°C under vacuum, and reagent-grade propylene oxide was used as received.

Polymer Synthesis

Polyamide IIId from Ia and IId

A mixture of 1.21 g (5 mmol) of **Ia,** 1.00 g (5 mmol) of **IId,** 0.5 g of calcium chloride, and 3.1 g (10 mmol) of triphenyl phosphite in 2.5 mL of pyridine and 8 mL of NMP was heated with stirring at 100°C for 3 h under nitrogen. The reaction mixture was poured into 500 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried 100°C under vacuum. The polymer weighed 1.96 g (97%) and had an inherent viscosity of 0.50 dL/g, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C. The IR spectrum (film) exhibited absorptions at 3400 and 3255 cm^{-1} (N—H) and 1655 cm^{-1} (C=O).

Other aramids were synthesized by similar procedure.

Polymer IIId from Ib and IId

A solution of 1.00 g (5 mmol) of **IId** in 10 mL of NMP was cooled to −25–−30°C on a dry ice–acetone bath. After that 3.5 mL of propylene oxide was added to the mixture, then 1.396 g (5 mmol) of **Ib** was added. The mixture was stirred at −10°C for 3 h under nitrogen. The solution thus obtained was poured into 500 mL of methanol. The precipitated polymer was collected by filtration, washed well with

Table I. Synthesis of Polyamides from Diacid and Diamines by Direct Polycondensation[a]

Polymer	Yield (%)	η_{inh}[b] (dL/g)	$\bar{M}_n$[c] (× 10^{-4})	$\bar{M}_w$[c] (× 10^{-4})	$\bar{M}_w/\bar{M}_n$
IIIa	80	0.22	0.30	0.78	2.6
IIIb	92	0.57	0.62	1.56	2.5
IIIc	93	0.37	0.61	1.87	2.8
IIId	97	0.50	0.89	2.39	2.7
IIIe	80	0.24	0.34	0.89	2.6
IIIf	50	0.10	0.01	0.03	3.0
IIIg	80	0.17	0.29	0.61	2.1
IIIh	99	0.27	0.23	0.88	3.8
IIIi	99	0.55	1.12	2.94	2.6
IIIj	100	0.68	1.53	3.17	2.1
IIIk	99	0.40	0.98	2.01	2.1
IIIl	98	0.46	2.06	4.38	2.1

[a] Reaction was carried out with 5 mmol of **Ia** and 5 mmol of **II**, 0.5 g of calcium chloride, and 3.1 g (10 mmol) of triphenyl phosphite in 2.5 mL of pyridine and 10 mL of NMP with stirring at 100°C for 3 h under nitrogen.

[b] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.

[c] Determined by GPC on the basis of polyoxyethylene calibration.

Table II. Synthesis of Polyamides from Diacid Chlorides and Diamines by Low-Temperature Solution Polycondensation with Different Acid Acceptors

	Polymer[a]	Polymer[b]				Elemental Analysis[c] (%)		
Polymer	η_{inh}[d] (dL/g)	η_{inh}[d] (dL/g)	$\bar{M}_n$[e] (× 10^{-+4})	$\bar{M}_w$[e] (× 10^{-4})	$\bar{M}_w/\bar{M}_n$	C	H	N
IIIa	0.35	0.38	0.6	0.8	1.4	—	—	—
IIIb	0.73	0.78	2.2	3.0	1.4	—	—	—
IIIc	0.58	0.58	2.4	3.3	1.4	77.55	5.26	7.70
						(80.18	4.98	6.90)
IIId	0.65	0.87	5.0	7.4	1.5	75.26	4.59	6.90
						(76.83	4.47	6.90)
IIIe	0.45	0.52	3.4	5.0	1.5	72.72	4.34	6.63
						(73.93	4.29	6.63)
IIIf	0.14	0.34	1.4	1.8	1.3	—	—	—
IIIg	0.24	0.66	4.3	5.8	1.3	63.20	3.89	6.20
						(64.45	3.36	5.18)
IIIh	0.36	0.37	1.5	1.8	1.2	—	—	—
IIIi	0.47	0.88	3.2	4.5	1.4	76.07	4.37	5.86
						(77.10	4.45	5.62)
IIIj	0.51	1.83	7.2	11.6	1.6	78.11	4.40	4.69
						(79.43	4.56	4.87)
IIIk	0.64	0.83	4.8	7.2	1.5	70.35	4.04	4.37
						(71.46	4.10	4.39)
IIIl	0.72	0.72	5.3	8.0	1.5	67.28	3.60	4.07
						(67.96	3.62	3.87)

[a] Reaction was carried out with 5 mmol of **Ib** and **II** in 10 mL of NMP and 1.22 g (12 mmol) of triethylamine as acid acceptor with stirring at 0–5°C for 3 h under nitrogen.

[b] Reaction was carried out with 5 mmol of **Ib** and **II** in 10 mL of NMP and 3.5 mL (50 mmol) of propylene oxide as acid acceptor with stirring at −10°C for 3 h under nitrogen.

[c] The values in parentheses are the calculated values.

[d] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.

[e] Determined by GPC on the basis of polyoxyethylene calibration.

Table III. Solubility of Polyamides[a]

Solvent	Polymer		
	IIIb	IIIc, IIIe, IIIi	IIIa, IIId, IIIf, IIIg, IIIh, IIIj, IIIk, IIIl
Conc. sulfuric acid	++	++	++
N-methyl-2-pyrrolidone	++	++	++
Dimethylformamide	++	++	++
Dimethyl sulfoxide	++	++	++
Pyridine	++	++	++
m-Cresol	++	++	++
Tetrahydrofuran	+	−	++
Acetone	−	−	−
Methanol	−	−	−

[a] (++) Soluble at room temperature, (+) soluble on heating or swelling, (−) insoluble.

hot methanol, and dried at 100°C under vacuum. The yield of the polymer was 1.93 g (95%) and the inherent viscosity was 0.87 dL/g in concentrated sulfuric acid.

ANAL. Calcd for $(C_{26}H_{18}N_2O_3)_n$: C, 76.83%; H, 4.47%; N, 6.90%. Found: C, 75.26%; H, 4.57%; N, 6.90%.

Other aramids were prepared by analogous procedure.

Measurements

IR spectra were recorded on a Hitachi EP-G3 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DSC-41M and TGA-40M, respectively. Dynamic mechanical analysis (DMA) were performed with a Toyoseiki Rheolograph-Solid in the tensile mode. Wide angle X-ray diffraction patterns were obtained at room temperature on a Rigakudenki RU-200 apparatus with nickel-filtered CuKα radiation (50 kV, 180 mA). Weight-average molecular weight ($\bar{M}_w$) and number-average molecular weight ($\bar{M}_n$) were determined by means of gel permeation chromatography (GPC) on the basis of polyoxyethylene calibration on a JASCO apparatus (eluent: dimethylformamide). Tensile properties were determined from stress–strain curves obtained with a Toyo Baldwin Tensilon UTM-II-20, and measurements were performed at room temperature using solution-cast film specimens (about 0.1 mm thick, 1.0 cm wide, and 5 cm gauge length) at an elongation rate of 20%/min.

RESULTS AND DISCUSSION

Polymer Synthesis

The direct polycondensation of aromatic diamines with dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents,[5] as well as low-temperature solution polycondensation of aromatic diamines with diacid chlorides,[6,7] are convenient methods for the preparation of polyamides on a laboratory scale. Aramides **IIIa–IIIl** were prepared from aromatic diamines **IIa–IIl** and 2,2′-bibenzoic acid **Ia** by the direct polycondensation, and the results are summarized in Table I. All the polymerizations proceed in homogeneous solution, and the aromatic polyamides thus obtained had inherent viscosities of 0.10–0.68 dL/g. The GPC curves of polyamides indicated that the $\bar{M}_w$ values were 3000–

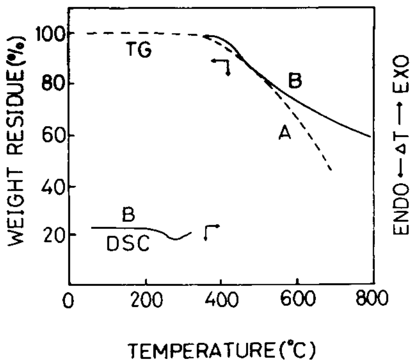

Figure 1. DSC and TG curves for polyamide **IIIj**: (A) in air, (B) in nitrogen. DSC heating rate = 20°C/min and TG heating rate = 10°C/min.

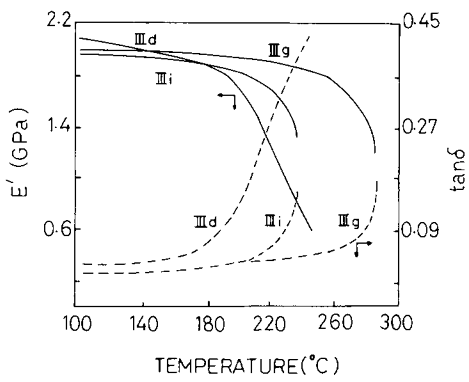

Figure 2. Storage modulus (E') and tanδ curves of polyamide films at a heating rate of 2°C/min at 10 Hz.

43800 relative to standard polyoxyethylene, and the $\bar{M}_w/\bar{M}_n$ values, a measure of molecular weight distribution, were 2.1–3.8.

A series of aramids could also be obtained readily by the low-temperature solution polycondensation of diacid chloride **Ib** with various aromatic diamines **IIa–III** in NMP in the presence of triethylamine or propylene oxide as the acid acceptor. Table II summarizes the results of the polymerization. The low-temperature solution polycondensation afforded the aramids having higher inherent viscosities compared with the direct polycondensation. In addition, the solution polycondensation using propylene oxide as the acid acceptor was generally more preferable than that using triethylamine for the preparation of higher molecular weight aramids. Thus, aramids **IIIa–IIIl** with inherent viscosities of 0.34–1.83 dL/g were successfully obtained by the low-temperature solution polycondensation using propylene oxide in NMP. These viscosity values corresponded to the $\bar{M}_w$ values of 8000–116000, and the ratios of $\bar{M}_w/\bar{M}_n$ were 1.2–1.6. The $\bar{M}_w/\bar{M}_n$ values were unexpectedly smaller than those from the direct polycondensation. The elemental analysis values of these aramids were in good agreement with the calculated values for the proposed structures (Table II). The IR spectra of the polymers showed characteristic amide absorptions near 3400-3250 cm^{-1} (N—H), and 1655 cm^{-1} (C=O).

Polymer Characterization

Table III shows the solubility behavior of the aramids. All the polymers were highly soluble in polar solvents such as DMAc, NMP, dimethyl sulfoxide, and *m*-cresol, and even in less polar pylidine. Thus, the solubility of aramids was greatly improved by the introduction of bulky 2,2'-biphenylylene unit into the polymer backbone. The solubility was very similar to that of the polyamides derived from 2,2'-diaminobiphenyl and dicarboxylic acid chlorides.[2] Polymers **IIIc–IIIe, IIIg,** and **IIIi–IIIl** could be cast into transparent and flexible films from the DMAc solutions.

Table IV. Thermal Behavior of Polyamides[a]

	T_g (°C)		$T_d{}^c$ (°C)		$T_{10}{}^c$ (°C)	
Polymer	DSC[a]	DMA[b]	In Air	In N_2	In Air	In N_2
IIIa	245	—	380	390	395	440
IIIb	285	—	330	350	430	410
IIIc	240	245	380	350	440	415
IIId	251	249	350	360	415	420
IIIe	250	263	350	360	420	420
IIIf	290	—	365	380	400	420
IIIg	275	287	330	355	385	400
IIIh	306	—	350	375	425	440
IIIi	226	238	350	360	425	430
IIIj	242	270	350	380	455	450
IIIk	244	261	360	365	440	445
IIIl	231	244	350	355	425	430

[a] Determined by DSC at a heating rate of 20°C/min in nitrogen.
[b] Determined by DMA at a heating rate of 2°C/min at 10 Hz.
[c] T_d and T_{10} are decomposition temperatures of initial and 10% weight loss, respectively, measured by TG at a heating rate of 10°C/min.

Table V. Mechanical Properties of Polyamides Films

	Polymer							
	IIIc	**IIId**	**IIIe**	**IIIg**	**IIIi**	**IIIj**	**IIIk**	**IIIl**
Tensil strength (MPa)	50	67	41	36	49	59	65	56
Elongation at break (%)	3.3	5.4	2.5	2.5	3.2	6.6	5.3	4.2
Tensile modulus (GPa)	1.7	1.8	1.7	1.6	1.7	1.5	1.8	1.5

The X-ray diffraction studies revealed that all the polyamides were amorphous. Thus, the amorphous nature of those polymers was reflected in their excellent solubility.

The thermal behavior of the polymers was evaluated by means of DSC, TG, and DMA. The DSC and TG, and DMA curves of the aramids are given in Figures 1 and 2, respectively, and the glass transition temperatures (T_g) and decomposition temperatures (T_d) obtained are listed in Table IV.

The T_gs of the polymers were observed in the range of 226–306°C, and decreased with decreasing rigidity and symmetry of the polymer backbone, and with increasing number of flexible linkages in the polymer main chain. The T_gs were somewhat higher than those of the corresponding aramids derived from 2,2′-diaminobiphenyl and aromatic diacid chlorides lying between 220 and 250°C.[2]

All the polymers except **IIIa** and **IIIg** were stable up to 350°C in both air and nitrogen, and the temperatures at 10% weight loss were above 400°C on the TG curves, and there is no obvious difference in thermal stability between the aramids obtained here and the similar polymers reported earlier.[2]

The mechanical properties of the solution cast films of the polyamides are tabulated in Table V. The tensile strength, elongation at break, and tensile modulus of the films were 36–67 MPa, 2.5–6.6%, and 1.5–1.8 GPa, respectively. The tensile strength of the aramid films were almost the same as that of the polyamide films based on 2,2′-diaminobiphenyl.[2] The modulus values obtained from the tensile test were in good agreement with those from the DMA measurement.

In conclusion, the introduction of bulky and rigid 2,2′-biphenylylene unit into polyamide backbones improved their solubility in various organic solvents. Since these aromatic polyamides with high molecular weights were amorphous and had T_gs in the range of 226–306°C, they are considered to be one of the promising processable and high-performance plastics.

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