

Preparation and Characterization of Aromatic Polyamides Based on Ether-sulfone-dicarboxylic Acids

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ABSTRACT: Two ether-sulfone-dicarboxylic acids, 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoic acid (Me-III) and 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoic acid (III), were prepared by the fluorodisplacement of 4,4'-sulfonylbis(2,6-dimethylphenol) and 4,4'-sulfonyldiphenol with *p*-fluorobenzonitrile, and subsequent alkaline hydrolysis of intermediate dinitriles. Using triphenyl phosphite (TPP) and pyridine as condensing agents, aromatic polyamides containing ether and sulfone links were prepared by the direct polycondensation of the dicarboxylic acids with various aromatic diamines in the *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride. The inherent viscosities of the resulting polymers were above 0.4 dL/g and up to 1.01 dL/g. Most of the polyamides were readily soluble in polar solvents such as NMP, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and afforded tough and transparent films by solution-casting. Most of the polymers showed distinct glass transition on their differential scanning calorimetry (DSC) curves, and their glass transition temperatures (T_g) were recorded between 212–272°C. The methyl-substituted polyamides showed slightly higher T_g s than the corresponding unsubstituted ones. The results of the thermogravimetry analysis (TGA) revealed that all the polyamides showed no significant weight loss before 400°C, and the methyl-substituted polymers showed lower initial decomposition temperatures than the unsubstituted ones. © 1997 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* **35**: 2421–2429, 1997

Keywords: ether-sulfone-dicarboxylic acids; aromatic poly(ether-sulfone-amide)s; direct polycondensation; triphenyl phosphite

INTRODUCTION

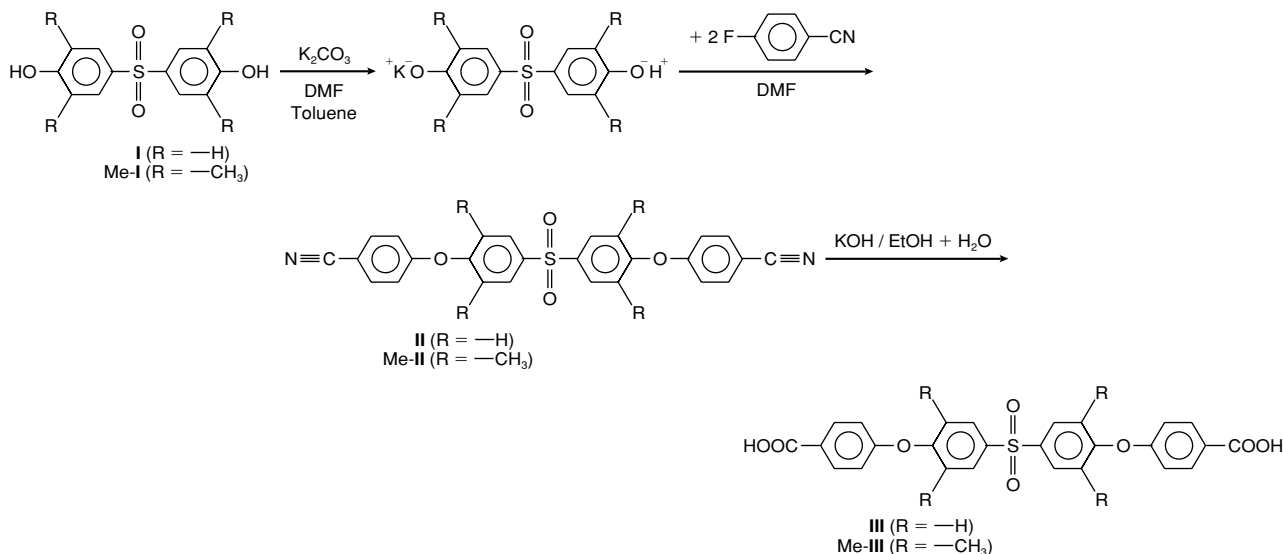
Wholly aromatic polyamides (aramids) are an important class of high-performance heat-resistant materials.^{1–2} For example, poly-*p*-phenyleneterephthalamide (Kevlar) and poly-*m*-phenyleneisophthalamide (Nomex) exhibit a number of excellent properties such as high thermal stability, chemical resistance, low flammability, and excellent mechanical properties as fibers. Fabrication of aramids, however, is difficult because of their

high melting or softening temperatures and limited solubility. One of the methods to improve the solubility of aromatic polyamides is the introduction of flexible groups such as sulfonyl, ether, isopropylidene, or hexafluoroisopropylidene group into the polymer chain.^{3–11}

Aromatic polyamides containing aryl ether or sulfone links generally have increased chain flexibility and lower glass transition temperatures than those crystalline polyaramids without these groups. A number of aromatic polyamides with both aryl ether and aryl sulfone links between amide groups have been prepared by polymerization of 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline (diamine IV₁ as shown in Scheme II) with

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Scheme 1.

the appropriate carboxylic acid derivative^{8,9} or by reacting the acid chloride of 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dibenzoic acid (diacid **III** as shown in Scheme I) with aromatic diamines.^{7,10} Polyamids of this general structure are of interest because they possess enhanced tractability and solubility characteristics.

The purpose of the present study was to modify the basic diacid structure **III** with methyl group substituents and to utilize the novel diacid (**Me-III**) in the preparation of aromatic polyamides. The effect of the ring substitution on polymer properties have been evaluated.

EXPERIMENTAL

Materials

4,4'-Sulfonyldiphenol (**I**) (from Sigma) and 4,4'-sulfonylbis(2,6-dimethylphenol) (**Me-I**) (from Aldrich) were used as received. *p*-Fluorobenzonitrile (from TCI), *N,N*-dimethylformamide (from Fluka), and toluene (from Alps) were used without previous purification.

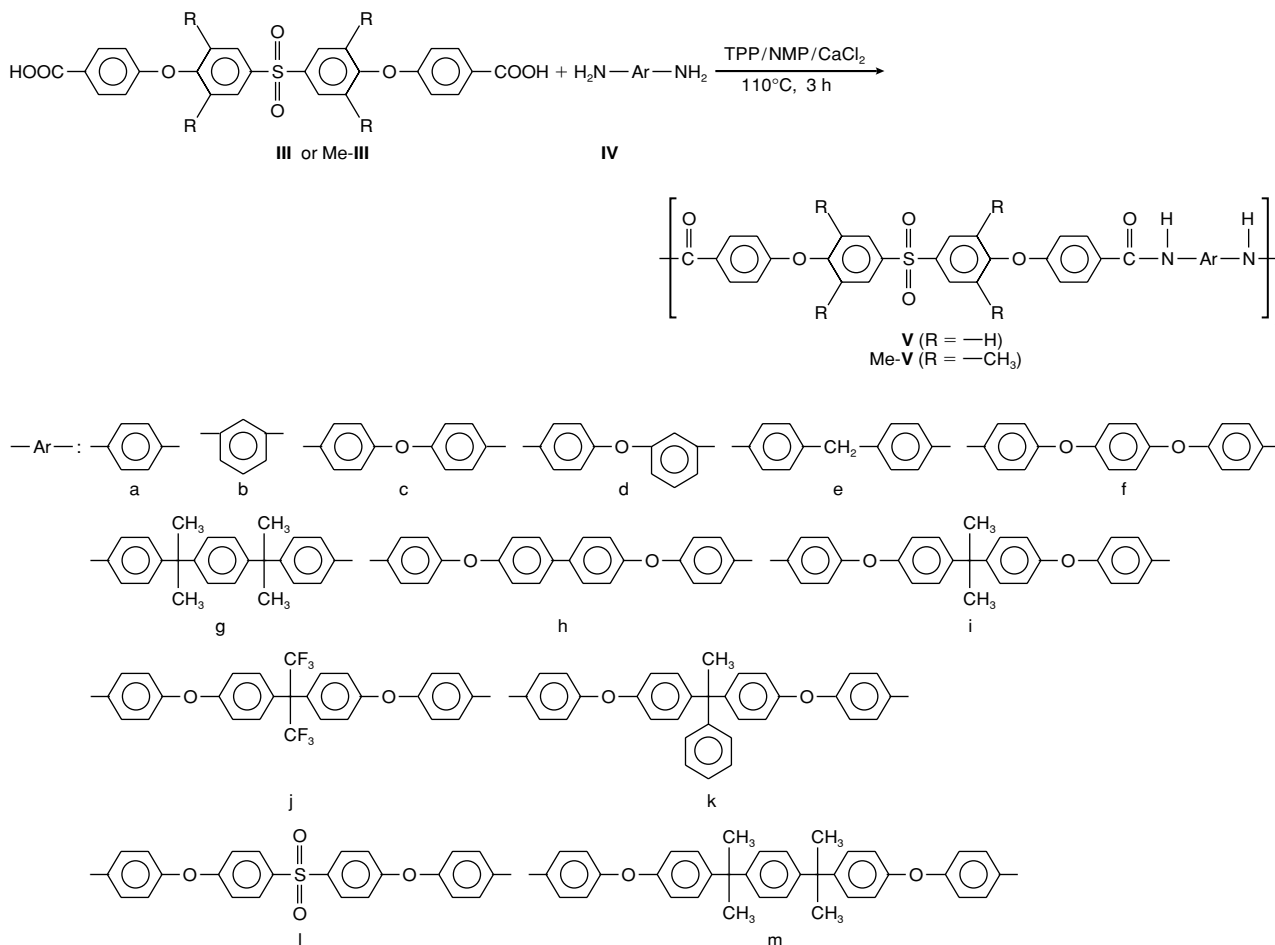
According to a reported method,¹² 4,4'-bis(4-aminophenoxy)biphenyl (**IV_h**), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**IV_i**), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**IV_j**), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**IV_k**), bis[4-(4-aminophenoxy)phenyl] sulfone (**IV_l**), and α,α' -bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**IV_m**) were pre-

pared by the aromatic nucleophilic substitution reaction of the corresponding biphenols and *p*-chloronitrobenzene in the presence of a base such as K₂CO₃, giving the bis(*p*-nitrophenoxy) compounds, and subsequent reduction of the dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst. *p*-Phenylenediamine (**IV_a**) (from TCI) was purified by vacuum sublimation, and *m*-phenylenediamine (**IV_b**) (from Janssen) was purified by vacuum distillation. The other diamines such as 4,4'-diaminodiphenyl ether (**IV_c**) (from TCI), 3,4'-diaminodiphenyl ether (**IV_d**) (from Mitsui Petrochemical Ind.), 4,4'-diaminophenylmethane (**IV_e**) (from TCI), 1,4-bis(*p*-aminophenoxy)benzene (**IV_f**) (from TCI), and α,α' -bis(4-aminophenyl)-1,4-diisopropylbenzene (**IV_g**) (from Mitsui Petrochemical Ind.) were used without purification. Commercially obtained anhydrous calcium chloride were dried under vacuum at 180°C for 10 h. Triphenyl phosphite (TPP) (from Wako) was used without previous purification. NMP and pyridine were purified by distillation under reduced pressure over calcium hydride.

Monomer Synthesis

4,4'-[Sulfonylbis(2,6-Dimethyl-1,4-phenylene)-dioxy]dibenzonitrile (**Me-II**)

4,4'-Sulfonylbis(2,6-dimethylphenol) (15.32 g, 0.05 mol) and K₂CO₃ (13.82 g, 0.1 mol) were suspended in a mixture of 100 mL of DMF and 60

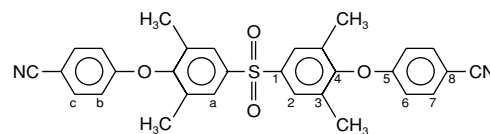


Scheme 2.

mL of toluene, and heated with stirring at reflux temperature using a Dean–Stark trap to remove the water azeotropically. After removal of the residual toluene, *p*-fluorobenzonitrile (12.11 g, 0.1 mol) was added, and heating was continued at 150°C for 6 h. Then, the reaction mixture was cooled and poured into 600 mL of water. The precipitated product was filtered off and dried (93.2% yield), and recrystallized from methanol to afford colorless needles of Me-II, mp 197–199°C. IR (KBr): 2232 cm⁻¹ (C≡N str.), 1282–1323 cm⁻¹ [asym. S(=O)₂ str.], 1141–1191 cm⁻¹ [sym. S(=O)₂ str.], 1241 cm⁻¹ (C—O str.). ¹H-NMR (δ ppm, in CDCl₃): 7.80 (s, 4H, H_a), 6.86 (d, 4H, H_b), 7.63 (d, 4H, H_c), 2.20 (s, 12H, —CH₃). ¹³C-NMR (δ ppm, in CDCl₃): 159.83 (C⁵), 153.92 (C⁴), 138.54 (C¹), 134.53 (C⁷), 132.96 (C³), 128.66 (C²), 118.42 (cyano carbon), 115.41 (C⁶), 105.80 (C⁸), 16.39 (methyl carbon).

Anal. Calcd for C₃₀H₂₄N₂O₄S (508.60): C,

70.85%; H, 4.76%; N, 5.51%. Found: C, 70.84%; H, 5.13%; N, 5.28%.

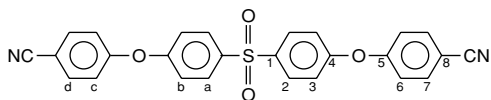


4,4'-[Sulfonylbis(1,4-Phenylene)dioxy]-dibenzonitrile (II)

The dinitrile II was prepared starting from 4,4'-sulfonyldiphenol and *p*-fluorobenzonitrile in an analogous procedure. Yield 99%, mp 201–203°C. IR (KBr): 2230 cm⁻¹ (C≡N str.), 1279–1325 cm⁻¹ [asym. S(=O)₂ str.], 1152–1172 cm⁻¹ [sym. S(=O)₂ str.], 1253 cm⁻¹ (C—O str.). ¹H-NMR (δ ppm, in CDCl₃): 8.03 (d, 4H, H_a), 7.20 (d, 4H, H_b), 7.20 (d, 4H, H_c), 7.73 (d, 4H, H_d). ¹³C-NMR (δ ppm, in CDCl₃): 159.69 (C⁴), 159.21

(C⁵), 137.15 (C¹), 134.42 (C⁷), 130.16 (C²), 119.68 (C³), 119.54 (C⁶), 118.19 (cyano carbon), 107.99 (C⁸).

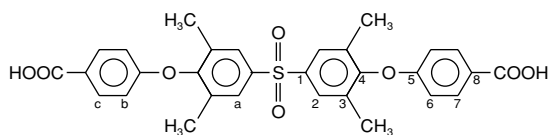
Anal. Calcd for C₃₄H₁₆N₂O₄S (452.49): C, 69.01%; H, 3.56%; N, 6.19%. Found: C, 68.60%; H, 3.85%; N, 5.59%.



4,4'-[Sulfonylbis(2,6-Dimethyl-1,4-phenylene)-dioxo]dibenzoic Acid (Me-III)

A suspension of dinitrile Me-II (19 g, 0.0374 mol) in 500 mL of 1 : 1 volume mixture of water and ethanol containing 56 g (1.0 mol) of KOH was refluxed for 20 h. The resulting hot clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and was acidified by conc. HCl to pH = 2–3, and the white precipitate was filtered off, washed with water and dried to get 19.0 g (95% yield) of carboxylic acid Me-III, mp 312–315°C. IR (KBr): 2400–3600 cm⁻¹ (O—H str.), 1688 cm⁻¹ (C=O str.), 1282 cm⁻¹ [asym. S(=O)₂ str.], 1164–1139 cm⁻¹ [sym. S(=O)₂ str.], 1232 cm⁻¹ (C—O str.). ¹H-NMR (δ ppm, in DMSO-*d*₆): 8.00 (s, 4H, H_a), 6.90 (d, 4H, H_b), 8.00 (d, 4H, H_c), 2.20 (s, 12H, —CH₃). ¹³C-NMR (δ ppm, in DMSO-*d*₆): 167.43 (carboxyl carbon), 160.50 (C⁵), 154.90 (C⁴), 138.88 (C¹), 133.59 (C⁷), 129.35 (C²), 132.72 (C³), 125.68 (C⁸), 115.27 (C⁶), 16.75 (methyl carbon).

Anal. Calcd for C₃₀H₂₆O₈S (550.63): C, 65.92%; H, 4.79%. Found: C, 65.36%; H, 4.72%.

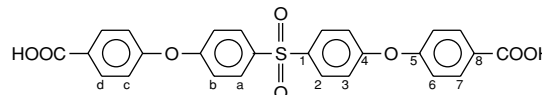


4,4'-[Sulfonylbis(1,4-Phenylene)dioxo]dibenzoic Acid (III)

Dicarboxylic acid III was prepared from the alkaline hydrolysis of dinitrile II in a similar procedure. Yield 95%, mp 288–290°C (DSC 292°C) (lit.⁷ 308–309°C; lit.¹³ 292–295°C). IR (KBr): 2400–3600 cm⁻¹ (O—H str.), 1680 cm⁻¹ (C=O str.), 1323–1294 cm⁻¹ [asym. S(=O)₂ str.], 1164–1154 cm⁻¹ [sym. S(=O)₂ str.], 1247 cm⁻¹ (C—O str.). ¹H-NMR (δ ppm, in DMSO-*d*₆): 8.01

(d, 4H, H_a), 7.30 (d, 4H, H_b), 7.20 (d, 4H, H_c), 8.02 (d, 4H, H_d). ¹³C-NMR (δ ppm, in DMSO-*d*₆): 166.58 (carboxyl carbon), 158.61 (C⁵), 160.16 (C⁴), 136.08 (C¹), 131.85 (C⁷), 130.04 (C²), 119.34 (C³), 127.10 (C⁸), 118.67 (C⁶).

Anal. Calcd for C₂₆H₁₈O₈S (490.49): C, 63.67%; H, 3.70%. Found: C, 63.62%; H, 3.86%.



Polymer Synthesis

A typical polymerization procedure is as follows. A mixture of 0.6832 g (1.25 mmol) of diacid Me-III, 0.1325 g (1.25 mmol) of *m*-phenylenediamine, 0.2 g of calcium chloride, 0.9 mL of TPP, 0.8 mL of pyridine, and 15 mL of *N*-methyl-2-pyrrolidone (NMP) was heated with stirring at 110°C for 3 h. The obtained polymer solution was trickled into 300 mL of methanol giving rise to a stringy precipitate, which was washed thoroughly with methanol and hot water, collected by filtration, and dried. The product was 0.816 g (Yield 99.7%), and the inherent viscosity of the polymer was 1.01 dL/g as measured in *N,N*-dimethylacetamide (DMAc) containing 5% LiCl at a concentration of 0.5 g/dL at 30°C. IR (film): 3344 cm⁻¹ (N—H str.), 1665 cm⁻¹ (C=O str.), 1301 cm⁻¹ [asym. S(=O)₂ str.], 1170–1151 cm⁻¹ [sym. S(=O)₂ str.], 1245 cm⁻¹ (C—O str.).

All other polyamides were synthesized by an analogous procedure as above.

Preparation of Polyamide Films

A solution of polymer was made by dissolving above 0.8 g of the polymer in 8 mL of DMAc to afford an approximate 10 wt % solution. The clear solution was poured into a 9-cm-diameter glass culture dish, which was placed in a 80°C oven overnight to remove the solvent. The semidried polyamide film was lifted from the glass surface and further dried in vacuo at 120°C for 6 h. The obtained films had about 0.1 mm in thickness and were ready for X-ray diffraction measurements and tensile tests.

Measurements

All melting points were determined on a Mel-temp II melting point apparatus and were uncorrected.

Table I. Inherent Viscosities, Average Molecular Weight, and Film Quality of Polyamides

Polymer ^a	η_{inh}^b (dL/g)	\bar{M}_w^c ($\times 10^{-4}$)	\bar{M}_n^c ($\times 10^{-4}$)	\bar{M}_w/\bar{M}_n	Film Quality ^e
V_a	0.62	— ^d	—	—	— ^f
V_b	0.74	14.40	5.89	2.44	Flexible
V_c	0.74	6.60	3.09	2.14	Flexible
V_d	0.56	5.91	2.60	2.27	Flexible
V_e	0.54	5.28	2.51	2.11	Flexible
V_f	0.69	7.01	3.06	2.29	Flexible
V_g	0.55	5.48	2.37	2.31	Flexible
V_h	0.86	—	—	—	Brittle
V_i	0.66	7.03	4.39	1.60	Flexible
V_j	0.60	7.76	4.34	1.79	Flexible
V_k	0.53	5.75	3.70	1.55	Flexible
V_l	0.58	6.31	3.99	1.57	Flexible
V_m	0.60	7.66	4.15	1.85	Flexible
Me- V_a	0.52	—	—	—	—
Me- V_b	1.01	8.91	4.71	1.88	Flexible
Me- V_c	0.64	8.59	4.42	1.94	Flexible
Me- V_d	0.62	7.83	4.60	1.70	Flexible
Me- V_e	0.50	6.24	3.65	1.71	Flexible
Me- V_f	0.59	—	—	—	Brittle
Me- V_g	0.42	6.91	4.16	1.66	Flexible
Me- V_h	0.71	—	—	—	Flexible
Me- V_i	0.53	7.20	4.03	1.79	Flexible
Me- V_j	0.51	6.36	4.08	1.56	Flexible
Me- V_k	0.40	5.67	3.56	1.59	Flexible
Me- V_l	0.40	5.79	4.07	1.42	Flexible
Me- V_m	0.40	6.71	3.68	1.82	Flexible

^a Polymerization was carried out using 1.25 mmol each of diacid and diamine monomers, 0.8 mL of pyridine, 0.9 mL of triphenyl phosphite, 0.2–0.3 g of CaCl₂, 1.5–2.5 mL of NMP at 110°C for 3 h.

^b Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl dissolved.

^c Determined by GPC, with DMF + 0.01 mol/L LiBr as the eluent and polystyrene as the standard.

^d Insoluble in the eluent of GPC measurements.

^e Films were cast by slow evaporation of polymer solutions in DMAc.

^f Insoluble in DMAc.

Elemental analyses were performed with a Perkin–Elmer C, H, N 2400 elemental analyzer. Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform spectrometer. ¹H-NMR and ¹³C-NMR spectra were measured at 30°C on a Jeol EX-400 NMR spectrometer with perdeuterio-dimethyl sulfoxide (DMSO-*d*₆) as an external reference, working at 400 and 100 Hz, respectively. The inherent viscosities of all polymers were determined at 0.5 g/dL concentration using a Cannon-Fenske viscometer thermostated at 30°C. 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 polystyrene calibration on a Shimadzu LC-6A apparatus (column: Tosoh TSK-GEL; eluent: DMF containing 0.01 mol/L of lithium bromide; pumping rate: 1 mL/min; detec-

tor: a refractive index detector; temperature: 40°C). Differential scanning calorimetry (DSC) analysis were performed on a Sinku Riko 7000 differential scanning calorimeter coupled to a Sinku Riko 7000 thermal analyzer at the heating rate of 10°C/min in flowing nitrogen (30 cm³/min). Thermogravimetric data were obtained on a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm³/min) at a heating rate of 20°C/min. Thermomechanical analysis (TMA) was conducted with a Rigaku TMA 8140 at a heating rate of 10°C/min in nitrogen. The wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) with film (or powder) specimens of about 0.1 mm thick on a Rigaku Geiger-Flex D-Max III_a X-ray diffrac-

Table II. Solubility Behavior of Polyamides^a

Polymer	Solvent ^b					
	DMF	DMSO	NMP	DMAc	<i>m</i> -Cresol	THF
V _a	—	—	—	—	—	—
V _b	+	+	+	+	+	—
V _c	+	+	+	+	+	—
V _d	+	+	+	+	+	—
V _e	+	+	+	+	+	—
V _f	+	+	+	+	+	—
V _g	+	+	+	+	+	+h
V _h	—	—	+	—	—	—
V _i	+	+	+	+	+	+
V _j	+	+	+	+	+	+
V _k	+	+	+	+	+	+h
V _l	+	+	+	+	+	—
V _m	+	+	+	+	+	+
Me-V _a	—	—	—	—	—	—
Me-V _b	+	+	+	+	+	—
Me-V _c	+	+	+	+	+	—
Me-V _d	+	+	+	+	+	—
Me-V _e	+	+	+	+	+h	—
Me-V _f	—	—	+	+	—	—
Me-V _g	+	+	+	+	+h	—
Me-V _h	—	—	+	—	—	—
Me-V _i	+	+	+	+	+	+h
Me-V _j	+	+	+	+	+	+
Me-V _k	+	+	+	+	+	+
Me-V _l	+	+	+	+	+	—
Me-V _m	+	+h	+	+	+	+

^a +: Soluble at room temperature; +h: soluble on heating; —: insoluble even on heating.

^b DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; NMP: *N*-methyl-2-pyrrolidone.

tometer, using Ni-filtered CuK α radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$. An Instron universal tester Model 1130 with a load cell 5 kg was used to study the stress–strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at the room temperature with film specimens (0.5 wide, 6 long, and about 0.1 mm thick) and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Monomer Synthesis

The dicarboxylic acid monomers which containing both sulfone and ether linkages, that is, 4,4'-[sulfonylbis(2,6 - dimethyl - 1,4 - phenylene)dioxy] -

dibenzoic acid (Me-**III**) and 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoic acid (**III**), were prepared by a two-step synthetic route outlined in Scheme I. In the first step, the intermediate dinitriles 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzonitrile (Me-**II**) and 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzonitrile (**II**) were obtained from the nucleophilic fluorodisplacement of *p*-fluorobenzonitrile with the potassium phenolates of 4,4'-sulfonylbis(2,6-dimethylphenol) (Me-**I**) and 4,4'-sulfonyldiphenol (**I**) in *N,N*-dimethylformamide (DMF). The dinitriles were then readily converted into the corresponding dicarboxylic acids by alkaline hydrolysis. The yield was high (>90%). The structures of intermediate dinitriles Me-**II** and **II** and dicarboxylic acids Me-**III** and **III** were confirmed by elemental analysis and IR and NMR spectroscopy. The mp of diacid **III** was reported to be 292–295°C (ref. 13) and 306–308°C (ref. 7), respectively, by

two groups. The value we observed is close to that reported by the former. It was found that diacid **III** prepared in this work melted in the 288 to 290°C range in a capillary and showed a sharp melting endotherm in the range of 290 to 293°C (peak temperature 292°C) on its DSC curve.

Polymer Synthesis

Serial polyamides V_{a-m} and Me- V_{a-m} having ether and sulfone groups in main chains were prepared by a phosphorylation reaction according to Yamazaki,¹⁴ which was carried out under 110°C for 3 h by reacting diacid **III** and Me-**III**, respectively, with various aromatic diamines IV_{a-m} in NMP containing dissolved $CaCl_2$ using triphenyl phosphite and pyridine as condensing agents. All the structures of the diamines and polyamides are shown in Scheme II. Due to insolubility, polyamides V_a and Me- V_a precipitated out of the reaction media in the early stage. In other cases, all the polymerization reactions proceeded homogeneously throughout the reaction. As shown in Table I, all the polymers were obtained in quantitative yields with inherent viscosities of 0.40–1.01 dL/g. The GPC curves indicated that \bar{M}_w values of the polyamides were in the range of 52,000 to 144,000, relative to standard polystyrene, and the polydispersity index \bar{M}_w/\bar{M}_n ranged from 1.42 to 2.44. Except for polyamides V_a and Me- V_a , all polyamides were soluble in DMAc and could be cast into free standing films. The films made from V_h and Me- V_f were noncreasable, and other polyamide films were flexible and tough.

The structure of these polyamides was ascertained by IR spectroscopy. Some characteristic absorptions appeared in the IR spectrum, such as N—H stretching near 3350 cm^{-1} , C=O stretching near 1665 cm^{-1} , S(=O)₂ stretching near 1300 cm^{-1} and 1150 cm^{-1} , and aryl ether stretching near 1245 cm^{-1} .

Properties of Polymers

The qualitative solubility behavior of all the polyamides is included in Table II. With the exception of polyamides V_a and Me- V_a , all other polyamides were soluble in DMAc and NMP. Most of the polyamides were also readily soluble in DMF, dimethylsulfoxide (DMSO), and *m*-cresol. Polyamides V_h , Me- V_f , and Me- V_h showed somewhat limited solubility, probably due to moderate crystallinity as evidenced by the X-ray diffraction patterns. In general, these polyamides revealed good solubility

Table III. Tensile Properties of Polyamide Films

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (GPa)
V_b	75	7	1.51
V_c	66	10	1.20
V_d	68	7	1.39
V_e	63	11	1.23
V_f	65	10	1.14
V_g	69	10	1.19
V_i	56	18	1.12
V_j	64	8	1.16
V_k	68	9	1.23
V_l	61	9	1.18
V_m	70	9	1.06
Me- V_b	77	8	1.49
Me- V_c	71	10	1.38
Me- V_d	72	9	1.32
Me- V_e	69	10	1.16
Me- V_g	64	8	1.28
Me- V_h	77	14	1.37
Me- V_i	67	9	1.14
Me- V_j	66	9	1.21
Me- V_k	70	9	1.21
Me- V_l	70	9	1.27
Me- V_m	67	9	1.17

due to the presence of ether and sulfone links in the backbone, and the methyl substituents on the aromatic ring seemed do not significantly affect their solubility behavior.

All the polyamides that showed high solubility exhibited amorphous patterns in the wide-angle X-ray diffraction measurement, and they could be solution-cast into transparent, flexible, and tough films. The tensile properties of these flexible films are given in Table III. The films had tensile strengths of 56–77 MPa, elongations at break of 7–18%, and initial moduli of 1.06–1.51 GPa. All polymer films did not show yield points on their stress–strain curves except for polyamide V_i . The elongation at break of these films is low, so they behave as strong and hard materials.

Thermal properties of all the polyamides were evaluated by thermogravimetry analysis (TGA), DSC, and thermomechanical analysis (TMA). The thermal behavior data of all the polymers are summarized in Table IV. Rapid cooling from the elevated temperature (about 300–350°C) to room temperature in air yield more amorphous samples so that in almost all cases the T_g s could be easily measured in the second heating traces of DSC. The middle of baseline shift on the second DSC

Table IV. Thermal Properties of Polyamides

Polymer	T_g^a (°C)	T_s^b (°C)	T_d^c (°C)		Char Yield ^c (%)
			In N ₂	In Air	
V_a	— ^e	— ^f	489	480	52.7
V_b	239	233	484	484	55.8
V_c	238	222	509	505	51.5
V_d	223	220	499	497	52.2
V_e	237	222	488	488	60.5
V_f	220	221	502	493	51.6
V_g	212	236	476	465	49.7
V_h	220	—	507	487	51.0
V_i	217	224	501	504	45.6
V_j	226	223	512	508	53.0
V_k	230	228	505	500	54.8
V_l	241	208	507	499	45.8
V_m	213	213	500	501	46.9
Me- V_a	—	—	445	425	39.8
Me- V_b	271	227	433	427	59.1
Me- V_c	272	259	453	440	52.9
Me- V_d	258	248	435	439	56.1
Me- V_e	—	246	432	433	48.5
Me- V_f	—	—	440	440	57.5
Me- V_g	257	252	439	431	39.5
Me- V_h	268	246	439	437	47.0
Me- V_i	248	246	441	440	53.2
Me- V_j	251	239	449	447	51.8
Me- V_k	249	243	444	445	46.8
Me- V_l	266	232	443	440	52.8
Me- V_m	234	227	444	447	44.7

^a Baseline shifts in the second heating DSC traces, with a heating rate of 20°C/min.

^b Softening temperatures measured by the TMA (penetration method) with a load of 5 g at a heating rate of 10°C/min.

^c Decomposition temperatures at which 10% weight loss were recorded by TG at a heating rate of 20°C/min.

^d Residual weight (%) when heated to 800°C in nitrogen.

^e No discernible transitions were observed.

^f Did not measure.

heating trace was judged as T_g . The T_g s of the methyl-substituted polyamides stayed in the 234 to 272°C range, and those of the unsubstituted polyamides were in the range of 212 to 241°C. The difference in T_g values between the methyl-substituted polyamides and the corresponding unsubstituted analogues are attributed to the hindrance effect of the chain rotation in the methyl-substituted polymers.¹⁵ The T_g values of some polyamides such as those of **V_b**, **V_c**, and **V_e** are lower than those reported in literature⁷ may be attributed to lower molecular weights (η_{inh} values). The softening temperatures (T_s , which may be considered as apparent T_g) of polymer films measured by TMA are also included in Table IV. In most cases, the T_s values were lower than T_g s. This difference may be explained by the fact that these ether and sulfone-containing

polyamides exhibited a certain degree of plasticity near T_g .

The representative TG diagrams of polyamides **V_b** and Me-**V_b** in air and nitrogen are shown in Figure 1. Polymer **V_b** showed a very similar TG behavior in nitrogen and air atmospheres below 550°C, but when the temperature was increased above 550°C, the polymer showed a rapid weight loss and decomposed nearly completely at 750°C in air. As can be seen from Figure 1, the presence of methyl substituents on the aromatic rings led to an earlier decomposition, due to the less thermally stable nature of aliphatic groups. The TG data of all polyamides are listed in Table IV. The polyamides without methyl substituents lost 10% weight at temperatures in the range of 465 to 509°C, and the methyl-substituted polyamides in the range of 425 to 457°C.

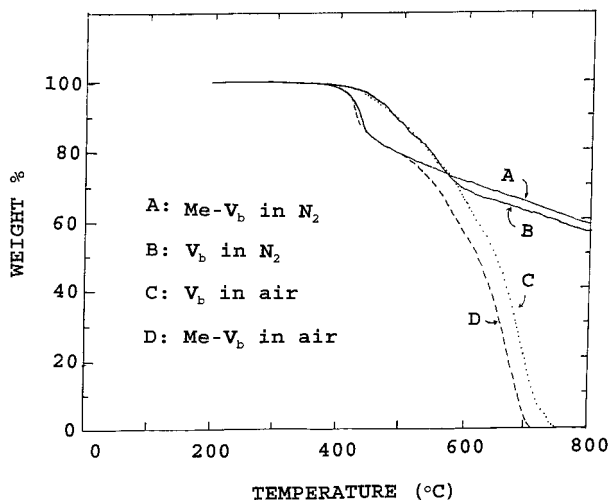


Figure 1. TG thermograms for polyamides V_b and $Me-V_b$ at a heating rate of $20^\circ\text{C}/\text{min}$.

CONCLUSIONS

The solution direct polycondensation of 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoic acid or 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoic acid with aromatic diamines, using triphenyl phosphite and pyridine as condensing agents, to generate moderate to high molecular weight polyamides with aryl ether and sulfone groups was successful. The polyamides had inherent viscosities of 0.40–1.01 dL/g. Most of them could be cast into flexible and strong films. The methyl-substituted polyamides had higher T_g but lower initial decomposition temperature than the corresponding unsubstituted polymers.

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REFERENCES AND NOTES

1. P. E. Cassidy, *Thermally Stable Polymer*, Dekker, New York, 1980.
2. H. H. Yang, in *Aromatic High-Strength Fibers*, John Wiley & Sons, New York, 1989.
3. S.-H. Hsiao and C.-P. Yang, *J. Polym. Sci. Part A: Polym. Chem.*, **28**, 2501 (1990).
4. H. Manami, M. Nakazawa, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **28**, 465 (1990).
5. C.-P. Yang and W.-T. Chen, *Makromol. Chem.*, **193**, 2323 (1991).
6. C.-P. Yang and J.-H. Lin, *J. Polym. Sci. Part A: Polym. Chem.*, **31**, 2153 (1993).
7. C. Chiriac and J. K. Stille, *Macromolecules*, **10**, 712 (1977).
8. G. L. Brode, G. T. Kwiatkowski, and A. W. Bedwin, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 575 (1974).
9. J. Adduci, L. L. Chapoy, G. Jonsson, J. Kops, and B. M. Shinde, *J. Appl. Polym. Sci.*, **28**, 2069 (1983).
10. S. B. Idage, B. B. Idage, B. M. Shinde, and S. P. Vernekar, *J. Polym. Sci. Part A: Polym. Chem.*, **28**, 583 (1983).
11. N. Avella, G. Maglio, R. Palumbo, F. Russo, and M. C. Vignola, *Makromol. Chem. Rapid. Comm.*, **14**, 545 (1993).
12. S.-H. Hsiao, C.-P. Yang, and C.-K. Lin, *J. Polym. Res.*, **2**, 1–12 (1995); *Chem. Abstr.*, **123**, 287811g.
13. Von G. Lorenz, M. Gallus, W. Giessler, F. Bodesheim, H. Wieden, and G. E. Nischk, *Makromol. Chem.*, **130**, 65 (1969).
14. N. Yamazaki, M. Matsumoto, and F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1373 (1975).
15. F. Keitoku, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **32**, 317 (1994).