

Polyaramides Containing Arylene Sulfone Ether Linkages*

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Synopsis

Polyamides containing arylene sulfone ether linkages were synthesized from 4,4'-[sulfonylbis (*p*-phenyleneoxy)] dibenzoyl chloride (SPCl), 3,3'-[sulfonylbis (*p*-phenyleneoxy)] dibenzoyl chloride (SMCl) and various aromatic diamines (ARD), by solution and interfacial polymerization techniques. In solution polymerization, the effect of various acid acceptors such as propylene oxide (PO), lithium hydroxide (LiOH) in the presence of lithium chloride (LiCl), and triethylamine (TEA) on the molecular weight of the polyamides was studied. The effect of structure of various aromatic diamines on molecular weight and thermal properties of polyamides was also studied. The polyamides prepared were characterized by solution viscosity, elemental analysis, thermo-gravimetric analysis, differential scanning calorimetry, and x-ray diffraction. Physical and thermal properties of polyamides prepared from SPCl and ARD were compared with the polyamides prepared from SMCl and ARD.

INTRODUCTION

Aromatic polyamides are well known for their high temperature stability, excellent mechanical properties and high thermooxidative stability. However, these polymers suffer because of their insolubility in organic solvents. Of various methods tried to improve their solubility in organic solvents, introduction of aromatic sulfone and ether groups in the polymer backbone met with much success, without affecting other properties. Thus aromatic polyamides containing aryl ether, aryl sulfone, or aryl sulfone ether linkages are well known in the literature¹⁻⁴ for their superior solubility in organic solvents in addition to excellent chain flexibility and tractability, high thermooxidative stability, and mechanical properties.⁵⁻⁸ Generally, these polymers are amorphous and have low glass transition temperatures. They have good potential for commercial exploitation. Recently, they have been proposed as new candidates for thermotropic liquid crystalline polymers.⁹

The present work was undertaken to study comparatively the effect of the structures of various aromatic diamines on the properties of polyamides obtained from para- and meta-linked diacids containing sulfone ether linkages. Polyamides were prepared by both solution and interfacial polymerization techniques. In the solution polymerization method, various acid acceptors such as propylene oxide, lithium hydroxide in the presence of lithium chloride, and triethylamine were used and their effect on molecular weight of the polyamides was studied. The present study also describes the synthesis of

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4,4'-[sulfonylbis (*p*-phenyleneoxy)] dibenzoic acid (SPA) and 3,3'-[sulfonylbis (*p*-phenyleneoxy)] dibenzoic acid (SMA) by a modified route which gives high yields in a short time. Reported methods^{10,11} require 16–40 h for the reaction and give low yields. The present method gives 90% yield of the ditolyl compounds in 5 h and 80% yield of the corresponding diacids.

EXPERIMENTAL

Materials

1,3-Phenylene diamine (MPDA) and 1,4-phenylene diamine (PPDA) (Fluka, AG, West Germany) were purified by vacuum sublimation.

4,4'-Diaminodiphenyl (Benzidine) (Sisco, Bombay) was purified by recrystallization from ether.

4,4'-Diaminodiphenylmethane (MDA) (Bayer, AG, West Germany) was purified by distillation under reduced pressure followed by recrystallization from benzene.

4,4'-Diaminodiphenylether (ODA) (EGA, Chemie., West Germany) was purified by recrystallization from tetrahydrofuran.

4,4'-Diaminodiphenylsulfone (SDA) (Fisions, Philadelphia) was purified by recrystallization from ethanol.

p-Cresol and *m*-cresol (Sisco, Bombay) were purified by distillation under reduced pressure.

4,4'-Dichlorodiphenylsulfone (DCPS) (Fluka, AG, Switzerland) was used as received.

N-Methyl-2-pyrrolidone (NMP) (Fluka, AG, Switzerland), *N,N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) (SD's, Bombay) were dried over molecular sieves and distilled under reduced pressure.

Potassium fluoride (KF), Propylene oxide (PO), lithium hydroxide (LiOH), lithium chloride (LiCl), and triethylamine (TEA) (Loba Chemie, Bombay) were purified by standard procedures.

4,4'-[Sulfonylbis (*p*-phenyleneoxy)] dibenzoyl chloride (SPCl) and 3,3'-[sulfonylbis (*p*-phenyleneoxy)] dibenzoyl chloride (SMCl) were prepared in our laboratory and used after recrystallization from the appropriate solvents.

Instrumental Methods

Infrared spectra were recorded on a Perkin Elmer spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian T-60, Bruker WH 90 MHz spectrophotometer with TMS as an internal standard.

Ubbelohde viscometers were used to determine inherent viscosities of polymer solutions having concentrations of 0.5 g/100 mL in dimethylformamide. A constant temperature bath was maintained at 30°C.

Thermogravimetric analyses were obtained with a Netzsch STA 409 Thermogravimetric Analyzer in a flowing air environment. Heating rate used for the determinations was 5°C min⁻¹. Temperature was measured by a Pt-Pt Rh (10%) thermocouple.

Differential scanning calorimetry thermograms were obtained with a Perkin-Elmer Differential Scanning Calorimeter DSC 2 equipped with Thermal Analysis Data Station (TADS). Rate of heating used was 20°C min⁻¹.

The x-ray diffractograms were obtained with a Phillips x-ray unit (Phillips generator, PW-1730) and a nickel filtered CuK_α radiation.

Monomer Synthesis

4,4'-[Sulfonylbis (p-phenyleneoxy)] Ditoluene (SPM)

To a three-necked 250-mL round-bottomed flask, equipped with reflux condenser, thermowell, nitrogen gas inlet tube, and stirring arrangement was added 8.65 g (0.08 mol) *p*-cresol, 4.49 g (0.08 mol) potassium hydroxide and 75 mL DMSO. The reaction mixture was heated to 70°C with stirring, water of neutralization was removed under vacuum with some quantity of DMSO. To the resulting potassium salt was added 11.49 g (0.04 mol) 4,4'-dichlorodiphenylsulfone, 2.0 g potassium fluoride and 50 mL dry DMSO.

The mixture was heated at 125°C under nitrogen atmosphere with stirring for 5 h. After cooling, the reaction mixture was poured into water. The product was washed 4 to 5 times with water and extracted with dichloromethane. The dichloromethane layer was dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure and recrystallization from methanol yielded 16.4 g (95%) of pure SPM, *mp* 128°C.

The SPM was characterized by infrared (IR), ^1H NMR, mass spectral, and elemental analysis.

ANAL. Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_4\text{S}$ (430): C, 72.55%; H, 5.11%. Found: C, 72.25%; H, 5.24%.
Mass Spectrum: Molecular ion (M^+) peak at 430.

4,4'-[Sulfonylbis (p-phenyleneoxy)] Dibenzoic Acid (SPA)

To a 250-mL four-necked round-bottomed flask, equipped with an efficient mechanical stirrer, a reflux condenser, thermowell, and addition funnel were added 12.9 g (0.03 mol) of SPM, 150 mL water, and 100 mL pyridine. The temperature was raised to 95°C and solid KMnO_4 was added portionwise to maintain a slow reflux which was continued for 3 h. The excess KMnO_4 was destroyed by adding methanol. The MnO_2 was removed by filtration and washed with a large volume of boiling water and the washings were combined with the filtrate. The filtrate, after removal of excess pyridine, was treated with activated charcoal and acidified with dilute HCl. The precipitated acid was collected by filtration, washed with water, then dissolved in sodium bicarbonate solution, again treated with activated charcoal and finally acidified with HCl to obtain 11.76 g (80%) of SPA after recrystallization from dioxane, *mp* 306–308°C.

The SPA prepared by this method was characterized by IR, ^1H NMR, mass spectral, and elemental analysis.

ANAL. Calcd for $\text{C}_{26}\text{H}_{18}\text{O}_8\text{S}$ (490): C, 63.67%; H, 3.67%. Found: C, 63.26%; H, 3.76%.
Mass spectrum: Molecular ion (M^+) peak at 490.

4,4'-[Sulfonylbis (p-phenyleneoxy)] Dibenzoyl Chloride (SPCl)

To a 100-mL round-bottomed flask equipped with reflux condenser, guard tube, and stirring arrangement, was added 4.9 g (0.01 mol) diacid (SPA) and 40 mL thionyl chloride. The mixture was heated to the reflux temperature for 2 h, after which time 3–4 drops of DMF were added. Heating continued for

another 2 h, and the mixture was left overnight at room temperature. The thionyl chloride was removed under reduced pressure at 40–50°C. The dry crude product was recrystallized from dry benzene to yield 4.8 g (91%) of pure SPCL, *mp* 184–186°C.

The diacid chloride prepared was characterized by IR, ¹H NMR, mass spectral, and elemental analysis.

ANAL. Calcd for C₂₆H₁₆O₆SCl₂ (526): C, 59.20%; H, 3.04%. Found: C, 59.10%; H, 3.00%.

Mass spectrum: Molecular ion (M⁺) peak at 526.

3,3'-[Sulfonylbis (p-phenyleneoxy)] Ditoluene (SMM)

To a three-necked 250 mL round-bottomed flask, equipped with reflux condenser, thermowell, nitrogen gas inlet tube, and stirring arrangement was added 8.65 g (0.08 mol) *m*-cresol, 4.49 g (0.08 mol) potassium hydroxide, and 75 mL DMSO. The reaction mixture was heated to 70°C with stirring. Water of neutralization was removed under vacuum with some quantity of DMSO. To the resulting potassium salt was added 11.49 g (0.04 mol) 4,4'-dichlorodiphenylsulfone, 2.0 g potassium fluoride, and 50 mL dry DMSO.

The mixture was heated at 125°C under nitrogen atmosphere with stirring for 5 h. After cooling, the reaction mixture was poured into water. The product was washed 4 to 5 times with water and extracted with ether. The ether layer was dried over anhydrous sodium sulfate. Removal of solvent and distillation under reduced pressure yielded 16.0 g (93%) of pure SMM, *bp* 260–5°C/8 mm.

The SMM prepared was characterized by IR, ¹H NMR, mass spectral, and elemental analysis.

ANAL. Calcd for C₂₆H₂₂O₄S (430): C, 72.55%; H, 5.11%. Found: C, 72.40%; H, 5.20%.

Mass spectrum: Molecular ion (M⁺) peak at 430.

3,3'-[Sulfonylbis (p-phenyleneoxy)] Dibenzoic Acid (SMA)

To a 250-mL four-necked round-bottomed flask, equipped with an efficient mechanical stirrer, a reflux condenser, a thermowell, and addition funnel was added 12.9 g (0.03 mol) of SMM, 150 mL water, and 100 mL pyridine. The temperature was raised to 95°C and solid KMnO₄ was added portionwise to maintain a slow reflux, and was continued for 3 h. The excess KMnO₄ was destroyed by adding methanol. The MnO₂ was removed by filtration and washed with a large volume of boiling water; the washings were combined with the filtrate. After removal of excess pyridine, the filtrate was treated with activated charcoal and acidified with dilute HCl. The precipitated acid was collected by filtration, washed with water, then dissolved in sodium bicarbonate solution, again treated with activated charcoal, and finally acidified with HCl to obtain 11.46 g (78%) of SMA after recrystallization from methanol, *mp* 230–232°C.

The SMA prepared by this method was characterized by IR, ¹H NMR, mass spectral, and elemental analysis.

ANAL. Calcd for C₂₆H₁₈O₈S (490): C, 63.67%; H, 3.67%. Found: C, 63.56%; H, 3.78%.

Mass spectrum: Molecular ion (M⁺) peak at 490.

3,3'-(Sulfonylbis(p-phenyleneoxy)) Dibenzoyl Chloride (SMCl)

To a 100-mL round-bottomed flask equipped with a reflux condenser, guard tube, and stirring arrangement, was added 4.9 g (0.01 mol) diacid (SMA) and 40 mL thionyl chloride. The mixture was heated to the reflux temperature for 2 h, after which time 3–4 drops of DMF was added. Heating continued for another 2 h and the mixture was left overnight at room temperature. The thionyl chloride was removed under reduced pressure at 40–50°C. The dry crude product was recrystallized from a mixture of dry dichloromethane and petroleum ether to yield 4.75 g (90%) of pure SMCl, *mp* 120–122°C.

The diacid chloride prepared was characterized by IR, ¹H NMR, mass spectral, and elemental analysis.

ANAL. Calcd for C₂₆H₁₆O₆SCl₂ (526): C, 59.20%; H, 3.04%. Found: C, 59.30%; H, 3.16%.

Mass spectrum: Molecular ion (M⁺) peak at 526.

Solution Polymerization

A typical example of solution polymerization follows:

A 100-mL three-necked round-bottomed flask was charged under nitrogen with 0.216 g (0.002 mol) of PPDA and 25 mL of dry NMP. After cooling the solution to 0°C, 1.0 mL propylene oxide was added. The mixture was then cooled to –10°C and with vigorous stirring 1.05 g (0.002 mol) of diacid chloride (5) was added. Five mL of dry NMP was used to wash the diacid chloride flask and addition funnel. The solution was stirred at this temperature for 1 h and then 24 h at room temperature. The viscous solution obtained was slowly poured into a large volume of methanol (300 mL) with vigorous stirring. The precipitated fibrous polymer was collected by filtration, washed well with methanol (3–4 times) and dried.

The polycondensation reactions of diacid chloride (5) with various aromatic diamines (6) were carried out in NMP, under the same conditions.

Interfacial Polymerization

A typical example of interfacial polymerization is as follows:

A 250-mL high-speed reactor was charged with 0.2162 g (0.002 mol) of PPDA, and 0.212 g (0.002 mol) sodium carbonate in 50 mL distilled water. To this solution was added 1.05 g (0.002 mol) of diacid chloride (5) in 50 mL dichloromethane at 0°C. The reaction mixture was then stirred vigorously for 20 min and poured into methanol. The precipitated polymer was separated by filtration, washed with water, acetone, and dichloromethane. Finally, the polymer was dried under high vacuum at 70°C. The same procedure was used to prepare other polyamides.

Polymer Solubility

The solubility of polyamides was determined at 3% concentration in various solvents. All the polymers dissolved in aprotic polar solvents such as dimethylformamide (DMF), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), *m*-cresol, and dichloroacetic acid, except

polyamides 7a, 7c, 8a, and 8c (for nomenclature see Fig. 1) which were soluble with difficulty in these solvents. The polymers were insoluble in nonpolar solvents such as benzene, toluene, petroleum ether, and carbon tetrachloride.

RESULTS AND DISCUSSION

Ditolyl compounds such as 4,4'-[sulfonylbis (*p*-phenyleneoxy)] ditoluene (SPM) and 3,3'-[sulfonylbis (*p*-phenyleneoxy)] ditoluene (SMM) are generally synthesized by reacting potassium or sodium salts of corresponding phenols

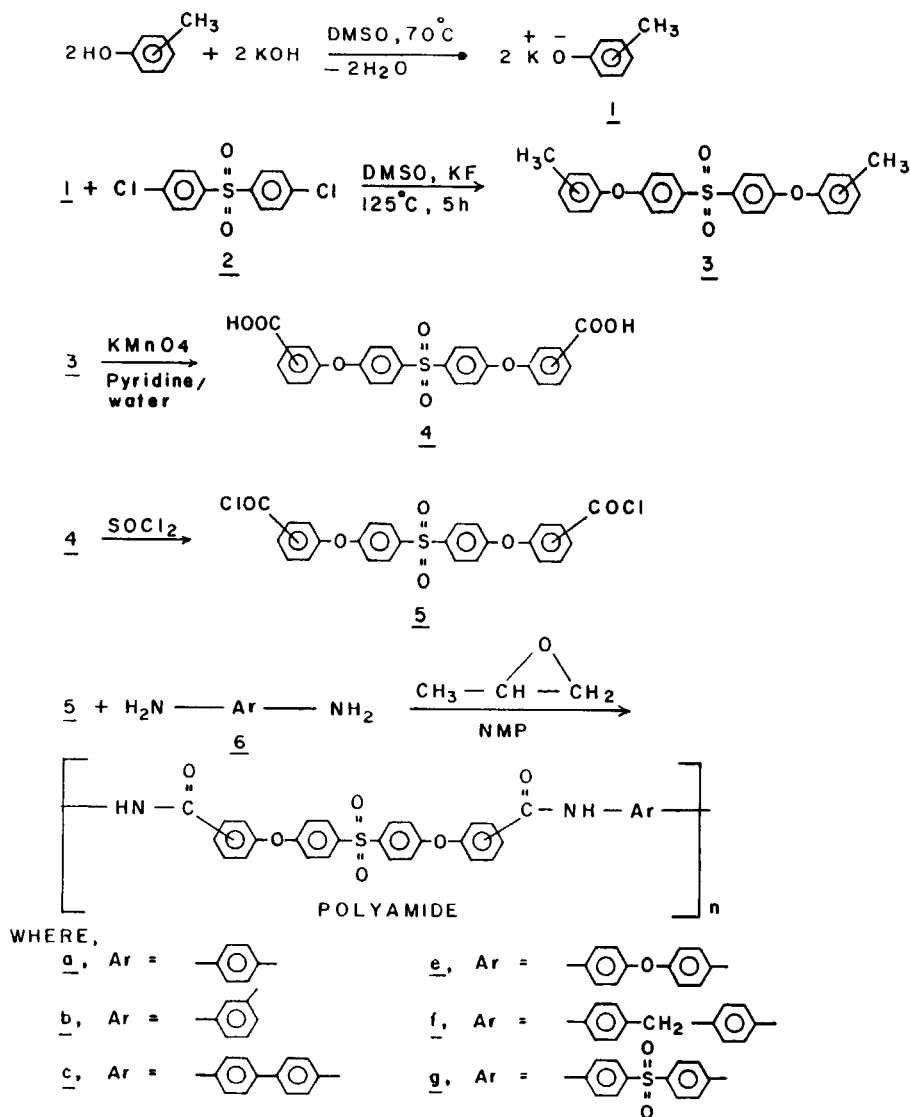
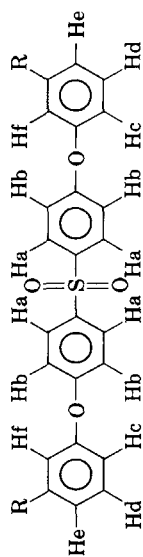


Fig. 1. Preparation of polyamides containing arylene sulfone ether linkages.

TABLE I
IR and NMR Spectral Data

Sr. no. (1)	Abbreviation (2)	R Substituent (3)	IR (Nujol), cm^{-1} (4)	$^1\text{H NMR}^a$, δ ppm						
				Ar-Ha (5)	Ar-Hb (6)	Ar-Hc (7)	Ar-Hd (8)	Ar-He (9)	Ar-Hf (10)	
1.	SPM ^b	CH ₃	2910 (C-CH ₃), 1590 (<-CH, Ar), 1300, 1320, 1110, 1150 (-SO ₂ -), 1260 (Ar-O-Ar)	7.80 (8H, <i>d</i>) (<i>J</i> = 8 Hz) 2.36 (6H, <i>s</i>)	Hb Hc Hd Ha Ha Hb Hc Hd Hb Hc Hd	6.9 (4H, <i>d</i>) (<i>J</i> = 4 Hz)	7.0 (4H, <i>d</i>) (<i>J</i> = 4 Hz)	7.80 (8H, <i>d</i>) (<i>J</i> = 8 Hz)	-	-
2.	SPA ^c	COOH	2550 (-OH), 1680 (>C=O), 1590 (<-CH, Ar), 1295, 1330, 1110, 1160 (-SO ₂ -), 1250 (Ar-O-Ar)	8.0 (8H, <i>d</i>) (<i>J</i> = 8 Hz) 3.04 (2H, <i>s</i> , br)*	Hb Hc Hd Ha Ha Hb Hc Hd Hb Hc Hd	7.18 (4H, <i>d</i>) (<i>J</i> = 5 Hz)	7.28 (4H, <i>d</i>) (<i>J</i> = 6 Hz)	8.0 (8H, <i>d</i>) (<i>J</i> = 8 Hz)	-	-
3.	SPC ^b	COCl	1750 (>C=O), 1590 (<-CH, Ar), 1310, 1330, 1110, 1160 (-SO ₂ -), 1250 (Ar-O-Ar)	8.17 (4H, <i>d</i>) (<i>J</i> = 8 Hz)	Hb Hc Hd Ha Ha Hb Hc Hd Hb Hc Hd	7.11 (4H, <i>d</i>) (<i>J</i> = 8 Hz)	7.20 (4H, <i>d</i>) (<i>J</i> = 8 Hz)	8.02 (4H, <i>d</i>) (<i>J</i> = 8 Hz)	-	-



4.	SMM ^b	CH ₃	2910 (-C-CH ₃), 1590 (-CH, Ar), 1285, 1295, 1110, 1150 (-SO ₂ -), 1250 (Ar-O-Ar)	7.76 (4H, d) (J = 8Hz) 2.36 (6H, S)	7.1 (2H, m)	7.26 (2H, dd)	7.56 (2H, m)	7.26 (2H, S)
5.	SMA ^c	COOH	2560 (-OH), 1690 (>C=O), 1590 (-CH, Ar), 1285, 1295, 1110, 1160 (-SO ₂ -), 1250 (Ar-O-Ar)	8.0 (4H, d) (J = 8Hz) 3.51 (2H, S, br)*	7.42 (2H, m)	7.6 (2H, dd)	7.86 (2H, m)	7.6 (2H, S)
6.	SMCl ^b	COCl	1740 (>C=O), 1590 (-CH, Ar), 1285, 1295, 1110, 1160 (-SO ₂ -), 1250 (Ar-O-Ar)	7.82 (4H, d) (J = 8Hz)	7.26 (2H, m)	7.46 (2H, dd)	7.73 (2H, m)	7.46 (2H, S)

*Exchangeable with D₂O.

^aS = Singlet, d = doublet, dd = doublet of doublet, m = multiplet, s = singlet, br = broad.

^bNMR spectra were recorded in CDCl₃.

^cNMR spectra were recorded in DMSO d₆.

with 4,4'-dichlorodiphenylsulfone in DMSO under various conditions. However, these methods require long reaction times of nearly 40 h and give only a 60% yield.¹¹ In the present study, the reaction is carried out in the presence of potassium fluoride (KF), which gives high yields (> 90%) in a short time (~ 5 h). The ditolyl compounds thus obtained were oxidized to dicarboxylic acids by KMnO_4 , further converted to diacid chlorides by thionyl chloride in good yields and characterized by infrared, ^1H NMR, mass spectral, and elemental analysis, the details of which are given in Table I.

The para- and meta-linked diacid chlorides, 4,4'-[sulfonylbis (*p*-phenyleneoxy)] dibenzoylchloride and 3,3'-[sulfonylbis (*p*-phenyleneoxy)] dibenzoylchloride, thus obtained were reacted with various aromatic diamines by solution and interfacial polymerization techniques, to give polyamides of general structures as shown below:

TABLE II
Properties of Polyamide Series 7a-f and 8a-f

Polyamide (1)	Solution polymerization $\eta_{inh}^d \text{ dL} \cdot \text{g}^{-1}$			Interfacial polymerization $\eta_{inh}^d \text{ dL} \cdot \text{g}^{-1}$	Yield %	Elemental analysis ^g		
	PO ^a (2)	LiOH/LiCl ^b (3)	TEA ^c (4)			C% (7)	H% (8)	N% (9)
7								
a	1.02 ^e	0.75 ^e	0.48 ^e	1.20 ^e	99	68.10 (68.32)	4.12 (3.91)	5.00 (4.98)
b	0.94	0.62	0.40	1.00	98	68.70 (68.32)	3.96 (3.91)	4.92 (4.98)
c	1.12 ^e	0.80 ^e	0.52 ^e	1.32 ^e	98	71.36 (71.47)	4.00 (4.08)	4.40 (4.39)
d	1.86	1.42	0.84	1.98	99	69.96 (69.72)	4.16 (3.97)	4.30 (4.28)
e	0.78	0.46	0.36	0.92	98	71.88 (71.77)	4.36 (4.29)	4.20 (4.29)
f	0.70	0.42	0.32	0.84	99	64.90 (64.95)	3.86 (3.70)	4.10 (3.98)
8								
a	0.75 ^f	0.46 ^f	0.35 ^f	0.98 ^f	98	68.14 (68.32)	4.00 (3.91)	4.86 (4.98)
b	0.59	0.36	0.26	0.80	99	68.56 (68.32)	3.88 (3.91)	4.90 (4.98)
c	0.92 ^f	0.64 ^f	0.48 ^f	1.07 ^f	99	70.86 (71.47)	3.96 (4.08)	4.10 (4.39)
d	1.04	0.74	0.44	1.50	98	69.88 (69.72)	4.10 (3.97)	4.20 (4.28)
e	0.68	0.44	0.23	1.79	99	72.00 (71.77)	4.40 (4.29)	4.00 (4.29)
f	0.65	0.41	0.25	0.72	98	64.68 (64.95)	3.80 (3.70)	4.16 (3.98)

^a Propylene oxide = 1.00 mL.

^b Lithium hydroxide = 0.168 g, lithium chloride = 0.170 g.

^c Triethylamine = 0.56 mL.

^d determined in dimethyl formamide at 30°C.

^e determined in 96% sulfuric acid at 30°C.

^f determined in *N*-methyl-2-pyrrolidone at 30°C.

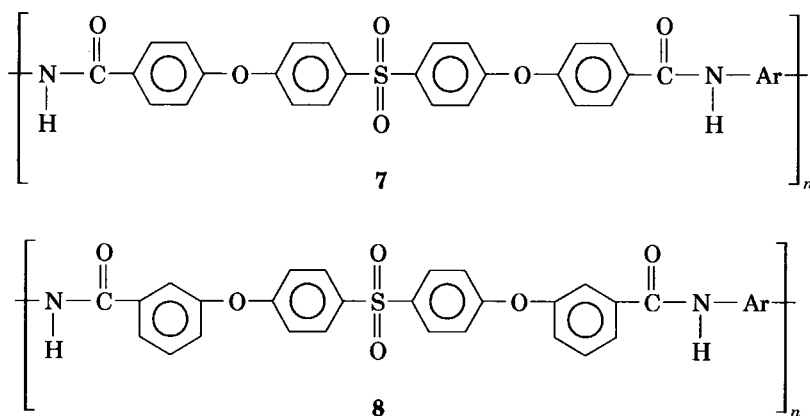
^g Values in parenthesis indicate the corresponding calculated values.

TABLE III
Thermal Characteristics of Polyamide Series 7a-f and 8a-f

Polyamide	T_g (°C)	IDT (°C)	Temperature at various % residual weight (°C)					IPDT (°C)	T_{max} (°C)
			10%	20%	30%	40%	50%		
7									
a	260	410	440	498	532	552	561	510	540
b	245	430	470	517	542	560	570	582	588
c	255	420	460	506	530	548	562	525	542
d	260	398	438	478	504	518	528	532	538
e	250	412	463	492	508	520	532	502	528
f	240	390	419	469	524	542	538	514	548
8									
a	250	403	432	494	522	542	549	514	554
b	220	435	471	522	547	564	579	604	610
c	235	429	463	514	536	556	569	540	549
d	245	405	445	486	511	524	531	543	548
e	240	420	473	501	516	526	534	510	536
f	230	397	429	480	531	548	561	517	568

Abbreviations: T_g = glass transition temperature; IDT = initial decomposition temperature; IPDT = integral procedural decomposition temperature; T_{max} = temperature for maximum rate of decomposition.

general structures as shown below:



where the Ar group indicates the structures of diamines 6a-f (Fig. 1). Most of the polyamides prepared formed tough, transparent, and flexible films. They have been characterized by IR, solution viscosity, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, and x-ray diffraction. The properties of para- and meta-linked polyamide series 7a-f and 8a-f are summarized in Tables II and III.

Both the solution and interfacial polymerization techniques give polymers in high yields. The elemental analyses for carbon, hydrogen, and nitrogen are in good agreement with the calculated values.

Effect of Acid Acceptors

In order to obtain a high-molecular weight polymer by the solution polymerization technique, the acid formed during polycondensation must be removed continuously using acid acceptors. In the present study, three acid acceptors, namely propylene oxide, lithium chloride/lithium hydroxide, and triethylamine were used. It was observed that the polyamides obtained using propylene oxide had the highest molecular weights and that those obtained using triethylamine had the lowest molecular weights. This may be due to the

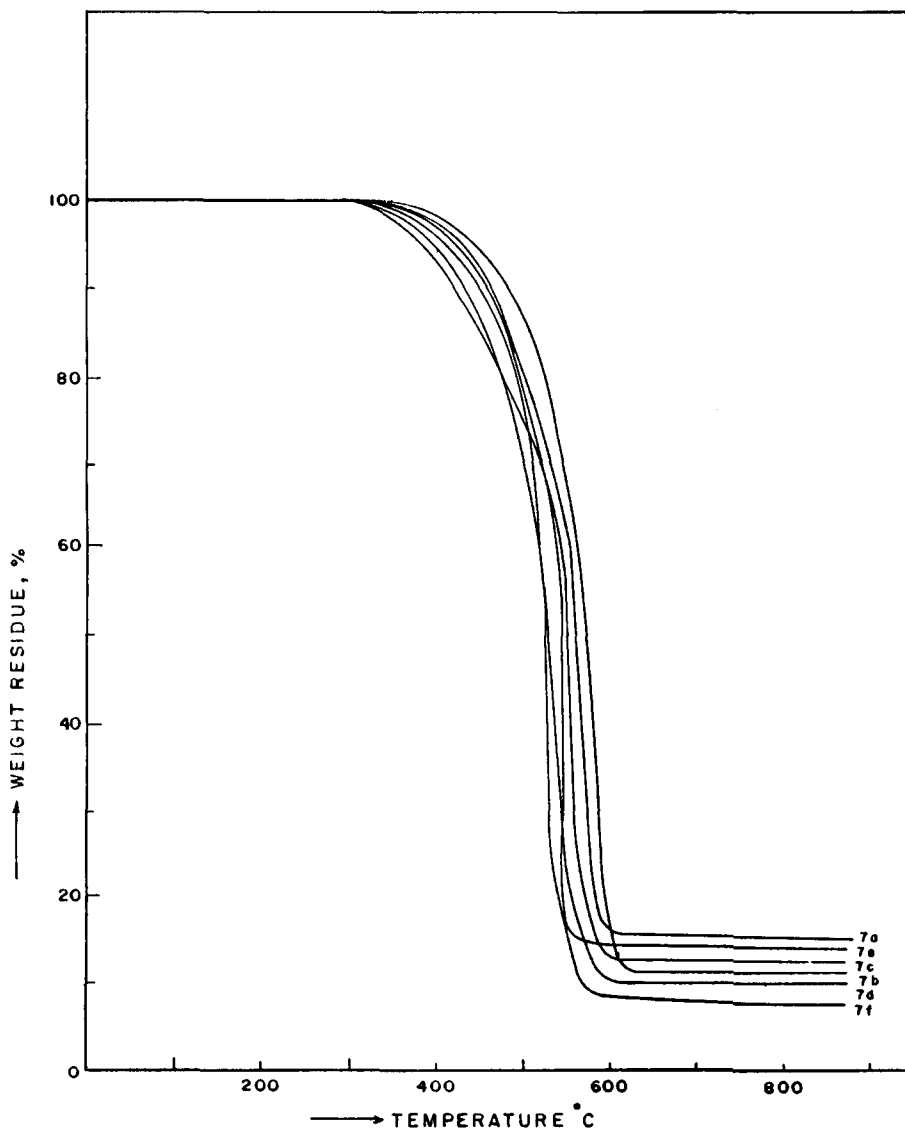


Fig. 2. Thermogravimetric analyses of sulfone ether containing polyamide series 7a-f.

hydrolysis of polyamide chains in the presence of strong base such as triethylamine.

Viscosity

Viscosity is directly related to molecular weight of the polymer. In the present study, it was observed that the inherent viscosity of polyamides obtained by interfacial polymerization is higher than that from solution polymerization. Similarly, less bulky diamines also give polyamides of higher inherent viscosity as expected. The lowest viscosity obtained in the case of the polyamides synthesized from the sulfone-containing diamine (6f) may be attributed to its low basicity.

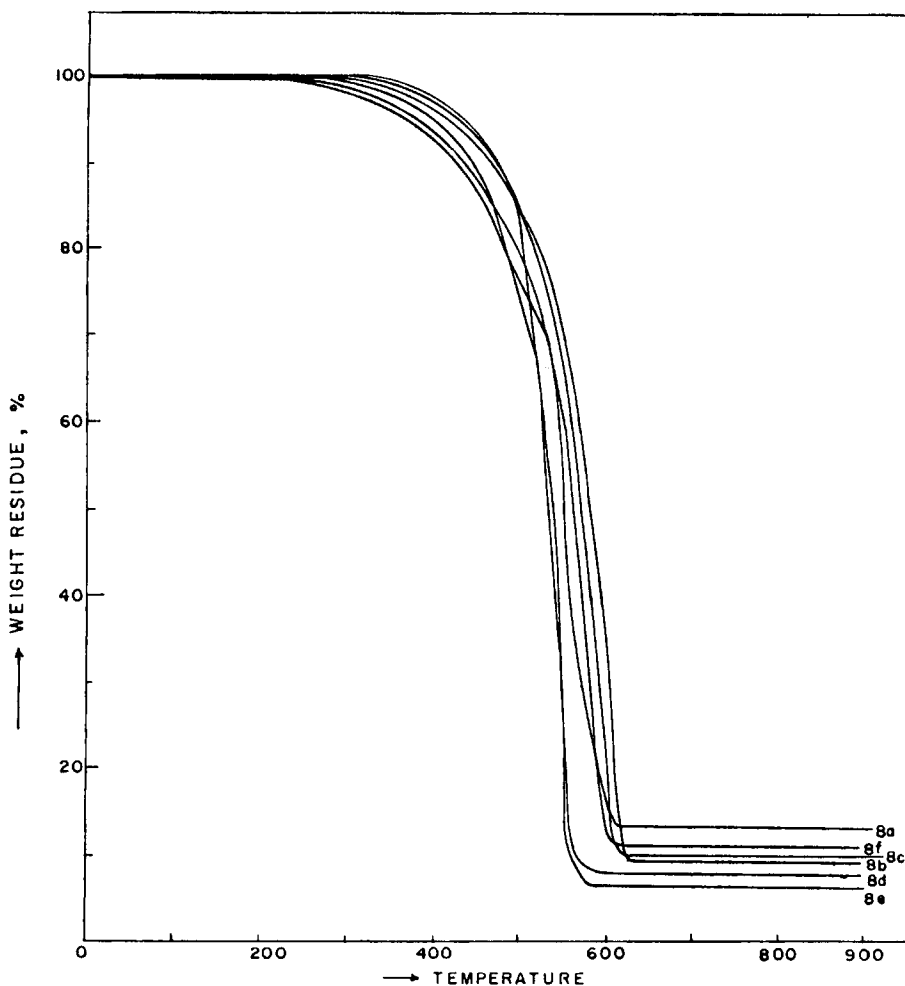


Fig. 3. Thermogravimetric analyses of arylene sulfone ether containing polyamide series 8a-f.

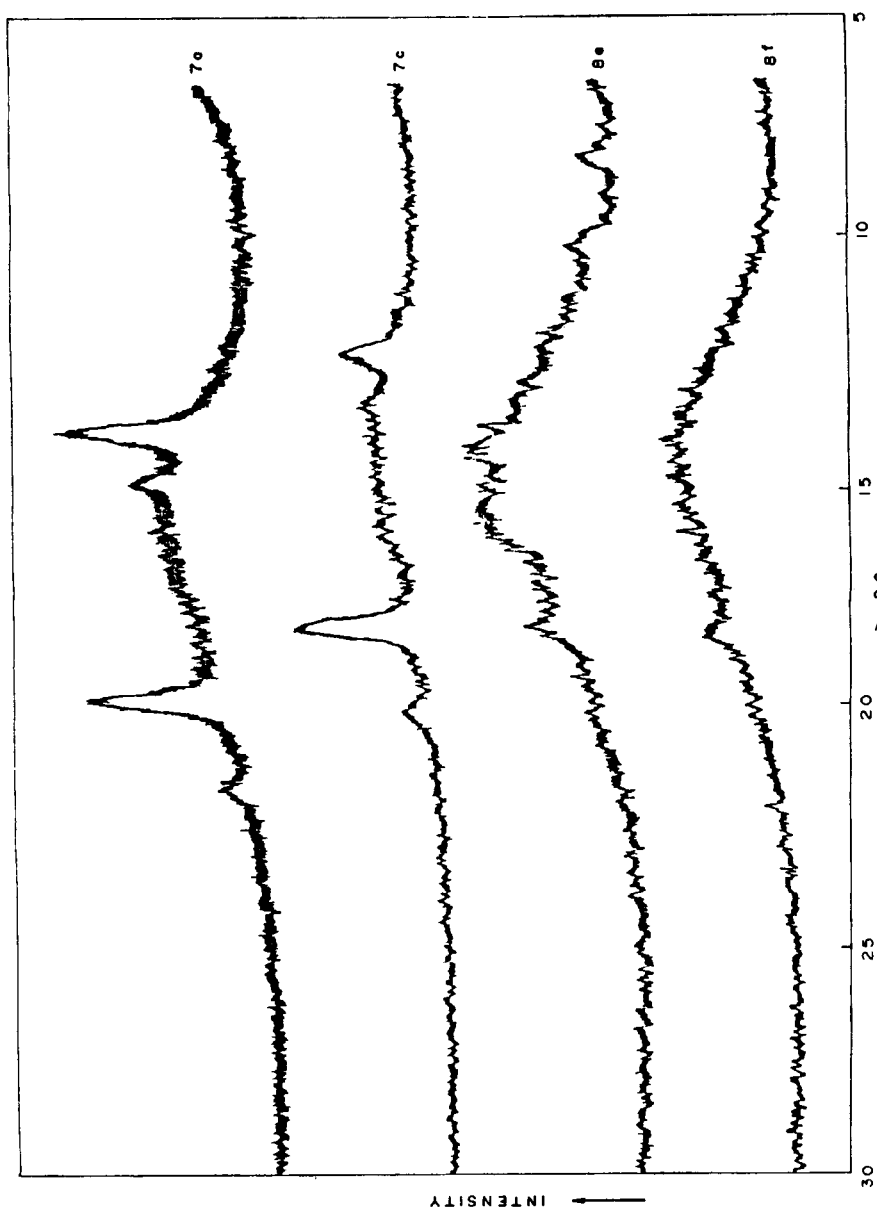


Fig. 4. X-ray diffractograms of polyamides 7a, 7c, 8e, and 8f.

Thermal Behavior

Aromatic polyamides are known for their high thermal stability. In the present study, the thermal stability of the polyamides was studied by thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetry (DTG). The samples were heated at a constant rate of $5^{\circ}\text{C min}^{-1}$ in air. Temperatures for different weight losses were determined from the TGA curves and are tabulated in Table III. The initial decomposition temperature (IDT), integral procedural decomposition temperature (IPDT), and the temperature for maximum rate of decomposition (T_{max}) were calculated from the original thermograms and are also listed in Table III. Figures 2 and 3 illustrate the thermograms for polyamide series 7a-f (para-linked polyamides) and 8a-f (meta-linked polyamides), respectively. Polyamides prepared from meta-linked diacid have marginally higher thermal stability than the corresponding polyamides prepared from para-linked diacid. Similarly, polyamides prepared from meta-linked diamines (6b) showed greater thermal stability compared to that of para-linked diamines.

The DSC results showed that the glass transition (T_g) values for the polyamide series 7a-f are slightly higher than the polyamide series 8a-f. Both the polyamides 7b and 8b prepared from the meta-linked diamine 6b, have the lowest T_g value in their respective series.

X-Ray Behavior

The crystalline nature of the polyamides was studied by x-ray diffraction. The polyamides 7a and 7c prepared from the more rigid diamines showed partially crystalline behavior. The polyamides of the series 8a-f showed an amorphous x-ray behavior. The representative x-ray diffractograms are shown in Figure. 4.

CONCLUSIONS

4,4'-[Sulfonylbis (*p*-phenyleneoxy)] dibenzoic acid and 3,3'-[sulfonylbis (*p*-phenyleneoxy)] dibenzoic acid were synthesized by a modified route and used for the preparation of a series of polyamides containing the arylene sulfone ether linkages employing various acid acceptors. Propylene oxide afforded the highest molecular weight polyamides. All the polyamides prepared from the meta-linked aromatic diamine showed marginally superior thermal properties as compared to the corresponding para-linked diamines.

References

1. G. L. Brode, J. H. Kawakami, G. T. Kwiatkowski, and A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 575 (1974).
2. G. T. Kwiatkowski, G. L. Brode, J. H. Kawakami, and A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 589 (1974).
3. C. Chirac and J. K. Stille, *Macromolecules*, **10**, 712 (1974).
4. J. Adduci, L. L. Chapoy, G. Jonsson, J. Kops, and B. M. Shinde, *J. Appl. Polym. Sci.*, **28**, 2069 (1983).
5. R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale, and C. N. Merriman, *J. Polym. Sci., Part A-1*, **5**, 2375 (1967).

6. W. F. Hale, A. G. Farnham, R. N. Johnson, and R. A. Clendinning, *J. Polym. Sci.*, Part A-1, **5**, 2399 (1967).
7. G. L. Brode, *The Chemistry of Sulfides*, A. V. Tobolsky, Ed., Wiley, New York, 1968, pp. 133-144.
8. J. M. Lancaster, B. A. Wright, and W. W. Wright, *J. Appl. Polym. Sci.*, **9**, 1955 (1965).
9. J. Adduci, L. L. Chapoy, G. Jonsson, J. Kops, and B. M. Shinde, *Polym. Eng. Sci.*, **21** (11), 712 (1981).
10. V. G. Lorenz, M. G. Gallus, W. Giessler, F. Bodesheim, H. Wieden, and G. L. Nischk, *Die Makromol. Chemie*, **130**, 65 (1969).
11. H. R. Lubowitz, Fr. pat. 2,030, 905 (1970) (CA 75: 64581w).

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