

Polyimides and Polyamide–Imides Containing Arylene Sulfone Ether Linkages*

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Synopsis

Polyimides and polyamide–imides containing arylene sulfone ether linkages were synthesized from 4,4'-bis(4-isocyanatophenoxy) diphenylsulfone (SPI), 4,4'-bis(3-isocyanatophenoxy) diphenylsulfone (SMI), pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), and trimellitic anhydride (TMA) using one-step method. The diisocyanates SPI and SMI were synthesized from 4,4'-bis(4-carboxyphenoxy) diphenylsulfone (SPA) and 4,4'-bis(3-carboxyphenoxy) diphenylsulfone (SMA) by a Weinstock-modified curtius rearrangement method. All the polycondensation reactions were carried out in *N*-methyl-2-pyrrolidone (NMP) and the polymers obtained were characterized by infrared spectroscopy, solution viscosity, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction.

INTRODUCTION

Aromatic polyamides, polyimides, and polyamide–imides with aryl ether, aryl sulfone, or aryl sulfone ether linkages are well known in the literature.^{1–4} Generally these polymers are amorphous and have low glass transition temperature, superior chain flexibility and tractability, high thermooxidative stability, and excellent mechanical properties.^{5–8} Unlike other aromatic polyimides and polyamide–imides, they have better solubility in organic solvents and hence they have potential of commercial interest. Recently, they have been proposed as new candidates for thermotropic liquid crystalline polymers.⁹

Polyimides are conventionally prepared by the reaction of a diamine and dianhydride in a polar solvent. A soluble polyamic acid intermediate formed by this reaction is converted to an insoluble polyimide by heat or by chemical reaction.¹⁰ Another method for synthesizing polyimide is by reacting a diisocyanate with a dianhydride in which a seven-membered ring intermediate¹¹ is formed which rearranges with elimination of carbon dioxide, to form a polyimide. It can also be prepared by the reaction of an aromatic diisocyanate with a tetracarboxylic diester which on heating forms a polyimide with the elimination of alcohol.¹² Naoya¹³ prepared polyimides by hydrogen transfer polymerization of pyromellitic acid diimide and diisocyanates in polar solvents in the presence of a tertiaryamine catalyst. Thus the synthesis and characterizations of a number of polyimides and mixed polyimides having different structures have been reported in the literature.^{14–20} They have low solubility in organic solvents and hence various modifications have been tried to improve their solubility. One of

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them is the introduction of sulfone and ether linkages in the polymer backbone which met with some success.²¹

Our investigation relates to the synthesis of 4,4'-bis(4-isocyanatophenoxy) diphenylsulfone (SPI) and 4,4'-bis(3-isocyanatophenoxy) diphenylsulfone (SMI) from the corresponding diacids via diacylazides by a Weinstock-modified curtius rearrangement and a comparative study of the synthesis and characterization of the polyimides and polyamide-imides prepared therefrom.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) (KOCH-LIGHT, U.K.) was purified by recrystallization from dry acetic anhydride.

3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) (Gulf Oil Chem Co., Houston, TX) was purified by sublimation under reduced pressure at 260–270°C/mm Hg.

Trimellitic anhydride (TMA) (Fluka, A.G., Switzerland) was purified by recrystallization from dry acetic anhydride.

N-methyl-2-pyrrolidone (NMP) (Fluka, A.G., Switzerland), *N,N*-dimethylacetamide (DMAC) (SD's Bombay) were dried over molecular sieves and distilled under reduced pressure.

Triethylamine (TEA) and ethylchloroformate (ECF) (E. Merck, Bombay) were purified and distilled before use.

Sodium azide (SAZ) (IDPL, Hyderabad) was activated by trituration with hydrazine and precipitated with acetone from the water solution.

4,4'-bis(4-carboxyphenoxy) diphenylsulfone (SPA) and 4,4'-bis(3-carboxyphenoxy) diphenylsulfone (SMA) were prepared and purified by the method described in the literature.²²

Diisocyanates SPI and SMI were prepared in our laboratory and used after recrystallization from the appropriate solvents.

Instrumental Methods

IR spectra were recorded on a Perkin-Elmer spectrophotometer. 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 *N,N*-dimethylacetamide. 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.

The differential scanning calorimetry thermograms were obtained with a Perkin-Elmer differential scanning calorimeter DSC 2 equipped with a thermal analysis data station (TADS). The 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 radiations.

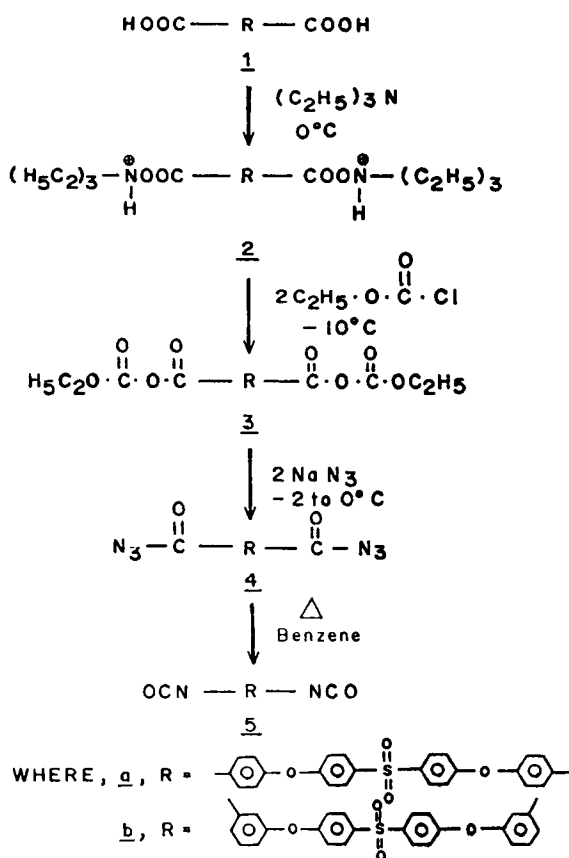


Fig. 1. Preparation of diisocyanates containing arylene sulfone ether linkages.

Diisocyanate Synthesis

4,4'-Bis(4-azidocarbonylphenoxy)diphenylsulfone (SPAZ)

Into a 250-mL three-necked RB flask, equipped with a mechanical stirrer, dropping funnel, and thermowell, were placed 4.9 g (0.01 mol) of 4,4'-bis(4-carboxyphenoxy)diphenylsulfone (SPA) and 40 mL acetone. The suspension was cooled to 0°C and 2.02 g (0.02 mol) of triethylamine in 15 mL acetone was added over a period of 10 min. The reaction mixture was stirred for a further 10 min and then a solution of 2.17 g (0.02 mol) ethylchloroformate in 15 mL acetone was added at 0°C over a period of 10 min. The resulting reaction mixture was stirred for 1 h at the same temperature and then a solution of 1.30 g (0.02 mol) sodium azide in 60 mL of water was added dropwise. Finally, the reaction mixture was stirred for 4 h at 0°C and then poured into 200 mL ice-cold water. The solid obtained was collected by filtration, dissolved in dichloromethane, and dried over anhydrous sodium sulphate. After filtration, dichloromethane was removed under reduced pressure to obtain 4.6 g (85%) of pure SPAZ, mp = 113–115°C (decomp.)

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

ANAL: Calcd. for C₂₆H₁₆N₆O₆S: C, 57.78%; H, 2.96%. Found: C, 57.35%; H, 3.0%.

TABLE I
 IR and NMR Spectral Data

Sample no.	Abbreviation	<i>R</i> substituent	IR (Nujol) (cm ⁻¹)	¹ H-NMR ^a δ (ppm)					
				Ar-Ha	Ar-Hb	Ar-Hc	Ar-Hd	Ar-He	Ar-Hf
1	SPAZ ^b	CON ₃	2120 (—N ₃), 1690 (C=O), 1590 (—CH, Ar), 1300, 1320, 1110, 1160 (—SO ₂ —), 1250 (Ar—O—Ar)	8.06 (4H, d) (<i>J</i> = 8 Hz)	7.04 (4H, d) (<i>J</i> = 8 Hz)	7.13 (4H, d) (<i>J</i> = 8 Hz)	7.95 (4H, d) (<i>J</i> = 8 Hz)	—	—
			2280 (—NCO), 1590 (—CH, Ar) 1300, 1320, 1110, 1150 (—SO ₂ —), 1260 (Ar—O—Ar)	7.80 (4H, d) (<i>J</i> = 8 Hz)	7.50 (4H, d) (<i>J</i> = 8 Hz)	7.00 (4H, d) (<i>J</i> = 8 Hz)	6.70 (4H, d) (<i>J</i> = 8 Hz)	—	—
3	SMAZ ^b	CON ₃	2140 (—N ₃), 1690 (C=O) 1590 (—CH, Ar), 1300, 1320, 1110, 1150 (—SO ₂ —) 1260 (Ar—O—Ar)	7.86 (4H, d) (<i>J</i> = 8 Hz)	7.02 (4H, d) (<i>J</i> = 8 Hz)	7.31 (2H, m)	7.46 (2H, dd)	7.73 (2H, m)	7.46 (2H, s)
			2260 (—NCO), 1590 (—CH, Ar) 1300, 1330, 1110, 1160 (—SO ₂ —), 1250 (Ar—O—Ar)	7.82 (4H, d) (<i>J</i> = 8 Hz)	6.97 (4H, d) (<i>J</i> = 8 Hz)	6.73 (2H, m)	7.26 (2H, dd)	6.82 (2H, m)	7.28 (2H, s)

^a s = singlet, d = doublet, dd = doublet of doublet, m = multiplet.

^b NMR spectra were recorded in CDCl₃.

^c NMR spectra were recorded in DMSO d₆.

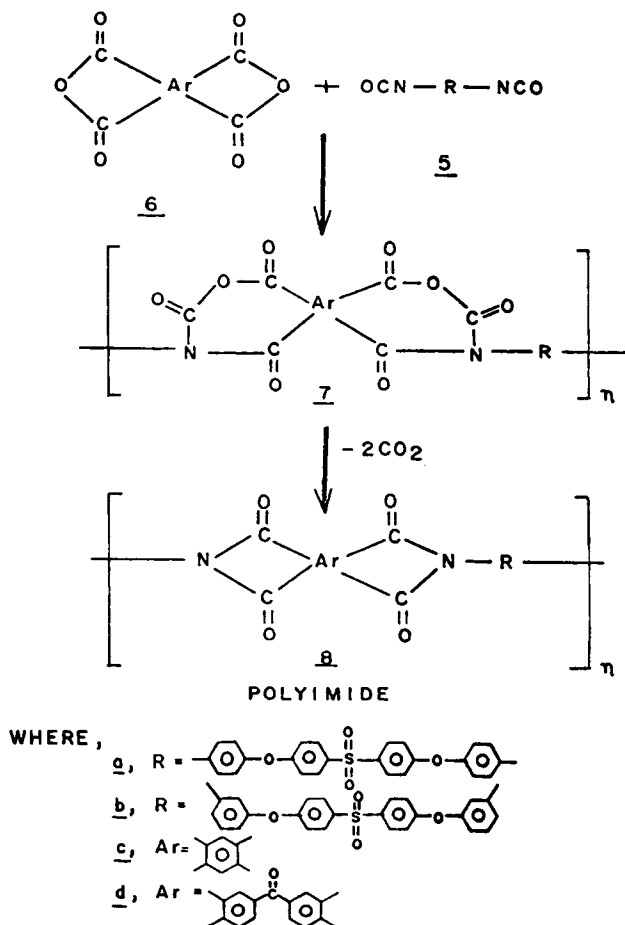


Fig. 2. Preparation of polyimides containing arylene sulfone ether linkages.

4,4'-Bis(4-isocyanatophenoxy)diphenylsulfone (SPI)

To a 100-mL RB flask, equipped with a reflux condenser and calcium chloride guard tube, were placed 2.70 g (0.05 mol) of SPAZ in 35 mL dry benzene. The solution was refluxed for 12 h. The benzene was removed by distillation under reduced pressure. The residue after recrystallization from dry benzene gave 2.30 g (95%) of pure SPI, mp = 53–55°C.

The SPI prepared was characterized by IR, $^1\text{H-NMR}$, mass spectral and elemental analysis.

ANAL: Calcd. for $\text{C}_{26}\text{H}_{16}\text{N}_2\text{O}_6\text{S}$: C, 64.46%; H, 3.30%; N, 6.61%. Found: C, 64.20%; H, 3.40%; N, 6.56%. Mass spectrum: molecular ion (M^+) peak at 484.

4,4'-Bis(3-azidocarbonylphenoxy)diphenylsulfone (SMAZ)

The SMAZ was prepared by the reaction of 4,4'-bis(3-carboxyphenoxy) diphenylsulfone (SMA) with triethylamine, ethylchloroformate, and sodium azide under the same reaction conditions, as used for the SPAZ derivative. The product obtained was dissolved in dichloromethane and dried over anhydrous sodium

TABLE II
Properties of Polyimides and Polyamide-imides

Sample no.	Polymer abbreviation	Reactants		η_{inh}^a (dL g ⁻¹)	Elemental analysis ^b		
		Dianhydride	Diisocyanate		C %	H %	N %
<u>Polyimides</u>							
1	8ca	PMDA	SPI	0.43	66.10 (66.44)	3.10 (2.93)	4.60 (4.56)
2	8cb	PMDA	SMI	0.32	66.24 (66.44)	3.00 (2.93)	4.66 (4.56)
3	8da	BTDA	SPI	0.38	64.86 (65.00)	3.52 (3.40)	4.48 (4.33)
4	8db	BTDA	SMI	0.30	64.92 (65.00)	3.56 (3.40)	4.44 (4.33)
<u>Polyamide-imides</u>							
5	12a	TMA	SPI	0.41	67.26 (67.34)	3.46 (3.40)	4.80 (4.76)
6	12b	TMA	SMI	0.38	67.28 (67.34)	3.48 (3.40)	4.90 (4.76)

^a Determined in *N,N*-dimethylacetamide at 30°C.

^b Values in parentheses indicate the corresponding calculated values.

PMDA = pyromellitic dianhydride; BTDA = 3,3',4,4'-benzophenone tetracarboxylic dianhydride; SPI = 4,4'-bis(4-isocyanatophenoxy) diphenylsulfone; SMI = 4,4'-bis(3-isocyanatophenoxy) diphenylsulfone.

sulfate. The dichloromethane was removed under reduced pressure to obtain 4.40 g (82%) of pure SMAZ, mp = 108–110°C (decomp.).

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

ANAL: Calcd. for C₂₆H₁₆N₆O₆S: C, 57.78%; H, 2.96%. Found: C, 57.68%; H, 2.84%.

4,4'-Bis(3-isocyanatophenoxy)diphenylsulfone (SMI)

The SMI was prepared from 4,4'-bis(3-azidocarbonylphenoxy) diphenylsulfone (SMAZ) under the same reaction conditions as used for the SPI derivative. The product obtained was recrystallized from dry benzene to give 2.20 g (92%) of pure SMI, mp = 48–50°C.

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

ANAL: Calcd. for C₂₆H₁₆N₂O₆S: C, 64.46%; H, 3.30%; N, 6.61%. Found: C, 64.40%; H, 3.42%; N, 6.52%. Mass spectrum: molecular ion (M⁺) peak at 484.

Polyimide Synthesis

A typical example for the preparation of polyimide 8 ca is as follows: Into a 50-mL three-necked RB flask, equipped with a thermometer, nitrogen gas inlet, and gas outlet connected to barium hydroxide solution, were placed 0.9680 g (0.002 mol) of diisocyanate (5a) and 20 mL dry NMP. To this solution, 0.4362 g (0.002 mol) of PMDA (6c) was added in small quantities over a period of 15–20 min at 0°C. The reaction mixture was stirred at this temperature for 0.5

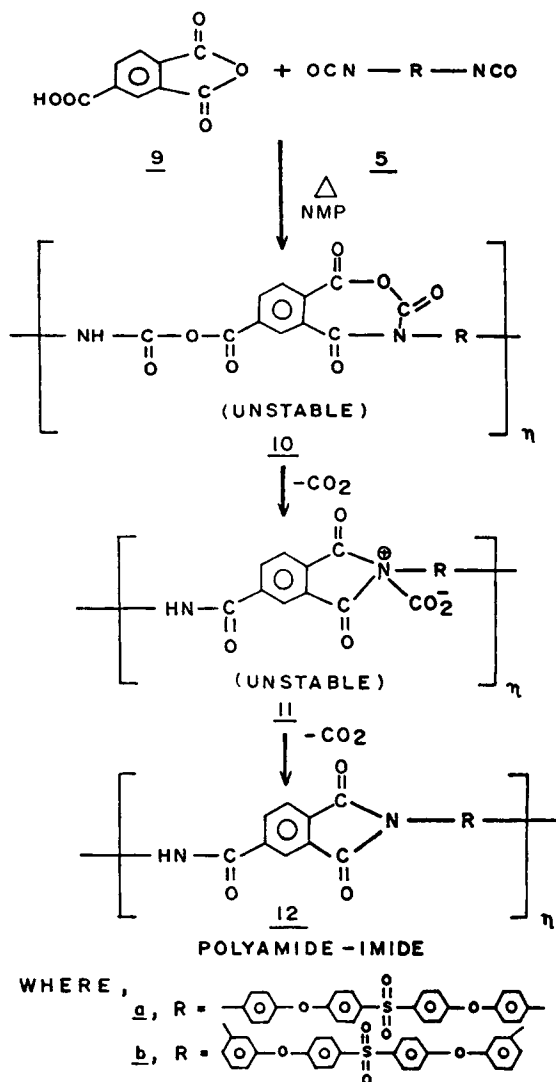


Fig. 3. Preparation of polyamide-imides containing arylene sulfone ether linkages.

h and then slowly heated to 40°C, at which temperature it was held for 2.5 h. The temperature was then slowly raised to 90°C and maintained for 2.0 h. CO₂ gas evolution was observed at this temperature. Finally, the reaction mixture was heated at 130–140°C for 24 h after which the reaction mixture was poured into 100 mL water and the polymer was filtered off, washed several times with methanol, and then dried at 100°C under reduced pressure. The same procedure was followed to prepare polyimides 8cb, 8da, and 8db.

The polyamide-imide polymers 12a and 12b were also prepared by following the same procedure of polyimides.

Polymer Solubility

The solubility of polyimides and polyamide-imide polymers was determined at 3% concentration in various solvents. All the polymers dissolved in aprotic

TABLE III
Thermal Behavior of Polyimides and Polyamide-imides

Sample no.	Polymer abbreviation	T_g^a (°C)	IDT ^b (°C)	Temperature at various % residual weight					IPDT ^c (°C)	T_{max}^d (°C)
				10%	20%	30%	40%	50%		
Polyimides										
1	8ca	280	405	441	479	497	515	520	519	530
2	8cb	260	443	495	540	553	565	575	539	590
3	8da	272	400	450	490	513	528	545	507	550
4	8db	230	456	505	535	555	563	568	552	580
Polyamide-imides										
5	12a	220	459	475	485	500	515	531	497	540
6	12b	200	495	515	530	555	570	585	529	590

^a T_g = glass transition temperature.

^b IDT = initial decomposition temperature.

^c IPDT = integral procedural decomposition temperature.

^d T_{max} = temperature for maximum rate of decomposition.

polar solvents such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), *N,N*-dimethylacetamide (DMAC), *N*-methyl-2-pyrrolidone (NMP), *m*-cresol, and dichloroacetic acid. These polymers were insoluble in nonpolar solvents such as benzene, toluene, petroleum ether, and carbon tetrachloride.

RESULTS AND DISCUSSION

Arylene Sulfone Ether Diisocyanates

In the present work, two diisocyanates namely, 4,4'-bis(4-isocyanatophenoxy) diphenylsulfone (SPI) and 4,4'-bis(3-isocyanatophenoxy) diphenylsulfone (SMI) containing arylene sulfone ether linkages were synthesized in quantitative yields from the corresponding diacids via diacylazide intermediates by a Weinstock-modified curtius rearrangement method, with a view to avoid phosgenation route for the preparation of diisocyanates. The reaction scheme for the preparation of diisocyanates is as shown in Figure 1. These diisocyanates (SPI and SMI) together with two new diacylazides (SPAZ and SMAZ) were characterized by IR, ¹H-NMR, mass spectral and elemental analysis, the details of which are given in Table I.

Arylene Sulfone Ether Polyimides

A series of polyimides containing arylene sulfone ether linkages have been prepared from the reaction of pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-bis(4-isocyanatophenoxy) diphenylsulfone (SPI) and 4,4'-bis(3-isocyanatophenoxy) diphenylsulfone (SMI) at low temperature by one-step method. The reaction scheme for the preparation of polyimides is as shown in Figure 2. All these polycondensation reactions were carried out in *N*-methyl-2-pyrrolidone (NMP) under

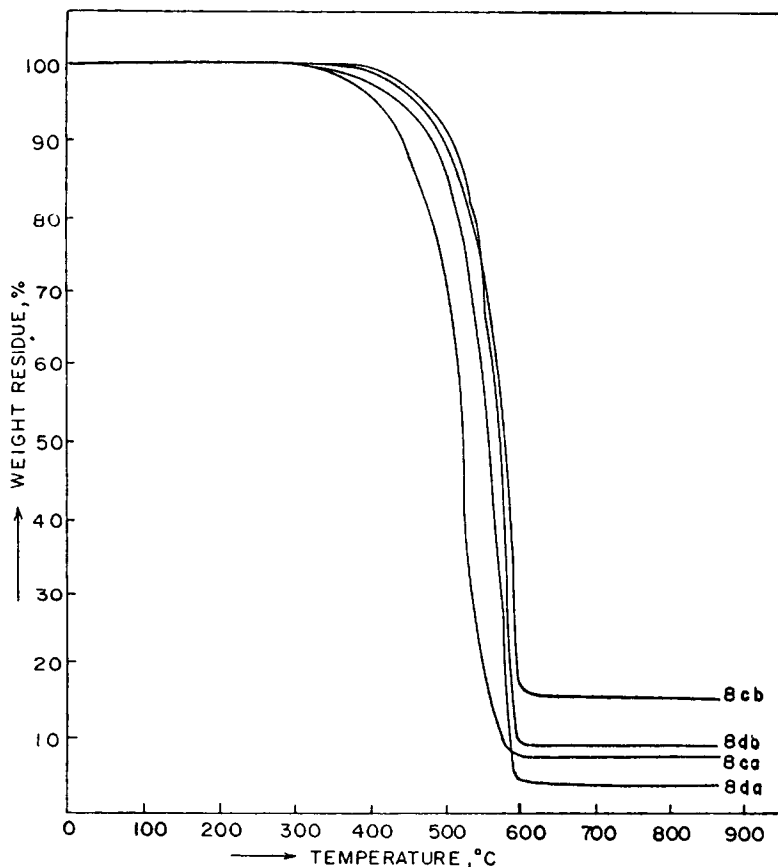


Fig. 4. Thermogravimetric analyses of arylene sulfone ether containing polyimides 8ca, 8cb, 8da and 8db.

the same conditions. The polymers prepared were characterized by infrared spectra, solution viscosity, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. All the polymers prepared were soluble in aprotic polar solvents and had film forming properties.

The properties of polyimides 8ca, 8cb, 8da, and 8db are summarized in Table II. The polyimides prepared from PMDA have higher inherent viscosities as compared to that of polyimides prepared from BTDA. Similarly, polyimides prepared from meta-linked diisocyanate have lower inherent viscosities as compared to that of polyimides prepared from para-linked diisocyanate. The elemental analyses values for carbon, hydrogen, and nitrogen are in good agreement with the calculated values.

The effect of diisocyanate structure on the thermal stability of polyimides was studied by thermooxidative degradation. To evaluate this effect, thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) were performed simultaneously by heating the polymer at a constant rate of $5^{\circ}\text{C min}^{-1}$ in air. Temperatures for different weight losses and initial decomposition temperature (IDT) values were calculated from the original TGA curves and are listed in Table III. The integral procedural decomposition temperature (IPDT) values were calculated from

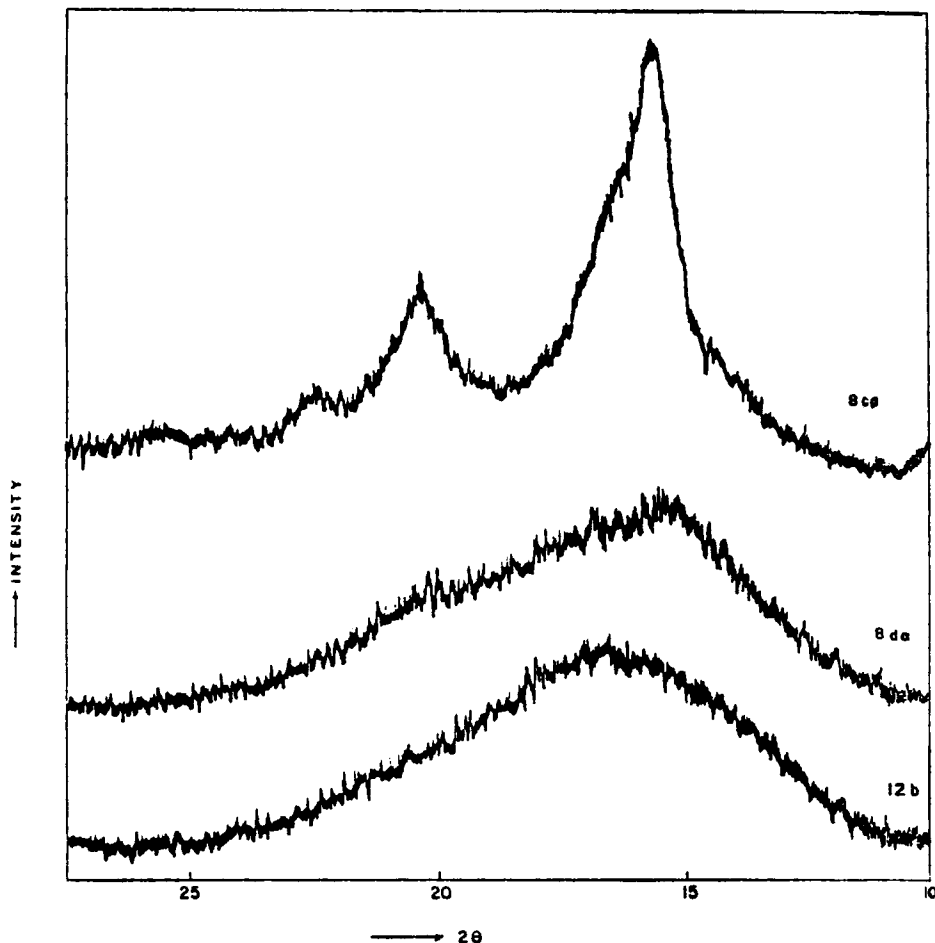


Fig. 5. X-ray diffractograms of polyimides 8 ca, 8 da and polyimide-imide 12b.

the original TGA curve by following the method of Doyle.²³ The temperature for maximum rate of decomposition (T_{max}) values were calculated from the DTG curve. The thermograms for polyimides 8ca, 8cb, 8da, and 8db are illustrated in Figure 4.

Fairly good thermal stability was observed in both the PMDA and BTDA polyimide series. Polyimides 8cb and 8db prepared from the meta-linked diisocyanate (5b), showed greater thermal stability than the polyimides 8ca and 8da prepared from the para-linked diisocyanate (5a). They also showed lowest percent weight loss at high temperatures. The DSC results showed that the glass transition temperature (T_g) values of both the PMDA and BTDA polyimides prepared from the nonlinear meta-linked diisocyanate (5b) are lower as compared to the T_g values of polyimides prepared from the linear para-linked diisocyanate (5a).

The crystalline nature of the polyimides was studied by X-ray diffraction. All the polyimides showed an amorphous X-ray pattern, except polyimide 8ca. The polyimide 8ca shows partial crystallinity as indicated by the X-ray diffractograms which are shown in Figure 5.

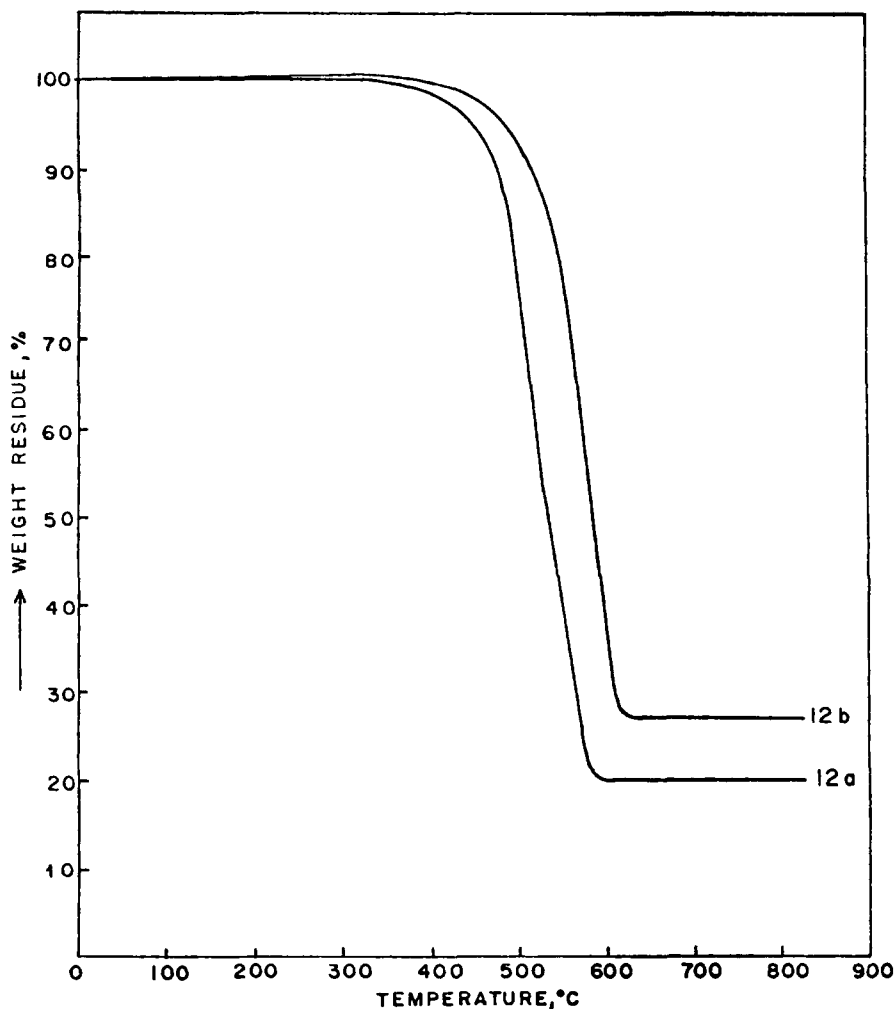


Fig. 6. Thermogravimetric analyses of arylene sulfone ether containing polyamide-imides 12a and 12b.

Arylene Sulfone Ether Polyamide-Imides

Polyamide-imides containing arylene sulfone ether linkages have been prepared from the reaction of trimellitic anhydride (TMA) and 4,4'-bis(4-isocyanatophenoxy) diphenylsulfone (SPI) and 4,4'-bis(3-isocyanatophenoxy) diphenylsulfone (SMI) at low temperature by one-step method. The reaction scheme for the preparation of polyamide-imides is as shown in Figure 3. All the polycondensation reactions were carried out in *N*-methyl-2-pyrrolidone (NMP) under identical conditions. The polymers prepared were characterized by infrared spectra, solution viscosity, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. All the polymers prepared were soluble in aprotic polar solvents and had film forming properties.

The properties of polyamide-imides 12a and 12b are summarized in Table II. The polyamide-imide polymer 12a prepared from PMDA have higher inherent viscosity as compared to the polyamide-imide 12b, prepared from BTDA.

The thermal properties of polyamide-imides 12a and 12b are as shown in Table III. Temperatures for different weight losses and IDT values were calculated from the original thermograms. The IPDT values were calculated from the original TGA curve by following the method of Doyle²³ and T_{\max} values were calculated from the DTG curve. The thermograms for polyamide-imide 12a and 12b are illustrated in Figure 6.

Fairly good thermal stability was observed in both the polyamide-imides. The polyamide-imide 12b prepared from the meta-linked diisocyanate (5b) showed greater thermal stability than the polyamide-imide 12a, prepared from the para-linked diisocyanate (5a). It also showed lowest percent weight loss at high temperatures.

The glass transition temperature (T_g) is lower in case of polyamide-imide 12b, prepared from the meta-linked diisocyanate as compared to the polyamide-imide 12a, prepared from the para-linked diisocyanate, as indicated by the DSC results.

The crystallinity of the polyamide-imides was studied by X-ray diffraction. Both the polymers showed an amorphous X-ray pattern. The representative X-ray diffractograms are shown in Figure 5.

CONCLUSIONS

1. The diisocyanates namely 4,4'-bis(4-isocyanatophenoxy) diphenylsulfone (SPI) and 4,4'-bis(3-isocyanatophenoxy) diphenylsulfone (SMI) were successfully synthesized from the corresponding dibenzoic acids in quantitative yields by a Weinstock-modified curtius rearrangement.
2. The diisocyanates obtained by this method are of pure grade and can be directly used for the synthesis of polyimides and polyamide-imides.
3. Polyimides and polyamide-imides containing arylene sulfone ether linkages were prepared by reacting these diisocyanates with dianhydrides by the one-step method in good yields.
4. All the polymers prepared were soluble in aprotic polar solvents and had film-forming properties.
5. Polyimides and polyamide-imides based on the meta-linked diisocyanate showed superior thermal stability with low glass transition temperature as compared to the corresponding polymers prepared from the para-linked diisocyanate.

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