

# Poly-1,2,4-Triazoles Containing Arylene Sulfone Ether Linkages\*

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## Synopsis

Poly-1,2,4-triazoles containing arylene sulfone ether linkages have been synthesized by the reaction of polyhydrazide precursors and aniline in polyphosphoric acid at 260°C. The polyhydrazide intermediates were prepared from arylene sulfone ether containing dihydrazides and aromatic diacidchlorides via solution and interfacial polycondensation. These polymers and their intermediates were characterized by infrared, solubility, solution viscosity, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction.

## INTRODUCTION

In recent years, the investigation of thermally stable linear polymer systems has received increased emphasis, due largely to demands for heat-resistant synthetics as laminates, films, and fibrous materials. Many polymers containing heterocyclic units joining aromatic nuclei have been explored in the quest for thermally stable materials. Thermostable heterocyclic polymers such as polybenzimidazoles, polyimides, polyoxadiazoles, polybenzoxazoles, and polytriazoles have been the subject of active research for a number of years. A literature survey reveals that negligible attention has been paid to the polytriazole polymers,<sup>1-3</sup> which are known to be better heat-resistant.

It is reported that arylene sulfone ether containing polyamides, polyimides, and polyamideimides show good thermal stability<sup>4-11</sup> and better solubility in various organic solvents. The solution cast films of these macromolecules were flexible and exhibited good adhesion to metal and glass surfaces. In contrast, similar polyamide, polyimide, and polyamideimide polymers which do not contain sulfone ether group in their repeating structures are insoluble in organic solvents and, therefore, are not very useful for heat stable coatings and films.

This paper is a continuation of our ongoing research leading to the development of arylene sulfone ether containing polymers and reports the synthesis and characterization of arylene sulfone ether containing poly-1,2,4-triazoles.

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## EXPERIMENTAL

### Materials

4,4'-[Sulfonylbis(*p*-phenyleneoxy)]dibenzoic acid (SPA),<sup>12</sup> 3,3'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoic acid (SMA),<sup>12</sup> 4,4'-[sulfonylbis(*p*-phenyleneoxy)]dimethylbenzoate (SPME), 3,3'-[sulfonylbis(*p*-phenyleneoxy)]dimethylbenzoate (SMME), 4,4'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoylhydrazine (SPHZ), and 3,3'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoylhydrazine (SMHZ) were prepared in our laboratory and used after recrystallization from the appropriate solvents.

Aniline (ANE) (SISCO, Bombay) was fractionally distilled under reduced pressure and the water white distillate was stored under nitrogen in a sealed amber-colored bottle in the refrigerator. Polyphosphoric acid (PPA) (Matheson, Coleman and Bell) was used as received. Dichloromethane (DCM) (SD's, Bombay) was dried on anhydrous calcium chloride and fractionally distilled, the middle cut fraction collected. *N*-methyl-2-pyrrolidone (NMP) (Fluka, A.G., Switzerland) *N,N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) (SD's, Bombay) were dried over molecular sieves and distilled under reduced pressure.

### Instrumental Methods

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer. NMR spectra were recorded on a Varian T-60, Bruker WH90 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. The heating rate used for the determinations was 5°C min<sup>-1</sup>. The 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 for the determinations was 20°C min<sup>-1</sup>.

The X-ray diffractograms were obtained with a Phillips X-ray unit (Phillips generator, PW 1730) and nickel-filtered CuK<sub>α</sub> radiations.

### Preparations

#### *4,4'*-[Sulfonylbis(*p*-Phenyleneoxy)]dimethylbenzoate (SPME)

To a 50-mL R.B. flask, equipped with reflux condenser and stirring arrangement was added 4.90 g (0.01 mol) of 4,4'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoic acid (SPA), excess of methanol and 0.20 g of concd sulfuric acid and the mixture was refluxed for 10 h. On cooling, the acid was neutralized with ammonia and the excess methanol was removed by distillation. The product,

which solidified on cooling, was filtered at the pump, washed with water three to four times, and dried. The recrystallization from methanol afforded 4.60 g (94%) of pure SPME, mp 138–140°C.

The structure of SPME was determined by IR, <sup>1</sup>H-NMR and mass spectral and elemental analysis.

ANAL: Calcd for C<sub>28</sub>H<sub>22</sub>O<sub>8</sub>S: C, 64.86%; H, 4.24%. Found: C, 64.74%; H, 4.30%.

Mass spectrum: Molecular ion (M<sup>+</sup>) peak at 518.

### 3,3'-[Sulfonylbis(*p*-Phenyleneoxy)]dimethylbenzoate (SMME)

The SMME was prepared by the reaction of 3,3'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoic acid (SMA) with methanol in presence of concd sulfuric acid under the same reaction conditions as used for SPME derivative. The product, which solidified on cooling, was filtered at the pump, washed with water three to four times, and dried. The recrystallization from methanol afforded 4.56 g (93%) of pure SMME, mp 128–130°C.

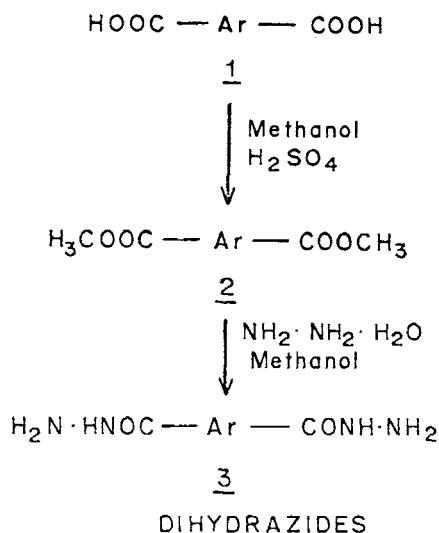
The structure of SMME was determined by IR, <sup>1</sup>H-NMR and mass spectral and elemental analysis.

ANAL: Calcd for C<sub>28</sub>H<sub>22</sub>O<sub>8</sub>S: C, 64.86%; H, 4.24%. Found: C, 64.80%; H, 4.34%.

Mass spectrum: Molecular ion (M<sup>+</sup>) peak at 518.

### 4,4'-[Sulfonylbis(*p*-Phenyleneoxy)]dibenzoylhydrazine (SPHZ)

To a 100-mL R.B. flask, equipped with reflux condenser and stirring arrangement, was added 5.18 g (0.01 mol) of 4,4'-[sulfonylbis(*p*-



Where,

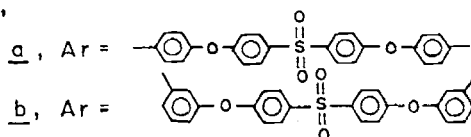
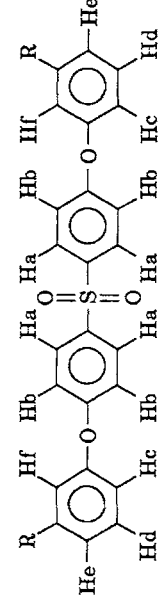
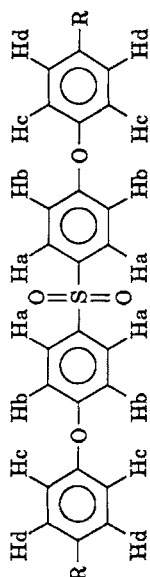


Fig. 1. Preparation of arylene sulfone ether containing dihydrazides.

TABLE I  
IR and NMR Spectral Data

No.	Abbreviation	Substituent —R	IR(Nujol), $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR, $\delta$ (ppm)					
				Ar—Ha	Ar—Hb	Ar—Hc	Ar—Hd	Ar—He	Ar—Hf
1	SPME	—COOCH <sub>3</sub> <sup>b</sup>	1720 (—COO— stretching), 1590 (—CH aromatic), 1285, 1150, 1110 (—SO <sub>2</sub> — stretching), 1250 (Ar—O—Ar stretching)	8.0 (4H, d) ( <i>J</i> = 8.0 Hz)	6.96 (4H, d) ( <i>J</i> = 6.0 Hz)	7.08 (4H, d) ( <i>J</i> = 6.0 Hz)	7.84 (4H, d) ( <i>J</i> = 8.0 Hz)	—	—
2	SPHZ	—CONH·NH <sub>2</sub> <sup>c</sup>	3300 (—NH·NH <sub>2</sub> —), 1635 (—CO—Str—), 1590 (—CH aromatic), 1300, 1150, 1110 (—SO <sub>2</sub> — stretching), 1250 (Ar—O—Ar stretching)	7.96 (4H, d) ( <i>J</i> = 8.0 Hz)	7.1 (4H, d) ( <i>J</i> = 6.0 Hz)	7.24 (4H, d) ( <i>J</i> = 6.0 Hz)	7.88 (4H, d) ( <i>J</i> = 8.0 Hz)	—	—



3	SMME	—COOCH <sub>3</sub> <sup>b</sup>	1720 (—COO— stretching), 1590 (—CH aromatic), 1290, 1150, 1110 (—SO <sub>2</sub> — stretching) 1250, (Ar—O—Ar stretching)	7.88 (4H, d) (J = 8.0 Hz) 3.86 (6H, s) —OCH <sub>3</sub>	7.0 (4H, d) (J = 8.0 Hz)	7.3 (2H, m)	7.44 (2H, dd)	7.72 (2H, m)	7.44 (2H, s)
4	SMHZ	—CONH·NH <sub>2</sub> <sup>c</sup>	3300 (—NH·NH <sub>2</sub> stretching), 1630 (—CO—, stretching), 1590 (—CH aromatic), 1290, 1150, 1110 (—SO <sub>2</sub> — stretching), 1250 (Ar—O—Ar)	7.92 (4H, d) (J = 8.0 Hz) <sup>d</sup> 9.78 (2H, brs) —CONH	7.1 (4H, d) (J = 8.0 Hz)	7.32 (2H, m)	7.50 (2H, dd)	7.70 (2H, m)	7.50 (2H, s)

<sup>a</sup> s = singlet, d = doublet, dd = doublet of doublet, m = multiplet, br = broad.

<sup>b</sup> NMR spectra were recorded in CDCl<sub>3</sub>.

<sup>c</sup> NMR spectra were recorded in DMSO d<sub>6</sub>.

<sup>d</sup> Exchanges with D<sub>2</sub>O.

phenyleneoxy] dimethylbenzoate (SPME), 1.50 g (0.03 mol) of hydrazine hydrate, and 50 mL dry methanol. The reaction mixture was refluxed for 12 h. The solid product which precipitates during the reaction was collected by filtration and washed two to three times with methanol. The recrystallization from a mixture of dichloromethane and petroleum ether afforded 5.0 g (96%) of pure SPHZ, mp 210–212°C.

The structure of SPHZ was determined by IR, <sup>1</sup>H-NMR and mass spectral and elemental analysis.

ANAL: Calcd for C<sub>26</sub>H<sub>22</sub>O<sub>6</sub>N<sub>4</sub>S: C, 60.23%; H, 4.24%. Found: C, 60.16%; H, 4.20%.

Mass spectrum: Molecular ion (M<sup>+</sup>) peak at 518.

### *3,3'-[Sulfonylbis(p-Phenyleneoxy)]dibenzoylhydrazine (SMHZ)*

The SMHZ was prepared by the reaction of 3,3'-[sulfonylbis(*p*-phenyleneoxy)] dimethylbenzoate (SMME) with hydrazine hydrate in presence of methanol under the same reaction conditions, as used for the SPHZ derivative. The solid product which precipitates during the reaction was collected by filtration and washed two to three times with methanol. The recrystallization from a mixture of dichloromethane and petroleum ether afforded 4.90 g (94%) of pure SMHZ, mp 100–102°C.

The structure of SMHZ was determined by IR, <sup>1</sup>H-NMR and mass spectral and elemental analysis.

ANAL: Calcd for C<sub>26</sub>H<sub>22</sub>O<sub>6</sub>N<sub>4</sub>S: C, 60.23%; H, 4.24%. Found: C, 60.20%; H, 4.32%.

Mass spectrum: Molecular ion (M<sup>+</sup>) peak at 518.

### *Diacidchlorides*

Terephthaloyl chloride (TPCl), mp 79–81°C, and isophthaloyl chloride (IPCl), mp 43–44°C, were prepared from the corresponding acids by standard procedures and purified before use.

## **Polymerizations**

The polyhydrazides were prepared by using solution and interfacial polycondensation methods.

### *Solution Polymerization*

A 100-mL three-necked R.B. flask, equipped with thermowell, guard tube, nitrogen inlet tube, and stirring arrangement was charged under nitrogen with 1.036 g (0.002 mol) of 4,4'-[sulfonylbis(*p*-phenyleneoxy)] dibenzoyl hydrazine (**3a**) and 20 mL of dry NMP. After cooling the solution to –10°C and with vigorous stirring, 0.4060 g (0.002 mol) of terephthaloyl chloride (**4c**) was added portionwise over a period of 15 min. 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 (200 mL) with vigorous stirring. The precipitated polymer was collected by filtration, washed well with methanol (three to four times), and dried.

TABLE II  
Properties of Polyhydrazides

No.	Polymer abbreviation	Reactants		Yield (%)	Solution viscosity <sup>a</sup> $\eta_{inh}$ (dL g <sup>-1</sup> )			Elemental analysis <sup>b</sup>		
		Dihydrazide	Diacidchloride		Solution polymerization	Interfacial polymerization	C %	H %	N %	
1	5 ac	SPHZ <sup>c</sup>	TPCl <sup>e</sup>	98.0	0.52	0.63	62.80 (62.96)	3.80 (3.70)	8.76 (8.64)	
2	5 ad	SPHZ <sup>c</sup>	IPCl <sup>f</sup>	98.0	0.48	0.58	62.92 (62.96)	3.86 (3.70)	8.56 (8.64)	
3	5 bc	SMHZ <sup>d</sup>	TPCl <sup>e</sup>	97.0	0.44	0.56	62.82 (62.96)	3.68 (3.70)	8.68 (8.64)	
4	5 bd	SMHZ <sup>d</sup>	IPCl <sup>f</sup>	96.0	0.40	0.51	62.90 (62.96)	3.74 (3.70)	8.60 (8.64)	

<sup>a</sup> Determined in dimethylformamide at 30°C.

<sup>b</sup> Values in parenthesis indicate the corresponding calculated values.

<sup>c</sup> SPHZ = 4,4'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoylhydrazine.

<sup>d</sup> SMHZ = 3,3'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoylhydrazine.

<sup>e</sup> TPCl = terephthaloyl chloride.

<sup>f</sup> IPCl = isophthaloyl chloride.

The other polycondensation reactions of dibenzoylhydrazines with diacid chlorides were carried out in NMP under the same conditions.

### Interfacial Polymerization

A 250-mL high-speed stirring reactor was charged with 1.036 g (0.002 mol) of dibenzoylhydrazine (**3a**) and 0.212 g (0.002 mol) of sodium carbonate in 50 mL distilled water. To this solution was added 0.4060 g (0.002 mol) of diacid chloride (**4c**) in 50 mL dichloromethane at 0°C. The reaction mixture was then stirred vigorously for 20 min and was poured into methanol. The precipitated polymer was separated by filtration and washed with water, acetone, and dichloromethane. Finally, the polymer was dried under high vacuum at 70°C. The same procedure was used for other polymers.

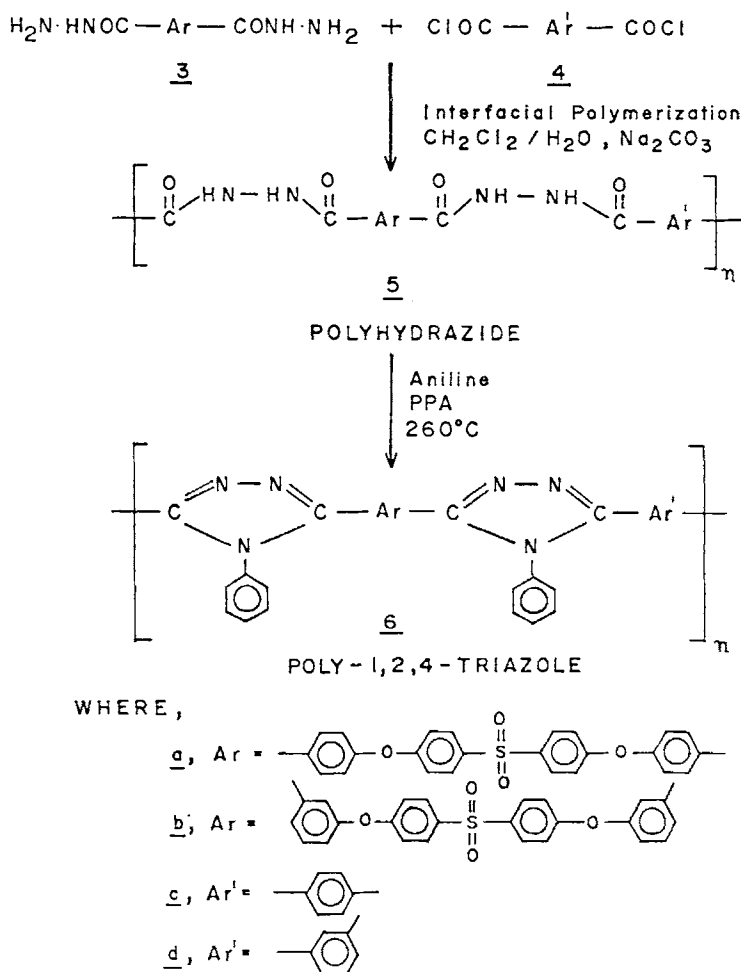


Fig. 2. Preparation of arylene sulfone ether containing poly-1,2,4-triazoles.



TABLE III  
Properties of Poly-1,2,4-Triazoles

No.	Polymer abbreviation	Reactants		Yield (%)	Solution viscosity $\eta_{inh}^a$ (dl g <sup>-1</sup> )	Elemental analysis <sup>b</sup>		
		Polyhydrazide	Aniline			C %	H %	N %
1	6 ac	5 ac	ANE	96.0	0.44	72.40 (72.44)	3.88 (3.94)	10.92 (11.00)
2	6 ad	5 ad	ANE	97.0	0.39	72.48 (72.44)	3.84 (3.94)	10.94 (11.00)
3	6 bc	5 bc	ANE	98.0	0.36	72.52 (72.44)	3.98 (3.94)	11.10 (11.00)
4	6 bd	5 bd	ANE	97.0	0.32	72.42 (72.44)	3.92 (3.94)	11.16 (11.00)

<sup>a</sup> Determined in dimethylformamide at 30°C.

<sup>b</sup> Values in parenthesis indicate the corresponding calculated values.

### *Synthesis of Poly-1,2,4-Triazoles*

A typical synthesis of polytriazole from polyhydrazide is as follows: To a 100-mL R.B. flask, equipped with reflux condenser and stirring arrangement, was added 2.0 g of polyhydrazide (**5ac**), 10 mL of aniline, and 40 mL of polyphosphoric acid. The reaction mixture was heated at 260°C for 3 h. The clear reaction mixture obtained was then poured in excess of distilled water. The precipitated polymer was filtered and washed with water, with 10% sodium hydroxide solution, again with water, and finally with methanol. The polymer obtained was dried under high vacuum at 70°C. The same procedure was used to prepare other polytriazoles.

### *Polymer Solubility*

The solubility of polyhydrazides and poly-1,2,4-triazoles was determined at 3% concentration in various solvents. All the polymers dissolved in aprotic 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

Carboxylic hydrazides or symmetrical carboxylic dihydrazides have been prepared by the reaction between carboxylic acid,<sup>13</sup> ester,<sup>14</sup> anhydrides,<sup>14</sup> or carbonyl chlorides<sup>15</sup> with hydrazine or carboxylic hydrazides respectively. The reactions of esters with hydrazine or with 80–100% hydrazine hydrate is generally regarded to be quantitative while other with acid derivatives frequently lead to undesirable mixtures of mono-, di-, tri-, and tetraacylhydrazines.<sup>14,16 18</sup>

In the present work, we have synthesized dihydrazides containing arylene sulfone ether links by the reaction of carboxylic acid esters and hydrazine hy-

drate in quantitative yields. The scheme for the preparation of dihydrazides is shown in Figure 1. The structures of dicarboxylic acid esters and dihydrazides were elucidated by IR, NMR, and mass spectral analysis, the spectral data of which is given in Table I.

Four polyhydrazides have been prepared by the interfacial and solution polycondensation of 4,4'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoylhydrazine (SPHZ) and 3,3'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoylhydrazine (SMHZ) with terephthaloyl and isophthaloyl chloride. The polymers thus obtained were characterized by elemental analysis, IR, and solution viscosity. The properties of polyhydrazides are summarized in Table II. Infrared spectrums and elemental analyses are in good agreement with the assigned structure. These polymers are soluble in all aprotic polar solvents. The inherent viscosities of these polymers vary from 0.40 to 0.63 dL/g in dimethylformamide and are higher in polymers synthesized by interfacial polycondensation tech-

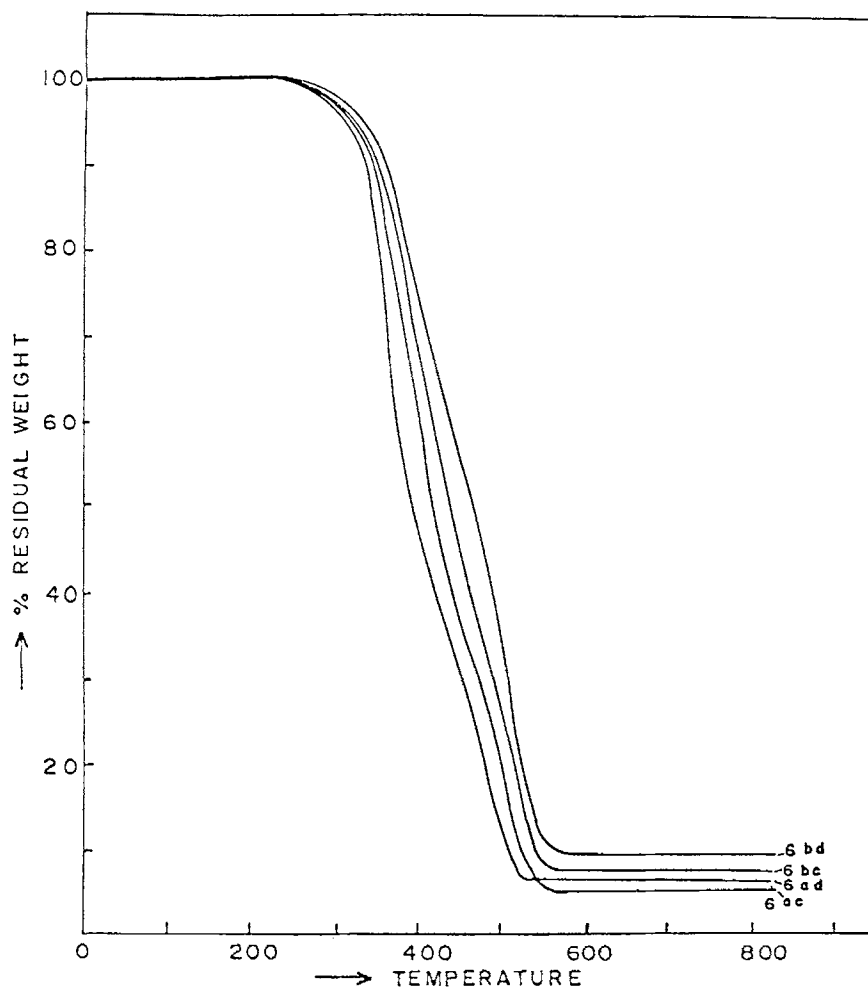


Fig. 3. Thermogravimetric analyses of poly-1,2,4-triazoles 6ac, 6bc, 6ad, and 6bd.

TABLE IV  
Thermal Characteristics of Poly-1,2,4-Triazoles

No.	Polymer abbreviation	$T_g^a$ (°C)	IDT <sup>b</sup> (°C)	Temperature at various % residual weight (°C)					IPDT <sup>c</sup> (°C)	$T_{max}^d$ (°C)
				10%	20%	30%	40%	50%		
1	6 ac	270	323	340	365	385	400	415	400	530
2	6 ad	250	324	335	350	360	375	390	405	525
3	6 bc	210	342	350	375	395	420	440	420	557
4	6 bd	204	350	365	385	410	435	465	418	550

<sup>a</sup>  $T_g$  = glass transition temperature.

<sup>b</sup> IDT = initial decomposition temperature.

<sup>c</sup> IPDT = integral procedural decomposition temperature.

<sup>d</sup>  $T_{max}$  = temperature for maximum rate of decomposition.

nique. Similarly, they are comparatively lower in polyhydrazides prepared from meta-linked dihydrazides than those prepared from the para-linked dihydrazides.

These polyhydrazides (prepared by interfacial method) have been converted to respective *N*-aryl substituted 1,2,4-triazoles by reacting them with aniline at 260°C in polyphosphoric acid (PPA). The cyclization proceeds by the elimination of water molecules as shown in Figure 2. The reaction is complete in 3 h and was monitored by infrared spectroscopy. The polymers thus obtained were characterized by infrared spectrum, solution viscosity, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. The properties of these polymers are summarized in Table III.

All the polymers are white solids. The elemental analyses and IR spectra are in good agreement with the structures shown in Figure 2. These polymers are soluble in aprotic polar solvents like DMF, DMAC, DMSO, and NMP. The inherent viscosities of these polymers in DMF varies from 0.32 to 0.44 dL/g, which are lower than the corresponding polyhydrazides.

The thermal stability of these polymers was studied by thermogravimetric analysis. The samples were heated in air at a constant rate of 5°C min<sup>-1</sup>. The original thermograms of para- and meta-linked polytriazoles are illustrated in Figure 3. Initial decomposition temperature (IDT) and the temperatures for different weight losses were determined from original TGA curves and are tabulated in Table IV. The integral procedural decomposition temperature (IPDT) was calculated by following the method of Doyle.<sup>19</sup> The temperature for maximum rate of decomposition ( $T_{max}$ ) was calculated from the DTG curve.  $T_{max}$  and IPDT values show that the polytriazoles have good thermal stability. Polytriazoles prepared from meta-linked polyhydrazides showed marginally greater thermal stability than that of polytriazoles prepared from para-linked polyhydrazides. They also showed the lowest percent weight loss at high temperatures.

The DSC results showed that the glass transition temperature ( $T_g$ ) for the para-linked polytriazoles are slightly higher than meta-linked polytriazoles.

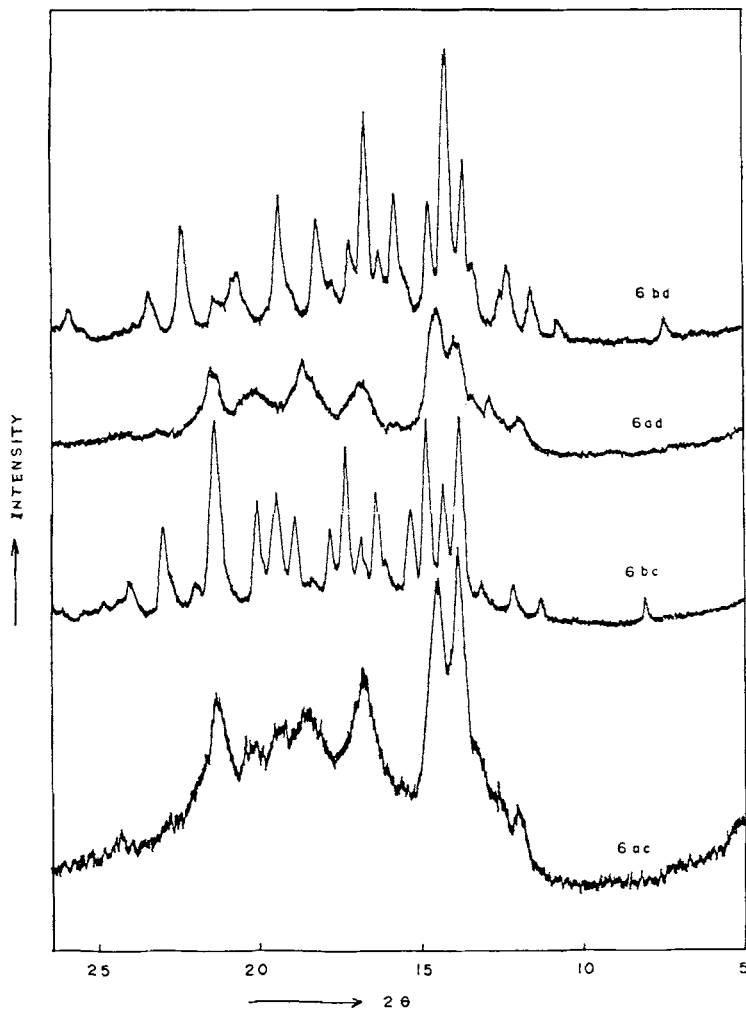


Fig. 4. X-ray diffractograms of poly-1,2,4-triazoles 6ac, 6bc, 6ad, and 6bd.

The polytriazoles prepared from the meta-linked polyhydrazide have the lowest  $T_g$  value in their respective series.

The crystallinity of the polytriazoles was studied by X-ray diffraction. All the polytriazoles showed partial crystallinity in their respective X-ray diffractograms, which are shown in Figure 4.

### CONCLUSIONS

1. The dihydrazides, namely 4,4'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoylhydrazine (SPHZ) and 3,3'-[sulfonylbis(*p*-phenyleneoxy)]dibenzoylhydrazine (SMHZ), were successfully synthesized from the corresponding dibenzoic acids in quantitative yields.

2. The dihydrazides obtained by this method are of pure grade and can be directly used for the preparation of polytriazoles via polyhydrazide intermediates.
3. Polyhydrazides containing arylene sulfone ether linkages were prepared by reacting these dihydrazides with diacidchlorides in good yields and polytriazoles were prepared therefrom by chemical reaction in presence of PPA and aniline in good yields.
4. All the polymers prepared were soluble in aprotic polar solvents and had film forming properties.
5. Polyhydrazides and polytriazoles based on meta-linked dihydrazide showed marginally superior thermal stability with low glass transition temperatures as compared to the corresponding polymers prepared from para-linked dihydrazides.

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