

# Aromatic Polyesters. I. Synthesis and Characterization of Poly(4,4'-Thiodiphenyl Phthalate)s

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## Synopsis

Poly(4,4'-thiodiphenyl phthalates) (iso/tere) have been synthesized using both low temperature step-growth and phase-transfer catalyzed polymerization techniques. These polymers were characterized using conventional techniques like elemental analysis, solubility characteristics, X-ray diffraction, infrared, and proton nuclear magnetic resonance spectroscopy. 4,4'-Thiodiphenyl dibenzoate was used as a model compound.

## INTRODUCTION

The aromatic polyesters are known to be fairly thermostable and have good thermooxidative stabilities. However, they are not very amenable to processing. Incorporation of linkages like ether, sulfide, sulfone, etc., may enhance their processability without any significant loss in their overall thermal performance. Moreover, incorporation of those linkages are known to enhance resistance to solvent and environmental stress crazing of the parent polymers. However, surprisingly very little information is available on the synthesis and properties of these polymers.

We have undertaken a systematic study on the synthesis, characterization, and analysis of structurally related polymers having these linkages with similar neighboring unit. The present paper reports the successful utilization of both low temperature condensation polymerization using thionyl chloride and pyridine<sup>1</sup> as well as phase-transfer catalyzed<sup>2</sup> methods followed by detailed characterization of poly(4,4'-thiodiphenyl phthalates) (designated as I for isophthalate and T for terephthalate structures).

## EXPERIMENTAL

Chloroform (B.D.H.) tetraethyl ammonium chloride (Aldrich), sodium hydroxide (B.D.H.), benzene (GR, E. Merck, India), were used without further purification. Dimethyl formamide (DMF) (E. Merck) was allowed to stand over magnesium sulfate for 24 h and distilled under reduced pressure ( $\approx 20$  torr). Pyridine (B.D.H.) was refluxed over sodium hydroxide followed by distillation. Thionyl chloride (B.D.H.) was distilled before use. Terephthalic acid (E. Merck) was purified via sodium salt which after recrystallization from water was reconverted to the acid by acidification with mineral

acid,<sup>3</sup> and isophthalic acid (Kochlight, U.K.) was crystallized from aqueous ethanol.<sup>3</sup> Terephthaloyl chloride and isophthaloyl chloride were distilled under reduced pressure ( $\approx 20$  torr) through a short Vigreux column and recrystallized from hexane.<sup>3,4</sup> Thiodiphenol (TDP) was received as a gift sample from M/s Crown Zellerbach Corp. and was used without further purification. Thorin (Aldrich) was used as received. Benzil (SRL, Extrapure) was washed with alkali and crystallized from benzene.<sup>3</sup>

### Polymer Synthesis

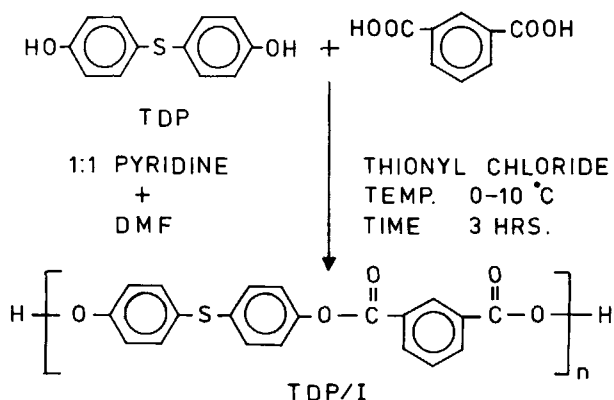
Poly (4,4'-thiodiphenyl phthalate)s were prepared by the following methods.

#### *Low Temperature Condensation Polymerization in Solution* (Scheme 1)

A typical synthetic procedure is outlined below:

To a 250-mL two-necked flask, equipped with a stirrer and thermometer, a solution of 0.415 g (2.5 mmol) of isophthalic acid in 5 mL of pyridine was added. The reaction mixture was cooled to bring down the temperature of the solution to below 0°C. Freshly distilled thionyl chloride [0.66 g (5.5 mmol)] was added, and the solution was stirred for approximately 3 min. Subsequently, 0.535 g (2.5 mmol) of TDP dissolved in 5 mL of DMF was added to the reaction mixture and the polymerization was carried out at 10°C for approximately 3 h under continuous stirring. The polymer was isolated by pouring the solution into 500 mL of cold distilled water and recovered by filtration. It was thoroughly washed and dried overnight in an oven at 50–60°C. The polymer was further purified by repeated reprecipitation and subsequently dried:

$$\text{yield} = 0.90 \text{ g (94.7\%)}, \quad [\eta] = 0.39 \text{ dL/g}, \quad \bar{M}_n = 15,700$$



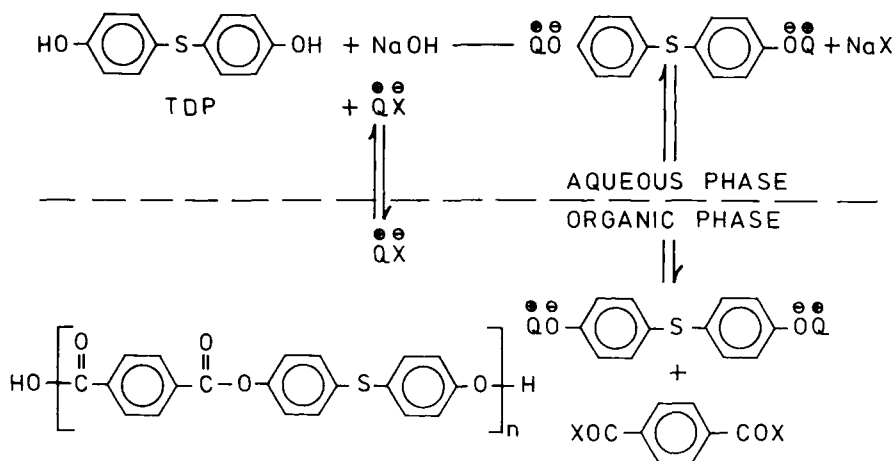
Scheme 1. A typical low temperature step-growth solution polymerization of sulfur-containing aromatic polyester.

*Phase Transfer Catalyzed Polycondensation (Scheme 2)*

A typical synthetic method is outlined below:

In a 250-mL, two-necked flask equipped with a stirrer a solution of 4.2 g (0.105 mol) of sodium hydroxide in 30 mL of distilled water and 10.90 g of TDP (0.05 mol) was used. A solution of 11.165 g (0.055 mol) of terephthaloyl chloride in 30 mL chloroform was added in the reaction mixture followed by 1.01 g (0.01 mol) of tetraethyl ammonium chloride ( $C_2H_5)_4N^+Cl^-$ . The reaction mixture was stirred at a very high speed at room temperature ( $\approx 25^\circ C$ ) for 10–15 min. The resulting polymer was filtered and washed thoroughly with distilled water. The polymer was purified by reprecipitation and dried in a vacuum oven at 50–60°C:

$$\text{yield} = 20 \text{ g (90\%)}, \quad [\eta] = 0.42 \text{ dL/g}, \quad \bar{M}_n = 16,500.$$



Scheme 2. A typical phase-transfer catalyzed step-growth polymerization of sulfur-containing aromatic polyester.

4,4'-Thiodiphenyl dibenzoate (TDP/BA) was synthesized by using the low-temperature condensation method in homogeneous medium as described above. Viscosity measurements were carried out in DMF at  $30 \pm 0.01^\circ C$  using an Ubbelohde suspended level viscometer. Intrinsic viscosity was calculated by using the Soloman-Ciuta equation.<sup>5</sup> Number-average molecular weight ( $\bar{M}_n$ ) was measured in DMF at  $90 \pm 0.1^\circ C$  using a Knauer (West Germany) vapor pressure osmometer. Purified benzil was used for calibration.

The melting point was determined by a conventional melting point apparatus. Elemental microanalysis of these polymers and 4,4'-thiodiphenyl dibenzoate for carbon, hydrogen, and sulfur<sup>6</sup> were done. Infrared spectroscopy was recorded with a Perkin-Elmer Model 237B spectrometer using KBr pellets. <sup>1</sup>H-NMR spectra were recorded on a Varian EM 390, 90-MHz NMR spectrometer using DMSO-d<sub>6</sub> as solvent and tetramethylsilane as internal standard. X-ray diffraction patterns were recorded with DORN-I (USSR) X-ray diffractometer using Ni-filtered CuK<sub>α</sub> radiation. The percentage of crys-

TABLE I  
Physical Characteristics of Poly(4,4'-Thiodiphenyl Phthalate)s and Related Model Compound

Polyesters and model compound	[ $\eta$ ] in DMF at 30 $\pm$ 0.01°C (dL/g)	$\bar{M}_n$	Melting point (°C)	Elemental Analysis (%)				Crystallinity (%)
				C	H	S	O	
Poly(4,4'-thiodiphenyl terephthalate) (TDP/T)	0.44	17,700	$\approx$ 300	66.88	3.46	9.18	18.47 (calculated)	48.19
				69.00	3.42	9.10	18.48 (found)	
Poly(4,4'-thiodiphenyl isophthalate) (TDP/I)	0.39	15,700	$\approx$ 300	68.36	3.46	9.18	18.47 (calculated)	46.53
				68.73	3.50	9.20	18.57 (found)	
4,4'-Thiodiphenyl dibenzoate (TDP/BA)	—	—	175	73.24	4.25	7.50	15.00 (calculated)	—
				73.25	4.20	7.53	15.02 (found)	

tallinity of these polymers were determined from the intensity of both crystalline and amorphous scatter by the Hermans-Weidinger method.<sup>7</sup>

## RESULTS AND DISCUSSION

Poly(4,4'-thiodiphenyl phthalate)s (TDP/T or I) and the model compound 4,4'-thiodiphenyl dibenzoate (TDP/BA) can readily be synthesized by the procedure outlined above. Some characteristics of these polymers are summarized in Table I, including elemental analytical data. These polymers are soluble in most aprotic solvents (DMF, DMAC, DMSO), highly polar solvents like *N*-methyl pyrrolidone, pyridine, and partially soluble in ether solvents (THF). The structure of the repeating unit of these polymers have been confirmed both by IR and <sup>1</sup>H-NMR spectroscopy, as well as by elemental analysis.

### Infrared Spectroscopy

The IR spectra of dihydroxy reactant (TDP), model compound TDP/BA, and polyesters TDP (T/I) are shown in Figure 1. The frequencies (cm<sup>-1</sup>) of

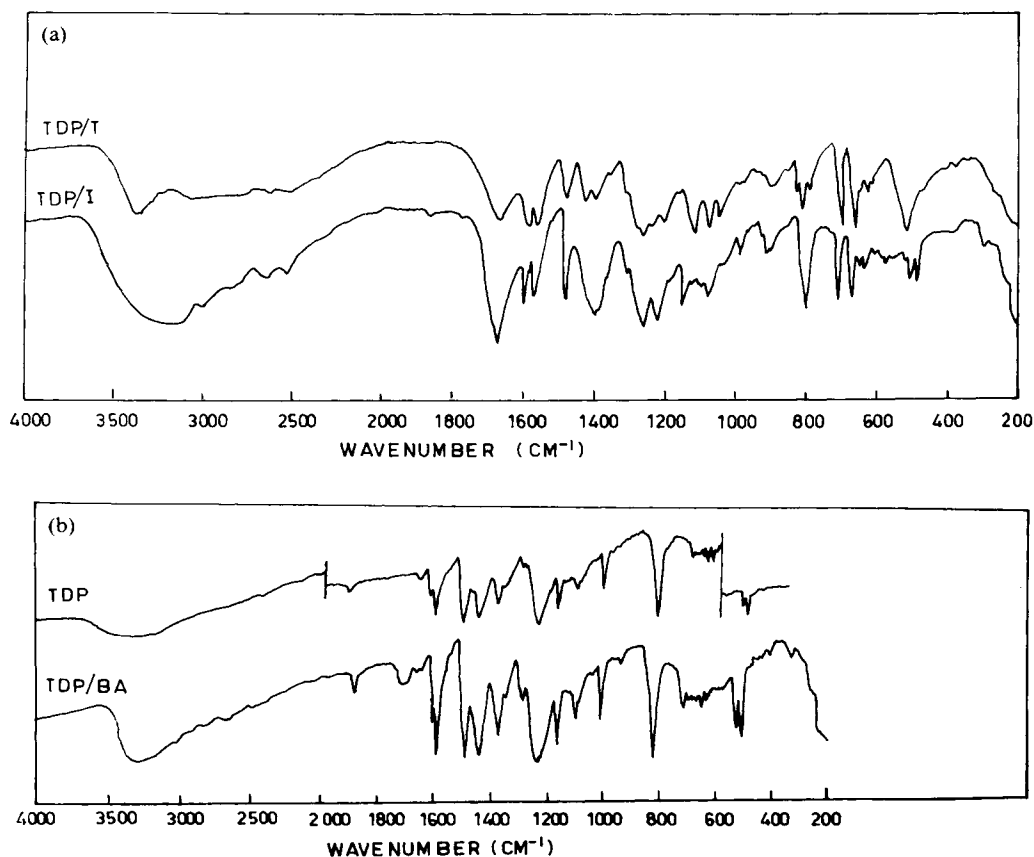
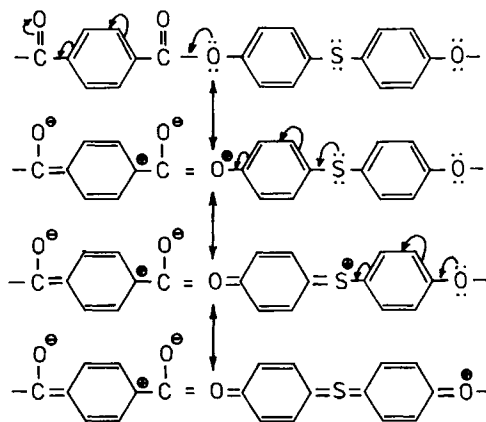


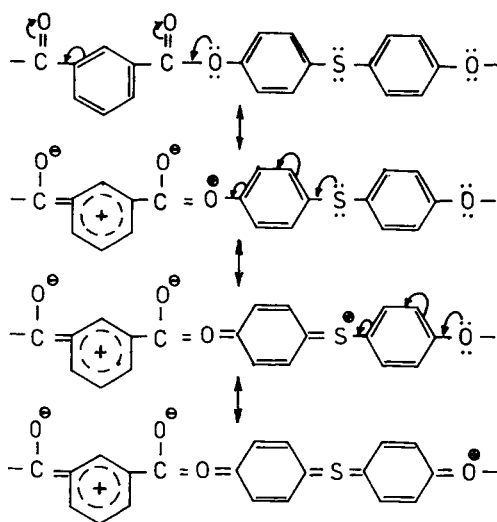
Fig. 1. (a) IR of TDP/T and TDP/I; (b) IR of 4,4'-thiodiphenyl dibenzoate [TDP/BA] and TDP.

TABLE II  
Important IR Absorbances of TDP, TDP/BA, TDP/T, and TDP/I

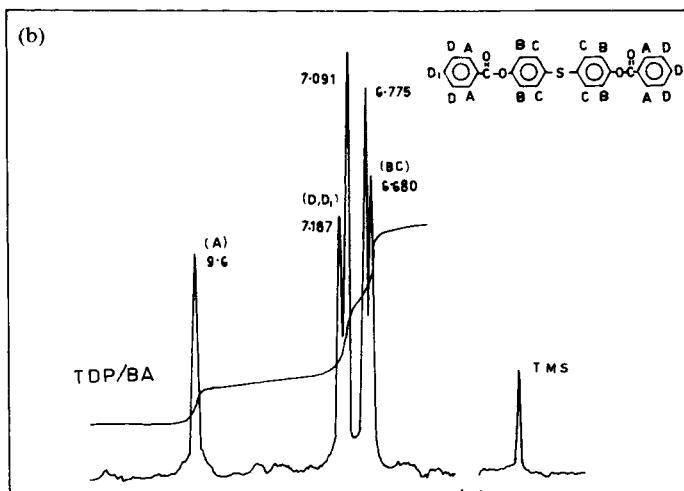
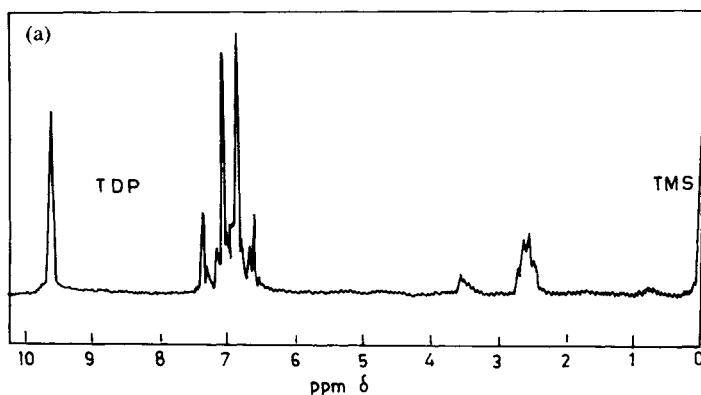
Assignment	TDP	TDP/BA	TDP/T	TDP/I
(1) 1,4-disubstituted benzene	490	505 520	505 520	510 520
(2) 1,4-disubstituted benzene	—	—	570	—
(3) 1,3-disubstituted benzene ring	—	—	—	600
(4) C—S—C linkage	615 630	630 650	630 (W)	630 650
(5) 1,3-disubstituted benzene prominent due to ester linkage	—	—	—	690
(6) —C—O— benzoate	—	700–710	730	730
(7) Para-disubstituted benzene out of plane C—H bond	810	820	820	820
(8) Disubstituted benzene and C—S—C stretching	920	930	920–940	920–940
(9) Partly 1,4-disubstitution partly C—S—C stretching	1000	1010	1015	1010
(10) C—O—C dibenzoate	—	—	1110 (Tere)	1095 (ISO)
(11) C=S [C—S—C] predominantly double bond character	1160	1165	1165 (W)	1170
(12) Phenolic C—S stretching	1230	1220	1235	1235
(13) C=O of benzoate	—	1280–1290	1280	1280
(14) Phenyl —C—O stretching	1275	1375	1380 (W)	1375 (W)
(15) Phenyl (in-plane)	1445	1440	1420	1420
(16) Phenyl C—H (in-plane)	1495	1490	1505	1490
(17) Phenyl C—C (in-plane)	1590	1585	1580	1580
(18) Phenyl —H (out of plane) and 1,3-disubstitution	1605	1600	1600 (W)	1605
(19) Aryl ester of aromatic acid (C=O benzoate)	—	1680–1720	1680–1700	1680–1700
(20) C—S—C linkage	1895	1885	1875	1875



Scheme 3. Resonance structures of poly(4,4'-thiodiphenyl terephthalate) [TDP/T].



Scheme 4. Resonance structure of poly(4,4'-thiodiphenyl isophthalate) [TDP/I].

Fig. 2. (a)  $^1\text{H-NMR}$  spectroscopy of thionylidiphenol (TDP); (b)  $^1\text{H-NMR}$  spectroscopy of TDP/BA.

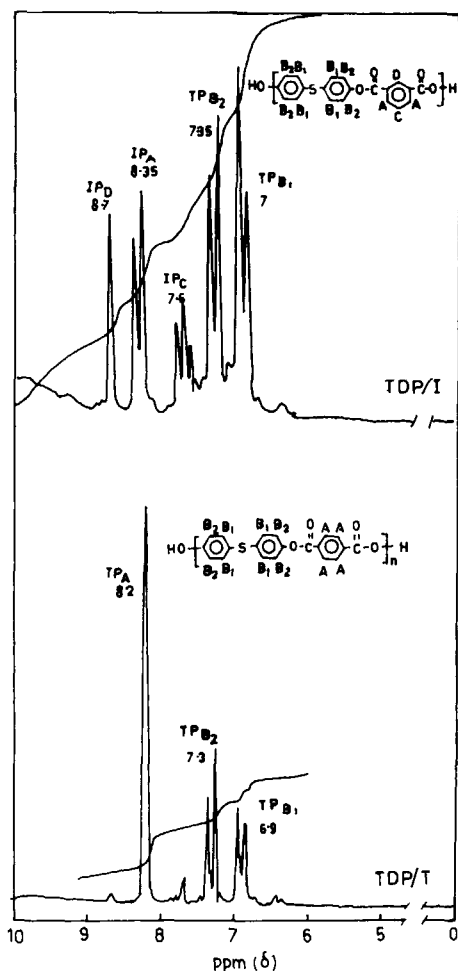


Fig. 3. <sup>1</sup>H-NMR spectroscopy of poly(4,4'-thiodiphenyl terephthalate) [TDP/T] and poly(4,4'-thiodiphenyl isophthalate) [TDP/I].

the important peaks/bands along with their assignments are given in Table II. In TDP, strong absorptions at 490, 505, 810, and 1000  $\text{cm}^{-1}$  confirm the 1,4-disubstituted benzene ring and at 615, 630, 920, 1000, 1070–1100, and 1160  $\text{cm}^{-1}$  confirm the presence of C—S—C linkages in the molecule.<sup>6</sup>

The effect of conjugation (Schemes 3–4) on the absorption bands of —S— linkage and 1,4-disubstituted benzene by incorporation of carboxylate groups in TDP(T/I) and TDP/BA indicates that the absorptions due to 1,4-disubstituted benzene are shifted to 505 (510 in case of TDP/I) and 520  $\text{cm}^{-1}$  (from 490 and 505  $\text{cm}^{-1}$ , respectively), whereas, absorptions due to C—S—C linkages are shifted to 630 and 650  $\text{cm}^{-1}$  (from 615 and 630  $\text{cm}^{-1}$  in TDP, respectively) also due to conjugation (Schemes 3 and 4). Other assignments of interests are the band at 570  $\text{cm}^{-1}$  for 1,4-disubstitution in TDP/T, at 500 and 690  $\text{cm}^{-1}$  for 1,3-disubstitution present only in TDP/I, and C—O—C dibenzoate stretch at 1110 and 1095  $\text{cm}^{-1}$  in TDP/T and TDP/I, respectively (absent both in TDP and TDP/BA).



### NMR Spectroscopy

The  $^1\text{H-NMR}$  spectra of these compounds are shown in Figures 2 and 3. For TDP, quartet at 6.66–7.36  $\delta$  are caused by the four protons associated with each of the two benzene rings. Protons closer to  $-\text{S}-$  linkages ( $\text{TP}_{\text{B}_1}$ ) are at lower  $\delta$  values, whereas those close to  $-\text{O}-$  linkages ( $\text{TP}_{\text{B}_2}$ ) are at higher  $\delta$  values. A singlet at 9.65  $\delta$  corresponds to the proton present in the  $-\text{OH}-$  group at chain end.

For TDP/BA, the doublet at 6.68–6.775  $\delta$  corresponds to protons (B and C) of benzene nuclei in both the sides of the  $-\text{S}-$  linkage, the doublet at 7.691–7.187  $\delta$  corresponds to six protons (D and  $\text{D}_1$ ) present in the dibenzoate unit, and the singlet at 9.6  $\delta$  corresponds to four hydrogen atoms (A) present in the dibenzoate unit closer to carboxylate group.

For TDP/T, a singlet at 8.2  $\delta$  is caused by the four protons ( $\text{TP}_{\text{A}}$ ) of terephthalic, whereas for TDP/I a singlet at 8.75  $\delta$  is caused by the proton ( $\text{IP}_{\text{D}}$ ) present in isophthalic in between two ester groups. The doublet at

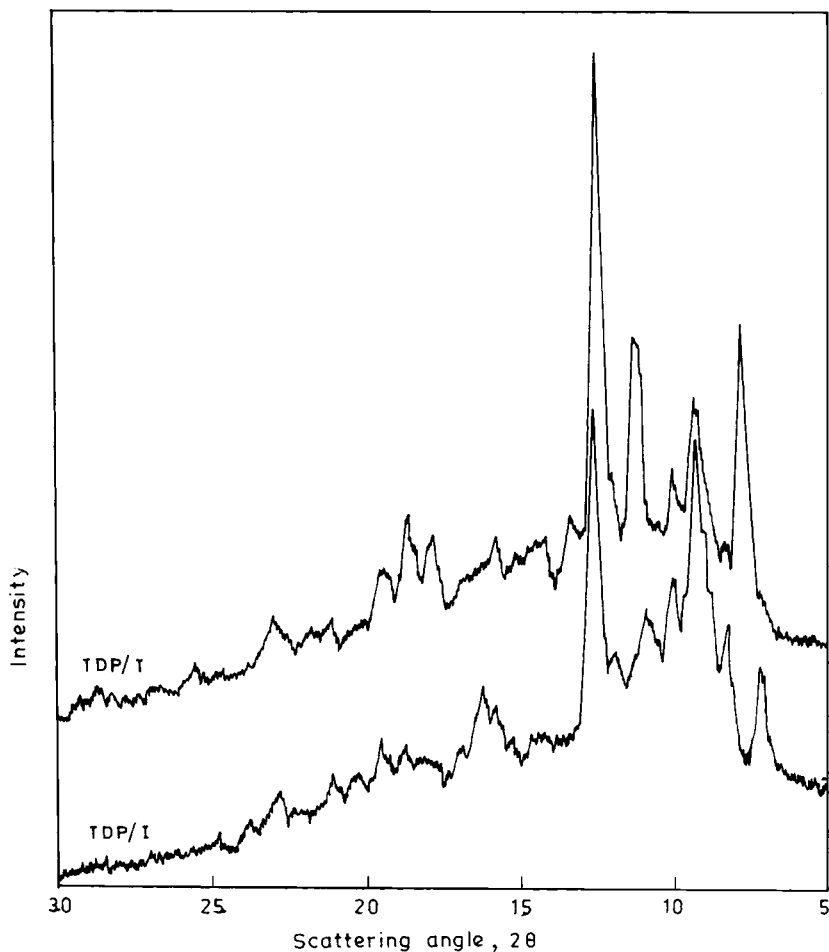


Fig. 4. X-ray diffraction patterns of poly(4,4'-thiodiphenyl terephthalate) [TDP/T] and poly(4,4'-thiodiphenyl isophthalate) [TDP/I].

8.3–8.45  $\delta$  is caused by two protons ( $IP_A$ ) present in isophthalic and nearby the ester linkages. Multiplets at 7.3–7.4  $\delta$  are caused by the proton ( $IP_C$ ) present in isophthalic and away from ester linkages. Multiplets at 7.3–7.40  $\delta$  are due to four protons ( $TP_{B2}$ ) present in the diphenol unit of the polyester and away from the thio group. Multiplets at 6.85/6.9–7.0  $\delta$  correspond to four protons ( $TP_{B1}$ ) present in diphenol next to the thio group. A peak at 9.8  $\delta$  may be due to protons present in —OH end groups.

X-ray diffraction patterns of TDP (T/I) are shown in Figure 4. They are partially crystalline in nature and under identical synthetic condition: TPD/T is slightly more crystalline (see Table I). At present, no further attempt has been made to elucidate crystal structure of these polymers.

### CONCLUSIONS

Wholly aromatic polyesters containing flexible sulfide linkage can easily be prepared by low temperature step-growth polymerization. Structure elucidation by various techniques confirmed their repeat unit. The presence of resonance-stabilized conjugated structures in these systems has also been confirmed by IR spectroscopy. It may thus be reasonably expected that these polymers may show good thermal stability coupled with marginal flexibility. These polymers are partially crystalline in nature with melting point around 300°C. These polymers are found to be soluble only in aprotic, highly polar and ether solvents.

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