

# Flameproofed Polyesters Prepared by Direct Polycondensation of Aromatic Dicarboxylic Acids and Brominated Bisphenols with Tosyl Chloride and *N,N'*-Dimethylformamide in Pyridine

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## Synopsis

Brominated aromatic polyesters were successfully prepared by reacting isophthalic acid and terephthalic acid with *p*-toluenesulfonyl chloride in pyridine in the presence of *N,N'*-dimethylformamide, followed by treating with a pyridine solution of tetrabromobisphenols. The tetrabromobisphenols were synthesized by a facile bromination of their corresponding bisphenols in aqueous acetic acid solution under mild conditions. The polycondensation was significantly affected by the reactivity of bisphenols and the solubility of the resulting polymers in the reaction media. Tetrabromobisphenols with positive linking groups between the aromatic rings and better solubility of the resulting polymers give a more favorable result. The products were nonflammable having limiting oxygen index 59–62 (ASTM D2863-77) without much sacrifice in thermal stability.

## INTRODUCTION

The aromatic polyesters have been prepared by several methods. Among the more widely used methods were melt polycondensation, low temperature interfacial polymerization, high temperature solution, and low temperature solution polymerization.<sup>1–3</sup> Recently, several workers have reported a facile synthesis of aromatic polyester by a direct polycondensation of dicarboxylic acids with bisphenols in the presence of condensing agents, which include triphenylphosphine,<sup>4</sup> arylsulfonyl chloride,<sup>5,6</sup> triphenylphosphine dichloride,<sup>7</sup> diphenyl chlorophosphate,<sup>8</sup> thionyl chloride,<sup>9</sup> phosphorous oxychloride,<sup>10</sup> etc. One of the most simple and effective methods operative under mild conditions is that reported by Higashi and co-workers,<sup>6</sup> in which arylsulfonyl chlorides in pyridine in the presence of *N,N'*-dimethylformamide (DMF) is used for the preparation of high-molecular-weight polyester directly from dicarboxylic acids and bisphenols as well as hydroxybenzoic acid with no substantial amounts of oligomers being formed.

Organic bromides have long been recognized as effective flame retardants for polymeric materials, and there is a large amount of data in the literature on the topic. Many patents have dealt with the preparation of flameproofed aromatic polyesters by introducing bromine into the polymer chain.<sup>11–13</sup> The synthesis of brominated aromatic polyesters by a direct polycondensation has

not been reported yet. Our objective is to synthesize some brominated bisphenols and to study the direct polymerization of them with dicarboxylic acids by toluenesulfonyl chloride (tosyl chloride, TsCl) in the presence of DMF. The thermal stability and flame retardancy of the resulting polymers are also investigated.

## EXPERIMENTAL

### Reagents

Isophthalic acid and terephthalic acid (Wako Pure Chemical Ind., Ltd.) were extra pure grade and used without further purification. Phenolphthalein (Fluka AG), *p,p'*-biphenol, 4,4'-thiodiphenol, bisphenol S (Tokyo Kasei Kogyo Co. Ltd.), and bromine (Wako) were used as received. 3,3',5,5'-Tetrabromobisphenol A (TBBPA) and 3,3',5,5'-tetrabromobisphenol A bis(hydroxyethyl) ether (TBBPABHE) were supplied by a local supplier and purified by recrystallization from hot methanol. Other chemicals such as *p*-toluenesulfonyl chloride, pyridine, and *N,N'*-dimethylformamide (Wako) used as condensing agents were used as received. The phenols and 1,1,2,2- (sym-) tetrachloroethane (Wako) used in the measurement of polymer solution viscosities were reagent grade and used without further purification.

### Synthesis of Tetrabromobisphenols

A typical preparation of a tetrabromobisphenol is as follows. Into a 300 mL flask, 0.03 mol of 4,4'-thiodiphenol (6.6 g) was dissolved in 150 mL of glacial acetic acid, and a small quantity of water was added as the hydrogen bromide acceptor. To this solution, 0.132 mol (10 g) of bromine, measured from a burette, was added slowly with stirring. The reaction was initially carried out at room temperature (about 25°C) over a period of about 10 min. The flask was transferred to a warm water bath of 60°C when the reaction medium appeared turbid. White solids precipitated gradually from the reaction medium as the reaction proceeded. A persistent yellow color indicated that the reaction was complete. Finally, the reaction temperature was held at 80°C for 1 h to ensure complete bromination. After cooling, the crude 3,3',5,5'-tetrabromo-4,4'-thiodiphenol (TBTDP) was filtered. The product was occasionally colored with bromine, which was removed by adding a few drops of sodium bicarbonate solution. To purify TBTDP, the crude product was crystallized from hot acetone. The yield was 9.7 g (60%). Similarly, 3,3',5,5'-tetrabromobisphenol S (TBBPS, 73% of yield), 3,3',5,5'-tetrabromo-4,4'-bisphenol (TBBP, 75%), and 3,3',5,5'-tetrabromophenolphthalein (TBPP, 80%) were prepared from their corresponding bisphenols by the same procedure as above.

### Polymer Synthesis

#### *Copolycondensation of TBBPA with IPA and TPA*

A solution of tosyl chloride (6.5 mmol) in pyridine (5 mL) and DMF (1.5 mmol) was maintained at room temperature for 30 min and added to a mixed solution of IPA and TPA (2.5 mmol total with various ratios) in

pyridine (5 mL). The mixture was maintained at room temperature for 30 min and then at 120°C for 10 min to effect a clear solution. To this solution 2.5 mmol of TBBPA in 5 mL of pyridine was added at 120°C over 20 min. The whole solution was maintained at 120°C (bath temperature) for 3 h, and the resulting polymer solution was poured into methanol to precipitate the polymer. The polymer separated was washed in boiling methanol for 30 min.

#### *Preparation of Various Br-Containing Polyesters*

A solution of TsCl (6.5 mmol) in pyridine (5 mL) and DMF (1.5 mmol) was maintained at room temperature for 30 min and added to the mixture of equimolar amounts (1.25 mmol) of IPA and TPA in pyridine (5 mL). The reaction mixture was maintained at room temperature for 10 min and then at 120°C for 10 min. To this mixture tetrabromobisphenols (2.5 mmol) in pyridine (5 mL) were added over 20 min, and the whole solution was heated at 120°C for 3 h. Polymers were separated by working up as described above.

#### *Copolycondensation of IPA / TPA (1 / 1) with TBBPA and TBBP*

To the hot reaction mixture of TsCl (6.5 mmol), DMF (1.5 mmol), IPA (1.25 mmol), and TPA (1.25 mmol) in pyridine (10 mL) prepared as described above, a mixed solution of TBBPA and TBBP (2.5 mmol total with various ratios) was added at 120°C for 3 h. Polymers were separated by working up as described above.

### **Characterization**

A Jasco IRA-2 grating infrared spectrophotometer, a JEOL-JNM-PMX 60 NMR spectrometer, and a JEOL FX-90Q FT NMR spectrometer were utilized to identify the structures of monomers and polymers. Inherent viscosities of all polymers were determined at 0.5 g/dL concentration in symtetrachloroethane/phenol, 40/60 (by weight), at 30°C using a Cannon-Fenske viscometer.

Limiting oxygen index (LOI) determinations were made using a Suga ON-1 meter (made in Japan). The LOI value is defined as the minimum concentration of oxygen in the mixture of oxygen and nitrogen, expressed as volume percent, that will just support flaming combustion of a material initially at room temperature. According to the standard method of ASTM D2863-77, the test specimens with about 0.5 mm thickness, 5 cm width, and 14 cm length were cut from the polymer film to be tested. The flaming of the specimen past the 100-mm reference mark was judged to meet the criterion of burning.

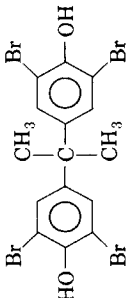
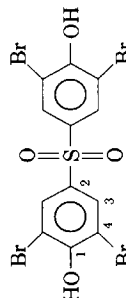
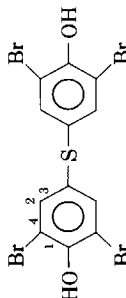
Thermogravimetric (TG) data were obtained using a DuPont 951 thermogravimetric analyzer coupled to a DuPont 1090 thermal analyzer. Experiments were performed on  $10 \pm 2$  mg samples heated in flowing nitrogen (50 cc/min) at a heating rate of 10°C/min.

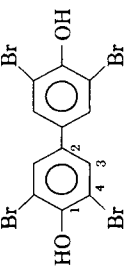
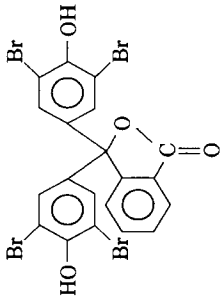
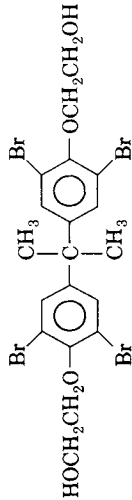
## **RESULTS AND DISCUSSION**

### **Synthesis of Tetrabromobisphenols**

There were six tetrabromobisphenols utilized in this study and four of them were prepared from their corresponding unbrominated bisphenols, namely,

TABLE I  
Structures, Molecular Weights, Melting Points, and Chemical Shifts of Various Tetrabromobisphenols

Tetrabromobisphenols	MW	mp (°C)	<sup>1</sup> H chemical shifts of aromatic protons (δ <sub>ppm</sub> )	<sup>13</sup> C chemical shifts (δ <sub>ppm</sub> relative to TMS = 0)			
				C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
 3,3',5,5'-tetrabromobisphenol A (TBBPA)	543.8	177	7.25/CDCl <sub>3</sub>	—	—	—	—
 3,3',5,5'-tetrabromobisphenol S (TBBPS) <sup>a</sup>	565.8	270	8.28/DMSO-d <sub>6</sub>	155.71	133.61	131.66	111.94
 3,3',5,5'-tetrabromo-4,4'-thiodiphenol (TBTDP) <sup>b</sup>	533.6	201	7.55/DMSO-d <sub>6</sub>	150.94	134.80	127.32	112.26

 <p>3,3',5,5'-tetrabromo-4,4'-biphenol (TBBP)<sup>c</sup></p>	501.8	280	7.83/DMSO <sub>d6</sub>	141.14	131.38	129.60	112.07
 <p>3,3',5,5'-tetrabromophenolphthalein (TBPP)<sup>d</sup></p>	633.9	291	7.30/DMSO <sub>d6</sub>	—	—	—	—
 <p>3,3',5,5'-tetrabromobisphenol A bis (2-hydroxyethyl) ether (TBBPABHE)</p>	631.9	117	7.33/CDCl <sub>3</sub>	—	—	—	—

<sup>a</sup> Calcd for C<sub>12</sub>H<sub>6</sub>O<sub>2</sub>Br<sub>4</sub>S: C, 25.47; H, 1.07; Br, 63.69. Found: C, 25.54; H, 0.98; Br, 63.60.

<sup>b</sup> Calcd for C<sub>12</sub>H<sub>6</sub>O<sub>2</sub>Br<sub>4</sub>S: C, 26.99; H, 1.13; Br, 58.89. Found: C, 26.89; H, 0.94; Br, 58.82.

<sup>c</sup> Calcd for C<sub>12</sub>H<sub>6</sub>O<sub>2</sub>Br<sub>4</sub>: C, 28.72; H, 1.20; Br, 56.40. Found: C, 28.72; H, 1.02; Br, 56.27.

<sup>d</sup> For protons on the bromine-substituted benzene rings.

TBBPS, TBTDP, TBBP, and TBPP. The ability of the hydroxyl group to permit electron release into the aromatic ring renders the system extremely reactive toward electrophilic substitution, particularly at the ortho position of bisphenols. Catalysts, such as aluminum or ferric halides, are quite unnecessary, and direct bromination even under mild conditions usually leads to introduction of bromine at all available ortho positions. The structures of products were identified by IR, NMR, and elemental analyses. The structures, molecular weights, melting points, and some NMR data of these tetrabromobisphenols are shown in Table I.

Figure 1 shows typical difference of  $^1\text{H-NMR}$  spectra between a bisphenol and a brominated bisphenol. The spectrum of 4,4'-thiodiphenol shows two AB doublets of the aromatic protons between 7 and 8 ppm, and, if reacted with bromine to TBTDP, the resonance peak of aromatic protons would transform to a singlet at  $7.55 \delta_{\text{ppm}}$ . The broad hump at the downfield is peculiar to the hydroxyl group. Furthermore, the bromination of bisphenol would cause some variance in the  $^{13}\text{C}$ -chemical shifts. As shown in Figure 2, as an example, the chemical shift of the ortho carbons of bisphenols shift to a higher magnetic field due to the increase of electron density after grafting the bromine atom, and the intensity of its resonance peak weakens, which is attributed to a longer spin-lattice relaxation time. Hence, in the spectrum of TBTDP [Fig. 2(b)], we can easily measure the  $^{13}\text{C}$  resonance of C-Br at  $112.26 \delta_{\text{ppm}}$ .

Figures 3(a), (b), and (c) are the IR spectra of TBBP, TBTDP, and TBBPS, respectively, which reveal aromatic hydroxyl absorptions at  $3380 \text{ cm}^{-1}$ . The fingerprints of these spectra show a great difference in comparison with their corresponding unbrominated bisphenols, and all of these spectra show the characteristic absorptions of C-Br stretching or bending vibration between  $600$  and  $900 \text{ cm}^{-1}$ . The elemental analyses of these tetrabromobisphenols agree well with the calculated values.

### Polymer Synthesis

The copolymers of TBBPA with a mixture of different parts of isophthalic acid (IPA) and terephthalic acid (TPA) were prepared using the Higashi reaction medium.<sup>6</sup> As listed in Table II, polymer precipitation took place at early stage of the reaction and led to a low-molecular-weight oligomer when TBBPA homopolymerized with IPA or TPA or copolymerized with the mixture of higher parts of IPA or TPA. The copolymers between 1/2 and 1/1 were all extremely soluble and showed the higher inherent viscosities obtainable with this polymerization system. Copolymer of TBBPA with IPA and TPA produced a higher inherent viscosity than that of homopolymer with IPA or TPA, probably because the copolycondensation might proceed readily due to lower crystallinity and better solubility of the copolymer in the reaction media. DSC and X-ray diffraction studies of TBBPA-IPA/TPA (1/1) copolymer indicated that it had equally low crystallinity. These copolymer samples charred during testing and showed a very high LOI between 58 and 59. The substitution of terephthaloyl units for isophthaloyl units showed little effect on the limiting oxygen index.

Various other bromine-containing aromatic polyesters were prepared under the similar condition for TBBPA-IP/TPA copolymer (Table III). Tetrabromobisphenols with positive substituents, such as TBBPA or TBPP,

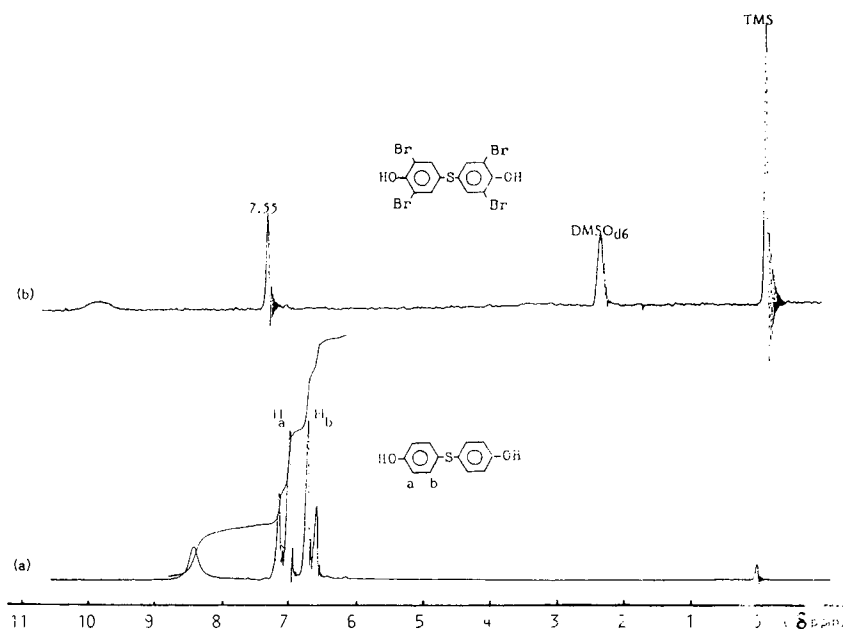


Fig. 1. <sup>1</sup>H-NMR spectra of (a) 4,4'-thiodiphenol in CDCl<sub>3</sub> and (b) 3,3',5,5'-tetrabromo-4,4'-thiodiphenol in DMSO<sub>d6</sub>.

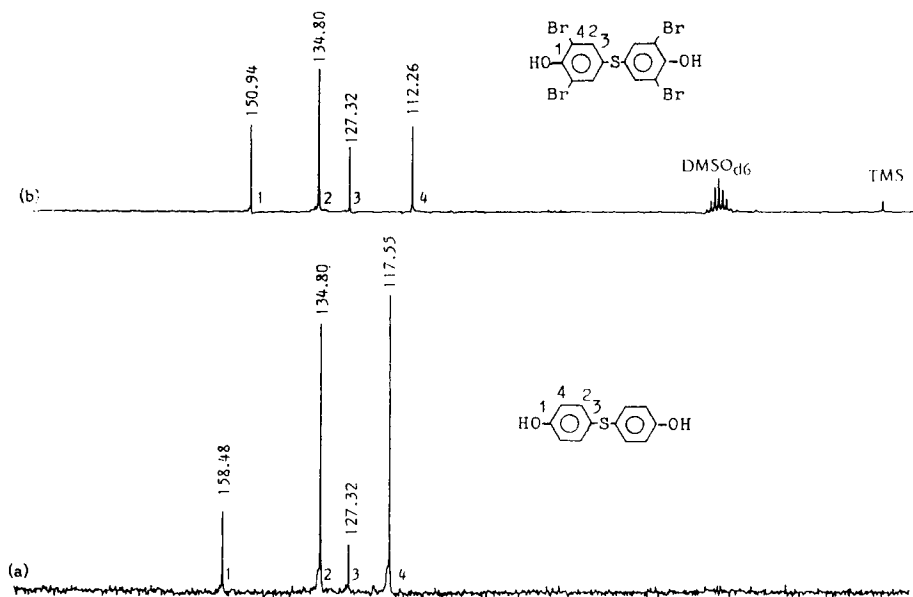


Fig. 2. <sup>13</sup>C-NMR spectra of (a) 4,4'-thiodiphenol in CDCl<sub>3</sub> and (b) 3,3',5,5'-tetrabromo-4,4'-thiodiphenol in DMSO<sub>d6</sub>.

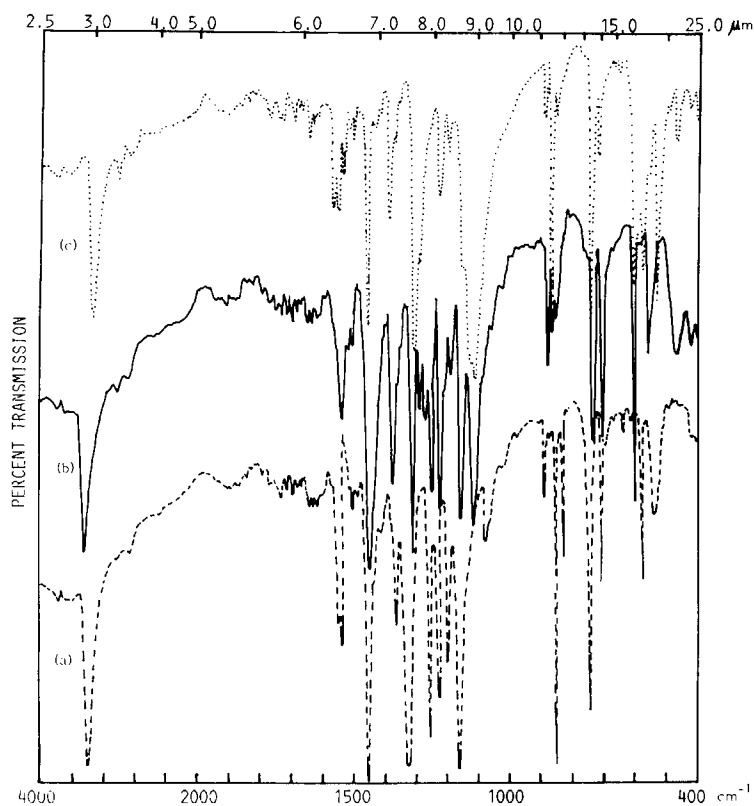


Fig. 3. IR spectra of tetrabromobisphenols: (a) TBBP; (b) TBTDP; (c) TBBPS.

TABLE II  
Copolymerization of TBBPA with IPA and TPA by Direct Polymerization  
with TsCl/DMF/Pyridine<sup>a</sup>

Dicarboxylic acid	State <sup>c</sup>	$\eta_{inh}$ (dL/g) <sup>d</sup>	LOI <sup>e</sup>
IPA	ppt	0.13	—
IPA/TPA <sup>b</sup>	ppt	0.24	—
	Clear	0.47	58.5
	Clear	0.80	58.0
	Clear	0.90	59.0
	Clear	0.81	58.5
	Clear	0.50	58.0
	ppt	0.20	—
TPA	ppt	0.11	—

<sup>a</sup> IPA + TPA = 2.5 mmol; TBBPA = 2.5 mmol; pyridine = 15 mL; DMF = 1.5 mmol; aging condition = rt (10 min) and 120°C (10 min).

<sup>b</sup> Molar ratio

<sup>c</sup> ppt = precipitation occurring during the reaction, clear: homogeneous reaction.

<sup>d</sup> Measured in phenol/sym-tetrachloroethane, 60/40 (weight), at 30°C.

<sup>e</sup> Limiting oxygen index.



TABLE III  
Various Aromatic Polyesters of IPA/TPA and Bisphenols  
Prepared by Using TsCl/DMF/Pyridine<sup>a</sup>

Polymers	Bisphenols	State	$\eta_{inh}$ (dL/g) <sup>b</sup>	LOI <sup>c</sup>
P-1 <sup>d</sup>	TBBPA	Clear	0.90	59.0
P-2	TBBPS	ppt	0.32	—
P-3	TBTDP	Clear	0.34	—
P-4 <sup>e</sup>	TBBP	ppt	0.23	—
P-5 <sup>f</sup>	TBPP	Clear	0.72	61.0
P-6 <sup>g</sup>	TBBPABHE	Clear	0.48	43.5
P-7	BPA <sup>h</sup>	Clear	0.95	29.5
—	TBPP/TBBP <sup>i</sup> (1/1)	Clear	0.70	61.5
—	TBBPA/TBBP <sup>i</sup> (1/1)	Clear	0.85	59.5

<sup>a</sup> IPA = TPA = 1.25 mmol; bisphenol = 2.5 mmol; TsCl = 6.5 mmol; Py = 15 mL; DMF = 1.5 mmol.

<sup>b</sup> Measured in phenol/sym-tetrachloroethane, 60/40 (by weight), at 30°C.

<sup>c</sup> Limiting oxygen index.

<sup>d</sup> Calcd for C<sub>23</sub>H<sub>14</sub>O<sub>4</sub>Br<sub>4</sub>: C, 40.98; H, 2.09. Found: C, 41.16; H, 1.98.

<sup>e</sup> Calcd for C<sub>20</sub>H<sub>8</sub>O<sub>4</sub>Br<sub>4</sub>: C, 38.01; H, 1.27. Found: C, 38.04; H, 1.27.

<sup>f</sup> Calcd for C<sub>28</sub>H<sub>12</sub>O<sub>6</sub>Br<sub>4</sub>: C, 44.02; H, 1.58. Found: C, 44.12; H, 1.55.

<sup>g</sup> Calcd for C<sub>27</sub>H<sub>22</sub>O<sub>6</sub>Br<sub>4</sub>: C, 42.55; H, 2.91. Found: C, 42.59; H, 2.86.

<sup>h</sup> BPA = bisphenol-A.

<sup>i</sup> TBPP = TBBP = TBBPA = 1.25 mmol.

afforded better results than those with negative substituents, such as TBBPS or TBTDP. The polycondensation with aliphatic diols such as TBBPABHE gave a less favorable result. The reaction of TBBP with the mixture of equal parts of IPA and TPA gave a reaction mixture containing substantial amounts of polymer precipitates due to the high crystallinity of biphenyl units, giving only an oligomer having inherent viscosity of 0.23 dL/g. A homogeneous reaction, improved solubility, and a higher viscosity was obtained by mixing TBBP with TBBPA or TBPP in this polymerization system. The higher LOI

TABLE IV  
Copolyesters of IPA/TPA and Mixed TBBPA/TBBP  
Prepared by TsCl/DMF/Pyridine<sup>a</sup>

TBBPA/TBBP <sup>b</sup>	State	$\eta_{inh}$ (dL/g) <sup>c</sup>
1/0	Clear	0.90
4/1	Clear	0.88
2/1	Clear	0.90
1/1	Clear	0.85
1/2	Gum	0.87
1/3	ppt	0.50
1/4	ppt	0.30
0/1	ppt	0.23

<sup>a</sup> IPA = TPA = 1.25 mmol; TsCl = 6.5 mmol; DMF = 1.5 mmol; TBBPA + TBBP = 2.5 mmol.

<sup>b</sup> Molar ratio.

<sup>c</sup> Measured in phenol/tetrachloroethane, 60/40 (by weight), at 30°C.

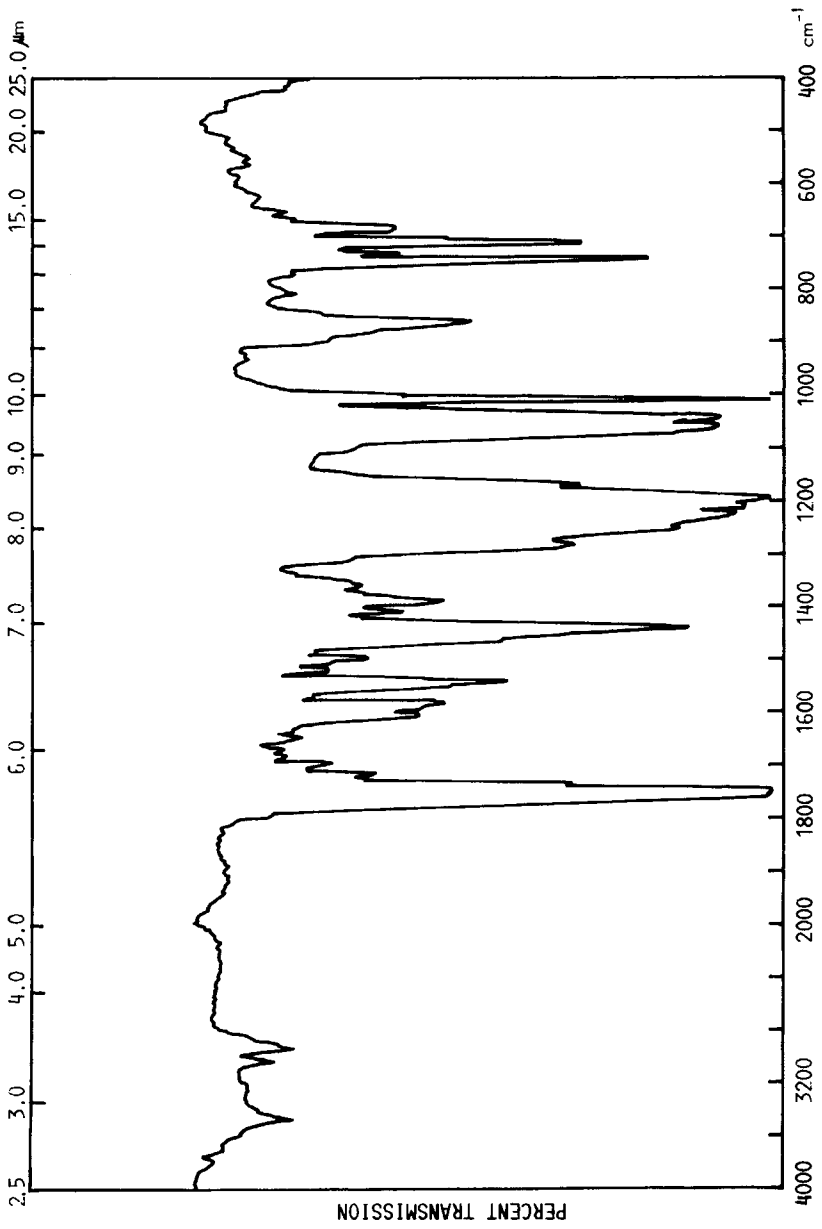


Fig. 4. IR spectrum of TPA/IPA (1/1)-TBBPA/TBPP (1/1) copolyester.

TABLE V  
Results of Thermogravimetric Analyses<sup>a</sup>

Polymers	$T_D^i$ (°C)	$T_D^{50}$ (°C)	Wt <sup>R</sup> (%)
P-1	381	488	30
P-2	382	501	35
P-3	363	474	29
P-4	385	564	40
P-5	382	518	35
P-6	358	380	20
P-7	410	520	21

<sup>a</sup> $T_D^i$  and  $T_D^{50}$  are the temperatures where initial and 50% weight loss were observed. Wt<sup>R</sup> stands for the weight percent of residue remaining after the sample was heated to 600°C.

value of the copolymer film derived from TBPP than that from TBBPA may be attributed to its higher aromaticity.

The reaction of the mixture of TBPP and the proper quantity of TBBPA with equimolar amounts of IPA and TPA could proceed nearly homogeneously in pyridine. However, an unfavorable result was obtained if the amount of TBPP was more than 50 mol %. For a mixture of TBBPA/TBBP at a molar ratio of 1/2, a gummy product was produced. If the ratio was less than 1/3, a low viscosity value was obtained due to polymer precipitation at an early stage of the reaction (see Table IV). This indicates that the polycondensation is affected significantly by the solubility of the resulting polymer in the reaction medium.

Figure 4 shows a typical IR spectrum of a brominated aromatic polyester, revealing a carbonyl absorption at  $1760\text{ cm}^{-1}$  and no absorption in the region

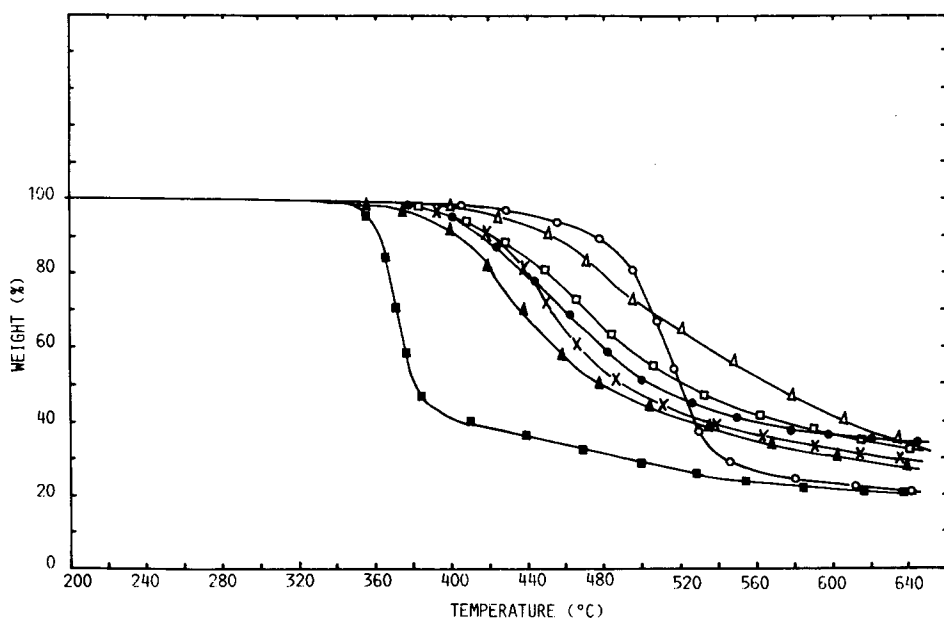


Fig. 5. TG thermograms of polyesters P-1 (×), P-2 (●), P-3 (▲), P-4 (△), P-5 (□), P-6 (■), and P-7 (○), with heating rate  $10^\circ\text{C}/\text{min}$  in  $\text{N}_2$ .

of the hydroxyl group. Other bands of the ester C—O group occurs at 1050 and 1220  $\text{cm}^{-1}$ , and bands corresponding to bromine atoms appear between 600 and 900  $\text{cm}^{-1}$ .

The thermal stability of the polymers was studied by thermogravimetry. Table V summarizes the initial decomposition temperatures observed by TG analyses ( $T_D^i$ ) and temperatures ( $T_D^{50}$ ), where 50 wt % loss was observed. The table also presents weight residues,  $\text{Wt}^R$ , at 600°C. Figure 5 shows the TG curves used in this study to obtain the data included in Table V, along with weight loss data for non-bromine-containing polymer P-7.

Inspection of these thermograms indicates that brominated aromatic polyesters are less stable than unbrominated one, but with a higher char yield. This is to be expected since a substitution of the aromatic rings reduced stability. The earlier weight losses corresponding to the liberation of HBr are clearly evident for the brominated aromatic polyesters, and the thermal stability of brominated aromatic polyesters depends on the linking groups between the aromatic rings. In regard to the linking atoms or groups, the thermal stability of rigid ones, such as biphenyl or phenolphthalein units, is superior to that of flexible ones, such as isopropyl,  $\text{SO}_2$ , and S. This may be caused by the rodlike molecular chains which pack together well and restrict the motion of the molecular chain and hence gives better stability. As might be expected, the least stable of these polymers was the one containing aliphatic carbon-carbon linkage, such as P-6 derived from TBBPABHE.

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