

Synthesis and Properties of Aromatic Polyesters and Brominated Polyesters Derived from α,α' -Bis(4-hydroxyphenyl)-1,4(or 1,3)-diisopropylbenzene

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Abstract: The interfacial polycondensation technique was used for the preparation of polyarylates and brominated polyarylates. Polyarylates and brominated polyarylates were prepared by mixing a solution of diacid chloride such as terephthaloyl chloride, isophthaloyl chloride, or their mixture in dichloromethane with an aqueous alkaline solution of α,α' -bis(4-hydroxyphenyl)-1,4(or 1,3)-diisopropylbenzene or α,α' -bis(4-hydroxy-3,5-dibromophenyl)-1,4(or 1,3)-diisopropylbenzene using triethylbenzylammonium chloride as the phase transfer agent. Moderate to high molecular weight polyarylates with η_{inh} up to 1.27 dL/g were obtained, and most of them could be cast into tough and flexible films depending on the polymer composition. In general, polymers containing more 1,3-isomer or isophthaloyl chloride moieties gave transparent and flexible films and had lower glass transition temperatures and higher solubility. Although these polymers have two isopropylidene linkages in their repeating units, they still exhibit moderately high thermal stability and show no obvious weight loss before 400 °C. The introduction of bromine on the polymer backbone caused a decrease of inherent viscosity, crystallinity, and thermal stability of the polyarylates, while causing an increase in glass transition temperature and a great enhancement of fire retardancy.

Keywords: Polyarylates, Brominated polyarylates, Interfacial polycondensation, α,α' -Bis(4-hydroxyphenyl)-1,4(or 1,3)-diisopropylbenzene.

Introduction

Polyarylates are an important class of high performance engineering plastics which have found application in a variety of areas [1, 2]. They are usually described as aromatic polyesters derived from aromatic dicarboxylic acids and diphenols. The reactions of aromatic dicarboxylic acids and diphenols were first noted by Conix [3] in 1957. The acid chloride and the diacetate routes were noted as feasible synthesis procedures to obtain polyarylates of high molecular weight. Levine and Temin [4], Eareckson [5], Morgan and Kwolek [6], and a number of Russian investigators, specifically Korshak and Vinogradov [2], were also early contributors to the technical literature regarding the synthesis of polyarylates. Bier [7] in a review article in 1974 discussed the synthesis and properties of polyarylates. Attractive mechanical and electrical properties were noted along with favorable economics and feasible

synthesis routes. Interestingly, the same year (1974) Unitika announced the first commercial production of U-polymer (a polyarylate based on bisphenol A and tere/iso phthalates).

Three feasible routes for obtaining high molecular weight polyarylates have been reported. In the first, the aromatic diacid is converted to the acid chloride followed by condensation with the diphenol. The second route involves the preparation of the diphenyl ester of the aromatic diacid followed by reaction with the diphenol. The third process involves the preparation of the diacetate of the diphenol followed by condensation with the aromatic diacid. Among these techniques, interfacial polycondensation [8, 9] became a major polyarylate-forming process since 1957 with the works of Conix [3], Eareckson [5], and Morgan [10]. This method is a highly effective procedure for the rapid preparation of polymers in high molecular weight and in a easily isolatable form. Hence, at present, the interfacial polycondensation is

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still a very popular means for screening new polyarylates [11-13] due to its particular advantages.

Although the commercial polyarylates based on bisphenol A exhibited attractive electrical and mechanical properties, its melt viscosity was noted to be high, and thus its injection moldability was considered to be a limitation. Polyarylates based on α,α' -bis(4-hydroxyphenyl)-1,4(or 1,3)-diisopropylbenzene (BPP or BPM) (a bisphenol containing one more cumyl unit than bisphenol A) and tere/iso phthaloyl chloride have been reported to exhibit improved melt moldability under shear stress [14-16]. Although the polyarylates based on bisphenol BPP or BPM have been prepared in some patent references, little information is known about this kind of polymer. The present study deals with the synthesis and basic characterization of several polyarylates from these two bisphenols. This paper also describes the synthesis of two new brominated bisphenols of BPP and BPM and summarizes the synthesis and basic characterization of brominated polyarylates from these two novel monomers. Effects of the incorporation of bromine on the properties, such as solubility, crystallinity, thermal properties, and flame retardancy, of polyarylates will be discussed.

Experimental

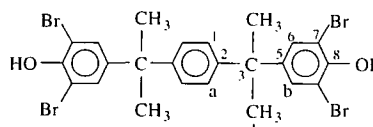
1. Materials

α,α' -Bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (BPP) and α,α' -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene (BPM) were used as received from Mitsui Petrochemical Ind. (Japan). Bromine (Wako) and glacial acetic acid (Wako) were used without further purification. Terephthaloyl chloride (TPC) (Wako) and isophthaloyl chloride (IPC) (Fluka) were purified by vacuum distillation. Triethylbenzylammonium chloride (TEBAC) (TCI), used as a phase transfer agent, was used as received.

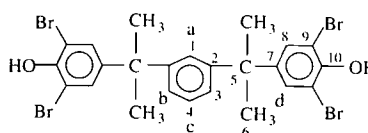
2. Monomer Synthesis

A detailed procedure for the preparation of α,α' -bis(4-hydroxy-3,5-dibromophenyl)-1,4-diisopropylbenzene (TBBPP) is described as follows. In a 500 mL flask, 11.43 g (0.033 mol) of α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (BPP) was dissolved in 200 mL of glacial acetic acid, and 15 mL of water was added as the hydrogen bromide acceptor. To this solution, 21 g (0.132 mol) of bromine was added slowly with stirring. The reaction was initially carried out at room temperature over a period of about 30 min. The flask was transferred to a warm water bath of 60 °C for 1 hr when the reaction medium appeared turbid. White solids precipitated gradually from the reaction medium as the reaction proceeded.

After cooling, 200 mL of water was added and the product was filtered, washed with 20 wt% aqueous sodium bicarbonate (NaHCO_3) and water, and dried. Yield 92%, mp. 191 °C. IR (KBr): 3480 cm^{-1} [O-H str.], 1477-1553 cm^{-1} [arom. C=C str.], 737 cm^{-1} [C-Br str.]. ^1H NMR (δ ppm, in CDCl_3): 9.77 (s, -OH), 7.27 (s, 4H, H_b), 7.13 (s, 4H, H_a), 1.54 (s, 12H, - CH_3). ^{13}C NMR (δ ppm, in CDCl_3): 148.81 (C_8), 146.96 (C_2), 145.10 (C_5), 130.63 (C_6), 126.35 (C_1), 111.96 (C_7) (aromatic carbons), 41.75 (quaternary carbon, C_3), 30.27 (methyl carbon, C_4). Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_2\text{Br}_4$ (662.04): C, 43.54%; H, 3.35%. Found: C, 43.27%; H, 3.49%.



α,α' -Bis(4-hydroxy-3,5-dibromophenyl)-1,3-diisopropylbenzene (TBBPM) was prepared by the bromination of α,α' -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene in an analogous procedure, yield 93%; mp. 152 °C. IR (KBr): 3494 cm^{-1} [O-H str.], 1475-1560 cm^{-1} [arom. C=C str.], 737 cm^{-1} [C-Br str.]. ^1H NMR (δ ppm, in CDCl_3): 7.19 (s, 4H, H_d), 7.05 (m, 4H, H_{a-c}), 1.52 (s, 12H, - CH_3). ^{13}C NMR (δ ppm, in CDCl_3): 149.10 (C_{10}), 148.77 (C_2), 145.10 (C_7), 130.48 (C_8), 128.38 (C_4), 124.70 (C_1), 124.39 (C_3), 111.77 (C_9) (aromatic carbons), 42.24 (quaternary carbon, C_5), 30.43 (methyl carbon, C_6). Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_2\text{Br}_4$ (662.04): C, 43.54%; H, 3.35%. Found: C, 43.69%; H, 3.30%.



3. Polymer Synthesis

A typical polymerization procedure for polyester B-T/I(1/1) is as follows. In a 50 mL flask, 0.8662 g (2.5 mmol) of α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (BPP) and 0.02 g of triethylbenzylammonium chloride (TEBAC) were dissolved in 6 mL of 1 M aqueous sodium hydroxide. The bisphenol solution was further diluted with 19 mL of water to a concentration of about 0.1 M. To the magnetically stirred solution was added all at once a solution of 0.2538 g (1.25 mmol) each of TPC and IPC in 10 mL of dichloromethane, and an additional 2.5 mL was used to rinse the residual acid chlorides. The two-phase mixture was vigorously stirred at room temperature for 30 min. The mixture was poured into

500 mL of hot water containing a small amount of hydrochloric acid to remove dichloromethane. After cooling, the precipitated polymer was collected by filtration and dried. Yield 99%. The inherent viscosity of the polymer [B-T/I(1/1)] in *sym*-tetrachloroethane/phenol (40/60 wt%) mixture was 1.21 wt% dL/g, measured at a concentration of 0.5 g/dL at 30 °C.

All other polymers were synthesized by a similar procedure.

4. Measurements

Melting points were measured in capillaries on a MEL-TEMP II apparatus. Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform spectrometer. ¹H NMR and ¹³C NMR spectra were measured at 30 °C on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-d₆) as an external reference, working at 400 and 100 MHz, respectively. Elemental analyses were run in a Perkin-Elmer model 240 C, H, N analyzer. The inherent viscosities of all polymers were determined at 0.5 g/dL concentration using a Cannon-Fenske viscosimeter thermostated at 30 °C. Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) were determined by means of gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Shimadzu LC-6A apparatus (column: Tosoh TSK-GEL; eluent: tetrahydrofuran; flow rate: 1 cm³/min; temperature: 40 °C; detector: refractive index detector). Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko 7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analyzer at the heating rate of 20 °C/min in flowing nitrogen (30 cm³/min). Thermogravimetric data were obtained on a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm³/min) at a heating rate of 20 °C/min. The wide-angle X-ray diffraction measurements were performed at room temperature (about 25 °C) with film (or powder) specimens of about 0.1 mm thick on a Rigaku Geiger-Flex D-Max III_a X-ray diffractometer, using Ni-filtered CuK_α radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of 2θ = 5-40°. An Instron universal ester Model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick); an average of at least five individual determinations were used. The oxygen indices of the polymers were measured using a Suga ON-1 meter (made in Japan).

The limiting oxygen index (LOI) is defined as

the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that is necessary to ignite and to support a flame. According to the standard method of ANSI/ASTM D2863-77 (September 1977, p. 752), five test specimens with about 0.5 mm thickness, 5 cm width, and 14 cm length were cut from the polymer film to be tested. Flaming of the specimen past the 100 mm reference mark was judged to meet the criterion of burning.

Results and Discussion

1. Monomer Synthesis

According to the procedure reported in one of our earlier publications [17], the tetrabromobisphenols used in this work, bis(4-hydroxy-3,5-dibromophenyl)-1,4-diisopropylbenzene (TBBPP) and α,α'-bis(4-hydroxy-3,5-dibromophenyl)-1,3-diisopropylbenzene (TBBPM), were prepared from their corresponding bisphenols, such as α,α'-bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (BPP) and α,α'-bis(4-hydroxyphenyl)-1,3-diisopropylbenzene (BPM), by bromination in acetic acid under mild conditions. The structures of tetrabromobisphenols were identified by elemental analysis, FTIR, ¹H NMR and ¹³C NMR spectroscopy. Figure 1 shows the FTIR spectra for

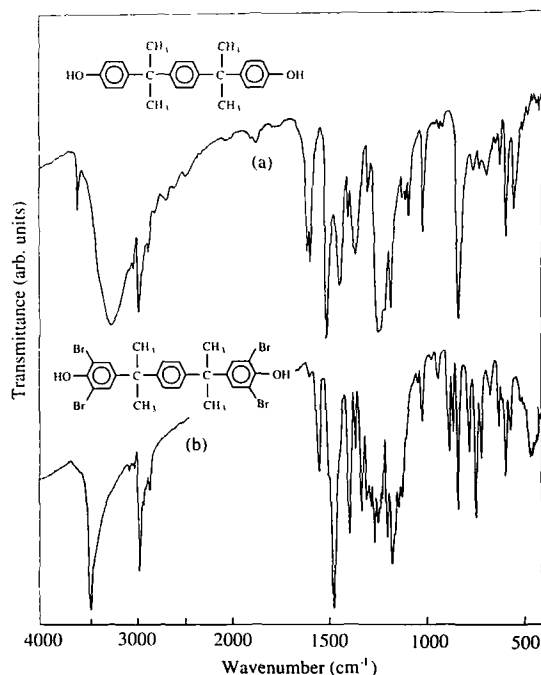


Figure 1. IR spectra of (a) α,α'-bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (BPP) and (b) α,α'-bis(4-hydroxy-3,5-dibromophenyl)-1,4-diisopropylbenzene (TBBPP).

bisphenol BPP and tetrabromobisphenol TBBPP, respectively. When BPP is brominated to TBBPP, an absorption near 730 cm^{-1} corresponds to the C-Br stretching appears, and the broad intermolecular hydrogen bonded band from about 3000 to 3500 cm^{-1} is reduced considerably and shifted to higher frequencies, possibly due to the presence of bromine atoms which interfere with the hydrogen bonding.

Figure 2 shows typical difference of ^1H NMR spectra between bisphenol BPP and brominated bisphenol TBBPP. As shown in the spectrum of BPP, the magnetically equivalent protons (H_b) on the central benzene ring give rise to a singlet at $\delta 7.05\text{ ppm}$, and the nonequivalent protons (H_a and H_c) on the outer benzene rings show two AB doublets centered at $\delta 7.00$ and 6.98 ppm , respectively. The singlet at $\delta 1.52\text{ ppm}$ is due to the isopropylidene protons of BPP and TBBPP. When BPP is brominated to TBBPP, the doublet resonance of H_b is transformed to a singlet at $\delta 7.27\text{ ppm}$ due to lack of coupling. The downfield shift of the signal may be due to the inductive effect of bromine atom. The comparative ^{13}C NMR spectra of bisphenol BPP and brominated bisphenol TBBPP are shown in Figure 3; all carbon atoms give separate and assignable resonances. After grafting the bromine

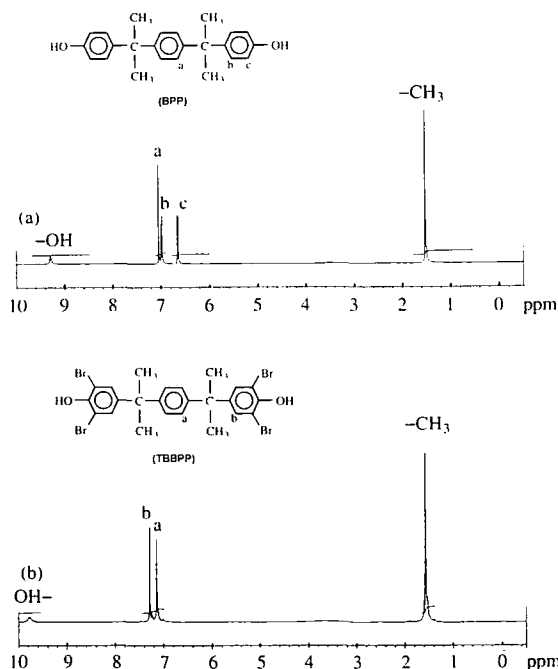


Figure 2. ^1H NMR spectra of (a) α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (BPP) in DMSO-d_6 and (b) α,α' -bis(4-hydroxy-3,5-dibromophenyl)-1,4-diisopropylbenzene (TBBPP) in DMSO-d_6 .

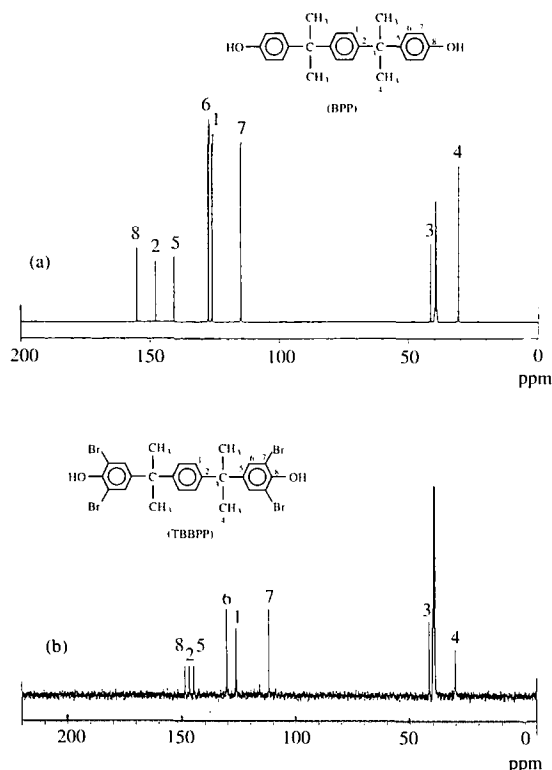
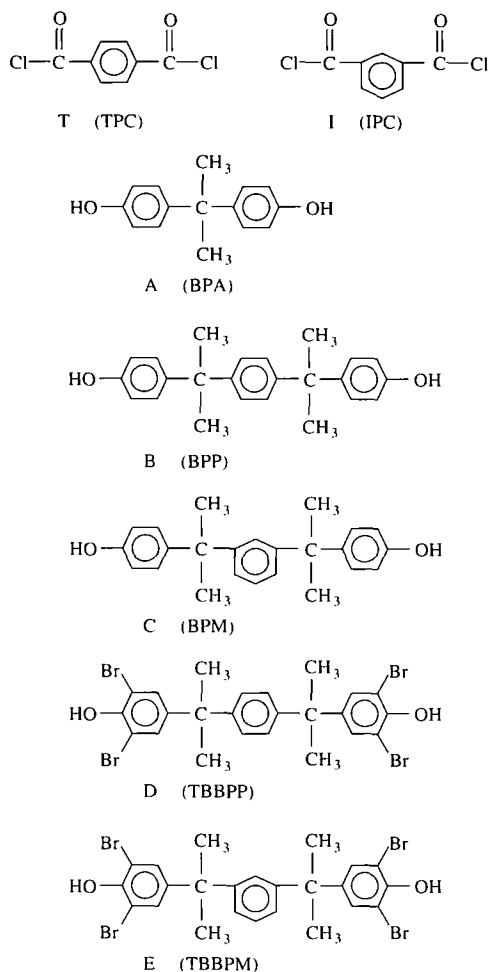


Figure 3. ^{13}C NMR spectra of (a) α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (BPP) in DMSO-d_6 and (b) α,α' -bis(4-hydroxy-3,5-dibromophenyl)-1,4-diisopropylbenzene (TBBPP) in DMSO-d_6 .

atom, the resonance signals of C_7 and C_8 carbons move to higher field, possibly due to the increase of electron density induced by the bromine atom from the electron-rich oxygen atom. Downfield shifts of C_5 and C_6 resonances may be attributed to the inductive effect of the bromine atom.

2. Polymer Synthesis

Polyarylates were conveniently synthesized by the phase-transfer catalyzed polycondensation of aromatic diacid chlorides with bisphenols [5, 8]. For convenience sake, the bisphenols were further coded from A to E, and the diacid chlorides are coded T and I, as illustrated in Scheme 1. The polycondensation of bisphenols A-E or their mixtures with diacid chlorides TPC, IPC, or their mixtures leading to isopropylidene-containing polyarylates were carried out in dichloromethane aqueous sodium hydroxide system using triethylbenzylammonium chloride (TEBAC) as a phase transfer agent (Scheme 2), which is known to be the most effective means for producing high molecular weight polyarylates [18]. The results of polycondensation and the properties of polyester films are



Scheme 1. Structures and Codes of Monomers.

summarized in Table I. Polymer precipitation or emulsification of the reaction system occurred during the polycondensations of these bisphenols with TPC. This phenomenon may be due to the poor solubility of the resultant polyarylates, possibly caused by their high degree of crystallinity. These polyterephthalates could not be dissolved in suitable organic solvents for viscosity measurement or film casting. Incorporation of a proper quantity of IPC moiety into the polyterephthalate backbone enhanced the solubility of the resulted polymers. Hence, in most copolycondensation cases using mixed TPC/IPC, the polymerization proceeded homogeneously (a well-defined two-phase system was observed), giving rise to polymers with reasonable inherent viscosities which could afford tough and flexible films. However, an early precipitation occurred in the reaction media of TBBPP (D) with TPC or IPC, or mixed TPC/IPC (1/1), retard-

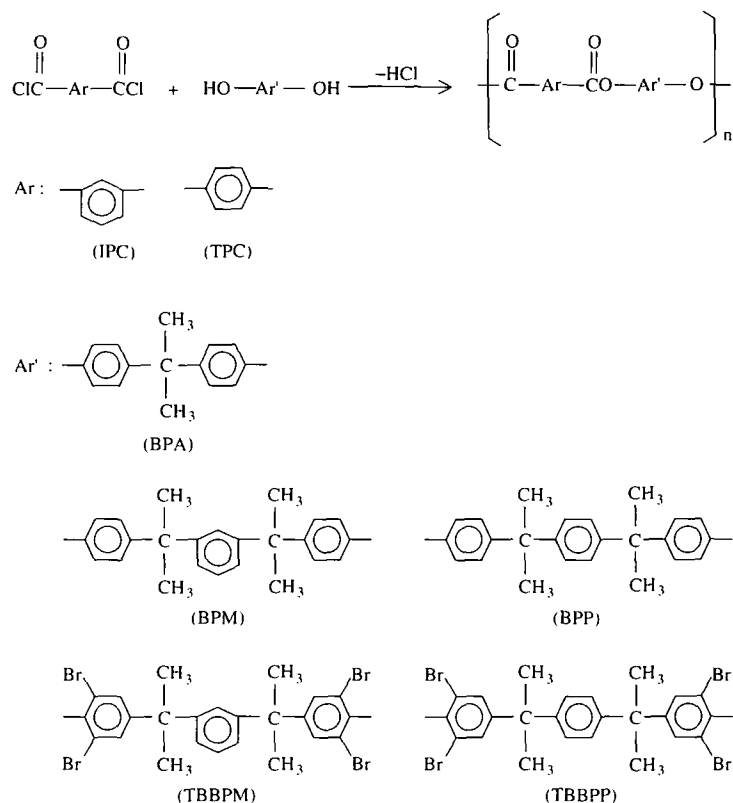
ing the formation of high molecular weight product. This result implies that the introduction of bromine decreases the solubility of polyester in dichloromethane, probably attributable to the increase of cohesive energy between molecules. This problem was circumvented through reacting the BPA (A)/TBBPP (D) mixture with mixed TPC/IPC. As shown in Table I, polymer A/D(1/1)-T/I(1/1) had a moderately high inherent viscosity of 0.75 dL/g and could be cast into a tough film. In general, the reaction system forming suspension or emulsion afforded an inferior result with respect to inherent viscosity of the resulting polymer. The inherent viscosities of the polymers thus obtained were in the range of 0.28-0.40 dL/g, and self-supported films could not be obtained from these polymers. On the contrary, the reaction systems which maintained clear, well-defined two-phase throughout the reaction produced polymers with higher inherent viscosities. As shown in Table I, the polymers thus produced exhibited inherent viscosities between 0.45 dL/g and 1.73 dL/g. The average molecular weights of three representative polyesters with moderate to high inherent viscosities of 0.50-0.98 dL/g were determined by GPC, and the results are included in Table II. Their weight-average molecular weights (\bar{M}_w) estimated by GPC curves were in the range of 47,000-102,000 relative to polystyrene standard. As expected, the higher the viscosity, the higher the molecular weight.

The structure of these polyesters was confirmed by IR spectroscopy. Figure 4 shows the typical IR spectra of representative polyesters B-T/I(1/1) and D-T/I(1/1). Some characteristic absorptions appeared in the IR spectra, such as C-H stretching near 3000 cm^{-1} , C=O stretching near 1750 cm^{-1} , and aromatic ether stretching near 1200 cm^{-1} .

3. Properties of Polymers

3.1 Solubility

The qualitative solubility behavior of some polyarylates is summarized in Table III. As mentioned previously, the solubility of the polymers obtained from bisphenol BPP (B) or BPM (C) with TPC is poor, and they are insoluble in all the solvents tested. However, combinations of BPP or BPM with IPC or equal parts of TPC and IPC led to polyarylates with enhanced solubility. Polyarylates containing BPM moiety revealed greater solubility than those containing BPP moiety, ascribable to the less unsymmetric structure. Copolymerization of TPC with mixed bisphenols of BPP and BPM disrupted the regularity of the polymer chain; hence, copolymer B/C(1/1)-T exhibited higher solubility than homopolymers B-T and C-T. The introduction of bromine onto the polymer chain led to a decreased solubility,



Scheme 2. Preparation of Polyesters.

for example, the polyarylates synthesized from tetrabromobisphenol TBBPM (E) with TPC, IPC, or their mixtures were hardly soluble in the organic solvents tested. Probably due to low molecular weight, the *p*-isomer TBBPP (D)-derived brominated polyarylates D-T/I(1/1) and D-T still maintained good solubility. In general, these polyarylates showed better solubility in chlorinated hydrocarbons such as dichloromethane, chloroform, *sym*-tetrachloroethane, and *p*-chlorophenol, but they revealed less solubility in polar aprotic solvents such as DMF.

3.2 Crystallinity and Tensile Properties

The crystallinity of the polymers was examined by wide-angle X-ray diffraction. The X-ray diffraction patterns of some representative polyarylates are shown in Figure 5. Polyarylates B-T/I(100/0), B-T/I(75/25), and C-T/I(100/0) revealed one stronger peak reflection between $2\theta = 15\text{--}25^\circ$, indicative of a high degree of crystallinity. This corresponds to their

poor solubility. As mentioned above in Table I, except for some polyarylates which had low inherent viscosity and embrittled upon film-casting, the others could be cast into flexible films. All of these flexible films gave amorphous diffraction patterns. The results of X-ray diffraction measurement also indicated that copolymerization or the introduction of bromine decreased the crystallinity of the polyarylates. It is reasonable because copolymerization disrupts the regularity of the polymer chain, and incorporation of bromine atoms on the backbone interrupts the close-packing of polymer chains. The tensile properties of some flexible films are given in Table IV. The films had a tensile strength of 23-53 MPa, elongation at break of 2-6%, and initial modulus of 1.3-1.8 GPa. They behave as strong and rigid materials. Only the film of polyester C-T/I(1/3) necked during tensile testing.

3.3 Thermal Properties and Flame Retardancy

Table I. Preparation of polyesters^(a).

Polymer Code	$\eta_{inh}^{(b)}$ (dL/g)	Appearance of Reaction Solution	Film ^(c) Quality
A-T/I (1/1) ^(d)	1.28	Well-defined two phases	F, T
B-T	-	Emulsion	-
B-T/I (3/1)	0.35	Emulsion	-
B-T/I (1/1)	1.21	Well-defined two phases	F, ST
B-T/I (1/3)	1.73	Well-defined two phases	F, T
B-I	0.55	Well-defined two phases	F, T
C-T	-	Emulsion	-
C-T/I (3/1)	0.87	Well-defined two phases	F, ST
C-T/I (1/1)	0.50	Well-defined two phases	F, T
C-T/I (1/3)	0.68	Well-defined two phases	F, ST
C-I	0.62	Well-defined two phases	F, T
D-T	-	Suspension	-
D-T/I (1/1)	0.37	Suspension	B
D-I	0.28	Suspension	B
E-T	-	Suspension	B
E-T/I (1/1)	0.65	Well-defined two phases	F, T
E-I	0.68	Well-defined two phases	F, T
A/D (3/1)-T/I (1/1)	0.61	Well-defined two phases	F, T
A/D (1/1)-T/I (1/1)	0.75	Well-defined two phases	F, T
A/D (1/3)-T/I (1/1)	0.37	Suspension	B
A/E (3/1)-T/I (1/1)	0.64	Well-defined two phases	F, T
A/E (1/1)-T/I (1/1)	0.65	Well-defined two phases	B
A/E (1/3)-T/I (1/1)	0.45	Well-defined two phases	B
B/C (1/1)-T	0.40	Emulsion	B
B/C (1/1)-T/I (1/1)	0.98	Well-defined two phases	F, T
B/C (1/1)-I	0.33	Emulsion	B

(a) Polymerization was carried out with 2.5 mmol of bisphenols, 2.5 mmol of diacid chlorides and 0.02 mg of TEBAC in 12.5 mL (25 mL for brominated polyesters) of methylene chloride and 6.0 mL of 1 M aqueous sodium hydroxide at room temperature for 1 hr.

(b) Measured at a concentration of 0.5 g/dL in *sym*-tetrachloroethane/phenol (40:60 by weight) at 30 °C; -: insoluble.

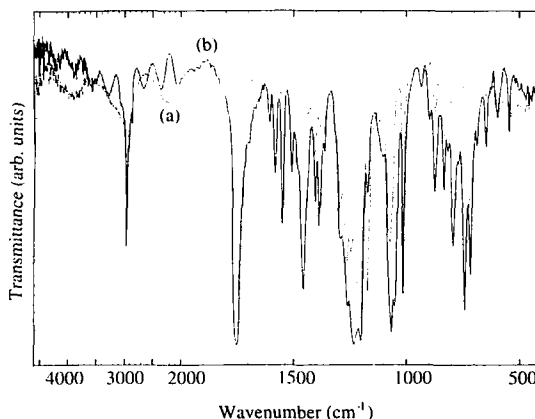
(c) Films were cast from polymer solutions in *sym*-tetrachloroethane. F: flexible, B: brittle, T: transparent, ST: semi-transparent, -: insoluble.

(d) Molar ratio, T: TPC, I: IPC.

Table II. Average molecular weights of some representative polyesters^(a).

Polymer Code	η_{inh} (dL/g)	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
B/C (1/1)-T/I (1/1)	0.98	10.2	7.0	1.5
C-T/I (1/1)	0.62	9.6	7.5	1.3
C-I	0.50	4.7	2.6	1.8

(a) \bar{M}_w and \bar{M}_n were determined by GPC, using tetrahydrofuran as the eluent and polystyrene as the standard.

**Figure 4.** IR spectra of polyesters (a) B-T/I(1/1) and (b) D-T/I(1/1).

Thermal properties of all the polyarylates were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The glass transition temperature (T_g), 10% weight loss temperature (T_{10}) in nitrogen, and char yield at 800 °C in nitrogen of all polymers are summarized in Table V. Rapid cooling from the elevated temperatures (about 350 °C) to room temperature in air yields more amorphous samples so that in almost all cases the T_g s could be easily measured in the second heating traces of

DSC. The base-line shift on the second DSC heating trace was judged as T_g . The bisphenol BPM (C)-derived polyarylates containing flexible *m*-phenylenediisopropylidene structure revealed lower

Table III. Solubility of polymers^(a).

Polymer code	Solvent ^(b)						
	CH ₂ Cl ₂	CHCl ₃	<i>sym</i> -TCE	<i>m</i> -cresol	<i>p</i> -CIPhOH	THF	DMF
B-T	-	-	-	-	-	-	-
B-T/I (1/1)	s	+h	+	-	+h	-	-
B-I	+	+	+	s	+	+h	-
C-T	-	-	-	-	+h	-	-
C-T/I (1/1)	+	+	+	+h	+	+	s
C-I	+	+	+	+	+	+	+
B/C (1/1)-T	s	+h	+	-	+	-	-
B/C (1/1)-T/I (1/1)	+	+	+	+	+	+	+h
B/C (1/1)-I	+	+	+	+	+	+	+
D-T	-	-	s	-	s	-	-
D-T/I (1/1)	+	+	+	+	+	+	s
D-I	+h	+h	+	+	+	+	s
E-T	s	+h	s	s	+h	s	-
E-T/I (1/1)	s	s	s	s	+h	s	s
E-I	s	s	s	s	+h	s	-

(a) +: soluble, -: insoluble, s: swelling, +h: soluble on heating. Measured at 2% solids at room temperature.

(b) *sym*-TCE: *sym*-tetrachloroethane; *p*-CIPhOH: *p*-chlorophenol; THF: tetrahydrofuran; DMF: *N,N*-dimethylformamide.

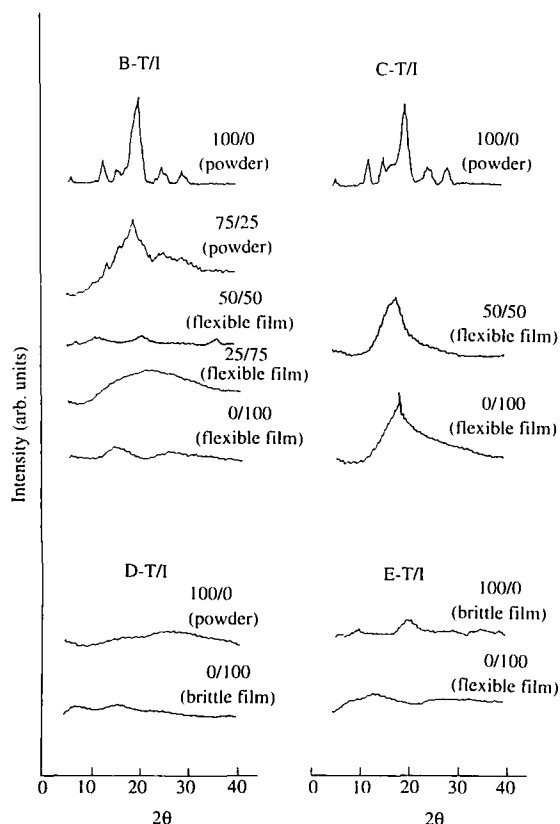


Figure 5. X-ray diffraction patterns of some representative polyesters.

Table IV. Tensile properties of polyester films.

Polymer Code	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
B-T/I (1/1)	-	53	6	1.3
B-T/I (1/3)	-	52	5	1.3
B-I	-	42	4	1.4
C-T/I (3/1)	-	32	3	1.8
C-T/I (1/1)	-	23	3	1.3
C-T/I (1/3)	29	28	6	1.4
C-I	-	30	2	1.6

T_g s than the corresponding *p*-isomeric BPP (B)-derived ones by about 50-70°C. The T_g values of B- and C-derived polyarylates are in the range of 158-220°C and 86-126°C, respectively. Comparison of T_g s of the polyarylates obtained from BPA (A), BPP (B), and BPM (C) with equimolar TPC and IPC showed that the introduction of one more cumyl unit leads to a decrease in T_g . The result also implies that polyarylates containing BPP or BPM moiety probably exhibited lower melting viscosity, or higher tractability, than those containing BPA moiety. In general, the introduction of bromine on the polymer backbone resulted in an increase of T_g values, owing to the steric hindrance of the movement of the polymer chain. For example, the TBBPP (D)-derived brominated polyarylates revealed higher T_g s than the corresponding BPP (B)-derived ones, and the T_g values of bromine-containing TBBPM (E)-polyarylates were also higher than the corresponding BPM (C)-

Table V. Thermal properties of polyesters.

Polymer Code	T _g ^(a) (°C)	T _i ^(b) (°C)	T ₁₀ ^(c) (°C)	Residue ^(d) (wt%)
A-T/I (1/1)	198	482	483	16.2
B-T	220	488	462	21.6
B-T/I (3/1)	187	492	492	20.6
B-T/I (1/1)	182	483	484	24.0
B-T/I (1/3)	180	481	485	28.4
B-I	158	493	489	19.7
C-T	—	493	486	19.6
C-T/I (3/1)	122	491	493	23.3
C-T/I (1/1)	126	489	492	23.3
C-T/I (1/3)	120	484	480	23.2
C-I	86	483	480	16.4
D-T	215	438	433	33.4
D-T/I (1/1)	204	429	435	31.9
D-I	194	435	437	34.4
E-T	152	424	427	33.4
E-T/I (1/1)	168	439	444	30.0
E-I	177	435	438	33.6
A/D (3/1)-T/I (1/1)	172	434	443	26.4
A/D (1/1)-T	207	430	442	19.5
A/D (1/1)-T/I (1/1)	198	425	437	13.9
A/D (1/1)-I	190	432	438	28.9
A/D (1/3)-T	212	427	434	25.7
A/D (1/3)-T/I (1/1)	198	430	441	29.4
A/D (1/3)-I	187	425	437	25.7
A/E (3/1)-T/I (1/1)	157	425	437	25.4
A/E (1/1)-T/I (1/1)	—	422	430	29.6
A/E (1/3)-T/I (1/1)	162	429	434	29.3
B/C (1/1)-T	150	491	493	24.1
B/C (1/1)-T/I (1/1)	135	480	482	23.3
B/C (1/1)-I	127	485	484	18.1

(a) Determined by DSC with a heating rate of 10 °C/min under nitrogen.

(b) Initial decomposition temperatures determined by TG with a heating rate of 20 °C/min in nitrogen.

(c) Temperatures at which 10% weight loss were recorded by TG.

(d) At 800 °C in nitrogen.

polyarylates.

As a representative example, the TG curves of polyarylate B-T/I(1/1) in air and nitrogen are depicted in Figure 6. Polyarylate B-T/I(1/1) did not show obvious weight loss up to 480 °C in nitrogen, whereas it decomposed rapidly between 490-530 °C. There was about 24% residual char left at 800 °C in nitrogen. In air, the polymer decomposed initially at a lower temperature, oxidative degradation continued above 500 °C, and the polymer decomposed completely at about 670 °C. A comparison of thermal behavior of polyarylate B-T/I(1/1) with that of bromine-substituted polyarylate D-T/I(1/1) in nitrogen is illustrated in Figure 7, and it reveals that the latter is lower by 50 °C due to the earlier decomposition of C-Br. However, the brominated polyarylate D-T/I(1/1) exhibited higher residue char than the non-brominated polyarylate B-T/I(1/1) at elevated temperatures (above

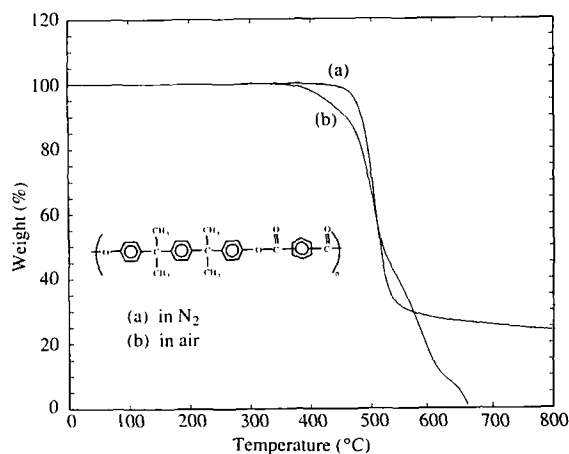


Figure 6. TG curves of polyarylate B-T/I(1/1) (a) in N₂ and (b) in air.

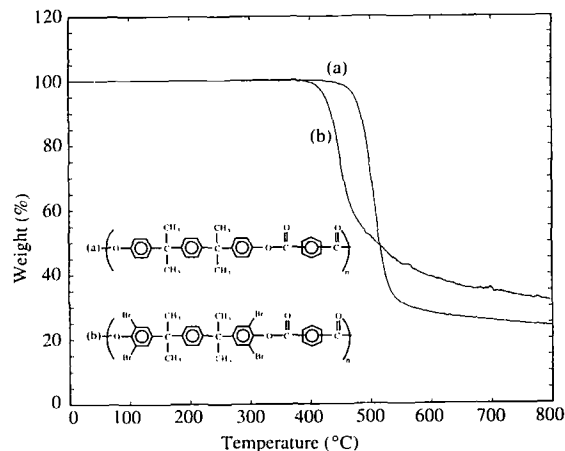


Figure 7. TG curves of polyarylates (a) B-T/I(1/1) and (b) D-T/I(1/1) in N₂.

550 °C). This implies that the former probably possesses higher flame retardancy than the latter. All other polyarylates showed a similar thermal behavior. Some TG data are included in Table V.

The limiting oxygen index (LOI) values of four representative polyarylates are presented in Table VI. It is observed that the LOI values increase with the bromine content in the polymer backbone. In other words, the introduction of bromine on the polymer backbone caused a great enhancement of flame retardancy.

Conclusion

Table VI. Limiting oxygen index (LOI) of brominated copolyesters containing various bromine content.

Polymer Code	Br (wt%)	LOI
A-T/I (1/1)	0	26.5
A/E (3/1)-T/I (1/1)	17.2	35.0
A/E (1/1)-T/I (1/1)	27.9	42.5
E-T/I (1/1)	35.2	48.5

Polyarylates and brominated polyarylates with inherent viscosities of 0.28-1.73 dL/g were synthesized by the interfacial polycondensation from α,α' bis(4-hydroxyphenyl)-1,4(or 1,3)-diisopropylbenzene or their tetrabromobisphenols with mixed terephthaloyl chloride/isophthaloyl chloride of various ratios. Precipitation or emulsification occurred in each homo-polycondensation reaction of these bisphenols with terephthaloyl chloride, producing low molecular weight products. Copolymerization with appropriate quantities of isophthaloyl chloride enhanced the solubility of the resulting copolymers, giving rise to products with higher inherent viscosities. Most of the polymers could be cast into good-quality and creasable films. In general, polyesters containing more 1,3-isomeric bisphenol or isophthaloyl chloride moieties could be cast into transparent and flexible films, and had lower glass transition temperatures together with higher solubility. These polyarylates possessed reasonable thermal stability, and they showed no significant weight loss below 400 °C. The introduction of bromine on the polyarylate backbone led to a decrease in solubility, crystallinity, and thermal stability, while resulting in an increase in glass transition temperature and a great enhancement in fire-retardancy.

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