

# Preparation and Properties of Brominated Poly(arylcaboxylate)s via Interfacial Polycondensation

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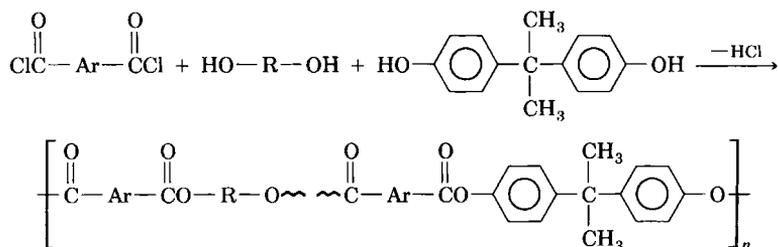
## Synopsis

The interfacial polycondensation method has been used for the preparation of brominated poly(arylcaboxylate)s. Brominated poly(arylcaboxylate)s can be prepared easily by mixing a solution of diacid chloride in a water-immiscible organic solvent with an aqueous alkaline solution of bisphenol in the presence of catalyst such as quaternary ammonium salts. First, in a dichloromethane–water system using triethylbenzylammonium chloride (TEBAC) as the catalyst a series of 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane (3,3',5,5'-tetrabromobisphenol A, TBBPA) with isophthaloyl (I) and terephthaloyl chlorides (T) has been prepared and some properties as inherent viscosity, solubility, crystallinity, and flammability have been measured. Copolymers prepared from TBBPA and mixed T/I with 33/67–67/33 molar ratios show good solubility and amorphous nature, and can be cast into transparent and tough films with limiting oxygen index of 58–59 (ANSI/ASTM D2683-77). Second, the effects of some variables as the nature of organic phase and catalysts, concentration of reactants, and basicity of aqueous phase on the interfacial polycondensation of TBBPA with equal parts of T and I [T/I (50/50)] was investigated in some detail. Among the solvents tested dichloromethane was found to be the best solvent and quaternary ammonium salts such as TEBAC and tetra-*n*-butylammonium bromide (TBAB) were highly efficient catalysts. Poly(arylcaboxylate)s with the highest molecular weights were obtained at an acid chloride concentration of 0.2 mol/L in dichloromethane and a concentration of TBBPA of 0.1 mol/L in alkali when TEBAC was used as catalyst. A maximum of inherent viscosity was obtained at two equivalent amounts of alkali corresponding to bisphenol. Polycondensation of several combinations of T/I (50/50) with some other tetrabromobisphenols, such as 3,3',5,5'-tetrabromo-4,4'-biphenol, 3,3',5,5'-tetrabromobisphenol S, 3,3',5,5'-tetrabromo-4,4'-thiodiphenol, and 3,3',5,5'-tetrabromophenolphthalein, were carried out with limited success. Whereas, a more favorable result could be obtained by the mixed copolycondensation of these tetrabromobisphenols and bisphenol A (BPA) with T/I (50/50). Finally, the copoly(arylcaboxylate)s from TBBPA, BPA, T, and I were prepared and characterized. The incorporation of bromine on the polymer backbone caused a decrease of inherent viscosity, glass transition temperature, crystallinity, and thermal stability of copolyarylates, whereas it caused a great enhancement of flame retardancy.

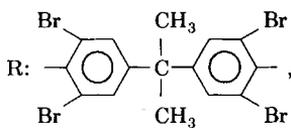
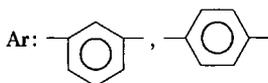
## INTRODUCTION

Interfacial polycondensation came into prominence as a major polyester-forming technique about 30 years ago with the works of Conix<sup>1</sup> and Eareckson.<sup>2</sup> The preparation of a great many aromatic polyesters via interfacial synthesis have been reported in the literature,<sup>2–5</sup> and polyesters derived from 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and isophthaloyl (I) and terephthaloyl chloride (T) have been commercialized. The method is a highly effective procedure for the rapid preparation of polymers in high molecular weight and in a easily isolated form. At present, the interfacial polycondensation is still a very popular means for screening new polyesters<sup>6,7</sup> due to its particular advantages.

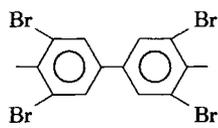
It is well known that the incorporation of halogen substitution into polymer chains has led to flame-retardant polymers and fibers.<sup>8</sup> There are many patent references dealing with the preparation of flame-resistant polyesters by means of interfacial polycondensation from T and I with halogenated bisphenols. A popular type of bisphenol has been 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane (3,3',5,5'-tetrabromobisphenol A, TBBPA) and its homologs.<sup>9-17</sup> Little investigation, however, has been reported on the effect of variables of the polymer preparations. In this article, the effects of some variables as the diacid chloride composition, the nature of organic phase and catalysts, concentration of reactants, and the amount of alkali on the interfacial polycondensation of T, I, and TBBPA are reported. A study is also made of the interfacial polycondensation of other tetrabromobisphenols with T and I and of copolycondensation of them and bisphenol A with the same acid chlorides [eq. (1)]. Some properties, such as crystallinity, thermal stability, thermal transition, and flame retardancy, of the brominated poly(arylcarylate)s will be discussed.



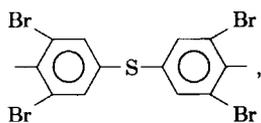
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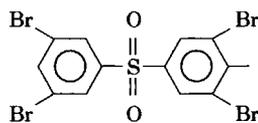
(TBBPA),



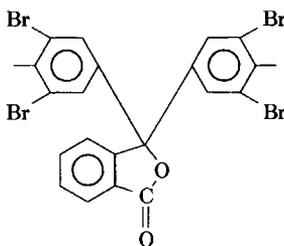
(TBBP),



(TBTDP),



(TBBPS)



(TBPP)

## EXPERIMENTAL

### Materials

2,2-Bis(4-hydroxy-3,5-dibromophenyl)propane (3,3',5,5'-tetrabromobisphenol A, TBBPA) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, BPA) were obtained commercially and purified by recrystallization from methanol and toluene, respectively. 3,3',5,5'-Tetrabromo-4,4'-biphenol (TBBP; mp 280°C), 3,3',5,5'-tetrabromobisphenol S (TBBPS; mp 270°C), 3,3',5,5'-tetrabromo-4,4'-thiodiphenol (TBTDP; mp 201°C), and 3,3',5,5'-tetrabromophenolphthalein (TBPP; mp 291°C) were prepared according to the method described in our previous work<sup>18</sup> from the bromination of their corresponding bisphenols in aqueous acetic acid solution under mild conditions.

Commercial isophthaloyl chloride (I) and terephthaloyl chloride (T) were purified by vacuum distillation before use.

Sodium lauryl sulfate (SLS), 18-crown-6-ether (18-C-6-E), and all quaternary ammonium salts, such as tetraethylammonium bromide (TEAB), tetra-*n*-butylammonium bromide (TBAB), triethylbenzylammonium chloride (TEBAC), trimethylbenzylammonium chloride (TMBAC), cetyltrimethylammonium bromide (CTMAB), cetyltrimethylammonium chloride (CTMAC), and cetyldimethylammonium bromide (CEDMAB) were used as received from Tokyo Kasei Kogyo Co., Ltd. All the solvents employed were purified by distillation.

### Polymerization

The general process of preparation of poly(arylcarylate)s is as follows. In a 100-mL flask were placed 2.5 mmol of tetrabromobisphenols or their mixtures with BPA and 5.1 mL of 1M aqueous sodium hydroxide. Until the bisphenols were dissolved completely 0–50 mL of water together with 0.12 mmol of catalyst such as TEBAC were added to the solution. To the magnetically stirred solution was added quickly a solution of total 2.5 mmol of T and I in 5–22.5 mL of water-immiscible organic solvent, and an additional 2.5 mL of the solvent used to rinse the residue of diacid chlorides. The two-phase mixture was vigorously stirred with a stirring rate of about 3000 rpm at room temperature (about 20°C) for 1 h. The mixture was poured into 500 mL of hot water containing a small amount of hydrochloric acid. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried at 80°C *in vacuo*.

The polymer samples used in flammability and tensile tests were prepared on a larger scale in a three-necked 500-mL round-bottomed reactor equipped with a home blender. The polyester films were cast from the solution in *sym*-tetrachloroethane. The polymer films were dried thoroughly in a vacuum oven at 150°C for 10 h previous the flammability and tensile tests.

### Measurements

Inherent viscosities of all polymers were determined by using a Cannon-Fenske viscometer on a concentration of 0.5 g/dL.

The oxygen indices of the polymers were measured by using 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.

A DuPont 910 differential scanning calorimeter and a DuPont 951 thermogravimetric analyzer connected to a DuPont 1090 thermal analyzer were employed to study the transition data and thermal stability of decomposition onset temperature and char yield, respectively, for all polymers. The differential scanning calorimetry (DSC) was run under a nitrogen stream at a flow rate of 30 cc/min and at a heating rate of 10°C/min. The thermogravimetric (TG) analysis was determined under a nitrogen or air flow of 50 cc/min with a heating rate of 10°C/min.

Wide-angle x-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa with nickel-filtered  $\text{CuK}_\alpha$  radiation (40 kV, 20 mA). The scanning rate was 4°/min. Measurements were performed with powder sample or on film specimens of about 0.5 mm thickness.

Tensile properties were determined from stress-strain curves with an Instron Universal Tester Model 1130 with a load cell 5 kg at a drawing speed of 5 cm/min. Measurements were performed at 20°C on film specimens (about 0.1 mm thick, 5 mm wide, and 5 cm long) and an average of at least five individual determination was used.

## RESULTS AND DISCUSSION

### Effect of Diacid Chloride Structure on the Synthesis and Property of Polymer

The interfacial polymerization procedure, discussed in this article, was described in literature.<sup>1-5</sup> Interfacial synthesis of poly(arylcarylate)s involves the mixing of a solution of acid chloride in a water-immiscible organic solvent with an aqueous alkaline solution of bisphenol in the presence of catalyst such as quaternary ammonium salts or sodium lauryl sulfate. As the two solutions are brought into intimate contact, polymerization proceeds in or across the interface between the two phases. The reaction proceeds extremely rapidly at room temperature and may be complete in a matter of minutes.

Eareckson<sup>2</sup> found that in a given solvent system copolymers formed in higher molecular weights than homopolymers for the polycondensation of bisphenol A (BPA) with terephthaloyl chloride (T) and isophthaloyl chloride (I). In the present article, we substitute 3,3',5,5'-tetrabromobisphenol A (TBBPA) for BPA, and the results of polymerization are summarized in Table I, where the quaternary ammonium salt, TEAC, is used as a catalyst and dichloromethane is used as the solvent of the organic phase. Both homopolymers TBBPA-T and TBBPA-I tend to crystallize and are insoluble in the reaction media, as a result they are rapidly to form precipitates in a few minutes. The copolymers of TBBPA with T and I produced a more favorable result than that of homopolymer with T or I, possibly because the copolycon-

TABLE I  
Properties of TBBPA-T/I Copolymers<sup>a</sup>

T/I molar ratio	$\eta_{inh}^b$ (dL/g)	Solubility <sup>c</sup>	Film toughness <sup>d</sup>	LOI
100/0	insoluble	insoluble	—	—
83/17	1.26	1, 2, 3	brittle	—
75/25	1.26	1, 2, 3, 4, 5 (hot)	tough	58.5
67/33	1.09	1, 2, 3, 4, 5 (hot)	tough	58
50/50	1.16	1, 2, 3, 4, 5	very tough	59
33/67	0.97	1, 2, 3, 4	very tough	58.5
20/80	0.93	1, 2, 3, 4	brittle	—
0/100	insoluble	insoluble	—	—

<sup>a</sup>Polymerization was carried out with 0.025 mol of TBBPA and 0.025 mol of T + I in the presence of 0.16 g of TEAC in 125 mL of dichloromethane and 250 mL of 0.2M aqueous sodium hydroxide (51 mL of 1M aq. NaOH and 204 mL of water) at 20°C for 1 h.

<sup>b</sup>Measured at 0.5 g/dL concentration in *sym*-tetrachloroethane/phenol (40 : 60 by weight) at 30°C.

<sup>c</sup>Measured at 2% solids at room temperature in the following solvents: (1) *m*-cresol (2) *sym*-tetrachloroethane, (3) *p*-chlorophenol, (4) chloroform, (5) dimethylformamide.

<sup>d</sup>Films were cast from the *sym*-tetrachloroethane solutions.

densation might have proceeded more readily due to lower crystallinity and better solubility of the copolymer in the reaction media. These copolymers can be readily prepared in high molecular weight and their inherent viscosity shows a tendency to increase with the content of T. This may be due to the fact that the para-oriented rings tend to lie in extended conformation thus behaving as rod-like molecules difficult to move in solution. They are soluble in *m*-cresol and tetrahydrofuran and are extremely soluble in halogenated

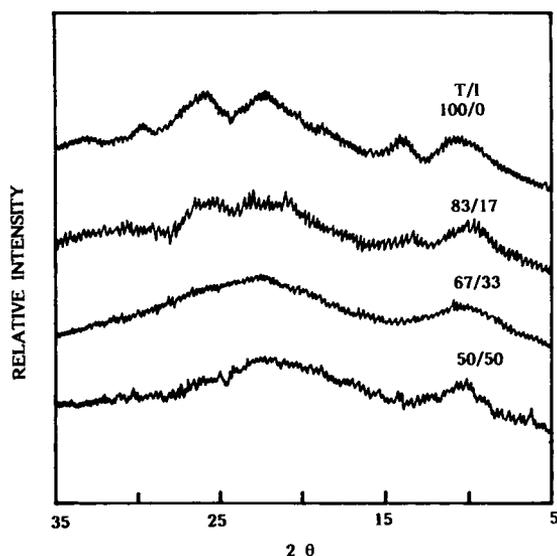


Fig. 1. X-ray diffraction patterns of TBBPA-T/I copolymers.

hydrocarbons such as dichloromethane, tetrachloroethane, *p*-chlorophenol, and chloroform, but are difficult to dissolve in amide-type solvents such as *N,N*-dimethylformamide (DMF). Copolymers with T/I between 67/33 and 33/67 (mol %) can be cast to yield strong, very tough, and transparent films from *sym*-tetrachloroethane solutions. The cast films of copolymers with higher part of T or I revealed lower transparency and embrittled, probably caused by the enhancement of crystallinity, as indicated by the x-ray diffraction patterns (Fig. 1). These copolymer samples charred during flammability 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, as found in our previous work.<sup>18</sup>

Subsequently, the preparation of TBBPA-T/I (50/50) copolymer was examined intensively and some polycondensation variables as nature of organic phase and catalysts, concentration of reactants, and basicity of aqueous phase were studied in some detail. Moreover, the effect of bisphenol structure on polycondensation will also be investigated.

### Factors Affecting Copolycondensation of TBBPA and T/I (50/50)

#### *Nature of Organic Phase*

The choice of solvents for interfacial polycondensation is very important in determining the molecular weight of the resulting polymer. Eareckson<sup>2</sup> has shown that liquids which are solvents, such as dichloromethane and trichloroethylene, or near-solvents, such as toluene and xylene, for the polymer allow formation of high molecular weight polymer in an interfacial polycondensation of BPA with the mixture of equal parts of T and I with sodium lauryl sulfate as catalyst. In the present work, study of the effect of the organic phase on the inherent viscosity and yield of brominated polyarylates from TBBPA and T/I (50/50) with TEAC as catalyst showed that the best results are obtained when dichloromethane is used as the organic solvent. Chloroform gave moderate results, whereas, except in nitrobenzene, less favorable results were produced in aromatic hydrocarbons such as toluene, chlorobenzene, and *o*-xylene (see Table II). In the latter case, the polymer is too insoluble in the organic phase so that the unswollen polymer film did not permit migration of the acid chloride molecules and thus the molecular weight of the polymer being formed was very low. Copolymers with low molecular weight were obtained by using trichloroethylene and tetrachloroethane as organic solvents, although they are good solvents for the copolymer. This problem arises because the nature of the solvent not only influences the rate of the desired reaction but also the rates of side reactions and even determines catalyst activity. Basically the solvent affects the permeability of the polymer film and the interfacial tension between phases. Further, the solvent can determine the limiting molecular weight of the polymer that can remain in solution. Because so many parameters are governed by the solvent, so far no generalization about solvent contributions adequately fits all experimental results. In subsequent work dichloromethane was used as the organic solvent.

TABLE II  
 Synthesis of TBBPA-T/I (50/50) Copolymer in Various  
 Solvent-Water Systems with TEBAC as a Catalyst<sup>a</sup>

Solvent for acid chlorides	Polymer	
	Yield (%)	$\eta_{inh}^b$ (dL/g)
Chloroform	97	0.86
Dichloromethane	98	1.21
<i>sym</i> -Tetrachloroethane	92	0.47
Trichloroethylene	87	0.35
<i>o</i> -Xylene	70	0.28
Toluene	65	0.25
Chlorobenzene	62	0.22
Nitrobenzene	95	0.73

<sup>a</sup>Polymerization was carried out with 5 mmol of TBBPA and 5 mmol of T/I (50/50) in the presence of 30 mg of TEBAC in 25 mL of the organic solvent and 50.5 mL of 0.2M aqueous sodium hydroxide (5.1 mL of 1M aq. NaOH and 45.4 mL of water) at 20°C for 1 h.

<sup>b</sup>Measured at a concentration of 0.5 g/dL in *sym*-tetrachloroethane/phenol (40:60 by wt) at 30°C.

### Effect of Catalyst

The effect of catalysts on polycondensation in a dichloromethane-water system is summarized in Table III. In the absence of catalyst the reaction system became an emulsion, probably due to the hydrolysis of the acid chloride end group of polymers or oligomers, leading to very low molecular weight of the resulting poly(arylcarylate)s. A well-defined two-phase system was observed when the reaction was catalyzed by the quaternary ammonium salts, with the exception of TEAB. With the same conditions of 0.1M of TBBPA in alkali and 0.2M of acid chlorides in dichloromethane TEBAC catalyst gave the best result, and TBAB gave moderate result; however, TBAB gave a more favorable result ( $\eta_{inh}$  of polymer up to 1.6 dL/g) than TEBAC when the concentration of reactants increased to 0.25M in aqueous phase and to 0.25M in organic phase. Moreover, from the rough observation of the appearance of the reaction medium, TBAB seems to catalyze the polyesterification faster than TEBAC. The viscous polymer mass in organic phase was usually formed not more than 5 min after mixing two reactant phases in the case catalyzed with TBAB. The less lipophilic TMBAC, or those with longer aliphatic chain of cetyl group, such as CTMAB, CTMAC, and CEDMAB, showed to be somewhat less effective. The quaternary ammonium salts were described as a phase transfer agent which acted to transfer the aqueous reactant into the organic phase and make it available for reaction there.<sup>19-21</sup> The commonly accepted explanation of the promoter role is that the agent serves to replace the sodium as the gegen ion  $[R_4\overset{\oplus}{N}O^{\ominus}-R-\overset{\ominus}{O}NR_4^{\oplus}]$  for the phenoxide ion and thus enhances the solubility (and hence diffusion rate) of phenoxide in the organic phase.<sup>22</sup> The different effects of the above discussed quaternary ammonium salts may be attributed to the difference of the diffusion rate of their corresponding gegen ions into dichloromethane.

TABLE III  
 Synthesis of TBBPA-T/I (50/50) Polyarylate with Various  
 Catalysts in a Dichloromethane-Water System<sup>a</sup>

Catalyst <sup>b</sup>	Polymer	
	Yield (%)	$\eta_{inh}^c$ (dL/g)
None	35	0.10
TEAB	82	0.31
TBAB	97	0.81 (1.6) <sup>d</sup>
TEBAC	98	1.21 (0.6) <sup>d</sup>
TMBAC	96	0.66
CTMAB	95	0.56
CTMAC	96	0.50
CEDMAB	96	0.55
18-C-6-E	92	0.37
SLS	52	0.20

<sup>a</sup> Polymerization was carried out with 5 mmol of TBBPA and 5 mmol of T/I (50/50) in the presence of 0.12 mmol of the catalyst in 25 mL of dichloromethane and 50.5 mL of 0.2M aqueous sodium hydroxide at 20°C for 1 h.

<sup>b</sup> TEAB: tetraethylammonium bromide; TBAB: tetrabutylammonium bromide; TEBAC: triethylbenzylammonium chloride; TMBAC: trimethylbenzylammonium chloride; CTMAB: cetyltrimethylammonium bromide; CTMAC: cetyltrimethylammonium chloride; CEDMAB: cetyldimethylammonium bromide; 18-C-6-E: 18-crown-6-ether; SLS: sodium lauryl sulfate.

<sup>c</sup> Measured at 0.5 g/dL concn. in *sym*-tetrachloroethane/phenol (40 : 60 by wt) at 30°C.

<sup>d</sup> Polymerization was carried out with 5 mmol of TBBPA and 5 mmol of T/I (50/50) in the presence of 0.12 mmol of catalyst in 20.0 mL of dichloromethane and 20.5 mL of 0.5M aqueous sodium hydroxide (10.2 mL of 1M eq. NaOH and 10.3 mL of water) at 20°C for 1 h.

Recently Lee et al.<sup>23</sup> found by means of UV determination that the transfer rate of bisphenolate and the rate of polycondensation were increased with increasing lipophilicity of the phase transfer agent. Numerous experiments with good reproducibility of results convinced us that these phase transfer agents employed in the TBBPA-T/I system behaved in the manner like that described by Lee. 18-Crown-6-ether, which is a highly efficient catalyst for producing some polyesters<sup>6</sup> with high molecular weight, showed a less favorable result. Interestingly, the commonly used dispersing agent, sodium lauryl sulfate, was found to be very ineffective as catalyst for the interfacial polycondensation reaction of TBBPA with phthaloyl chlorides.

#### Concentration of Reactants

Figure 2 illustrates the existing relationship between the viscosity of the obtained poly(arylcarboxylate) and the concentration of the solutions of the starting materials at various concentration of both components. As can be seen the dependence of the inherent viscosity of the poly(arylcarboxylate)s on the concentration of TBBPA in the aqueous alkaline phase showed that 0.1 mol/L is optimal in both instances of 0.25 and 0.167 mol/L of diacid chlorides in dichloromethane. The yield of the polyarylate is considerably less related to the concentration than the molecular weight and fluctuates between 80 and 95%. Usually, higher concentrations of the diacid chloride result in higher

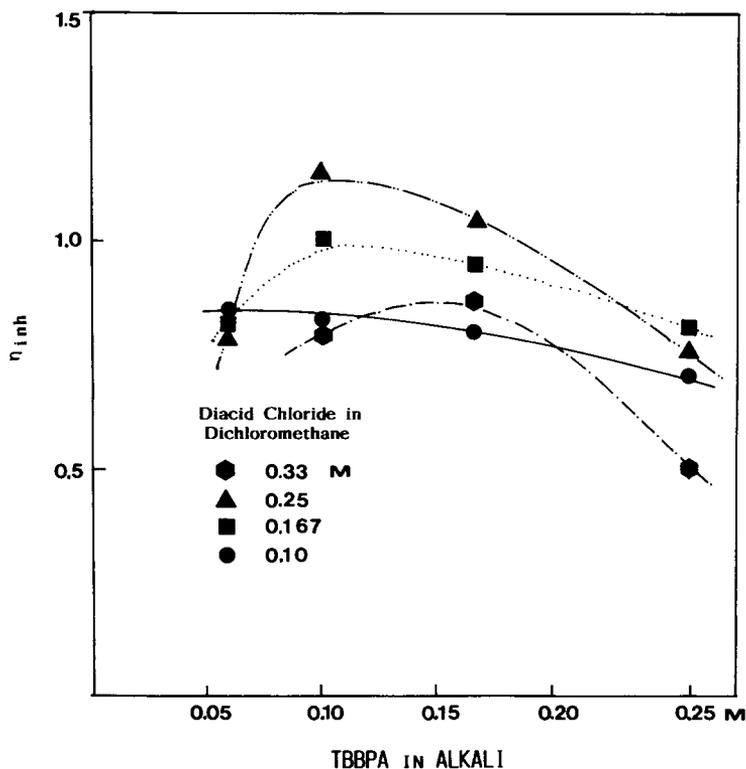


Fig. 2. Inherent viscosity of TBBPA-T/I (50/50) poly(arylcarboxylate) versus concentration of TBBPA in alkali solution at various concentrations of acid chloride in dichloromethane.

molecular weights. Polyarylates with the highest molecular weights were obtained at an acid chloride concentration of 0.2 mol/L and a concentration of TBBPA of 0.1 mol/L. Whereas, at too higher concentrations of acid chloride (and, thus, the increased concentration of polymer species), interchain contacts increase until a contact network is formed and semisolid pastes or precipitates are produced. At this point polymerization is greatly decreased in rate because of the lower mobility of the polymer chains and the decreased diffusion rate of the intermediates. This leads to a lowering of the average molecular weight and a broadening of molecular weight distribution as described by Morgan.<sup>22</sup>

#### *Basicity of Aqueous Phase*

In poly(arylcarboxylate) synthesis, alkali is essential because of the necessity for phenoxide ion as a reactant. The inherent viscosities of polymers at different amounts of alkali are shown in Table IV. Insufficient alkali, of course, produced a low molecular weight product because of the comparatively slow rate of reaction between un-ionized phenol and acid chloride. Excess alkali apparently has no deleterious effect on molecular weight. A high molecular weight in terms of inherent viscosity still could be obtained at seven-fold equivalent amounts of alkali employed, and the highest viscosity

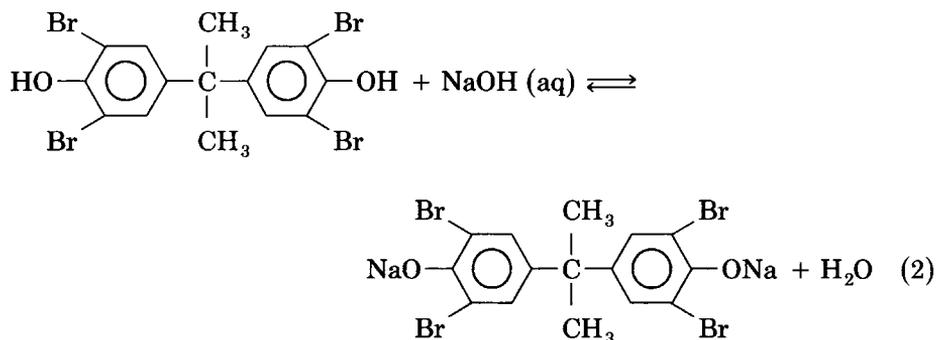
TABLE IV  
Effect of the Basicity of Aqueous Phase on the Preparation of  
TBBPA-T/I (50/50) Polyarylate in a Dichloromethane-Water System<sup>a</sup>

Amount of NaOH in aqueous phase [g (mmol)]	Initial pH value of aqueous phase	Polymer	
		Yield (%)	$\eta_{inh}^b$ (dL/g)
0.15 (3.75)	9.8	58	0.28
0.20 (5)	10.0	98	1.10
0.25 (6.25)	10.8	98	1.16
0.40 (10)	12.0	98	1.56
0.60 (15)	12.2	97	1.34
0.80 (20)	12.4	97	1.39
1.00 (25)	12.4	93	1.12
1.40 (35)	12.5	95	1.19
2.00 (50)	12.5	76	0.57

<sup>a</sup> Polymerization was carried out with 2.5 mmol of TBBPA and 2.5 mmol of mixed T/I (50/50) in the presence of 15 mg of TEBAC in 12.5 mL of dichloromethane and 25 mL of water containing dissolved various amounts of sodium hydroxide at 20°C for 1 h.

<sup>b</sup> Measured on 0.5 g/dL concentration in *sym*-tetrachloroethane/phenol (40 : 60 by wt) at 30°C.

was obtained at two-fold equivalent amounts of alkali corresponding to the phenol groups. To elucidate the reason, we may consider the equilibrium of bisphenol in alkali [eq. (2)]:



In the presence of phase transfer agent, the phenoxide ion will be converted to the gegen ion and transferred into the organic phase to proceed the polycondensation reaction with acid chloride. Thus, increasing the concentration of excess sodium hydroxide in the water phase favors the equilibrium to the right-hand side of eq. (2), and hence enhance the transfer rate of phenoxide ion into organic phase. This causes enhanced reaction rate and reduced probability of the hydrolysis of acid chloride, leading to a higher molecular weights of resulting poly(arylcarylate)s. Whereas, too much excess of alkali could lead to increased hydrolysis of the formed arylylate linkages and as a result lead to a lower molecular weight. For instance at 10-fold equivalent amounts of alkali, the yield and inherent viscosity of polymer decreased dramatically.

Optimal points in inherent viscosity were found upon changing other variables also. There was a maximum product viscosity [ $\eta_{inh}$  of TBBPA-T/I (50/50) poly(arylcaboxylate) up to 1.89 dL/g] associated with slow addition of comer, i.e., most of the diacid chloride solution is added in one portion (up to 95% of the stoichiometric amount) and then the remaining amount is added gradually. Moreover, it was found that in the reaction of equal parts of T and I with bisphenolate of TBBPA the maximum inherent viscosity of the polymer was reached at an equimolar ratio of bisphenol/acid chloride, although, it was sometimes observed that the maximum molecular weight occurred at other than an equimolar monomer ratio for other types of bisphenols. The effect of stoichiometry of reactants on the interfacial polycondensation for various bisphenols with diacid chlorides will be reported in a separate report.

### Preparation and Properties of Various Brominated Copoly(arylcaboxylate)s

Several other brominated copoly(arylcaboxylate)s were prepared from various tetrabromobisphenols such as TBBP, TBBPS, TBTDP, and TBPP with T/I (50/50) under the similar conditions for TBBPA-T/I (50/50) copolymer (Table V). These brominated bisphenols gave much lower inherent viscosities than did TBBPA. The lower inherent viscosity in the case of TBBP and TBBPS is attributable to the low solubility of the resulting polymers, whereas the less favorable results obtained from TBPP is explained by conversion of phenolphthalein in an alkaline medium to a monohydric phenol (blue dianion).

In addition to the copoly(arylcaboxylate)s from these tetrabromobisphenols with the mixture of T and I we also prepared some mixed poly(arylcaboxylate)s.

TABLE V  
Copolymers of T/I (50/50) and Various Tetrabromobisphenols or Their Mixtures with BPA<sup>a</sup>

Bisphenols <sup>b</sup>	Polymer				
	Yield (%)	$\eta_{inh}^c$ (dL/g)	Film property <sup>e</sup>	Br (wt %)	LOI
TBBP	97	insoluble	—	50.6	—
TBBP/BPA(33/67)	98	1.09	flexible	24.8	45.5
TBBPS	95	insoluble (0.25) <sup>d</sup>	—	45.9	—
TBBPS/BPA(33/67)	96	0.59	flexible	26.9	44.5
TBTDP	94	0.44	flexible	48.1	65.5
TBTDP/BPA(33/67)	96	0.64	flexible	27.7	51.5
TBPP	75	0.15	brittle	41.8	—
TBPP/BPA(20/80)	92	0.47	flexible	13.7	36.0
TBPP/BPA(10/90)	97	1.10	flexible	7.1	31.5

<sup>a</sup>Polymerization was carried out with 0.025 mol of bisphenols and 0.025 mol of mixed T/I (50/50) in the presence of 0.16 g of TEBAC in 125 mL of  $CH_2Cl_2$  and 255 mL of 0.2M aqueous NaOH at 20°C for 1 h.

<sup>b</sup>TBBP: 3,3',5,5'-tetrabromo-4,4'-biphenol; TBBPS: 3,3',5,5'-tetrabromobisphenol S; TBTDP: 3,3',5,5'-tetrabromo-4,4'-thiodiphenol; TBPP: 3,3',5,5'-tetrabromophenolphthalein.

<sup>c</sup>Measured at 0.5 g/dL concn. in *sym*-tetrachloroethane/phenol (40:60 by wt) at 30°C.

<sup>d</sup>Measured in *sym*-tetrachloroethane.

<sup>e</sup>Films were cast from *sym*-tetrachloroethane solutions.

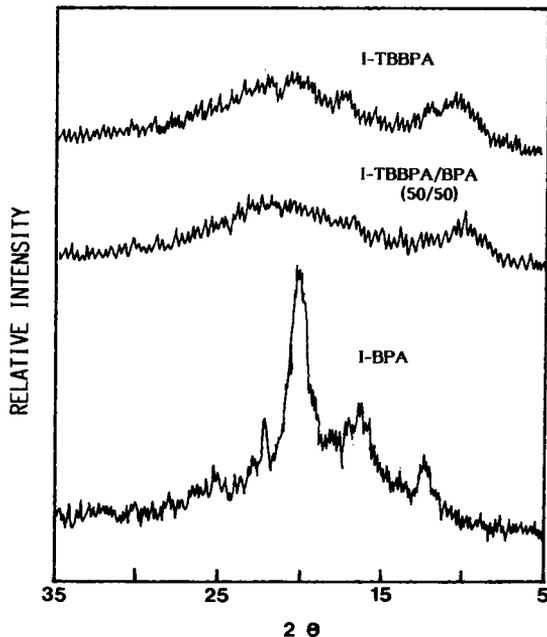


Fig. 3. X-ray diffraction patterns of poly(arylcarboxylate)s prepared from I, BPA, and TBBPA.

boxylate)s from their mixtures with BPA. A higher inherent viscosity was obtained probably due to the higher reactivity of BPA and the better solubility of the resulting copoly(arylcarboxylate)s by the introduction of the BPA moiety in the polymer backbone. Strong and flexible films could be cast from their polymer solutions in *sym*-tetrachloroethane. The high yield of polymer obtained ensured that most of the tetrabromobisphenol moiety was incorporated in the polymer chain. The polymer films showed highly fire-resistant. The LOI values increase with the content of bromine on the polymer backbone.

Subsequently the properties of mixed poly(arylcarboxylate)s from TBBPA, BPA, T, and I were investigated in some detail since they could be prepared with higher molecular weights. First the homopoly(arylcarboxylate)s of I with TBBPA and BPA and the copoly(arylcarboxylate)s of I and 50:50 TBBPA/BPA were synthesized and characterized with viscosity, x-ray diffraction, and DSC measurements. As shown in Figures 3 and 4, the crystallinity of poly(arylcarboxylate)s was decreased significantly by copolymerization. The properties of homo- and copoly(arylcarboxylate)s from I, TBBPA, and BPA are summarized in Table VI. A strong and flexible film of I-TBBPA/BPA (50/50) copoly(arylcarboxylate) could be cast from the polymer solution in *sym*-tetrachloroethane due to its amorphous nature. The reduction in viscosity in the case of the copolyarylate from equal parts of TBBPA and BPA is attributable to the lower reactivity of TBBPA (or more correctly, of its phenoxide ion) in interfacial polycondensation. This is probably due to steric hindrance of the formation of the intermediates activated complex and to reduced corner reactivity; both effects are caused by the

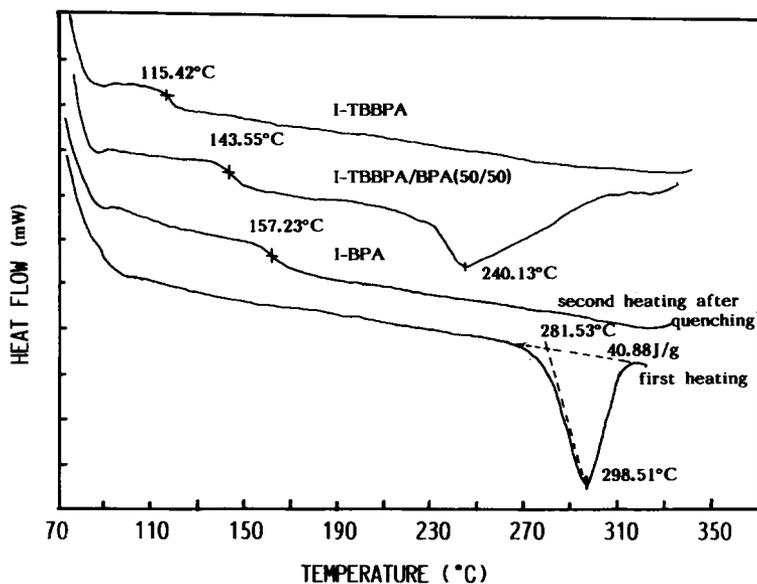


Fig. 4. DSC curves of poly(arylcarylate)s prepared from I, I, BPA, TBBPA.

presence of bulky bromine substitution on the aromatic rings, which increases the stability of the phenolate ion and decreases its reactivity for condensation. The decrease in glass transition temperature ( $T_g$ ) of copolymer may be explained by an increase of free volume caused by the bromine substitution. Similar behavior has been observed for the other halogenated polyesters<sup>24</sup> and polyamides.<sup>25</sup>

Finally, the copoly(arylcarylate)s of TBBPA, BPA, and T/I (50/50) were prepared and characterized. DSC and x-ray diffraction studies of these copolymers indicated that they had equally low crystallinity. A fall in inherent viscosity and  $T_g$  is also found in the brominated copolymers, as shown in Table VII. TG curves of the copoly(arylcarylate)s are shown in Figure 5 and the data of the onset of initial decomposition and tempera-

TABLE VI  
Properties of Poly(arylcarylate)s Prepared from I, TBBPA, and BPA<sup>a</sup>

Bisphenol	Polymer				
	Yield (%)	$\eta_{inh}^b$ (dL/g)	Film property <sup>c</sup>	$T_g^d$ (°C)	$T_m^d$ (°C)
BPA	98	1.53	brittle	156	281
BPA/TBBPA (50/50)	98	0.77	flexible	143	235
TBBPA	97	insoluble	—	115	—

<sup>a</sup> Preparation conditions: bisphenols = I = 5 mmol,  $CH_2Cl_2$  = 25 mL, 1M aq. NaOH = 5.1 mL, water = 45.4 mL, TEAC = 0.03 g, temperature = 20°C, time = 1 h.

<sup>b</sup> Measured at 0.5 g/dL in *sym*-tetrachloroethane/phenol (40/60 by wt) at 30°C.

<sup>c</sup> Films were cast from *sym*-tetrachloroethane solutions by slow evaporation of the solvent.

<sup>d</sup> Determined by DSC with a heating rate of 10°C/min in nitrogen.

TABLE VII  
Viscosities, Thermal Behavior Data, and LOI of Copoly(arylarcoylate)s Prepared from T/I (50/50) with Mixtures of TBBPA and BPA<sup>a</sup>

Polymer code	BPA/TBBPA mole ratio	$\eta_{inh}^b$ (dL/g)	$T_g^c$ (°C)	TGA data <sup>d</sup>		Br wt % in polymer	LOI
				IDT <sup>e</sup> (°C)	$T_d$ max <sup>f</sup> (°C)		
Co-1	100/0	1.94	200	445 (396) <sup>g</sup>	500	0	30.5
Co-2	75/25	0.94	201	423	490	18.3	40.8
Co-3	60/40	0.87	195	425	475	26.4	45.7
Co-4 <sup>h</sup>	50/50	1.07	184	423	475	31.0	48.3
Co-5	25/75	1.04	134	423	465	40.3	51.5
Co-6	0/100	1.16	133	420 (375)	460	47.4	59.5

<sup>a</sup> Polymerization was carried out with 0.025 mol of bisphenols and 0.025 mol of mixed T/I (50/50) in the presence of 0.16 g of TEBAC in 125 mL of CH<sub>2</sub>Cl<sub>2</sub> and 255 mL of 0.2M aqueous NaOH at 20°C for 1 h.

<sup>b</sup> Determined on a 0.5 g/dL polymer solution in *sym*-tetrachloroethane/phenol (40/60 by wt) at 30°C.

<sup>c</sup> Determined by DSC with a heating rate of 10°C/min under nitrogen.

<sup>d</sup> Data analyzed in nitrogen with a heating rate of 10°C/min.

<sup>e</sup> IDT: the onset of initial decomposition temperature.

<sup>f</sup>  $T_d$  max: temperature at maximum decomposition.

<sup>g</sup> Values in parentheses were determined in an air flow.

<sup>h</sup> ANAL. Calcd for (C<sub>46</sub>H<sub>32</sub>O<sub>8</sub>Br<sub>4</sub>)<sub>n</sub>: C, 53.52%; H, 3.12%; Br, 30.96%. Found: C, 53.40%; H, 3.53%; Br, 30.72%.

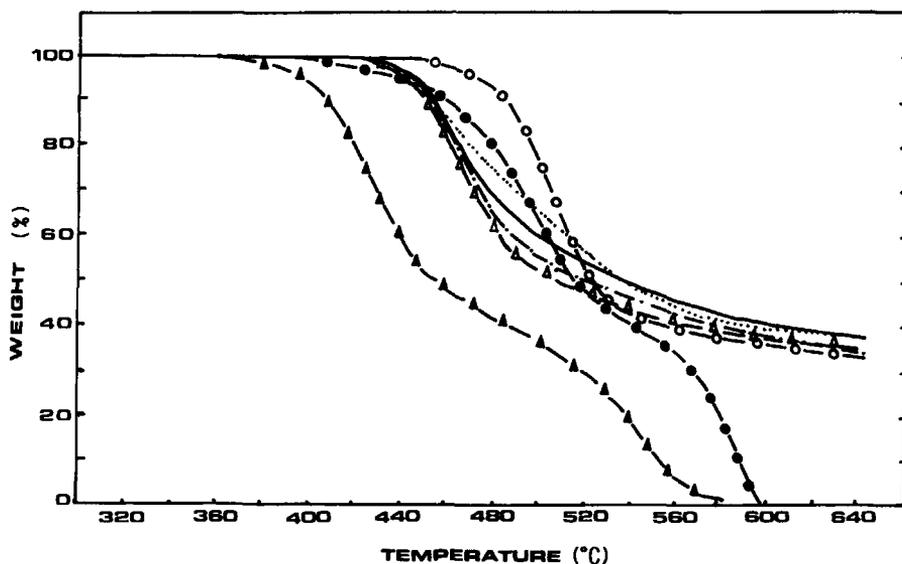


Fig. 5. TG curves of polymers Co-1 (—○— in N<sub>2</sub>, —●— in air), Co-2 (···), Co-4 (—), Co-5 (---), and Co-6 (—△— in N<sub>2</sub>, —▲— in air), with a heating rate of 10°C/min in N<sub>2</sub>, except where indicated.

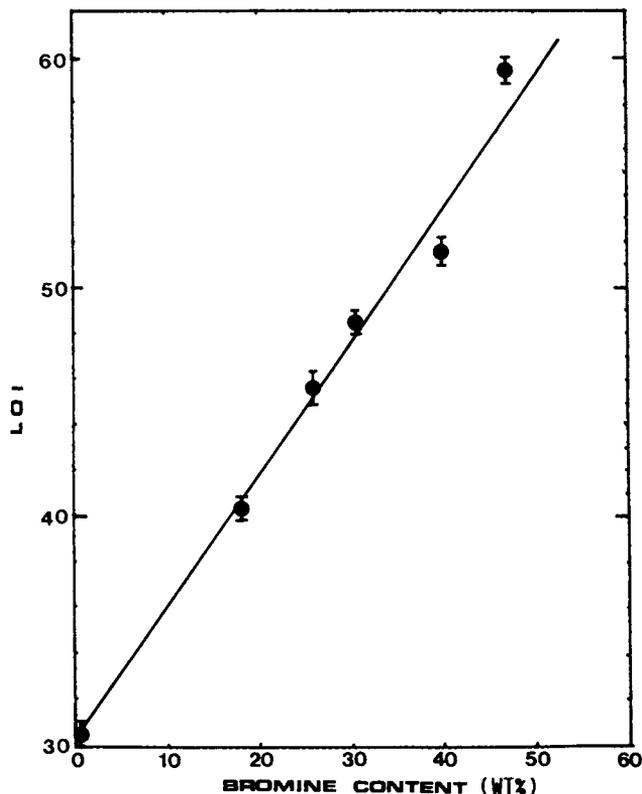


Fig. 6. Limiting oxygen index versus bromine content in the copolyarylates prepared from T/I (50/50) with the mixture of BPA and TBBPA.

ture at maximum decomposition are also listed in Table VII. It is observed that the substitution of bromine in the poly(arylcarylate)s leads to the decrease of the starting temperature of decomposition and the increase of residue in nitrogen. A comparison of the initial decomposition temperature of TBBPA-T/I (50/50) copoly(arylcarylate) with that of BPA-T/I (50/50) copolymer reveals that the former is lower by 25°C in nitrogen and 21°C in air due to the earlier decomposition of C-Br. The decomposition of copoly(arylcarylate)s with bromine-substitution starts between 420 and 425°C, and the rapid weight loss occurs in the region 450–500°C under nitrogen.

The LOI values of the copoly(arylcarylate)s are shown in the last column of Table VII. They approximately increase linearly with the bromine content in the polymer backbone as shown in Figure 6. The relationship between LOI value and bromine content in the copoly(arylcarylate) of T/I (50/50) with TBBPA and BPA shows as eq. (3):

$$\text{LOI} = 30.5 + 0.6X \quad (3)$$

where  $X$  is the concentration (wt %) of bromine in the TBBPA/BPA-T/I (50/50) copoly(arylcarylate)s.

Colorless, transparent, and flexible films could be cast from the tetrachloroethane solutions of all of the polymers Co-1 through Co-6. Typical mechanical properties of a film of polymer Co-4 were tensile strength of 98 MPa, elongation at break of 10%, and tensile modulus of 1.9 GPa.

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