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Preparation and properties of flame-retardant polycarbonates and copolycarbonates from 3,3′,5,5′-tetrabromobisphenol AF and bisphenol A

Der-Jang Liaw* and Ping Chang
Department of Chemical Engineering, National Taiwan Institute of Technology, Taipei, Taiwan 106, Republic of China
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Brominated fluorine-containing homopolycarbonates and copolycarbonates of varied unit ratio were synthesized from 3,3′,5,5′-tetrabromobisphenol AF and bisphenol A polycondensed with trichloromethyl chloroformate and a phase-transfer catalyst at 25°C. All polycarbonates were examined with i.r. spectra, elemental analyses (EA), inherent viscosity, X-ray diffraction, solubility, contact angle, tensile stress, d.s.c., t.g.a. and LOI. Polycarbonates of moderate to large molar mass and inherent viscosities up to 0.77 dl g^{-1} were obtained in high yields with tetra-*n*-butylammonium bromide as a catalyst, sodium hydroxide as a base and 1,2-dichloroethane as medium. The homopolycarbonate of greatest inherent viscosity reflects that bisphenol A, having an electron-releasing group, increases nucleophilic properties of the phenolate anion. The X-ray diffraction diagram showed that all polycarbonates were essentially semicrystalline. Almost all polycarbonates, except the homopolycarbonate based on bisphenol A, were soluble in acetone, NMP, DMF, THF, chloroform, pyridine, nitrobenzene and 1,1,2,2-tetrachloroethane at room temperature. The contact angles of the polycarbonates were found in the range 64–85°. The wettabilities of polycarbonates increased with increasing mass fraction of bromine atoms. The tensile stress shows that the films become more pliable with increasing fluorine atom content. The homopolycarbonate based on tetrabromobisphenol AF has the highest T_g at 206°C. The t.g.a. curves show that $T_d^{10\%}$ of polycarbonates was in the range 446–477°C in nitrogen. The LOI of homopolycarbonates based on bisphenol A and tetrabromobisphenol AF were found at 25.5 and 93, respectively. The results show that homopolycarbonate and copolycarbonates containing tetrabromobisphenol AF have great thermal stability and flame retardancy. © 1997 Elsevier Science Ltd.

(Keywords: 3,3′,5,5′-tetrabromobisphenol AF; LOI; thermal stability)

INTRODUCTION

Aromatic polycarbonates are commercially exploited as engineering plastics in various fields because of their good thermal and chemical stabilities[1–3]. Among many aromatic polycarbonates prepared from various bisphenols, bisphenol A-based polycarbonate is recognized to be about the best performing engineering plastic[4,5]. Only a few authors reported a polycarbonate based on bisphenol AF[6,7], and there are few details about brominated bisphenol AF-based polycarbonates.

In general, aromatic polycarbonates present problems in processing due to their solvent resistance and high glass transition temperatures, by virtue of their rigid structures. Extending our previous research[8,9], we synthesized polycarbonates containing fluorine atoms, because fluorine atoms improve the solubility[7–10] of polymers and increase their thermal stability[7–10]. Organic bromides have long been recognized to be effective flame retardants for polymeric materials, and there is a lot of data about them. Many patents describe the preparation of flame-proofed aromatic polyesters on introducing bromine into the polymer chain[11,12]. A bisphenol of a popular type is 3,3′,5,5′-tetrabromobisphenol A (TBBPA) and its homologues[9,11–14]. In general, the incorporation of halogen substituents into the polymer chain leads to increased flame retardancy and decreased thermal stability[15,16]. Thus, polymers containing bromine and fluorine atoms should be excellent candidates to improve flame retardancy while retaining good thermal stability.

Commercial polycarbonates are produced mainly through polycondensation in solution with phosgene as a carbonylation agent[17]. Because phosgene vapour is extremely toxic, this synthetic method is unfavourable for polycarbonate preparation on a laboratory scale.

We prepared a widely varied unit ratio with a phase-transfer catalyst and polycondensation of 3,3′,5,5′-tetrabromobisphenol AF (TBBPAF) and bisphenol A (BPA) with trichloromethyl chloroformate. Trichloromethyl chloroformate is a liquid that is handled more easily than phosgene for polycarbonate syntheses[7,18]. The effect of bromine and fluorine content on the physical properties of the polycarbonates and copolycarbonates,

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* To whom correspondence should be addressed

such as solubility, mechanical, surface properties, thermal properties and flame retardancy, are discussed in detail.

EXPERIMENTAL

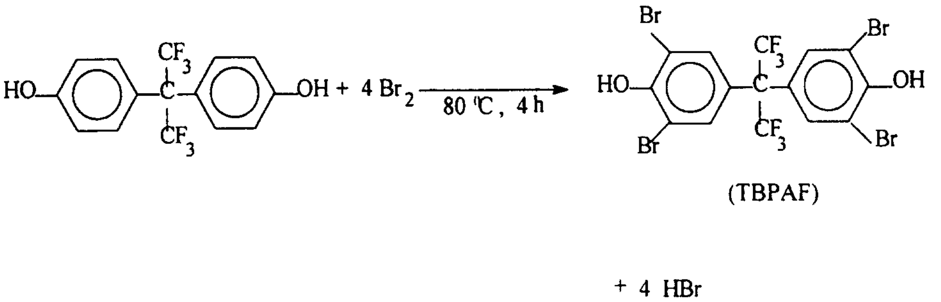
Materials

Bisphenol AF was recrystallized from benzene; m.p. 163–165°C, and likewise commercial bisphenol A; m.p. 155–156°C. Bromine (Merck Co., Germany), trichloromethyl chloroformate (Janssen Chemical, Belgium), and quaternary ammonium salts such as tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylammonium chloride (TBAC), benzyltriethylammonium bromide (BTEAB) and benzyltriethylammonium chloride (BTEAC) were used as purchased. All solvents were distilled before use.

Preparation of monomers

3,3′,5,5′-Tetrabromobisphenol AF[19]. A spherical flask (1 l) equipped with a dropping funnel was charged with bisphenol AF (33.6 g, 0.1 mol) and distilled water (500 ml). While the suspended mixture was heated from 30 to 80°C, bromine (65 g, 0.41 mol) was added to the reaction flask through the dropping funnel during 40 min. The flask was maintained about 80°C for 4 h. After the reaction was completed, the crude product was washed with aqueous sodium sulfite solution and distilled water to remove residual hydrogen bromide.

The final product was dried *in vacuo* at 60°C for 24 h. A white powder of m.p. 256°C was obtained; the yield was over 94%. The reaction took place according to equation (1):



(TBPAF)

+ 4 HBr

(1)

Anal. Calcd for $C_{15}H_6O_2F_6Br_4$: C, 27.6%; H, 0.9%; Found: C, 27.6%; H, 1.0%.

Polymerization

Homopolycarbonate from tetrabromobisphenol AF and trichloromethyl chloroformate. In a flask, tetrabromobisphenol AF (3.23 g, 5.00 mmol), TBAB (1.01 g, 3.15 mmol) and sodium hydroxide (1.14 g, 28.5 mmol) were dissolved in water (30 ml), and then 1,2-dichloroethane (DCE, 30 ml) was added. To this mixture, trichloromethyl chloroformate (1.49 g, 7.50 mmol) dissolved in DCE (7.5 ml) was added dropwise during 10 min with vigorous agitation at 25°C. The two-phase mixture was stirred at that temperature for 2 h. The organic layer was separated, washed repeatedly with water, and then added dropwise to methanol (300 ml). The precipitated powdery polymer was collected, rinsed thoroughly with methanol and dried under vacuum at 60°C for 24 h. The yield was 91%. The inherent viscosity of the polymer in dimethylformamide (DMF) was 0.31 dl g^{-1}, measured at a concentration 0.5 g dl^{-1} at 25°C. I.r. (KBr): 1793 cm^{-1} (C=O).

Copolymerization

Copolymerization of tetrabromobisphenol AF and bisphenol A with trichloromethyl chloroformate at various feed ratios in DCE was carried out at 25°C for 2 h. A typical copolymerization procedure of tetrabromobisphenol AF/bisphenol A (50/50) proceeded as follows. Into a flask was charged tetrabromobisphenol AF (1.61 g, 2.5 mmol), bisphenol A (0.58 g, 2.5 mmol), TBAB (1.01 g, 3.15 mmol), sodium hydroxide (1.14 g, 28.5 mmol), water (30 ml) and DCE (30 ml). To the vigorously stirred mixture was added a solution of trichloromethyl chloroformate (1.49 g, 7.5 mmol) in DCE (7.5 ml) in portions during 10 min at 25°C. After being stirred at 25°C for 2 h, the organic phase was collected and washed well with water. The fibrous polymer was isolated on pouring the solution into methanol (300 mL). The yield was 90%; the inherent viscosity was 0.58 dl g^{-1} in DMF at 25°C. I.r. (KBr): 1772 cm^{-1} (C=O).

Measurements

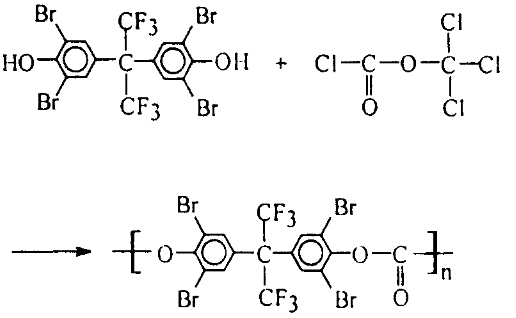
I.r. spectra were measured in the range 4000–400 cm^{-1} for the synthesized monomers and polymers in KBr discs (JASCO IR-700 spectrometer). The inherent viscosities, η_{inh}, were measured with an Ubbelohde viscometer at a concentration 0.5 g dl^{-1}. Elemental analyses of the monomers were made with a Perkin–Elmer 2400 instrument. X-ray diffraction diagrams of powders were recorded on an X-ray diffractometer (Philips model PW 1710). The LOI was determined on a SUGA instrument according to JIS K7201. Contact angles of polymers were measured with a contact-angle meter (Kernco, GIII). Static contact angles were measured at 25°C and 65% relative humidity through the use of a sessile drop of volume 2 μl. Tensile properties were determined from stress–strain curves (Toyo Baldwin Tensilon UTM-II) at an elongation rate 25% min^{-1}. Measurements were carried out at 25°C with film specimens (4 mm wide, 20 mm long and *ca.* 0.05 mm thick) and the average of at least five individual determinations was taken.

RESULTS AND DISCUSSION

Homopolycarbonate

Tetrabromobisphenol AF-based homopolycarbonate was synthesized at 25°C with the two-phase polycondensation of 3,3′,5,5′-tetrabromobisphenol AF and trichloromethylchloroformate in a system of organic solvent and aqueous alkaline solution with a quaternary ammonium salt—TBAB, TBAC, BTEAB or BTEAC.

Chlorinated hydrocarbons, dichloromethane, tetrachloromethane, 1,2-dichloroethane, and nitrobenzene served as organic media [equation (2)]:

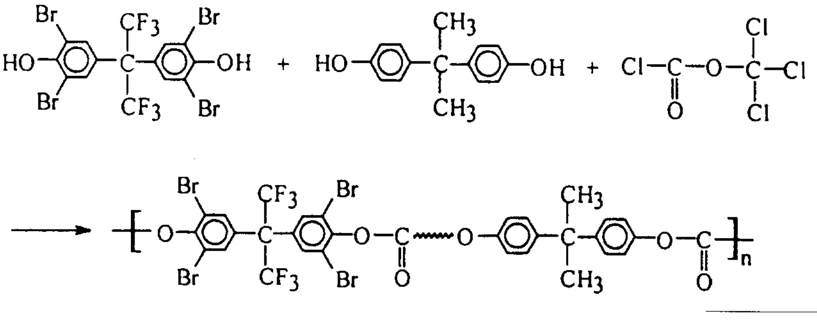


(2)

Reaction conditions and results are summarized in *Table 1*. According to the yield and inherent viscosity of the polymers, the use of TBAB as a phase-transfer catalyst, sodium hydroxide as a base, and DCE as organic medium were suitable to prepare polycarbonates of large molar mass at high yield. The optimum reaction conditions were found to be of TCF (7.5 mmol), TBAB (3.15 mmol), aqueous sodium hydroxide (*ca.* 1 M 30 ml 28.5 mmol), and DCE (37.5 ml), with tetrabromobisphenol AF (5 mmol), leading to formation of tetrabromobisphenol AF-based homopolycarbonate of inherent viscosity 0.31 dl g^{-1} in high yield at about 25°C for 2 h. Although polymers of large molar mass were obtained with dichloromethane and nitrobenzene as organic solvents, the yields were small. This two-phase technique would be effective for various diols in syntheses of polycarbonates.

Copolycarbonate

Brominated bisphenol AF and bisphenol A random copolycarbonates were synthesized on reacting the respective mixtures of tetrabromobisphenol AF/bisphenol A (feed molar ratios of 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100) with trichloromethyl chloroformate under the most suitable conditions, i.e. in the system of DCE and aqueous sodium hydroxide with two phases and TBAB as a catalyst [equation (3)]:



(3)

Table 2 shows that the ratio of tetrabromobisphenol AF/bisphenol A in copolymers as calculated on the basis of the carbon content. According to *Table 2*, the inherent viscosities of the copolycarbonates decreased with increasing feed ratio of tetrabromobisphenol AF to bisphenol A, although the yields were still high. This phenomenon may have resulted because tetrabromobisphenol AF is less nucleophilic due to strongly electron-withdrawing trifluoromethyl groups at the *para* position and bromine atoms on the ring, than bisphenol A.

Table 1 Synthesis of TBBPAF-based homopolycarbonates by two-phase polycondensation with trichloromethyl chloroformate[a]

	Reaction conditions		Polymer	
Run	Solvent[b]	Catalyst	Yield (%)	η_{inh}[c] (dl g^{-1})
1	DCM	TBAB	83.9	0.29
2	DCM	TBAC	85.7	0.21
3	DCM	BTEAC	64.5	0.16
4	DCM	BTEAB	67.2	0.09
5	TCM	TBAB	87.4	0.14
6	TCM	BTEAC	81.8	0.13
7	DCE	TBAB	90.2	0.31
8	DCE	TBAC	91.4	0.27
9	DCE	BTEAC	74.3	0.10
10	DCE	BTEAB	70.0	0.13
11	NB	TBAB	92.5	0.18
12	NB	BTEAC	89.7	0.11

[a] TBBPAF (5.00 mmol) and TCF (7.5 mmol) in the organic solvent (37.5 mL) and water (30 ml) were polymerized in the presence of catalyst (3.15 mmol) and sodium hydroxide (28.5 mmol) at 25°C for 2 h.
[b] Abbreviations: DCM, dichloromethane; TCM, tetrachloromethane; DCE, 1,2-dichloroethane; NB, nitrobenzene
[c] Measured at a concentration 0.5 g dl^{-1} in DMF at 25°C

The formation of polycarbonates was confirmed with i.r. spectra or elemental analysis. *Figure 1* shows i.r. spectra of three typical polycarbonates (tetrabromobisphenol AF/bisphenol A: 100/0, 50/50 and 0/100). I.r. spectra of homopolycarbonates based on bisphenol A and tetrabromobisphenol AF exhibited the characteristic carbonate carbonyl absorption at 1765 and 1793 cm^{-1}, respectively. The absorption wavenumber is increased because of the electron-withdrawing characteristics of the bromine atom and trifluoromethyl group. The peak of brominated copolycarbonates assigned to bromine appeared at 724 cm^{-1}. Methyl absorptions of homopolymer based on bisphenol A and copolymers were exhibited at 2958 cm^{-1}. Absorption attributed to hydroxyl groups in the diols almost disappeared, which implies the formation of polymers of moderate to large molar mass. Elemental analyses of both homopolymers (*Table 2*) agreed with compositions calculated for the proposed structures.

Polymer properties

All fluorine-containing polycarbonates were highly soluble in such solvents as acetone, NMP, DMF, THF, chloroform, pyridine, nitrobenzene, 1,1,2,2-tetrachloroethane and polar aprotic solvents at room temperature, whereas bisphenol A-based homopolycarbonate was entirely insoluble in DMSO, *m*-cresol and acetone even on heating. Fluorine-containing polycarbonates and bromine atoms on the benzene ring in polycarbonates favour greater solubility than for bisphenol A-based homopolycarbonate. Liaw *et al.* reported that solubility increases with flexible hexafluoroisopropylene

Table 2 Synthesis and thermal properties of 3,3′,5,5′-tetrabromobisphenol AF- and bisphenol A-based homopolycarbonates and copolycarbonates[a]

	Polymer					
Feed ratio: 3,3′,5,5′-tetrabromobisphenol AF/bisphenol A	Unit ratio[b] 3,3′5,5′-tetrabromobisphenol AF/bisphenol A	Yield[c] (%)	η_{inh}[d] (dl g^{-1})	$T_d^{10\%}$[e] (°C)	RM[f] (%)	T_g[g] (°C)
100/0	100/0	91	0.31	477	77	206
80/20	81/19	91	0.48	472	74	193
60/40	61/39	89	0.52	464	70	172
50/50	52/48	90	0.58	459	65	166
40/60	40/60	89	0.45	451	67	164
20/80	22/78	87	0.75	449	61	149
0/100	0/100	88	0.77	446	60	141

[a] Brominated bisphenol AF (5.00 mmol) and TCF (7.5 mmol) in DCE (37.5 ml) and water (30 ml) were polymerized in the presence of TBAB (3.15 mmol) and sodium hydroxide (28.5 mmol) at 25°C for 2 h

[b] The unit ratio of 3,3′,5,5′-tetrabromobisphenol AF/bisphenol A in the copolymers was estimated from elemental analysis

[c] The yield was calculated on the basis of the theoretical structure

[d] Measured at a concentration 0.5 g dL^{-1} in DMF at 25°C

[e] Temperature of 10% loss of mass observed by t.g.a. at a heating rate 10°C min^{-1} in nitrogen

[f] Residual mass at 500°C

[g] Determined by d.s.c. at a scan rate 10°C min^{-1}

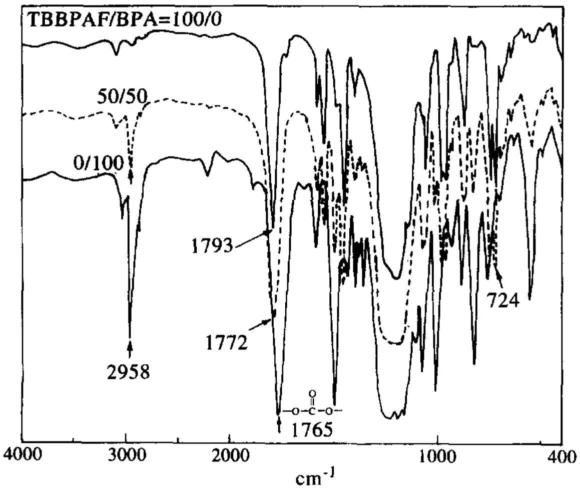


Figure 1 The i.r. spectra of polycarbonates (TBBPAF/BPA: 100/0, 50/50, 0/100)

groups between rigid phenyl rings in the polymer backbone[10].

X-ray diffraction patterns of four typical polycarbonates (tetrabromobisphenol AF/bisphenol A: 100/0, 60/40, 40/60 and 0/100) are shown in *Figure 2* with intensity as a function of 2θ; θ is the angle of diffraction (Bragg angle). The X-ray measurements indicated that all polycarbonates were essentially semicrystalline. As shown in *Figure 2*, the intensities of signals of polycarbonates slightly decreased on increasing the molar ratio of tetrabromobisphenol AF. Brominated polycarbonates are only slightly crystalline. Nagata *et al.*[15] reported that polyamides incorporating halogen substituents on the ring led to decreased crystallinity in terms of their larger van der Waals radius.

The thermal behaviour of polycarbonates was evaluated by means of t.g.a. and d.s.c; the results are summarized in *Table 2*. The t.g.a. curves of all polymers exhibited a 10% loss of mass at 446–477°C and residual mass 60–77% at 500°C in nitrogen. The thermal stability of polycarbonates derived from tetrabromobisphenol AF was remarkably improved relative to that of polycarbonates derived from bisphenol AF. Saegusa *et al.*[7] reported that the thermal stability of polymers was clearly improved on introducing an increased fluorine content.

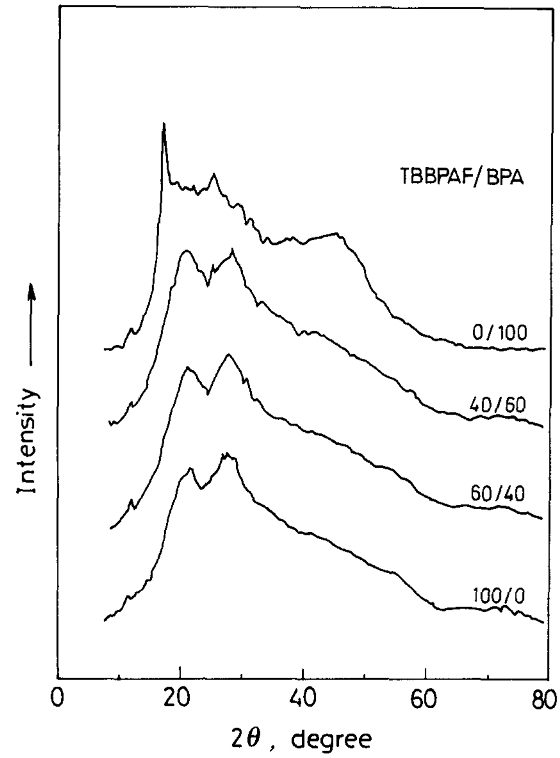


Figure 2 The X-ray diffraction patterns of polycarbonates (TBBPAF/BPA: 100/0, 60/40, 40/60, 0/100)

T_g of bisphenol A- and tetrabromobisphenol AF-based homopolycarbonate were 141 and 206°C, respectively. T_g of copolymers tended to increase monotonically between T_g of the two homopolymers as the proportion of tetrabromobisphenol AF was increased. T_g is reported to be 169°C for bisphenol AF-based homopolycarbonate[7]. T_g of brominated homopolycarbonate derived from tetrabromobisphenol AF is higher than that of unbrominated polycarbonate.

Figure 3 shows stress–strain curves for films of four typical polycarbonates (tetrabromobisphenol AF/bisphenol A: 80/20, 50/50, 20/80, 0/100). Polycarbonate

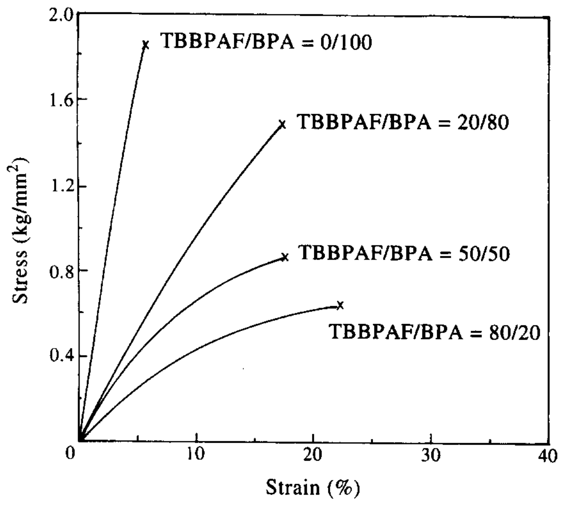


Figure 3 The stress–strain curves of polycarbonates (TBBPAF/BPA: 80/20, 50/50, 20/80, 0/100)

Table 3 Contact angle and limiting oxygen index of polycarbonates

Tetrabromobisphenol AF/bisphenol A/molar ratio	Contact angle[a] θ_w (deg)	Br[b] (%)	LOI
100/0	64.0	47.2	93.0
81/19	67.5	43.4	76.0
61/39	71.0	38.1	67.0
52/48	74.0	35.1	63.0
40/60	76.0	30.2	52.0
22/78	81.0	20.3	39.0
0/100	85.0	0.0	25.5

[a] Contact angle of water was measured at 25°C in air
[b] Mass fraction of bromine

(tetrabromobisphenol AF/bisphenol A: 100/0) formed no film on solution casting (in DMF). The elongation at break exceeded 17% for tetrabromobisphenol AF-containing copolycarbonates. This result indicates that the introduction of fluorine atom into the polycarbonate of bisphenol A type makes films more pliable. Saegusa *et al.*[7] reported that increased flexibility of films of fluorine-containing polycarbonates may be attributed to weaker intermolecular forces between polymer chains. Relative to the unbrominated bisphenol AF-based polycarbonate[7], the elongation of brominated polycarbonates decreased.

Contact angles (θ_w) of TBBPAF/BPA copolycarbonates are summarized in *Table 3* and *Figure 4*. The contact angles are in the range 64–85°. As shown in *Figure 4*, the contact angles of the copolymers tended to decrease monotonically as the proportion of TBBPAF was increased. However, in general, the contact angle should increase with increasing fluorine atom content. This result may be due to the bromination of the polymer increasing its overall hydrophilicity[19,20] irrespective of the content of fluorine. The critical surface tension (γ_c) of bisphenol A-based homopolycarbonate is 45×10^{-3} N m^{-1} at 20–25°C[21]. *Figure 5* presents the Zisman plot for TBBPAF/BPA: 50/50 copolycarbonate obtained with mixtures of butanol and water as wetting liquids at 25°C in air. γ_c was about 23×10^{-3} N m^{-1} (*Figure 5*), which is remarkably less than that of bisphenol A-based homopolycarbonate. This phenomenon may be due to the presence of fluorine groups with smaller surface energies[7].

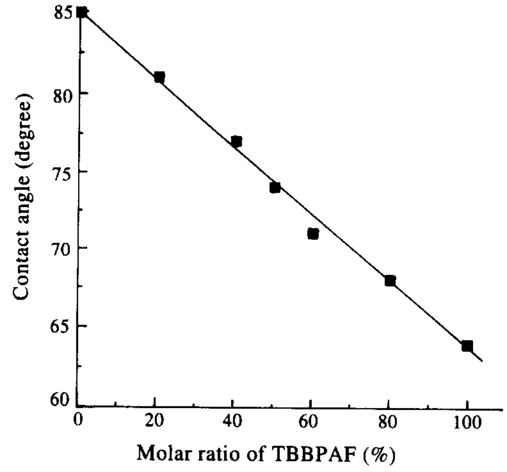


Figure 4 Contact angles of TBBPAF/BPA copolycarbonates

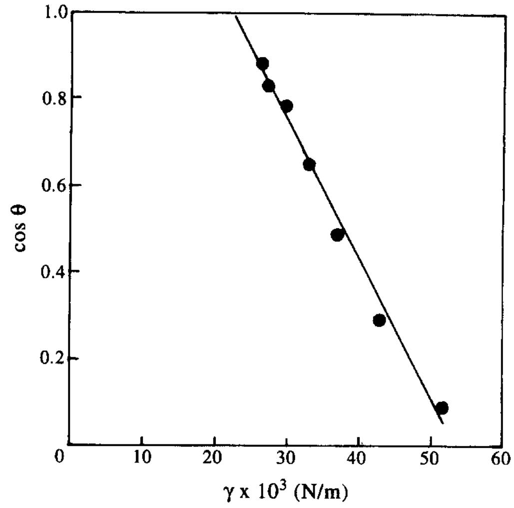


Figure 5 Plot of the cosine of the contact angle, θ, made by droplets of a series of *n*-butanol–water mixtures on TBBPAF/BPA = 50/50 copolycarbonate at 25°C

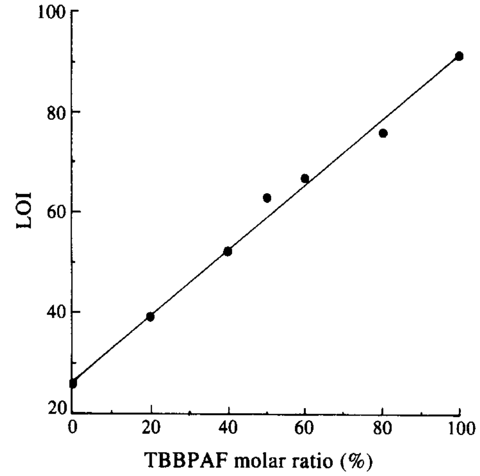


Figure 6 LOI value of TBBPAF/BPA copolycarbonates

The value of LOI of homopolycarbonates and copolycarbonates are presented in *Table 3*. LOI of bisphenol A- and tetrabromobisphenol AF-based homopolycarbonate were 25.5 and 93, respectively. The LOI of the polymers increases approximately with the proportion of tetrabromobisphenol AF in the polycarbonate backbone (*Figure 6*). The relationship between LOI and the content of tetrabromobisphenol AF in the copolymers follows equation (4)

$$\mathrm{LOI} = 25.5 + 0.651X \tag{4}$$

in which X is the molar percentage of tetrabromobisphenol AF in the copolycarbonates. The polycarbonate derived from tetrabromobisphenol AF has good flame retardancy, as indicated by the large limiting oxygen index 93.

CONCLUSIONS

Brominated polycarbonates and copolycarbonates were successfully synthesized on polycondensation of brominated bisphenol AF and/or bisphenol A with trichloromethyl chloroformate and a phase-transfer catalyst at 25°C. The homopolycarbonate of greatest inherent viscosity ($0.77\,\mathrm{dl\,g^{-1}}$) may reflect that bisphenol A having an electron-releasing group increases the nucleophilic properties of the phenolate anion. X-ray diffraction measurements on powders showed that all polycarbonates were essentially semicrystalline. Almost all polycarbonates were soluble in acetone, NMP, DMF, THF, chloroform, pyridine, nitrobenzene, 1,1,2,2-tetrachloroethane. Polycarbonates containing brominated bisphenol AF were more wettable than homopolycarbonate based on bisphenol A. T_g of brominated bisphenol AF-based homopolycarbonate was 206°C, much greater than for homopolycarbonate based on bisphenol A or bisphenol AF. These polymers obtained from aromatic bisphenols lost no mass below 394°C in nitrogen. Polycarbonates derived from brominated bisphenol AF have good thermal stability and flame retardancy, as indicated by the large limiting oxygen index 93.

ACKNOWLEDGEMENTS

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