

# Synthesis and characterization of copolycarbonates from melt transesterification

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Novel copolycarbonates of six types were prepared via melt polycondensation of various aromatic and aliphatic diphenyl dicarbonates and monomers, including bisphenol A, bisphenol S, bis[4-( $\beta$ -hydroxyethoxy)phenyl]sulfone and bisphenol AF, giving copolycarbonates in four series of each type. The copolycarbonates were characterized with infra-red spectra, inherent viscosity, differential scanning calorimetry, thermogravimetric analysis, X-ray diffraction, solubility and contact angle measurements. Copolycarbonates had inherent viscosities in the range 0.28–0.45 dl g<sup>-1</sup>. The copolycarbonates were soluble in *N*-methylpyrrolidinone, dimethylformamide, pyridine, dimethylsulfoxide and phenol. The glass transition temperatures ( $T_g$ ) of the copolycarbonates were in the range 79–159°C. Copolycarbonates containing bromine have a higher  $T_g$  and a lower  $T_d^{10}$  (temperature at which there is 10% loss of mass). These brominated copolycarbonates have good flame retardancy, indicated by their large limiting oxygen index in the range 52–70. Copolycarbonates based on tetrabromobisphenol S are more wetttable than copolymers without bromine. Copyright © 1996 Elsevier Science Ltd.

(Keywords: diphenyl dicarbonate; copolycarbonate; characterization)

## INTRODUCTION

Aromatic polycarbonates are commercially exploited as an engineering plastic in various fields because of their good thermal and chemical stabilities. Polycarbonates are produced commercially by interfacial polymerization and melt transesterification. The most commonly used monomers are bisphenol A and phosgene<sup>1–6</sup>. Commercial polycarbonates are produced mainly through polycondensation in solution at low temperature with phosgene as a carbonylation agent. Because phosgene vapour is extremely toxic, this preparative method is unfavourable for polycarbonate synthesis on a laboratory scale<sup>7</sup>.

A homopolycarbonate such as bisphenol A polycarbonate is a widely used engineering thermoplastic because of its high performance. Numerous copolycarbonates based on bisphenol A and assorted other diphenols have been prepared to improve on the properties of the homopolymers<sup>2,8,9</sup> such as solubility, crystallinity, flame retardancy and thermal ageing characteristics. Among the most significant characteristic of copolymers in general is their chain sequence architecture. Many authors have addressed the synthesis of copolycarbonates by phosgenation<sup>10,11</sup> or melt transesterification<sup>12–14</sup>. The disadvantage of phosgenation is that it is difficult to control the preparation of bischloroformate. Furthermore, all structures of polycarbonates prepared by melt transesterification

originated in order to synthesize thermotropic liquid-crystalline polycarbonates<sup>12–14</sup>.

We synthesized novel aromatic and aliphatic copolycarbonates from diphenyl dicarbonates of six types by melt transesterification. The purpose of our work was to investigate the effect of structures of copolycarbonates on the physical properties and reactivity by introducing an electron-releasing group or electron-withdrawing group, an aromatic group or aliphatic group, and bromine substituents into the main chains. The effect of bromine atoms, ether groups and linear alkylene groups on the physical properties of copolycarbonates, such as solubility, surface properties and thermal behaviour, is discussed in detail.

## EXPERIMENTAL

### Materials and measurement

Bisphenol S (Hailsun Chemical Co., Taiwan) was purified by recrystallization from a solution in methanol and benzene (1:3 v/v) (1 g to 6 ml of solvent), m.p. = 248°C<sup>15</sup>. Bisphenol AF was recrystallized from benzene, m.p. = 163–165°C, as was commercial bisphenol A, m.p. = 155–156°C. Ethylene carbonate, bromine, phenyl chloroformate and zinc acetate were purchased (Merck Co.). The solvents were purified according to standard methods. I.r. spectra were recorded in the range 4000–400 cm<sup>-1</sup> for the synthesized monomers and polymers in KBr discs (Jasco IR-700 spectrometer). The inherent viscosities  $\eta_{inh}$  were measured in an

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**Table 1** Results of syntheses of diphenyl dicarbonates

Dicarbonate	$T_m$ (°C)	Yield (%)	I.r. <sup>a</sup> (cm <sup>-1</sup> )	Elemental analysis (%)									
				C		H		O		S		Br	
				Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
A BPADC	88	82	1772	74.38	74.36	5.24	5.13	20.56	20.51	-	-	-	-
B BPAFDC	107	91	1765	60.57	60.41	3.26	3.12	<sup>b</sup>	<sup>b</sup>	-	-	<sup>b</sup>	<sup>b</sup>
C BPSDC	161	96	1772	63.69	63.67	3.73	3.67	26.04	26.10	6.54	6.53	-	-
D HEPSDC	130	81	1752	61.57	62.28	4.59	4.50	28.22	27.68	5.52	5.53	-	-
E TBBPSDC	199	86	1779	38.50	38.70	1.76	1.74	15.53	15.90	7.88	7.95	39.78	39.70
F 1,4-BTDC	79	95	1750	65.77	65.50	5.57	5.54	28.66	28.69	-	-	-	-

<sup>a</sup> Wavenumber of -O-C(=O)-O- peak, in KBr discs<sup>b</sup> F prevents the determination of O and Br with elemental analysis

Ubbelohde viscometer at a concentration 0.5 g dl<sup>-1</sup> in *N*-methylpyrrolidinone (NMP). Elemental analysis of the monomers was carried out (Perkin-Elmer 2400 instrument). X-ray diffraction patterns were recorded of powders with an X-ray diffractometer (Philips model PW 1710). Samples for d.s.c. measurements (Du Pont 9000) were heated in aluminium pans at a rate of 10°C min<sup>-1</sup>. <sup>13</sup>C n.m.r. spectra were recorded (Bruker AM-300 WB FT-NMR spectrometer). Samples for thermogravimetric analysis (Du Pont 9900 instrument) were heated under nitrogen at 10°C min<sup>-1</sup>. The LOI (limiting oxygen index) was determined (SUGA instrument) according to ASTM D 2863-77. 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 use of a sessile drop of volume 2 μl.

#### Monomer synthesis

**Bisphenol S diphenyl dicarbonate (BPSDC (compound C)).** Phenyl chloroformate (0.42 mol) was added dropwise to bisphenol S (0.2 mol), pyridine (0.46 mol) and tetrahydrofuran (THF) (300 ml) below 10°C during 30 min. The mixture was reacted for another 4 h at 25°C and poured into water. The precipitate was filtered out and washed with aqueous Na<sub>2</sub>CO<sub>3</sub> (10%) several times, recrystallized from ethyl acetate, and then dried at 60°C overnight under vacuum. The final product was a white powder (m.p. 161°C) in 96% yield.

**Other monomers.** Bisphenol A diphenyl dicarbonate (BPADC (A)), bisphenol AF diphenyl dicarbonate (BPAFDC (B)), bis[4-(β-hydroxyethoxy)phenyl]sulfone (HEPS) diphenyl dicarbonate (HEPSDC (D)), tetrabromobisphenol S diphenyl dicarbonate (TBBPSDC (E)) and 1,4-butanediol diphenyl dicarbonate (1,4-BTDC (F)) were prepared as described for BPSDC<sup>12</sup>.

#### Polymerization

**Copolycarbonate C1.** Bisphenol A (10 mmol), bisphenol S diphenyl dicarbonate (10 mmol) and zinc acetate (50 mg) under a nitrogen atmosphere were stirred mechanically in a spherical glass vessel for 1 h at 170°C, then for 30 min at 200°C, and for another 30 min at 220°C. The temperature was then raised to 260°C at 4000 Pa for 30 min and to 300°C at 550 Pa for another 30 min.

Copolymers of types A, B, C, D and F were synthesized as described for C1.

**Copolycarbonate E1.** Bisphenol A (10 mmol), tetrabromobisphenol S diphenyl dicarbonate (10 mmol) and zinc acetate (50 mg) were stirred mechanically at 210°C for 1 h under a nitrogen atmosphere. The reaction continued for another hour at 240°C. The temperature was then raised to 280°C at 4000 Pa for 1 h and to 300°C at 550 Pa for 30 min. The inherent viscosity was measured at a concentration of 0.5 g dl<sup>-1</sup> in NMP at 25°C.

Other copolycarbonates of type E were synthesized as described for E1.

## RESULTS

### Characterization of monomers

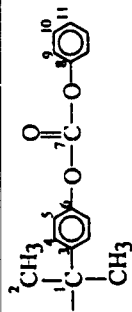
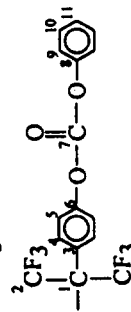
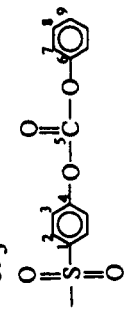
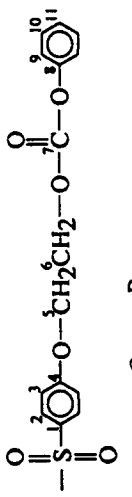
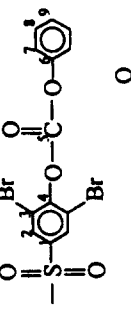
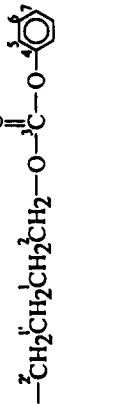
Diphenyl dicarbonates were synthesized from phenyl chloroformate and various diols. The diphenyl dicarbonate monomers obtained in higher yield were characterized by elemental analysis, melting point and i.r. spectra (KBr discs) as shown in Table 1. The C=O absorptions of diphenyl dicarbonate monomers were in the range 1750–1779 cm<sup>-1</sup>; the C=O wavenumbers of aliphatic monomer (HEPSDC) and alkylene monomer (1,4-BTDC) were smaller than for aromatic monomers. The melting points of diphenyl dicarbonates were in the range 79–199°C. According to Table 1, the results of elemental analysis agreed satisfactorily with theoretical values. Table 2 presents the characterization of new diphenyl dicarbonates by <sup>13</sup>C n.m.r. spectra (chemical shifts vs. tetramethylsilane, TMS). The signals near 152–155 ppm belong to the carbonyl groups of diphenyl dicarbonate.

### Polymerization of diphenyl dicarbonates with various diols

Several copolycarbonates (A1–F4) were prepared by melt polycondensation of various diphenyl dicarbonates and diols in the presence of zinc acetate as transesterification catalyst. Diols including bisphenol A (1), bisphenol S (2), bis[4-(β-hydroxyethoxy)phenyl]sulfone (HEPS) (3) and bisphenol AF (4) were used. Scheme 1 illustrates the synthesis of copolymers from the reaction of various diphenyl dicarbonates with diols in melt polycondensation. The polymers obtained were characterized by inherent viscosity, i.r. spectra, X-ray diffraction, solubility, thermogravimetric analysis (t.g.a.), differential scanning calorimetry (d.s.c.), contact angle ( $\theta_w$ ) and limiting oxygen index (LOI).

Table 3 presents i.r. data of the copolycarbonates<sup>15–18</sup>. For instance, the i.r. spectrum of copolycarbonate A2

Table 2 <sup>13</sup>C n.m.r. chemical shifts (vs. TMS) of diphenyl dicarbonates

Dicarbonate	Structure	Solvent <sup>a</sup>	δ (ppm)										
			1	2	3	4	5	6	7	8	9	10	11
A		A	43.1	31.0	149.3	128.7	121.4	150.0	152.8	152.1	121.9	130.4	127.0
B		A	63.6	127.2	122.2	130.4	116.0	152.3	152.6	152.0	121.8	132.3	131.5
C		D	138.7	129.9	121.1	154.2	150.7	150.3	122.9	128.8	126.6		
D		D	133.8	129.6	121.1	161.7	66.1	66.7	153.0	150.6	115.3	129.0	126.1
E		A	135.5	130.3	115.9	162.9	154.2	152.1	121.8	130.2	126.8		
F		A	25.8	68.9	154.3	152.3	122.0	130.3	126.8				

<sup>a</sup> A: acetone-d<sub>6</sub>; D: DMSO-d<sub>6</sub>

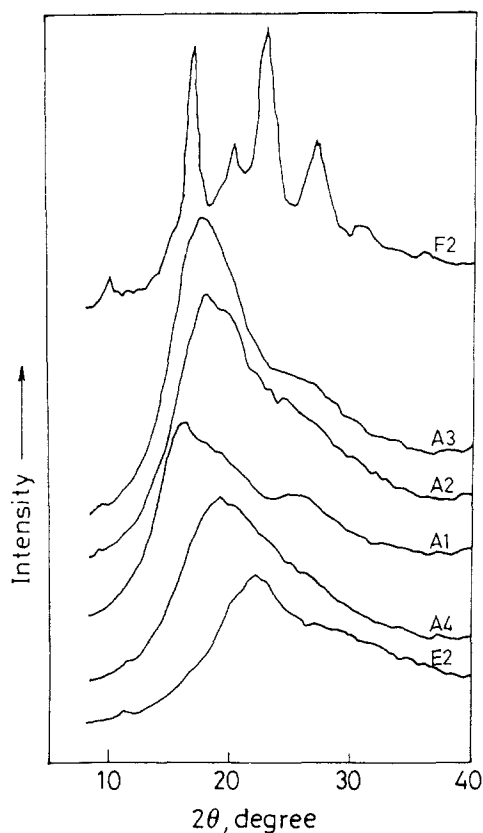
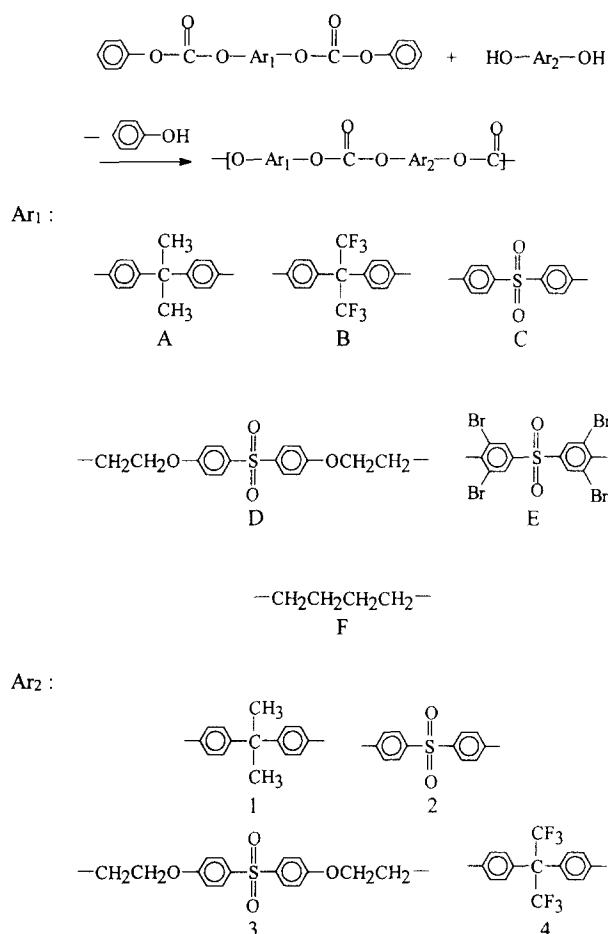


Figure 1 X-ray diffraction patterns of copolymers

Scheme 1

Table 3 I.r. spectra of copolycarbonates

Polymer code	Wavenumber (cm <sup>-1</sup> ) in KBr				
	C=O	C-O-C	-CH <sub>3</sub>	-SO <sub>2</sub>	C-Br
A1	1766	1241	2958		
A2	1765	1250	2958	1144, 1302	
A3	1759	1248	2956	1142, 1300	
A4	1771	1240	2960		
B1	1772	1246	2966		
B2	1772	1250	-	1143, 1298	
B3	1760	1243	-	1143, 1310	
B4	1774	1240			
C1	1766	1245	2958	1143, 1304	
C2	1770	1240	-	1148, 1310	
C3	1743	1246	-	1140, 1308	
C4	1769	1241	-	1145, 1311	
D1	1750	1240	2956	1145, 1308	
D2	1744	1246	-	1145, 1310	
D3	1736	1248	-	1155, 1310	
D4	1755	1250	-	1142, 1305	
E1	1766	1247	2956	1156, 1308	789
E2	1777	1245	-	1155, 1310	794
E3	1758	1248	-	1145, 1305	788
E4	1772	1250	-	1148, 1313	786
F1	1754	1243	2952		
F2	1759	1251		1144, 1316	
F3	1743	1246		1147, 1311	
F4	1760	1250			

that showed a C=O mode at 1765 cm<sup>-1</sup> and a -C-O-C- mode at 1250 cm<sup>-1</sup> indicates the presence of a carbonyl group in a BPA-BPS copolycarbonate. The i.r. spectra show that the wavenumber of the C=O mode in copolycarbonates containing an aliphatic or alkylene group is less than that of copolycarbonates based on an aromatic group.

X-ray diffraction measurements of the polymers indicated that all copolycarbonates were essentially amorphous except those based on 1,4-BTDC. Copolycarbonates derived from 1,4-BTDC were semicrystalline. X-ray diffraction patterns of some typical copolymers appear in Figure 1 with intensity as a function of 2θ; θ is the angle of diffraction (Bragg angle). Copolycarbonate F2 has the greatest crystallinity, possibly because introducing a linear alkylene group into a polymer backbone favours regular packing of the polymer chain. However, the copolycarbonate E2 containing bromine, which has a large van der Waals radius and which disturbs the molecular arrangement, has the least diffraction intensity<sup>7,19,20</sup>.

Table 4 shows the qualitative solubility behaviour of copolycarbonates. Almost all copolycarbonates were soluble in NMP, dimethylformamide (DMF), pyridine, dimethylsulfoxide (DMSO) and phenol but insoluble in typical organic solvents such as acetone, methanol and 1,4-dioxane. The solubility of copolycarbonates containing fluorine (type B and series 4) greatly exceeded that of other copolycarbonates. Several researchers reported that solubility is improved with flexible hexafluoroisopropylidene groups between rigid phenyl rings in the polymer backbone<sup>21,22</sup>. The solubility of copolycarbonates containing bisphenol S (type C and series 2) is less

**Table 4** Solubility of copolycarbonates in various solvents<sup>a</sup>

Polymer code	Acetone	THF	NMP	Methanol	DMSO	DMF	Pyridine	Chloroform	1,4-Dioxane	Phenol
A1	-	+	++	-	+-	+-	+-	+	+	+
A2	-	+	++	-	+-	+	+	+-	+-	+
A3	-	++	++	-	++	++	++	++	++	+
A4	++	++	++	-	++	++	++	++	++	+
B1	+-	+-	+-	-	+-	+-	+-	+	-	+-
B2	+-	++	+	-	+	++	++	+-	+-	+
B3	++	++	++	-	++	++	++	+-	+-	+
B4	++	++	++	-	++	+	++	+	+	+
C1	-	-	++	-	++	+-	++	+	-	+
C2	-	-	++	-	++	++	++	-	-	+
C3	-	+-	++	-	++	++	++	-	-	+
C4	+	+-	++	-	++	++	++	+-	+-	+
D1	-	-	+-	-	+-	+-	+-	+-	+-	+-
D2	-	-	+	-	++	+	++	-	-	+
D3	+-	+-	++	-	++	++	++	-	+-	+
D4	+	+	++	-	+-	++	++	+-	+-	+
E1	+	++	++	-	++	++	++	+-	+-	+
E2	+-	+	++	-	++	++	++	-	+-	+
E3	+-	++	++	-	++	++	++	-	+	+
E4	++	++	++	-	++	++	++	+-	++	+
F1	-	+	++	-	+-	+	++	+-	+-	+
F2	-	-	++	-	+-	+	+-	-	-	+
F3	-	-	++	-	++	++	++	-	+-	+
F4	+	+	++	-	++	++	++	-	+-	+

<sup>a</sup> Solubility: ++, soluble at 25°C; +, soluble on heating to 60°C; +-, partially soluble; -, insoluble

than that of copolycarbonates containing bisphenol A (type A and series 1). Liaw *et al.*<sup>19</sup> reported that polyesters containing a sulfonyl group, which has a small van der Waals radius, have a relatively large degree of crystallinity. The HEPS-based copolycarbonates (type D and series 3) containing the oxyethylene unit are more soluble than copolycarbonates based on BPS. Copolycarbonates having a linear alkylene group in the backbone (type F) are less soluble than copolycarbonates of type D because the latter has flexible ether linkages in its main chain<sup>23</sup>.

The inherent viscosities and thermal behaviours of copolycarbonates are summarized in Table 5. The copolycarbonates had moderate inherent viscosities, 0.28–0.45 dl g<sup>-1</sup>.

The copolycarbonates synthesized from bisphenol A (series 1) have greater inherent viscosities than copolycarbonates based on bisphenol S (series 2), HEPS (series 3) and bisphenol AF (series 4). This phenomenon may reflect that diols having an electron-releasing group increased the nucleophilic properties of the phenolate anion<sup>18</sup>. As diol 3 having an aliphatic oxyethylene unit (series 3) cannot form an alcoholate anion, it seems difficult for nucleophilic attack to proceed on the carbonyl group to give the polymer of decreased inherent viscosity. In comparison with the various diphenyl dicarbonates, the copolycarbonates prepared from BPADC (type A) have a smaller inherent viscosity. However, copolycarbonates prepared from BPAFDC (type B), BPSDC (type C) and HEPSDC (type D) have larger inherent viscosities. This phenomenon may reflect that an electron-withdrawing group, such as sulfonyl or hexafluoropropane, introduced into the diphenyl dicarbonate facilitates formation of the phenoxy anion, thus increasing their reactivities.

The thermal behaviour of copolycarbonates was evaluated by means of t.g.a. and d.s.c. The glass

**Table 5** Thermal properties of copolymers

Polymer code	$\eta_{inh}^a$ (dl g <sup>-1</sup> )	$T_g$ (°C)	$T_d^{10b}$ (°C)	Residual mass at 500°C (%)
A1	0.42	135	407	25.0
A2	0.30	134	404	28.8
A3	0.28	92	353	15.4
A4	0.33	138	410	33.7
B1	0.45	141	413	35.1
B2	0.34	135	407	39.6
B3	0.31	105	365	28.8
B4	0.34	148	443	45.1
C1	0.39	138	403	36.8
C2	0.30	132	380	45.3
C3	0.30	101	347	30.1
C4	0.37	143	410	47.4
D1	- <sup>c</sup>	120	385	20.5
D2	0.39	111	365	30.9
D3	0.35	79	353	20.2
D4	0.43	135	396	36.7
E1	0.34	151	364	59.8
E2	0.31	146	361	64.4
E3	0.30	125	343	54.2
E4	0.32	159	371	64.9
F1	0.43	101	369	13.3
F2	0.37	98	360	24.6
F3	0.33	89	354	19.7
F4	0.36	107	374	20.2

<sup>a</sup> Measured at a concentration of 0.5 g dl<sup>-1</sup> in NMP at 25°C

<sup>b</sup>  $T_d^{10}$  is the temperature at which 10% loss of mass was observed

<sup>c</sup> Insoluble in NMP

transition temperatures ( $T_g$ ) are presented in Table 5. The glass transition temperatures of copolycarbonates were in the range 79–159°C. The effect of diol and diphenyl dicarbonate on the glass transition of copolycarbonates is discussed in detail. Among the four diols,

$T_g$  of copolycarbonates (series 4) prepared from BPAF is the highest. Copolycarbonates based on BPS (series 2) or HEPS (series 3) have a lower  $T_g$ . This may reflect that BPS and HEPS have a characteristically electron-withdrawing sulfonyl group, which favours both decreased reactivity and inherent viscosity of polycarbonates<sup>19</sup>. Furthermore, the copolycarbonates (series 3) based on HEPS have the lowest  $T_g$  because flexible ether linkages are present in the polymer backbone<sup>16</sup>. In comparison with the diphenyl dicarbonate, copolycarbonates derived from brominated bisphenol S diphenyl dicarbonate (**E1–E4**) have a higher  $T_g$ . Liaw *et al.*<sup>17</sup> and Marks<sup>11</sup> reported that  $T_g$  of a brominated polycarbonate exceeds that of an unbrominated polycarbonate. Among copolycarbonates based on unbrominated diphenyl dicarbonate, the BPAFDC-based copolycarbonates (**B1–B4**) have the greatest  $T_g$  because of the fluorine atom. The  $T_g$  of copolycarbonates of type **D** (**D1–D4**) and type **F** (**F1–F4**) containing aliphatic oxyethylene and alkylene groups, respectively, is smaller than for copolycarbonates of other types. The thermal stabilities of copolycarbonates was tested with thermogravimetry. Table 5 summarizes the temperature ( $T_d^{10}$ ) at which 10% loss of mass was observed, and the mass residues at 500°C. The  $T_d^{10}$  of copolycarbonates was in the range 343–443°C and the residual mass was in the range 15.4–64.9%. Among copolycarbonates based on various bisphenols and an aliphatic diol, the copolycarbonates (series 4) synthesized from BPAF have the highest  $T_d^{10}$ . Thus, thermal stability of copolymers was clearly improved on introduction of fluorine atoms (series 4)<sup>7</sup>. Copolycarbonates prepared from HEPS (series 3) had the least  $T_d^{10}$  and residual mass at 500°C, because of the flexible ether linkage of the polymer<sup>17,18</sup>. Copolycarbonates based on BPS (series 2) have smaller  $T_d^{10}$  than copolycarbonates based on BPA (series 1) because of its lower reactivity. However, greater residual mass was observed for copolycarbonates based on BPS and BPAF because of their sulfone and hexafluoroisopropylidene groups, respectively. Copolycarbonates derived from aromatic diphenyl dicarbonates (BPAFDC, BPSDC and BPADC) have greater  $T_d^{10}$  than copolycarbonates derived from aliphatic or brominated aromatic diphenyl dicarbonates. According to Table 5 polymers (type **E**) having bromine atoms degraded at the lowest temperature but yielded the greatest char, because hydrogen bromide is easily evolved from bromine-containing polymers during thermal degradation<sup>17,18</sup>. Although copolycarbonates BPA/HEPS, prepared from either HEPSDC/BPA (**D1**) or BPADC/HEPS (**A3**), have similar structures, **D1** and **A3** have distinct thermal behaviours. The greater  $T_g$  and  $T_d^{10}$  of **D1** may reflect the greater inherent viscosity of copolycarbonate **D1**, synthesized from the BPA diol having an electron-releasing group, whereas diphenyl dicarbonate (HEPSDC) has an electron-withdrawing group.

The wettability data of copolycarbonate films for water at 25°C in air are compiled in Table 6. The contact angles ( $\theta_w$ ) of copolycarbonates were in the range 40–93°. Compared with diols, copolycarbonates derived from BPAF (series 4) have the greatest contact angles, perhaps due to the presence of the hydrophobic trifluoromethyl groups of BPAF<sup>7,17</sup>. The copolycarbonates derived from HEPS (series 3) have the smallest contact angles ( $\theta_w$ ), possibly reflecting both the hydrophilic sulfonyl group

Table 6 Wettability and flame retardation of copolycarbonates

Polymer code	Contact angle $\theta_w$ (deg)	LOI
A1	84	
A2	77	
A3	64	
A4	89	
B1	89	
B2	83	
B3	76	
B4	93	
C1	80	29
C2	78	34
C3	60	30
C4	82	35
D1	74	
D2	70	
D3	68	
D4	80	
E1	54	52
E2	45	55
E3	40	50
E4	62	70
F1	81	
F2	76	
F3	73	
F4	84	

and the more polar surfaces of polycarbonates on the introduction of oxyethylene units. This phenomenon was also observed by Hu *et al.*<sup>24</sup> for a biodegradable copolymer poly(ethylene glycol)/poly(L-lactide). Copolycarbonates of type **F** have greater contact angles than those of types **C**, **D** and **E** because of the hydrophobic alkylene group in the backbone. The copolycarbonates derived from TBBPSDC (type **E**) have the smallest contact angle ( $\theta_w$ ), perhaps due to the bromination of polymers, which increases their overall hydrophilicity<sup>20,25</sup>.

The measured LOI values are also shown in Table 6. All brominated copolycarbonates based on brominated bisphenol S (type **E**) have greater fire resistance than the corresponding unbrominated copolycarbonates (type **C**). Several researchers reported that halogen imparts flame retardation to polyphosphonates<sup>20,26,27</sup>, polyamides<sup>28</sup> and polyesters<sup>29–31</sup>, thus resulting in increased LOI. The LOI of bisphenol S (**C2** and **E2**) and bisphenol AF based (**C4** and **E4**) copolycarbonates exceed those of corresponding polycarbonates based on bisphenol A (**C1** and **E1**), possibly due to the presence of sulfonyl and hexafluoropropane groups in addition to the phenyl rings. The LOI of copolycarbonates derived from HEPS (**C3** and **E3**) are less than those of copolycarbonates based on bisphenol S (**C2** and **E2**), possibly because HEPS containing the oxyethylene group has a greater ratio of oxygen to carbon than bisphenol S.

## CONCLUSIONS

Novel copolycarbonates were prepared successfully on melt transesterification from aromatic and aliphatic diphenyl dicarbonates of six types with diols of four kinds. Diols having an electron-releasing group such as bisphenol A increased the nucleophilic properties of the phenolate anion to increase the inherent viscosity. Diols

such as bisphenol AF and bisphenol S having an electron-withdrawing group gave less favourable results. Diols having an aliphatic oxyethylene unit gave the least favourable result of inherent viscosity. Diphenyl dicarbonates having an electron-withdrawing group easily form the phenoxy anion, thus increasing their reactivities. The greatest inherent viscosity is obtained from the reaction of diphenyl dicarbonate containing an electron-withdrawing group with diol having an electron-releasing group. Diffraction diagrams showed that copolycarbonates of types **A**, **B**, **C**, **D** and **E** were amorphous but copolycarbonates of type **F** were semicrystalline. Copolycarbonates containing bromine atoms have superior  $T_g$  and flame retardation.

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#### REFERENCES

- Schnell, H. *Angew. Chem.* 1956, **68**, 33
- Schnell, H. 'Chemistry and Physics of Polycarbonates', Wiley Interscience, New York, 1964
- Bottenbruch, L. *Encycl. Polym. Sci. Technol.* 1969, **10**, 710
- Bela, V. F. and Guenter, S. *Angew. Makromol. Chem.* 1982, **108**, 41
- Jacob, S. and Stejskal, E. O. *Macromolecules* 1985, **18**, 368
- Floudas, G. and Higgins, J. S. *Macromolecules* 1993, **26**, 1676
- Saegusa, T., Kuriki, M., Kawai, A. and Nakamura, S. *J. Polym. Sci. (A) Polym. Chem.* 1990, **28**, 3327
- Freitag, D., Grigo, U., Mueller, P. and Nouvertne, W. in 'Encyclopedia of Polymer Science and Technology', Vol. 11, Wiley, New York, 1987, p. 648
- Christopher, W. and Fox, D. 'Polycarbonates', Reinhold, New York, 1962
- Tenigul, M., Parson, I. W., Hay, J. N. and Haward, R. N. *Polymer* 1983, **24**, 1313
- Marks, M. J. *J. Appl. Polym. Sci.* 1994, **52**, 467
- Sato, M., Hirata, T., Takemo, N. and Mukaida, K. *Makromol. Chem.* 1991, **192**, 139
- Sun, S. J. and Chang, T. C. *J. Polym. Sci. (A) Polym. Chem.* 1993, **31**, 2711
- Sun, S. J. and Chang, T. C. *J. Polym. Sci. (A) Polym. Chem.* 1993, **31**, 2237
- Liaw, D. J. and Shen, W. C. *Angew. Makromol. Chem.* 1992, **199**, 171
- Liaw, D. J. and Shen, W. C. *Angew. Makromol. Chem.* 1992, **200**, 137
- Liaw, D. J. and Chang, P. *J. Appl. Polym. Sci.* submitted
- Liaw, D. J. and Chen, P. S. *J. Polym. Sci. (A) Polym. Chem.* 1996, **34**, 885
- Liaw, D. J. *J. Polym. Sci. (A) Polym. Chem.* 1995, **33**, 605
- Liaw, D. J. and Chen, P. S. *Polymer* 1995, **36**, 4491
- Liaw, D. J. and Wang, K. L. *J. Polym. Sci. (A) Polym. Chem.* in press
- Yang, C. P. and Chen, W. T. *J. Polym. Sci. (A) Polym. Chem.* 1993, **31**, 1571
- Ghassemi, H. and Hay, A. S. *Macromolecules* 1994, **27**, 3116
- Hu, S. G., Liu, H. J. and Pan, I. L. *J. Appl. Polym. Sci.* 1993, **50**, 1391
- Garti, N. and Aserin, A. *J. Dispers. Sci. Technol.* 1987, **8**(2) 113
- Liaw, D. J. and Shen, W. C. *Polymer* 1993, **34**, 1336
- Liaw, D. J. and Wang, D. W. *React. Polym.* in press
- Yang, C. P. and Hsiao, S. H. *J. Polym. Sci. (A) Polym. Chem.* 1990, **28**, 871
- Yang, C. P. and Hsiao, S. H. *J. Appl. Polym. Sci.* 1988, **36**, 1221
- Kenichi, H., Isamu, H., Kenji, Y. and Daisuke, S. *Ger. Offen.* 2606279 1976
- Albert, W. *US Pat.* 4322521 1982