

Synthesis and Characterization of Alternating Block Copolycarbonates Containing Constituent Groups of Polysulfone

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Abstract: A series of alternating and alternating block copolycarbonates containing the constituent groups of polysulfone was synthesized through a multi-step solution condensation method. For the regulation of block length, monodisperse oligomers were prepared by using a large excess of the bisphenols and were subsequently incorporated into the copolymer chains. Separating the unreacted bisphenols from the oligomers by dissolution/precipitation steps took advantage of solubility differences. The structures of the monomers, oligomers, and copolymers were characterized and confirmed by GPC, NMR spectroscopy, mass spectrometry, and elemental analysis. Monodispersity of the oligomers, which is critical for control over the block length in the copolymers, was confirmed by GPC and mass spectrometry. Of the two constituent groups of the polysulfone, the sulfone linkage stiffens the polycarbonate copolymer chain, while the ether linkage softens it.

Keywords: alternating, copolymer, oligocarbonate, polycarbonate, polysulfone.

Introduction

Our effort for the preparation of alternating block copoly-carbonate containing sulfone and ether linkages is prompted by the need for a model copolymer system for studying the relaxation behavior of bisphenol A polysulfone (PSF) based on that of bisphenol A polycarbonate (PC). Another purpose for the preparation of the copolymers is to investigate the effect of structural change by incorporating the structural units of PSF on stiffness of PC chain. PC is one of the most widely used engineering plastics, which possess excellent toughness, moderate heat resistance, and optical clarity. As it is widely recognized that the macroscopic mechanical properties of PC is related to the existence of the pronounced secondary relaxation of the polymer, numerous studies on the structure modifications including block copolymers of PC have been reported to study the effect of chemical structure on the mechanical properties.¹⁻⁴ The modifications have focused on the structure variation in the phenylene ring or in the connector group between the rings. PSF is one of super engineering plastics with better heat resistance and chemical stability over PC. As PSF is widely used for gas separation membranes, there have been many studies on the structural variations of PSF and their structure-permeability relation-

ship.⁵⁻⁹ The modifications on the PSF structures have been mostly putting various substituents on the phenylene rings in attempts to separate the chains. However, to the best of our knowledge, no attempt on the synthesis of copolymers that have the structural units of both PSF and PC has been reported.¹⁰

We report the design and synthesis of a series of copolymers, in which structural units of PC and PSF are alternating. Units such as isopropylidene diphenyl, diphenyl ether, and diphenyl sulfone are linked by carbonate group to form the copolymers. Copolymers that have tetramethyl-substituted phenylene rings are also prepared. In addition, alternating block copolymers that possess either bisphenol A or tetramethyl bisphenol A tr carbonate were synthesized. In polycondensation reactions interfacial polymerization technique is usually advantageous over solution polymerization for obtaining high molecular weight of the polymers.^{11,12} In this study, however, multi-step solution condensation route was employed, since alternating structure and the control of block length was more desirable than high molecular weight of the copolymers.^{13,14} For alternating block copolycarbonates that possess ether and sulfone units, the preparation of oligocarbonate with controlled length is critical. Although some previous studies have reported the preparation of block copolycarbonates from oligocarbonates, the block length seemed not to be precisely controlled.¹⁴⁻¹⁸ In this study, to ensure the monodispersity of block length, we used a large

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excess of bisphenol followed by the repeated dissolution/precipitation steps.

Experimental

Materials. Bisphenol A (BPA), bis(4-hydroxyphenyl) sulfone (BPS), and tetramethyl bisphenol A (TMBPA) were purchased from Aldrich, and bis(4-hydroxyphenyl) ether (BPO) and bis(4-hydroxy-3,5-dimethylphenyl) sulfone (TMBPS) were purchased from TCI. BPO was purified by passing through a column of silica gel (70-230 mesh) with tetrahydrofuran (THF) followed by recrystallization, while the other bisphenols were used as received. Phosgene, supplied as a gas from Matheson, was condensed in toluene at dry ice/acetone temperature before use. THF, toluene, and methylene chloride (MC) were purchased from JT Baker, and were dried over 4 Å molecular sieve before use. Other reagents used were purchased from either Aldrich or JT Baker and used without further purification, unless otherwise mentioned.

Synthesis of Bisphenol Bischloroformates. For the preparation of BPA bischloroformate (B-BCF), in a 1,000 mL reactor equipped with a mechanical stirrer, a condenser, and a dropping funnel, 500 mL of dry toluene was charged, and phosgene (79.14 g, 0.8 mol) was condensed over 1 h at dry ice/acetone temperature. After replacing the dry ice/acetone bath with an ice bath, a solution of BPA (22.83 g, 0.1 mol) and *N,N*-dimethylaniline (DMA, 30.30 g, 0.25 mol) in 250 mL of THF was added over 2 h. The reaction mixture was warmed slowly to room temperature and was allowed to stand for 12 h. Unreacted phosgene and most of the solvents were removed by bubbling nitrogen gas followed by applying reduced pressure. The mixture was diluted with 500 mL of toluene, and the solids were filtered off. The solution was passed through a column of silica gel (70-230 mesh), and the column was washed with toluene. After toluene was evaporated, the product was recrystallized using *n*-hexane: yield: 89%. ¹H NMR (CDCl₃, ppm): 1.61 (s, 6H, *i*-PrCH₃), 7.06 (d, 4H, PhH), 7.18 (m, 4H, PhH). MALDI-TOF MS: *m/z* = 353.17 (M + H)⁺, 375.00 (M + Na)⁺. Anal. Calcd for C₁₇H₁₄Cl₂O₄: C 57.81; H 4.00. Found: C 57.37; H 3.88.

The procedure for the synthesis of the other bischloroformates is identical to the one described above. E-BCF: yield 87%. ¹H NMR (CD₂Cl₂, ppm): 7.03-7.09 (m, 4H, PhH), 7.20-7.26 (m, 4H, PhH). MALDI-TOF MS: *m/z* = 326.32 (M + H)⁺, 348.03 (M + Na)⁺. Anal. Calcd for C₁₄H₈Cl₂O₅: C 51.40; H 2.47. Found: C 50.94; H 2.25.

S-BCF: yield 85%. ¹H NMR (CD₂Cl₂, ppm): 7.28-7.35 (m, 4H, PhH), 7.88-7.95 (m, 4H, PhH). MALDI-TOF MS: *m/z* = 374.96 (M + H)⁺. Anal. Calcd for C₁₄H₈Cl₂O₆S: C 44.82; H 2.15; S 8.55. Found: C 45.28; H 2.28; S 8.82.

T-BCF: yield 75%. ¹H NMR (CD₂Cl₂, ppm): 1.60 (s, 6H, *i*-PrCH₃), 2.13 (s, 12H, PhCH₃), 6.96 (s, 4H, PhH). MALDI-TOF MS: *m/z* = 408.94 (M + H)⁺, 430.92 (M + Na)⁺. Anal.

Calcd for C₂₁H₂₂Cl₂O₄: C 61.62; H 5.42. Found: C 61.28; H 5.33.

Z-BCF: yield 78%. ¹H NMR (CD₂Cl₂, ppm): 2.30 (s, 12H, PhCH₃), 5.32 (s, 4H, PhH), 7.66 (s, 4H, PhH). MALDI-TOF MS: *m/z* = 430.88 (M + H)⁺, 452.82 (M + Na)⁺. Anal. Calcd for C₁₈H₁₆Cl₂O₆S: C 50.13; H 3.74; S 7.43. Found: C 50.61; H 3.76; S 7.45.

Synthesis of Bisphenol Tricarbonates: B3 and T3 Oligomers. For the preparation of BPA tricarbate (B3), BPA (91.32 g, 0.40 mol) in 350 mL of THF and pyridine (7.91 g, 0.10 mol) were charged in a 1,000 mL reactor equipped with a mechanical stirrer and a dropping funnel. B-BCF (8.83 g, 0.025 mol) in 400 mL of THF was added dropwise through a dropping funnel at ice bath temperature. The reaction stood for 12 h at room temperature after removing the ice bath. After the salts were filtered off and most of THF and pyridine were evaporated, the concentrated solution (about 100 mL) was dissolved in 200 mL of 2-propanol and poured into 2 L of water to remove residual pyridine. The precipitated white solids were filtered, dissolved in 500 mL of 2-propanol, and diluted with about three portions of water until reprecipitation occurred. The dissolution/precipitation steps using 2-propanol/water were repeated more than 5 times for complete elimination of unreacted BPA: yield 68%. ¹H NMR (CDCl₃, ppm): 1.57 (s, 12H, *i*-PrCH₃, outside), 1.61 (s, 6H, *i*-PrCH₃, inside), 6.66-7.01 (m, 8H, PhH, outside), 7.08-7.18 (m, 16H, PhH, inside). MALDI-TOF MS: *m/z* = 759.09 (M + Na)⁺. Anal. Calcd for C₄₇H₄₄O₈: C 76.61; H 6.02. Found: C 76.65; H 6.11.

The procedure for TMBPA tricarbate (T3) was the same to that for B3 except for the monomers, TMBPA and TMBPA BCF (T-BCF), and the use of methanol instead of 2-propanol for purification: yield 72%. ¹H NMR (CDCl₃, ppm): 1.53 (s, 12H, *i*-PrCH₃, outside); 1.54 (s, 6H, *i*-PrCH₃, inside), 2.13 (s, 12H, PhCH₃, outside), 2.18 (s, 24H, PhCH₃, inside), 6.75 (s, 4H, PhH, outside), 7.19 (s, 8H, PhH, inside). MALDI-TOF MS: *m/z* = 927.34 (M + Na)⁺. Anal. Calcd for C₅₉H₆₈O₈: C 78.29; H 7.57. Found: C 77.81; H 7.56.

Synthesis of Alternating Copolycarbonates. The alternating copolymers were prepared by condensation of equimolar amounts of a bisphenol and a BCF of desired combination. The preparation of TE is described here. BPO (10.11 g, 0.05 mol) in 150 mL of MC was first charged in a 500 mL reactor equipped with a stirrer, a dropping funnel, and a condenser, and pyridine (9.89 g, 0.125 mol) was added. T-BCF (20.47 g, 0.05 mol) in 200 mL of MC was added dropwise to the solution through the dropping funnel for 1 h at 35 °C. The reaction was allowed to stand for 12 h at room temperature. After the solids were filtered off, the solution was poured into methanol for precipitation. A couple of dissolution/precipitation operations using MC/methanol were effected for purification before final drying. ¹H NMR (CD₂Cl₂, ppm): 1.65 (s, 6H, *i*-PrCH₃), 2.19 (s, 12H, PhCH₃), 7.00 (s, 4H, PhH), 7.23-7.26 (q, 8H, PhH). Anal. Calcd for

(C₃₃H₃₀O₇)_n: C 73.59; H 5.61. Found: C 73.48; H 5.40.

The procedure for the synthesis of the other alternating copolycarbonates is identical to the one described above. TS. ¹H NMR (CD₂Cl₂, ppm): 1.60 (s, 6H, *i*-PrCH₃), 2.20 (s, 12H, PhCH₃), 7.00 (s, 4H, PhH), 7.43-8.03 (q, 8H, PhH). Anal. Calcd for (C₃₃H₃₀O₁₀S)_n: C 67.56; H 5.15; S 5.47. Found: C 67.43; H 5.12; S 5.44.

BE. ¹H NMR (CD₂Cl₂, ppm): 1.71 (s, 6H, *i*-PrCH₃), 7.05-7.19 (m, 8H, PhH), 7.22-7.31 (m, 8H, PhH). Anal. Calcd for (C₂₉H₂₂O₇)_n: C 72.19; H 4.60. Found: C 71.91; H 4.36.

BS. ¹H NMR (CD₂Cl₂, ppm): 1.65 (s, 6H, *i*-PrCH₃), 6.90-7.17 (q, 8H, PhH), 7.27-8.02 (q, 8H, PhH). Anal. Calcd for (C₂₉H₂₂O₈S)_n: C 65.65; H 4.18; S 6.04. Found: C 65.33; H 4.15; S 5.95.

TZ. ¹H NMR (CD₂Cl₂, ppm): 1.63 (s, 6H, *i*-PrCH₃), 2.22 (s, 12H, PhCH₃), 2.35 (s, 12H, PhCH₃), 7.00 (s, 4H, PhH), 7.71 (s, 4H, PhH). Anal. Calcd for (C₃₇H₃₈O₈S)_n: C 69.14; H 5.96; S 5.00. Found: C 69.15; H 5.81; S 4.83.

The synthetic procedure for the alternating copolymers containing B3 or T3 was similar to that for the alternating copolycarbonates, except that *N,N*-dimethyl-4-aminopyridine (DMAP) was used as the cocatalyst with pyridine. For example, DMAP (0.015 mol) was added to pyridine (0.065 mol) in the reaction of B3 (0.03 mol) and Z-BCF (0.03 mol) for the preparation of B3Z. ¹H NMR (CD₂Cl₂, ppm): 1.55 (d, 18H, *i*-PrCH₃, B3 unit), 2.17 (s, 12H, PhCH₃, Z unit), 7.00-7.15 (m, 24H, PhH, B3 unit), 7.55 (s, 4H, PhH, Z unit). Anal. Calcd for (C₆₅H₅₈O₁₄S)_n: C 71.28; H 5.34; S 2.93. Found: C 71.12; H 5.30; S 3.03.

The procedure for the synthesis of the other alternating block copolycarbonates is identical to the one described above. B3E. ¹H NMR (CD₂Cl₂, ppm): 1.70 (s, 6H, *i*-PrCH₃, B3 unit), 7.05 (m, 4H, PhH, E unit), 7.16 (m, 12H, PhH, B3 unit), 7.25 (m, 4H, PhH, E unit), 7.95 (m, 12H, PhH, B3 unit). Anal. Calcd for (C₆₁H₅₀O₁₃)_n: C 73.93; H 5.09. Found: C 73.89; H 4.82.

B3S. ¹H NMR (CD₂Cl₂, ppm): 1.61 (m, 6H, *i*-PrCH₃, B3 unit), 7.08 (m, 12H, PhH, B3 unit), 7.20 (m, 12H, PhH, B3 unit), 7.36 (m, 4H, PhH, E unit), 7.93 (m, 4H, PhH, E unit). Anal. Calcd for (C₆₁H₅₀O₁₄S)_n: C 70.51; H 4.85; S 3.09. Found: C 70.97; H 5.00; S 3.11.

T3E. ¹H NMR (CD₂Cl₂, ppm): 1.63 (s, 18H, *i*-PrCH₃), 2.23 (s, 36H, PhCH₃, T3 unit), 6.96 (s, 12H, PhH, T3 unit), 7.06-7.26 (m, 8H, PhH, E unit). Anal. Calcd for (C₇₃H₇₄O₁₃)_n: C 75.63; H 6.43. Found: C 75.60; H 6.17.

T3S. ¹H NMR (CD₂Cl₂, ppm): 1.60 (s, 18H, *i*-PrCH₃), 2.16 (s, 36H, PhCH₃, T3 unit), 6.90 (s, 12H, PhH, T3 unit), 7.29-7.95 (q, 8H, PhH, S unit). Anal. Calcd for (C₇₃H₇₄O₁₄S)_n: C 72.62; H 6.18; S 2.66. Found: C 72.62; H 6.13; S 2.69.

Characterization. ¹H NMR spectra were recorded on a Bruker AMX-500 spectrometer at room temperature. Deuterated MC or chloroform was used as the solvent. IR spectra were obtained on a Perkin Elmer 750X FT-IR spectrometer.

Elemental analysis was carried out with a LECO CHNS-932 analyzer. MALDI-TOF mass spectral data were obtained using a Bruker Biflex IV with 2,5-dihydroxybenzoic acid as the matrix. Molecular weight of the copolymers was measured using GPC at 35 °C on three PLGel Mix polystyrene gel columns that were connected to a Viscotek LR125 laser refractometer at a flow rate of 1.0 mL/min. THF was used as the eluting solvent, and the results were calibrated using polystyrene standards. GPC traces for the trimers were obtained by Waters Styragel HR 3 columns and Waters 2487 Dual λ UV absorbance detector. Glass transition temperature was determined by DSC (TA 2920) at a heating rate of 20 °C/min.

Results and Discussion

Monomers. The units incorporated in the copolymers are shown in Figure 1, and the steps for the synthesis and the code designation for the intermediates and copolymers are shown in Scheme 1.

BCF of the bisphenols were synthesized following the general procedures previously reported,^{14,15} which employed excess of phosgene in the presence of DMA as the acid acceptor at temperatures below room temperature. More excess of phosgene, four to eight times, over bisphenol was used in this study to ensure chloroformate groups. The complete absence of hydroxyl group is critical for the high molecular weight of the alternating copolymers that is prepared later from BCF. FT-IR and ¹H NMR spectra of the BCFs indicated that no hydroxyl group remained from starting bisphenol or was converted from BCF during the purification procedure. Figure 2 shows FT-IR spectra of BPA, B-BCF and B3. By the conversion from BPA to B-BCF, the absorption band around 3300 cm⁻¹, which is characteristic of hydroxyl group, disappears, and new bands of chloroformate around 1720 cm⁻¹ (C=O) and 1300 cm⁻¹ (C-O) are observed. Hydroxy absorption band emerges again in the spectrum of B3 oligomer.

Oligomers. Securing the oligocarbonates having exactly three BPA (B3) or TMBPA (T3) units is essential for the preparation of the well-defined alternating block copolycarbonates in this study. There have been several efforts to prepare the BPA or TMBPA oligocarbonates with controlled block lengths. Jho and Yee synthesized the oligomers with six and nine units through the imbalanced feeding of the

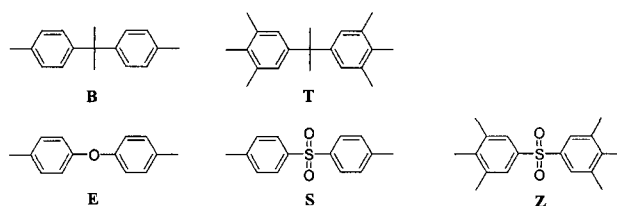
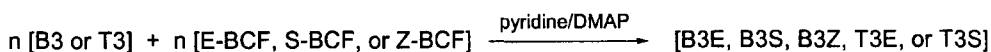
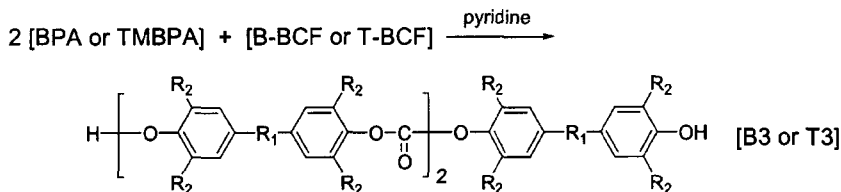
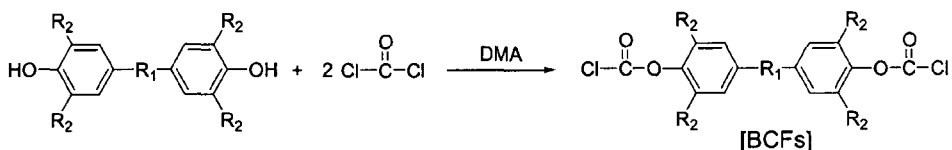


Figure 1. The monomeric unit and code in copolycarbonates.

Scheme I



R ₁	R ₂	Bisphenol	Bischloroformate	Code in Copolymers
C(CH ₃) ₂	H	BPA	B-BCF	B
O	H	BPO	E-BCF	E
SO ₂	H	BPS	S-BCF	S
C(CH ₃) ₂	CH ₃	TMBPA	T-BCF	T
SO ₂	CH ₃	TMBPS	Z-BCF	Z

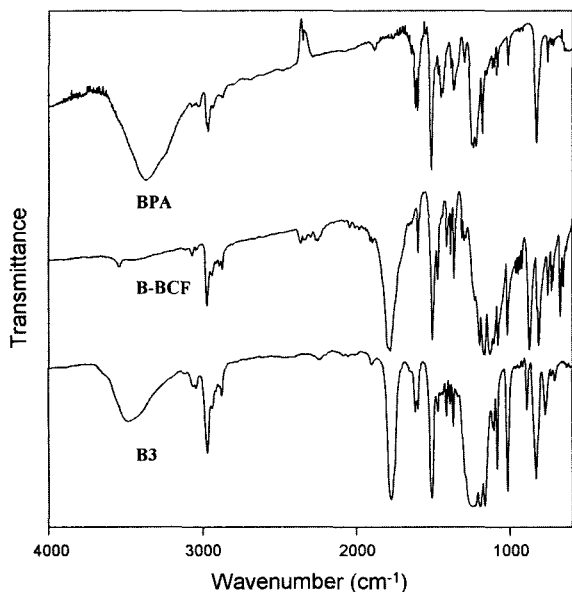


Figure 2. IR spectra of BPA, B-BCF, and B3.

bisphenols and BCFs.¹⁴ The oligomers were inherently polydisperse with the polydispersity indices around 1.4, as characterized by GPC. Direct condensation of two equivalent

of BPA and one equivalent of B-BCF was reported as an effort to prepare B3.^{15,16} Although the polydispersity index was not stated, the oligomer was not thought to be monodisperse. Xiao and Yee employed monosodium salt of BPA, two equivalents of which is reacted with one equivalent of BPA to form B3.¹⁷ Some polydispersity appeared to be unavoidable due to the partial equilibrium between the phenyl oxide and the phenyl hydroxyl groups, which they admitted, and the possible existence of BPA disodium salt. A similar protection technique was proposed by Klug *et al.*,¹⁸ who prepared BPA oligocarbonates of the block lengths of three and longer by using benzylcarbonate as a protecting group. The oligomers were relatively monodisperse with the polydispersity indices between 1.08 and 1.14, which was possibly due to the susceptibility of the inside carbonate linkage to the deprotecting hydrogenolysis reagent.

As the B3 or T3 oligomers prepared by the previous efforts appeared to suffer from polydispersity, we decided to make a rather simple approach. B-BCF or T-BCF was reacted with large excess of its bisphenol, and resulting B3 or T3 was purified by repeated dissolution/precipitation steps. The BCF was diluted by solvent and added to the bisphenol very slowly at a low temperature to minimize the formation of higher oligomers than trimers. Separation of unreacted BPA from B3 was effected by repeated dissolution/precipitation

steps taking advantage of the small difference in solubility in 2-propanol. As it turned out that 2-propanol is a good and a poor solvent for BPA and B3, respectively, water was added to the 2-propanol solution until B3 first precipitated out. For the separation of T3, methanol was used instead of 2-propanol.

The amount of excess bisphenol that gives trimer free from higher oligomers was determined by trial and error.

Figure 3 shows the GPC traces for the B3 and T3 prepared with different amount of excess bisphenols. It is indicated that an excess of BPA as large as eight-times is needed for B3 free from higher oligomers. On the other hand, four-time excess TMBPA is sufficient to obtain relatively monodisperse T3, which is probably due to the lower reactivity of TMBPA compared to that of BPA. The monodispersity of the oligomers was confirmed by MALDI-TOF mass spectra,

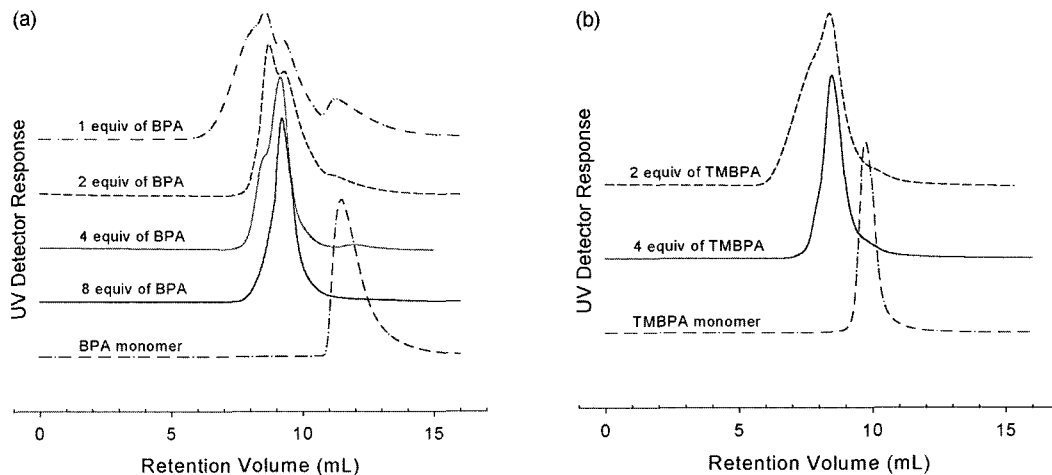


Figure 3. GPC traces of the oligomers prepared with different amount of excess bisphenols; (a) B3 and (b) T3.

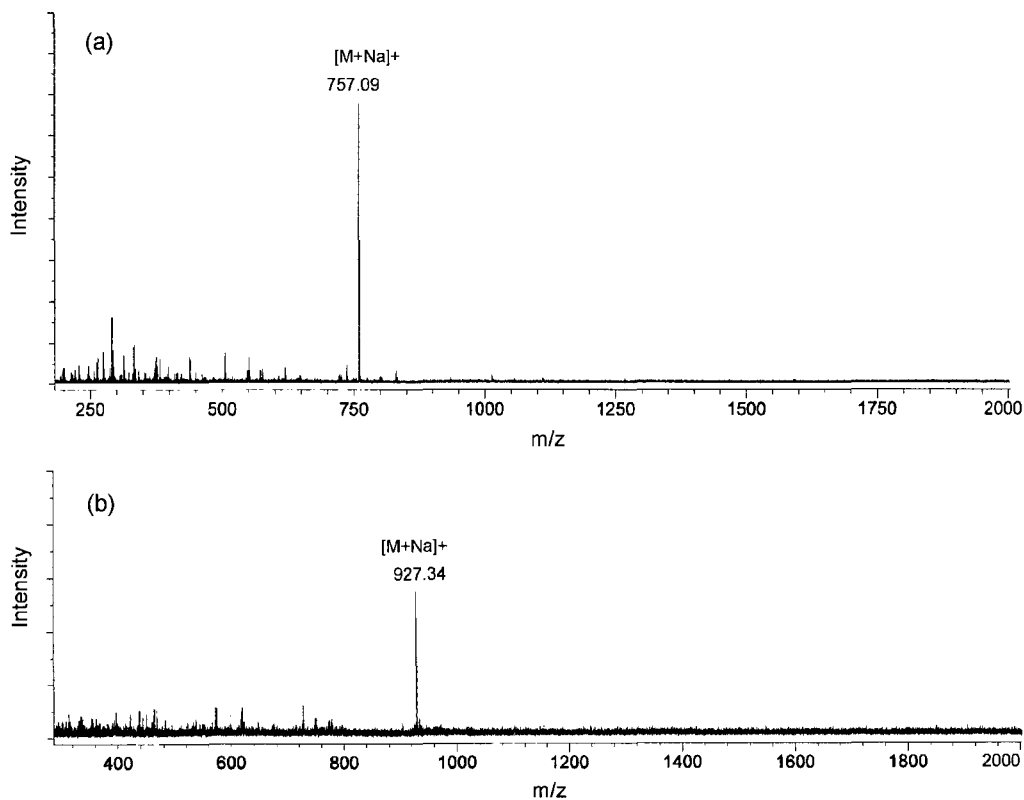


Figure 4. MALDI-TOF mass spectra of (a) B3 and (b) T3.

which are shown in Figure 4. In both spectra, no peak with considerable abundance is observed other than the main peaks for B3 and T3. The additional experimental results including elemental analysis and NMR also support the monodispersity. In mass spectra main peaks are observed at the molecular weight of the respective oligomers. No peak with considerable abundance was observed at the molecular weight of higher oligomers. The observation that a large excess of bisphenol is necessary for monodisperse oligomers indicates that the previous attempts employing imbalanced feed were prone to be of polydispersity.

Copolymers. The alternating copolymers, BE, BS, TE, TS, and TZ, were prepared by the polycondensation of B-BCF or T-BCF and a bisphenol of desired combination. Although the bisphenols were of different reactivity, it appeared that all the bisphenols reacted readily with B-BCF and T-BCF to give high molecular weight copolymers. Table I shows that the molecular weight and its distribution of the copolymers are comparable to those of the commercial PC. The structure of these copolymers was characterized by ¹H-NMR. In the spectrum for TE shown in Figure 5(a), the peak integrals of the phenylene proton in T unit (c) and those in E unit (d and e) are the same. These peaks and the methyl proton peaks appear free from side peaks due to the blockiness, which indicate the alternating feature of this copolymer.

For the preparation of alternating block copolymers, B3 or T3 was polycondensed with the E-, S-, or Z-BCF. To avoid the complication in the purification of B3- or T3-BCF, the other side of the combination was bischloroformated and reacted with B3 and T3. As shown in Table I the copolymers containing B3 are of higher molecular weight than those containing T3, which may be due to the lower reactivity

Table I. Molecular Weight and Glass Transition Temperature of the Copolymers

Polymer	M_n (g mol ⁻¹)	M_w/M_n	T_g (°C)
BE	23,300	2.03	140
BS	15,400	2.05	172
TE	27,700	2.01	163
TS	22,000	2.02	180
TZ	20,200	2.16	229
B3E	45,300	2.28	143
B3S	15,600	2.05	156
B3Z	13,400	2.06	190
T3E	9,690	2.00	171
T3S	10,600	2.26	208
PC*	17,800	2.07	150

*A commercial polycarbonate, Lexan 141 from GE Plastics.

of T3. The T3 copolymers, however, were tough enough for film casting or compression molding. In the NMR spectrum for B3Z (Figure 5(b)), the integral ratios between methyl protons (a and b) and between phenylene protons (c, d, and e) are 3/2 and 3/1, respectively. In addition there is no side peak besides these peaks, which confirms the 3/1 alternating block structure of this copolymer.

Glass transition temperatures of the copolymers listed in Table I reflect the relative rigidity of constituent groups. The polymers containing tetramethyl substituted phenylene units, T, Z, or both, are of significantly higher T_g s. It is also noted

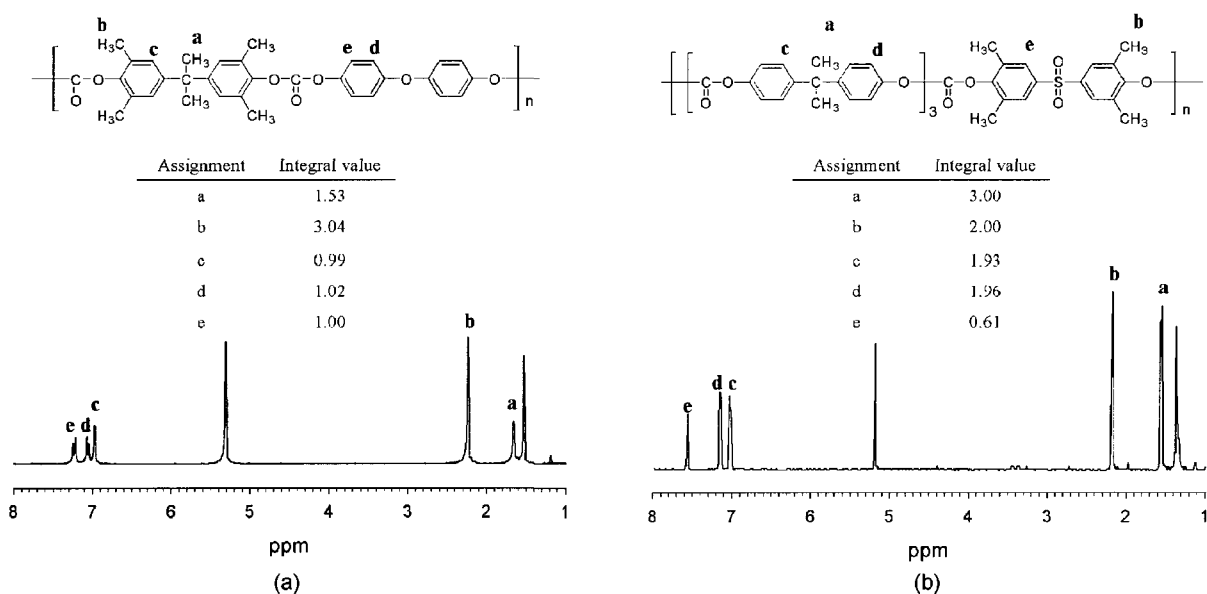


Figure 5. ¹H NMR spectra of the copolymers; (a) TE and (b) B3Z.

that glass transition temperature decreases with the incorporation of flexible ether linkage (E) and increases by bulky and polar sulfone group (S). When T_g s of the copolymers are compared with each other and with those of PC (BB, 150°C), tetramethyl bisphenol A PC (TT, 200°C),¹⁵ and their alternating copolymer (BT, 170°C),¹⁶ rigidity of the units increases in the order of $E < B < S < T < Z$. Detailed investigation on relaxation behaviors and mechanical properties of the alternating block copolymers is out of the scope of this work and will be discussed in future.

Conclusions

Alternating and alternating block copolycarbonates containing the constituent groups of polysulfone were successfully prepared through multi-step solution polycondensation. For the preparation of monodisperse trimers, a large excess of four to eight times bisphenols over bischloroformates were necessary, which were traced by GPC of the oligomers. In addition, repeated dissolution/precipitation steps using solubility difference were also necessary for the separation of impurities. Molecular weight of the copolymers was high enough to be comparable with commercial PC. Structure of the synthesized bischloroformates, oligomers, and copolymers was confirmed by ¹H NMR, mass spectroscopy, and elemental analysis. Incorporating tetramethyl groups or sulfone linkages into the copolymer increases glass transition temperature probably due to the bulky and polar sulfone group, while ether linkage lowers T_g .

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References

- (1) A. F. Yee and S. A. Smith, *Macromolecules*, **14**, 54 (1981).
- (2) C. Xiao, J. Y. Jho, and A. F. Yee, *Macromolecules*, **27**, 2761 (1994).
- (3) C. J. G. Plummer, C. L. Soles, C. Xiao, J. Wu, H. H. Kausch, and A. F. Yee, *Macromolecules*, **28**, 7157 (1995).
- (4) J. Wu, C. Xiao, A. F. Yee, C. A. Klug, and J. Schaefer, *J. Polym. Sci., Part B: Polym. Phys.*, **39**, 1730 (2001).
- (5) C. L. Aitken, W. J. Koros, and D. R. Paul, *Macromolecules*, **25**, 3424 (1992).
- (6) C. L. Aitken, W. J. Koros, and D. R. Paul, *Macromolecules*, **25**, 3651 (1992).
- (7) I. W. Kim, K. J. Lee, J. Y. Jho, H. C. Park, J. Won, Y. S. Kang, M. D. Guiver, G.P. Roberson, and Y. Dai, *Macromolecules*, **34**, 2908 (2001).
- (8) K. Ghosal, R. T. Chern, B. D. Freeman, W. H. Daly, and I. I. Negulescu, *Macromolecules*, **29**, 4360 (1996).
- (9) J. H. Kim, J. E. Yoo, and C. K. Kim, *Macromol. Res.*, **10**, 209 (2002).
- (10) B. U. Kang, J. A. Lee, and J. Y. Jho, *J. Ind. Eng. Chem.*, **5**, 77 (1999).
- (11) H. Vernaleken, *Interfacial Synthesis*, F. Millich, C. E. Carraher, Jr., Eds., Marcel Dekker, New York, 1977, Vol. 2, Chapter 13, pp 111.
- (12) B. G. Kim, M. S. Gong, and J. H. Kim, *Korea Polym. J.*, **2**, 109 (1994).
- (13) S. W. Lee, W. Huh, Y. S. Hong, and K. M. Lee, *Korea Polym. J.*, **8**, 261 (2000).
- (14) J. Y. Jho and A. F. Yee, *Macromolecules*, **24**, 1590 (1991).
- (15) J. Liu and A. F. Yee, *Macromolecules*, **31**, 7865 (1998).
- (16) J. Wu, C. Xiao, A. F. Yee, C. A. Klug, and J. Schaefer, *J. Polym. Sci., Part B: Polym. Phys.*, **39**, 1730 (2001).
- (17) C. Xiao and A. F. Yee, *Macromolecules*, **25**, 6800 (1992).
- (18) C. A. Klug, J. Wu, C. Xiao, A. F. Yee, and J. Schaefer, *Macromolecules*, **30**, 6302 (1997).