Syntheses of Alternating Multiblock Copolycarbonates with Controlled Block Lengths

Jae Y. Jho and Albert F. Yee*

Macromolecular Research Center and Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, Michigan 48109

Received July 31, 1990

ABSTRACT: A series of alternating multiblock copolymers containing the carbonates of bisphenol-A (BPA) and tetramethylbisphenol-A (TMBPA) were synthesized. To control the block length, a multistep solution polycondensation method was employed. Through the unbalanced feeds of comonomers, two types of oligomers with regulated molecular weights were prepared and subsequently condensed to form a copolymer. Block lengths were determined with ^1H NMR, and the structures of the copolymers were characterized with ^{13}C NMR. The copolymers were found to have single glass transitions irrespective of block lengths.

Introduction

Our effort to prepare multiblock copolycarbonates is motivated by the need for a model copolymer system for studying the secondary relaxation motion in bisphenol-A polycarbonate (BPA-PC).[1] Another purpose for the preparation of the copolymers is to develop a polymer that has higher modulus and higher glass transition temperature than BPA-PC without losing the ductility of BPA-PC. In view of these purposes, the polycarbonate of 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane(tetramethylbisphenol-A polycarbonate, TMBPA-PC) is selected as the second component. TMBPA-PC is a high-modulus polymer with a high T_g of 200 °C and its secondary relaxation temperature is far apart from that of BPA-PC.[2] Furthermore, TMBPA-PC is miscible with BPA-PC, and thus the block copolymers would not be expected to exhibit phase separation.

For the syntheses of polycarbonates, the interfacial condensation of phosgene and bisphenols is generally used due to the fact that high molecular weights of products are readily obtained. A high molecular weight copolycarbonate also could be obtained through the interfacial condensation of BPA and TMBPA in the presence of phosgene.[3] For the copolymers in the present study, however, the incorporation of blocks with controlled molecular weights is more important than the high molecular weight of the copolymer. Since, in an interfacial synthesis, balanced stoichiometry is kept at the limited interfacial reaction site, the control of molecular weight through the gross imbalance of monomer feeds cannot be achieved. As a result, an interfacial route was avoided and a multistep solution synthesis route was followed. Solution methods for preparing polycarbonates had been developed earlier,[4,5] and the general principles of these techniques were observed in this experiment.

A brief description of the synthetic route is given here. First, the monomers TMBPA, TMBPA bis(chloroformate), and BPA bis(chloroformate) were prepared. Oligomers were then prepared by reacting BPA and TMBPA with their corresponding bis(chloroformates). Finally, polycondensation of the oligomers was accomplished by converting the hydroxyl groups of TMBPA oligomers to bis(chloroformate) groups, followed by condensing with hydroxyl-terminated BPA oligomers to yield alternating multiblock copolymers. The alternating copolymer was prepared through direct polycondensation of BPA bis(chloroformate) with TMBPA. The details of the synthetic method as well as the characterization techniques used in each step are discussed in this paper.

Discussion

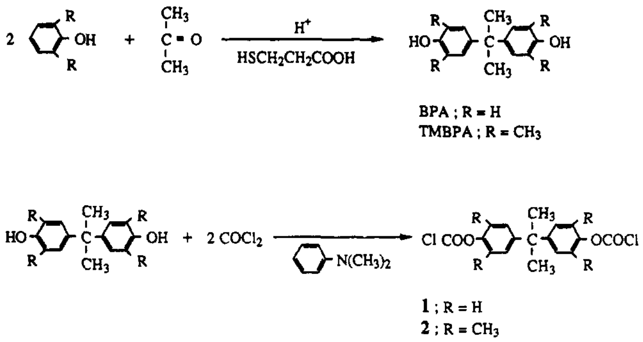
Monomers. Bisphenols used in this study must be of high purity to avoid a change in the backbone structure of the resulting polycarbonates due to isomeric impurity.[6] For the present experiment, BPA was purchased at 99+% purity and was used without further purification. TMBPA was synthesized by reacting 2,6-dimethylphenol with acetone in the presence of dry HCl as shown in Scheme I. The procedure for the synthesis of BPA[6] was followed, including the use of a fourfold excess of 2,6-dimethylphenol instead of a twofold stoichiometric amount. Repeated recrystallization from methanol/water (55/45 volume ratio) gave a pure product.

Bis(chloroformates) of BPA (**1**) and TMBPA (**2**) were synthesized by introducing excess phosgene in the presence of an acid acceptor (Scheme I). **1** had been reportedly prepared with various catalysts.[7,8] In the present experiment, *N,N*-dimethylaniline, which is known to be nonreactive to the resulting formate group, was chosen as the acid acceptor. The procedure followed was the generalized procedure for the syntheses of bis(chloroformates), which employs the extremely slow addition of a large excess of phosgene into the solution of bisphenol at a dry ice/acetone temperature to prevent premature reaction.[9] Subsequent addition of the tertiary amine acceptor was also carried out very slowly to prevent possible coupling reactions. Toluene was used as a solvent for both bisphenols, though small amounts of dry THF were added for the complete dissolution of BPA. Although a chloroformate group is not known to be as reactive to the moisture in the air as an acyl chloride group is, care has to be exercised during the purification procedure to avoid the transformation of the chloroformate group to the hydroxyl group. Flash column chromatography was successfully employed using toluene as an eluent. On a TLC plate, the product had $R_f = 0.6$, and the only other spot located was at $R_f = 0.0$. Recrystallization was effected with a small amount of *n*-hexane. In the ^1H NMR spectra of the bis(chloroformates) collected, peaks for the hydroxyl group were not found, which indicated that all hydroxyl groups were converted to chloroformate groups and that no hydroxyl group was formed during the separation procedure.

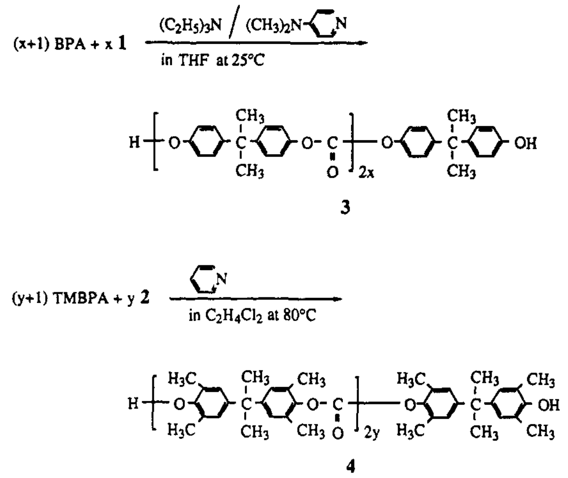
Oligomers. For the syntheses of most block copolymers containing polycarbonates, polycarbonate blocks have been formed and incorporated in situ. In a typical procedure, the preformed block of the other component is reacted, in many cases interfacially, with bisphenol-A in the presence of phosgene. This general procedure could not be employed in this experiment, since the size of the poly-

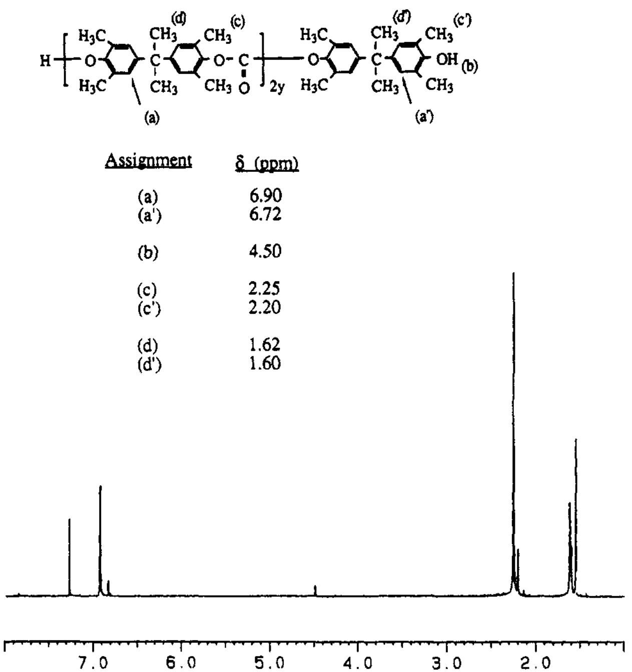
0024-9297/91/2224-1590$02.50/0

Scheme I



Scheme II





Assignment	δ (ppm)
(a)	6.90
(a')	6.72
(b)	4.50
(c)	2.25
(c')	2.20
(d)	1.62
(d')	1.60

Figure 1. ^{1}H NMR spectrum of a TMBPA oligocarbonate.

carbonate block could not be controlled by this method. As an alternative method, the BPA block and the TMBPA block were produced by the solution condensation of bisphenols and their bis(chloroformates) and then were incorporated in the copolymer chain (Scheme II). This method enables one to control the molecular weight through the imbalance of the monomer feed, which is well described by Caruther's equation.[10] This method also ensures that, through the feeding of the calculated excess of bisphenols over their bis(chloroformates), the product oligomers possess hydroxyl functionalities. For the syntheses of polycarbonates, only a few polycondensation reactions were performed in a single liquid solution,[5,11,12] in which pyridine was used as either a catalyst or a catalyst/solvent at room temperature. The modification was necessary because the reactivities of BPA and TMBPA are different. The reactivity of TMBPA to acylation is lower than that of BPA as revealed experimentally.[13,14] Despite the expected resonance effect due to electron-donating methyl substituents, the measured acidity of TMBPA is only a little less than that of BPA,[3] which indicates that a steric effect plays a major role in the reduction of the reactivity of TMBPA. As a result, for the preparation of TMBPA oligocarbonates (4), the solution reaction was run at a higher reaction temperature (80 °C) with pyridine to circumvent the low reactivities of TMBPA and TMBPA bis(chloroformate). For the BPA oligocarbonates (3), an entirely different catalyst system was employed. 3 prepared with pyridine catalyst showed broad molecular weight distributions, with polydispersities close to 3.0, presumably due to the higher reactivities of the monomers compared to those of the TMBPA monomers. Since those polydispersities were not judged to be tolerable in this study, the reactions were carried out at a lower temperature (room temperature) with an alternative catalyst system. Triethylamine was used with a small amount (5 mol %) of 4-(dimethylamino)pyridine, which is known as the "super acylating catalyst". Triethylamine performed better than pyridine in this reaction, which was also experienced by other researchers.[15] Several oligomers with different molecular weights were prepared by systematically varying the ratios of monomer feeds.

The molecular weights of the oligomers, which will be the block lengths in the copolymer chain, were determined in the NMR spectra by virtue of the fact that the chemical shifts of protons in the terminal units of the oligomer chains are different from those in the middle parts of the chain. As shown in the spectra of 4 (Figure 1) all methyl protons and ring protons have small extra peaks separated from their main peaks. By counting the relative numbers of protons in the terminal units and those in the rest of the chains, we could obtain simple relationships between the integrated peak ratios and the molecular weights. Since, in the determination of the molecular weights of 3, the integration was not as clear as in 4, further separation of the small peak from the main peak was attempted to confirm the results of the calculations. Trichloroethyl chloroformate, a common protecting group for a phenolic hydroxyl group,[16] was used to convert the hydroxyl groups in BPA oligomers to trichloroethyl carbonate groups. After conversion of the hydroxyl end groups in the oligomers to trichloroethyl carbonate groups, the small peak for the methyl protons in the terminal units merged with the main peak, and the ethyl protons in the end group caused a peak at 4.88 ppm, which enabled an easier and clearer calculation of the relative peak areas. The peak position of the ethyl protons and the quantitative yield of the reaction were confirmed with a model compound we prepared, BPA *trichloroethyl carbonate*. In the end, the average degrees of polymerization calculated from these peak ratios were found to be in good agreement with those calculated directly. The results of the molecular weight determinations of the oligomers used in the copolymer preparation are shown in Table I.

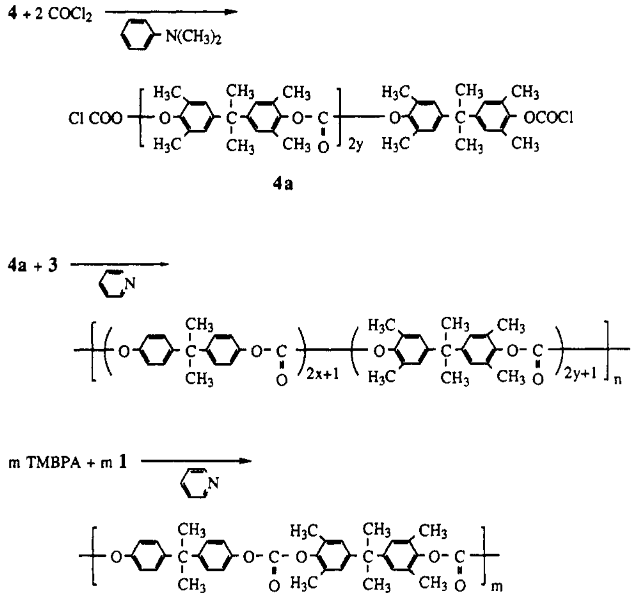
Since having well-defined blocks in the copolymer chain is critical in this study,[1] narrow molecular weight distributions of the oligomers are desirable. As described by an early theory of polycondensation, the polydispersities

Table I
Characterization of the Oligomers Prepared

oligomer	$\bar{x}_n$[a]	$\bar{M}_n$[b]	PD[c]
B6	6.2	1550	1.30
B9	8.8	2200	1.57
T6	6.4	1950	1.28
T9	9.2	2800	1.42

[a] Number-average degree of polymerization obtained from NMR characterizations. [b] Number-average molecular weight calculated from NMR results. [c] Polydispersity measured by GPC.

Scheme III



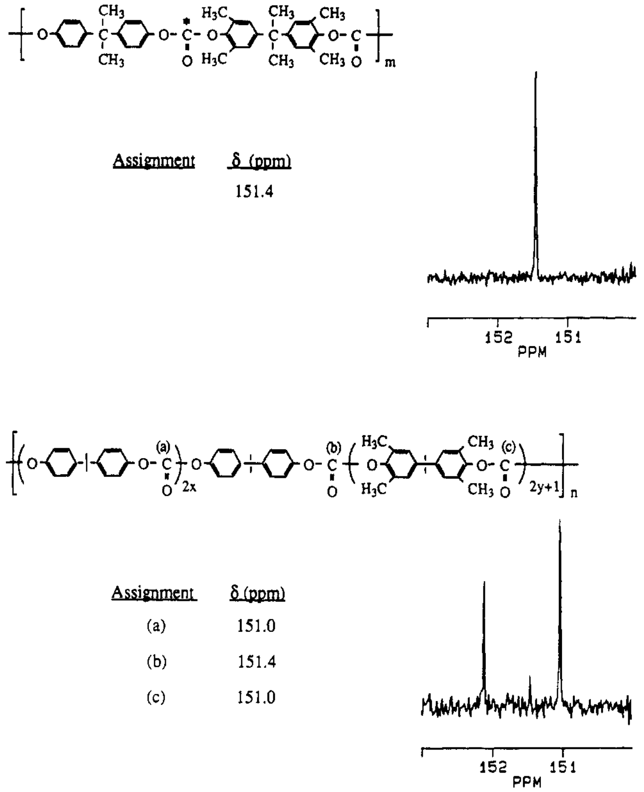


Figure 2. ^{13}C NMR spectra of the alternating copolycarbonate and a multiblock copolycarbonate showing carbonyl carbon chemical shifts.

for the imbalanced polymerization are expected to be smaller than those obtained with the balanced monomer feed.[17] The polydispersities of the oligomers prepared were determined by GPC to be in the range between 1.3 and 1.6. These molecular weight distributions are not considered to be so excessive as to cause problems in interpreting the dynamic mechanical results of the copolymers based on these oligomers. Further efforts to fractionate these oligomers, therefore, were not made.

Copolymers. For combining the two oligomers to form a copolymer chain, several synthetic routes were sought and tried. Since both oligomers prepared have hydroxyl end groups, if these oligomers were directly condensed, the block lengths in the copolymer chain would be different from the molecular weights of the oligomers. In fact, if the hydroxyl-terminated oligomers are directly condensed, no matter whether an interfacial or solution process is used, the formation of homopolymers through self-condensation would be favored over copolymers through cross-condensation because of the difference in the reactivities of the hydroxyl groups in BPA oligomers and TMBPA oligomers. As a result, the conversion of the end groups of one block species was necessary. In this experiment, as shown in Scheme III, the hydroxyl groups of 4 were converted to chloroformate groups, since the TMBPA oligomer has better solubility in toluene, which is the solvent for the bis(chloroformylation). The procedure followed was the same as that used in the bis(chloroformylation) of monomers. After the reaction was stopped, the excess phosgene was completely removed from the system to prevent any remaining phosgene from taking part in the next step of the reaction. The bis(chloroformate)-terminated TMBPA oligomers obtained were immediately used in the next step, viz., condensation with the hydroxyl-terminated BPA oligomers, without being retrieved.

The molecular weights of the resulting copolymers were not reproducibly high due to a slight imbalance between 3 and bis(chloroformylated) 4. To solve this problem, a series of small-scale experiments designed to predetermine the optimum ratio of coreactants was conducted. The result suggested that starting the bis(chloroformylation) reaction with a slight excess of TMBPA oligomers would give sufficiently high molecular weight copolymers. In the large-scale experiments, calculated ratios of about 1.05 usually gave sufficiently high molecular weights. In addition to the alternating multiblock copolymers described above, an alternating copolymer was made by direct polycondensation of 1 and TMBPA. Since the control of equimolar balance was readily achievable in this polycondensation, high molecular weight alternating copolymer was obtained without any difficulty. An alternating copolymer and two multiblock copolymers, listed at Table II, were prepared in large scale to study their dynamic mechanical and mechanical properties.[1] Also, the homopolymer of TMBPA carbonate was prepared by the polycondensation of TMBPA and 2.

The incorporation of two oligomers in a copolymer was confirmed in the ^{13}C NMR spectrum (Figure 2). The carbonyl carbon peaks were identified through the ^{13}C NMR spectra of the model compounds diphenyl carbonate (DPC), phenyl xylyl carbonate (PXC), and dixylyl carbonate (DXC), which have carbonyl carbons in environments almost identical with those in copolymers. The incorporation of oligomers in the copolymer chains was confirmed by comparing the chemical shifts, and the results are summarized in Table III. The alternating copolymer has only one carbonyl carbon peak at 151.4 ppm due to the interlinking carbonyl groups between the BPA and TMBPA units, which is confirmed by the peak position of PXC. On the other hand, block copolymers have two

Table II
Characterization of the Polymers

polymer	block length[a]	$\overline{M_n}$[b]	[η],[c] dL/g	T_g,[d] °C
BPA-PC		25 900	0.47	148
TMBPA-PC		32 800	0.50	200
B1T1	1/1	22 400	0.38	167
B6T6	6/6	32 200	0.54	179
B9T9	9/9	22 600	0.37	176

[a] Average number of repeating units in each block species (rounded from NMR results). [b] Number-average molecular weight determined by GPC calibrated with polystyrene. [c] Limiting viscosity number (intrinsic viscosity) measured in chloroform at 25 °C. [d] Glass transition temperature determined by DSC at 10 °C/min heating rate.

Table III
^{13}C NMR Analyses of Copolymers

sample	δ(C*═O), ppm		
model compounds			
diphenyl carbonate (DPC)	152.0		
phenyl xylyl carbonate (PXC)		151.3	
dixylyl carbonate (DXC)			150.7
polymers			
BPA-PC	151.9		
TMBPA-PC			151.0
alternating copolymer		151.4	
multiblock copolymers	152.1	151.4	151.0

additional carbonyl carbon peaks due to the carbonyl groups inside the blocks.

The molecular weights of the oligomers were maintained intact during the polycondensation by using the solution method described above, and the measured number-average molecular weights of the oligomers were taken as the block lengths in the copolymer chain where they were incorporated. To confirm that the block lengths remained unchanged during the reaction, two tests were carried out. First, the molecular weight of the intermediate bis(chloroformylated) 4 was checked to ensure that it was the same as that before bis(chloroformylation), which indicated that no change in molecular weight occurred at the first step of the reaction. Second, the possibility of transesterification reaction during the copolycondensation was examined by a test reaction with model compounds. To test the possibility of an ester exchange, DPC and DXC were mixed and stirred at 80 °C in the presence of pyridine, which duplicated the conditions of the second step of the polymerization process. After 12 h, the reaction mixture was examined on a TLC plate (7/3 *n*-hexane/ethyl acetate), on which R_f values for the DPC, PXC, and DXC were 0.49, 0.52, and 0.56, respectively. The mixture after the reaction showed only two spots at the R_f's of 0.49 and 0.56, in addition to a spot for pyridine at 0.22. This indicates that no transesterification reaction had occurred and therefore it would not occur at the second step of polymerization. This result, combined with the result of the first test, demonstrates the fact that the block lengths in the copolymer chains are the same as those of the oligomers.

The prepared polymers have high enough molecular weights for film casting and molding. Although determination of absolute molecular weights was impossible, the molecular "sizes" of the copolymers were measured and compared with that of a commercial BPAPC (Lexan 141 from General Electric). From the results of dilute-solution viscometry and GPC, as shown in Table II, the sizes of the copolymers prepared appeared to be comparable to that of the commercial material, which has a $\overline{M_w}$ about 30 000 and a polydispersity between 2.5 and 3.0. From these results, it is estimated that an average of at least four pairs of oligomers are incorporated in a copolymer chain.

The single-phase nature of the copolymers was examined. The cast films were transparent, and single glass transitions were found by DSC scans (10 K/min.). The T_g's of the copolymers were located at temperatures intermediate between the T_g's of the two homopolymers. The slightly lower glass transition temperature of the alternating copolymer compared to that of the block copolymers is thought to be due to the lack of rigid TMBPA carbonate blocks along the chain.[1]

Experimental Section

Materials and General Procedures. Phosgene was supplied either as a gas from Matheson Gas Co. or as a 20 wt % (1.93 M) solution in toluene from Fluka Chemicals Co. Tetrahydrofuran (THF) and toluene were distilled from lithium aluminum hydride and sodium metal, respectively. Bisphenol-A (BPA, 99+ %), anhydrous 1,2-dichloroethane (DCE), *N*,*N*-dimethylaniline (DMA), 4-(dimethylamino)pyridine (DMAP), 2,6-dimethylphenol (DMP), and β,β,β-trichloroethyl chloroformate (TCECF) were purchased from Aldrich Chemical Co. and used without further purification. TLC was performed on Analtech TLC plates followed by visualization at 254 nm. Flash column chromatography was performed on either 28–200 mesh (grade 12) or 230–400 mesh (60 Å) silica gel particles. NMR spectra were obtained on a Bruker WM-360 FT-NMR spectrometer.

2,2-Bis(3,5-dimethyl-4-hydroxyphenyl)propane (TMBPA). Dry HCl gas was passed through a mixture of DMP (150 g, 1.25 mol), acetone (30 g, 0.5 mol), β-mercaptopropionic acid (5 mL), and calcium chloride (15 g) for 9 h, during which period the temperature was kept at 60 °C to suppress the formation of isomeric products. After the mixture cooled to room temperature, it was diluted with cold water and precipitates were filtered. The yellow solid was recrystallized from methanol/water (55/45) several times to yield white needlelike crystals: yield 76%; mp 160–162 °C. Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.56; H, 8.59. ^{1}H NMR (DMSO, TMS): δ 7.92 (s, 2 H, hydroxyl), 6.71 (s, 4 H, aromatic), 2.05 (s, 12 H, ring-substituted methyl), 1.48 (s, 6 H, methyl).

2,2-Bis(4-((chlorocarbonyl)oxy)phenyl)propane (1). In a 500-mL flask equipped with a dry ice/acetone-topped condenser, mechanical stirrer, gas inlet line, and gas outlet line with an aqueous NaOH trap, BPA (57 g, 0.25 mol) in toluene/dry THF (300 mL/50 mL) was cooled to −70 °C with a dry ice/acetone bath. Phosgene (100 g, 1.0 mol) was condensed into this solution over 1.5 h. The cold bath was replaced with an ice bath, and DMA (66.6 g, 0.55 mol) was added at 0–5 °C over 0.5 h. The mixture was warmed very slowly to room temperature and was allowed to stand overnight. Toluene (200 mL) was added to dilute the mixture, and unreacted phosgene and THF were removed under reduced pressure. After solids were filtered off, the solution was passed through the column of silica gel (230–400 mesh), and the column was washed with toluene until no more product was found in the eluent on a TLC plate ($R_f \sim 0.7$). After toluene was evaporated under reduced pressure, the product was recrystallized from *n*-hexane as white crystals: yield 79%; mp 91–94 °C. Anal. Calcd for $C_{17}H_{14}Cl_2O_4$: C, 57.81; H, 4.00; Cl, 20.08. Found: C, 57.84; H, 3.99; Cl, 20.42. ^{1}H NMR ($CDCl_3$, TMS): δ 7.4–7.1 (m, 8 H, aromatic), 1.70 (s, 6 H, methyl).

2,2-Bis(3,5-dimethyl-4-((chlorocarbonyl)oxy)phenyl)propane (2). The procedure was identical with the one for 1, except that the reaction was carried out in a toluene solution: yield 70%; mp 84–86 °C. Anal. Calcd for $C_{21}H_{22}Cl_2O_4$: C, 61.62; H, 5.42; Cl, 17.32. Found: C, 62.06; H, 5.83; Cl, 17.92. ^{1}H NMR ($CDCl_3$, TMS): δ 6.90 (s, 4 H, aromatic), 2.20 (s, 12 H, ring-substituted methyl), 1.60 (s, 6 H, methyl).

BPA Oligocarbonates (3). For the calculated number-average degree of polymerization of 9, BPA (22.8 g, 0.1 mol) and 1 (28.2 g, 0.08 mol) in 300 mL of dry THF were cooled to 0–5 °C. DMAP (1.0 g, 8×10^{-3} mol) dissolved in 20 mL of THF was added dropwise followed by the slow addition of triethylamine (22.2 mL, 0.16 mol). White precipitates, formed upon the addition of DMAP, were dissolved by the addition of triethylamine. The temperature was slowly raised to room temperature, and the reaction mixture was allowed to stand for 6 h. After the precipitates were filtered off, the solution was poured into methanol, and the precipitated white solids were washed with water and methanol several times. The product was reprecipitated with chloroform and methanol; yield 87%. ^{1}H NMR ($CDCl_3$, TMS): δ 7.30–7.12 (m, aromatic, middle), 7.12–6.70 (q, aromatic terminal), 4.70 (s, 2 H, hydroxyl), 1.67 (s, methyl, middle), 1.64 (s, methyl, terminal).

TMBPA Oligocarbonates (4). For the calculated number-average degree of polymerization of 9, TMBPA (28.4 g, 0.1 mol) and 2 (32.7 g, 0.08 mol) dissolved in 200 mL of DCE were heated to 80 °C. Pyridine (81 mL, 0.32 mol) was added over 10 min. The mixture was refluxed for 8 h and cooled to room temperature. After the solids were filtered off, the solution was poured into methanol to give white precipitates. The product was washed with water and methanol, dried, and reprecipitated with chloroform and methanol; yield 72%. ^{1}H NMR ($CDCl_3$, TMS): δ 6.90 (s, aromatic, middle), 6.72 (s, aromatic, terminal), 4.50 (s, 2 H, hydroxyl), 2.25 (s, ring-substituted methyl, middle), 2.20 (s, ring-substituted methyl, terminal), 1.62 (s, methyl, middle), 1.60 (s, methyl, terminal).

2,2-Bis(4-((((trichloroethyl)oxy)carbonyl)oxy)phenyl)-propane (5). TCECF (4.14 mL, 0.03 mol) in 20 mL of DCE was added dropwise to an ice-cold solution of BPA (2.28 g, 0.01 mol) in 20 mL of DCE and 5 mL of dry pyridine. The mixture was stirred at room temperature for 6 h and washed successively with 2% aqueous HCl, water, 5% sodium bicarbonate, and water. The organic extract was dried over magnesium sulfate, and DCE was evaporated to give white crystals. Recrystallization was effected from *n*-heptane: yield 95%; mp 61–63 °C. Anal. Calcd for $C_{21}H_{18}Cl_6O_6$: C, 43.56; H, 3.13; Cl, 36.73. Found: C, 43.73; H, 3.18; Cl, 37.04. ^{1}H NMR ($CDCl_3$, TMS): δ 7.3–7.1 (m, 8 H, aromatic), 4.88 (s, 4 H, methylene), 1.67 (s, 6 H, methyl).

Trichloroethyl BPA Oligocarbonates. The procedure was identical with the one for 5 except that more DCE was used for dilution of the reaction mixture after it was allowed to stand for 18 h. A white powder product was obtained after washing with *n*-heptane rather than recrystallization. ^{1}H NMR ($CDCl_3$, TMS): δ 7.3–7.1 (m, aromatic), 4.88 (s, 4 H, methylene), 1.67 (s, methyl).

Multiblock Copolycarbonates. For the copolymer with block lengths of 9 for each component, 4 (27.6 g, 0.01 mol) in 200 mL of toluene was cooled to −70 °C, and phosgene (5 g, 0.05 mol) dissolved in toluene was added slowly. DMA (2.7 g, 0.022 mol) in 20 mL of toluene was added at 0–5 °C over 0.5 h. The mixture was warmed very slowly to room temperature and was allowed to stand overnight. After the solids were filtered off, unreacted phosgene and toluene were distilled out under reduced pressure. The greenish concentrated oil was added to 3 (22.6 g, 0.01 mol) in 400 mL of DCE. The mixture was heated to 80 °C and pyridine (4 mL, 0.05 mol) was added at once through the condenser. The reaction was refluxed for 8 h and cooled to room temperature. After the precipitates were filtered off, the solution was poured into methanol to give a white product. Purification was effected by reprecipitation with chloroform and methanol. The ^{13}C NMR result is shown in Figure 2.

Alternating Copolycarbonate. TMBPA (28.4 g, 0.1 mol) and 1 (35.3 g, 0.1 mol) in 200 mL of DCE were heated to 80 °C. Pyridine (24.3 mL, 0.3 mol) was added at once through the condenser. The reaction mixture was allowed to reflux for 4 h and cooled to room temperature. After the precipitates were filtered off, the solution was poured into methanol for precipitation. The polymer was reprecipitated with chloroform and methanol. The ^{13}C NMR result is shown in Figure 2.

Bis(2,6-dimethylphenyl) Carbonate. DMP (10 g, 0.082 mol) in 50 mL of toluene and 50 mL of pyridine was cooled to 0 °C under an argon atmosphere. Phosgene (4.8 g, 0.048 mol) in toluene was added over 0.5 h. The temperature was slowly raised to room temperature, and the reaction mixture was allowed to stand for 1.5 h. After the solids were filtered off, the yellow solution was washed with water three times. The organic phase was dried over magnesium sulfate, and toluene was distilled out under reduced pressure to give pale yellow crystals. Repeated recrystallization from methanol gave white crystals: yield 71%; mp 117–120 °C. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.89; H, 6.68. ^{13}C NMR ($CDCl_3$): δ 150.7 (s, carbonyl), 148.3 (s, 2 C, O-substituted aromatic).

Phenyl 2,6-Dimethylphenyl Carbonate. Phenol (9.4 g, 0.1 mol) and DMP (12.2 g, 0.1 mol) in 100 mL of toluene were cooled to 0 °C under an argon atmosphere. Pyridine (50 mL) and DMAP (244 mg, 2×10^{-3} mol) were added. Phosgene (15 g, 0.15 mol) in toluene was added over 0.5 h. The mixture was warmed slowly to room temperature and allowed to stand for 2 h. After the precipitates were filtered off, the yellow solution was washed with cold water three times and dried over magnesium sulfate. The concentrated solution obtained after the evaporation of toluene was passed through a column of silica gel (28–200 mesh) and further eluted by toluene. A portion corresponding to R_f = 0.52 on the TLC plate (7/*n*-hexane/ethyl acetate) was collected. By evaporation of toluene, white crystals were obtained. Purification of the product was effected by distillation under reduced pressure (180 °C/17 mmHg); mp 36–38 °C. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.80; H, 5.79. ^{13}C NMR ($CDCl_3$): δ 151.3 (s, 1 C, carbonyl), 151.1 (s, O-substituted aromatic, phenyl side), 148.3 (s, 1 C, O-substituted aromatic, dimethylphenyl side).

Acknowledgment. This research was supported by the National Science Foundation (Grant No. DMR-8714981). We are grateful for support and discussions provided by Dr. John Campbell of the General Electric Corporate Research and Development Center and Drs. John Osby and Philip Yang of the Dow Chemical Co.

References and Notes

(1) Jho, J. Y.; Yee, A. F. *Macromolecules*, accepted for publication.
(2) Yee, A. F.; Maxwell, M. A. *J. Macromol. Sci., Phys.* **1980**, *B17*, 543.
(3) Vernaleken, H. In *Interfacial Synthesis*; Millich, F., Carraher, C. E., Jr., Eds.; Marcel Dekker: New York, 1977; Vol. II, Chapter 13.
(4) Schnell, H. *Chemistry and Physics of Polycarbonates*; Interscience: New York, 1964; Chapter 2.
(5) Morgan, P. W. *Macromolecules* **1970**, *3*, 536.
(6) Saunders, K. J. *Organic Polymer Chemistry*; Chapman and Hall: London, 1973; Chapter 16.
(7) Matzner, M.; Barclay, R. J.; Merriam, C. N. *J. Appl. Polym. Sci.* **1965**, *9*, 3337.
(8) Schnell, V. H.; Bottenbruch, L. *Makomol. Chem.* **1963**, *57*, 1.
(9) Barclay, R., Jr.; Sulzberg, T. In *Condensation Monomers*; Stille, J. K., Campbell, T. W., Eds.; Wiley-Interscience: New York, 1972; Chapter 8.
(10) Odian, G. *Principles of Polymerization*, 2nd ed.; Wiley: New York, 1981; Chapter 2.
(11) McGrath, J. E.; Ward, T. C.; Wnuk, A. J. *Polym. Eng. Sci.* **1977**, *17*, 647.
(12) Serini, V.; Vernaleken, H.; Schnell, H. German Offen. 2 211 956, 1973.
(13) Korshak, V. V.; Vinogradova, S. V.; Kuchanov, S. I.; Vasnev, V. A. *J. Macromol. Sci., Rev. Macromol. Chem.* **1976**, *C14*, 27.
(14) Campbell, J., Corporate Research Center, General Electric Co., Schenectady, NY, personal communication, 1986.
(15) Scriven, E. F. *Chem. Soc. Rev.* **1983**, *12*, 129.
(16) Windholz, T. B.; Johnston, D. B. R. *Tetrahedron Lett.* **1967**, *27*, 2555.
(17) Case, L. C. *J. Polym. Sci.* **1960**, *48*, 27.