Preparation and Polymerization of Bisphenol A Cyclic Oligomeric Carbonates

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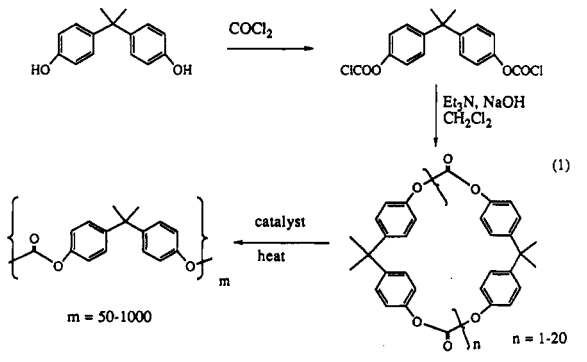
ABSTRACT: A selective, high-yielding procedure for the preparation of Bisphenol A cyclic oligomeric carbonates via a triethylamine-catalyzed hydrolysis/condensation reaction of bis(chloroformate) is described. The reaction produces cyclic oligomers in 80–90% yield, along with about 15% high molecular weight polymer, but with almost total exclusion of linear oligomers. The structure of the amine catalyst controls the selectivity of cyclic vs linear vs polymer formation. Use of other amine catalysts can lead to different products. Use of pyridine as catalyst, for example, affords linear oligomers in 99% yield, with very low yields of cyclics. Polymerization of the cyclic oligomers to polycarbonate with M_w = 50 000–300 000 is achieved by heating at 300 °C for 15 min in the presence of various basic catalysts. The preparation of authentic oligomeric linear and cyclic materials is also described.

Introduction

A research program on the chemistry of cyclic oligomeric aromatic carbonates was initiated several years ago to determine whether cyclic oligomers might be useful as reactive intermediates for the preparation of high molecular weight polycarbonate. The attractiveness of using cyclic oligomeric carbonates to prepare polycarbonate was based on the expectation that the low molecular weight oligomeric materials would have significantly lower viscosities than high molecular weight polycarbonate, thus facilitating reactive processing. Other advantages of using cyclic carbonates for reactive processing were based on the anticipation that no volatile or nonvolatile byproducts would be liberated during the polymerization and that very high molecular weights should be achievable. The major goals of the research program were twofold: discovery of an efficient means of preparation of cyclic oligomeric aromatic carbonates and development of procedures, catalysts, and conditions under which the cyclics could be conveniently polymerized. The achievement of these goals has been reported in a preliminary fashion;[1] this paper relates the details of the preparation and polymerization of Bisphenol A cyclic oligomeric carbonates.

Discrete cyclic aromatic carbonates have been known for some time, but their utility has been limited for two reasons: (1) Procedures for preparation of cyclic carbonates were nonselective and low-yielding, necessitating tedious separations. (2) Polymerization and processing were hampered by the fact that the individual cyclic oligomers are very high melting solids (melting points >350 °C). This paper reports a hydrolysis/condensation reaction of Bisphenol A bis(chloroformate) (eq 1), which



affords the selective formation of a *mixture* of cyclic oligomeric carbonates that is nearly devoid of linear oligomers and which has a melting point of about 200 °C. Because the cyclics are formed selectively, the crude mixture of cyclics can be polymerized directly, leading to very high molecular weight polycarbonate.

Experimental Section

Materials and Instruments. Reagent-grade solvents and chemicals were used without further purification. Dow Parabis was used as the source of Bisphenol A. Purified, crystalline Bisphenol A bis(chloroformate), prepared via a modification of the Wingfoot procedure,[2] was used for early studies, and a slightly oligomeric mixture of bis(chloroformate)s, prepared according to the procedure of Brunelle et al.,[3] was used for process optimization. Proton NMR spectra were recorded on a Varian EM-390 NMR or a GE QE-300 spectrometer; ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. All are in $CDCl_3$ and reported in parts per million vs TMS. FTIR spectra were measured on a Nicolet 5DXC spectrophotometer and are reported in cm^{-1}. Melting points were measured on a Thomas-Hoover melting point apparatus or on a Mel-Temp hot stage. HPLC analyses were performed on a Du Pont Model 850 liquid chromatograph with detection at 254 and 285 nm or on a Perkin-Elmer HPLC system comprising a Model 410 pump, ISS-100 autoinjector, and LC-235 diode array detector. The diode array detector was used for generation of UV spectra. THF/water gradients were used for elution of products on C-8 reverse-phase columns. Gradients used for analysis were as follows.

Program 1: *Analysis for BPA, Bis(phenyl carbonate) Capped Oligomers, and Hydroxy-Terminated Linear Oligomers.* Solvent A, 30% THF/water; solvent B, THF. Step 1, 10–70% B over 15 min at exponent −1; step 2, 70–100% B over 1 min at exponent 1; step 3, 100% B for 2 min; step 4, 100% B to 10% B over 2 min (recycle).

Program 2: *Analysis for Cyclics, Linears, and Polymer.* Solvent A, 30% THF/water; solvent B, THF. Step 1, 40–75% B over 15 min at exponent −2; step 2, 75–100% B over 3 min at exponent 1; step 3, 100% B for 4 min; step 4, 100% to 40% B over 2 min (recycle).

Both instruments were interfaced with a Nelson Analytical Model 2600 chromatography data system, used for data reduction. Size exclusion chromatography was performed on the Du Pont HPLC, using chloroform/1% ethanol as the eluent, and a pair of Du Pont mixed-bed size exclusion columns. Weight- and number-average molecular weights were obtained from the Nelson Analytical GPC software, using polystyrene standards (Waters).

Starting Materials. (a) Bisphenol A Bis(chloroformate). Bisphenol A (228.3 g, 1.00 mol) and CH_2Cl_2 (750 mL) were stirred mechanically in a 2-L, three-neck flask fitted with a phosgene dip tube and an efficient condenser while cooling in an ice bath

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to 0 °C. Phosgene was admitted into the reactor at a rate of 3.0 g/min for 70 min (210 g of $COCl_2$; 2.12 mol); all precautions necessary were taken in working with this extremely toxic gas. A solution of freshly distilled diethylaniline (300 g, 2.00 mol) in 200 mL of CH_2Cl_2 was added carefully over 30 min, while the temperature of the reaction was maintained at 0 °C. (Use of diethylamine rather than dimethylaniline allows one to work at 0 °C and obviates the use of excess phosgene, as recommended by Wingfoot.[2]) After addition was complete, the reaction was warmed to ambient temperature over 1 h with gentle sparging with nitrogen. At this point, a clear solution was obtained. Over 2 h, the reaction was warmed with a water bath to about 40–50 °C with more forceful sparging with nitrogen to remove excess phosgene. Gases exiting from the condenser were vented through a caustic scrubber. After all phosgene was removed, 1.0 L of toluene was added, and the methylene chloride was removed in vacuo. Diethylaniline hydrochloride precipitates from the reaction and can be removed by filtration. Evaporation affords the crude BPA bis(chloroformate), which can be purified by recrystallization from hexane. Often a blue color is evident, probably due to formation of small amounts of dialkylaminobenzophenones during the phosgenation, and a second recrystallization may be necessary. In a solid state, the BPA bis(chloroformate) is stable for many months if moist air is excluded.

(b) Bisphenol A Bis(chloroformate) (Interfacial Procedure). Bisphenol A 0.50 mol, 114 g and 375 mL of CH_2Cl_2 were placed in a 2-L, five-neck flask equipped with a phosgene dip tube, a mechanical stirrer, a pH probe, a thermometer, a chilled condenser, and a port for addition of 25% NaOH using a Masterflex peristaltic pump attached to a Cole-Parmer pH controller. Twenty-five milliliters of water was added, and the reactor was immersed in a −10 °C ice bath. When the reaction temperature reached 15 °C, phosgene was bubbled in at a rate of 3 g/min for 33 min (99 g, 1.00 mol); 25% NaOH was added via the pH controller throughout the reaction to maintain a pH between 3 and 5 (controller set point of 4.0), while the temperature was controlled between 15 and 18 °C. After phosgene addition was complete, the pH was raised to between 9 and 10 (set point of 9.0) and maintained in that range until no more phosgene was detected (using phosgene detector paper; about 15–20 min). NaCl which had precipitated from solution was redissolved by addition of 200 mL of water. Stirring was stopped, and the two layers were allowed to separate. The organic layer was separated and washed with 1 N HCl, affording 0.5 L of a 1.0 M solution of BPA bis(chloroformate)/CH_2Cl_2, which can be used directly in cyclization reactions. Derivatization of a sample with phenol/Et_3N and analysis by HPLC revealed the composition to be 88% BPA bis(chloroformate), 8% dimer bis(chloroformate), and a total of 3% trimer and tetramer bis(chloroformate)s.

The purity of BPA bis(chloroformate) is best determined via derivatization and HPLC analysis. Derivatization is achieved as follows.

(c) Analysis Derivatization and HPLC. Approximately 0.5 mL of crude chloroformate/CH_2Cl_2 solution from above (or 100 mg of solid BPA bis(chloroformate) dissolved in 0.5 mL of CH_2Cl_2) was added dropwise to 1.0 g of phenol and 1.0 g of Et_3N in 10 mL of CH_2Cl_2 at 0 °C, over 2 min. If the chloroformates were added too fast, some polymerization resulted. The derivatized sample was washed with 15 mL each of 1 N HCl, 0.1 N HCl, and water and was then evaporated to dryness. All the derivatization and washing steps can be conveniently carried out in a 1-oz vial. After redissolution in THF (5 mL; sometimes addition of a few drops of water is necessary if triethylamine hydrochloride precipitates as fine needles), analysis is carried out by HPLC on a reverse-phase, THF–water system, using a C-8 or C-18 column, at a flow rate of 2.0 mL/min. A Du Pont C-8 Golden Series column and program 1 above were used. All products absorb at 254 nm, and any mono(chloroformate)s, BPA, and linear oligomers absorb strongly at 285 nm. An authentic sample of BPA bis(phenyl carbonate) (mp 104–105 °C; lit.[4] mp 102–103 °C) can be made from reaction of BPA, phenyl chloroformate, and triethylamine via conventional procedures.

(d) Bisphenol A Mono(triethylsilyl) Ether (1). Bisphenol A (114 g, 0.50 mol) was dissolved in 1.0 L of dry THF and treated with 0.2 equiv of triethylamine (10.1 g, 100 mmol). The solution was cooled to 0 °C and treated with 0.2 equiv of chlorotriethylsilane (34.0 g, 100 mmol) by adding a solution of the chlorosilane in 100 mL of CH_2Cl_2 over 30 min. After an additional hour, the solution was warmed to room temperature, and 500 mL of ether was added to help precipitate triethylamine hydrochloride. The mixture was filtered through a fritted glass funnel to remove triethylamine hydrochloride. The filtrate was evaporated to near dryness and redissolved in 500 mL of CH_2Cl_2. Upon seeding with BPA, a large amount of BPA crystallized. VPC analysis of the filtrate indicated that the CH_2Cl_2 soluble portion consisted of 80% BPA mono(triethylsilyl) ether, 7% bis(silyl) ether, and 13% BPA. The BPA was removed by filtration, washing with CH_2Cl_2, and the filtrate was cooled in the refrigerator and reseeded, removing more BPA. Finally, the CH_2Cl_2 solution was washed twice with 1.0 N NaOH to remove residual BPA. VPC analysis indicated that the product contained only 1% BPA, 91% BPA mono(triethylsilyl) ether, and 8% bis(silyl) ether. This material can normally be used without further purification, although pure samples can be obtained by flash column chromatography (silica gel, hexane/ethyl acetate), which will make future product purification easier. The product is an oil. ^1H NMR 0.752 (6 H, q, J = 7.8 Hz), 0.958 (9 H, t, J = 7.8 Hz), 1.60 (6 H, s), 5.3 (1 H, br s), 6.682 and 6.738 (4 H, d of d, J = 8.6 and 16.8 Hz), 7.55 (4 H, d, J = 8.6 Hz); ^{13}C NMR 5.03, 6.69, 31.12, 41.74, 114.73, 119.26, 127.74, 127.96, 127.96, 143.37, 143.73, 153.14, 153.26; FTIR (neat) OH (broad) at 3300–3400, strong absorptions at 1607.5, 1510.4, 1263.1, 1240.5, 1175.5, 1013.5, 912.13, 833.32, 745.64, and 735.13 cm^{-1}.

Bisphenol A Oligomeric Linears. (a) Linear Bisphenol A Carbonate Dimer (3). Crude silyl ether 1 from above (3.434 g, 10.0 mmol) and bis(2,4-dinitrophenyl)carbonate (2.00 g, 5.00 mmol) were stirred in 100 mL of CH_2Cl_2 at 0 °C and treated with triethylamine (1.01 g, 10.0 mmol) and 4-(dimethylamino)pyridine (61 mg, 0.5 mmol; 5% catalyst). After stirring for 2 h at 0 °C, the reaction was quenched with 25 mL of 1.0 N HCl and extracted into CH_2Cl_2. After an additional wash with 0.1 M HCl, the CH_2Cl_2 solution was washed twice with cold 1.0 M NaOH to remove dinitrophenol and then again with 0.1 N HCl. Drying and evaporation provided the crude product, linear BPA carbonate dimer bis(triethylsilyl) ether, which was an oil and which was pure by TLC.

Deprotection of the silyl ether was achieved via acid-catalyzed hydrolysis in methanol/CH_2Cl_2. The crude silyl ether was dissolved in 3:1 MeOH/CH_2Cl_2 and was treated with about 50 mg of p-toluenesulfonic acid. Analysis by TLC indicated that desilylation occurred almost instantly at ambient temperature. The product was evaporated and purified by column chromatography, affording 2.21 g of white solid (92%). Recrystallization from CH_2Cl_2/EtOAc gave mp 174–175 °C (lit.[5] mp 172–172.5 °C). The material was about 97% pure by HPLC and had a 254/280 nm area ratio of 0.41. Bisphenol A has an area ratio of 0.19. ^1H NMR 1.632 (12 H, s), 5.101 (2 H, s), 6.708 (4 H, d, J = 8.6 Hz), 7.065 (4 H, d, J = 8.7 Hz), 7.135 (4 H, d, J = 8.7 Hz), 7.235 (4 H, d, J = 8.7 Hz); ^{13}C NMR 31.01, 42.14, 114.85, 120.2, 127.92, 127.96, 142.5, 148.77, 149.08, 153.51; FTIR ($CHCl_3$) C=O at 1787.9, sharp O—H at 3587.8, broad O—H at 3200–3250 cm^{-1}.

(b) Linear Bisphenol A Carbonate Trimer (4). Crude silyl ether 1 from above (3.434 g, 10.0 mmol) and BPA bis(chloroformate) (1.765 g, 5.00 mmol) were stirred in CH_2Cl_2 at 0 °C and treated with triethylamine (1.01 g, 10 mmol), reacting for 2 h at 0 °C. The crude product was worked up by extraction into CH_2Cl_2 and washing with HCl (1.0 N and then 0.1 N). After evaporation, the product was dissolved in 1:1 methanol/CH_2Cl_2 and treated with ca. 10 mg of toluenesulfonic acid. After 1 h at room temperature, TLC analysis indicated complete deprotection to the linear uncapped trimer 4. The linear trimer was purified by column chromatography, affording 3.20 g of white amorphous solid (87%), with mp 84–86 °C, which was found to be 98% pure by HPLC analysis. The 254/280 area ratio of linear trimer IV is 0.68. ^1H NMR 1.621 (12 H, s), 1.653 (6 H, s), 5.482 (2 H, s), 6.681 (4 H, d, J = 8.57 Hz), 7.03–7.247 (20 H, m); ^{13}C NMR 30.95, 31.03, 42.14, 42.61, 114.88, 120.20, 120.39, 127.94, 127.99, 142.32, 148.37, 148.77, 148.96, 149.16, 152.41, 153.67; FTIR ($CHCl_3$) C=O at 1769.0, O—H at 3597 (sharp) and 3200–3300, strong absorptions at 2973, 1511, 1259, 1082, 1016, and 832 cm^{-1}.

(c) Bisphenol A Mono(triethylsilyl) Ether Mono(chloroformate) (2). Purified silyl ether 1 from above (6.88 g, 20.0 mmol) was dissolved in 100 mL of toluene and cooled to −10 °C

in a salt bath. The solution was phosgenated at that temperature, taking all necessary precautions, for 5 min, at a flow rate of 0.5 g of $COCl_2$/min. After phosgenation was complete, a solution of dimethylaniline/toluene (2.42 g, 20.0 mmol; 10 mL of toluene) was added over 20 min. The solution formed a precipitate, dimethylaniline hydrochloride. The reaction was warmed to ambient temperature, sparged with nitrogen to remove excess phosgene, and then filtered, washed with 1 N HCl, dried, and evaporated. The crude chloroformate was used without further purification. Derivation with PhOH/Et_3N according to the procedure above and analysis by HPLC indicated that the product was about 93% pure, containing a small amount of starting material. FTIR showed a C=O at 1788.8 cm^{-1} and no O—H. ^1H NMR 0.730 (q, J = 7.7 Hz, 6 H, Si–CH_2), 0.989 (t, J = 7.7 Hz, 9 H, Si–CH_2CH_3), 1.628 (s, 6 H, *gem*-dimethyl), 6.748 (d, J = 8.6 Hz, 2 H, aromatic ortho to triethylsiloxy), 7.038 and 7.068 (pair of overlapping d, J = 8.9, 9.0 Hz, 4 H, aromatic), and 7.235 (d, J = 8.8 Hz, 2 H, aromatic ortho to chloroformate group).

(d) Linear Bisphenol A Carbonate Tetramer (5). Chloroformate **2** (10% of the product from above; 2.0 mmol) and linear dimer **3** (482 mg, 1.00 mmol) were stirred in 20 mL of CH_2Cl_2 at 0 °C and treated with Et_3N (205 mg, 2.0 mmol). Workup and deprotection similar to methods above afforded linear tetramer **5** in 53% yield after chromatography. HPLC analysis showed 254/280 area ratio of 0.88. mp 157–161 °C; ^1H NMR 1.612 (s, 12 H, *gem*-dimethyl), 1.647 (s, 12 H, *gem*-dimethyl), 5.39 (br s, 2 H, O–H), 6.639 (d, J = 8.4 Hz, 4 H, C–H ortho to phenols), 7.01–7.245 (multiplet, 28 H, aromatic); ^{13}C NMR 30.98, 31.06, 42.16, 42.63, 114.89, 120.23, 120.41, 127.93, 127.97, 128.02, 142.33, 148.42, 148.78, 148.98, 149.19, 152.47, 153.67; FTIR C=O at 1769.9, H—O at 3600, other strong absorptions at 1015.7, 1164.1, 1194.8, 1247.9, and 1508.4 cm^{-1}.

(e) Linear Bisphenol A Carbonate Pentamer (6). Chloroformate **2** (10% of the product from above; 2.0 mmol) and linear trimer **4** (736 mg, 1.0 mmol) were stirred in 20 mL of CH_2Cl_2 at 0 °C and treated with Et_3N (205 mg, 2.0 mmol). Workup and deprotection of the silyl groups similar to methods above afforded linear pentamer **6** in 77% yield after chromatography. HPLC analysis showed the 254/280 area ratio to be 1.39. mp 173–177 °C; ^1H NMR 1.633 and 1.669 (s, 30 H, *gem*-dimethyls), 4.92 (br s, 2 H, O–H), 6.680 (d, J = 10.6 Hz, 4 H, C–H ortho to phenols), 7.047–7.260 (m, 36 H, aromatic); ^{13}C NMR 30.90, 30.96, 31.03, 42.11, 42.54, 42.89, 114.76, 120.14, 120.31, 127.91, 148.33, 148.75, 148.91, 148.93, 149.06, 152.29, and 153.52; FTIR C=O at 1770.1, O—H at 3600, other strong absorptions at 1015.7, 1164.1, 1194.8, 1215.2, 1222.4, 1246.9, and 1507.7 cm^{-1}.

Bisphenol A Oligomeric Cyclics. (a) Bisphenol A Carbonate Cyclic Trimer (7). Linear trimer **4** (370 mg, 0.50 mmol) and bis(2,4-dinitrophenyl)carbonate (200 mg, 0.50 mmol) were dissolved together in 25 mL of CH_2Cl_2 (no reaction occurs in the absence of base) and were added via syringe pump to 50 mL of CH_2Cl_2 containing 1.1 mmol of Et_3N (111 mg) and 0.025 mmol of 4-(dimethylamino)pyridine (3 mg; 5% catalyst) at 0 °C over 1 h. After stirring for 1 h, the reaction was worked up by washing sequentially with water, HCl, NaOH, and HCl. After drying and evaporation, the amorphous solid product was analyzed by HPLC, showing 60% cyclic trimer, 15% cyclic hexamer, and 5% cyclic nonamer. All the cyclic oligomers had 254/280 area ratios of 40–50. Smaller amounts of linear contaminants were also noticed. Cyclic trimer was separated by column chromatography and recrystallized from carbon disulfide and then from benzene, affording fine cubic crystals with mp 345–350 °C (lit.[16] mp 350 °C).

(b) Bisphenol A Carbonate Cyclic Tetramer (8). A solution of linear trimer (736 mg, 1.00 mmol) **4** and BPA bis(chloroformate) (353 mg, 1.00 mmol) in 20 mL of CH_2Cl_2 was added over 2 h to an excess of Et_3N (300 mg, 3.0 mmol) in 50 mL of CH_2Cl_2 at 0 °C. Workup of the reaction by extraction into CH_2Cl_2 and washing with HCl and water afforded the crude product, which HPLC analysis indicated contained the following mixture: cyclic tetramer (55%), cyclic octamer (20%), and cyclic dodecamer (8%). Cyclic tetramer has a 254/280 area ratio of 50. Small amounts of linear materials were also present. Cyclic tetramer was separated by column chromatography and purified by recrystallization from benzene (mp 368–72 °C; lit.[14,15] mp 375 °C).

(c) Bisphenol A Carbonate Cyclic Pentamer (9). Reaction of 1.00 mmol each of linear tetramer **5** and BPA bis(chloroformate) under conditions similar to those listed above afforded 35% cyclic pentamer (254/285 nm area ratio of 53) and 13% cyclic decamer.

(d) Bisphenol A Carbonate Cyclic Hexamer (10). Reaction of 1.00 mmol each of linear pentamer **6** and BPA bis(chloroformate) under condition similar to those above afforded 60% cyclic hexamer (254/285 area ratio of 56) and 9% cyclic dodecamer.

Cyclization Reactions. (a) Attempted Cyclization via Pseudo High Dilution. A solution of BPA (2.28 g, 10.0 mmol) and BPA bis(chloroformate) (3.53 g, 10.0 mmol) in 1:1 THF/CH_2Cl_2 (50 mL) was added to a cold solution of Et_3N (2.2 g, 22 mmol) in 50 mL of CH_2Cl_2 over 2 h. After complete addition and stirring for an additional hour, the reaction was worked up via extraction into CH_2Cl_2 and washing with HCl and water. HPLC analysis indicated that cyclic tetramer was the major product, as well as fair amounts of cyclic trimer and pentamer. A significant amount of BPA remained unreacted, and high levels of linear materials were present. This product distribution is represented in the trace shown in Figure 1. An identical reaction, but using pyridine as the base, gave the HPLC trace shown in Figure 2.

(b) Cyclization via Phase-Transfer Catalysis. Reactions of BPA disodium salt with bis(*o*-nitrophenyl) carbonate, bis(2,4-dinitrophenyl) carbonate, bis(methylsalicyl) carbonate, phosgene, and BPA bis(chloroformate) catalyzed by a variety of phase-transfer agents in a variety of solvents were all carried out in a similar manner. BPA disodium salt (2.72 g, 10.0 mmol) and PTC agent were stirred in 50 mL of solvent at temperatures from room temperature to 50 °C. The reactive agent was added in 20 mL of the same solvent over 1–2 h. In the case of the nitrophenyl carbonates, 5% DMAP was used as an additional catalyst, added along with the phenoxide. Reactions were all quenched by addition of acid, extracted into CH_2Cl_2, and washed with HCl and water. HPLC analysis indicated various amounts of cyclics, linears, and polymer. The product represented by the HPLC trace shown in Figure 3 resulted from reaction of BPA disodium salt in toluene at 75 °C, adding BPA bischloroformate over 1 h, and using 1,6-hexanediylbis[4-(dihexylamino)pyridinium bromide][28] as the phase-transfer catalyst (1% molar).

General Procedure for Preparation of Macrocyclic Aromatic Carbonates. A 1.0-L Morton flask equipped with a mechanical stirrer and condenser was charged with 200 mL of CH_2Cl_2, 7.0 mL of water, 3.0 mL of 9.75 M NaOH (29 mmol), and 2.4-mL of Et_3N (17.25 mmol). The mixture was heated to reflux and vigorously stirred, and a solution of BPA bis(chloroformate) (200 mL of 1.0 M in CH_2Cl_2) was added subsurface over the tip of the impeller at 6.7 mL/min by using a peristaltic pump. Concurrently, 59 mL of 9.75 M NaOH (575 mmol) was delivered over 25 min by using a dropping funnel, and 2.4 mL of Et_3N was added over 28 min by using a syringe pump. Within 10 min after complete bischloroformate addition, the phases were separated and washed with 1.0 M HCl and then with water three times. Concentration of the product in vacuo afforded a nearly quantitative yield of product containing 85% cyclics by HPLC analysis (Figure 4). Alternatively, the cyclics and polymer can be isolated by spraying the product/CH_2Cl_2 solution into rapidly stirred water at 85–95 °C. A typical distribution of cyclic oligomers was 5% dimer, 18% trimer, 16% tetramer, 12% pentamer, 9% hexamer, and 25% higher oligomeric cyclics. The level of linear oligomers was approximated by doping a known quantity of authentic linear trimer into the crude product, noting the increase in size of the trimer peak at 285 nm, which determined the level of linear trimer. By use of the known relative response factors for Bisphenol A, linear dimer, trimer, and tetramer, the total level of linear oligomeric impurities could be calculated to about 0.01–0.05%.

Washing the crude cyclics/polymer product with 5 volumes of acetone provided a solution of pure cyclics in about 75% yield (the high molecular weight polymer and macrocyclic carbonates with more than ca. 15 repeat units are insoluble in acetone). The mixed macrocyclic oligomers have mp 200–210 °C. FTIR shows no phenolic O—H and a strong C=O at 1770.6 cm^{-1}. ^{13}C NMR absorptions were found at 28.3, 30.27, and 30.87 (methyls), 42.29 and 42.53 (quaternary carbons), 120.2–120.4 and 127.7–127.9 (unsubstituted aromatics), 148.2–149.05 (substituted aromatics), and 152.1–152.2 (carbonyls). ^1H NMR (300 MHz) major resonances associated with BPA carbonates were 7.26 (d, J = 8.8, 4 H), 7.17

(d, J = 8.8, 4 H), and 1.69 (s, 6 H); minor resonances associated with cyclic dimer and trimer are also observed (vide infra). Field desorption shows parent ions at 508, 762, 1016, 1270, 1524, and 1778 m/e. HPLC elution using a THF/water gradient on a C-8 reverse-phase column showed the following pattern:

component	retn time, min	254/285 nm area ratio
cyclic dimer	3.10	17.5
cyclic trimer	4.29	46.6
cyclic tetramer	5.68	49.65
cyclic pentamer	6.91	52.65
cyclic hexamer	8.07	56.26
cyclic heptamer	9.125	51.5
cyclic octamer	10.10	50.7
cyclic nonamer	11.02	50.2

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.36; H, 5.21.

Preparation of Linear Oligomers. A reaction was carried out by using the same procedure described above for the preparation of macrocyclic carbonates, except that pyridine was used as the amine catalyst rather than triethylamine. Identical reaction workup provided a white solid with mp 140–145 °C. HPLC analysis (Figure 5) indicated selective formation of linear oligomers, by comparison of retention times and 254/285 nm values to those of Bisphenol A and authentic linear dimer, trimer, and tetramer. HPLC elution using the same THF/water gradient as for cyclics analysis showed the following pattern:

component	retn time, min	254/285 nm area ratio
Bisphenol A	1.69	0.187
linear dimer	2.077	0.408
linear trimer	2.626	0.679
linear tetramer	3.417	0.879
linear pentamer	4.496	1.39
linear hexamer	5.635	1.47
linear heptamer	6.673	1.61
linear octamer	7.618	1.69
linear nonamer	8.496	2.16
linear decamer	9.326	2.05

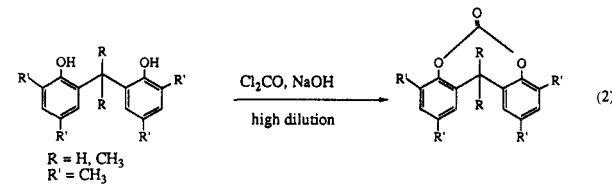
FTIR showed an O—H absorption at 3597 cm^{-1} and a C=O absorption at 1770.2 cm^{-1}. ^1H NMR (300 MHz) major resonances associated with carbonate linkages were 7.26 (d, J = 8.9, 4 H), 7.18 (d, J = 8.9, 4 H), and 1.69 (s, 6 H); minor resonances associated with phenolic end groups (about 10%) were 7.08 (m), 6.70 (m), and 4.91 (s). ^{13}C NMR absorptions were found at 30.892 (methyls), 42.05 and 42.54 (quaternary carbons), 114.65, 114.78 (phenolic carbon), 119.90–120.75 and 127.52–128.21 (unsubstituted aromatics), 142.20, 148.28–149.03 (substituted aromatics), 152.214, and 153.635 (carbonyls). Field desorption mass spectrum showed parent peaks at 272, 482, 736, and 990 m/e. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.80; H, 5.42.

Polymerization Reactions. BPA cyclic oligomeric carbonate (0.5 g of dried powder) and catalyst solution were dissolved together and re-evaporated to a powder. The powder was placed in a dry test tube, and the test tube was sealed with a septum. The powder was heated to 300 °C under nitrogen for 30 min. After cooling, the product was analyzed by gel permeation chromatography. Molecular weights in Table II are relative to polystyrene. In experiments utilizing diphenyl carbonate as a chain terminator, the carbonate was dissolved along with the cyclics and catalyst. Figure 7 shows a GPC trace of starting cyclic oligomers and crude polymerization product.

Background

Literature on cyclic aliphatic carbonates and esters is fairly extensive.[6] Preparation of cyclic carbonates from ethylene or propylene glycol is straightforward and is favored thermodynamically. However, aliphatic polycarbonates have not generally been useful materials due to their thermal instability (decomposition to olefin, CO_2, and an alcohol)[7] and lack of ductility. Furthermore, polymerization of these cyclic precursors normally leads to polymers with significant amounts of cyclic present at equilibrium. Hocker et al. have recently circumvented many of these difficulties by using the cyclic carbonates of 2,2-dialkyl-1,3-propanediols as precursors to aliphatic polycarbonates.[8]

Cyclic polyesters and polycarbonates were prepared in the 1930s by Carothers[9] via thermal depolymerization reactions of linear polyesters and polycarbonates, using distillation to remove the more volatile cyclic esters and carbonates. In the mid-1960s, Prochaska was granted patents on the preparation of monomeric cyclic carbonates with 7- or 8-membered rings, formed from 2,2′-bisphenols, such as 2,2′-biphenol or compounds obtained via condensation of p-cresol with formaldehyde (eq 2).[10] The



(2)

monomeric cyclic carbonates were prepared either directly, via phosgenation of the 2,2′-bisphenols, or by a vacuum distillation–transesterification reaction in a technique similar to that used by Carothers,[9] starting from an ortho,-ortho polycarbonate. The method was extended by Prochaska to many other systems having ortho,ortho carbonates, such as low molecular weight phenol–formaldehyde resins. This work has recently been reinvestigated by Kricheldorf and Jensson, who have examined the ring-opening polymerization of o,o'-biphenol carbonate in some detail.[11]

The cyclic carbonates of 2,2′-bisphenols could be polymerized to high molecular weight polymers at temperatures of 200–280 °C in the presence of potassium carbonate. Work carried out some years later by Juliano[12] indicated that polymerization of Prochaska's monomeric cyclic carbonates could be initiated by polymeric anions (such as obtained from anionic polymerization of polystyrene with n-BuLi. High molecular weight block copolymers were obtained, but degradation to lower molecular weights occurred within hours. Probably, the strained monomeric carbonate polymerized to linear polymers and then reached equilibrium as a series of cyclic oligomeric carbonates formed via back-biting, with significant amounts of oligomers present at equilibrium because of the ortho,ortho relationship in the bisphenol. An analogy for this behavior can be seen in polyester chemistry, where one finds that only about 1% cyclic oligomers are found in poly(butylene terephthalate) [1–2% with poly(ethylene terephthalate)], whereas up to 8.5% cyclic oligomer can be found in poly(ethylene isophthalate) or poly(ethylene phthalate) under equilibrating conditions.[13]

In 1962, Schnell and Bottenbruch reported the preparation of the cyclic tetrameric carbonate of Bisphenol A (BPA).[14] They found that cyclic tetramer could be formed preferentially from reaction of BPA with BPA bis(chloroformate), in reactions carried out at 0.05 M concentration. In more detailed publications on the subject, yields as high as 21% were reported, for a variety of bisphenols.[15] It was also reported that the melting point of the cyclic tetramer from BPA was 375 °C and that it could be polymerized at its melting point with or without catalyst, affording very high molecular weight polycarbonate.

Prochaska was granted a patent[16] on the preparation of cyclic dimers and trimers of various bisphenols, although only the cyclic trimer of BPA was reported. An improved

process for preparing BPA cyclic trimer was reported by Moody at about the same time.[17] Whereas Prochaska used direct phosgenation of BPA in dilute solution in methylene chloride and pyridine as the source of base, Moody carried out a slow addition of BPA bischloroformate to pyridine and a small amount of water, effecting a high dilution reaction (final concentration of 0.03 M, with reaction time of 1.75 h).

Results and Discussion

When attempts were made to reproduce either the Prochaska/Moody results or the Schnell work, HPLC analyses of the products obtained from reactions of BPA with BPA bis(chloroformate) indicated mixtures containing predominantly *linear* oligomeric products (presumably formed from adventitious water) and only low levels of cyclics, even at concentrations as low as 0.01 M. The use of high-pressure liquid chromatography, using detection at various wavelengths, as an analytical tool revealed that such reactions were not selective for cyclic formation. Even pseudo high dilution conditions,[18] wherein a solution of BPA in THF (or of BPA disodium salt in water) was added concurrently with a solution of BPA bis(chloroformate) in CH_2Cl_2 slowly via syringe drive to a solution of amine in CH_2Cl_2, gave cyclic oligomeric carbonates contaminated with significant levels of linear materials. Previously, cyclic trimer and tetramer had been isolated via a series of precipitations and crystallizations, from methylene chloride/petroleum ether, ethylene chloride, carbon disulfide, and benzene.[14-17] Repeating the literature examples, but at a somewhat higher concentration (0.10 M), we were able to isolate only about 10% of the desired BPA cyclic tetramer and less than 5% of the cyclic trimer.

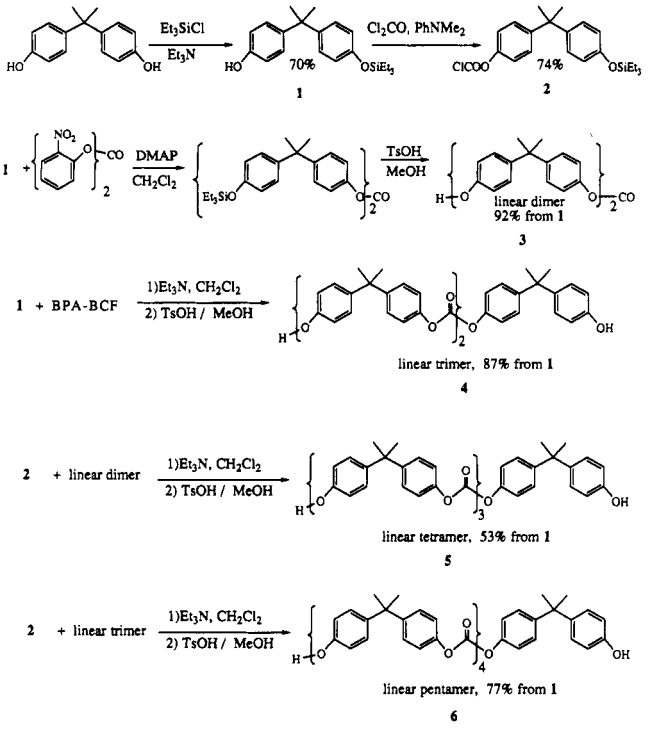
Preparation of Authentic Materials. Our efforts in cyclic oligomeric carbonate chemistry began with the synthesis of authentic low molecular weight linear and cyclic BPA oligocarbonates in unequivocal fashion (Schemes I and II). Bisphenol A was monoprotected[19] via reaction of excess BPA with chlorotriethylsilane and Et_3N in CH_2Cl_2 at 0 °C. Excess BPA was removed by crystallizing most of it from the CH_2Cl_2 solution at low temperature and by washing out the remainder with NaOH.[20] The mono(triethylsilyl) ether of BPA (1) was converted to its chloroformate (2) via reaction with phosgene and dimethylaniline, according to the Wingfoot[2] method.

Reaction of monoprotected bisphenol 1 with *o*-nitrophenyl carbonate in CH_2Cl_2 with catalysis by 4-(dimethylamino)pyridine[21] followed by deprotection of the silyl ether with toluenesulfonic acid/MeOH afforded a 92% yield of linear dimer 3. Reaction of monoprotected bisphenol 1 with BPA bis(chloroformate) at low temperature in methylene chloride followed by deprotection with *p*-TsOH/MeOH led to an 87% yield of linear trimer 4. Reaction of linear dimer with protected chloroformate 2 in CH_2Cl_2, using Et_3N as base, at 0 °C followed by removal of the triethylsilyl group with *p*-TsOH/MeOH afforded linear tetramer 5 in 53% yield, and similar reaction of linear trimer afforded linear pentamer 6 in 77% yield.

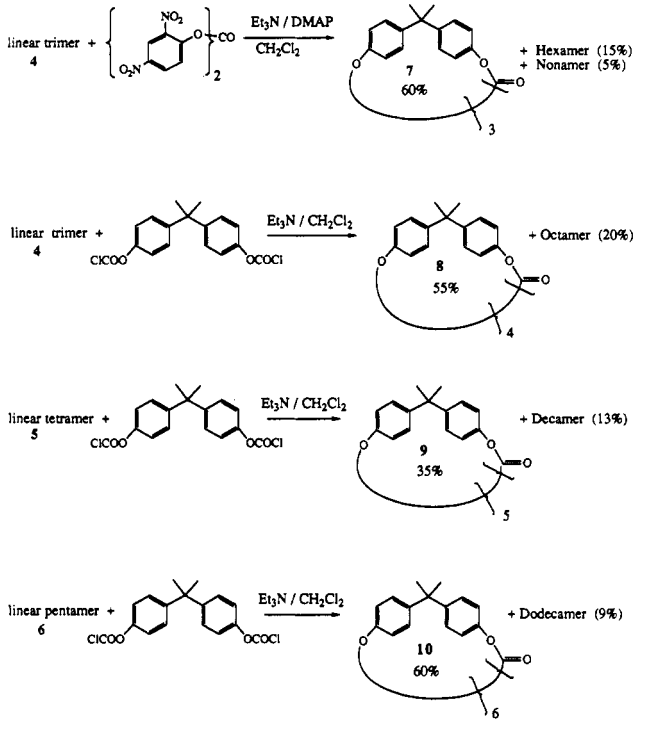
All of the linear oligomers were solids crystallized from EtOAc/hexane. Their identities were confirmed by NMR, FTIR, mass spectral, and HPLC analyses. Reverse-phase HPLC using a THF/water system gave excellent separation of materials and indicated that these phenol-terminated oligomers had significant absorption at 285 nm, with 254/285-nm absorbance ratios of about 0.5–2.

Authentic cyclic oligomeric materials were prepared by using pseudo high dilution techniques.[18] Rather than relying on reaction of monomeric species to afford oligomeric cyclics of three or more members, the discrete linear

Scheme I
Preparation of Oligomeric Linears



Scheme II
Preparation of Authentic Cyclic Oligomers



oligomers were used as starting materials. Thus, reaction of linear dimer with BPA bis(chloroformate) at high dilution led to cyclic trimer 7 (22%), cyclic hexamer (28%), and cyclic nonamer (12%). Alternatively, reaction of linear trimer with bis(2,4-dinitrophenyl) carbonate, catalyzed by DMAP, led to cyclic trimer (60%), hexamer (15%), and nonamer (5%). Since 2 + 1 or 3 + 0 condensations were performed, only every third oligomer was obtained as a cyclic. Smaller amounts (<5%) of linear materials were also obtained. The discrete cyclic oligomers were easily isolated by flash chromatography. Cyclic tetramer (8), pentamer (9), and hexamer (10) were similarly obtained via reaction of BPA bis(chloroformate) with linear tri-

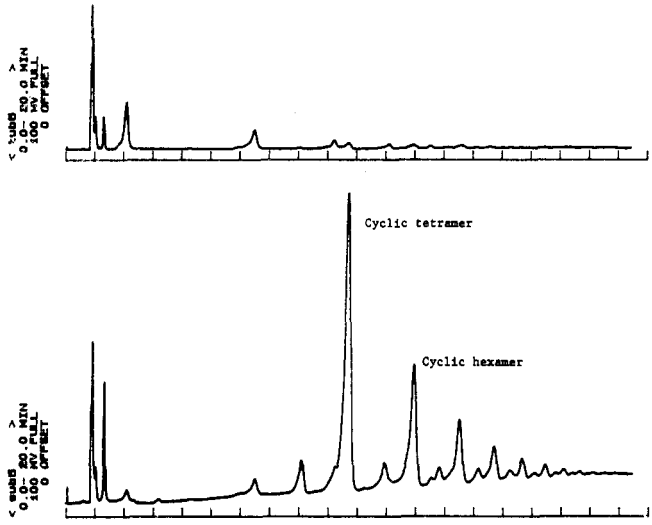


Figure 1. Result of attempted cyclization via condensation of BPA with BPA bis(chloroformate) using stoichiometric DMAP: (top trace) detection at 285 nm, 0.10 AU full scale; (bottom trace) detection at 254 nm, 0.10 AU full scale.

mer, tetramer, and pentamer, respectively. In each case, smaller amounts of the $(x + 1)_n$ oligomers were also obtained from the linears with DP = x, although the amounts diminished as the ring sizes increased (Scheme II).

In each case the cyclic oligomeric carbonates were separated from linear materials by column chromatography, with the cyclics eluting faster than the more polar linears. Recrystallization gave solids in all cases, with trimer and tetramer being highly crystalline. IR analysis showed no O–H absorption, and all compounds had 254/285-nm ratios of 40–50 (vs 0.25–1.2 for the linear oligomers). Mass spectral analyses confirmed the identity of the cyclics. With the authentic materials in hand, our attention was turned toward a method for effecting a selective conversion of BPA into cyclic oligomeric carbonates.

Preparation of Oligomeric Cyclic Carbonates. The first attempts at preparation of cyclic oligomeric polycarbonates were similar to those previously reported.[14-17] Simultaneous addition (via mechanical syringe pump) of solutions of BPA/THF and BPA bis(chloroformate) in CH_2Cl_2 to a solution of Et_3N in CH_2Cl_2 at 0 °C over 8 h led to 20–30% cyclic oligomeric carbonates by HPLC analysis. Cyclic tetramer was the major product, although cyclics from trimer to decamer were noted. However, the remainder of the material consisted of oligomeric linear species, some of which were terminated with phenolic hydroxyl, the remainder of which would be either chloroformate- or diethylurethane-terminated.[22] Although the yield was improved to 40–60% by using DMAP as the base, this product mixture was not deemed to be useful for further conversion to polymer without removal of the residual linears. A representative HPLC trace is shown in Figure 1. It is interesting to note that previous workers[14-17] had used pyridine as the base in a similar reaction. In our hands, such reactions afforded predominantly *linear* oligomers, with small amounts of cyclic tetramer and hexamer detected as the only cyclic oligomeric products (Figure 2).[23]

The use of phase-transfer catalysis (PTC) techniques[24] to effect the high dilution conditions necessary for high-yielding cyclics preparation were next investigated. PTC methods have been used in the preparation of oligomeric polyformals[25] (from reaction of BPA, NaOH, and CH_2Cl_2) and, more recently, to prepare macrocyclic lactones.[26] In

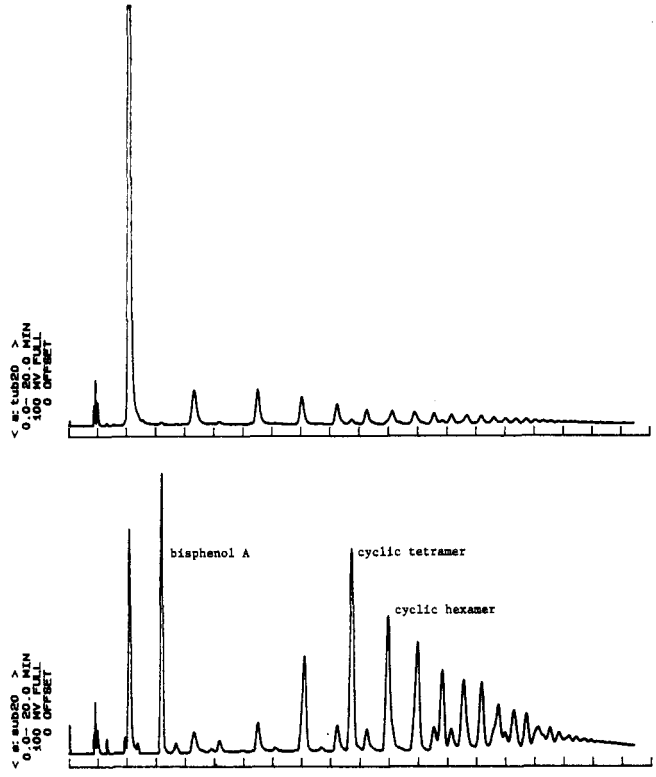


Figure 2. Result of attempted cyclization via condensation of BPA with BPA bis(chloroformate), using pyridine as base: (top trace) detection at 285 nm, 0.10 AU full scale; (bottom trace) 254-nm detection, 0.10 AU full scale.

operation, the PTC catalyst achieves pseudo high dilution conditions by controlling the amount of anionic reagent soluble in the organic phase. For example, if 1% tetrabutylammonium bromide were used as the catalyst, one would expect that the maximum concentration of BPA dianion to be solubilized in the organic phase would be 0.005 equiv. Slow addition of a bis(chloroformate) in organic solution would then achieve low concentrations of both reagents in the organic phase, favoring intramolecular rather than intermolecular reactions; final product concentrations could still be reasonably high, however, since the cyclic products, once formed, should be inert to the reaction conditions.

Reactions of BPA disodium salt with bis(*o*-nitrophenyl)[21] carbonate, bis(2,4-dinitrophenyl) carbonate, bis(methylsalicyl) carbonate,[27] phosgene, or BPA bis(chloroformate) catalyzed by a variety of phase-transfer agents in a variety of solvents were investigated. The best results were obtained in reaction of anhydrous BPA disodium salt with BPA bis(chloroformate) in toluene at 75 °C by using a bis(ammonium) salt[28] as the PTC catalyst. In this manner, 50–67% cyclics were obtained and were nearly devoid of linear contamination, except for starting BPA (see HPLC trace, Figure 3). Unfortunately, this technique proved to be rather cumbersome in operation and did not yield product of the purity desired. This method stands, however, as the first phase-transfer technique for preparation of cyclic oligomeric carbonates.

Bayer chemists have reported the preparation of *macro*cyclic polycarbonates (i.e., cyclics with molecular weights of 15 000–30 000), using BPA bis(chloroformate) in a hydrolysis/condensation reaction.[29] Horbach et al. reported a procedure wherein BPA bis(chloroformate) was reacted with triethylamine, NaOH, and CH_2Cl_2 at high pH, high triethylamine, and low temperature to form a high molecular weight cyclic polycarbonate, with weight-average molecular weights of at least 15 000, and less than 0.3–0.8 endgroups per polycarbonate molecule (i.e., 15–40% lin-

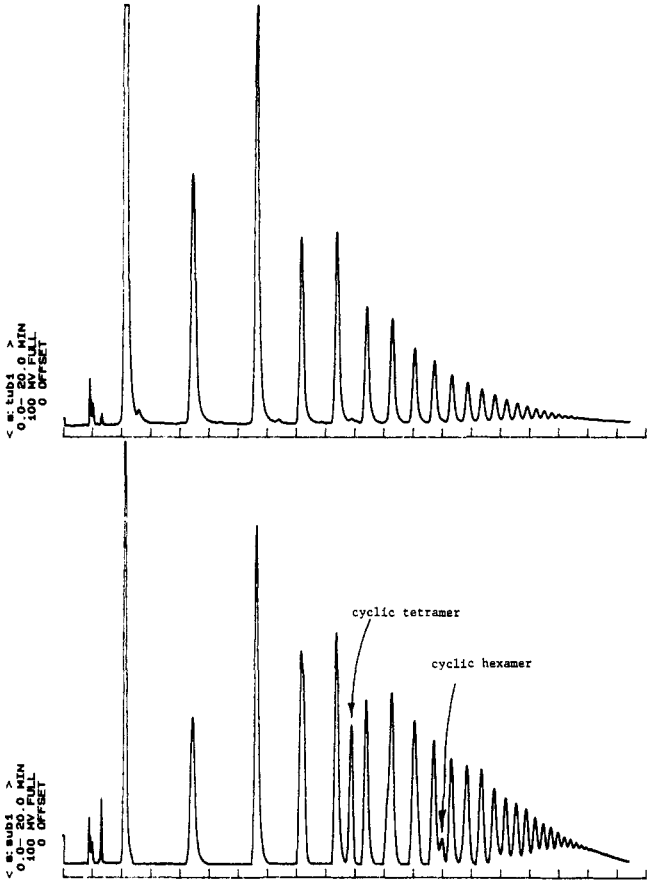


Figure 3. Result of cyclization via PTC reaction of BPA disodium salt with BPA bis(chloroformate): (top trace) detection at 285 nm, 0.10 AU full scale; (bottom trace) 254-nm detection, 0.10 AU full scale.

ears). The Bayer chemists were interested in high molecular weight cyclic polycarbonates presumably because these materials should have inherently higher hydrolytic stability than a linear polymer of the same molecular weight; assuming one reaction per molecule, for simplicity, a nucleophilic attack on a carbonate group would not alter the molecules' molecular weight. The analytical techniques used to show that the high molecular weight polymer was cyclic were based on measurements of endgroups per molecule (although no method for endgroup analysis was given) and information from an amidization reaction using piperidine.[30] Although the results of the amidization experiment are not conclusive,[31] the data suggest that the Bayer chemists obtained predominantly cyclic materials with a selectivity of macrocycles vs linears of about 60–85%. No data suggesting the presence (or absence) of *oligomeric* cyclic materials were presented in any of the Bayer papers. However, since all the BPA bis(chloroformate) was added at once in the Bayer procedure, it is likely that oligomeric products were not formed, since the reactant concentrations were high.

We were nonetheless intrigued by the possibility of using a hydrolysis/condensation reaction for the preparation of oligomeric cyclic carbonates. If *cyclic* carbonates could be formed selectively in such reactions, then slow addition of BPA bis(chloroformate) solution to a mixture of Et_3N, NaOH, and CH_2Cl_2 should lead to formation of the desired low molecular weight oligomeric cyclics, because high concentrations of chloroformate oligomers would never be present; thus, *intra*molecular reactions should be favored over *inter*molecular reactions. In this manner, pseudo high dilution conditions would be achieved by addition of a single monomer rather than by an attempt to balance phenol and bis(chloroformate) endgroups, as

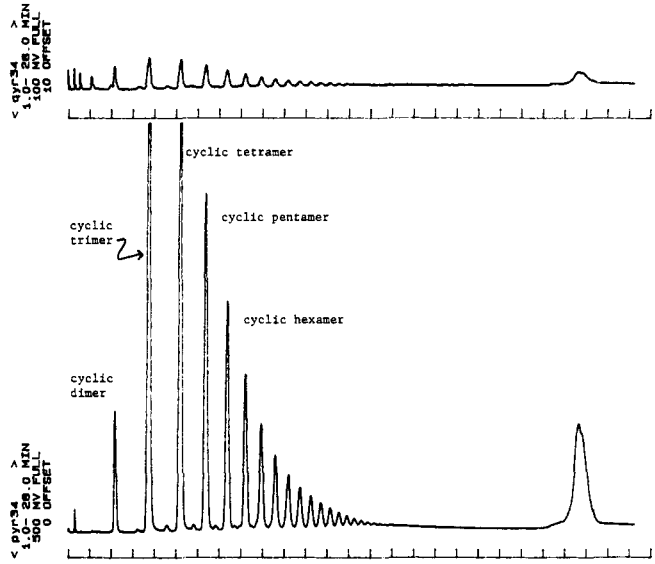


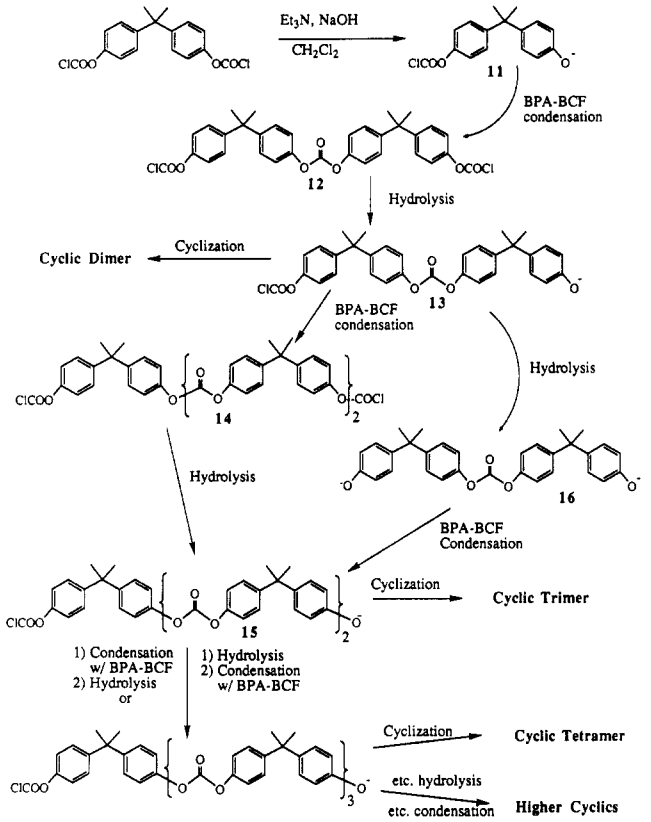
Figure 4. Result of triethylamine-catalyzed cyclization via hydrolysis/condensation of BPA bis(chloroformate): (top trace) detection at 285 nm, 0.10 AU full scale; (bottom trace) 254-nm detection, 0.50 AU full scale.

in previous efforts.

When such an experiment was carried out, it was found not only that cyclic oligomeric carbonates were formed but also that virtually *no oligomeric linear materials were present*. The HPLC traces in Figure 4 show the crude product from an interfacial cyclization reaction. The product is composed only of oligomeric cyclics and high molecular weight polymer in about an 85/15 ratio. The very small peaks between the cyclics are not linears, but rather ortho,para mixed cyclics, formed from the small amounts of *o,p*-BPA present in the BPA starting material. The levels of linear oligomers in the reaction products were estimated by doping authentic linear trimer into the reaction product and analyzing by HPLC, with detection at 285 nm. By use of this method, it was calculated that the level of linear oligomers was 0.01–0.03% of the total. This means that the selectivity for cyclics/linears in this reaction is about 10 000 to 1! This selectivity toward cyclics vs linears is far greater than the 60–85% selectivity found in previous preparations of BPA cyclic carbonates.[14-17] A range of cyclics from cyclic dimer through the oligomer with $n = 26$ were formed, with the majority of material (>90%) having a degree of polymerization of less than 10. Cyclic dimer was formed in 5–10% yield in these reactions, with the low yields due to the fact that ring strain makes formation of dimer somewhat more difficult than the higher oligomeric cyclics. The previously unreported cyclic dimer is readily isolated, and a crystal structure has been solved.[32] Cyclic dimer is subject to some ring strain, evident from a shift of about 10 cm^{-1} in the infrared (1780.9 cm^{-1}). The major byproduct from the reaction is high molecular weight polymer, which is represented by the broad peak near the end of the trace. The molecular weight of this polymer ranges between 40 000 and 100 000 (by gel permeation chromatography using polystyrene standards), depending on reaction conditions, but has not yet been characterized as a linear or cyclic material.

Under the conditions of this cyclization reaction, both hydrolysis and condensation must occur for BPA bis(chloroformate) to be converted first to a phenoxide and then to a carbonate. Controlling the ratio of hydrolysis to condensation is crucial, since excessive hydrolysis will lead to recovery of BPA or to oligomeric linears. Conversely, if hydrolysis occurs too slowly, then the concentration of BPA bis(chloroformate) will increase in the reaction

Scheme III
Formation of Cyclic Oligomers and Reincorporation of Linear Oligomers via Hydrolysis/Condensation Reactions of BPA-Bis(chloroformate)



medium, eventually leading to conditions that favor intermolecular reactions, affording polymer. Maintenance of the proper ratio of hydrolysis/condensation and sufficient reaction rates to prevent buildup of reactive oligomers was the key to successful cyclizations.

Neglecting, for the moment, the effects of amine catalysis, one can develop a model for the selective formation of cyclic vs linear oligomers (Scheme III). Under the conditions of the amine-catalyzed cyclization reaction, one molecule of BPA bis(chloroformate) must undergo one hydrolysis [forming mono(chloroformate) **11**] and one condensation reaction with a second molecule of BPA bis(chloroformate) to form dimer bis(chloroformate) **12**. Subsequent hydrolysis of intermediate **12** leads to the first intermediate (**13**) which is capable of cyclizing to the desired product (cyclic dimer) or which can react with a third molecule of BPA bis(chloroformate) to form a trimer bis(chloroformate) (**14**). Trimer bis(chloroformate) **14** next undergoes a hydrolysis reaction, forming trimer mono(chloroformate) **15**, which again can either cyclize or continue to grow via condensation with incoming BPA bis(chloroformate). Since the amount of incoming bis(chloroformate) is limited at any given time, intra- rather than intermolecular condensations are favored, affording good yields of cyclics vs polymer. Rapid reaction of the bischloroformates before concentrations build up is also ensured by the high catalyst levels. Any linear oligomers that may form in small amounts can be reincorporated into cyclics. For example, had intermediate **13** been hydrolyzed to linear dimer **16**, subsequent reaction with entering BPA bis(chloroformate) would lead to intermediate **15**, which can cyclize to the cyclic trimer. The pathway by which BPA bis(chloroformate) may be converted to cyclics or linears is shown in Scheme III.

The choice of triethylamine as the catalyst for this reaction was crucial. A number of other amine catalysts were utilized, to try to elucidate the mode of catalysis (Table I). Curiously, when pyridine was substituted for triethylamine in an otherwise identical reaction, only *linear* oligomers were obtained (note the significantly higher 285-nm absorptions in Figure 5). Merely by a change of catalysts, total selectivity toward either cyclics or linears can be achieved. When other amines were investigated,

Table I
Interfacial Hydrolysis/Condensation Reactions of Bisphenol A Bis(chloroformate) Using Various Catalysts[a]

catalyst	catalyst concn	% cyclics	products
Et_3N	0.1[b]	85	cyclics and polymer
Et_3N	0.005	<5	polymer and cyclics
pyridine	0.1	0	linears
pyridine	0.5	0	Bisphenol A
ethylpiperidine	0.1	58	cyclics and polymer
ethylpiperidine	0.05[b]	75	cyclics and polymer
n-Pr_3N	0.1	68	cyclics and polymer
n-Pr_3N	0.25[b]	84	cyclics and polymer
quinuclidine	0.1	<1	36% linears + polymer
quinuclidine	0.005[b]	34	polymer, cyclics, 1% linear
Et_3NMe	0.1	27	linears, cyclics, polymer
Et_2NMe	0.005[b]	64	cyclics, polymer, <1% linears
$EtNMe_2$, Me_3N, DABCO[c]	0.1	<1	linears
proton sponge,[d] i-Bu_3N, Et_4NOH	0.1	0	no reaction
n-Bu_4NBr, PEG 600[e]	0.1	0	no reaction
4-(dimethylamino)-pyridine	0.1	80	cyclics and polymer

[a] Cyclization according to procedure under Experimental Section, with final product concentration of 0.5 M. [b] Optimum concentration for cyclic formation. [c] 1,4-Diazabicyclo[2.2.2]octane. [d] 1,8-Bis(dimethylamino)naphthalene. [e] Poly(ethylene glycol), av M_w = 600.

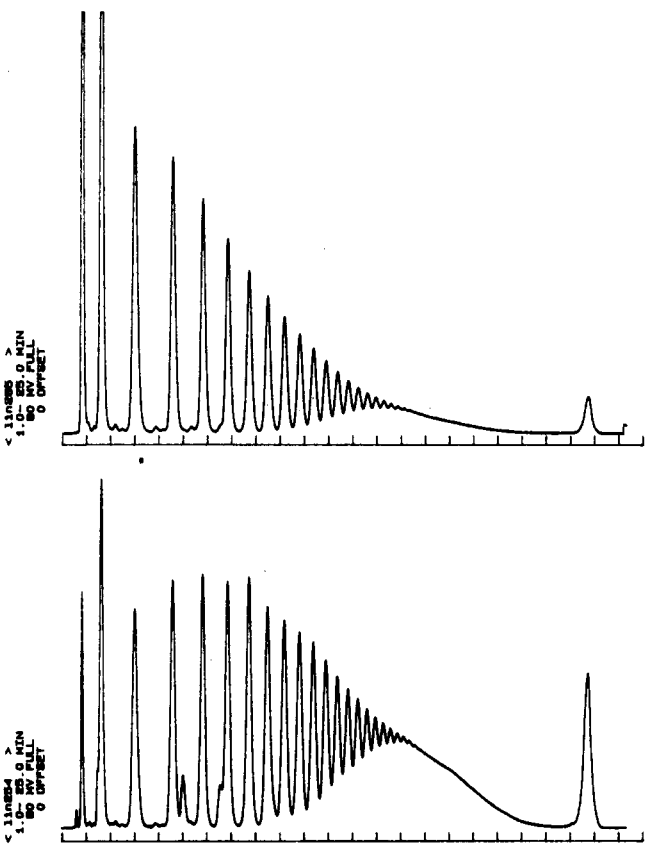


Figure 5. Formation of linear oligomers via pyridine-catalyzed hydrolysis/condensation of BPA bis(chloroformate): (top trace) 285-nm detection, 80 mV full scale; (bottom trace) 254-nm detection, 80 mV full scale.

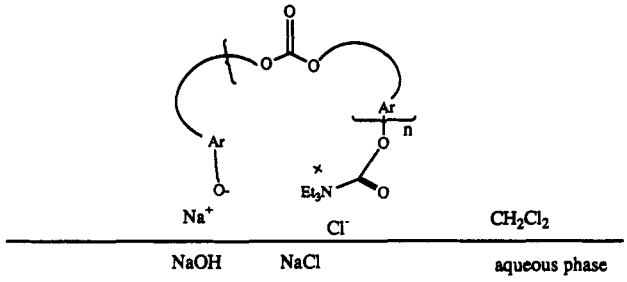


Figure 6.

it was found that heterocyclic aromatic or very unhindered amines gave mixtures of linear and cyclic products. More lipophilic amines, such as tributyl- or trihexylamine, afforded cyclics, but with significantly higher levels of polymer. Hindered amines (triisobutylamine or diisopropylethylamine) or basic but not nucleophilic amines (such as Proton Sponge) gave very slight reaction, with only a small amount of hydrolysis to BPA. Use of phase-transfer catalysts (n-Bu_4NBr or PEG) gave no reaction in the absence of amine or complete hydrolysis to BPA under more forcing conditions. It is interesting to note that merely by changing catalysts and carrying out reaction under identical conditions each of the five possible reaction results for reaction of BPA bis(chloroformate) (polymer, cyclics, linears, hydrolysis to BPA, and no reaction) may be selected. It is clear that the amine used as catalyst must be nucleophilic and soluble in the organic phase. More extensive work detailing the role of amine catalysis of this reaction will be reported subsequently.[33]

Formation of cyclics may be further enhanced by the interfacial nature of the reaction. Since the reaction takes place at pH 9–14, it seems likely that cyclization occurs via an intermediate with a phenoxide on one end of a short oligomeric chain and an acylammonium salt on the other. At high dilution, the ends of the oligomer chain are brought into close proximity by their attraction to the aqueous phase at the interface (Figure 6). It has been found that stirring rates and phase ratios can have important effects on the reaction. When ratios of water/CH_2Cl_2 typical of interfacial polymerization reactions (i.e., about 1:1) are used, rather casual stirring is optimum; adjustment of the aqueous/organic phase ratio can minimize stirring effects and permit emulsification-type stirring.[33]

A study of the reaction variables resulted in the following conditions for optimum yields of cyclics: *concentration*, maximum of 0.60 M at reaction end; *addition time*, more than 15 min, but less than 2 h (30-min reaction gave best results); *temperature*, reflux gave best results (reaction at 0 °C retained some chloroformates); *NaOH concentration*: not important (from 0.5 to 10 M NaOH gave similar results); *stirring*, dependent on phase ratio (good interphase mixing is important); *amine concentration*, optimum Et_3N concentration was 1.0–1.5% by volume in CH_2Cl_2 (0.07–0.11 M) (higher polymer levels are formed at either high or low amine concentrations); *type of amine catalyst*, triethylamine affords highest yields of cyclics. Extensive optimization of the cyclization reaction, including a detailed investigation of the individual and synergistic effects of reaction variables, will be reported subsequently.[33]

Polymerization Reactions. With cyclic oligomeric aromatic carbonates available, polymerization reactions were next investigated. It was anticipated that polymerization in the absence of a chain terminator would lead to very high molecular weight polycarbonates, but the rate of polymerization, and the extent of ring-chain equilibrium were unknown, since starting materials for polymerization of this type were previously unknown. Gel permeation chromatography of the cyclic oligomers (Figure 7, bottom trace) revealed their weight-average molecular weight to be about 1300, with dispersivity of 1.5 (relative to polystyrene standards). Heating the cyclics in glass test tubes under nitrogen gave a modest increase in molecular weight. When the polymerization reaction was catalyzed by lithium stearate or an organic titanate [bis(acetylacetonato)diisopropoxytitanium], polymerization at 300 °C led to polycarbonate with M_w = 250 000–300 000 in 0.5 h (Table II). Precipitation of the polymer into acetone and analysis of the soluble portion by HPLC showed that less than 0.25% cyclics remained after polymerization. The dispersivity of the polymer approached 2.0 (Figure 7, top trace). The molecular weight of the polymer could be controlled by the use of diphenyl carbonate as a chain terminator. Thus, addition of various levels of diphenyl carbonate into the polymerization reaction provided polycarbonates terminated with phenyl carbonate endgroups with molecular weights typical of commercial polycarbonate grades. A fundamental study on the polymerization of cyclic oligomeric carbonates has been reported in a preliminary paper.[34]

Additional work on development of catalysts and initiators for the polymerization of cyclic oligomeric carbonates has been recently reported.[35]

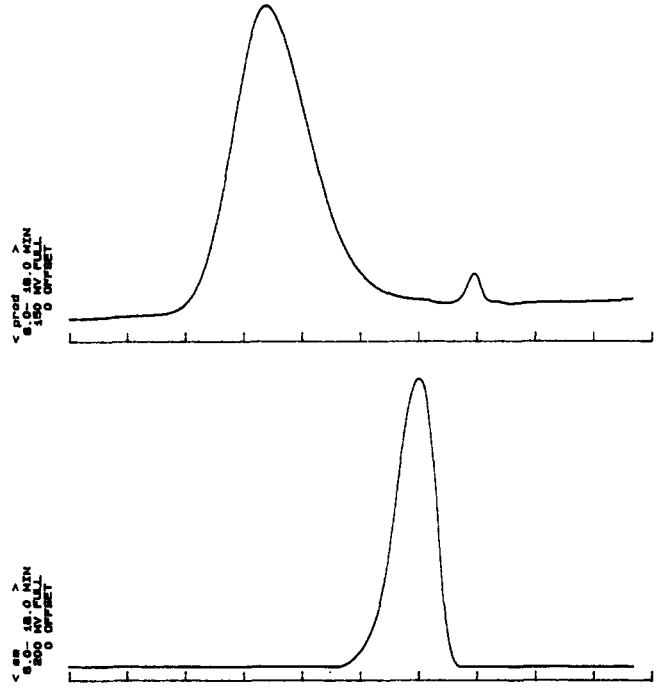


Figure 7. Gel permeation chromatography results for BPA oligomeric cyclics (bottom) and polymer resulting after heating at 300 °C for 15 min with 0.002 mol % titanate (top). Detection was at 254 nm.

Table II
Polymerization of BPA Cyclic Oligomeric Carbonates[a]

catalyst (mol %)	Ph_2CO_3	M_w	M_w/M_n
starting material		1 340	1.5
none		17 400	2.8
lithium stearate (0.5)		gel	
lithium stearate (0.1)		300 000	2.4
Tyzor AA (0.01)		265 000	2.2
Tyzor AA (0.002)		269 000	2.2
Tyzor AA (0.002)	1.0	117 000	2.1
Tyzor AA (0.002)	2.0	65 300	2.2

[a] All reactions were carried out at 300 °C for 0.5 h.

Conclusion

The preparation of cyclic oligomeric aromatic carbonates via a hydrolysis/condensation reaction of BPA bis(chloroformate) has been summarized. In this reaction, BPA bis(chloroformate) was added over a period of time to a stirred mixture of CH_2Cl_2, Et_3N, and NaOH. Under the proper conditions of triethylamine catalysis, selective formation of cyclic carbonates was achieved, with levels of linear oligomers controlled to less than 0.1%. The remarkably selective formation of cyclic oligomers seems to be principally controlled by the amine catalyst. Polymerization of the oligomeric cyclics leads to very high molecular weight polycarbonates in base-catalyzed reactions. The polymerization is complete in 30 min at 300 °C and leaves less than 0.25% cyclic oligomers at completion, leading to polymers with dispersivities of about 2. Further work on the mechanism of the cyclization reaction and on the fundamentals of the polymerization reaction will be reported in due course.

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