Polymer Bulletin 25, 583–590 (1991)

Polymer Bulletin

HPLC analysis of tetrabromobisphenol-A polycarbonate oligomers

Its application in interfacial phosgenation reaction

Jen-Tau Gu[1] and Chun-Shan Wang[2]

[1]Catalyst research Center, China Technical Consultants Inc., Toufen, Miaoli, Taiwan, Republic of China
[2]Department of Chemical Engineering, National Cheng-Kung University, Tainan, Taiwan, Republic of China

Summary

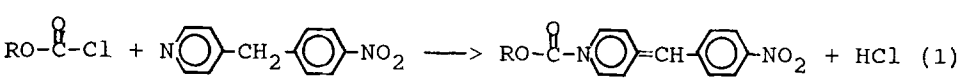
A liquid Chromatographic method for the oligocarbonates and chloroformate-containing oligomers at various stages in a typical tetrabromobisphenol-A polycarbonate phosgenation reaction has been developed. It has been discovered that triethyl amine, normally used as a catalyst for the polymerization, also acted as a chain terminator producing carbamate end-group oligomers. The characterization of the polymer and various types oligomers during phosgenation should allow a better understanding of polymerization mechanism and provide an important aid in defining the critical process parameters.

Introduction

Liquid chromatographic method for analysis of various oligomers in early stages of polycarbonate polymerization has been reported by this author(1). Tetrabromobisphenol-A poly-carbonate (TBBPA-PC) has been applied widely as ignition re-sistant polymer and as gas separation membrane for O_2/N_2(2). In the synthesis of TBBPA-PC, a reverse phase liquid chromatographic method was developed to fractionate and characterize the structure of oligomers. By applying a color development reagent, 4-(p-nitrobenzyl) pyridine (NBP), chromatographic analysis of chloroformate-containing oligomers has been developed.

Chemistry and Analysis

The reaction of 4-(p-nitrobenzyl) pyridine with a chloroformate results in a derivative that absorbs strongly in the visible region of electromagnetic spectrum:



(1)

The chromophoic species from the above reaction product are fairly stable within our normal LC conditions for chromatographic separation.

Experimental

LC Conditions

Hewlett Packard 1090M liquid chromatograph equipped with a scanning diode array detector was used. This detector can scan between 190 and 600 nm several times a second. The spectra were stored on a computer disc. LC column Spherisorb, ODS 2, 15 x 4 mm, 3 um from Scientific Glass Engineering with a flow rate of 0.5 ml/min were used. The signals at 295 and 254 nm were monitored. A typical sample prepartion was carried out by dissolving the polycarbonate solid film in THF or THF containing 1% of NBP (4-(p-nitrobenzyl)pyridine) for chloroformate. It was preferred to analyze the freshly prepared sample immediately to avoid any undersirable side reaction that may occur in the solution. This developed method was listed in following Table 1.

Table 1. The LC analysis condition of TBBPA-PC oligomers.

Time(min.)	% THF	% Water
0	60	40
40	80	20
50	100	0

Preparation of TBBPA-PC Using Triethylamine Catalyst

Into a 2-liter reaction flask equipped with a stirrer, PH electrode, phosgene inlet, reflux condenser, caustic addition inlet and a thermometer were placed water (250 ml), tetrabromobisphenol-A (108.8 g, 0.2 mole), methylene chloride (500 ml), triethylamine (0.736 g, 0.0073 mole) and phenol (0.13 g, 0.0014 mole). After adjusting the reactor solution to PH 10 with 50 % aqueous caustic solution. Phosgene (25.2 g, 0.255 mole) was added at the rate of 0.5 g/min. while maintaining PH at 10 by adding 50 % caustic solution. Reaction temperature was held at 25^{o}C by using a cooling bath. Reaction samples were taken at various stages of phosgenation to analyze oligomers. After the addition of phosgene was completed, the reaction mixture was diluted with methylene chloride (100 ml). Caustic solution was added to raise the PH to 12 and reaction mixture stirred until all chloroformate disappears. Total 50 % caustic consumed was 44.6 g (0.558 moles). After all chloroformate disappears additional phosgene was added to adjust the PH to 8. The organic layer was washed with dilute HCl and water. Polymer was precipitated by dilution with an equal volume of n-heptane.

Preparation of TBBPA Bischloroformate standard

Phosgene (19.8 g, 0.2 mole) was added slowly to a solution containing 87.7 g (0.161 mole) of TBBPA, 32 g (0.4 mole) of 50

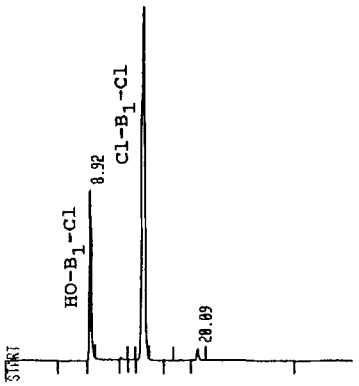


Fig.1. LC of mono- and bis-chloroformate(2 ppm) in NBP(2 ppm)/THF at UV430nm.

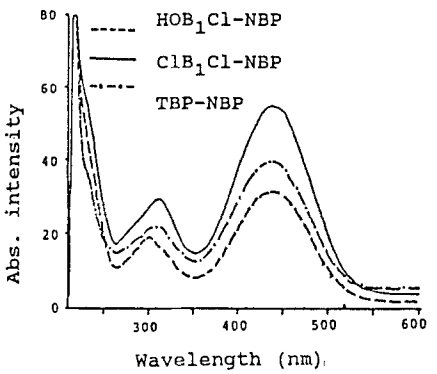


Fig.2. UV spectra of TBBPA bis-mono-chloroformate, and TBP chloroformate.

% aqueous sodium hydroxide, and 320 ml water at a flow rate of about 0.5 g/min. maintaining the reaction temperature at 28°C. As soon as the phosgene addition was completed, the white precipitates were collected by vacuum filtration, washing with deionized water and methanol. The precipitates were finally dried in vacuum oven overnight. Two major products, mono- and bis-chloroformates were formed. LC chromatogram and UV spectrum are shown in Figures 1 and 2.

Preparation of 2,4,6-Tribromophenol (TBP) Chloroformate

Phosgene (8 g, 0.08 mole) was added slowly to a solution containing 20.6 g (0.0645 mole) of TBP, 6.391 g (0.16 mole) of 50 % aqueous sodium hydroxide, and 128 ml water at a flow rate of about 0.2 g/min at 28°C. As soon as the phosgene addition was completed, the brown oil which precipitates from the reaction mixture was cooled to 0°C and scratched to obtain a light brown solid (23 g, 90.7 % yield). The product contained 86 % TBP chloroformate, 10 % unreacted TBP and 3 % di(2,4,6-tribromophenol carbonate. UV spectrum of TBP chloroformate/4-(p-nitrobenzyl)pyridine derivatives is shown in Figure 2.

Preparation of Diphenyl Carbonate as a TBBPA Standard

$$\text{TBBPA} + \text{PhO}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Cl} \xrightarrow{\text{Py./Tol.}} \text{PhO}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-B}_1\text{-O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{Cl} + \text{HO-B}_1\text{-O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OPh} \qquad (2)$$

Phenyl chlorofromate (0.337 g, 0.0024 mole) was added to a solution containing 0.5436 g (0.001 mole) of TBBPA, 0.266 g (0.0036 mole) of pyridine and 20 ml toluene. After refluxing for 1 hour, the solvent was removed by evaporation. The reside dissolved in 20 ml methylene chloride was washed once with dilute HCl, twice with dilute NaOH, and three times with deionized water. Finally, an equal volume of n-heptane was added to precipitate white solids. The precipitates were collected by vacuum filtration and dried in vacuum overnight. The product consisted of two major components, mono- and di-phenylcarbonate esters of TBBPA. Further purification was

achieved by silica gel (70-230 mesh) column using n-heptane as eluent. The identification of diphenyl dicarbonate of TBBPA was done by IR ($V_{C=O}$ 1787 cm^{-1}, v_{C-O} 1198 cm^{-1}), UV (Figure 3), and by mass spectrum (M^+ 785).

Results And Discussion

Ultraviolet and Visible Spectroscopy

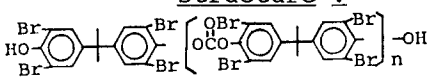
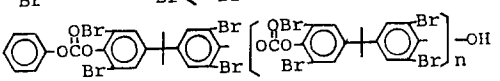
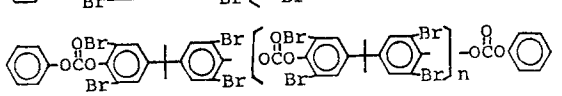
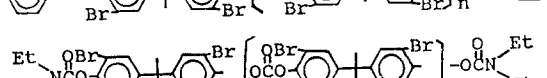
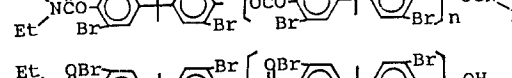
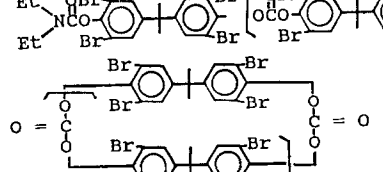
Both 4-(p-nitrobenzyl) pyridine and TBBPA chloroformates do not show any absorption above λ= 400 nm whereas the formed complex exhibits strong absorption at λ= 438 nm(1). No interference is expected in analyzing the complex when the λ= 430 nm is employed.

LC Analysis of Mono- and Bis-Chloroformates of TBBPA

Figure 1 is the chromatogram at λ = 430 nm of the lab-prepared mono-and bis-chloroformate of TBBPA and NBP derivatives. The component, Cl-B_1-H (RT = 11.914 min., B_1 means one unit of TBBPA, H means -OH end group) should give one half response compared with Cl-B_1-Cl (RT = 29.573) at λ= 430 nm. This has been verified by comparing the decrease of peak area ratio after dilution. Figure 2 is UV spectra of bis- and monochloroformate-NBP complexes.

LC Analysis of TBBPA-PC Oligomers

The assignment of LC peaks for oligomers from TBBPA-PC is based on : UV spectra, authentic samples or their model compounds and comparison with LC spectra of bisphenol-A polycarbonate(1). To obtain good chromatograms, extraction of oligomers from the polymer is necessary. This is achieved by addition of an equal volume of n-heptane to the methylene chloride solution of TBBPA-PC to precipitate the polymer. Oligomers are recovered by decanting top solution and evaporating the liquid. Possible TBBPA-PC oligomer structures are shown below :

Structure :	Symbol :
	HO-B_n-OH
	P-B_n-OH
	P-B_n-P
	A-B_n-A
	A-B_n-OH
	C_n

B : TBBPA repeating unit
P : Phenol (terminator)
A : Catalyst (diethylamine)
C_n: Cyclic Oligomers

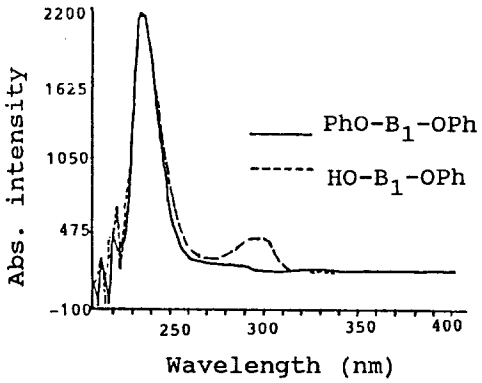


Fig.3. The UV spectra of mono- and di-phenylcarbonate.

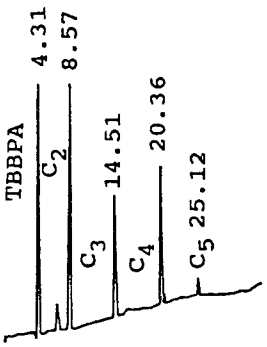


Fig.4. LC of cyclic oligomers

UV spectra of two model compounds, TBBPA and its diphenyl dicarbonate, are shown in Figure 3. TBBPA which representeds phenolic end-groups containing oligomers show a maximum absorbance at 295 nm, a longer wavelength than its diphenyl dicarbonate (ca 280 nm) which is model compound for cyclic oligomer (Cn) and phenol capped oligomers (PB_nP). The shift to a longer wavelength for phenolic end-groups compared with cyclic or phenol-capped oligomer is also observed in the case of bisphenol-A polycarbonate.

LC Analysis of Cyclic Oligomers

Significant quantity of cyclic TBBPA-PC oligomers are produced in the interfacial phosgenation reaction. The content of cyclic oligomers is dependent on several process parameters such as temperature, TBBPA phenolate concentration, mixing efficiency and caustic. Cyclic oligomers are prepared selectively in the presence of triethylamine catalyst at a dilute TBBPA bisphenolate concentration with high agitation(3,4,5). Figure 4 is the LC chromatogram of a phosgenation reaction following above procedure without phenol terminator and at detector wavelength of 254 nm. By comparing UV spectra of these oligomers with TBBPA (Figure 6), the LC peaks without maximum absorption at 295 nm are assigned to cyclic oligomers. Cyclic oligomers are found to have similar UV spectra (Figure 5). As in the case of PC from bisphenol-A, the peak at the shortest retention time is assigned as C_1 (the smallest ring with two TBBPA unit). Increasing the number of repeating units increases the elution time of the oligomers.

Identification of HO-B_n-OH Oligomers

HO-B_n-OH oligomers are obtained by hydrolyzing the chloroformate end group of the sample taken during polymerization without terminator and using 4-dimethylaminopyridine as a catalyst(6).

$$ClCO\text{-}B_n\text{-}OCCl \xrightarrow{H_2O} HO\text{-}B_n\text{-}OH \qquad (3)$$

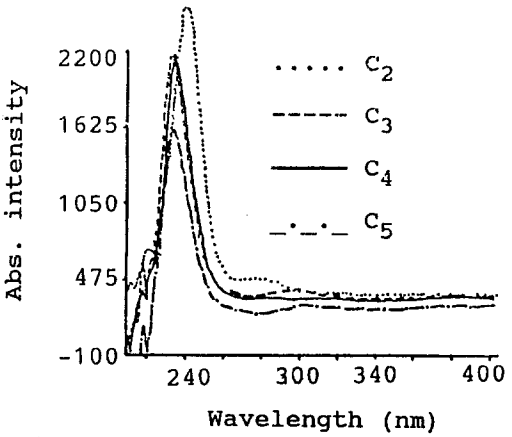


Fig.5. UV spectra of TBBPA, cyclic oligomers.

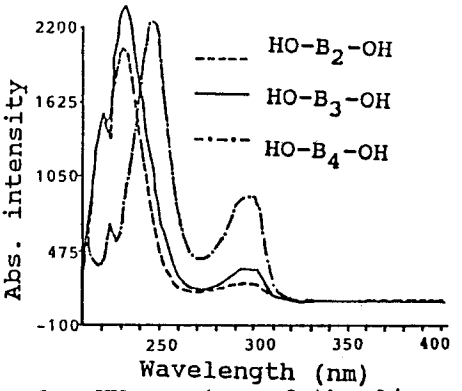


Fig.6. UV spectra of the linear oligomers with hydroxy terminator group.

Since no terminator is used, the possible structures are HO-Bn-OH or cyclic -Bn-. The UV spectra of the oligomers (Figure 6)are identical and have a maximum absorbance at 295 nm representing phenolic end-group containing oligomers. The absorbance ratio of 295 nm/235 nm has an inverse linear relationship to the ratio of OH number/benzene ring number (Figure 7). By comparing LC chromatograms and UV spectra of these samples with those of cyclic oligomers, it is possible to differentiate the linear oligomers from cyclic oligomers (Figure 8). Increasing the number of repeating units increases the elution time of the oligomers.

Determination of Carbamate End-group in TBBPA-PC

The liquid chromatogram of carbamate end-group oligomers is shown in Figure 9. This sample of polymer is synthesized without terminator using triethylamine as a catalyst. Since no termina-tor is used, the possible structures of oligomers are usually HO-B_n-OH of cyclic C_n. The chromatogram in Figure 9 contains several sets of doublets (RT = 12.18, 18.89 and 24.51 etc.,). One of the doublet peaks is assigned to cyclic

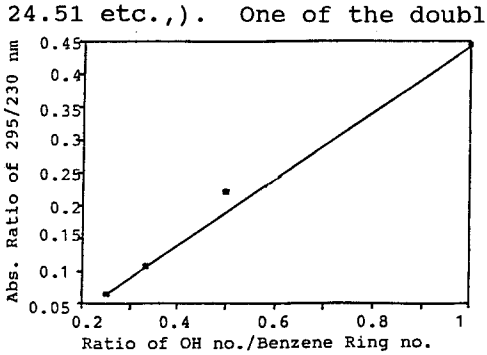


Fig.7. Abs. ratio (295/235 nm) vs the number ratio of OH/benzene ring.

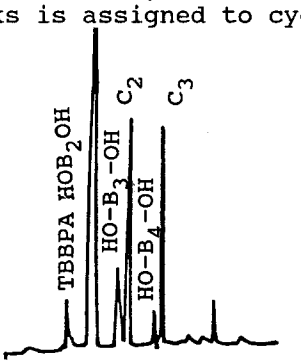


Fig.8. L. C. of HO-Bn-OH and cyclic oligomers.

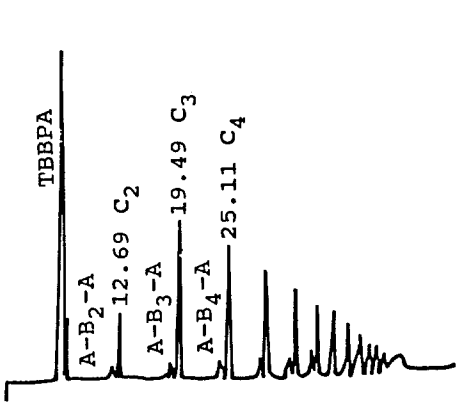


Fig.9. LC of cyclic and carbamate oligomers.

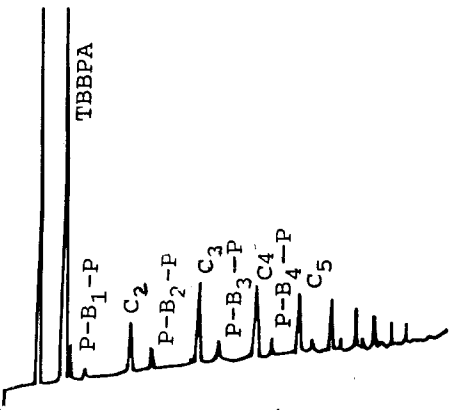


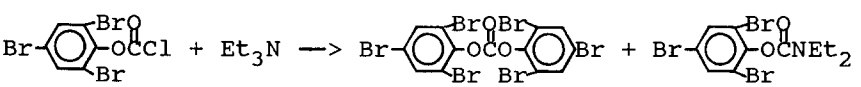
Fig.10. LC. of cyclic and phenol capping oligomers.

oligomer based on its retention time and UV spectrum. However, the other one does not contain phenolic end-group since its retention time (Figure 9) and UV spectra differs from phenolic end group oligomers (Figure 10). The UV spectra shows no maximum absorbance at 295 nm. The other peaks in the doublets are assigned to diethylamine carbamate end group oligomers (A-Bn-A) by comparing the retention time of the authentic sample made by the aminolysis of TBBPA bischloroformate with triethylamine or diethylamine.

$$Cl\overset{O}{\overset{\|}{C}}O\text{-}B_1\text{-}O\overset{O}{\overset{\|}{C}}Cl + Et_3N \longrightarrow (Et)_2N\overset{O}{\overset{\|}{C}}\text{-}B_1\text{-}O\overset{O}{\overset{\|}{C}}N(Et)_2 + 2EtCl$$

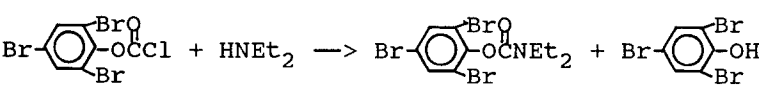
$$\text{"} \quad + Et_2NH \longrightarrow \quad \text{"} \quad + 2\ HCl \qquad (4)$$

Further evidence of carbamate end-group oligomer formation is achieved by the aminolysis of tribromophenol (TBP) chloroformate with triethylamine (5). Besides bis(2,4,6-tribromophenyl) carbamate (RT= 8.370), diethylamine carbamate of tribromophenol (RT = 4.775) is also produced. (Figure 11).



(5)

Authentic sample of diethylamine carbamate of tribromophenol is synthesized by the reaction of diethylamine with tribromochloroformate (6).



(6)

Figure 11a shows identical retention time (RT = 4.773) in liquid chromatogram as Figure 11b. Also the UV spectra are identical. The structures of TBP diethylcarbamate and bis-TBP-carbonate are confirmed by IR spectra and mass spectrum.

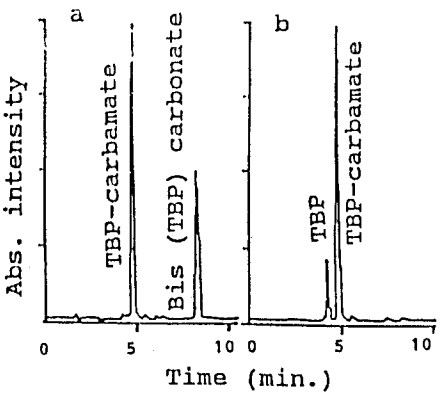


Fig.11. LC of TBP chloroformate (a) reacted with TEA or (b) reacted with DEA

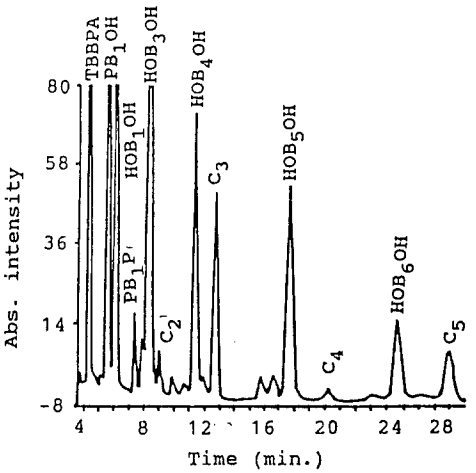


Fig.12. LC of oligomers from 2% mol. ratio PhOH/ TBBPA synthesis

The proposed mechanism of diethylamine carbamate end-group oligomers formation is due to the Hoffmann degradation reaction oftriethylamine-chloroformate complex where triethylamine acts as a terminator (7).

$$\sim\sim O\text{-}\overset{O}{\overset{\|}{C}}Cl + N(Et)_3 \longrightarrow \sim\sim O\text{-}\overset{OCl}{\overset{|}{\overset{\|}{C}}}N(Et)_2\text{-}CH_2CH_3 \longrightarrow \sim\sim O\text{-}\overset{O}{\overset{\|}{C}}N(Et)_2 + ClCH_2CH_3 \quad (7)$$

The bulkiness and electron withdrawal by bromine substituents at the ortho positions could be the reason for its low reactivity and the Hoffmann degradation. The search of better catalyst for the TBBPA-PC will be reported separately later.

Assignment of TBBPA-PC Oligomers

Figure 12 is the liquid chromatogram of TBBPA-PC oligomers using phenol as terminator. Their specific structures assignment is based on the above described characterization.

Acknowledgement

We thank the Catalyst Research Center and National Science Council for support of this work NSC 80-0405-E-198A-01.

References

1. J. T. Gu, F. C. Chang, J. Appl. Polym. Sci., 39,175(1990).
2. N. Murganandam, D. R. Paul, J. Membrane Sci., 34,185(1987).
3. D. J. Brunelle, T. L. Evans, T. G. Shannon, Polymer Preprints (ACS Div. Polym. Chem.), 30(2), 569 (1989).
4. E. P. Boden, D. J. Brunelle, T. G. Shannon, Polymer Preprints (ACS Div. Polym. Chem.) 30(2), 571 (1989).
5. D. J. Brunelle, and E. P. Boden, U.S. Pat. 4,727,134(1988).
6. D. B. G. Jaquiss, and V. Mark, U.S. Pat. 4,286,085 (1981).
7. P. G. Kosky and E. P. Boden, J. of Polym. Science, Polym. Chem. 28, 1507-1518 (1990).

Accepted December 27, 1990 S