HPLC Analysis of Polycarbonate Oligomers and Its Process Applications in the Interfacial Phosgenation Reaction

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Synopsis

A liquid chromatographic method for the oligocarbonates and chloroformate-containing oligomers at various stages in a typical polycarbonate phosgenation reaction has been developed. The accurate measurement of various types oligomers during phosgenation should allow for a better understanding of polymerization mechanism and provide great aid in defining the critical process parameters. Comparison of the total chloroformate concentration by accumulating every individual chloroformate-containing component and the standard colorimetric method shows close agreement.

INTRODUCTION

Liquid chromatography (LC) has gradually become a versatile analytical tool in numerous areas of chemistry since the first commercial instrument was available in early 1970s. The advancement of column and instrumentation technologies are mainly responsible for liquid chromatography being such a powerful tool of today equivalent to gas chromatography of the 1960s. LC applied to high molecular polymer has been rather limited due to the wide distribution of polymeric molecules and GPC is still considered the most appropriate method to characterize a high molecular weight polymer. However, in certain types of polymerization such as polycarbonate interfacial phosgenation, relatively lower MW oligomers of different endgroups dominate in the reaction. The distribution of various oligomers in early stages of polycarbonate polymerization is extremely important in the process optimization involving numerous process parameters. This is where LC can do the best to analyze these oligomers of different endgroups and supply the much-needed information, otherwise unobtainable. For example, if the quantitative measurement of each chloroformate-containing oligomer during various stages of phosgenation is achievable, understanding of phosgenation mechanism will be greatly improved and the critical process parameters can be controlled with confidence. Gur'yanova et al.[1] developed an LC method for polycarbonate using the THF/water solvent system which is unable to analyze the chloroformate-containing oligomers due to chloroformate hydrolysis during column separation. The previous method[1] can analyze only the oligocarbonates with OH end group. By applying the color development reagent, 4-(*p*-nitrobenzyl)pyridine (NPB), and the established LC method, chromatographic analysis of chloroformate-containing oligomers has been de-

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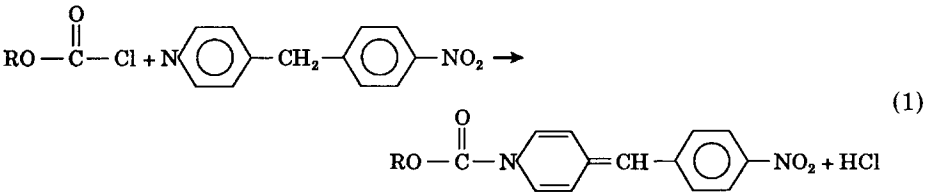
veloped. A complete reactor profile of chloroformate distribution from a typical phosgenation reaction has been achieved.

CHEMISTRY AND ANALYTICAL

4-(*p*-Nitrobenzyl)pyridine is well known for its extreme sensitivity towards acyl halides. Most of the earlier work with this reagent was limited in a few types of acyl halides.[2-4] Agree and Meeker[5] did more in-depth studies of this analytical technique with a wide variety of acyl chlorides and found that 4-(*p*-nitrobenzyl)pyridine reacted readily with most acid chloride and chloroformate. The reaction of 4-(*p*-nitrobenzyl)pyridine with a chloroformate results in a derivative that absorbs strongly in the visible region of the 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

A Hewlett Packard 1090A liquid chromatograph and an LC column Spherisorb, ODS2, 15 cm × 4 mm, 3 μm from Scientific Glass Engineering were employed in this study. A flow rate of 0.5 mL/min was used. Typical sample preparation is carried out by dissolving the polycarbonate solid film in THF or THF containing 1% NPB. It is preferable to analyze the freshly prepared sample immediately to avoid any undesirable side reaction that may occur in the solution. The LC solvent program for this developed method is listed in Table I.

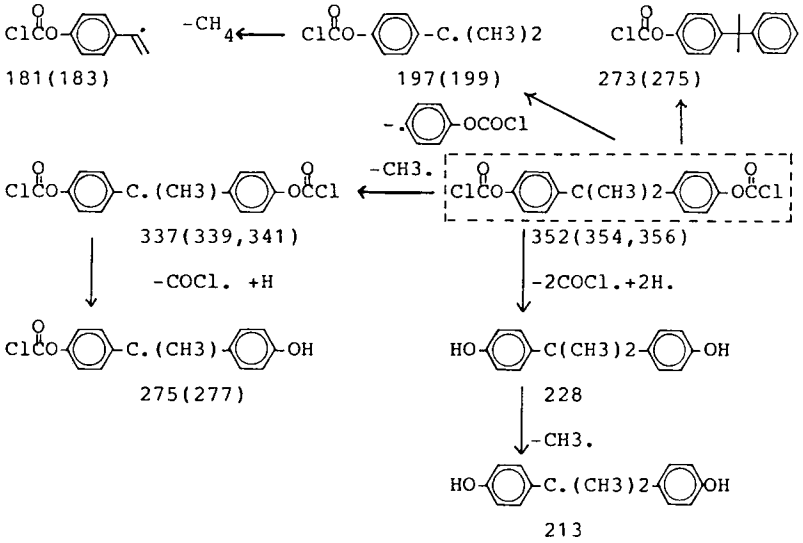
TABLE I
LC Analysis Conditions[a]

Program: Time (min)	H_2O (%)	THF (%)
0	45	55
40	20	80
60	0	100
65	0	100

[a] Column, Spherisorb ODS 2, 4 mm × 15 cm (3 μm); flow rate, 0.5 mL/min; temp, 20°C.

Preparation of Bischloroformate Standard

Phosgene [193 g (1.95 mol)] was added slowly to a solution containing 342.5 g bisphenol A (1.95 mol), 180 g sodium hydroxide (4.5 mol), and 2.4 L water at a flow rate of about 3.5 g/min, maintaining the temperature at 0–5°C. As soon as the phosgenation adding is completed, the white bischloroformate precipitates are collected by vacuum filtration, washing with deionized water and methanol. The precipitates are finally dried in vacuum overnight. The identification of this laboratory prepared bischloroformate was done by mass spectrum and the fragmentation is shown in Figure 1 and Scheme 1.



Scheme 1.

Phosgenation Minireactor Conditions

The detailed phosgenation procedures and conditions of this example run will be reported separately later.

RESULTS AND DISCUSSION

Ultraviolet and Visible Spectroscopy

The UV spectra of 4-(*p*-nitrobenzyl)pyridine, phenyl chloroformate, and colored derivative are shown in Figure 2. Both 4-(*p*-nitrobenzyl)pyridine and phenyl chloroformate do not show any absorption above $\lambda = 400$ nm whereas the formed complex exhibits strong absorption at $\lambda = 438$ nm. No interference is expected in analyzing the complex when the $\lambda = 430$ nm is employed. The absorbance of phenyl chloroformate NPB complex at $\lambda = 254$ nm (HPLC UV fixed detector wavelength) is approximately half of that at $\lambda = 438$ nm.

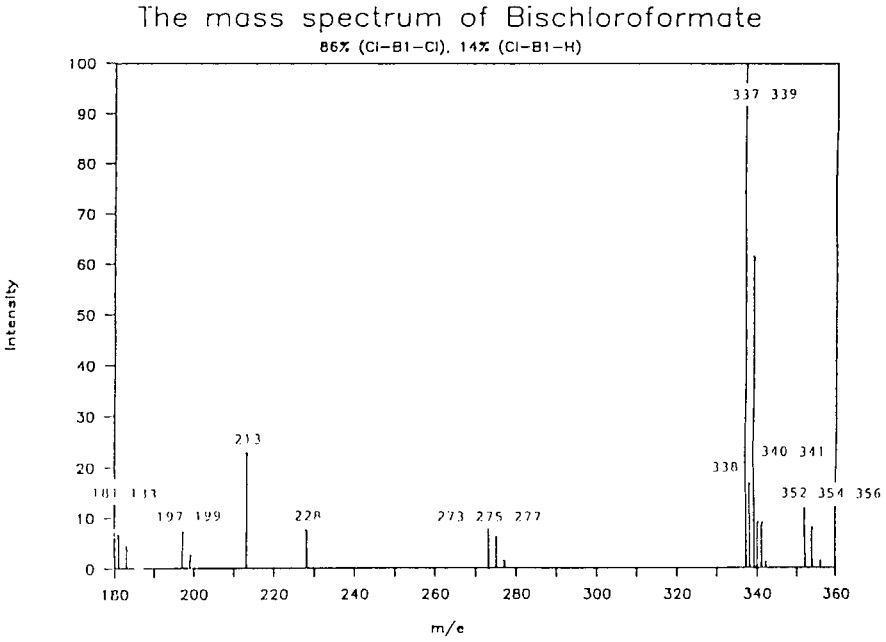


Fig. 1. The mass spectrum of bischloroformate.

LC Analysis of Bischloroformate

Figure 3 is the chromatogram at λ = 430 nm of the lab-prepared bischloroformate for chloroformate concentration standard and the results show only 86% purity based on chloroformate endgroup equivalence of the major peak,

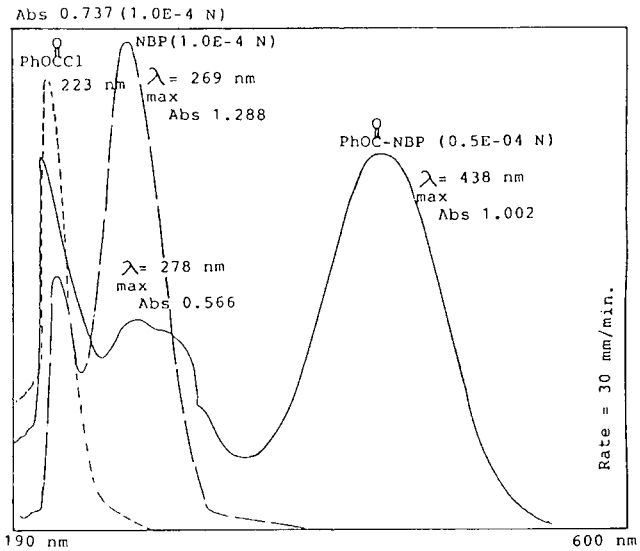


Fig. 2. The UV spectra of phenyl chloroformate, NBP, and their derivative.

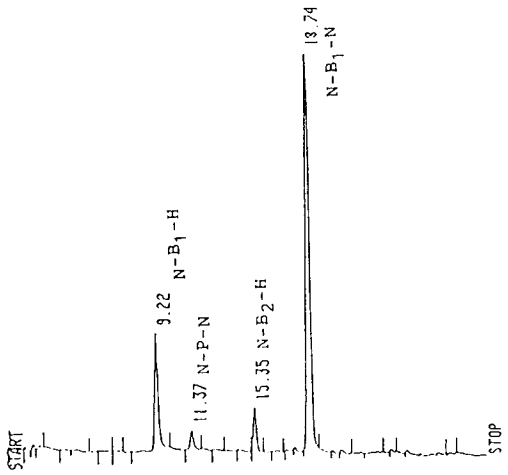


Fig. 3. Liquid chromatogram of bischloroformate (2 ppm) in NBP (2 ppm)/THF at UV 430 nm.

bischloroformate and NPB derivative, at an LC retention time (RT) of 18.84 min. The component, N–B_1–H (RT = 9.26 min, B_1 means one unit of bisphenol A, H means —OH endgroup), was identified simply by peak area increase from 14 to 79.6% while the major peak N–B_1–N is significantly reduced after the sample was stored for 2 days. The minor peak N–P–N (RT = 11.37 min) was identified by adding NPB solution into a phosgene-containing methylene solution. The presence of N–B_2–H (RT = 15.35 min) and N–B_1–H indicates minor dimerization and incomplete phosgenation did occur during the preparation of bischloroformate. The component H–B_1–N should give one half response compared with N–B_1–N at = 430 nm. This has been verified by comparing the decrease of peak area ratio after dilution. Figure 4 shows the slope of peak area ratio of H–B_1–N is about half of N–B_1–N.

LC Analysis of H–B_n–H Oligomers

The reactor samples from the early stages of phosgenation show the oligomers mainly the intermediated oligocarbonates with both end groups in hydroxy form (and chloroformate form). Chromatography of the hydroxyl-containing oligocarbonates is based on the separation according to their molecular weight and structural inhomogeneity. Figure 5 shows the chromatograms of a series samples taken from a typical phosgenation reactor using a detector wavelength λ = 254 nm. The chloroformate end groups of these samples were essentially hydrolyzed before or during column separation.

Identification of Cyclic Oligomers

Cyclic polycarbonate oligomers are formed in the interfacial phosgenation reaction which make up the significant portion of the total oligomer content. The content of cyclic oligomers is dependent on several process parameters such as temperature, phosgene feeding rate, and the addition of the caustic. Cyclic oligomers increase if the amine catalyst is present during phosgenation.[1,6]

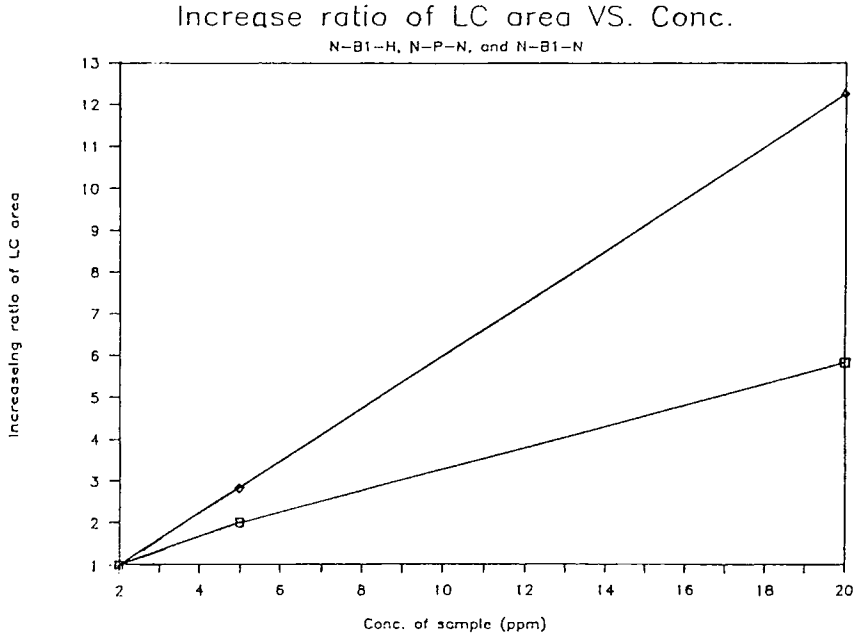


Fig. 4. The increasing area ratio vs. (+) concentration of N-B_1-N and (□) N-B_1-H at UV 430 nm.

Figures 6 and 7 are the LC chromatograms of a phosgenation intermediate without phenol terminator in the feed with detector wavelength at 254 and 280 nm, respectively. By comparing these two chromatograms, the peaks disappearing in Figure 7 are the cyclic oligomers. Quantitative UV analysis of the polycarbonate hydroxyl end group using λ = 287 nm was previously reported.[7]

Identification of N–B_n–N and N–B_n–H Oligomers

Figure 8 is the chromatograms of the same set of samples as shown in Figure 5 except for the addition of NPB and detector wavelength at 430 nm. The assignments of N-B_n-N and N-B_n-H are similar to those from the H-B_n-H series and their response ratios at λ = 254 430 nm have been taken into consideration. Figure 9 shows the plots of B_n of different end group combinations vs. LC retention time.

Chloroformate vs. Oligocarbonate

Three major classes of reactions are actually involved in the polycarbonate interfacial phosgenation reaction:

1. Phosgenation—to create chloroformate:

$$-\text{Ph}-\text{ONa} + \text{Cl}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{Cl} \rightarrow -\text{Ph}-\text{O}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{Cl} + \text{NaCl}$$

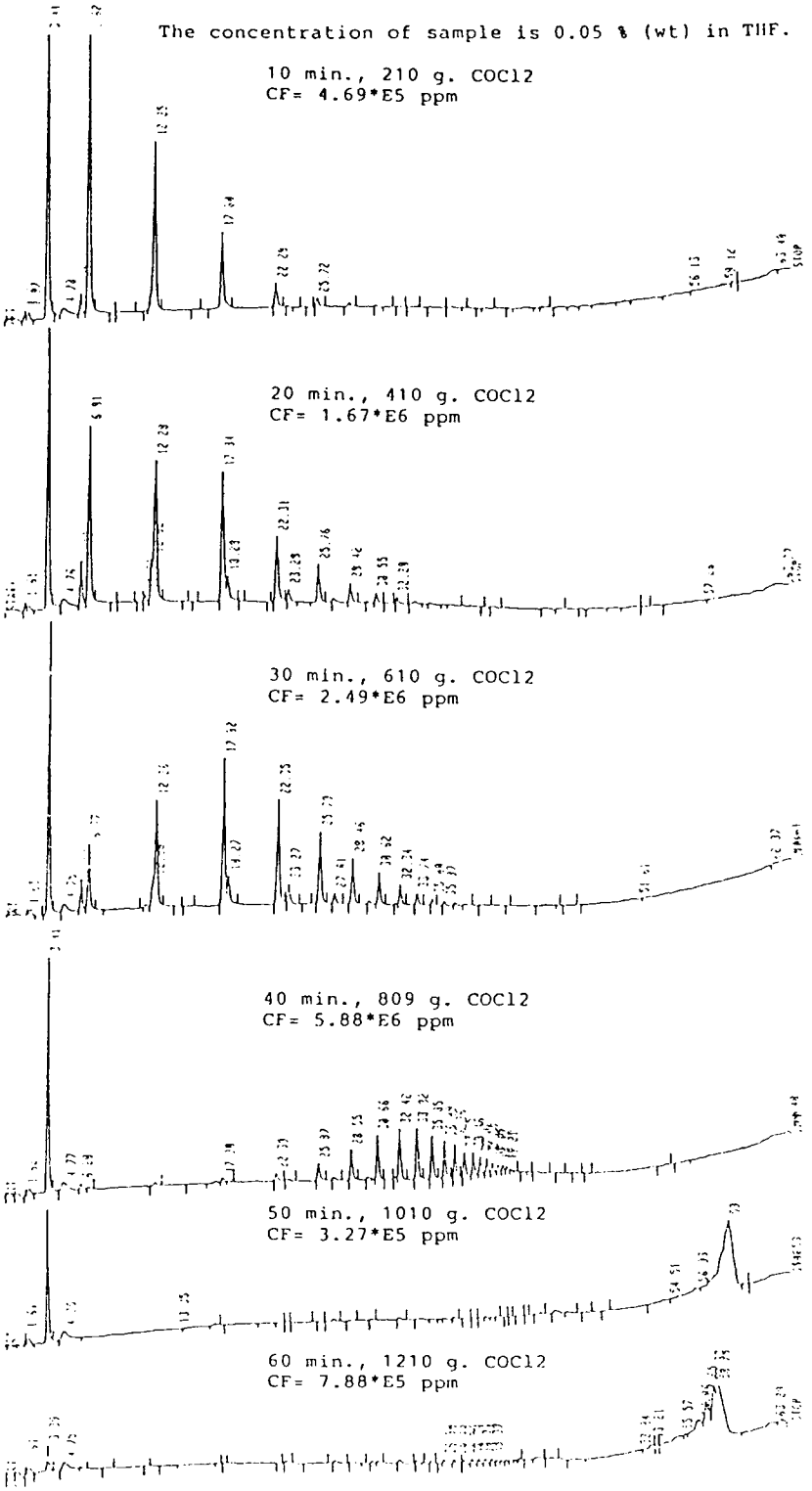


Fig. 5. Oligocarbonate reactor profile of a typical phosgenation reaction at UV 254 nm.

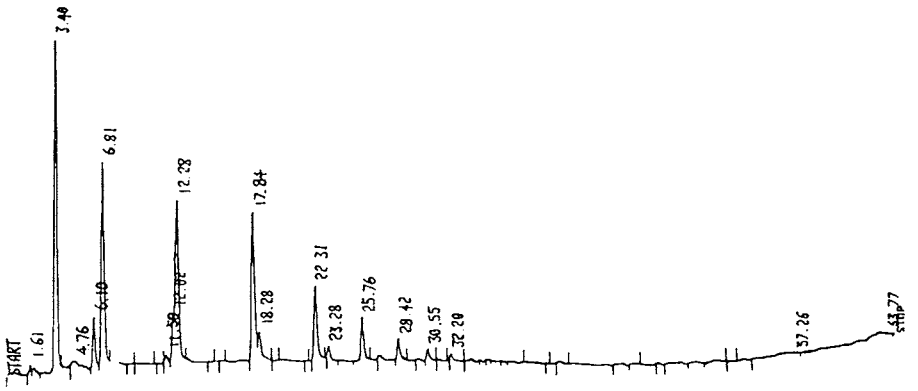


Fig. 6. Liquid chromatogram of a typical phosgenation reaction: 410 g $COCl_2$ (20 min), sample 0.05% in THF, λ = 254 nm.

2. Coupling reaction—to consume chloroformate and also produce oligocarbonates:

$$-Ph-ONa + Cl-\overset{\overset{O}{\|}}{C}-O-Ph \rightarrow -Ph-O-\overset{\overset{O}{\|}}{C}-O-Ph + NaCl$$

3. Hydrolysis—to consume phosgene, chloroformate, and caustic:

$$Cl-\overset{\overset{O}{\|}}{C}-Cl + 4NaOH \rightarrow Na_2CO_3 + 2NaCl + 2H_2O$$

$$-Ph-O-\overset{\overset{O}{\|}}{C}-Cl + 3NaOH \rightarrow -Ph-ONa + NaCl + Na_2CO_3 + H_2O$$

In the early stages of phosgenation reaction when the sodium bisphenate is still abundant, the hydrolysis of phosgene and chloroformate can be neglected

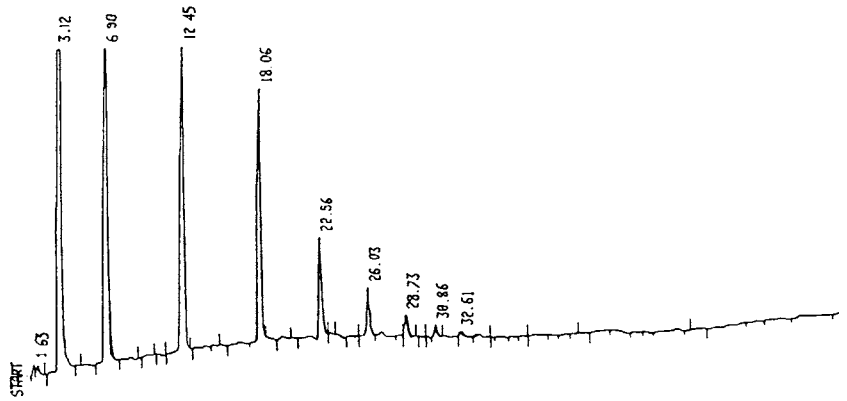


Fig. 7. Liquid chromatogram of a typical phosgenation reaction: 410 g $COCl_2$ (20 min), sample 0.05% in THF, λ = 280 nm.

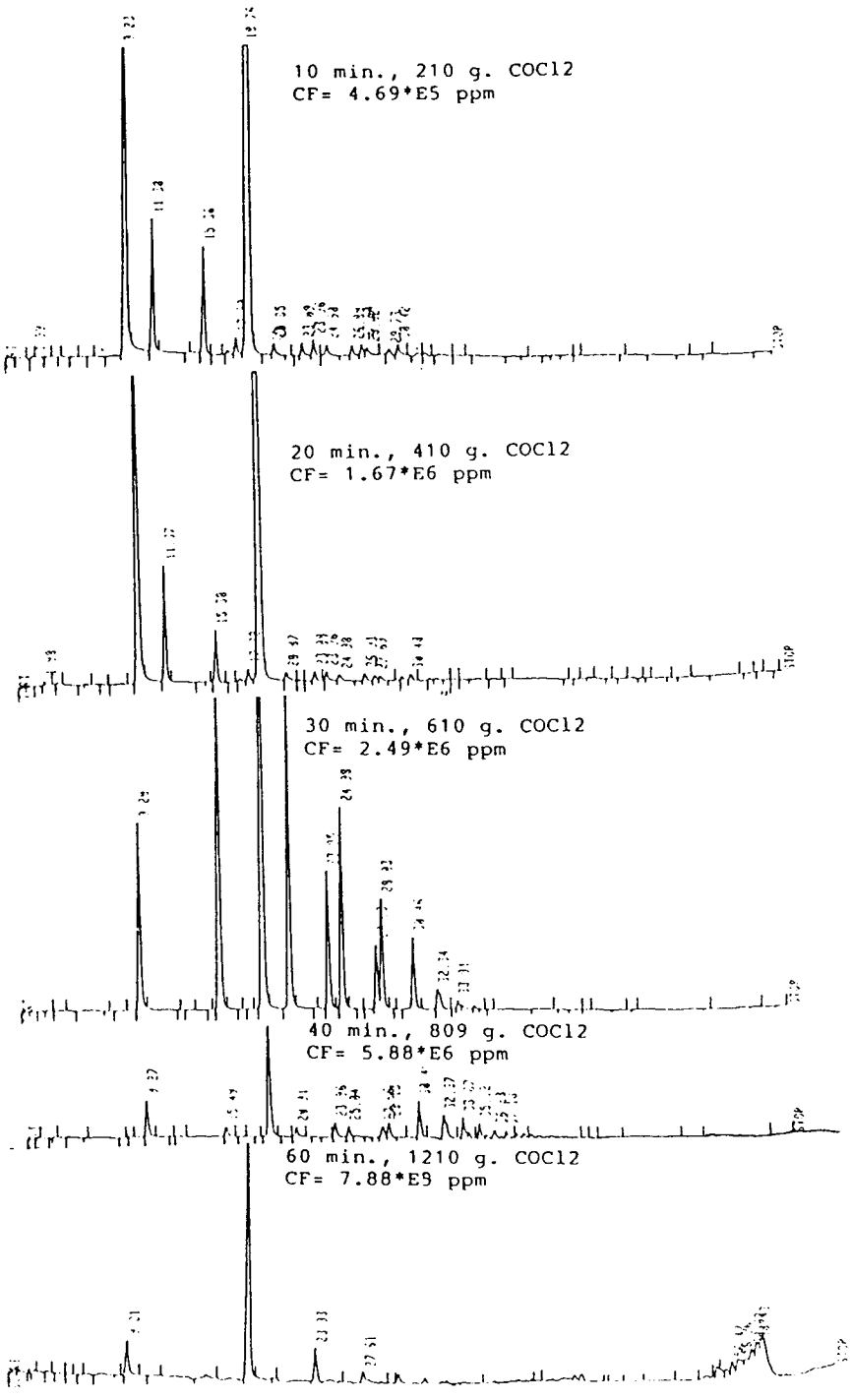


Fig. 8. Chloroformate reactor profile of a typical phosgenation reaction at UV 430 nm.

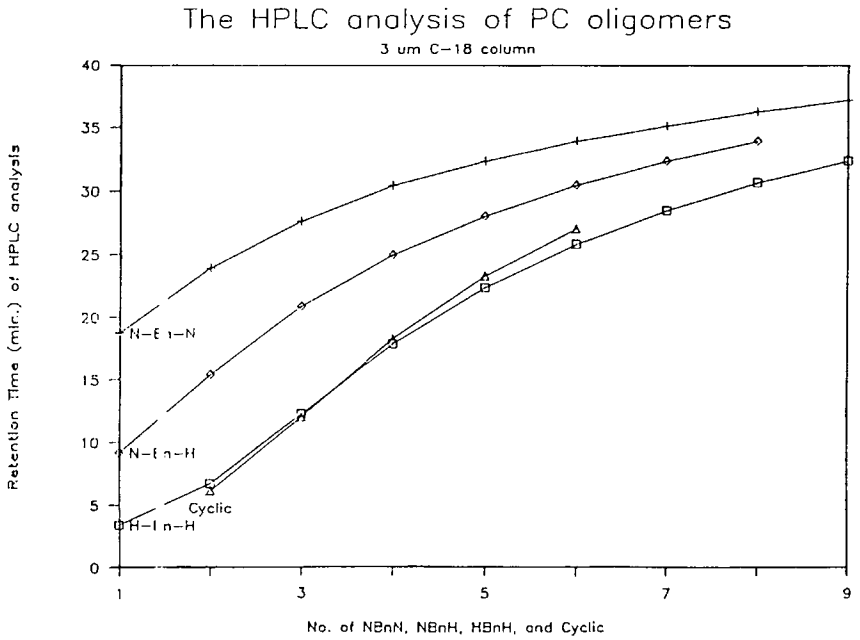


Fig. 9. Plots of B_n vs. LC retention time of various oligomers. (□) sample H–B_n–H; (△) sample cyclic $-OC(=O)O-B_n-$; (◇) sample N–B_n–H; (+) sample N–B_n–N.

because only an insignificant amount of the hydrolysis product sodium carbonate can be detected. If the phosgene loss can be neglected, all the phosgene fed into the reactor becomes either chloroformate or oligocarbonate (reactions 1 and 2). By employing this developed LC method, the relative and absolute quantity of chloroformate and oligocarbonate can be calculated. The example demonstrating how to calculate these values using chromatograms shown in Figure 10 is summarized in Table II. The results from Table II indicate that after 210 g of phosgene addition, 21.2% of the fed phosgene is in the form of chloroformate, and the remaining 78.8% in oligocarbonate. These results from the LC method can be verified by the material balance calculation shown in Table III. Based on above calculations, the oligocarbonate equivalent contents are the difference between the total fed phosgene equivalents and the chloroformate equivalents detected. Of course, minor adjustment for the phosgene loss through hydrolysis is necessary, especially in the later stages of reaction when the unreacted bisphenate in the aqueous phase is low. Such correction can be done by determining the sodium carbonate concentration in the aqueous by titration method.

Phosgenation Reactor Profile

Figure 8 shows the chromatograms of chloroformate distribution of a typical phosgenation reaction batch run at various stages of phosgene addition. The total chloroformate concentrations and intrinsic viscosity vs. time (g phosgene addition) are shown in Figure 11. The chloroformate concentration gradually increases to the time of second addition of caustic at 27 min whereas the intrinsic

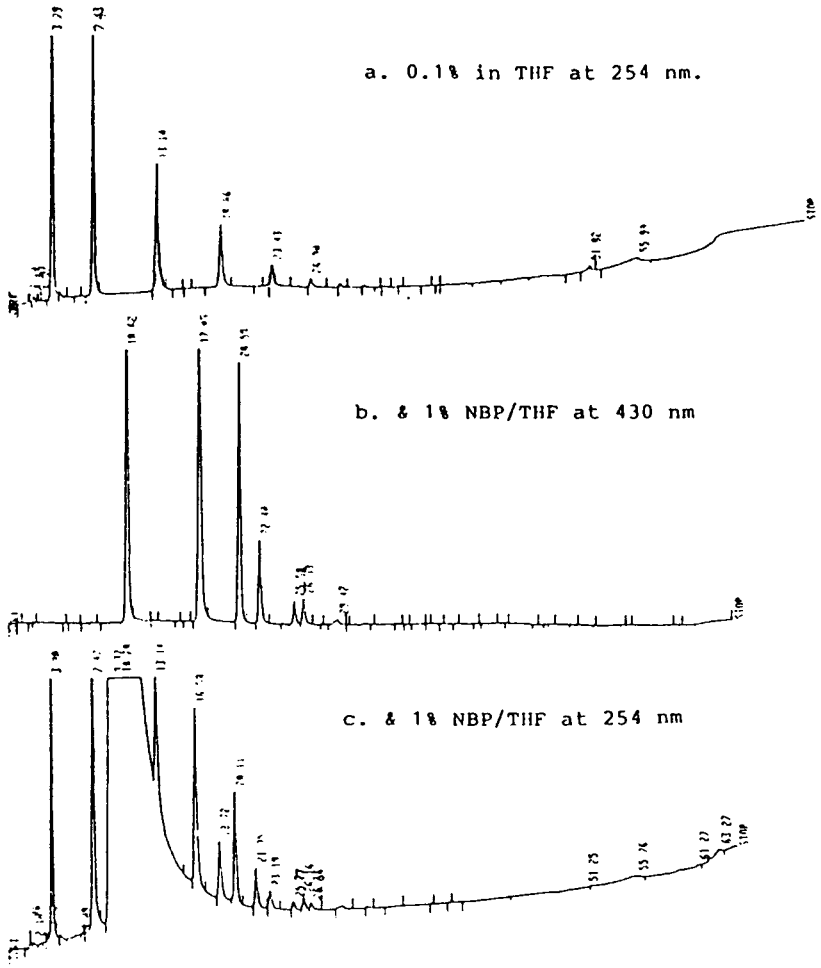


Fig. 10. Liquid chromatogram of a typical phosgenation reaction: 210 g $COCl_2$ (10 min), at UV 254 and 430 nm with NBP and at 254 nm without NBP.

viscosity increases very slowly. This results tends to indicate that, during early stages of phosgenation before second charge of caustic solution, polymerization is rather slow mainly through interfacial propagation by adding one bis unit at a time. The second charge of caustic solution by metering pump begins at the time (27 min) when 550 g of phosgene has already been fed into the reactor. The chloroformate concentration declines and the corresponding intrinsic viscosity is increased drastically following the second caustic addition and reaches a minimum at 47 min. The additional free caustic raises the pH value and catalyzes the coupling reaction rapidly. The second charge of caustic would certainly hydrolyze part of the chloroformate into sodium phenate. The additional sodium phenate is probably not the major driving force to cause such a dramatic increase in coupling rate. The relatively slower coupling rate observed before 27 min is probably due to the less emulsion and thus less interfacial contacting area. The degree of emulsion during phosgenation is increased gradually with the increase of phosgene addition.

TABLE II
Fraction of Chloroformate in 210 g $COCl_2$ Sample[a]

Components	Carbonate/ROCOCl	Corrected LC area	Relative eq. of carbonate	Relative eq. of ROCOCl
$H-B_1-H$	0/0	0	0	0
$H-B_2-H$	1/0	10.121	10.121	0
$H-B_1-N$	0/1	6.393	0	6.393
$H-B_3-H$	2/0	6.481	6.481	0
$H-B_2-N$	1/1	7.396	3.698	3.698
$H-B_4-H$	3/0	2.542	2.542	0
$N-B_1-N$	0/2	4.246	0	4.246
$H-B_3-N$	2/1	1.508	1.005	0.503
$H-B_5-H$	4/0	0.724	0.724	0
$N-B_2-N$	1/2	0.329	0.110	0.220
$H-B_4-N$	3/1	0.504	0.378	0.126
$H-B_6-H$	5/0	0.321	0.321	0
High M_w	5/1	31.06	31.06	0
Sum		71.624	56.439	15.185

[a] Data from Figure 10. CF % (Chloroformate wt %) = 21.2%.

CONCLUSIONS

1. A liquid chromatographic method for chloroformate-containing oligomers in the interfacial polycarbonate phosgenation process has been successfully developed.
2. This developed method can also be employed to calculate oligocarbonate concentration by subtracting the chloroformate from the total phosgene fed with some adjustment for hydrolysis.
3. A complete phosgenation reactor profile for oligomers with and without the chloroformate end group can be obtained.
4. Most coupling reactions occur at the interface and the rate is dependent of interfacial area and pH value.
5. The surface-active substances, such as —ONa and —OCOCl, increase the degree of emulsion and thus the interfacial area and the rate of polymerization.

TABLE III
Comparison of the Experimental and Calculated Chloroformate Concentrations

1. 210 g $COCl_2$ = 2.123 eq (in term of chloroformate and oligocarbonate formation)
2. Total organic weight in the reactor = 2794 g
3. If 21.2% of all the phosgene fed is in chloroformate form, we would expect % chloroformate in the organic phase to be % chloroformate = [2.12 (eq) × 79.5 (g/eq) × 100% × 21.2]/2794
   = 1.281%
4. Experimental results by colorimetry
   % chloroformate = (115 × 0.0074/120 × 6000) × 79.5/2794
   = 1.211%

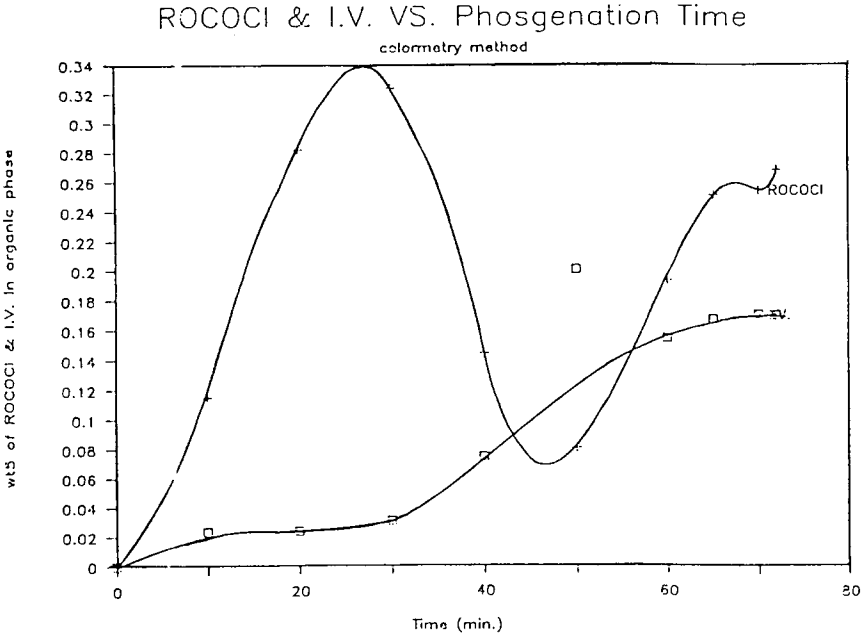


Fig. 11. (+) Total chloroformate (wt %) and (□) IV of a typical phosgenation reaction.

6. Better mechanistic understanding from this study suggests that a proper caustic adding program can smooth the reaction and reduce phosgene loss. The ideal caustic adding program is the one that can avoid suddenly changing the feeding rate and maintains a certain concentration of chloroformate throughout the reaction.

References

1. V. V. Gur'yanova, T. N. Prudskova, and A. V. Pavlov, *Int. Polym. Sci. Technol.*, **9,** 14 (1987) [transl. of *Plast. Messy,* **9,** 54 (1987)].

2. J. Epstein, R. W. Rosenthal, and R. J. Ess, *Anal. Chem.*, **27,** 1435 (1955).

3. A. Lamourous, *Mem. Poudres,* **38,** 383 (1956).

4. E. Sawicki, D. F. Bender, T. R. Hauser, R. M. Wilson, Jr., and J. E. Meeker, *Anal. Chem.*, **35,** 1479 (1963).

5. A. M. Agree and R. L. Meeker, *Talanta,* **13,** 1151 (1963).

6. M. Fieser and L. F. Fieser, *Reagents for Organic Synthesis,* Vol. 1, pp. 856–859. Wiley-Interscience, New York, 1967.

7. C. A. Pryde and M. Y. Hellman, *J. Appl. Polym. Sci.*, **25,** 2573 (1980).

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