The Interfacial Polycarbonate Reactions. I. Defining the Critical Process Parameters

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SYNOPSIS

Polycarbonate is prepared by the interfacial phosgenation and polycondensation of bisphenol A (BPA) in methylene chloride with caustic using triethylamine as a catalyst. In a typical batch reactor, where phosgenation and oligomerization proceed simultaneously, the critical process parameters are intermingled and are difficult to determine. Therefore, a semicontinuous process consisting of a series of static mixers for continuous phosgenation, followed by a batch reactor for oligomerization and polycondensation, was developed for better understanding of the reaction mechanisms. Phosgene hydrolysis was reduced greatly going from a batch to a continuous reactor (excess phosgene was reduced from 30 to 5%). Variables which influence the composition of intermediates are linear velocity, organic to aqueous volume ratio, PH (BPA to NaOH ratio), and phosgene to BPA ratio. These variables also affect BPA conversion, amount of phosgene hydrolysis, terminator capping efficiency, molecular weight, and molecular weight distribution of the resulted polycarbonate. Oligomerization takes place at the interface, and monochloroformates ($HO-B_n-OCOCl$) which contain both hydrophilic and lipophilic end groups, stay at the interface and, hence, react preferentially. Oligomers are analyzed by a newly developed HPLC technique.

INTRODUCTION

The interfacial phosgenation–polycondensation reaction between difunctional phenol and phosgene is the starting point for many commercial polymers of the carbonate family.[1] Since the reaction mechanisms of a typical batch phosgenation of bisphenol A (BPA) is complicated by simultaneous oligomerization, a semicontinuous process has been developed to control phosgenation and oligomerization separately. A series of static mixers are employed as plug flow reactors for the continuous phosgenation. The precooled organic (phosgene in methylene chloride) and aqueous (BPA in caustic) liquids are fed simultaneously and continuously into the static mixer reactors. The effluent from the static mixers is fed into a batch reactor to carry out subsequent oligomerization and polycondensation. Besides the substantial reduction in phosgene hydrolysis, from 8 to 10% for a typical batch reaction to merely 3 to

5% for the continuous phosgenation, the accurate measurement of various types of oligomers during phosgenation and oligomerization have allowed for a better understanding of the reaction mechanism, and have helped in defining the critical process parameters. These findings are discussed below.

EXPERIMENTAL

LC Conditions

A 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 are stored on a computer disc. LC column Spherisorb, ODS2, 15×4 mm, 3μm, from Scientific Glass Engineering, with a flow rate of 0.5 mL/min were used. The signals at 430 and 254 nm were monitored. Typical sample preparation is carried out by dissolving the polycarbonate solid film in THF or THF containing 1% of NBP (4-(p-nitrobenzyl)pyridine) for chloroformate. It is preferable to analyze the freshly

Table I   The LC Analysis Conditions for BPA–PC Oligomers

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

prepared sample immediately to avoid any undesirable side reaction that may occur in the solution. This method is listed in Table I.

Preparation of PC Using Triethylamine Catalyst–Batch Process

Into a 40-L reaction flask equipped with a stirrer, PH electrode, phosgene inlet, reflux condenser, caustic addition inlet, and a thermometer, are placed water (11.5 L), BPA (2515 g, 11.016 mol), methylene chloride (9.5 L), and phenol (31.1 g, 0.3305 mol). After adjusting the reactor solution to pH 12 with 50% aqueous caustic solution, phosgene (1414 g, 14.297 mol) is added at the rate of 20 g/min while maintaining pH at 12 by adding 50% caustic solution. Reaction temperature is held at 25°C by using a cooling bath. Reaction samples are taken at various stages of phosgenation to analyze oligomers. After the addition of phosgene is completed, the reaction mixture is diluted with methylene chloride (5.5 L). Caustic solution is added to raise the pH to 12, and then aqueous solution of triethylamine (7.255 g, 0.717 mol, 5% in water) is added. The reaction mix-
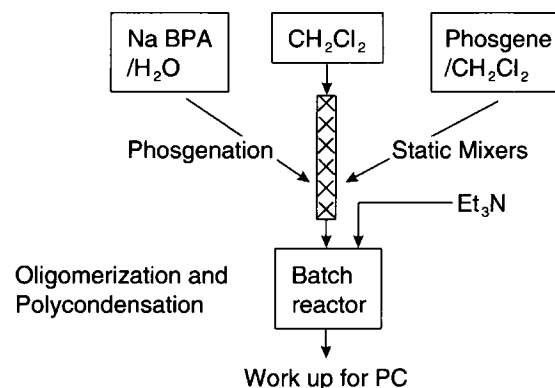
Scheme 1   Semicontinuous PC process. Na BPA/H_2O: BPA 2515 g, Phenol (or t-butyl phenol) 1–5% of BPA, $NaBH_4$ 2 g, NaOH (50%) 1982.4 g, H_2O 12.5 L; stir under N_2 atmosphere at 40–60°C for 30 min to obtain 16.8-kg solution, precooled to 10°C, flow rate 311 g/min. Phosgene/CH_2Cl_2: phosgene 1150 g in 4650 g of CH_2Cl_2 (or 20 wt %), precooled to 10°C, flow rate 106 g/min. CH_2Cl_2: CH_2Cl_2 16416 g, precooled to 1–5°C, flow rate 300 g/min.

ture stirred until all chloroformate disappears. Total 50% caustic consumed is 1430.3 g (35.758 mol). After all chloroformates disappear, additional phosgene is added to adjust the pH to 8. The organic layer is washed with dilute HCl and water. Polymer is precipitated by dilution with an equal volume of n-heptane.

Semicontinuous Process for BPA-PC

A simple block flow diagram for the semicontinuous process is shown in Scheme 1.

Table II   Various Combinations of Static Mixers

Character	T4-21	T6-21
Number of elements	21	21
Length (cm)	16.5	25
Vol (mL/unit)	3.24	13.07
Cross-section area (cm^2)	0.1963	0.5228
Min velocity (mL/min)	588.9	1568.4
Pressure (psi)	20/2 unit	19/2 unit
Different Combinations:	Linear Velocity T4-21 (cm/sec)	Retention Time (s)
T4-21*2 + T6-21*6	56.6–80.3	7.64–5.39
T4-21*2 + T6-21*6 + Parr R.	65.2	53.5
T4-21*2 + T6-21*3 + T4-21*4	58.4–59.6	5.11–5.01

Note: The static mixer was manufactured by Noritake Inc., Japan.

Raw material streams with the indicated flow rates are fed into a series of static mixers (type and specification are shown in Table II) maintaining reaction temperature around 13 to 17°C with a residence time of 3 to 8 s.

The effluent analyzed by HPLC typically contains 26 to 43% unreacted BPA, 36 to 50% $NaO-B_n-ONa$, 16 to 18% $NaO-B_n-OCOCl$, and 4 to 6% $Cl-OCO-B_n-OCO-Cl$. (B_1 means 1 unit of BPA, B_2, means 2 units and so forth). The effluent is fed into a 40-L batch reactor under agitation at 20 to 25°C for 30 min, with addition of 300 g caustic (50% aqueous solution) to maintain $pH \geq 12.5$. The reaction mixture is then stirred until all chloroformates disappear. Five percent aqueous triethylamine, 200 mL, is added and polycondensation proceeds at 20 to 25°C for 60 min. Layers are separated and the organic phase is first washed once with alkaline solution (150 g of 3% NaOH in 5 L H_2O), once with acid solution (100 g of 0.74% HCl in 5 L H_2O), and finally with 5 L of water 3 times. Polymer is precipitated by dilution with an equal volume of n-heptane.

RESULTS AND DISCUSSION

According to Noguchi,[2] 3 kinds of intermediates, $HO-B_n-OCOCl$, $ClOCO-B_n-OCOCl$, and $HO-B_n-OH$, are present during the phosgenation step. The distribution of these intermediates depends on reaction temperature, amount of caustic, and flow rate of phosgene. Only a few qualitative descriptions of these intermediates have been reported.[3] Because of the complexities of batch reactions, both phosgenation and coupling rates could not be measured in the above paper. With the semicontinuous process, we can divide the polycarbonate process into three sections: phosgenation, oligomerization, and poly-
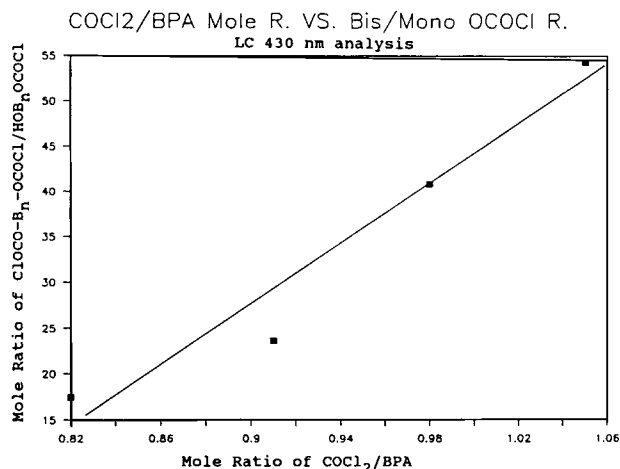

**Figure 1** The relationship of ClBnCl/HBnCl ratio vs. $COCl_2$/BPA mol ratio.

condensation. Process parameters affecting each section are discussed below.

Phosgenation Stage

The Effect of Phosgene/Bisphenol Ratio

Reactants are metered into static mixers by gear pumps and also monitored by electronic balances to control the exact ratio. With various ratios of phosgene/bisphenol, samples are taken at steady state and analyzed by the LC method[4] to determine their compositions in both aqueous and organic phases (shown in Scheme 2).

Since the LC area ratios, at 430 nm for NBP (4-(p-nitrobenzyl)pyridine) derivatives of chloroformates are equivalent to their mole ratios,[4] it is possible to calculate the ratio of $ClOCO-B_n-OCOCl/$ $HO-B_n-OCOCl$. These results are shown in Table III and Figure 1.
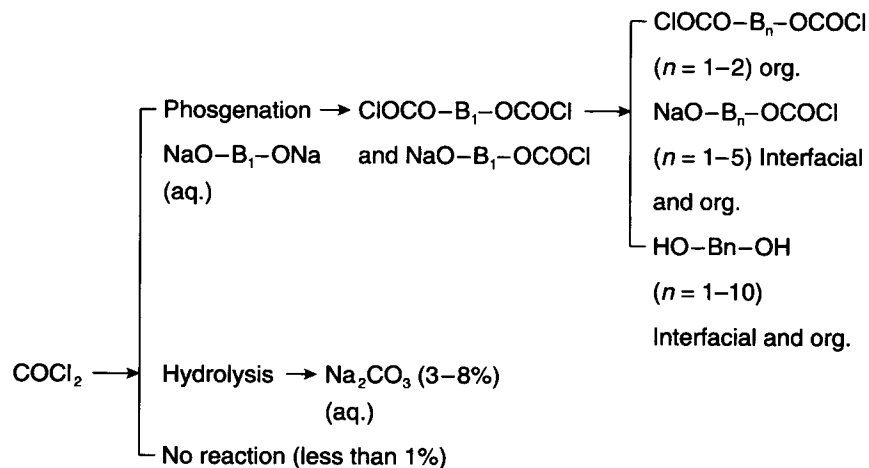
Scheme 2 LC analysis of phosgenation stage products.

Table III   The Mono- and Bischloroformate Percent of a Typical Semicontinuous PC Synthesis at Phosgenation Stage

	Time (min)	10	20	30	40
	$COCl_2$/BPA Mol Ratio	0.87	0.98	1.02	1.1
		Mol Ratio			
Detector UV 430 nm:					
Ph-B_1-N		0.6	0.56	0.41	0.67
H-B_1-N		7.66	17.38	9.96	11.13
H-B_2-N		45.62	40.7	34.28	31.91
N-B_1-N		14.14	18.52	28.06	34.24
H-B_3-N		17.97	14.03	15.01	12.52
N-B_2-N		0.71	0.58	0.93	0.95
H-B_4-N		7.37	5.47	7.11	5.57
H-B_5-N		3.26	2.03	3.25	2.42
H-B_6-N		2.67	0.73	1	0.59
Sum		100	100	100	100
Mol ratio of					
$ClOCO-B_n-OCOCl$/$HO-B_n-OCOCl$		0.1745	0.2361	0.4083	0.543

N = NBP, 4-(p-nitrobenzyl) pyridine.

The bis-/monochloroformates ratio increases with the higher phosgene/BPA ratio to the static mixer. The same result was reported by Noguchi[2] in a batch process with a higher flow rate of phosgene. The major component, HO-B_2-OCOCl (H-B_2-Cl), shown in Table III as its NBP derivatives H-B_2-N, can be produced from several routes as shown in Scheme 3.[2]

The Effect of Mixing

Better mixing produces higher yields of monochloroformate and reduces hydrolysis of phosgene.[3] As shown in Figure 2, better mixing resulting from the continuous static mixers has produced higher concentrations of monochloroformates than a batch reactor. The compositions at various phosgenation stages are shown in Table IV. The conversions of BPA increase rapidly with the increase in methylene chloride to aqueous volume ratio (MC/aq) from 0.8 to 1.0 (shown in Fig. 3). Conversions of BPA increase rapidly with higher linear velocity due to better mixing of the two reactant phases until too high a velocity reduces the residence time (as shown in Fig. 4). The optimum condition for BPA conversion at phosgenation stage using a T4-21 static mixer is at a linear velocity of 70 to 75 cm/s, with a residence time of around 7 s.

Hydrolysis of Phosgene

Since the hydrolysis of phosgene can be suppressed by the use of a higher concentration of BPA in the feed solution (increased reaction rate between BPA
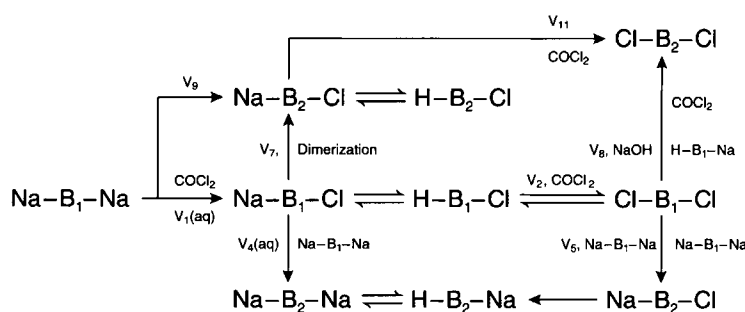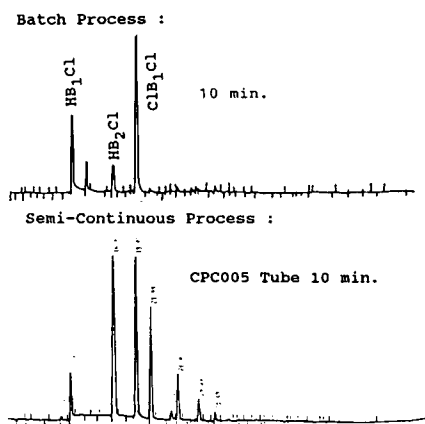

Scheme 3

Figure 2 LC analysis of monochloroformates, HB₁Cl and HB₂Cl, at phosgenation stage by a semicontinuous or a batch process.

Figure 3 BPA conversion vs. the vol ratio of org/aq at phosgenation stage [numerical numbers indicate the linear velocity (cm/s) of T4-21 static mixer].

and phosgene), the optimum solubility of BPA in caustic was determined (shown in Fig. 5). The optimum solubility (0.17 g of BPA per gram of a 6.7% NaOH solution at 20°C) was used for the semicontinuous process. Phosgene hydrolysis has been reduced dramatically from 8 to 10% for a batch process to 3 to 5% for the continuous phosgenation with the same BPA conversion (Fig. 6). This is attributed to an equal concentration of sodium bisphenolate
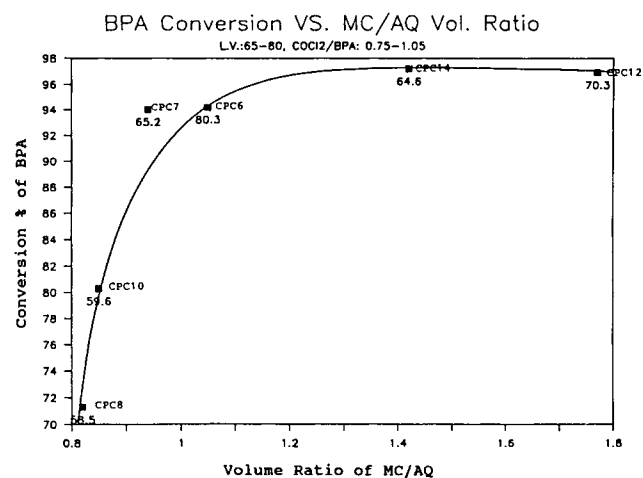
throughout the whole phosgenation stage for a continuous tubular reactor compared to very high and very low concentrations of sodium bisphenolate at the beginning and at the end of phosgenation for the batch reactor. The residual sodium bisphenolate in the effluent of the tubular reactor reacts completely in the following batch reactor (oligomeriza-

Table IV   The Relation of ROCOCl/OH Ratio vs. IV and Physical Properties

Run No.	CPC5	CPC6	CPC7	CPC8	CPC9	CPC10	CPC11	CPC12
Conversion % of BPA:								
Phosgenation	61.3	63.4	69.0	66.7	61.3	66.9	66.1	78.6
Tank 0 min	73.4	94.2	94	71.3	75.2	80.3	76.2	96.9
Linear V (cm/s)	56.6	80.3	65.2	58.5	58.4	59.6	100	70.3
Vol R (org/aq)	0.90	1.05	0.94	0.82	0.88	0.85	0.76	1.77
Mol R of COCl₂/BPA	0.94	1.06	0.80	0.83	0.85	0.88	0.88	0.88
Hydrolysis of COCl₂:								
Phosgenation	5.2	5.2	6.9	5.6	4.4	4.6	4.1	4.4
Tank 0 min	6.7	8.5	3.4	3.3	4.9	4.4	5.3	4.8
Abs of ROCOCl	288	160	187	249	244	186	300	111
UV (287/265)	0.010	0.025	0.012	0.048	0.103	0.098	0.11	0.026
Cl/OH ratio	27941	6250	14960	5188	2369	1898	2727	4253
IV (film)	0.335	0.324	0.347	0.282	0.326	0.377	0.319	0.321
IV (powder)	0.348	0.349	0.336	0.319	0.342	0.407	0.324	0.359
Tensile (kg/cm²)	648	648	655	673	624.7	614.9	648.3	647.8
DBTT (°C)	−2.5	−10	−7.5	−7.5	−12.5	−17.5	−2.5	−7.5
HDT (°C)	135.2	134.2	136.2					

Note. The terminator of CPC5 through CPC7 are phenol, others are *t*-butyl phenol (both terminators are 3 mol % of BPA).
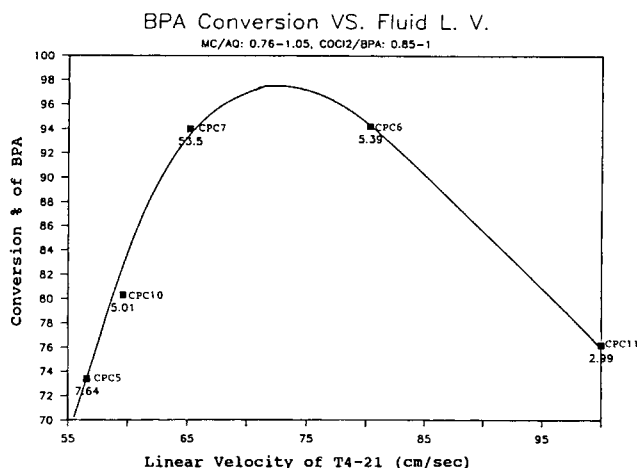
Figure 4 BPA conversion vs. the linear velocity of fluid in T4-21 static mixers [numerical numbers indicate the retention time (in seconds) in static mixers].

tion and polycondensation) without the use of excess phosgene while, for a typical batch process, 30% excess phosgene is required to achieve the same conversion of BPA.

Kinetic Rate Equations

Both phosgenation and hydrolysis are controlled by mass transfer and pH (diffusion control). The initial rates for these two reactions at an interface is expressed by the "liquid cage theory" in the following equations:

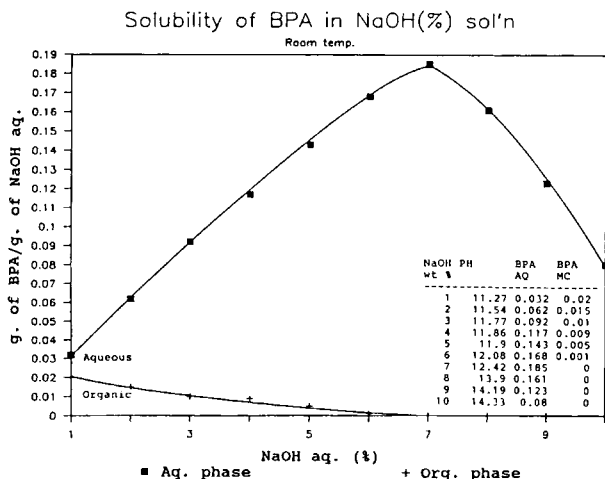Phosgenation rate $(R_p) = K_p*[COCl_2]*[RONa]$

$$(1)$$

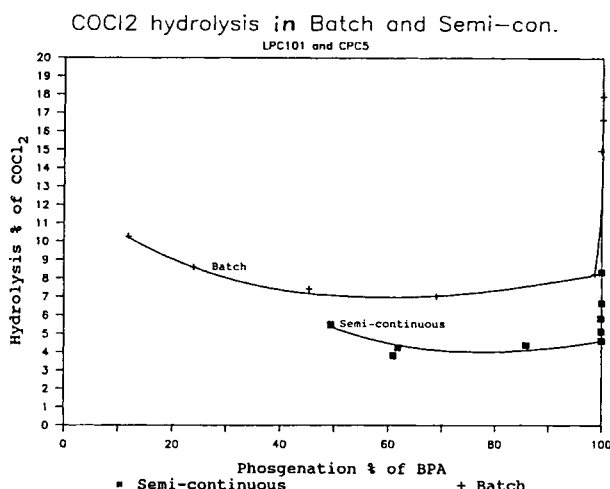Figure 5 The solubility curves of BPA in a caustic/CH$_2$Cl$_2$ two-phase solution.

Figure 6 The phosgene hydrolysis % vs. BPA conversion in a semicontinuous and a batch process.

Hydrolysis rate $(R_h) = K_h*[COCl_2]*[NaOH]$ (2)

$R_p/R_h = K_p/K_h*[RONa]/[NaOH]$ (3)

At the maximum point of BPA solubility curve (as shown in Fig. 5, 0.17 g BPA per 1 g NaOH 6.7% solution), the mol ratio of NaOH/BPA is calculated as follows:

[NaOH]/[BPA]

$$= [1*0.067/40]/[0.17/228.3] = 2.25$$

If the terminator is 3 mol % of BPA, and both terminator and BPA form RONa completely, then for 1 mol of BPA, there are 2.03 mol of RONa and (2.25 − 2.03) = 0.22 mol of NaOH.

Hydrolysis % of COCl$_2$ (H%) = $0.22*R_h/[2.03*R_p$

$$+ 0.22*R_h] = 1/[9.23*R_p/R_h + 1]$$

From eq. (3):

$$R_p/R_h = 2.03/0.22*K_p/K_h$$

H% = $1/[85.1*K_p/K_h + 1]$ or

$$K_h/K_p = 85.1/[1/H\% − 1] \quad (4)$$

For 5% COCl$_2$ hydrolysis in a semicontinuous process, the K_h/K_p is calculated, by eq. (4), to be 4.5, and for 8.6% of COCl$_2$ hydrolysis in a batch process, the K_h/K_p is about 8. Therefore, in order to complete the phosgenation of BPA and terminator, the excess phosgene has to be 5-8 mol % of BPA. Since hy-

drolysis of phosgene consumes twice as much caustic as normal phosgenation of BPA, extra caustic solution is required during the oligomerization stage to maintain pH above 12 (keeping ROH as RONa).

Oligomerization Stage

The composition of oligomers after phosgenation depend on the reaction temperature, mol ratio of BPA/NaOH, mixing efficiency (linear velocity and org/aq volume ratio) and mol ratio of $COCl_2$/BPA at the tube reactor. The relative reaction rates among oligomers can be observed through their individual rate of disappearance during the oligomerization stage. Samples are taken at various points and intervals during each stage of reaction, quenched with HCl, and analyzed for BPA conversion, phosgene hydrolysis, and oligomer composition. The effluent from the tube reactor is designated as tank 0 min, and samples taken from the batch reactor (every 10 min) are designated as tank 10 min, 20 min, . . . respectively. This information provides much help in understanding the relative reaction rates at the oligomerization stage.

Two samples were taken simultaneously after the steady state from static mixers, one from the middle of the tube reactor (T4-21*2 + T6-21*2), and another from the end of the tube reactor (T4-21*2 + T6-21*3 + T4-21*4), with retention times of 3.45 and 5.86 s, respectively. These were analyzed by LC (shown in Fig. 7). $H-B_1-Cl$ reduced from 26.4 to 16.4% (area %), $H-B_2-Cl$ increased from 28.8 to 43%, while $Cl-B_1-Cl$ changed slightly from 16.8 to 16.1%. This result indicated that $H-B_2-Cl$ was mostly from the dimerization of $H-B_1-Cl$ rather than from the reaction between $Cl-B_1-Cl$ and bisphenolate. This result can be understood easily from
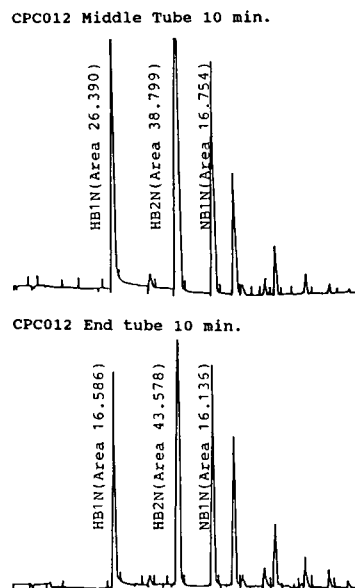

Figure 7 LC analysis of NBP-oligomers at different phosgenation periods, 3.45 s and 5.86 s, by a set of static mixer.

the structure of $H-B_1-Cl$, which contains both hydrophilic and lipophilic end groups that should exist mainly at the interface, hence, it reacts preferentially.

Similarly, runs 7 and 9 had the same oligomer distribution at the middle of tube reactor, however, at the end of phosgenation (tank 0 min), run 9 contained more $Cl-B_n-Cl$ than 7 (due to lower linear velocity, as shown in Tables IV and V, and hence, at the end of oligomerization (before Et_3N addition), it still had unreacted $Cl-B_n-Cl$ and also a lower molecular weight than #7. Both examples illustrate the faster coupling of monochloroformates over those

Table V   The LC Analysis of Chloroformate Oligomers for Runs #7, #9, and #12

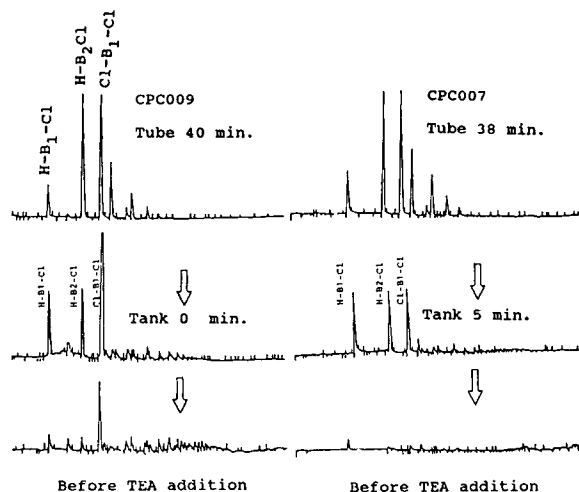| Oligomers (%)	HB_1Cl	HB_2Cl	ClB_1Cl	HB_3Cl	ClB_2Cl	HB_4Cl	HB_5Cl	HB_6Cl
Run 7								
Tube	10.7	25.4	40.7	11.1	1.8	6.0	3.3	1.1
Tank 0 min	27.8	30.9	34.5	6.8				
Before TEA addition	49.8	16.9	33.4					
Run 9								
Tube	5.6	27.8	45.4	10.1	2.7	4.7	2.7	1
Tank 0 min	28.1	25.2	46.7					
Before TEA addition	13.8	12.8	58.7	14.7				
Run 12								
Tube	27.9	37.6	23.1	6	1.2	1.1	2.6	0.5
Tank 0 min	35.9	23.1	15.1	6.5	1.7	1.3	8.4	8.3

Figure 8 LC analysis of chloroformate oligomers at oligomerization stage for runs 7 and 9.

of bischloroformates. Relative reaction rates of oligomers were further demonstrated by the reaction profiles shown in Figure 9. From the rate of disappearance of each oligomer, the following relative reaction rates were obtained:

$$H-B_2-Cl > H-B_1-Cl \gg Cl-B_1-Cl$$
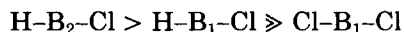
The reaction of BPA at the oligomerization stage was also examined. Run 12 has a higher concentra-

tion of monochloroformates (i.e., $H-B_1-Cl$ and $H-B_2-Cl$, as shown in Table V) than 9 after phosgenation. The unreacted bisphenolate in the aqueous phase was 3% and 20%, respectively for runs 12 and 9 [tank 0 min, as shown in Figure 10 (a and b)], and it took 20 and 60 min, respectively, for runs 12 and 9 to achieve a 99.9% conversion of BPA during the oligomerization stage.

Polycondensation Stage

Although an exact 1 : 1 mol ratio of two reactants, RONa and ROCOCl, constitutes a critical requirement for a high molecular weight polycarbonate product, an excess of ROCOCl is required to compensate for the hydrolysis loss of chloroformates during the polycondensation. If the hydrolysis of each family of chloroformates (monochloroformates and bischloroformates) can be obtained, the right
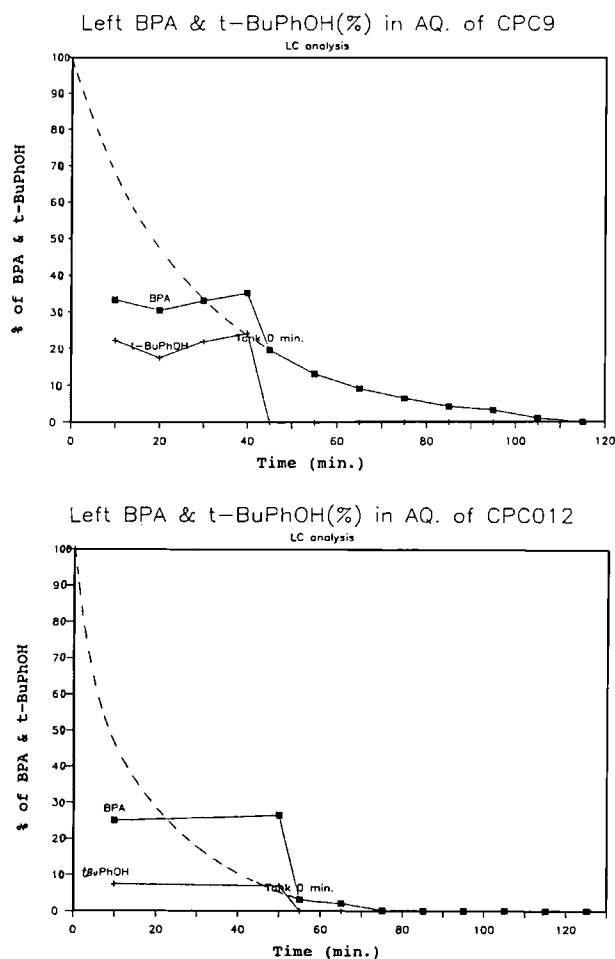

Figure 9 Chloroformates reactor profile of a typical semicontinuous oligomerization stage at UV 430 nm.

Figure 10 The BPA (aq.) conversion at oligomerization stage for runs 9 and 12.

ratio of ROCOCl/RONa can be calculated. However, due to the complex nature of interfacial hydrolysis in the presence of a catalyst, it is very difficult to determine.

In order to obtain an optimum ratio of ROCOCl/RONa before the addition of triethylamine, the reaction mixtures are analyzed by the colorimetry method: the absorbance at 430 nm (after addition of NBP to the diluted organic phase) will indicate the concentration of chloroformates.[4] The ratio of UV absorbances at 287/265 nm (287 nm is the absorbance of the OH group, and 265 nm is the absorbance of the CO group) will indicate the RONa content of oligomers. The ratios of the two reactants,[5] ROCOCl to RONa, have varied from $1.8*10^3$ to $2.8*10^4$ (as shown in Table IV), however, in spite of these variances, most of them have produced polycarbonate products with similar IV (intrinsic viscosity) and good physical properties.

CONCLUSIONS

1. Continuous phosgenation in static mixers, followed by a batch reactor for oligomerization and polycondensation, allow for better understanding of reaction mechanisms for interfacial polymerization of polycarbonate and defining the critical process parameters.
2. Phosgene hydrolysis has been reduced greatly from batch to continuous reactor (excess phosgene reduced from 30 to 5%).

3. Variables which influence the composition of intermediates are linear velocity, organic to aqueous volume ratio, pH (BPA to NaOH ratio) and phosgene/BPA ratio. These variables also affect BPA conversion, amount of phosgene hydrolysis, terminator capping efficiency, molecular weight, and molecular weight distribution of the resulted polycarbonate.
4. Most reactions take place at the interface, and the reaction rates depend on composition of intermediates. The reactivity of each component depends on its phase distribution. Monochloroformate reacts faster than bischloroformate.

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