The Interfacial Polycondensation of Tetrabromobisphenol-A Polycarbonate. II. Reactivities and Phase Distribution of Catalysts

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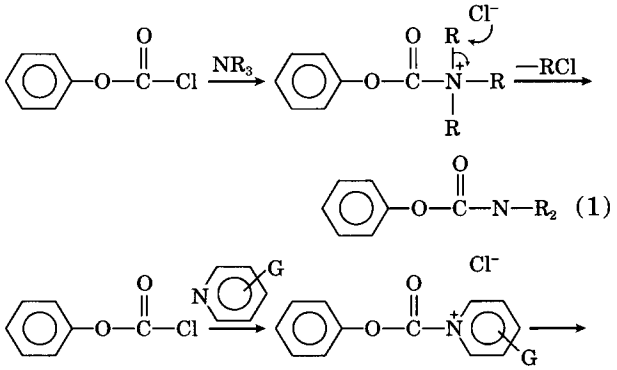
SYNOPSIS

Tetrabromobisphenol-A (TBBPA), a sterically hindered bisphenol, is known to give only low molecular weight polymers using the interfacial process. The low reactivity is attributed to the bulkiness and electron-withdrawing bromine substituents at the *ortho* positions. The optimum reaction conditions for the interfacial polymerization of TBBPA using pyridine derivatives as a catalyst have been developed. From the two-phase concentration distribution constant (K_e) and pK's values of triethylamine, 4-dimethylaminopyridine (DMAP), and TBBPA, the critical process parameters were obtained. Because of its high nucleophilicity and facile leaving character, the DMAP catalyst system produces a high molecular weight TBBPA-polycarbonate (PC) successfully. The profile of the process was followed to obtain a better understanding of the reaction mechanism. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In a previous study,[1] it was found that a membrane made from tetrabromobisphenol-A polycarbonate (TBBPA-PC) has high O_2/N_2 selectivity and is a good candidate for the polymer in membrane separation technology. Although high molecular weight TBBPA-PC, required for producing tough membranes, is readily prepared by the solution process in pyridine, the interfacial process only yielded low molecular weight TBBPA-PC.

From our previous studies[2,3] and Kosky and Boden's study,[4] the results could be attributed to steric hindrance created by bromine substituents and to side reactions leading to carbamates. The activity of the acyl ammonium salt was reduced either by an increase in the steric hindrance at the *ortho* position of bisphenol A or by an increase in the steric hindrance of tertiary aliphatic amine. By Kosky and Boden's proposal,[4] the unreacted amine is loosely associated with species within the reaction and does not exist as free amine. The decomposition of the acyl ammonium salt proceeds via nucleophilic displacement by Cl^- at the carbon attached to the positive nitrogen center to yield a carbamate byproduct. The larger the alkyl group of the tertiary amine, the more carbamate was formed.[3] The pyridine derivatives will not produce carbamates, and, especially, the pyridines with an electron-donating substituent have the best catalytic activity.[3,5] The mechanism of carbamate formation is shown by the following equations:



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Finally, the pH of the phosgenation step was controlled to optimize the concentration of monochloroformate oligomers.[6] Since the interfacial reaction is governed by the concentration of reactants in two phases, if the mixing efficiency or caustic feeding rate was not controlled perfectly, an exact 1 : 1 mol ratio of two reactants, RONa and ROCOCl, could not be obtained and the high molecular weight TBBPA–PC could not be achieved.

EXPERIMENTAL

Intrinsic Viscosity (IV) and GPC Measurement

The IV of TBBPA–PC was measured in 1% (g/mL) methylene chloride solution by an Ubbelode viscometer. The weight-average molecular weight and number-average molecular weight were measured in 1% (g/mL) methylene chloride solution by three GPC columns (Millipore Waters Part No. 10681, 7.8 × 300 nm, 3-column series connected). A TBBPA–PC standard was obtained from the Dow Chemical Co. and had a weight-average molecular weight of 145,000 with a dispersity of 4.8 (IV: 0.4354–0.4302). 4-Bromostyrene polymer had a weight-average molecular weight of 646,400 (IV: 0.0258).

Preparation of TBBPA–PC Using DMAP Catalyst

Into a 40 L reactor equipped with an anchor-type stirrer, phosgene inlet, reflux condenser, caustic addition inlet, and a thermometer were placed water (12.8 L), tetrabromobisphenol-A (2712 g, 5 mol), methylene chloride (14.83 L), *t*-butylphenol (0.24 g, 0.0025 mol), sodium borohydride (2.72 g), and sodium hydroxide (416 g, 10.4 mol). Phosgene (989 g, 10 mol) was added at a rate of 20 g/min while maintaining pH at 10–11 by adding a 50% caustic solution (1568 g, 19.6 mol, flow rate 63.42 g/min, start pumping into reactor after one-half of the phosgene has been added). Reaction temperature was maintained at 25°C by using a cooling jacket. Reaction samples were taken at various stages of phosgenation to analyze oligomers. After the addition of the phosgene was completed, the reaction mixture was diluted with methylene chloride (8 L). DMAP (2.52 g, 0.025 mol) was added and polycondensation started simultaneously. The reaction mixture was stirred for 1 h until all chloroformates disappeared. The level of chloroformate end groups was determined by HPLC and a colorimetric method.[7] After all chloroformate disappeared, additional phosgene was added to adjust the pH to 8. The organic layer was washed with dilute HCl and water. The polymer was precipitated by dilution with an equal volume of *n*-heptane.

Phase Distribution of TBBPA

TBBPA (0.1 g), water (5 mL), and methylene chloride (5 mL) were added to individual vials (20 mL). The pH of the aqueous phase was adjusted by adding sodium hydroxide or hydrochloric acid solution. The mixture was shaken vigorously by hand and permitted to phase-separate. A small sample from each phase was removed for LC analysis. From the ratio of TBBPA concentrations in two phases, the plot of Log(R) vs. pH was obtained (K_e = 0.000887, pK_1 = 7.42, pK_2 = 10) and is shown in Figure 1.

Phase Distribution of DMAP

A solution of DMAP (0.5 g) in methylene chloride (7 mL) and water (7 mL) was adjusted to pH's ranging from 3.24 to 12.55 by adding dilute HCl (10%) or NaOH (10%). After shaking vigorously for several minutes, each sample vial had reached equilibrium at room temperature. The organic and aqueous layers were separated and diluted with methylene chloride and water, respectively, followed by measurement of the UV absorbances at 256 nm for the organic phase and 280 nm for the aqueous phases.

From the ratio (R) of DMAP concentrations in the two phases, the plot of Log(R) vs. pH was obtained and is shown in Figure 2. By the first-order

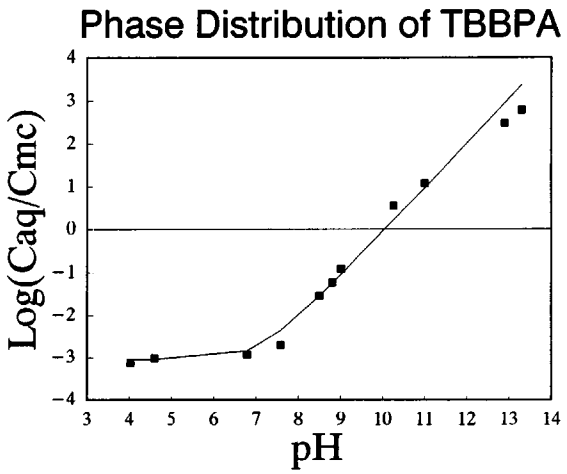

Figure 1 The phase distribution ratio vs. pH of TBBPA in the methylene chloride/water system: (■) exp.; (—) calculation.

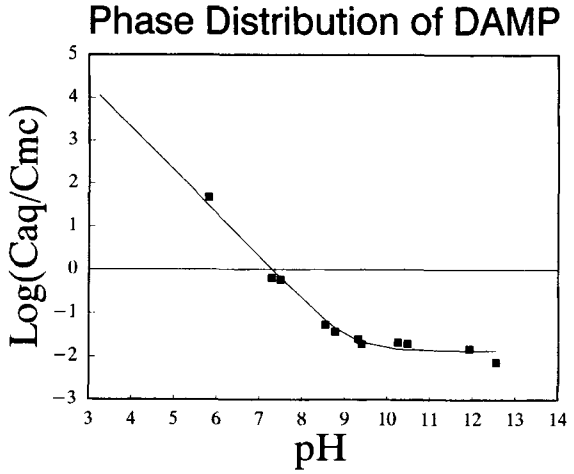

Figure 2 The phase distribution ratio vs. pH of DMAP in the methylene chloride/water system: (■) exp.; (—) calculation.

curve-fitting method, two linear equation coefficients were obtained for pH 10.25–11.93 and pH 7.29–9.39. A crosspoint can be calculated and the x-axis coordinate is proposed as the pK_b (10.515) of DMAP. Each experimental K_e (0.0049) was calculated from the pK_a and experimental R in eq. (1).

Phase Distribution of Triethylamine (TEA)

Since there is no UV absorbance for tertiary amines, the quaternary ammonium salts formed by the combination of the amine with methyl iodide (MeI) are used for measurement. Because the UV spectrum of TEA · MeI salt has an absorbance maximum at 230 nm, the detector wavelength for HPLC analysis was set at 230 nm to obtain the highest sensitivity. The phase distributions of TEA were determined as described below.

A solution of TEA (0.1N, 8 mL in methylene chloride) and water (8 mL) was adjusted to pH ranging from 7.5 to 12 by adding dilute HCl (10%) or dilute NaOH (10%). After shaking vigorously for several minutes, each sample vial (20 mL) had reached equilibrium at room temperature and the phases were left to separate. The organic layer (5 mL) was treated with excess methyl iodide (0.2N, 5 mL). After evaporation of methylene chloride, the residue was dissolved in acetonitrile (5 mL) and analyzed by HPLC for TEA in organic phase. The aqueous layer (5 mL) was adjusted to pH > 12 by adding NaOH (10%) and the free amine was extracted with methylene chloride (5 mL, three times). Because of the distribution coefficients at this pH, triple extraction with CH_2Cl_2 was sufficient to remove all of the amine from the aqueous phase. The pK_a and K_e values were calculated as in the above method and found to be $pK_a = 9.162$ and $K_e = 0.0136$ (Fig. 3).

RESULTS AND DISCUSSION

Phase Distribution and Acidities of Monomers and Catalysts

Data for phase distribution and acidity of TBBPA monomer and catalysts are useful in designing reaction conditions for interfacial polymerization.[8,9] Therefore, the phase distributions of TBBPA and DMAP catalyst in a methylene chloride/water system were determined. The phase distribution of phenols as a function of pH is shown in Scheme I. A plot of $\log(C_{aq}/C_{mc})$ vs. pH is shown in Figure 1. At pH > 8, a straight line with a slope of 1.4 was obtained (Fig. 1). This is unexpected as compared with the case of bisphenol A (Fig. 4) where the phase distribution ratio is constant at pH < 8 (slope = 0); the slope of line increases to 1.0 at intermediate pH and then eventually to 2.0 when pH > 11. The phenomenon is well described by Scheme I. This is because both the mono- and disodium salts of bisphenol A are essentially insoluble in methylene chloride, whereas TBBPA mono- and disodium salts are quite soluble in methylene chloride at pH < 9.0, resulting in a lower dependence on the pH of aqueous phase (slope < 2.0).

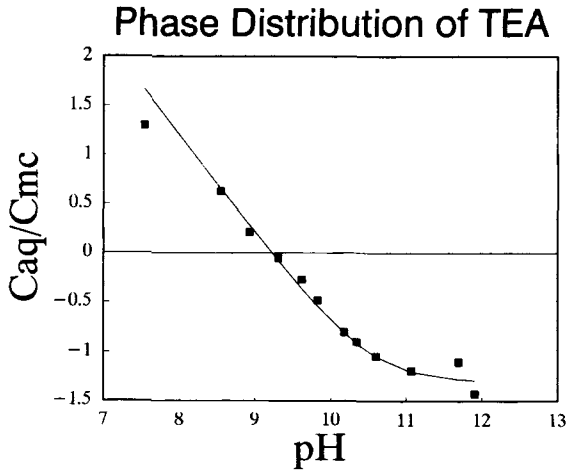

Figure 3 The phase distribution ratio vs. pH of TEA in the methylene chloride/water system: (■) exp.; (—) calculation.

CHEMICAL EQUILIBRIA

$$R\text{—Ph—OH} + \text{NaOH} \overset{K_c}{\rightleftharpoons} R\text{—Ph—ONa} + H_2O$$

$$\text{HO—Bis—OH} + \text{NaOH} \overset{K_1}{\rightleftharpoons} \text{NaO—Bis—OH} + H_2O \overset{K_2,\text{NaOH}}{\rightleftharpoons} \text{NaO—Bis—ONa} + H_2O$$

PHASE EQUILIBRIA

$$[\text{R—Ph—OH}]\text{org} \overset{K_e}{\rightleftharpoons} [\text{R—Ph—OH}]\text{aq}$$

PHASE DISTRIBUTION RATIOS

Monofunctional phenols

$$R = \frac{C_{aq}}{C_{org}} = K_e(1 + K_c[OH^-]_{aq})$$

Difunctional phenols

$$R = K_e(1 + K_1[OH^-]_{aq} + K_1 \cdot K_2[OH]^2_{aq})$$

Scheme I

Even though pK_a's of TBBPA cannot be determined accurately from the data in Figure 1, they are between 7 and 9 and lower than the corresponding values for bisphenol A. The experimental values of pK_a's of TBBPA (as shown in Table I) are 7.42 and 10, respectively, for the first and second phenolic groups. Note that TBBPA is much more soluble in methylene chloride than is bisphenol A. At pH 10, where the polymerization is performed, about 50% of the TBBPA is soluble in methylene chloride.

DMAP is a very effective catalyst for the polymerization of TBBPA. The phase distribution of DMAP as a function of pH is shown in Table I. Following the same approach outlined for phenols, one can derive an equation for amines:

$$R = C_{aq}/C_{mc} = K_e \times (1 + C_{H^+}/K_a) \qquad (3)$$

where C_{aq} and C_{mc} are concentrations of amine in aqueous and in methylene chloride phases, respectively.

At high pH ($C_{H^+} \rightarrow 0$), R will approach K_e, which is the phase distribution coefficient. At a low pH, the plot of log R vs. pH will yield a straight line with a slope of -1. Plots of log(R) vs. pH for both DMAP and TEA agree well with the expected trend. The best-fit value of K_e and pK_a's for the two amine systems are summarized in Table I. Note that the lines in Figures 2 and 3 are constructed from the calculated values of K_e and pK_a's values shown in Table I. At the pH used for the polymerization (pH 9–10), DMAP is about 10 times more soluble in methylene chloride than is TEA. The basicity of DMAP is lower than that of TEA.

Based on phase distribution and acidity data of TBBPA and the catalysts, optimum conditions for the polymerization of TBBPA can be estimated. For TBBPA, the polymerization pH should be between 8 and 10. The phase distribution of monohydroxyl and bishydroxyphenol as a function of pH is shown

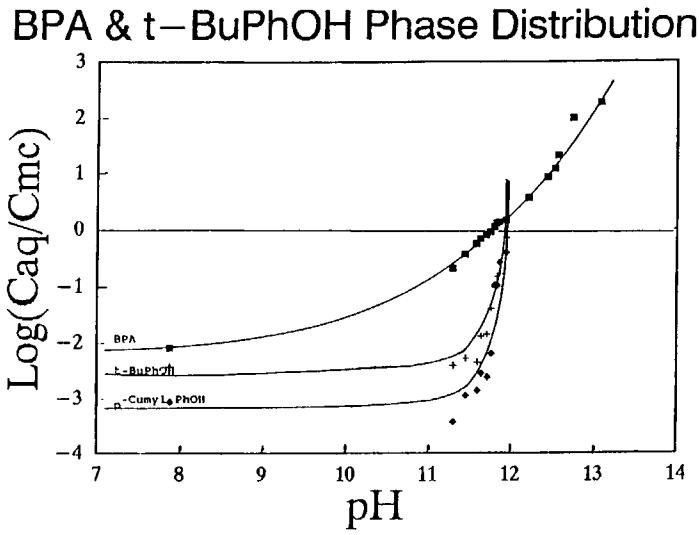

Figure 4 The phase distribution vs. pH of (■) BPA, (+) *t*-butylphenol, and (♦) cumylphenol in the methylene chloride/water system.

Table I Phase Distribution and Acidities of BPA, TBBPA, Terminators, and Amines Catalyst at Room Temperature

Name	K_e	pK_b	pK_{a_1}	pK_{a_2}
Bisphenol A	0.02100	4.200	9.80	11
	0.00272	4.41	9.59	10.2 (8)
TBBPA	0.00075	6.580	7.42	10
p-*t*-Butylphenol	0.00320	3.610	10.39[a]	
Phenol	0.20000	4.200	9.8[b]	
DMAP	0.00490	10.515	3.49	
TEA	0.01360	9.162	4.84	

[a] Ref. 10.
[b] Ref. 11.

in Scheme I. The K_e, pK_1, and pK_2 of TBBPA and *t*-butyl phenol are obtained by the curve-fitting method and are shown in Table I.

At low pH (< 8), the polymerization is slow since most TBBPA is in the phenol form. A pH higher than 10 can cause excessive hydrolysis of the phosgene by sodium hydroxide. Thus, the pH chosen was between 9.5 and 10.5 to obtain the largest amount of monochloroformate at the maximum population of monohydroxyl sodium salt of TBBPA (as shown in Fig. 5). For the TEA catalyst, the pH must be ≧ 12, whereas for DMAP, the pH ≧ 10.

Two polymerization procedures were studied: (a) polymerization using TEA as a catalyst (TEA mol % 0.05 and 5); phosgenation of sodium salt of TBBPA at pH 8.67–10.28 and the coupling of the oligomer at pH 11.44–11.77; and (b) polymerization using DMAP as the catalyst at pH 9.5–10.5.

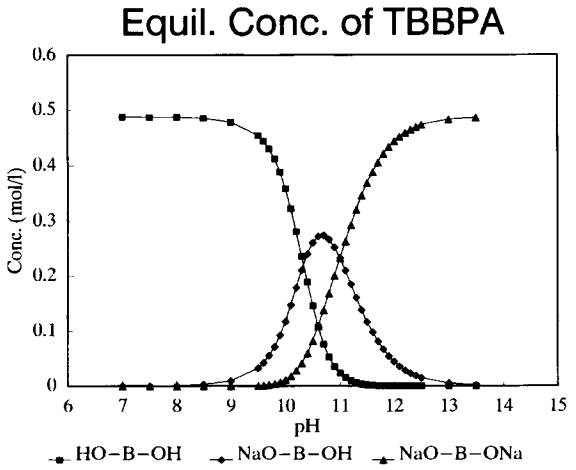

Figure 5 The calculated phase distribution of (■) HO—TBBis—OH, (♦) NaO—TBBis—OH, and (▲) NaO—TBBis—ONa in the methylene chloride/water system.

Polymerization Using TEA as Catalyst

Following the previous procedure,[4] phosgenation of the bisphenate solution at pH 10 and the coupling step at pH 12 were carried out in run #TB1002 and run #TB1003. Those results are shown in Table II.

The reaction profile for the polymerization was followed to understand why high molecular weight polymer cannot be obtained by this procedure. By HPLC analysis, the oligomers obtained at the end of phosgenation are terminated with chloroformate at both ends and have 3–4 repeating units of bisphenol (as shown in Fig. 6).

When the amount of TEA is 0.5% (run #TB1002), the molecular weight of the polymer did not increase significantly and the chloroformate end group did not change even though the reaction mixture was stirred for several hours. Increasing the TEA from 0.5 to 5%, the molecular weight increased and the IV increased from 0.0021 to 0.2869. This implies that part of the TEA is consumed in the termination of the polymer chain. As our previous study indicated,[3] the degradation of chloroformate–TEA complex occurs to give a carbamate end group.

Table II The IV of TBBPA–PC Catalyzed by TEA

Name	TEA Mol Ratio (%)	*t*-Butylphenol Mol Ratio (%)	IV
TB1002 (f)	0.5	3	0.0021
(p)	0.5	3	0.0987
TB1003 (f)	5.0	3	0.2869
(p)	5.0	3	0.4460

Film (f): casting in a dish; powder (p): ppt with *n*-heptane.

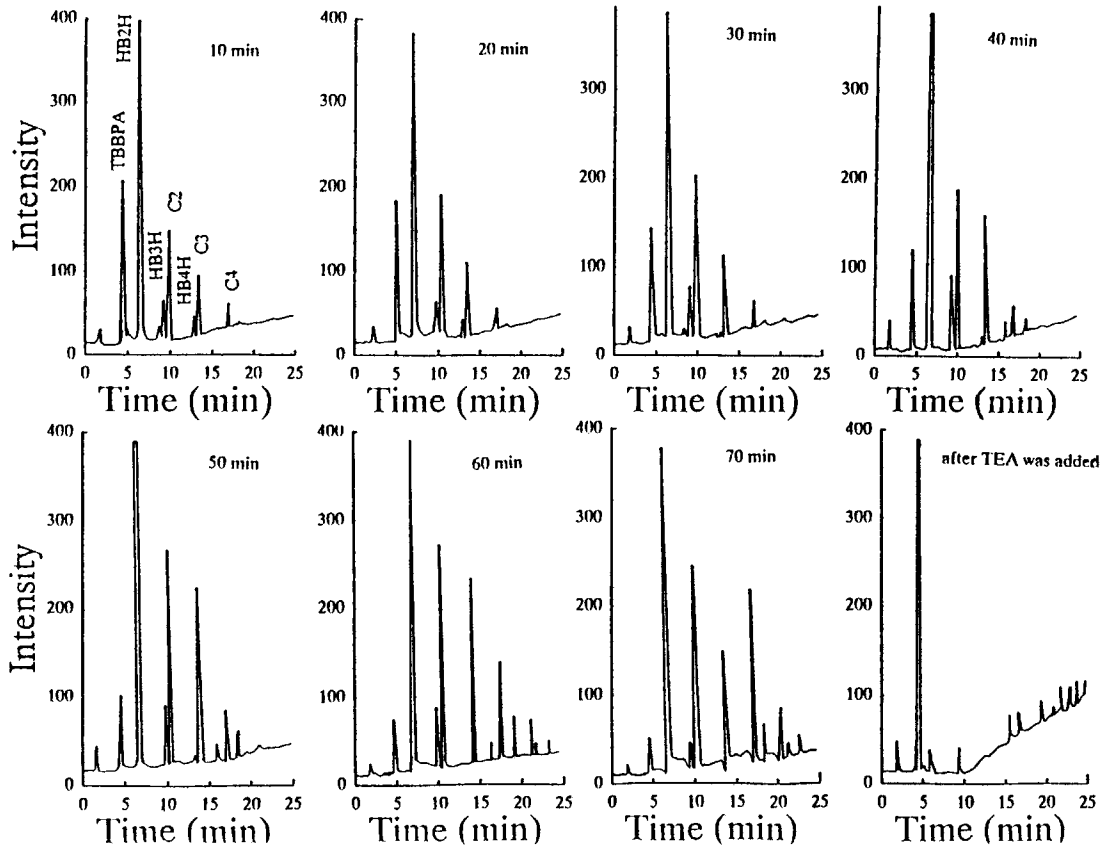

Figure 6 The reaction profile of a typical run of TBBPA–PC synthesis. (Oligocarbonates composition.)

This reaction terminates the polymer chain and consumes the TEA catalyst.

Polymerization Using Pyridine Derivatives as Catalyst

Pyridine derivatives were reacted with tribromophenyl chloroformate (TBPC) and formed the chloroformate–pyridine complex. They do not undergo degradation since the degradation process would involve breaking a π bond in the C=N group.[4] Note that C—N in the chloroformate–TEA complex is a single bond.

Besides the pH control in phosgenation, the amount of catalyst used is very important. The effect of catalyst level (DMAP) on molecular weight build is similar to the initiator for radical polymerizations. The higher the mol ratio of DMAP/TBBPA, the lower the IVs of the resulting polymers (as shown in Table III). Phosgenation at lower pH's (pH's ranged from 8.5 to 12) ultimately produces higher IV products (results shown in Table IV). Thus, high molecular weight TBBPA-PC can be synthesized

Table III The 6 IV vs. Mol Ratio of DMAP/TBBPA

Catalyst	Mol Ratio	IV
DMAP	1.0/1000	0.0671
DMAP	2.5/1000	0.0684
DMAP	5.0/1000	0.0654
DMAP	7.5/1000	0.0626
DMAP	10.0/1000	0.0546

Table IV The Intrinsic Viscosity of TB805, TB812, and TB820

Name	Phosgenation pH Range (Average)	IV of Film	IV of Powder
TB805	9.91–12.66 (10.71)	0.1957	0.2829
TB812	8.69–11.84 (10.10)	0.3959	0.4271
TB820	8.67–11.44 (9.62)	0.8197	0.9126

using controlled reaction conditions and a suitable catalyst.

During the phosgenation step, the reactants must be in contact at high concentrations to promote condensation and to minimize excessive phosgene hydrolysis, as well as to generate a suitable level of monochloroformates for the following polycondensation. The optimum solubility of TBBPA in the caustic was determined and used (See Fig. 7 for maximum solubility of TBBPA, 3.48 g of TBBPA per gram of a 6% NaOH solution at 30°C). The phosgene was blown into the reactor at a constant flow rate of 20 g/min throughout the phosgenation stage. The NaOH was added to the solution in a stepwise fashion (Fig. 8).

To maintain the pH value between 8.67 and 10.28, caustic addition was increased dramatically at the end of the reaction, because of the increased Na_2CO_3 resulting from phosgene hydrolysis (as shown in Fig. 9). To compare the activities of various catalysts at the same oligomer composition, samples were taken from the bottom of a stirred phosgenation reactor and polymerized by various catalysts. The polymerization results are listed in Table V. The highest IV was obtained by trimethylamine and DMAP catalysts. The least sterically hindered amine (trimethylamine) and DMAP did not produce the carbamate[3] but produced a high molecular weight product.

The advantage of DMAP over the other pyridine catalysts is probably due to its nucleophilicity and planar nature, the latter of which produces less steric hindrance with the *ortho*-brominated BPA upon formation of an acyl ammonium salt. The pK_a of DMAP also matches closely the pK_a of TBBPA and

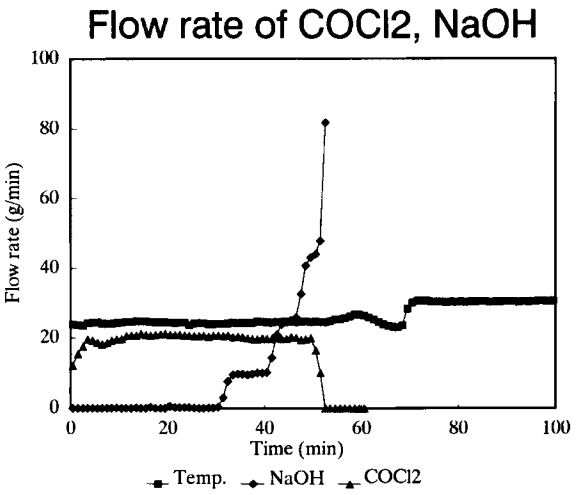

Figure 8 A typical run condition [flow rate of (▲) $COCl_2$, (♦) NaOH, and (■) temperature of TBBPA synthesis.

allows polycondensation at low pH. Therefore, the polymerization can be carried out at pH 9–10 to minimize hydrolysis side reactions. Although DMAP has lower basicity than do other pyridine derivatives, DMAP is a good nucleophile because of its resonant form and is also an excellent leaving group.

CONCLUSIONS

The reactivities and phase distributions of catalysts and monomers (TEA, DMAP, TBBPA, and BPA) and their effects on polymerization have been systematically investigated. The best catalysts among

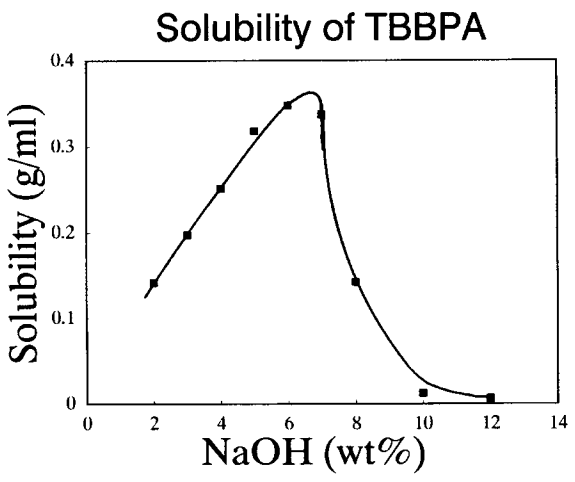

Figure 7 The solubility curve of TBBPA in the caustic solution.

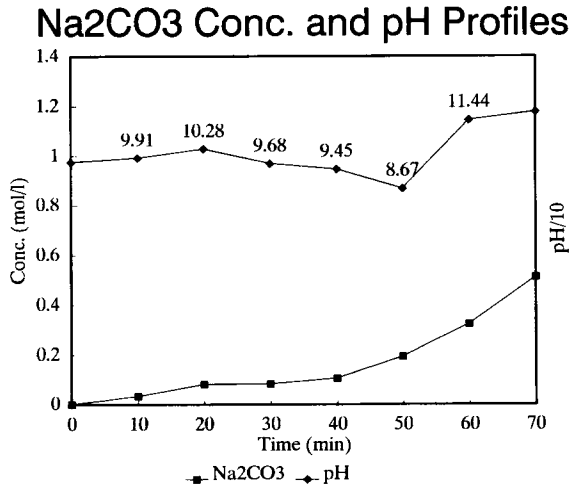

Figure 9 The pH value and the concentration of Na_2CO_3 of a typical run.

Table V Polymerization Results of TBBPA–PC Using Tertiary Amines and Pyridine Derivatives as Catalyst

No.	Name	IV of TB627	IV of TB703	IV of TB820
1	Trimethylamine · HCl	0.1175	0.0720	0.9191
2	Triethylamine	0.0145	0.0191	0.0374
3	Tripropylamine	0.0134	0.0169	0.0153
4	Tri-*n*-butylamine	0.0130	0.0164	0.0284
5	Piperidine, 1-methyl	0.2127	0.0680	
6	Piperidine, 1-ethyl	0.0171	0.0154	
7	Triethylenediamine	0.0601	0.0313	
8	DMAP	0.2127	0.0680	0.7029
9	4-Pyrrolidinopyridine		0.0674	
10	Imidazole, 1-methyl	0.0346	0.0541	
11	4-Phenylpyridine	0.0171	0.0154	0.0324
12	3-Phenylpyridine	0.0038	0.0142	0.0152
13	2,6-Dimethylpyridine			0.0100
14	4-Methylpyridine			0.0153
15	3-Methylpyridine			0.0198
16	2-Methylpyridine	0.0262	0.0260	0.0345
17	Pyridine	0.0144	0.0147	0.0121
18	3-Fluoropyridine			0.0122
19	4-Bromopyridine			0.0141
20	3-Bromopyridine			0.0114
21	4-Cyanopyridine			0.0096
22	3-Cyanopyridine			0.0095
23	1-Methylindole	0.0105	0.0131	

aliphatic amines and aromatic amines were found to be trimethylamine and DMAP. Using DMAP as a catalyst, a high molecular weight polycarbonate (IV up to 0.9, $M_w \geqq 200{,}000$) was successfully produced by the interfacial process. It was found that DMAP is a very effective catalyst in the polymerization of hindered diphenolic compounds. The effectiveness of the DMAP catalyst is attributed to its excellent nucleophilicity, planar nature, and leaving character, its inability to form carbamates from acyl ammonium salts, and to that DMAP is more soluble than is TEA in the methylene chloride phase and, hence, it increases the concentration of the chloroformate–DMAP complex.

APPENDIX

Note 1

(a) A small amount of chain stopper (0.05 mol % of TBBPA) was purposely used to obtain higher M_w TBBPA–PC and to differentiate the catalytic abilities of various amines and pyridine derivatives.

(b) The sodium borohydride was added to prevent oxidation of TBBPA disodium salt from air.

(c) The twofold excess of the phosgene was needed to compensate for the excessive hydrolysis of the phosgene in the TBBPA case. The phosgenation of 1 mol of TBBPA requires 2 mol of caustic, and hydrolysis of 1 mol phosgene requires 4 mol of caustic to maintain pH greater than 9.5, since NaOH effectively scavenges CO_2 to form Na_2CO_3. Therefore, the amount of caustic required for TBBPA–PC is 2 mol/mol TBBPA + 4 mol/mol phosgene hydrolyzed.

Note 2

The pK_a of the amine catalyst can be determined from the following equations:

$$R_3NH^+ \overset{K_a}{\rightleftharpoons} R_3N + H^+ \tag{A.1}$$

$$R_3N + H_2O \overset{K_b}{\rightleftharpoons} R_3NH^+ + OH^- \tag{A.2}$$

$$K_a = \frac{[R_3N][H^+]}{[R_3NH^+]} \tag{A.3}$$

$$K_b = \frac{[R_3NH^+][OH^-]}{[R_3N]} \tag{A.4}$$

$$K_a = \frac{[H^+][OH^-]}{K_b} = \frac{10^{-14}}{K_b} \quad (A.5)$$

$$pK_a = 14 - pK_b \quad (A.6)$$

Note 3

Revision to the paragraph on p. 851 that precedes the Results and Discussion in the authors' earlier paper [J.-T. Gu and C.-S. Wang, *J. Appl. Polym. Sci.*, **44,** 849–857 (1992)].

The effluent analyzed by HPLC typically contains 26–43 wt % unreacted BPA, 36–50 wt % NaO—B_n—ONa, 16–18 wt % NaO—B_n—OCOCl, and 4–6 wt % Cl—OCO—B_n—OCO—Cl. (B1 means 1 unit of BPA; B2, means 2 units; and so forth.) The effluent is fed into a 40 L batch reactor under agitation at 20–25°C for 30 min, with addition of 300 g caustic (50% aqueous solution) to maintain pH ≧ 12.5. Five percent aqueous triethylamine, 200 mL, is added and polycondensation proceeds at 20–25°C for 60 min until all chloroformates disappear.

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