

# Hydrolysis of Polycarbonate to Yield BPA

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## Synopsis

Elevated temperatures and high humidity decrease the molecular weight and impact strength of polycarbonate. Hydrolysis of injection molded polycarbonate (PC) bars stored in glass containers at 85°C and 96% relative humidity (RH) produced brown surface crystals within 30 days. Aging of PC bars at 96% RH and temperatures of 70°C and lower for longer periods of time formed a brown liquid coating on the PC. X-ray, DSC, and GPC measurements indicated that about 70 wt% of the surface crystals were bisphenol A (BPA). The remaining portion of hydrolysis products appeared to be higher molecular weight oligomers of BPA. The brown liquid was composed of supercooled liquid BPA, BPA oligomers, and water. Initial growth of BPA on the surface of a PC bar took place at the interface between the PC and the glass wall of the container. Apparently a water soluble extract from the glass container accelerated the hydrolytic degradation of PC; nevertheless, hydrolysis of PC occurred in the absence of glass—although at a slower rate. Hydrolysis studies were carried out on several commercial PC formulations. The PC resin containing only a heat stabilizer was least affected. Of the flame retardant grades, the brominated PC hydrolyzed less rapidly than these particular compositions containing alkali metal sulfonic acid salts. A glass fiber reinforced PC was less stable than its unfilled parent compound. A hydrolytic stabilizer was ineffective against the attack of water under these conditions.

## INTRODUCTION

Polycarbonate (PC) is a polymer with outstanding toughness. Paradoxically, it is known that the resistance of PC to stress cracking is lowered drastically when exposed to organic solvents like acetone or methylene chloride. Recently, it was shown that the critical crazing stress for PC bars is lowered significantly after exposure to high humidity and temperatures as low as 50°C.<sup>1</sup> Bair, Johnson, and Merriweather have found that the  $T_g$  of water-soaked PC can be lowered not only by hydrolytic degradation but also by plasticization.<sup>2</sup> Pryde and Hellman's GPC measurements of these humidity-aged samples revealed that considerable chain scission had occurred with an activation energy of 19 kcal/mole for the hydrolysis of polycarbonate.<sup>3</sup>

Recently, Pryde and Hellman have studied the hydrolysis of PC using IR and UV spectroscopy and GPC. PCs that were more completely end capped were more resistant to the onset of hydrolysis.<sup>4</sup> In this work, we report on the effects of high humidity and elevated temperatures on impact strength and molecular weight of PC bars and also on the analysis of crystals and liquids which form on the PC surfaces under these conditions.

## EXPERIMENTAL

### Materials

The commercial designations and descriptions of the PCs studied are listed in Table I. The study included standard bisphenol A (BPA)-phosgene polymers, flame retardant (FR) grades based on brominated BPA, and FR compositions containing alkali metal salts of sulfonic acids. The latter additives have been

TABLE I  
Polycarbonates Studied

Designation	Description
PC1	BPA PC, heat stabilized
PC2	Flame retardant (FR), brominated
PC3	FR, salt additive, pigmented
PC4	FR, salt additive, pigmented, hydrolytic stabilizer
PC5	FR, salt additive, hydrolytic stabilizer
PC6	FR, salt additive (higher concentration), hydrolytic stabilizer
PC7	FR, brominated, 10% glass fibers

described in the patent literature but have not been otherwise disclosed.<sup>5</sup> Some of the formulations evaluated contained a hydrolytic stabilizer of unrevealed nature.

### Test Methods

Izod impact tests were done according to ASTM D256 method A on bars 0.125 × 0.5 × 3 in., injection molded using a 2-oz capacity Arburg injection molding machine. The bars were notched before aging, with a cutter having a 0.030-in. radius rather than 0.010 in. as specified in ASTM D256. This was done so that ductile breaks would be obtained with all materials. Samples were treated in an autoclave at 125°C and 21 psig steam, and also heated under dry conditions at 125°C. Other specimens were aged at 85°C both dry and at 96% relative humidity (RH) obtained with a saturated aqueous potassium sulfate solution. These samples were placed in glass Mason jars for the 85°C environment. Five specimens were removed at each exposure period, conditioned for at least 24 hr at 23°C and 50% RH, and tested for impact strength.

Molecular weights were measured by gel permeation chromatography (GPC) using a Waters' HSGPC model #244 with a UV detector. PC samples were dissolved in tetrahydrofuran at 0.5% concentration and kept in a constant-temperature bath at 50°C overnight to ensure solubility. Each solution contained two drops of benzene which was used as an internal standard. Therefore, the calibration curve of every elution run was corrected by the elution volume of the peak height of benzene. The calibration curve was constructed by using GE's ND62 polycarbonate standard. The numbers reported are absolute values for polycarbonate. A computer program was written to determine the Schultz distribution, i.e., the cumulative weight fraction as a function of  $\log M_w$ . This procedure was used to separate the polymer, oligomer, and bisphenol A degradation product, but is not an absolute measure of the individual components.

Several experimental difficulties were encountered. The samples are in the form of cubes 1 mm on each side. However, the pellet size varies so that dimensions are not constant. In experiments in contact with glass, there is non-uniform contact of the surfaces. Furthermore, there is a gradation in products throughout the sample, since the reaction begins at the surface. In addition, small samples are used for GPC measurements. Owing to these difficulties, we have chosen not to report on comparative hydrolysis rates at this time.

Differential scanning calorimetry measurements were made with a Perkin-

Elmer DSC 2. Details of quantitative analysis by this method have been previously described.<sup>6</sup>

### EFFECT OF HYDROLYSIS ON IMPACT STRENGTH

Since Shea found that PC degraded readily on autoclaving and at 60°C,<sup>7</sup> our initial experiments were done at 125°C and 21 psig steam. The results in this accelerated test (Table II) showed that the standard bisphenol A-phosgene PC embrittled between 17 and 30 hr with a slight increase in molecular weight. Although this increase is small, it has been observed repeatedly before the onset of degradation. A brominated, flame-retardant PC2 embrittled in the same time. However, PC2 showed some evidence of hydrolysis in one molecular weight result. PC3, a flame-retardant grade containing a sulfonated organic salt additive, embrittled more rapidly and showed a significant decrease in molecular weight. Samples of all the formulations listed remained ductile after 30 hr of exposure at 125°C under dry conditions.

In order to obtain data more pertinent to actual exposure conditions, impact tests were conducted after aging at 85°C both dry and at 96% RH. All the compounds were ductile after 171 days at 85°C dry and showed only a slight yellowing. Under humid conditions, the standard PC was most stable, and an embrittlement time of more than 102 days. The brominated PC broke in a brittle manner between 14 and 30 days. The hydrolytically stabilized salt additive-type FR PC embrittled in 30 to 68 days; thus, it is not as resistant as PC1. This indicates that the additive system is probably causing acidic or alkaline-catalyzed hydrolysis depending on the nature of the added salt.

Embrittlement tests on PC1 conducted from 50 to 125°C under dry conditions are plotted in Figure 1 and yield an activation energy of 37 kcal/mole. This is close to the 35 kcal/mole value found for physical annealing by Legrand.<sup>8</sup> Izod embrittlement times at 85 and 125°C for all the materials studied show an acceleration of approximately two decades in time, comparable to the expected acceleration from the more complete data obtained on PC1. Embrittlement tests conducted at high humidities result in an activation energy of 30 kcal/mole, indicating the more rapid chemical degradation under these conditions.

Since the weight-average molecular weight ( $M_w$ ) data obtained by GPC measurements on these embrittled specimens (Table II) show generally that very little change in  $M_w$  occurred, it appears then that the mechanism responsible for embrittlement of PC at 125°C is mainly due to physical annealing. However, at temperatures below 80°C, chain scission begins to play an important role in the deterioration of mechanical properties (Fig. 1).<sup>1</sup>

TABLE II  
Hydrolysis of Molded Polycarbonate at 125°C, 21 psig Steam

Designation	Type	Izod embrittlement time, hr	$M_w \times 10^{-4}$	
			Before aging	After embrittlement
PC1	BPA PC, heat stabilized	17-30	2.68	2.80-2.83
PC2	FR, brominated PC	17-30	2.61	2.60-2.39
PC3	FR, salt additive, pigmented	6-9	2.95	1.93
PC4	FR, salt additive, pigmented, hydrolytic stabilizer	17-30	3.19	3.19-2.60

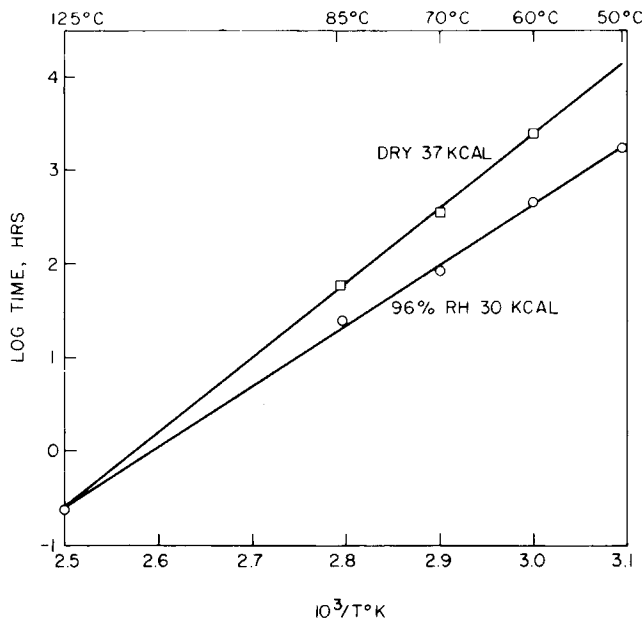


Fig. 1. Embrittlement time of polycarbonate vs. temperature and humidity.

After 30 days of storage in the glass jars at 85°C and 96% RH, brown crystals were observed on the surface of the PC1 bars. Initially, the crystals appeared to grow at or near the interface where the bars contacted the jar walls. At longer times and lower temperatures, a brown liquid partly coated the PC bars and clung in the form of droplets to the sides of the glass container. Analysis of this contamination was done microscopically and with differential scanning calorimetry.

### ANALYSIS

A scanning electron photomicrograph of a PC bar aged at 85°C under dry conditions for 102 days has an essentially featureless surface at 300× magnification except for a scratch mark [Fig. 2(A)]. However, identical PC bars aged for 102 days at 85°C and 95% RH have numerous large crystals coating the bars' surface [Figs. 2(B)–2(D)]. These crystals appeared to be etched into the surface during hydrolysis.

Crystals heated in a DSC from room temperature to 210°C showed several phase transitions (Fig. 3). First, 3.6 cal/g was liberated as the sample partially crystallized ( $\Delta H_c$ ) between 130 and 140°C. Second, following the exotherm, two melting transitions were detected with melting points,  $T_m$ , of 158 and 186°C and heats of fusion,  $\Delta H_f$ , of 24.0 and 4.3 cal/g, respectively. The sample was cooled at 40°C/min to 0°C with no sign of crystallization. Reheating the sample from 0 to 210°C indicated that the sample had glassified, for a  $T_g$  was found at 44°C. Crystallization occurred above  $T_g$  beginning at 81°C and terminated near 125°C with  $\Delta H_c$  equal to 13.8 cal/g. This was followed by melting with  $T_m$  and  $\Delta H_f$  equal to 134.3°C and 13.7 cal/g, respectively.

The melting, crystallization and vitrification behaviors of pure BPA and unknown crystals are similar (Fig. 3); thus, we concluded that the unknown crystals are largely BPA. From a comparison of  $\Delta H_f$  measurements we estimate that

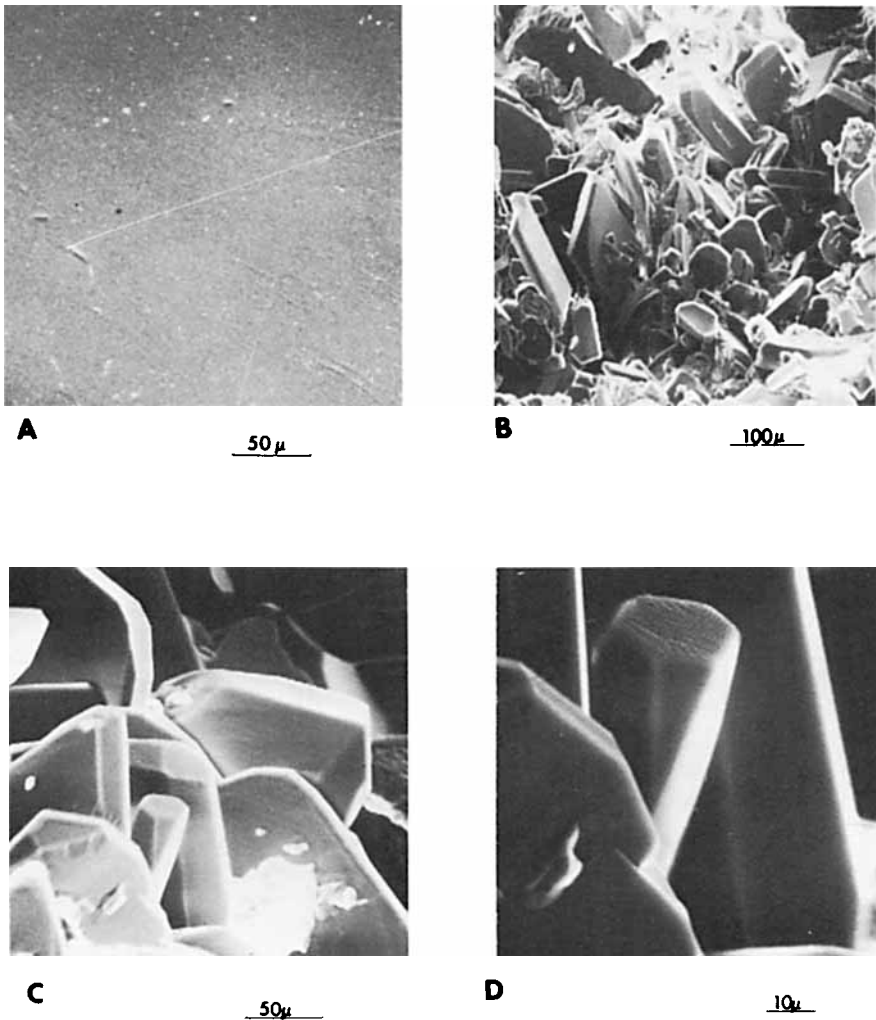


Fig. 2. Scanning electron photomicrographs of polycarbonate surface: (A) aged 102 days at 85°C, dry; (B)–(D) aged 102 days at 85°C, 96% RH.

the surface crystals are composed of approximately 70-wt % BPA. X-ray analysis of the unknown yielded a pattern identical to crystalline BPA.

As noted earlier, the crystals were brown in color whereas BPA crystals are white. We believe that the brown color is due to the presence of a small amount of degraded BPA or related products in the sample. Also, it was pointed out that brown crystals were present on the surface of hydrolyzed PC at 85° and a brown liquid coated the PC bars stored at 70°C and lower. This phenomenon is caused by the substance's tendency to remain as a supercooled liquid until heated above 80°C where rapid crystallization will occur.

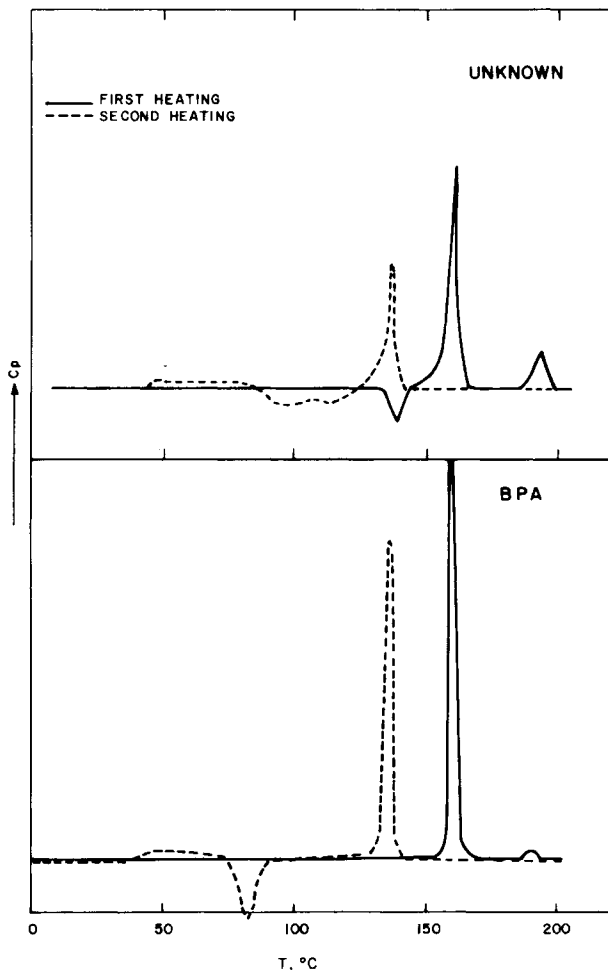


Fig. 3.  $C_p$  curves of unknown against BPA.

### MOLECULAR WEIGHT DETERMINATIONS

GPC measurements were made on the crystals removed from the surface of hydrolyzed PC (85°C and 96% RH) and showed that a large amount of BPA and higher-molecular-weight ( $M_w$ ) oligomers were present (Fig. 4). In comparison, the  $M_w$  of standard unaged PC is depicted by the dashed line in Figure 4 and shows relatively few low- $M_w$  species. In addition, one PC sample had BPA crystals removed from its surface. The  $M_w$  of the interior was 16,000; the original value was about 26,000. Clearly, hydrolysis occurs in the interior of the bar even though there is no detectable amount of BPA present.

Hydrolysis studies were conducted on a standard PC, a flame retardant, brominated PC, and two flame-retardant, salt additive-type PC compounds, which are hydrolytically stabilized. Molding pellets of these formulations were exposed at 85°C under three conditions: dry, at 96% RH in Teflon FEP beakers, and at 96% RH in contact with glass Mason jars. None of these PC compositions degraded in the dry condition. At 96% RH in Teflon FEP, all the samples degraded to some extent (Fig. 5). PC1, which contains only a heat stabilizer, was

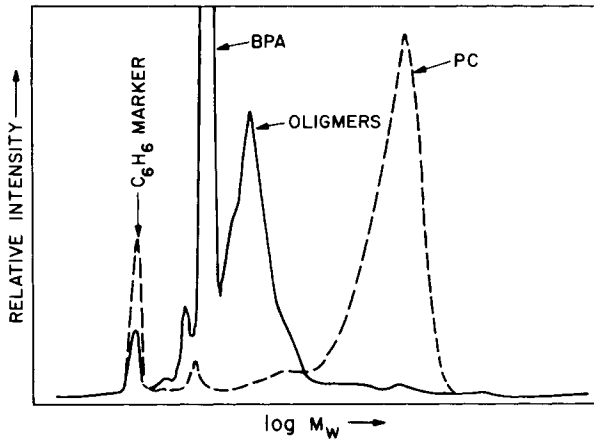


Fig. 4. GPC traces for crystals from hydrolyzed PC contrasted to standard, unaged PC: (—) crystals; (---) polymer.

least affected. The brominated PC2 was somewhat more resistant than the formulations containing the salt additives. The latter two compositions behaved similarly up to 500 hr. The hydrolysis reaction of PC5 became autocatalytic (Fig. 5) between 500 and 1000 hr. For samples in contact with the glass Mason jars, the relative rankings are the same, but the changes in  $M_w$  are more pronounced and occur at shorter times.

The data obtained from the separation of the relative ratios of polymers, oligomers, and bisphenol A (BPA) are given in Table III. The dry samples did not

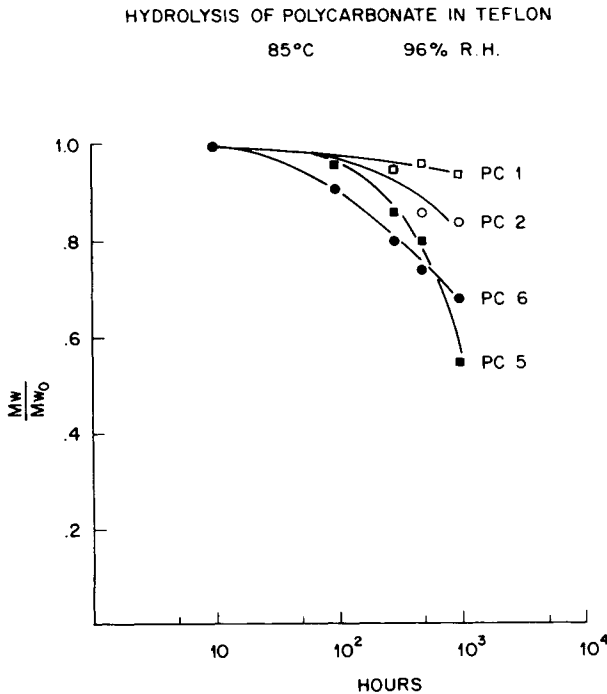


Fig. 5. Effect of time at 85°C, 96% RH on molecular weight of polycarbonate (pellets).

TABLE III  
Hydrolysis of Polycarbonate at 85°C<sup>a</sup>

Compound	Condi- tion	Degradation products, %														
		0 hr			100 hr			300 hr			500 hr			1000 hr		
		Poly- mer	Oligo- mer	BPA	Poly- mer	Oligo- mer	BPA	Poly- mer	Oligo- mer	BPA	Poly- mer	Oligo- mer	BPA	Poly- mer	Oligo- mer	BPA
PC1	Dry	94.9	3.4	1.7												
FEP	96% RH															
Glass	96% RH				85.0	7.0	8.0	94.9	3.2	1.9	63.5	14.5	22.0	94.67	3.57	1.76
PC2	Dry	96.2	2.48	1.4												
FEP	96% RH															
Glass	96% RH				85.0	7.0	8.0	88.7	6.3	5.0	63.5	14.5	22.0	86.79	6.26	6.95
PC5	Dry	94.93	3.48	1.59												
FEP	96% RH															
Glass	96% RH				93.88	3.69	2.43	94.52	3.19	2.29	93.88	3.79	1.91	94.30	3.8	0.0
					90.61	4.30	5.09	94.07	3.18	2.75	90.61	6.10	4.68	70.1	15.2	14.70
PC6	Dry	96.97	2.68	1.14												
FEP	96% RH															
Glass	96% RH				94.09	4.09	1.82	95.11	3.08	1.71	94.09	3.96	1.08	95.34	3.49	1.17
					94.04	3.96	2.0	93.73	4.02	2.22	94.04	6.1	2.3	55.13	16.09	28.78

<sup>a</sup> Data obtained on molding pellets.

<sup>b</sup> Bisphenol-A peak was slightly off scale indicating an even larger percentage.

<sup>c</sup> Other species with elution volumes similar to BPA make quantitative assessment of BPA below 2 wt % unmeaningful.



degrade. At 96% RH in Teflon FEP, the PC1 showed little change in the relative ratio of products although hydrolysis is occurring. The brominated PC2 reacted to produce a gradual increase in BPA and oligomers. The degradation products of PC6 changed very little in 1000 hr, whereas the PC5 reaction became autocatalytic between 500 and 1000 hr. For samples in contact with glass, massive hydrolysis took place, resulting in the formation of relatively large amounts of BPA even in the unmodified PC. Brominated PC did not seem to undergo this reaction as readily. The PC6 showed a substantial amount of BPA after 1000 hr while the PC5 had been converted completely to low molecular weight products.

### DISCUSSION OF GPC RESULTS

Pryde and Hellman<sup>4</sup> showed that in the hydrolysis of solid PC, the presence of phenolic end groups increases the overall rate. Hydrolysis occurs preferentially at linkages only once or twice removed from the phenolic end groups, giving rise to low molecular weight oligomers and BPA.

The reason for the accelerated rate of hydrolysis of samples in contact with glass is most likely the catalytic effect of the alkali leached from this soft glass. Catalysis can also occur when the system is acidic. Thus, the brominated PC was the only material which showed brown discoloration in the absence of glass contact. The production of acidic products could also account for the neutralizing effect of brominated PC in contact with glass and the resultant formation of a relatively low amount of BPA (Table III). The salt-modified PCs contain alkali metal sulfonic acid salts as flame retardant additives. Such additives can influence the reactions taking place. The most stable compound is PC1. Since it is the most nearly neutral system, it is the least affected.

The accelerating effect of glass on PC hydrolysis leads us to question the stability of PCs containing glass fibers. Impact bars were suspended in jars at 85°C and 95% RH for 48 and 100 days. Molecular weight measurements after exposure show that PC1 again is most stable (Fig. 6). The brominated PC2 degrades

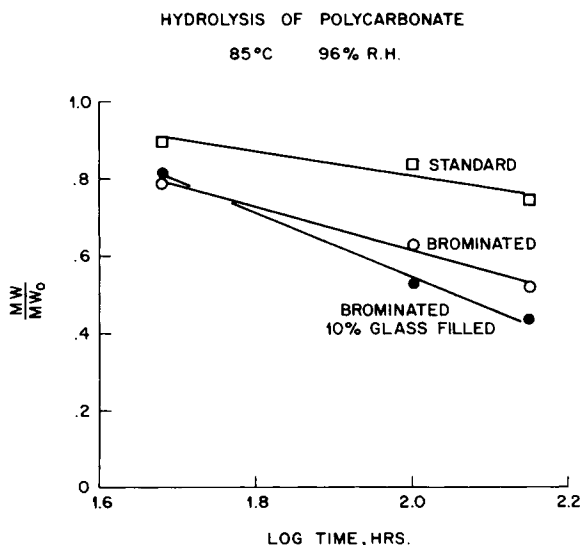


Fig. 6. Molecular weight change of various polycarbonates on hydrolysis (molded bars).

to some extent. The PC7 which contains brominated PC and 10% glass fibers hydrolyzes more rapidly. Even though the glass fibers are coated with a coupling agent which may not prove to be an effective barrier against diffusion of contaminants into the polymer, the ends are obviously uncoated and can lead to the catalytic effect.

## CONCLUSIONS

Aging of PC impact specimens at 125°C in steam shows that in the early stages of exposure, embrittlement was directly related to physical annealing rather than chemical degradation. However, during longer term aging at 85°C, hydrolytic breakdown of PC was observed and affected the embrittlement process. In addition, hydrolysis of polycarbonate (PC) bars stored in glass containers at 85°C and 96% RH produced brown surface crystals within 30 days. Aging of PC bars at 96% RH and temperatures of 70°C and lower for longer periods of time produced a brown liquid coating on the PC. X-ray, DSC, and GPC measurements indicated that about 70 wt % of the surface crystals was bisphenol A (BPA). The remaining portion of hydrolysis products appears to be higher-molecular-weight oligomers of BPA. The brown liquid was composed of supercooled liquid BPA, BPA oligomers, and water. Initial growth of BPA on the surface of a PC bar took place at the interface between the PC and the glass wall of the container. Apparently, an extract from the glass container accelerated the hydrolytic degradation of PC.

GPC measurements show that degradation does not occur in 1000 hr at 85°C in the dry state. At 96% RH, the unmodified PC was the most stable. Of the flame-retardant grades, the brominated PC hydrolyzed less rapidly than those containing the alkali metal sulfonic acid salts. PC with antihydrolysis additives was found to be ineffective against hydrolysis under these conditions. However, since this work was done, we have evaluated a hydrolytically stabilized flame-retardant PC containing alkali metal sulfonic acid salt having nearly equivalent performance to unmodified PC. It was found that a glass fiber-reinforced PC compound deteriorated more rapidly than its parent, unfilled formulation.

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## References

1. P. G. Kelleher and S. Matsuoka, *Proceedings of Conference on Plastics in Telecommunications II*, Sept. 1978, London, p. 12.
2. H. E. Bair, G. E. Johnson, and R. Merriweather, *J. Appl. Phys.*, **49**(10), 4976 (1978).
3. C. A. Pryde and M. Y. Hellman, *Polym. Prep., Am. Chem. Soc. Div. Polym.* **20**(2), 620 (1979).
4. C. A. Pryde and M. Y. Hellman, *J. Appl. Polym. Sci.*, **25**, 2573 (1980).
5. See for example U.S. Pat. 3,953,396.
6. H. E. Bair, in *Analytical Calorimetry*, Vol. 2, R. S. Porter and J. F. Johnson, Eds., Plenum, New York, 1970, p. 51.
7. J. W. Shea, C. J. Aloisio, and R. R. Cammons, *Proceedings of the Society of Plastics Engineers Annual Technical Conference*, April 25-28, 1977.
8. D. G. Legrand, *J. Appl. Polym. Sci.*, **13**, 2129 (1969).

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