

Solid State Hydrolysis of Bisphenol-A Polycarbonate.

I. Effect of Phenolic End Groups

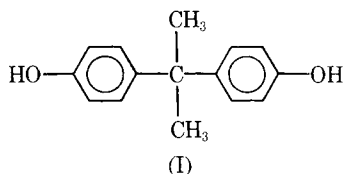
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Synopsis

Solid samples of a nonhydrolytically stabilized bisphenol-A polycarbonate were hydrolyzed at 125°C and 1.4 atm of steam. IR and UV techniques were used both to estimate the degree to which the unhydrolyzed polymer is capped by a chain-terminating agent and to determine the rate of hydrolysis as indicated by the formation of new phenolic end groups. The rate of formation of low-molecular-weight products, particularly bisphenol-A, was estimated by gel permeation chromatography studies. The combined results suggest that the degree of end-group capping is an important factor in the hydrolytic stability of the solid polymer. A model consistent with these results is proposed.

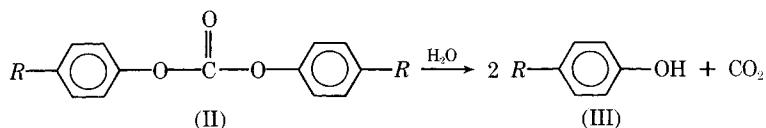
INTRODUCTION

Polycarbonates derived from 2,2-bis-(4-hydroxyphenyl)propane (bisphenol-A) (1) can be molded into parts exhibiting excellent strength and flexibility:



These properties may be diminished, however, by degradative processes such as photolysis and hydrolysis. Hydrolysis during molding operations can result in severe degradation, but it can be effectively minimized by carefully drying the polymer immediately before molding. Recent reports, however, suggest that hydrolysis may sometimes occur during long-term testing under conditions of temperature and humidity which are not much more severe than those encountered in some applications.^{1,2}

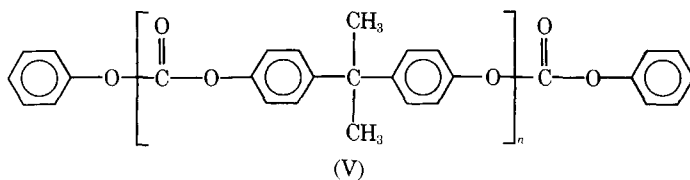
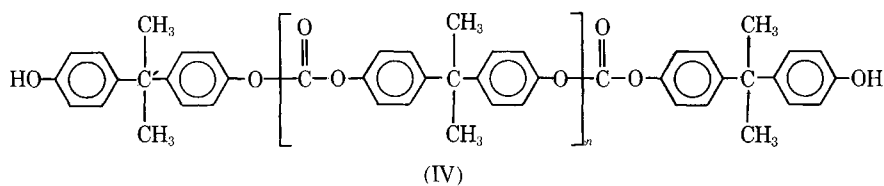
It is well known that hydrolysis of an aromatic carbonate (II) yields two molecules of a phenol, (III) and CO₂:



The intermediate half-ester of carbonic acid (or the corresponding anion) is not stable under the reaction conditions.

In a study directed toward understanding the greater relative hydrolytic stability of polymeric aryl carbonates compared to polymeric esters of aromatic carboxylic acids, Cooper and Williams¹ studied the behavior of a model carbonate compound, diphenyl carbonate, and compared it with that of a model aromatic ester, phenyl benzoate. The hydrolysis rates of both esters were measured in dioxane-water solutions. These authors found that diphenyl carbonate hydrolyzes most slowly in neutral solution. Addition of a strong base greatly accelerates the reaction, whereas addition of a strong acid causes only a moderate increase in rate. In all cases, however, the carbonate reacts more rapidly than phenyl benzoate, with the greatest difference in rates apparent in the neutral solutions. Thus the authors concluded that the observed resistance of polycarbonates to hydrolysis is not due to any inherent lack of reactivity of the carbonate linkage toward water and must therefore be related to factors which control hydrolysis of the bulk polymer.

In this study we have examined the chemical behavior of solid samples of a commercially available bisphenol-A polycarbonate under conditions of temperature and humidity conducive to rapid hydrolysis. The polymer used is a non-flame-retardant formulation containing no hydrolytic stabilizers. Like other commercially available polycarbonates, it is prepared using a chain-terminating agent. In this case phenol was used.⁴ Thus most of the polymer chains do not terminate in bisphenol-A units as shown in IV, but instead are end-capped with phenyl groups as in V:



Using two spectrometric methods, IR and UV, we have estimated the degree of capping in unhydrolyzed material and then measured the rate of hydrolysis as indicated by the formation of new phenolic end groups. Information as to the general patterns of attack on a molecular level was obtained by gel permeation chromatography (GPC) measurements of the amounts of small molecules such as bisphenol-A present after various hydrolysis times. The results from these two approaches indicate that capping by chain-terminating agents plays an important role in ensuring hydrolytic stability.

EXPERIMENTAL

Materials

The polymer used in this study was a commercially available formulation of a nonbranched bisphenol-A polycarbonate. It contains small amounts of thermal stabilizer, mold release agent and dye, but has no hydrolytic stabilizers, flame-retardant additives, fillers or pigments. The \bar{M}_w of the material used in this study is 26,800, as determined by gel permeation chromatography.

Deuteriochloroform (Merck; 99.8% minimum isotopic purity) was used as the solvent for the IR studies. Tetrahydrofuran was obtained from Waters Associates. Unstabilized grade was used for UV measurements and for the liquid chromatography study. Stabilized grade was used for the GPC experiments. Chloroform for the UV studies was Merck (ACS). The IR standard, *p-t*-butylphenol (Aldrich), was recrystallized from pentane to give needles, melting point 98–98.5°C. Bisphenol-A (Aldrich) was recrystallized from benzene to give crystals, melting point 154–155°C.

Hydrolysis

Pellets of the polymer were placed in a low, open Teflon container and subjected to hydrolysis at 125°C and 1.4 atm of steam in the presence of some air in a Pelton and Crane sterilizer. After removal from the sterilizer, the samples were dried under a stream of dry nitrogen. Uniform samples were prepared by dissolving 1–2 g of polymer in 15–20 ml methylene chloride and then rapidly evaporating the solvent using a vacuum oven.

IR Spectra

Solid-sample spectra were taken on 25- to 40- μ m polymer films cast from methylene chloride. Both these spectra and the nonquantitative solution spectra were obtained using a Perkin-Elmer 621 grating infrared spectrophotometer.

For the quantitative spectra, portions of the homogeneous samples prepared as described above were dissolved in deuteriochloroform to give 5–10 wt % solutions. The solutions were dried over molecular sieves (Linde 4A) for at least 24 hr before spectra were taken. Solutions of the standard, *p-t*-butylphenol, with concentrations in the 10^{-2} – $10^{-3}M$ range were prepared and similarly dried. No broadening of the phenolic absorption band was detected in even the most concentrated solutions.

The quantitative spectra were obtained using a Digilab model 15B Fourier transform spectrometer equipped with a glowbar source and a triglycine sulfate pyroelectric detector. A long-pass filter was used to remove visible light in order to facilitate data computation and storage. All solution spectra were taken using either 500 or 1000 scans at a nominal resolution of two wave numbers. Absorbances were calculated using an empty beam as a reference and then later corrected for solvent absorption by subtracting a solvent spectrum obtained using the sample cell.

UV Spectra

Portions of the homogeneous polymer samples were dissolved in chloroform to give solutions in the 10^{-2} to $10^{-4}M$ range using 254 as the gram molecular weight. For samples which had not been extensively hydrolyzed, the absorbances at 285 nm were measured using concentrated solutions which were subsequently diluted quantitatively for the 266-nm measurements. The spectra were obtained on a Cary 219 spectrophotometer using the automatic-baseline-correction option.

Gel Permeation Chromatography (GPC)

Samples for the low-molecular-weight product studies were prepared by dissolving the hydrolyzed pellets (5 g) in chloroform (50 ml) and then reprecipitating the polymer by adding a tenfold excess of acetone. The polymer was removed by filtration and then the solvent was evaporated from the filtrate. The acetone-soluble extracts thus obtained were dissolved in tetrahydrofuran (THF) and analyzed using a Waters High Speed GPC (model 244) equipped with a series of micro Styragel columns with pore sizes 500, 100, and 100 Å. Chromatograms were obtained using elution rates of 0.5 and 1.0 ml/min.

Assignments of peaks to bisphenol-A, phenol, diphenyl carbonate, and 2,6-di-*t*-butyl-4-methylphenol (the solvent stabilizer) were made by adding these materials to different polymer solutions and obtaining chromatograms under two or more different conditions. Assignment of the peak attributed to dimer is tentative. The areas under the peaks assigned to bisphenol-A and phenol were determined from the computer readout and then checked by weighing traces of the curves. The percentages of the other components were obtained by the second method only. Solutions of polymer samples hydrolyzed for 48 and 98 hr were analyzed at several concentrations to determine when significant deviations from Beer's law first became evident in the size of the oligomer peak. The chromatogram used in the actual analyses were generally those in which the size of the largest peak was one-half to two-thirds that size. A factor to be used in relating the area under each peak to material amount was determined for each available component by measuring its extinction coefficient at 254 nm using the UV spectrophotometer. The measured values in units of liter/mole cm were unhydrolyzed precipitated polymer (2.73); bisphenol-A (2.24); phenol (4.80); and diphenyl carbonate (1.81).

Liquid Chromatography (LC) Studies

Solutions of completely hydrolyzed polymer were prepared as follows. Samples (~1 g) of unhydrolyzed polymer and polymer hydrolyzed for 98 hr under the conditions described above were each dissolved in unstabilized tetrahydrofuran (~25 ml). Sodium hydroxide (0.5 g) was added along with 0.5–1 ml of water. The solutions were stirred under nitrogen at ~40°C for 8 hr. Each solution was adjusted to a pH of 5–6 by addition of hydrochloric acid and sodium bicarbonate. Sufficient sodium chloride was added to give saturated solutions, which were then extracted four times each with ~12 ml of THF. The organic extracts were diluted by a factor of 5 and 20- μ l samples were injected into a Waters liquid chromatograph. The eluting solvent was a 1:1 mixture of tetra-

hydrofuran and water. No difference was found for the chromatograms of the two samples as judged by the relative sizes of the peaks identified as phenol and bisphenol-A. This indicated that no significant amount of phenol had been lost from the sample hydrolyzed 98 hr as a solid.

RESULTS AND DISCUSSION

IR and UV Studies

The progress of the hydrolysis of polycarbonate may conveniently be followed by using either IR or UV spectroscopy to measure the changes in the concentration of free phenolic end groups. Both spectroscopic methods depend on the assumptions that the only significant contributions to the phenolic absorption are made by the hydroxyl groups of monomeric or terminal bisphenol-A and that by far the largest contributions to the aromatic absorptions are also made by bisphenol-A, either as monomer or incorporated into the polymer. The gel permeation chromatography data discussed later will show these assumptions to be acceptable.

In IR spectra taken using films of polycarbonate, the band attributed to the O—H stretching motion appears at about 3530 cm^{-1} , where it overlaps with the first overtone of the carbonyl absorption at $\sim 1760\text{ cm}^{-1}$. In dilute solutions in chloroform, the phenolic OH band is located at $\sim 3605\text{ cm}^{-1}$, but may be shifted to 3530 cm^{-1} by the addition of large amounts ($\sim 20\text{ wt } \%$) of ethyl carbonate. This suggests that the shift in the solid state is due to hydrogen-bonding interactions between the phenol and the carbonyl oxygen of the carbonate linkage.

Figure 1 shows the $3800\text{--}2800\text{ cm}^{-1}$ region of a spectrum of a partially hydrolyzed sample of polycarbonate in deuteriochloroform. This portion of the spectrum, which has been corrected for absorbance by the solvent at $\sim 3160\text{ cm}^{-1}$,

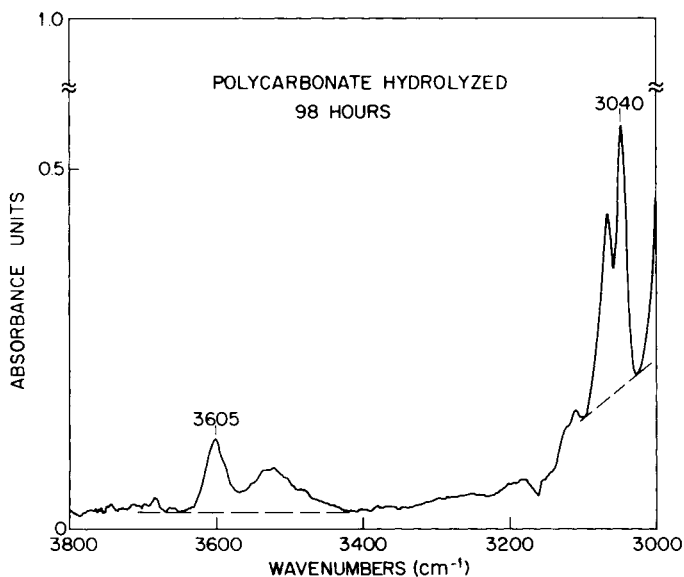


Fig. 1. IR spectrum (in deuteriochloroform) of a partially hydrolyzed polycarbonate sample. Spectrum corrected for absorption by residual C—H in solvent.

shows the phenolic absorption band at 3605 cm^{-1} , the carbonyl overtone, and the aromatic C—H absorption bands at 3060 and 3040 cm^{-1} . The peak at $\sim 3690\text{ cm}^{-1}$ is attributed to traces of water in the solution. The spectra were analyzed by comparing the base-to-peak heights of the 3605 and 3040 cm^{-1} bands. The ratio of aromatic hydrogens to phenolic groups is the same in the standard, *p*-*t*-butylphenol, as in the monomer, bisphenol-A. Thus the OH/CH absorption ratio (17.5:1) measured for a dilute ($3.5 \times 10^{-3}M$) solution of the standard can be used to calculate the number of units in each polymer sample as a function of the number of pairs of phenolic end groups present:

$$\begin{aligned} \text{units/OH pair} &= \frac{\text{OH/CH standard}}{\text{OH/CH polymer}} \\ &= \frac{17.5}{\text{OH/CH polymer}} \end{aligned} \quad (1)$$

The results obtained on sample pellets hydrolyzed for 0–152 hr are listed in Table I.

The UV analyses, like the IR studies, depend on measuring the size of the absorption band due to the phenolic groups. The analysis is less simple in this case, because the absorption due to the phenolic end groups overlaps that associated with the carbonate ester of bisphenol-A. Figure 2 shows the UV traces obtained for chloroform solutions of a partially hydrolyzed sample and an unhydrolyzed sample which had been precipitated to remove low-molecular-weight material. This latter sample was used as a model for a totally capped polymer. Bisphenol-A was used as the model for a pair of uncapped ends. The presence of uncapped ends in the partially hydrolyzed material is indicated by the growth of the peak at 285 nm . Shchori and McGrath⁵ have published a formula for determining molecular weights of uncapped polycarbonate in tetrahydrofuran solutions using the ratios of the absorptions at 285 and 266 nm . We have used this method by substituting appropriate constants for measurements made in chloroform:

$$\text{units/OH pair} = 3420/254[R \times 4.15/(1 - 0.22R) - 0.033] \quad (2)$$

In this equation, 3420 is the molar extinction measured at 285 nm for a dilute

TABLE I
Phenolic Content of Hydrolyzed Polycarbonate Samples

Hydrolysis time (hr)	Monomer units present per pair of phenolic groups	
	IR	UV ^a
0 ^b	2300	—
0	1400	2400
48	290	410
78	120	130
98	61	62
152	23	21
200		12
250		4.9
304		2.7

^a Ratios were calculated using the precipitated material as a model for completely capped polycarbonate.

^b Low-molecular-weight material removed by precipitation.

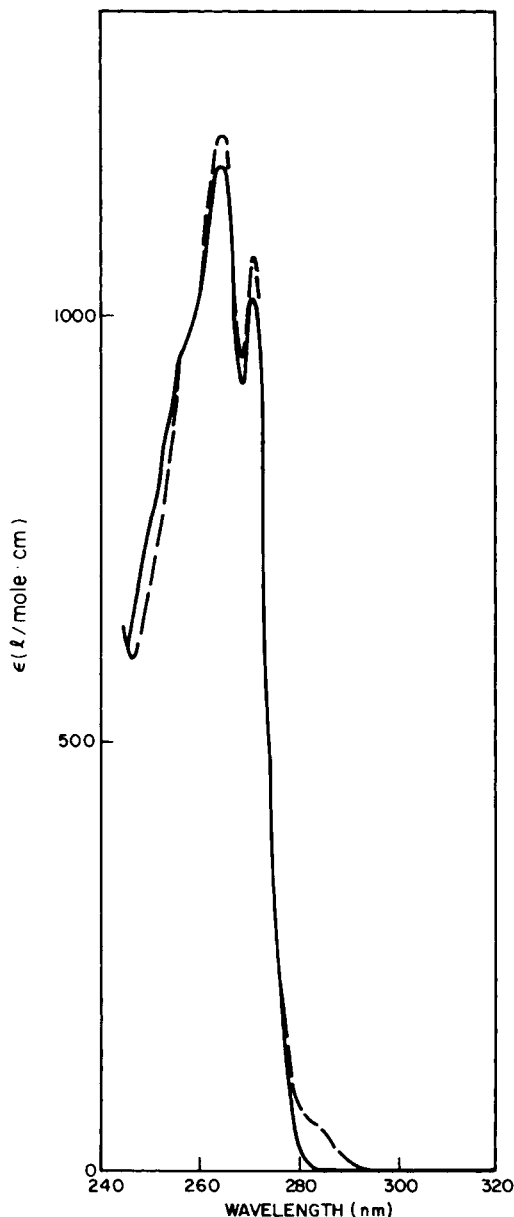


Fig. 2. UV spectra of a (—) capped polycarbonate sample before hydrolysis with all low-molecular-weight material removed and a (---) partially hydrolyzed sample (98 hr).

solution of bisphenol-A in chloroform and 254 is the formula weight of the repeat unit. R is the ratio of the absorbances at 285 and 266 nm measured for each sample, i.e., the ratio of phenolic to ester absorbances. The terms 4.15 and 0.033 are the absorptivities in liter/g cm of the capped polymer at 266 and 285 nm, respectively. The factor $0.22R$ corrects for the increased absorptivity at 266 nm due to uncapped ends [$0.22 = (E^{266}\text{BPA} - E^{266}\text{ capped polymer})/3420$]. The number of units per OH pair calculated for each sample from the UV data is shown in Table I.

The agreement between the IR and UV results is good for samples which have been hydrolyzed 98–152 hr. The number of units per pair obtained by the UV method may be slightly too high because the model compound does contain some uncapped ends (see below). The results obtained from the IR method, on the other hand, probably indicate too high a concentration of phenol groups in the unhydrolyzed and only slightly hydrolyzed samples. In contrast to the results reported by Horbach et al.,⁶ our studies indicate that for samples containing low concentrations of phenol, the apparent size of the absorption band at 3605 cm^{-1} is significantly increased by the presence of traces of water in the spectral solutions. A series of spectra taken on only slightly hydrolyzed samples showed that consistent results could be obtained between samples only if the size of the water absorption peak at 3690 cm^{-1} were the same. Increasing the amount of water in the sample could increase the measured phenol content in an unhydrolyzed sample by as much as a factor of 2. At higher phenol contents the effect is much smaller. Thus although the IR method described here is sufficiently sensitive to show relative differences between samples of uncapped polymers with \bar{M}_n 's in the range 500,000–1,000,000, provided that the samples contain similar amounts of water, the absolute value obtained may be in error. Although the UV method, in contrast, is not affected by water content, it is not sensitive enough for precise measurements at the extremely low phenolic group concentrations present in the unhydrolyzed material. For instance, in the polymer as received, the number of units per OH pair as measured by the method fell within the range of 1900–3000 with 2400 as an average value.

If the polymer used in this study were uncapped, the value of 2400 units per OH pair would correspond to an \bar{M}_n of $\sim 600,000$ g/mole. By dividing this number into 11,000 g/mole, the \bar{M}_n as determined by GPC, we estimate that 2% or less of the ends are uncapped. As seen from the IR results, the removal of small acetone-soluble molecules decreases the phenol content by $\sim 40\%$. Thus in the purified material, the degree of end-capping may be estimated as about 99%.

GPC Studies

Figure 3 shows the GPC traces obtained from the acetone-soluble portions of sample pellets which had been hydrolyzed for 0 and 152 hr. The proportional areas under each peak were determined and then related to material weight by multiplying by the appropriate ratio of small molecule versus polymer absorbance measured at 254 nm. The amount of each product in the total sample was then calculated using the known weight of the sample and the soluble fraction. The estimated weight percentages of BPA, phenol, diphenyl carbonate, and the products assumed to be dimer and trimer units found after various hydrolysis times are listed in Table II. These estimates may be subject to errors as high as $\pm 50\%$ for all the phenol measurements and $\pm (30\text{--}40)\%$ for those made on diphenyl carbonate. The estimates made for BPA are also subject to large error in the unhydrolyzed material, but the error limits should decrease rapidly as the peak height grows, with 10% being a reasonable estimate for the 78–98-hr samples. The peak attributed to dimer is poorly resolved in the samples which have not been extensively hydrolyzed. The error in the estimated weight of dimer at 78 hr may be $\pm 25\%$. This should decrease to about $\pm 10\%$ by 152 hr.

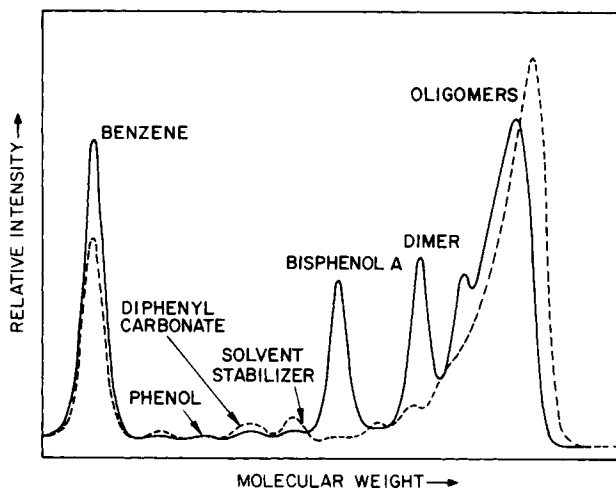


Fig. 3. Gel permeation chromatography traces of the acetone soluble portions of samples hydrolyzed (---) 0 and (—) 152 hr.

Rates and Patterns of Hydrolytic Attack

The spectroscopic data are reported in terms of concentration of phenolic end groups as a function of total bisphenol-A units. Because the great majority of the bisphenol-A units in the unhydrolyzed sample are present as the repeating unit (bisphenol-A plus carbonate linkage) we may use the change in phenolic concentration to calculate the number of linkages which have undergone scission by a given time:

$$s = \frac{\text{linkages per OH pair in unhydrolyzed PC}}{\text{linkages per OH pair in hydrolyzed PC}} - 1 \quad (3)$$

Of the total linkages present, the percentage which have reacted may then be calculated:

$$\% \text{ reaction} = \frac{s \times 100}{\text{linkages in initial unit}} \quad (4)$$

The overall reaction rates thus calculated from the IR and UV data in Table I are shown in Figure 4. The curves indicate that the reaction is subject to a marked autocatalytic effect. One possible explanation for this effect is that uncapped ends, which are initially present in extremely low concentration, cause the linkages adjacent to them to exhibit enhanced reactivity.

TABLE II
Low-Molecular-Weight Products in Hydrolyzed Polycarbonate

Hydrolysis time (hr)	Weight percent of product as determined by GPC analysis			
	Phenol	Diphenyl carbonate	BPA	Dimer
0	0.02	0.21	0.03	0.20
48	0.03	0.20	0.07	0.22
78	0.05	0.26	0.23	0.38
98	0.05	0.24	0.53	0.81
152	0.05	0.24	1.7	2.0
200	0.03	0.19	3.6	3.4

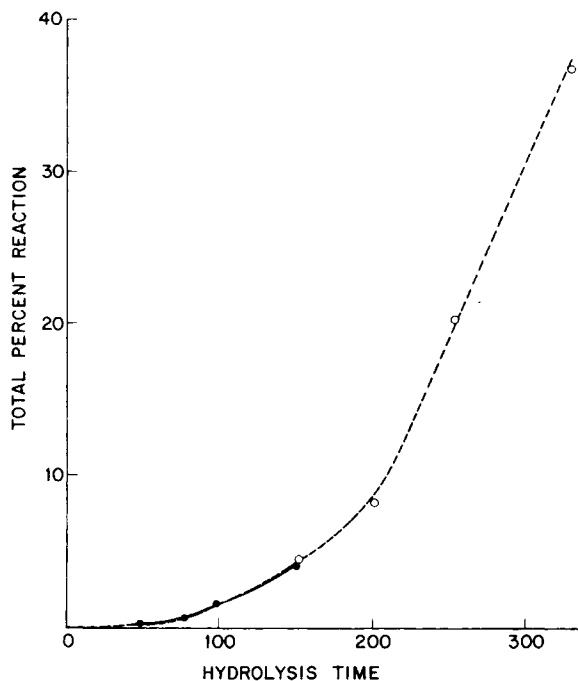


Fig. 4. Rate curve for total scissions in solid polycarbonate hydrolyzed at 125°C and 1.4 atm steam: (○) UV data, (●) IR data.

We define r_1 , the relative reactivity of a carbonate linkage adjacent to a terminal BPA unit, in eq. (5):

$$r_1 = \frac{S_t/F_{Lt}}{S_i/F_{Li}} \quad (5)$$

Here S_t is the rate of scission, during a given time interval, at carbonate linkages adjacent to terminal BPA units and S_i is the rate for all other scissions, i.e., scissions at internal linkages and at linkages to phenyl caps. The term F_{Lt} is the fraction of all the linkages which are adjacent to terminal BPA groups and F_{Li} is the remaining fraction, which includes all internal linkages as well as linkages at capped ends. Equation (5) is only truly valid, of course, for very short intervals at low conversion, i.e., when any reaction products formed in a given hydrolysis interval do not undergo significant reaction during that interval.

The rate of terminal scissions in an interval (S_t) may be estimated from the amount of BPA formed:

$$S_t = \frac{\text{wt \% BPA formed}}{100} \times \frac{\text{MW repeat unit (254)}}{\text{MW BPA (228)}} \quad (6)$$

The rate for all other scissions (S_i) is then

$$S_i = S - S_t \quad (7)$$

where S is the overall scission rate in the interval.

The total number of carbonate linkages L in a polycarbonate molecule is, of course, one less than the number of BPA units. For the relatively high \bar{M}_n material present early in the reaction, we may ignore both the contribution of the

extra BPA unit on each polymer and the contribution of any monomer. Thus,

$$L = \text{total BPA units in sample} \quad (8)$$

The number of terminal carbonate linkages adjacent to BPA units L_t is then approximately equal to the number of phenolic end groups on polymer molecules. Excluding only monomeric BPA from our definition of polymer, we obtain

$$F_{Lt} = \frac{L_t}{L} = \frac{\text{total OH—OH on free BPA}}{\text{total BPA units}} \quad (9)$$

and because

$$F_{Li} = 1 - F_{Lt} \quad (10)$$

by transposing and substituting in eq. (5), we have

$$r_i = \frac{S_t}{F_{Li}} \times \frac{1 - F_{Lt}}{S - S_t} \quad (11)$$

Equation (11) may now be evaluated using the experimental data. S_t will be found by using the differences in the weight percent of BPA found for each sample (Table II) in eq. (6). The total rate of scission S may be found by using eq. (4). The spectroscopic and GPC data may be used together to calculate F_{Lt} : the first term in eq. (9) may be found from the concentration of OH as a function of BPA units, and the second from the concentration of free BPA. Thus

$$F_{Lt} = 2 \left(\frac{1}{\text{units per OH pair}} - \frac{\text{wt \% BPA present}}{100} \times \frac{254}{228} \right) \quad (12)$$

where the first term is the average value during a given interval (Table I) and the wt % BPA is the average obtained from Table II.

Estimated values of the relative reactivities for the early stages of the reaction appear in Table III. The UV data were used to calculate the overall rates. The ranges were approximated by using reasonable maximum and minimum values based on the estimated errors in measurement for the amount of BPA formed in each interval.

The percentage errors in the calculated values of r_1 due to reaction of new terminal linkages formed in a given interval were estimated by

$$\% E = \Delta F_{Lt} \times S \times r_1 \quad (13)$$

where ΔF_{Lt} is the change in F_{Lt} between the beginning and end of the interval.

TABLE III
Apparent Relative Reactivities of Linkages Adjacent to Terminal BPA Units

Hydrolysis interval	r_1	Range ^a
48-78	118	200-60
78-98	48	87-25
98-152	33	52-21
152-200	19	38-10

^a Ranges were estimated by using the following error limits to determine maximum and minimum values for the amount of BPA formed in each interval: 48 hr (20%); 78 hr (15%); 98 hr (12%); 152 hr (10%) and 200 hr (8%).

Errors from this source increased slowly to give a maximum of $\pm 2\%$ error in the last interval (152–200 hr).

For the second carbonate linkage at an uncapped polymer end, rough estimates of the apparent relative reactivity (r_2) may be made by examining the changes in the size of the peak attributed to dimer units. In the interval of 78–152 hr, the weight of the dimer appears to increase just slightly more than that of BPA, suggesting that scission at the next-to-last linkage is about half as likely as at the final linkage at uncapped ends. The relatively low concentration of dimer at 200 hr suggests that hydrolysis of dimer may be significant at this point in the reaction.

Hydrolysis at the final linkage at a capped end, of course, yields phenol. The difference in phenol content between the samples hydrolyzed 0 and 98 hr (0.03%) is what we would expect if hydrolysis occurs at capped ends at the same rate as at internal sites. One possible explanation for the lack of growth in phenol content was that phenol could be lost during the hydrolysis. However, when two samples, one unhydrolyzed and the other hydrolyzed as the solid for 98 hr, were hydrolyzed completely with base, no difference was seen in the ratio of phenol to BPA peaks obtained using liquid chromatography. Therefore, we assume that formation and subsequent loss of phenol does not occur significantly this early in the reaction. The chromatographic techniques used here are not sufficiently sensitive to determine if the rate of scission at a capped end is identical to that measured for a typical internal linkage: variations by a factor of 2–3 in the rate might not be detected. However, the low rate of growth in phenol content early in the reaction clearly indicates that linkages at capped ends do not exhibit the high degree of enhanced reactivity shown by those linkages adjacent to terminal bisphenol-A units.

Effect of Phenolic Molecules

As was seen in Figure 4, the overall rate of hydrolysis of solid polycarbonate exhibits a pronounced autocatalytic effect which becomes evident before even 1% of the carbonate linkages have been destroyed. A part of this effect can be attributed to the large increase, through scissions occurring randomly along the chain, of uncapped ends and the concomitant increase in the number of reactive linkages adjacent or next-to-adjacent to terminal BPA units. However, the rate at which internal bonds undergo scission also increases markedly in the early stages of the reaction. This increase can be seen in Figure 5. The solid-line curve shows the rate at which scissions occur at linkages which are two or more units removed from terminal BPA units and are thus not expected to show significantly enhanced reactivity. The points used in this curve were estimated from the total number of scissions (s) by first subtracting the number of terminal scissions (s_t) and then further subtracting half of s_t to approximate the number of scissions occurring at the next-to-last linkages at uncapped ends. The leveling off in this curve in the 152- to 200-hr interval is probably due to a combination of the formation of BPA from further reactions of the products formed in that interval and the decreasing number of internal bonds.

Bair et al.⁷ showed that under the hydrolysis conditions used in this study, the initially low water content of samples of polycarbonate increased as the reaction continued. The rate of increase was larger at longer hydrolysis times.

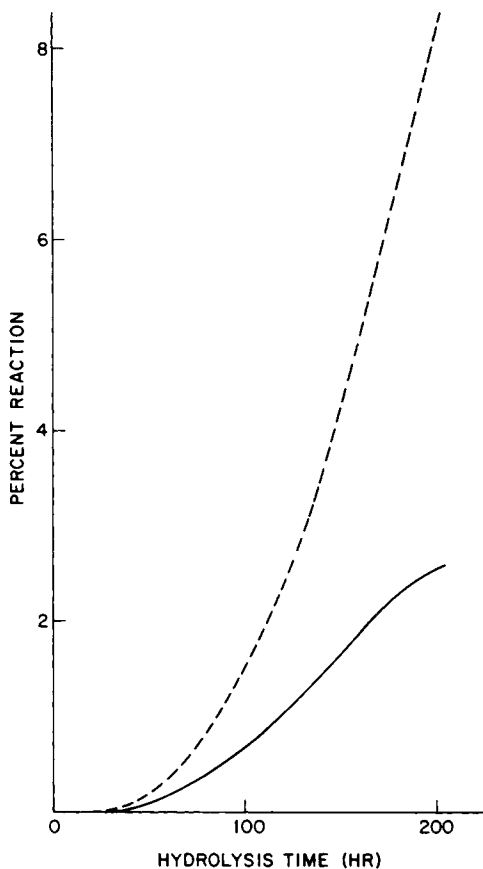


Fig. 5. Rate curves for (---) total vs. (—) internal scissions in solid polycarbonate.

This increased solubility of water can most reasonably be ascribed to the growing concentration of polar protic phenol groups. The increased water content alone will result in a higher rate of hydrolysis because water is the limiting reagent early in the hydrolysis. In addition, water and phenolic end groups may affect the reaction rate in other ways. The slightly acidic phenolic hydrogen may be donated to the carbonyl oxygen, resulting in general acid catalysis. Although studies of carbonate hydrolysis in aqueous solutions^{3,8} have given no evidence for general acid catalysis by phenol groups, this may be a more important factor in the solid state reaction. The shift of $\sim 80\text{ cm}^{-1}$ to lower frequencies for the O—H stretching band observed in the solid polymer suggests that there is significant hydrogen bonding in the ground state between the phenolic end groups and the carbonyl groups. Thus, interactions during the reaction would not require large changes in the positions of the participating molecules. Finally, either water or other phenolic groups may offer additional stabilizing interactions. Tillet and Wiggins⁸ found that in the neutral hydrolysis of 2-hydroxyethyl carbonate in water, the entropy of activation was consistent with that expected for a reaction requiring the proper orientation of several solvent molecules in the transition state.

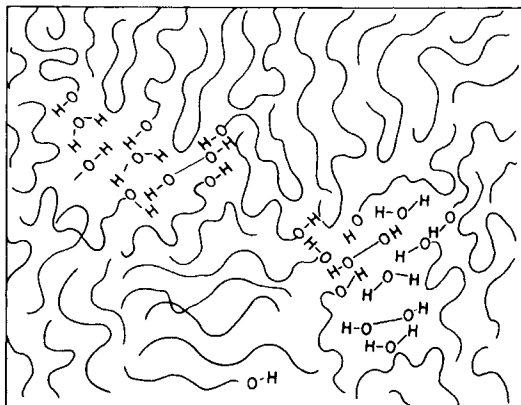


Fig. 6. Two-dimensional representation of partially hydrolyzed polycarbonate.

Both the enhanced reactivity of linkages near terminal BPA units and the autocatalytic increase in scissions at internal linkages are consistent with a model of the polymer shown in Figure 6. In this model, uncapped polymer ends and small, polar molecules such as dimer, BPA, phenol, and water all cluster together surrounded by regions containing the bulk of the polymer molecules and the phenyl-capped ends. In the unhydrolyzed polymer, the clusters would be small, but would grow as the hydrolysis proceeds. In this model the first and, to a lesser extent, the second linkages at uncapped ends extend into the region of polar molecules and are thus particularly susceptible to hydrolysis. Polymer molecules that border on or loop into the polar cluster will also be subject to attack. Thus, as clusters increase in size or number, the number of scissions occurring at internal sites will increase, both adding to the autocatalytic effect and causing an apparent decrease in the relative reactivity at linkages adjacent to terminal BPA units.

The results discussed here indicate that the general excellent ability of relatively pure polycarbonates to withstand conditions of high temperature and humidity without significant hydrolysis is dependent on their having a low content of polar molecules, because such molecules can either increase the solubility of water in the polymer or otherwise interact to increase the reaction rate. The thorough capping of phenolic end groups is obviously a major factor in minimizing the polar-group content of the polar content. However, many additives or their reaction products may also contribute to the polar content. Thus even neutral additives may deleteriously affect the hydrolytic stability of the formulation. In future studies, we will examine the effect of some common classes of additives on the hydrolysis rate. In addition, we will examine the rate of hydrolysis under somewhat milder conditions (85°C, 95% relative humidity) to determine if any significant changes are seen in the general pattern of hydrolytic attack when the reaction is carried out well below the glass transition temperature of the polymer.

The authors are grateful to R. J. Miner for supplying hydrolyzed polycarbonate samples and to D. L. Allara, G. E. Johnson, and G. N. Taylor for helpful comments.

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Received February 12, 1980

Accepted April 15, 1980