## References and Notes

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$$U''_m = \begin{bmatrix} 0 & 0.193 & 0 & 0.946 & 0 \\ 0.193 & 0 & 0 & 0 & 0.051 \\ 0 & 0 & 0 & 0.204 & 0.051 \\ 0.946 & 0 & 0.204 & 0 & 0 \\ 0 & 0.051 & 0.051 & 0 & 0 \end{bmatrix}$$

$$U''_r = \begin{bmatrix} 0.895 & 0 & 0.193 & 0 & 0 \\ 0 & 0 & 0 & 0.204 & 0.051 \\ 0.193 & 0 & 0 & 0 & 0.051 \\ 0 & 0.204 & 0 & 1 & 0 \\ 0 & 0.051 & 0.051 & 0 & 0 \end{bmatrix}$$

$$U' = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 1 & 1 & 0 \end{bmatrix}$$

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# Carbon-13 Nuclear Magnetic Resonance Study of the Hydrolysis of Bisphenol A Polycarbonate

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ABSTRACT: $^{13}$C NMR is an effective tool for the identification and quantitative measurement of the products formed in the hydrolysis of bisphenol A polycarbonate. The polymer, without additives, was hydrolyzed in steam at 125 °C. As the hydrolysis proceeded, the formation of products was followed by $^{13}$C NMR and gel permeation chromatography. The products formed were primarily bisphenol A, dimer, and higher oligomers. The polymer chain ends in the starting polycarbonate resin were identified as phenyl carbonate units. End group concentration was measured at each level of hydrolysis. The rates of formation of bisphenol A and dimer are compared to theoretically predicted values.

The degradation of polymers is a subject which has wide economic, technological, and scientific interest.[1-3] Cheng et al.[4] have shown $^{13}$C NMR to be an investigative tool of great utility in attempting to understand the oxidative degradation of polyethylene. The results of that work demonstrate that by $^{13}$C NMR one can unambiguously identify and measure the products formed as a function of the extent of oxidation. In this paper we wish to report the results of a $^{13}$C NMR study of the hydrolytic degradation of bisphenol A polycarbonate (poly[bis(4-hydroxyphenyl-2,2-propanediyl) carbonate]). It is the purpose of this study to identify products which result from the hydrolysis of polycarbonate and to record their concentration as a function of the extent of hydrolysis. $^{13}$C NMR is of particular value in this type of study because of its ability to identify unambiguously the products formed as the result of hydrolysis. Band overlap, which makes exact product identification difficult in infrared spectroscopy, is normally not a problem in $^{13}$C NMR. In addition, with proper attention paid to spin–lattice relaxation times ($T_1$) and nuclear Overhauser enhancements (NOE),[5] $^{13}$C NMR provides direct quantitative measurement of the various products formed.

A substantial effort has been made in recent years to elucidate the thermal and photooxidative degradation of polycarbonates.[6-9] This work has concentrated mainly on the effects of these degradation processes on the physical properties of the polymer and on the identification of volatile products. Few reports are available on the hydrolytic degradation of polycarbonate under conditions where significant thermal and photooxidative degradation do not occur. A recent study by Pryde and Hellman[10] is the first attempt to quantify rates of formation of bisphenol A upon hydrolysis. Gardner and Martin[11] have related the loss in mechanical properties to the degree of hydrolysis at fairly low temperatures (65–93 °C).

The hydrolysis of bisphenol A polycarbonate is generally presumed to follow the reaction of organic diaryl carbonates such as diphenyl carbonate. The reaction proceeds at an appreciable rate in neutral solution and is both acid and base catalyzed:[12]

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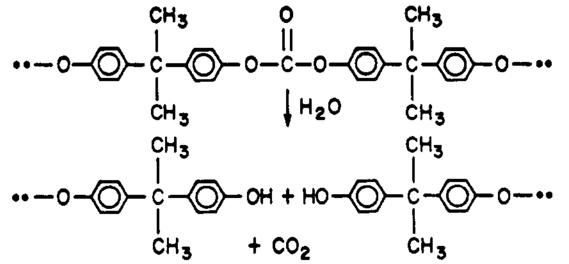
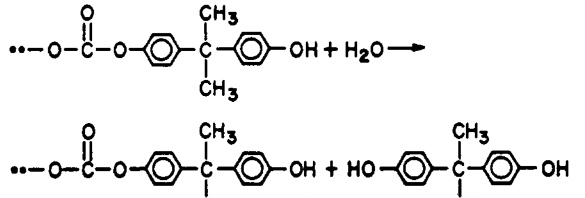


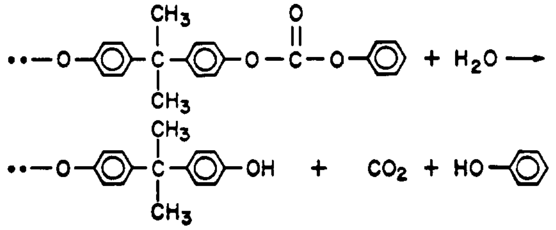
(1)

Two phenolic end groups are formed at each scission. Hydrolysis of the carbonate linkage adjacent to a chain end yields small-molecule products. Reaction of the normal chain end (i.e., not end capped) produces a phenolic chain end and bisphenol A:



(2)

If the chain is end capped with a phenyl or substituted-phenyl group, the products are a phenolic chain end and free phenol or a substituted phenol:



(3)

A pure polycarbonate resin which has not suffered any thermal oxidation is an important prerequisite for hydrolysis study. The presence of hydroxy compounds and water resulting from oxidation can cause chain scission via alcoholysis or hydrolysis. In addition, the presence of thermal stabilizers can be a complicating factor since certain classes of stabilizers can cause chain scission.[13] For these reasons, we have chosen to conduct the hydrolysis study on a polycarbonate powder which has no thermal history and contains no additives (see Experimental Section). O'Reilly et al.[14] have shown that a polycarbonate powder with a viscosity molecular weight of $4 \times 10^4$ contains about 17% crystallinity. Upon heating above the melting temperature and cooling a completely amorphous polymer can be obtained. The occurrence of crystallinity in the powder and the total absence of crystallinity in molded material should be kept in mind when comparing the results of degradation studies. Polycarbonate in the form of the extruded pellet was employed by Pryde and Hellman in their hydrolysis work.[10] One can assume such material to be totally amorphous. Therefore, comparison of rates of hydrolysis between that study and our results must be made cautiously, bearing in mind that the crystallinity of our powder, which has not been heated above the melting temperature, may cause a lower overall water content as compared to the pellet material.

## Experimental Section

**Material.** The polycarbonate employed is a General Electric Lexan 145-111 material which was received as a resin powder without thermal or hydrolytic stabilizers and without dyes or other additives. The starting material was found by GPC to have an $\bar{M}_n = 11\,530$ and $\bar{M}_w = 28\,200$ corresponding to an $\bar{M}_w/\bar{M}_n$ ratio of 2.45. The tetrahydrofuran used in the GPC measurement of the hydrolyzed polycarbonate was UV-grade material purchased from Waters Associates.

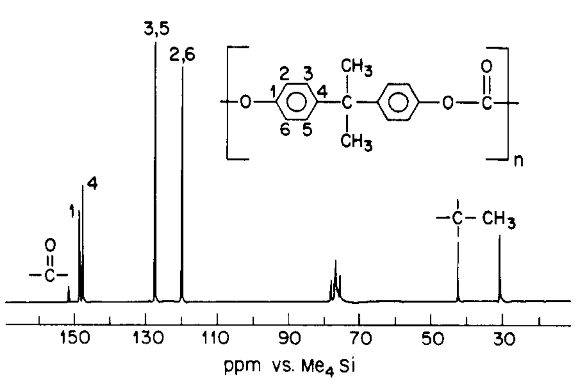


**Figure 1.** 25-MHz $^{13}$C NMR spectrum of undegraded bisphenol A polycarbonate resin, observed at ca. 20% concentration (w/v) in $CDCl_3$ at 34 °C.

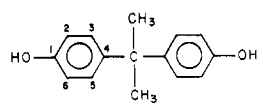
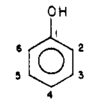
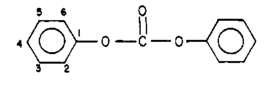
**Methods.** The hydrolysis of the polycarbonate resin was carried out in a Pelton and Crane steam sterilizer at a temperature of 125 °C and a pressure of 1.4 atm of steam and air. The polymer powder was spread in a thin layer (1–2 mm) in a Teflon tray. Water dripping from the metal surfaces of the sterilizer was prevented from reaching the polymer by means of a Teflon shield placed over the tray. At no time during the hydrolysis did the polycarbonate come into contact with any material other than Teflon. This is of particular importance since, as we have seen, the hydrolysis reaction is catalyzed by both acid and base. Contact with glass surfaces has been shown to accelerate hydrolysis in polycarbonate bars.[15] Following hydrolysis the samples were dried under vacuum at 25 °C for 24 h.

The model compound solutions and the polycarbonate solutions for $^{13}$C NMR measurements were prepared at a concentration of 15–20% (w/v) in Wilmad 18-mm cylindrical small-volume sample cells with a volume of 4.0 mL. In all cases the solvent was $CDCl_3$; HMDS was used as an internal reference. Measurements were made on a Varian XL-100 spectrometer with a $^{13}$C resonance frequency of 25.16 MHz. Spectra were recorded at a temperature of 34 °C. For each measurement the FID was stored in 8K computer locations. The $\pi/2$ sampling pulse width was 25 $\mu$s, the sweep width was 5000 Hz, the repetition time was 15.0 s, and all protons were noise decoupled. Between 1000 and 20 000 scans were required for each measurement, with the higher number of scans required for the lower levels of hydrolysis. The model compound solutions and polycarbonate solutions used in obtaining the GPC curves were prepared at a concentration of 1 mg/mL of tetrahydrofuran. Benzene was used as a reference marker. Measurements were made on a Waters Associates liquid chromatograph, using three micro-Styragel columns (500, 100, 100 Å) in series. An elution rate of 1.0 mL/min was employed for all samples. The area under each peak in the chromatogram was determined by measurement with a planimeter and by cutting and weighing. Essentially identical results were obtained by the two methods.

## Results and Discussion

The $^{13}$C NMR spectrum of polycarbonate was analyzed by Williams et al.[16] in a study of bisphenol A polycarbonate–poly(dimethylsiloxane) block copolymers. With the aid of model compounds these authors were able to assign all of the resonances unequivocally. Their assignments are employed in Figure 1, which represents the $^{13}$C NMR spectrum of the polycarbonate resin before hydrolysis. Considering our experimental conditions (see above), it is unlikely that the proper intensity ratios would be obtained for all carbons. One should expect differential nuclear Overhauser enhancements and a wide range of $T_1$ values for the various types of carbons in the polycarbonate repeat unit. This is conspicuously the case for the weak resonance of the carbonyl carbon at 152 ppm in Figure 1. In addition, the line width of the methyl resonance at 30 ppm is 3 times that of the quaternary carbon at 42 ppm.

Table I
$^{13}C$ NMR Chemical Shifts (ppm) for Model Compounds

| compound | shift | assignment |
|---|---|---|
|  | 153.42 | 1 |
| | 143.24 | 4 |
| | 128.05 | 3,5 |
| | 114.85 | 2,6 |
| | 41.83 | $-\underset{\vert}{\overset{\vert}{C}}-$ |
| | 31.16 | $-CH_3$ |
|  | 155.51 | 1 |
| | 129.70 | 3,5 |
| | 120.82 | 4 |
| | 115.43 | 2,6 |
|  | 152.06 | $-\overset{\overset{O}{\Vert}}{C}-$ |
| | 151.16 | 1 |
| | 129.61 | 3,5 |
| | 126.30 | 4 |
| | 120.93 | 2,6 |

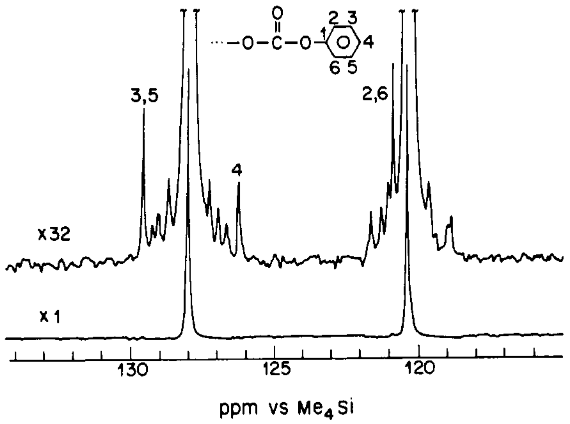


**Figure 2.** Aromatic region of 25-MHz $^{13}C$ spectrum of undegraded bisphenol A polycarbonate resin, observed in $CDCl_3$ at 34 °C. Spectrum at ×32 gain shows resonances of phenyl end caps.

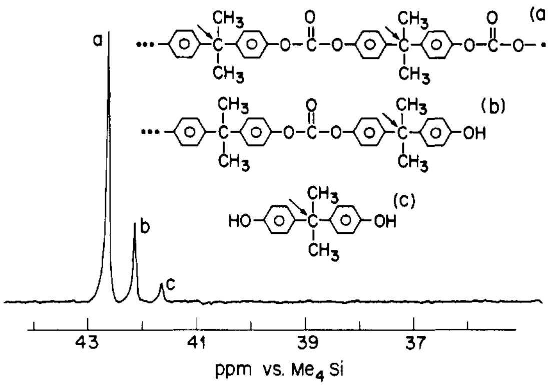


**Figure 3.** Quaternary aliphatic carbon region of 25-MHz $^{13}C$ spectrum of bisphenol A polycarbonate resin after 342-h exposure to steam at 125 °C. Observed in $CDCl_3$ at 34 °C.

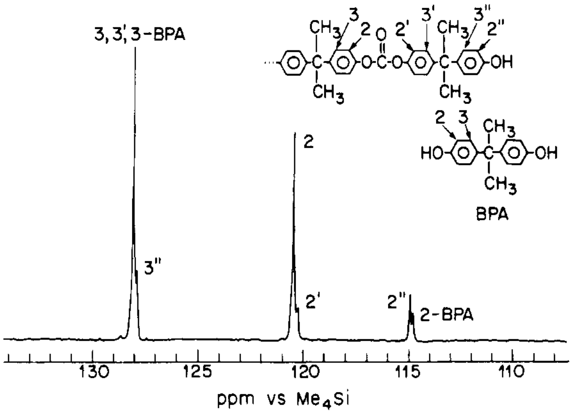


**Figure 4.** Aromatic C–H carbon region of 25-MHz $^{13}C$ spectrum of bisphenol A polycarbonate resin; same conditions as Figure 3.

The area ratio of these two carbon resonances is therefore 3:1, not the expected 2:1. For our experimental conditions, only the elimination of all NOE's and the shortening of all $T_1$'s by the use of paramagnetic quenching reagents[17,18] would make it possible to obtain spectra in which all carbon resonances are in the proper quantitative ratio. Unfortunately, the concentrations (0.05–0.1 M) of paramagnetic reagent required to achieve the desired condition produced unacceptable line broadening in our hydrolyzed polycarbonate samples. However, it was still possible to obtain quantitative data without quenching reagents by restricting quantitative measurements to comparison of resonances of the same carbon type.

The hydrolysis mechanism described in eq 2 and 3 results in the formation of bisphenol A and phenol. The $^{13}C$ chemical shifts of these two compounds and of diphenyl carbonate, a model for phenyl-capped chain ends, are listed in Table I. The assignments of bisphenol A were previously determined by Levy and Nelson.[19] GPC measurements on the polycarbonate powder before hydrolysis indicate the content of bisphenol A, phenol, or any other low molecular weight compound to be less than 0.02% by weight. A close examination of the aromatic region of the $^{13}C$ spectrum of the starting polycarbonate resin (Figure 2) indicates the presence of a terminal phenyl ring. The chemical shifts of 129.5, 126.2, and 120.9 ppm are in excellent agreement with those of diphenyl carbonate (Table I). The quaternary ring carbon should appear at ~151–153 ppm but due to a long $T_1$ and possibly reduced NOE it was not found in this spectrum. The concentration of phenyl end groups is measured from the relative heights of the –CH– ring carbon of the phenyl ring and the –CH– ring carbon of the backbone repeat unit. The measurement was initially performed by using various delay times to eliminate any possible error due to different $T_1$ values between internal and terminal rings. In addition, the measurement was carried out in the presence of 0.1 M chromium acetylacetonate [$Cr(acac)_3$] to eliminate all NOE's. The results establish that a delay of 15.0 s without a quenching reagent is sufficient to obtain quantitative data from these protonated carbons. The measurement of the end group is a direct measure of the number-average molecular weight. From the $^{13}C$ spectrum our resin was found to have an $\bar{M}_n$ of 14 900. This is to be compared with a GPC-determined value of 11 530.

It is possible that a small number of chains terminate in phenolic groups. From the $^{13}C$ spectrum we can set an upper limit for phenolic end groups in the starting resin at one per 1450 repeat units. With a $\overline{DP}_n$ of 58.6 (based on the NMR value for $\bar{M}_n$) we thus have no more than one phenolic end per 24.7 molecules. This indicates that at least 98% of the chain ends are capped by phenyl rings before hydrolysis.

A $^{13}C$ NMR spectrum representative of those recorded in this study is shown in Figures 3–5. The sample was hydrolyzed for 342 h. The spectrum has been divided into the three spectral regions of interest. In Figure 3, three distinct resonances are detected. The large peak at 42.8 ppm is assigned to the alkyl quaternary carbon of the

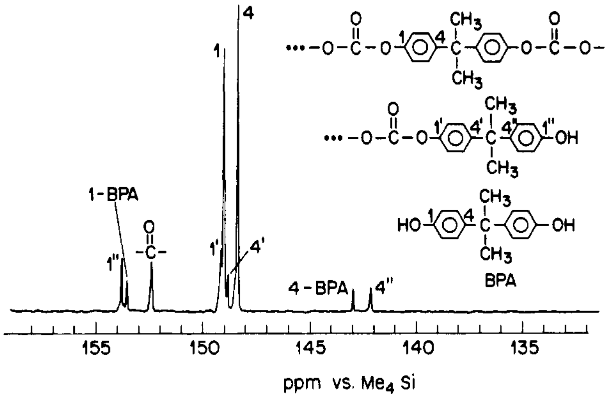
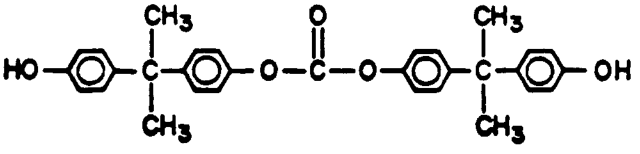


**Figure 5.** Carbonyl and quaternary aromatic carbon region of 25-MHz $^{13}$C spectrum of bisphenol A polycarbonate resin; same conditions as Figure 3.

polycarbonate repeat unit. The smallest peak at 41.7 ppm is the same carbon in bisphenol A. The resonance at 42.1 ppm is the alkyl quaternary carbon in the terminal phenolic structure resulting from the chain scission in eq 1. In Figure 4, the region of protonated aromatic carbons, we find two large resonances representing the protonated ring carbons of the polycarbonate repeat unit and smaller resonances due to the bisphenol A and the phenolic chain ends. The assignments of carbons 3'' and 2'' in the chain end are based on the shifts of similar carbons in bisphenol A. The assignments of 2' and 3' are made by comparison to similar carbons in the internal polycarbonate repeat unit. Figure 5 is the spectral region for aromatic quaternary carbons and carbonyl carbons. The two large resonances at 148.2 and 149.0 ppm and the smaller resonance at 152.3 ppm are carbons in the repeat unit. Peaks labeled 1-BPA and 4-BPA are assigned to bisphenol A (see Table I). Peak assignments 1'', 4'', 4', and 1' are based on the carbon's environmental similarity to carbons in bisphenol A and the polycarbonate repeat unit. A close examination of Figures 4 and 5 and spectra obtained on other samples shows no evidence for the presence of phenol. A control experiment indicates that under the experimental conditions used to carry out the hydrolysis phenol is completely vaporized.

Two types of carbons were used quantitatively in this study. The alkyl quaternary carbons were measured to determine the content of bisphenol A and the number of phenolic chain ends. The protonated aromatic carbons were measured in the determination of the number of phenyl end groups in each sample. In order to establish the reliability of such measurements a test sample was prepared containing the original nonhydrolyzed polycarbonate resin and a known quantity of bisphenol A. The NMR results using alkyl quaternary carbons at ~42 ppm as a quantitative probe are correct with a maximum error of ±3% under our experimental conditions. GPC measurement of the test sample produced results with an accuracy of ±4%.

The gel permeation chromatogram obtained for the 342-h hydrolyzed sample is presented in Figure 6. The assignment of the bisphenol A peak was determined from the measurement of the retention time of bisphenol A in the test sample. The preceding peak is assumed to correspond to "dimer", i.e.



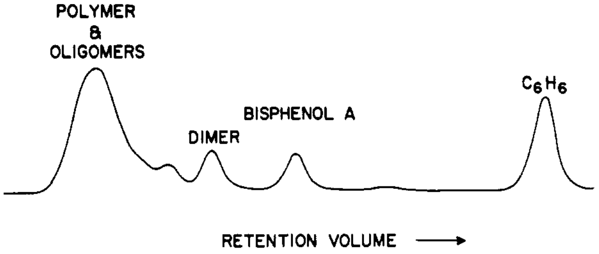


**Figure 6.** Gel permeation chromatogram of bisphenol A polycarbonate resin after 342 h of hydrolysis.

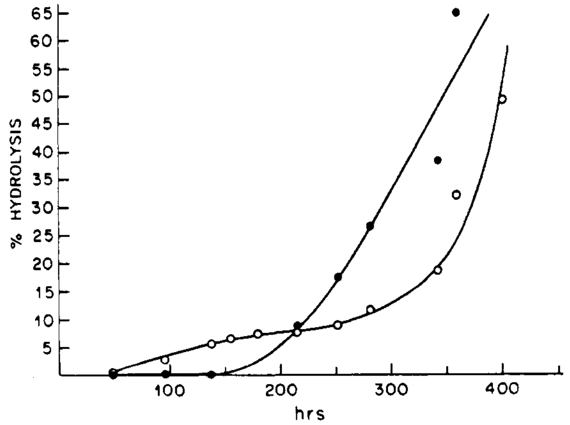


**Figure 7.** Percent of all bonds (open circles) and terminal bonds (filled circles) hydrolyzed as a function of time of exposure of bisphenol A polycarbonate resin to steam at 125 °C. These curves are based on NMR measurements.

No authentic sample of this material was available; it does not appear to have any unique carbon resonances which would permit evaluation by NMR. The amounts of "dimer" and bisphenol A were determined by area measurements of each peak and comparison to the total area of all peaks.

Figure 7 shows the results of hydrolyzing bisphenol A polycarbonate resin for periods ranging from 48 to 402 h. The open circles in the figure represent the percentage of all carbonate linkages which have been hydrolyzed as determined from the NMR results. The filled circles indicate the percentage of original phenyl end groups which have been removed. The curves demonstrate a large difference in reactivity of the terminal carbonate linkage with a phenyl end group compared to the internal linkages. During the initial 150 h of hydrolysis there appear to be only a very small number of phenyl end groups removed. However, after ca. 200 h the rate of hydrolysis for this type of terminal linkage accelerates and surpasses the overall rate of hydrolysis. We do not at present know the reason for this behavior. The data presented in Figure 7 clearly establish that at least in the early critical hours of hydrolysis the phenyl end groups are very stable and do not represent an initiation site for rapid hydrolysis. Only after the polymer has suffered advanced hydrolytic degradation do these groups become labile to hydrolysis.

It is also qualitatively evident from Figure 7 that the rate of hydrolysis of nonterminal carbonate linkages does not follow a first-order course or any other simple kinetic scheme. Hydrolysis is barely evident until after 30 h. After about 150 h, it is retarded somewhat, and later appears to accelerate. These changes no doubt reflect alterations in the water content (assumed to increase with time) and physical constitution of the material as reaction proceeds. We shall not attempt to rationalize them in detail. As will be seen in the next section, our procedure is to treat the reaction in terms of reduced time, i.e., in terms of the fraction of bonds broken whether or not this is linear in time.

## Bisphenol A and "Dimer" Formation

The rate of formation of bisphenol A is of particular significance in connection with proposed mechanisms of polycarbonate hydrolysis. It has been suggested,[10] for example, that scission at terminal bonds is preferred and that it accelerates as the reaction proceeds, resulting in a rate of appearance of bisphenol A substantially in excess of that expected for a random statistical process, particularly in early stages. In this section, we examine this question and also that of "dimer" formation.

The questions of molecular weight averages and formation of fragments of specified length in a chain scission process were considered many years ago by Montroll and Simha[20] and Simha.[21] We here derive similar relationships appropriate for our data on bisphenol A and "dimer" formation. We suppose that hydrolysis has taken place to an extent $p$, so that $p$ is the probability of bond scission. Consider a chain containing $n$ carbonate bonds, including those to the end-cap units. This chain will contain $n - 1$ bisphenol A units. Scission is assumed to be equally probable for all bonds. Let us number the units in the chain, including the end-cap units, as 0, 1, 2, ..., $n$ and introduce a random variable $X_i$ ($i = 0, 1, ..., n$) which takes the value 1 if the $i$th unit is now a free bisphenol A unit and 0 otherwise (i.e., if the unit is an original end unit or an internal unit with at most one carbonate bond broken). Because of the end-cap units

$$X_0 = X_n = 0$$

and, for $i = 1, 2, ..., n - 1$

$$\text{Prob}\,\{X_i = 1\} = p^2$$

since for the $i$th unit to be a free bisphenol A unit the adjacent bonds must both be broken, an event of probability $p^2$. The probability of a unit *not* being released as free bisphenol A is accordingly

$$\text{Prob}\,\{X_i = 0\} = 1 - p^2$$

The total number of bisphenol A units released is the random variable $\sum_{i=1}^{n-1} X_i$ and the average value of this sum is

$$m_n = (n - 1)\,\text{Prob}\,\{X_i = 1\} = (n - 1)p^2 \qquad (4)$$

where $m_n$ is the average number of bisphenol A molecules produced from chains of length $n$.

Let us now suppose that the original resin has a most-probable distribution of chain lengths characterized by a number-average degree of polymerization $\bar{P}_n$ (i.e., the number-average value of $n - 1$). The weight fraction of chains of length $x$, i.e., the fraction of bonds belonging to such chains, is

$$w_x = \frac{x}{\bar{P}_n^{\,2}} e^{-x/\bar{P}_n} \qquad (5)$$

For end-capped chains, the average number of monomers produced per original weight-average chain is

$$m = \int_1^\infty w_x m_x \, dx = \int_1^\infty \frac{p^2 x(x-1)}{\bar{P}_n^{\,2}} e^{-x/\bar{P}_n}\, dx \simeq \frac{p^2}{\bar{P}_n^{\,2}} \int_0^\infty x^2 e^{-x/\bar{P}_n}\, dx - \frac{p^2}{\bar{P}_n^{\,2}} \int_0^\infty x e^{-x/\bar{P}_n}\, dx$$

from which

$$m = 2p^2(\bar{P}_n - \tfrac{1}{2}) \qquad (6)$$

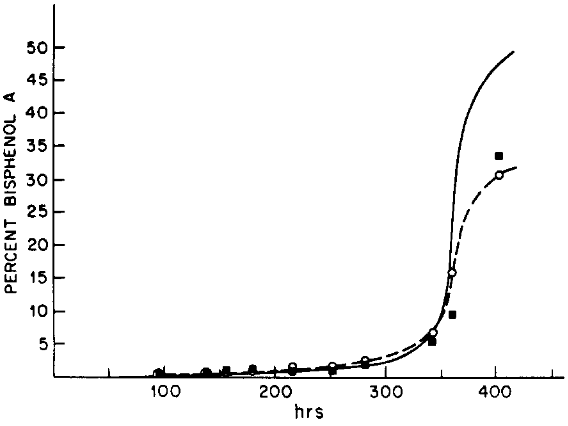


**Figure 8.** Experimental (○ = NMR; ■ = GPC) and calculated (solid line) rates of formation of bisphenol A in polycarbonate resin hydrolysis in steam at 125 °C. The dashed line has been fitted to the NMR data only.

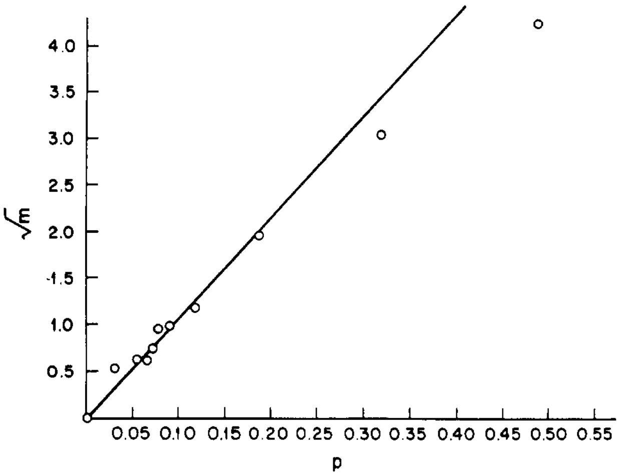


**Figure 9.** Plot of $m^{1/2}$ (where $m$ is the number of bisphenol A molecules produced per original weight-average polycarbonate chain) vs. $p$, the overall extent of carbonate bond hydrolysis. The line is a plot of eq 6.

In Figure 8, eq 6 is tested by plotting the production of bisphenol A, expressed as a fraction of the total amount possible if all bonds were broken, vs. time of hydrolysis. The NMR and GPC measurements are in acceptable agreement, particularly early in the reaction. They follow the same form as the plot of eq 6 and indicate an accelerating or autocatalytic reaction. There is an indication of a falling off, however, in the later stages, as the experimental production of bisphenol A falls behind the predicted value. This is more evident in Figure 9, in which $m^{1/2}$ (derived from NMR measurements only) is plotted vs. $p$ and compared with eq 6. In the earlier stages ($p \leq 0.25$), the experimental plot is linear, as expected. We conclude that the terminal carbonate bonds are observably (but not markedly) less reactive than the internal bonds. It should be realized that the appearance of acceleration in Figure 8 in part reflects the accumulation of free chain ends, at which only one cut suffices to release bisphenol A, and that to this extent the acceleration is statistical rather than real. (The anomalous behavior of the end-cap bonds perturbs this picture somewhat but not seriously; for example, at 360 h one may readily show that over 95% of the chain ends are free, yet the rate of bisphenol A release has fallen observably below that expected from eq 6.)

To treat the rate of release of dimer we define a random variable $Y_i$ ($i = 0, 1, ..., n - 1$) to be 1 if the $i$th and

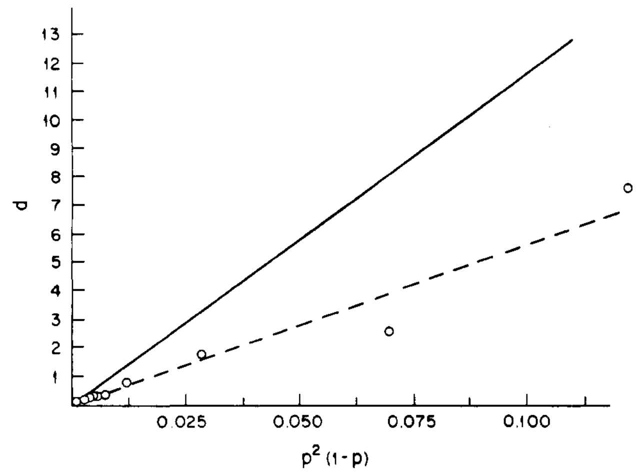


**Figure 10.** Plot of $d$, the number of "dimer" molecules produced per original weight-average polycarbonate chain, vs. $p^2(1-p)$. The solid line is a plot of eq 8. (The dashed line is a least-squares line through the experimental data.)

$(i+1)$th units together form a dimer and to be 0 otherwise. Then

$$Y_0 = Y_{n-1} = 0$$

$$\text{Prob}\,\{Y_i = 1\} = p^2(1-p) \qquad (i = 1, 2, ..., n-2)$$

$$\text{Prob}\,\{Y_i = 0\} = 1 - p^2(1-p) \qquad (i = 1, 2, ..., n-2)$$

$1 - p$ being the probability of *not* cutting a specified bond, in this case the adjacent one. The total number of dimers is the random variable $\sum_{i=1}^{n-2} Y_i$ and the average value of this sum is

$$\begin{aligned} d_n &= (n-2)\,\text{Prob}\,\{Y_i = 1\} \\ &= (n-2)p^2(1-p) \end{aligned} \tag{7}$$

For end-capped chains, the average number of "dimers" released per original weight-average chain is

$$\begin{aligned} d &= \int_1^\infty w_x d_x \,\mathrm{d}x \\ &\simeq 2p^2(1-p)(\bar{P}_n - 1) \end{aligned} \tag{8}$$

In the early stages of hydrolysis, when $p$ is small, (8) and (6) are roughly equal, as is reasonable since the release of both molecules requires two cuts at specified positions. Thus equal molar amounts of each should be observed so long as $p \ll 1$. In fact, however, the gel permeation chromatograms make it clear that approximately equal *weight* fractions of bisphenol A and "dimer" are produced throughout the hydrolysis, as already reported by Pryde and Hellman.[10] Thus the rate of formation of "dimer" is only about half that expected from eq 8; this is shown in Figure 10, in which the experimental $d$ is plotted vs. $2p^2(1-p)$ and compared with eq 8. We must conclude from this that, for reasons which are unknown, the penultimate carbonate bond is only half as reactive as the terminal bond, which itself (as we have seen) is slightly less reactive than the average internal bond.

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