Hydrolytic Aging of Polycarbonate. II. Hydrolysis Kinetics, Effect of Static Stresses

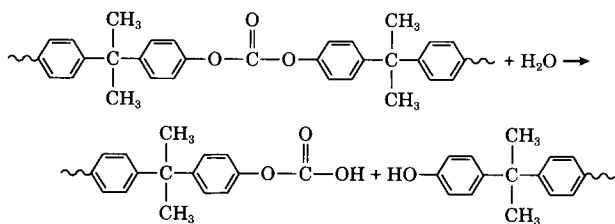I. GHORBEL,[1,*] N. AKELE,[2] F. THOMINETTE,[2] P. SPITERI,[3] and J. VERDU[2,†]

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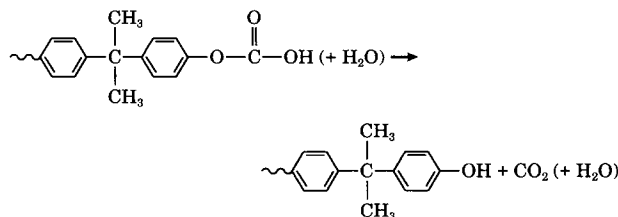
SYNOPSIS

Plaques of bisphenol A polycarbonate (PC) were exposed to a water-saturated atmosphere at temperatures ranging from 40 to 90°C for up to 7 months. Certain samples were exposed under tensile load at 60 and 90°C, 100% RH with stresses ranging from 3.7 to 8.7 MPa. The PC molecular weight was determined by steric exclusion chromatography, and the kinetic parameters for hydrolytic chain scission were determined. It appears clearly that in the presence of tensile stresses, the hydrolysis rate is increased (at both temperatures under study) by a factor of about 10. The stress effect cannot be represented by the Eyring–Zhurkov relationship because the activation volume appears as an increasing function of the temperature and a decreasing function of time. Some possible causes of the observed stress effects are discussed © 1995 John Wiley & Sons, Inc.

INTRODUCTION

There is relatively abundant literature data on the hydrolytic aging of polycarbonate (PC) at temperatures ranging between 40 and 100°C.[1-4] The mechanism can be described as follows:

The resulting acid carbonate undergoes easily a decarboxylation:

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This process can be therefore described as a random chain scission with accumulation of phenolic chain ends. Simple kinetics models based on the following assumptions have been often proposed:

1. The process is not diffusion controlled, and degradation is homogeneously distributed within the sample thickness.
2. The process is homogeneous at the morphological scale. In other words, the concepts of chemical kinetics can be applied to experimental results obtained on samples of typical size greater than 1 mm.
3. Chain scission is of apparent zero order (which involves in fact many hypotheses, which will be studied in detail in the discussion section). In this case:

$$N_t = \frac{M_{n0}}{M_{nt}} - 1 = Kt \qquad (1)$$

where N_t is the number of scissions per initial chain, M_{n0} and M_{nt} the respective molar masses before and after degradation, t the time, and K a pseudo-rate constant.

In many practical applications, the material can be mechanically loaded, which can affect its durability in various ways. Some of these effects are:

1. A shortening of the time to rupture under static or dynamic loading. Hydrolytic degradation but also presumably polymer plasticization by water are expected to play a significant role in this process.
2. An eventual mechanochemical degradation of the polymer. According to Kausch,[5] the contribution of mechanochemical processes to chain scission would be, however, negligible.
3. An eventual effect of stresses on the hydrolysis rate. Stress effects on polymer aging were recently reviewed,[6] but the papers devoted to hydrolysis are very scarce and their results often ambiguous. As a matter of fact, the stress effects are judged from purely mechanical criteria (generally time to rupture), whereas data on the hydrolysis conversion ratio are not available. Furthermore, most of the published work in this field deals with composite materials where multiple failure causes, for instance, due to interfacial degradation, coexist and where the great data scatter makes practically impossible a precise kinetic analysis.

A brief study of the problem of stress-activated polymer degradation shows that in order to reach valid conclusions, the following conditions must be satisfied:

1. The polymer must be 100% amorphous in order to avoid morphological heterogeneities of the degradation conversion. If the polymer is linear, it must be exposed to aging in glassy state in order to avoid extensive flow.
2. The aging process must be a pure random chain scission, competitive crosslinking would considerably complicate the interpretation of results.
3. The mechanism of chain scission must be simple enough to be accessible to kinetic analysis (which is rarely the case of branched-chain oxidation).
4. Precise molecular weight measurements have to be made.

It is obvious that there are only very few cases where all these conditions can be met. Polycarbonate hydrolysis would constitute the ideal case, provided that hypotheses (1), (2), and (3), which are essentially relative to the validity of kinetic data derived from molecular weight measurements, would be valid.

The aim of this article is to report some preliminary results on the hydrolysis of polycarbonate in the temperature range 40–100°C, and in the absence and presence of static stresses in the range 3–8 MPa, the stress intensity being such that no macroscopic damagement (e.g., no significant local stress overconcentration) was observed in the scale time of experiments.

EXPERIMENTAL

Material

All the tests were performed on extruded plaques of 2 mm thickness of an unstabilized polycarbonate industrial sample (LEXAN, G. E. Plastics) of which some physical properties were investigated in the first part of this article.[7] Dogbone specimens according to the French standard AFNOR NFT 51 054 were machined in the plaques, with the tensile direction parallel to the extrusion direction.

Exposure

Previously described[7] climatic chambers were used in saturated atmosphere (100% RH) at 40, 70, 80, and 90°C. Sample loading was performed with a creep machine, Mayes-TC 30 (3 tons capacity), operating at constant load level. For the chosen values of this latter, the applied stresses are far below the yield stress. During creep tests, the neck associated with viscoplastic flow has not been observed, and the deformation was considered homogeneous and uniform. The polymer is then tested in the viscoelastic range and the changes of cross-section area as the deformation proceeds can be neglected. The stress values reported in the following section are obtained by dividing the load by the initial cross section.

Molecular Weight Measurements

Steric exclusion chromatography (SEC) was used in the following conditions: The solvent was freshly distilled tetrahydrofuran at a 1.2 mL min^{-1} flow rate. Four columns: Shodex KF 802.5, 803, 804, and 805 were used. The detector was a refractometer Waters R 401. After exposure, the samples were dried and then stored in dark at 20°C. Steric exclusion chromatography analysis was made on sample sets corresponding to one day measurements in order to reduce dispersion.
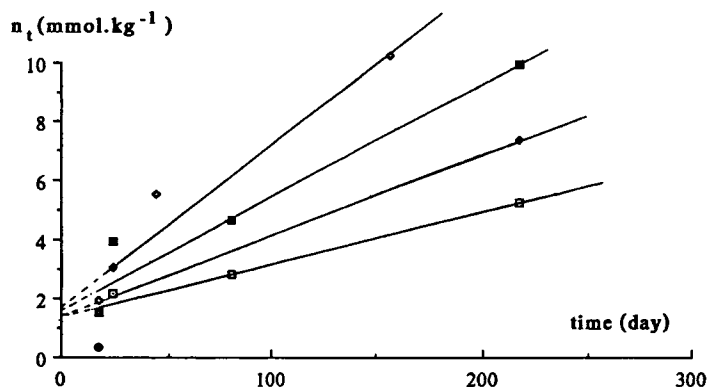
Figure 1   Time variation of the number of chain scissions per mass unit. ($\square$) 40°C; ($\blacklozenge$) 70°C; ($\blacksquare$) 80°C; ($\blacklozenge$) 90°C.

For each set, the chromatograph was calibrated with polystyrene standards (Polymer Laboratories). Only the chromatograms for which the solvent peaks were exactly superimposable were taken into account, otherwise, the analysis was repeated. Thanks to these precautions, a reproducibility of about ±5% was obtained.

RESULTS AND DISCUSSION

Hydrolysis of Unloaded Specimens

The number of chain scissions per mass unit n_t was determined according to:

$$n_t = \frac{1}{M_{nt}} - \frac{1}{M_{n0}}$$

where M_{nt} and M_{n0} are the values of the number-average molar weight, respectively, after and before exposure of duration t.

n_t was plotted against exposure time in Figure 1. It must be recalled that the complete hydrolysis conversion corresponds to $n_t = m^{-1} = 3.93$ mol kg^{-1} (m being the monomer unit molar weight). The conversion ratios under investigation are thus always lower than 0.25%.

In a first approach, we considered that the data scatter is such that only the highest conversion value is significant. In this case, only the average hydrolysis rate $\bar{r}$ can be determined as follows:

$$\bar{r} = \frac{n_t(\text{max})}{t(\text{max})}$$

where $t(\text{max}) = 214$ days at all temperatures except 90°C (153 days). The values of $\bar{r}$ are reported in Table I.

All the curves $n_t = f(t)$ display, however, a pronounced curvature in their initial part. The hydrolysis rate decreases sharply in the early days of exposure to reach a pseudo-stationary value when $n_t \approx 2 \times 10^{-3}$ mol kg^{-1}. There are possible explanations for such a behavior:

1. Kinetic control by the water diffusion into the polymer. This hypothesis can be rejected on the basis of previously reported arguments.[7]
2. Autoretardated character of the hydrolysis mechanism. This hypothesis will be examined in detail in a next article, but it can be already remarked that, for a single-step process, no one kinetic scheme (whatever the reaction

Table I   Kinetic Constant for the Hydrolysis of Unloaded Samples According to Both Hypothesis

Temperature	n_0 (10^{-3} mol kg^{-1})	k (mol kg^{-1} s^{-1})	$\bar{r}$ (mol kg^{-1} s^{-1})
40	1.5	1.9×10^{-10}	2.72×10^{-10}
70	1.5	3.05×10^{-10}	3.86×10^{-10}
80	1.5	5.2×10^{-10}	5.25×10^{-10}
90	1.5	6.4×10^{-10}	7.55×10^{-10}

order) could explain such rate changes at so low a conversion.

3. Protective end groups. The nature of initially present end groups is unknown. It could be imagined that the polymer under study contains protective end groups that avoid auto-catalysis in the early period of exposure. Indeed, in such a case, the expected behavior would be opposite to the observed one in which the initial curvature displays a positive concavity.

4. Two-step process. The sample under study would contain a low concentration (about 1.5 × 10⁻³ mol kg⁻¹, i.e., less than one group per every 10 chains), of highly reactive esters randomly distributed into the chains. They would disappear in the early hours of exposure and then the degradation rate would decrease until an almost constant value characteristic of the reactivity of "normal" carbonate groups. These highly reactive esters could result from the polycondensation process or from a limited thermal degradation during processing. The following alternative explanation could be also imagined: The initially present chain ends display a strong catalytic effect on hydrolysis; however, they are themselves highly reactive, so that they disappear rapidly in the early hours of exposure.

These considerations lead to a second approach in which the medium and long-term hydrolysis behavior (typically for $t \geq 21$ days) could be modeled as follows:

$$n_t = n_0 + kt \qquad (2)$$

n_0 corresponds to the concentration of highly reactive species ("abnormal" esters); k is a pseudo-zero-order rate constant for the hydrolysis of normal esters. The choice of zero order can be justified as follows:

In the most general case, the degradation rate can be expressed by

$$\frac{dn_t}{d_t} = K[E_t]^\alpha[H_2O]^\beta = K(E_0 - n_t)^\alpha[H_2O]^\beta$$
$$= KE_0^\alpha\left(1 - \frac{n_t}{E_0}\right)^\alpha[H_2O]^\beta \qquad (3)$$

where E_t and E_0 are the ester concentrations, respectively, before and after exposure of duration t.

For very low conversion, it can be written:

$$\frac{n_t}{E_0} \ll 1 \rightarrow \frac{dn_t}{d_t} \approx KE_0^\alpha[H_2O]^\beta = k. \qquad (4)$$

In the range of conversions under study, the deviations due to this approximation are largely negligible relatively to experimental incertitudes.

If K is a true constant obeying Arrhenius law, k must also obey this law with the same activation energy E:

$$k = k_0\exp(-E/RT). \qquad (5)$$

Finally, the degradation kinetics of unloaded samples, for times exceeding 21 days, can be well modeled using relations (2) and (5) using: $n_0 = 1.5 \times 10^{-3}$ mol kg⁻¹, $k_0 = 1.8 \times 10^{-6}$ mol kg⁻¹ s⁻¹, and $E = 23$ kJ mol⁻¹.

Recent unpublished measurements confirmed clearly the validity of this second approach, but both approaches will be used to compare the behavior of loaded and unloaded samples.

Hydrolysis of Loaded Samples

The results of measurements made on loaded samples and the corresponding kinetic data determined according to both above approaches are reported in Table II.

According to our hypothesis on the presence of labile esters responsible for the first kinetic step, n_0 has been considered independent of exposure conditions and equal to 1.5×10^{-3} mol kg⁻¹.

These results call for the following comments:

1. Tensile loading considerably accelerates hydrolysis. Both comparative approaches lead to the conclusion that, at both temperatures under study, the chain scission rate is increased by about one order of magnitude for stresses of few megapascals.

2. The formalism of Eyring–Zhurkov is often used in such studies to express the stress effect on process rate. Here, the rate constant k was plotted against reduced stress σ/T in Figure 2. It appears that the rate variations cannot be simply expressed by the Eyring–Zhurkov formula:

$$k = k_0\exp\frac{-(E - V\sigma)}{RT}.$$

Table II   Hydrolysis under Stress. Experimental M_n Values and Kinetic Data According to Two Approaches (See Text)

Temperature (°C)	Duration (h)	Stress (MPa)	M_{nt} kg mol^{-1}	n_t mmol kg^{-1}	k mol kg^{-1} s^{-1}	$\bar{r}$ mol kg^{-1} s^{-1}
90	3672	0	31.34	10.0	6.4×10^{-10}	7.55×10^{-10}
90	213	3.7	34.4	7.5	7.8×10^{-9}	9.8×10^{-9}
90	168	3.9	37.5	5.0	5.8×10^{-9}	8.3×10^{-9}
90	254	3.9	36.6	5.6	4.5×10^{-5}	6.1×10^{-9}
90	309	3.9	35.8	6.2	4.2×10^{-9}	5.6×10^{-9}
90	65	4.4	32.2	9.4	3.4×10^{-8}	4.0×10^{-8}
90	—	0	—	—	$\approx 2.1 \times 10^{-10(a)}$	$\approx 3.4 \times 10^{-10(a)}$
90	1071	8.7	28.6	13.3	3×10^{-9}	3.4×10^{-9}
70	2006	8.7	27.7	14.4	1.8×10^{-9}	2.0×10^{-9}

As a matter of fact, the curve relative to the exposure at 90°C seems to show that the activation volume V is an increasing function of the stress σ. Furthermore, the activation volume would be at least 3 times higher at 90°C than at 60°C.

3. Several exposure times were studied in two cases: 90°C, 3.9 MPa and 60°C, 8.7 MPa. It appears that in both cases, the pseudo-zero-order rate constant k (e.g., also the pseudo-activation volume V) is a decreasing function of exposure time. In other words, loading is less and less effective as a "hydrolysis catalyst" at increasing exposure times.

Mechanism of Stress Effect on Hydrolysis Rate

Only two types of mechanisms can be invoked to explain the observed stress effects on hydrolysis rate.

Physical Mechanisms

They are linked to stress effects on polymer permeability to water. In glassy polymers, tensile or shear loading leads to free volume[8] or "defects"[9] creation. Schematically, the physical state of the polymer in the conditions T, σ corresponds to the physical state of the unstressed polymer at $T + \Delta T$ where ΔT is positive and can be majored using:

$$T < T + \Delta T < T_g.$$

Sorption studies revealed that the water coefficient of diffusion and solubility in PC are increasing functions of the temperature.[10] For the sample thickness under study, diffusion cannot control the hydrolysis kinetics.[7] In contrast, according to Eq. (3), the chain scission rate is expected to increase with the water solubility. In the simplest case, hydrolysis would be first order relatively to water and ester concentrations so that
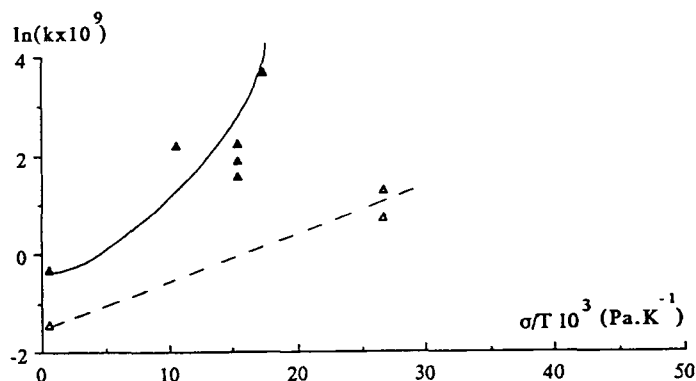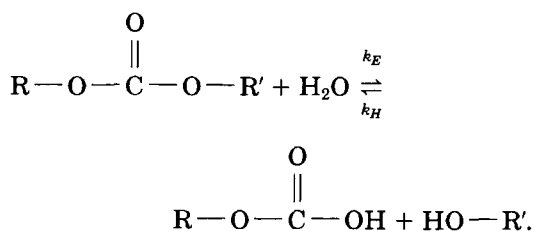

Figure 2   Eyring plot of hydrolysis rate. (▲) 60°C; (▲) 90°C.

$$K = KE_0[H_2O].$$

The pseudo-zero-order rate constant would be then proportional to the water concentration and would thus increase under tensile loading. It is difficult to explain variations of one order of magnitude by this process. In principle, compression loading is expected to have opposite effects to the tensile one, which suggests a possible way to check this hypothesis.

Chemical Effects

There are many possible ways for a stress effect on the chain scission rate:

1. Mechanically induced homolytic chain scissions according to Zhurkov[11] could contribute to the whole degradation rate. It has been experimentally verified that there is no molecular weight significant change in the time scale under study, for PC samples exposed under tension in dry atmosphere. This hypothesis can be thus rejected.
2. Tensile stresses disfavor the recombination of chain ends. According to this hypothesis, the carbonate hydrolysis would be equilibrated:

$$\begin{array}{c}
\text{O} \\
\parallel \\
\text{R}-\text{O}-\text{C}-\text{O}-\text{R}' + \text{H}_2\text{O} \underset{k_H}{\overset{k_E}{\rightleftharpoons}}
\end{array}$$

$$\begin{array}{c}
\text{O} \\
\parallel \\
\text{R}-\text{O}-\text{C}-\text{OH} + \text{HO}-\text{R}'.
\end{array}$$

If hydrolysis occurs in a stressed chain segment, the scission of this latter favors a relaxation whose result is a separation of chain ends as for the rupture of a spring under tension. This separation leads to a decrease of the probability of recombination expressed by the rate constant k_t. A decrease of k_E leads to an increase of the whole chain scission yield. It is noteworthy that the decarboxylation of the terminal carbonic acid could completely suppress the recombination.
3. Tensile stresses induce elastic deformations of valence angles in the carbonate group. These deformations can lead to a decrease of the activation energy of the rate controlling

step (which would in principle justify the use of the Eyring–Zhurkov model).
4. According to Robertson,[12] tensile stresses induce conformational changes. The chains are enriched in conformations of the highest potential energy, resulting in "kink" formation by local shear stresses. These structural changes can affect the hydrolysis rate if, for instance for steric reasons, hydrolysis is conformation sensitive.

The observed decrease of k (and $\bar{r}$) with the time of exposure for stressed samples can be attributed to relaxation effects leading to a homogenization of the stress distribution over polymer skeleton bonds. This hypothesis suggests that the physical aging could eventually influence the stress effect on hydrolysis rate, which can be experimentally verified.

CONCLUSIONS

It has been clearly shown that tensile stresses accelerate noticeably the polycarbonate hydrolysis. In the temperature interval under consideration, the stress effect could be expressed by the so-called activation volume V whose order of magnitude would be $V \approx 1.6 \pm 0.8 \ 1 \ \text{mol}^{-1}$, e.g., 8 ± 4 monomer units. It appears, however, that V is a decreasing function of exposure time and an increasing function of the temperature so that the Eyring–Zhurkov relationship applied to hydrolysis rate would have a poor predictive value. Among the possible causes of such stress effects, chemical ones (direct stress effects on hydrolysis or indirect effect through a conformational change) seem to be the most probable.

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