values gives a difference in $\Delta H°$ of 1.03 kcal/mol, and a difference of $\Delta S°$ of 1.98 eu or of $T\Delta S°$ of 0.59 kcal/mol.

A decomposition of the swelling process itself (phenol entering the Nylon) into its enthalpy and entropy components is not yet possible due to a lack of adequate enthalpy data. It is of interest to note that the Hammett equation has been applied to the enthalpy term alone in a study[8] of the hydrogen bonding of phenol with small-molecule donors.

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Solid State Photochemistry of Polycarbonates

A. GUPTA,* A. REMBAUM, and J. MOACANIN

Energy and Materials Research Section, Jet Propulsion Laboratory, Pasadena, California 91103.

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PhotoFries rearrangement observed on photolysis of aryl esters and carbonates has been the subject of numerous mechanistic investigations[1-10] as have α-C–C or -C–O bond homolysis and 1,3-acyl shifts occurring in a broad class of β,γ-unsaturated ketonic chromophores.[15-17] Meyer and Hammond[10] reported that gas-phase photolysis of phenyl acetate yields not only the photoFries product but products anticipated on the basis of formation of methyl radicals on α-C–O bond homolysis during the rearrangement. On the other hand Bellus,[3] and more recently Humphrey[2] et al., have concluded that although α-C–O bond homolysis is an ubiquitous side reaction obtained on photolysis of aryl esters, carbonates, or polymers thereof, photoFries rearrangement in these systems is a concerted 1,3-acyl shift originating from the first $\pi^* \leftarrow n$ singlet. Here we report quantum yield of photoFries rearrangement in a polycarbonate film as functions of temperature and humidity. We conclude that the mechanism and quantum yield of photoFries rearrangement in the solid state is markedly different from that in other media. In the homogeneous amorphous phase it is a concerted process proceeding either from the $\pi^* \leftarrow n$ singlet, in which case it must be subject to considerable self quenching, or from a triplet. The latter is presumably the first triplet since the lifetime of higher triplets is expected to be very short in condensed (solid) phase. We have also monitored the rate of chain scission as a function of irradiation period using FTIR (Fourier transform infrared spectroscopy) and gel permeation chromatography (GPC). It will be further demonstrated that the measurement of lifetime of the parent excited state is essential if a model of photodegradation of the film is to be developed, particularly when conversion is appreciable. Reports on transient detection and kinetics as well as development of such a model will be the subject of a future communication. The data used in these calculations were reported by Kolyer and Mann.[1]

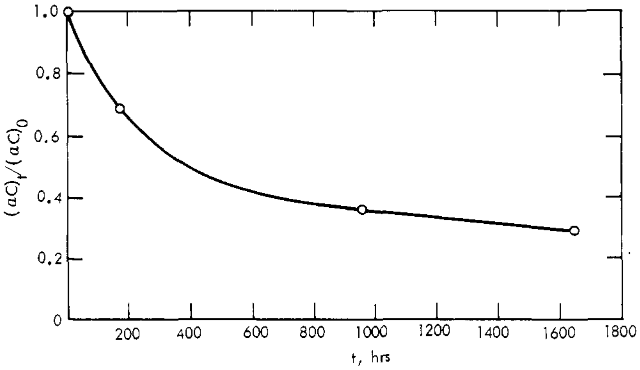

Figure 1. Rate of Lexan photodegradation (measured by following increase in A_{360} for a 24-h exposure) vs. age of lamp in hours.

Experimental Section

Experimental techniques and data handling are detailed in ref 1. The following test environments were used:

a. Indoor Testing Chamber. This chamber consists of a box fitted with a 2500 W ozone-free, high pressure Xenon lamp, blowers, and safety devices such as air-flow and temperature sensors. Spectral characterization of the lamp was carried out as a function of the age of lamp. It was found that there was a drop in the ultraviolet output in the region 300–310 nm, but no decrease at wavelengths higher than 310 nm. This drop in ultraviolet output reduces the initial rate of Lexan photodegradation. We may plot increase in absorbance at 360 nm for a 24-h exposure of fresh Lexan films vs. age of the lamp. This plot may be integrated to obtain the integrated UV intensity absorbed by Lexan when tests are carried out for long periods ($\lesssim$50 h) as a function of total duration of the test. This plot is shown in Figure 1 and has been used to correct all observed rates of Lexan photodegradation.

Short-wavelength ultraviolet was filtered with a Pyrex filter, so that the spectral distribution resembled air mass 1 solar irradiance. Infrared was filtered with a water filter in order to obtain a better control of the temperature. Humidity could be controlled by enclosing the sample in quartz vessels containing the requisite partial pressure of water vapor. Control runs were carried out in inert gas atmospheres.

b. EMMA and EMMAQUA. These are solar concentrators set up at DSET, Inc., of Phoenix, Ariz. and consist of aluminum mirrors mounted on a steel frame tracking the sun. The nominal acceleration factor is 800%, although deviation could be caused by loss of reflectivity of the mirrors, particularly in certain spectral regions. Samples are placed in a holder cooled by a blower and they may receive periodic (15 minutes) spray of deionized water (EMMAQUA).

c. Outdoor Exposure Tests. Samples were placed outdoors in Miami, Fla. and Phoenix, Ariz. at 45° south and in horizontal positions.

Absorbance at 360 nm was measured in a Cary 16. Weathered samples obtained through the courtesy of Dr. Kolyer were examined by using FTIR (ATR) spectroscopy and gel permeation chromatography (solvent CH_2Cl_2).

Initial rate studies were carried out with these data assuming that ϵ_{360} of phenyl salicylate is 1.1 L mol^{-1} cm^{-1}. Light input was estimated by multiplying the integrated input of the lamp (as a function of wavelength) to the absorbance of the film as a function of wavelength and integrating the resulting function in the range 290–340 nm.

Results and Discussion

UV-vis spectra of the film and its solution in dichloromethane are presented in Figure 2. The solution follows Beer's law up to the highest concentration used (12.3 mg/mL). Weak shoulders are observed at 322 nm and 308 nm. A Gaussian analysis of the spectrum reveals that the main Lexan absorption extends to 340 nm. The long-wavelength absorption may be attributed to a low-flying $\pi^* \leftarrow n$ singlet, or to the first triplet or a combination

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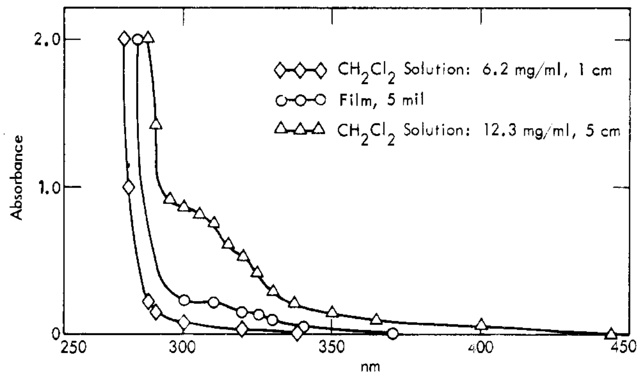


Figure 2. Electronic absorption spectra of Lexan in solution (CH_2Cl_2) and prepared in form of films. $(aC)_t/(aC)_0$ = increase in absorbance at 360 nm for a 24-h exposure at lamp age t divided by the increase in absorbance at 360 nm for a 24-h exposure at lamp age 0.

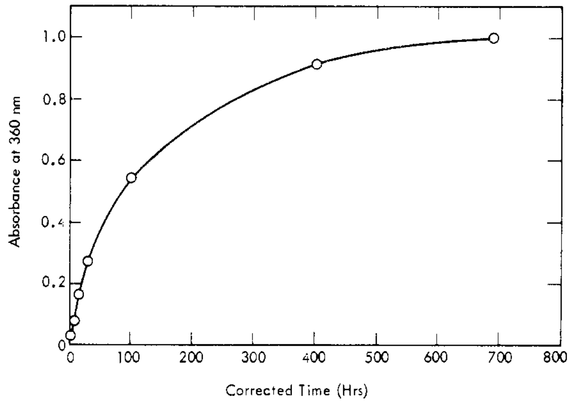


Figure 3. Photodegradation of Lexan films as a function of exposure period. Data have been corrected for aging of the lamp using the correction factor derived from Figure 1; see text. Polycarbonate films at 26.1 °C; 0% R.H; W = 6.07 mW/cm^2. Corrected time is the time equivalent of the actual integrated incident radiation if lamp aging did not occur.

of both. The absorption at 322 nm is presumably due to salicylate end groups in the polymer; hence, we calculate that the concentration of these groups in the polymer is 6×10^{-5} per mer, taking $\epsilon_{322} = 7300$ L mol^{-1} cm^{-1}.[2,11] This concentration of hydroxyl groups produces an extremely weak and broad absorption at around 3300 cm^{-1}. The assignment of the 305-nm band is uncertain, but presumably it is due to ester-type absorption. The assignment of 322 nm is confirmed by the fact that this band grows in intensity on photodegradation of the film.

GPC elution profiles of degraded films are presented in Figure 3. Evidence of chain scission also comes from FTIR (ATR) spectra and from observed monotonic decrease of T_g on photodegradation in air or under N_2. FTIR (ATR) spectra of the films (as a function of time of exposure) were recorded and difference spectra obtained. The carbonyl stretch appears at 1780 cm^{-1} while C–O and C–C bands occur at 1220, 1185, and 1160 cm^{-1}, respectively. The 1510-cm^{-1} absorption may be attributed to para-substituted phenyl groups. On weathering the carbonyl stretch loses intensity as well as the C–C and C–O bands, while hydroxyl absorption increases and broad new carbonyl peaks appear at 1740 (cm^{-1}) and between 1700 and 1640 cm^{-1}. These results indicate that photoFries rearrangement[2-6] is occurring and C–O bond scission is taking place. Chain scission is also indicated by decrease of T_g with time, the rate of which has the same profile as the rate of photoFries rearrangement.[1] We therefore assume that the "yellowing" or increase in A_{360} in the films is due to the formation of photoFries products. The following mechanistic scheme is proposed to model this system:

$$L \xrightarrow{h\nu} L^{1*} \xrightarrow{k_{isc}} L^{3*} \xrightarrow{k_{d_2}} L \qquad (1)$$

$$L \xrightarrow{h\nu} \rightarrow L^* \xrightarrow{k_{d_1}} L_1 \qquad (2)$$

$$L^* \xrightarrow{k_2} L_1 \qquad (3)$$

$$L_1 \xrightarrow{h\nu} L^*_1 \qquad (4)$$

$$L^*_1 \xrightarrow{k_{d_3}} L_1 \qquad (5)$$

$$L^*_1 \rightarrow L_2 \qquad (6)$$

$$L_2 \xrightarrow{h\nu} L^*_2 \xrightarrow{k_{d_4}} L_2 \qquad (7)$$

$$L^* + L_1 \xrightarrow{k_4} L + L^*_1 \qquad (8a)$$

$$L^* + L_1 \xrightarrow{k_5} L + L_1 \qquad (8b)$$

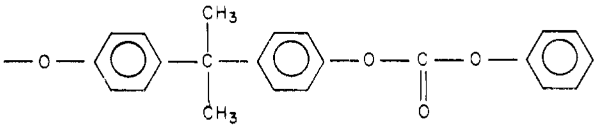
$$L^* + L_2 \xrightarrow{k_6} L + L^*_2 \qquad (9a)$$

$$L^* + L_2 \xrightarrow{k_7} L + L_2 \qquad (9b)$$

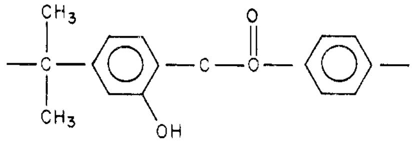
$$L^*_1 + L_2 \xrightarrow{k_8} L_1 + L^*_2 \qquad (10a)$$

$$L^*_1 + L_2 \xrightarrow{k_9} L_1 + L_2 \qquad (10b)$$

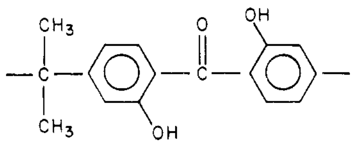
Here we show light absorption by Lexan, L, photoFries rearrangement of phenyl salicylate (L_1), competitive light absorption by L_1, generation of 2,2′-dihydroxybenzophenone (L_2), and so on. The energy transfer processes (eq 8, 9, and 10) appear to be exothermic while the corresponding quenching processes are feasible and have been demonstrated in simple mono- and bichromophoric systems.[12] In this scheme we made no assumptions about the nature of the reactive excited state. Comments on this subject are deferred to a later section.



L



L_1



L_2

Let us define

$$I_{L_i}(t) = \frac{I_0 a_{L_i}(t)}{a_L(t) + a_{L_1}(t) + a_{L_2}(t)} \qquad (1')$$

Table I

incident light intensity (300–400 nm), mW/cm^2	temp, °C	humidity, %	$\phi_i\phi_p$
6.07	26.1	0	0.005 ± 0.002
6.07	26.1	100	0.007 ± 0.003
4.4	26.1	0	0.003 ± 0.001
4.4	55.1	0	0.004 ± 0.002
4.4	55.1	100	0.005 ± 0.002

Table II

humidity, %	light intensity (300–400 nm), nW/cm^2	activation energy, kcal/mol	preexponential factor[a]
0	6.07	3.5 ± 0.6	1.0
0	4.4	4.0 ± 0.6	
100	6.07	1.2 ± 0.3	16
100	4.4	1.3 ± 0.3	
50	6.07	2.7 ± 0.4	6.5

[a] Relative to 0% RH, 6.07 mW/cm^2 light intensity.

When I_0 is the total light absorbed, and $a_{\mathrm{L}_i}(t)$ are the absorbances at time t.

$$\phi_i = k_i/\sum k_i \qquad (2')$$

when k_i is the rate of formation of L*, the reactive excited state from L^{1*}, the primary excited state, and k_i is the reciprocal of lifetime of L^{1*}.

$$\tau_{\mathrm{L}^*} = 1/[k_2 + \sum k_\mathrm{d} + (k_4 + k_5)L_1 + (k_6 + k_7)L_2] \qquad (3')$$

the lifetime of L* when concentrations of L$_1$ and L$_2$ are L_1 and L_2 respectively, and $\tau_{\mathrm{L}^*_1} = 1/[k_3 + k_{\mathrm{d}_3} + (k_8 + k_9)L_2]$, the lifetime of L$^*_1$. τ_L and τ_{L_1} may be measured in a Lexan film through nanosecond laser flash kinetic spectroscopy for varying concentrations of L$_1$ and L$_2$. Then

$$\mathrm{d}L_1/\mathrm{d}t = k_2 I_\mathrm{L}(t)\phi_i\tau_{\mathrm{L}^*} - k_3\tau_{\mathrm{L}^*_1}[I_{\mathrm{L}_1}(t) + k_4 L^*_1 I_\mathrm{L}(t)\phi_i]$$

and

$$\mathrm{d}L_2/\mathrm{d}t = \tau L^*_1 k_3[I_{\mathrm{L}_1}(t) + k_4 L_1\phi_i I_\mathrm{L}(t)\tau_{\mathrm{L}^*}]$$

If we use radiation of wavelength such that $a_\mathrm{L} >> a_{\mathrm{L}_1}, a_{\mathrm{L}_2}$ for the duration of test (e.g., 275 nm) $I_{\mathrm{L}_1,\mathrm{L}_2}(t) = 0$ then

$$\mathrm{d}L_1/\mathrm{d}t = I\phi_i\tau_{\mathrm{L}^*}(k_2 - k_3 k_4\tau_{\mathrm{L}^*_1}\mathrm{L}_1)$$

and

$$\mathrm{d}L_2/\mathrm{d}t = I\phi_i\tau_{\mathrm{L}^*_i}k_3 k_4\tau_{\mathrm{L}^*\mathrm{L}_1}$$

However, the data were taken using a high-pressure xenon arc; therefore, we shall only deal with initial rates, $(\mathrm{d}L_1/\mathrm{d}t)_{\mathrm{L}_1=0}$ and $(\mathrm{d}L_2/\mathrm{d}t)_{L_1,L_2=0}$

$$(\mathrm{d}L_2/\mathrm{d}t)_{L_1,L_2=0} = 0$$

and

$$(\mathrm{d}L_1/\mathrm{d}t)_{L_1=0} = I_0\phi_i\phi_\mathrm{p}$$

when

$$(k_2\tau_{\mathrm{L}^*})_{L_1=0} = \frac{k_2}{k_2 + \sum k_\mathrm{d}} = \phi_\mathrm{p}$$

$\phi_i\phi_\mathrm{p}$ being the initial or intrinsic quantum yield of product formation.

Table I gives $\phi_i\phi_\mathrm{p}$ values under various conditions. Figure 3 shows a typical degradation profile. Here absorbance at 360 nm has been plotted vs. time.

Table II gives the activation energies and preexponential factor of the initial rates. The activation parameters were calculated from initial rates using the equation $r = r_0 e^{-E/RT}$ when r_0 is the preexponential factor and $r = [\mathrm{d}\Delta A_{360}/\mathrm{d}t](t \rightarrow 0)$. These activation parameters nevertheless apply to $\phi_i\phi_\mathrm{p}$ since $r = \phi_i\phi_\mathrm{p} \times I(t)$, and absorbed light intensity $I(t)$ is independent of temperature. The errors in determination of the initial quantum efficiency arise largely out of errors in measurement of I, and hence the activation parameters could be measured more precisely than quantum efficiencies.

The very low quantum efficiency measured on the film is in contrast to those reported[3] on dilute solution of polycarbonate (~0.18). Mechanistic discussions[2-10,15-17] of photoFries rearrangement have included consideration of a radical process initiating from C–O bond homolysis and a concerted molecular rearrangement involving 1,3 or 1,5 shifts. It was proposed that an internal conversion takes place to a lower lying $\pi^* \leftarrow$ n state from the $\pi^* \leftarrow$ n state, which is followed by the molecular rearrangement.[2] In view of the observed two orders of magnitude difference between quantum yields in solution and in solid state it is unlikely that the rearrangement is a radical process, occurring from the same excited state both in solution and in solid state. Such a conclusion would imply that rearrangement of the radical pair is strongly hindered in the solid state, whereas recombination is facile. The activation energy of the photorearrangement would then have to be higher than what we observe. A similar argument also rules out the molecular rearrangement mechanism from the $\pi^* \leftarrow$ n singlet proposed for photoFries rearrangement occurring in dilute solution. The drastic decrease in quantum yield without a concomitant increase in activation energy means either that the reactive excited state is the $\pi^* \leftarrow$ n singlet and it undergoes considerable self-quenching (either to the ground state or the first triplet) or that the rearrangement takes place from a different excited state in the solid state. A suitable candidate would be lowest triplet which would then explain why the rearrangement is strongly quenched as concentrations of L$_1$ and L$_2$ build up. Obviously, part of the self-inhibition arises out of competitive absorption by the photo products since back energy transfer (reverse of eq 8, 9, and 10) is not feasible both on energetic grounds and because of reported short lifetime[13] of orthohydroxybenzophenone triplets, but absorbance calculations indicate that this screening effect cannot explain the total extent of inhibition. We therefore propose the energy transfer processes (eq 8, 9, and 10) as at least partially responsible for the UV-stabilizing effect exhibited by 2,2′-dihydroxybenzophenone. Reviews of excited state energetics and reaction pathways for similar β,γ-unsaturated systems have been published by Houk[15] and Dauben.[16] Nanosecond flash kinetic experiments both on solution and the films themselves are expected to yield excited state lifetimes of both Lexan (L) and phenylsalicylate (L$_1$). These lifetimes together with results from transient quenching studies now in progress should resolve this question.

In general, it appears the lowering of the activation energy in the presence of water vapor may be caused by greater stabilization of the transition state through solvation than the parent excited state or radical pair. Such extra stabilization is expected since any weakening of α-C–O bonds will allow the oxygen to hydrogen bond more effectively with water. The increase in the preexponential factor indicates a decrease in entropy of activation. The screening effect of the photoproducts is likely to be attenuated in the presence of water, inasmuch as it has been shown[14] that in polar protic solvents 2,2′-dihydroxy-

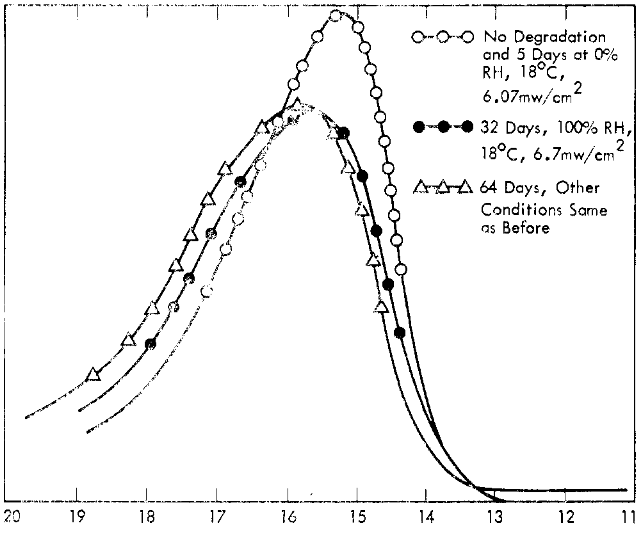


Figure 4. GPC traces of Lexan films after they have undergone photodegradation in the solid state.

benzophenone emits phosphorescence presumably because the intromolecular hydrogen bond is disrupted with resultant increase in the triplet lifetime. Neither the mechanism nor the relative magnitudes of reaction rates change significantly when water is introduced to the system.

It is well known that chain scission is another major mode of photodegradation in this system.[3,10,11] In the radical pair mechanism, these two modes of photodegradation arise from the same primary process, e.g., the C–O bond homolysis. On the other hand, if we propose that the parent excited state of photoFries rearrangement is the first triplet, it is possible that chain scission is an independent process, probably taking place from the $\pi^* \leftarrow n$ singlet. The evidence for chain scission on photodegradation in the solid state is (1) loss of C–O and C–C bond intensities in the FTIR (ATR) spectra, (2) GPC elution profiles of degraded film samples dissolved in $CHCl_3$ (Figure 4), and (3) decrease in T_g and tensile strength as photodegradation proceeds. These plots indicate that chain scission is inhibited as photoFries products build up.

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Why the Phase Boundaries Should be Sharp in Most Phase-Separated Block Copolymers

SONJA KRAUSE

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received May 24, 1978*

Recently, it was found[1] that the glass transition temperatures of the styrene microphases as determined by DSC and DTA measurements in low molecular weight diblock and triblock copolymers of styrene with dimethylsiloxane, butadiene, isoprene, and ethylene oxide depended only on the molecular weight of each styrene block in the block copolymer molecules. The value of this glass transition temperature, T_g, did not depend on the chemical nature of the rubbery blocks, on the position of the styrene block or blocks within the block copolymer molecule, or on the percentage composition of the block copolymer. The chemical nature and/or molecular weight of the rubbery block influenced the T_g of the styrene microphase only when the molecular weight and composition of the block copolymer was near that at which microphase separation no longer takes place.

These data strongly suggest that the nature of the styrene microphase is exactly the same in all the block copolymer samples investigated. If there is any mixing of blocks of different chemical nature in the glassy microphases, it must be exactly the same for all samples. This is highly unlikely for rubbery phases that are as different as butadiene and isoprene are from dimethylsiloxane and ethylene oxide. Among other things, the compatibility of the oligomers of the different rubbers with styrene oligomers is quite different, and this difference should carry over into differences in homopolymer miscibility. For example, it was found that hexamers of styrene and dimethylsiloxane are immiscible at room temperature and have an upper critical solution temperature of 35 °C.[2] A 10-mer of styrene and a 15-mer of isoprene, on the other hand, were miscible at room temperature and had an upper critical solution temperature of −30 °C.[3] In support of the lesser compatibility of poly(dimethylsiloxane) with polystyrene, one may note that the solubility parameter of dimethylsiloxane is much farther from that of polystyrene than are the solubility parameters of polybutadienes or of polyisoprenes,[4] no matter what their microstructure.

It seems to me that the only way to preserve the similar nature of the styrene microphases (made up of styrene blocks with molecular weights 5000 to 20 000) in the different block copolymers in view of the different compatibilities of the respective homopolymers is to assume that there is virtually no mixing between segments of rubbery and glassy blocks in the glassy microphase.

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