

The Ultraviolet Activation Spectrum of Polycarbonate

P. A. MULLEN and N. Z. SEARLE, *American Cyanamid Company,
Central Research Division, Stamford, Connecticut 06904*

Synopsis

Previous work has shown that a polymeric phenyl salicylate and a polymeric dihydroxybenzophenone are formed during the irradiation of polycarbonate with non-spectrally dispersed ultraviolet light. In the present studies the photodegradation of polycarbonate film has been investigated as a function of irradiating wavelength using spectrally dispersed light from a xenon arc between 2300 and 6300 Å. Maximum changes in absorbance at 3200, 3600, and 4000 Å were induced in the sample by irradiating wavelengths between 2800 and 2900 Å. The wavelength sensitivity of an extruded sample of polycarbonate is compared with results obtained for a solution-cast thin film of the material. The results of the present study support the stepwise photodegradation mechanism of polycarbonate previously reported and suggest the possibility of an additional photodegradation process.

INTRODUCTION

Increased light stability for a given polymer system may generally be attained either through improvements in formulation or by the incorporation of a protective ultraviolet absorber. Such improvements often depend upon a knowledge of the polymer activation spectrum which is the relative extent of photodegradation as a function of wavelength of incident light. An activation spectrum of polycarbonate was obtained by following the changes in absorbance induced in the material by radiation of various wavelengths.

In studies on polycarbonate with nonspectrally dispersed light a mechanism of photodegradation was proposed based on changes produced in the absorption spectrum of the sample.² The proposed mechanism involves the photochemical formation of a polymeric phenyl salicylate from the polycarbonate and the subsequent rearrangement of the salicylate to yield a polymeric dihydroxybenzophenone. The present work using a solution-cast film supports this mechanism. The experimental results also suggest the formation of additional photodegradation products.

In order to demonstrate the effect of sample preparation and thickness on the activation spectrum of polycarbonate, the experimental activation spectrum of an extruded polycarbonate sample is included for comparison.

EXPERIMENTAL

Instrumentation

The light source employed to obtain the activation spectrum was a Hanovia 900-W xenon arc. Wavelengths from 2300 Å to 6300 Å were dispersed across the sample, which was secured in the focal plane at the exit port of the spectrograph. The method of dispersing energy from this lamp across a sample by means of a fast quartz-prism spectrograph has been described previously.^{1,3} The dispersion of the spectrograph was found to range from less than 50 Å/mm at the short wavelength end to more than 300 Å/mm at 4100 Å. No determination of dispersion between 4100 and 6300 Å has been made.

Optical changes were followed using a Cary Model 14 spectrophotometer with an adapter to convert the instrument into a scanning microdensitometer.⁴ The adapter, fitted with a ca. 0.25-mm slit, is used to scan continuously across the sample at a predetermined wavelength (scan wavelength) or to obtain the absorption spectrum of any desired 0.25-mm-wide section of the film. The relation between wavelength of irradiation and chart trace had been obtained previously by photographing the emission lines of a low-pressure mercury arc at the focal plane of the spectrograph and scanning the plate with the microdensitometer (Cary 14 Plus adapter) exactly in the same way as the sample is scanned.

It had been determined by irradiation with undispersed ultraviolet light that photodegradation of polycarbonate results in the formation of degradation products having absorption bands centered at ca. 3200 and ca. 3600 Å. The extent of photodegradation of the polycarbonate with dispersed energy was therefore measured across the sample, i.e., as a function of incident irradiation wavelength, using scan wavelengths of 3200 and 3600 Å. A measure of yellowing was obtained with a scan wavelength of 4000 Å. The unirradiated sample was scanned from edge to edge on a rigid support at each scan wavelength to obtain a baseline. Repeated scans after irradiation at each scan wavelength showed the change in absorbance as a function of irradiating wavelength and time of irradiation.

Materials

A ca. 0.1-mil solution-cast film and a 10-mil extruded film of General Electric Lexan polycarbonate (a bisphenol A polycarbonate) were used in this investigation. The thin film was cast from chloroform solution and air dried.

RESULTS AND DISCUSSION

Solution-Cast Film

The absorption spectrum of unirradiated polycarbonate and the absorption spectra of the film after various irradiation times are presented in

Figure 1. The absorption spectra of the irradiated sample were taken of that area of the film showing maximum increase in absorbance after irradiation, i.e., in that 0.25-mm-wide area corresponding to irradiation wavelengths at the maximum of the activation spectrum. The absorption spectra after irradiation were corrected for the absorption of the unirradiated film and are given in Figure 2. All absorption curves have been plotted as relative to absorbance at 4000 Å.

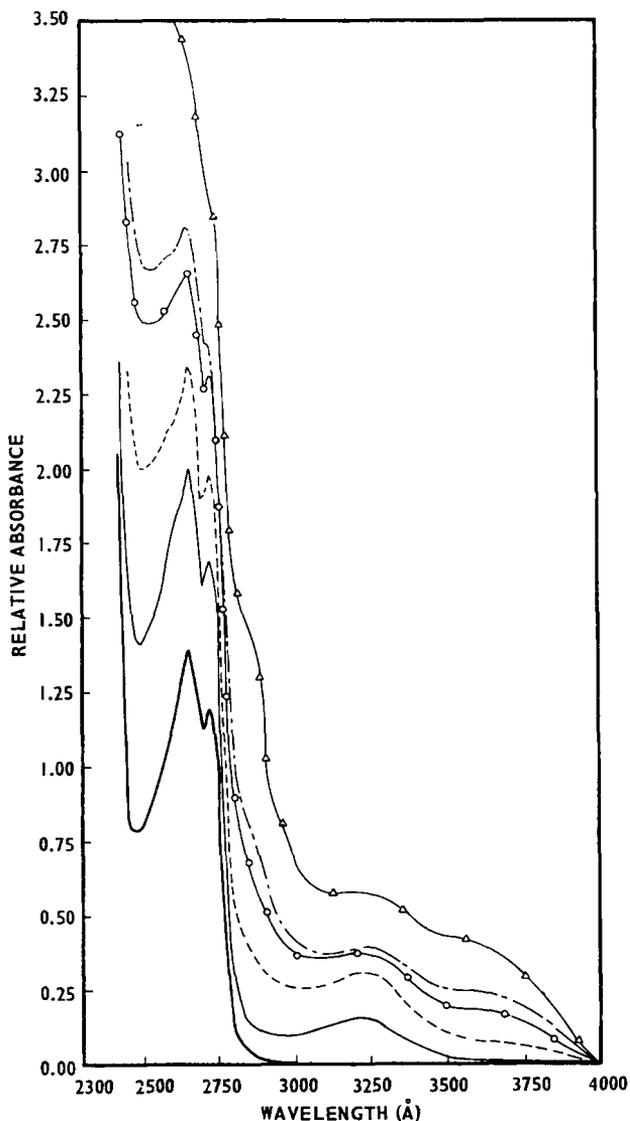


Fig. 1. Absorption spectrum of General Electric Lexan polycarbonate solution-cast film (~ 0.1 mil): (—) no irradiation; (---) irradiated 15 min; (· · ·) irradiated 1.5 hr; (O—O) irradiated 4.5 hr; (—□—) irradiated 8 hr; (Δ — Δ) irradiated 44 hr.

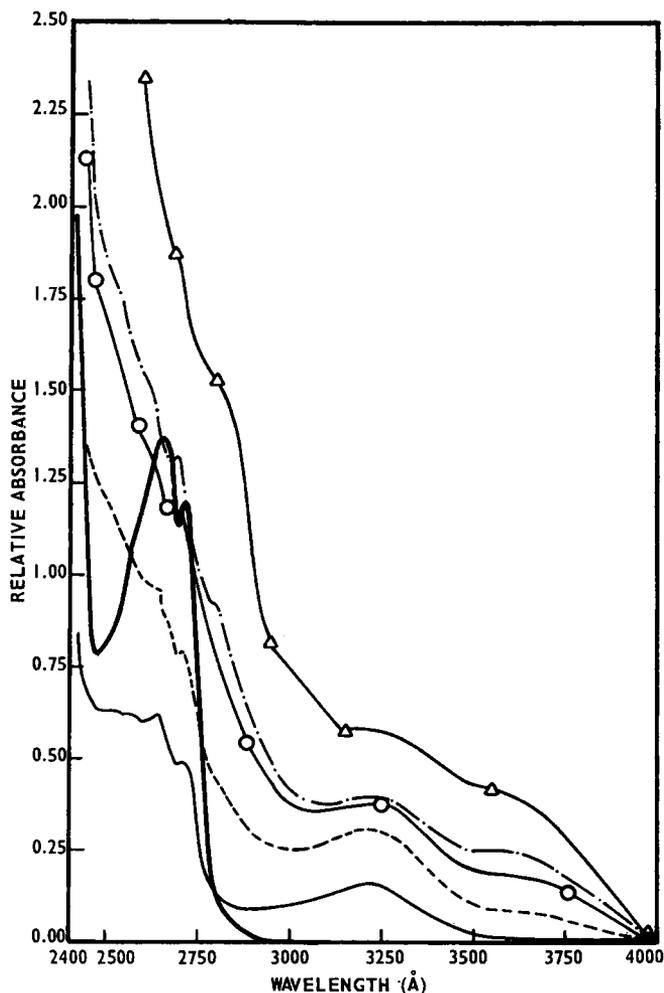


Fig. 2. Absorption spectrum (corrected) of General Electric Lexan polycarbonate solution-cast film (~ 0.1 mil): (—) no irradiation; (---) irradiated 15 min; (· · ·) irradiated 1.5 hr; (O—O) irradiated 4.5 hr; (- - -) irradiated 8 hr; (Δ — Δ) irradiated 44 hr.

The activation spectrum of the thin polycarbonate film at various irradiation times from 5 min to $22\frac{1}{4}$ hr is presented in Figures 3, 4, and 5 for scan wavelengths of 3200, 3600, and 4000 Å, respectively. The plots are presented as increase in absorbance versus wavelength of irradiation in Angström units. If we assume that the increase in absorbance at 3600 and 3200 Å is caused by the photochemical formation of a polymeric dihydroxy benzophenone (DHB) and a polymeric phenyl salicylate (PS), respectively, it may be stated that the activation spectrum given in Figures 3 and 4 show no evidence for the formation of a polymeric DHB during the first 5-min irradiation period. After 15 min irradiation, the increase in absorbance due to the formation of the polymeric PS at 3200 Å was 0.17, whereas the in-

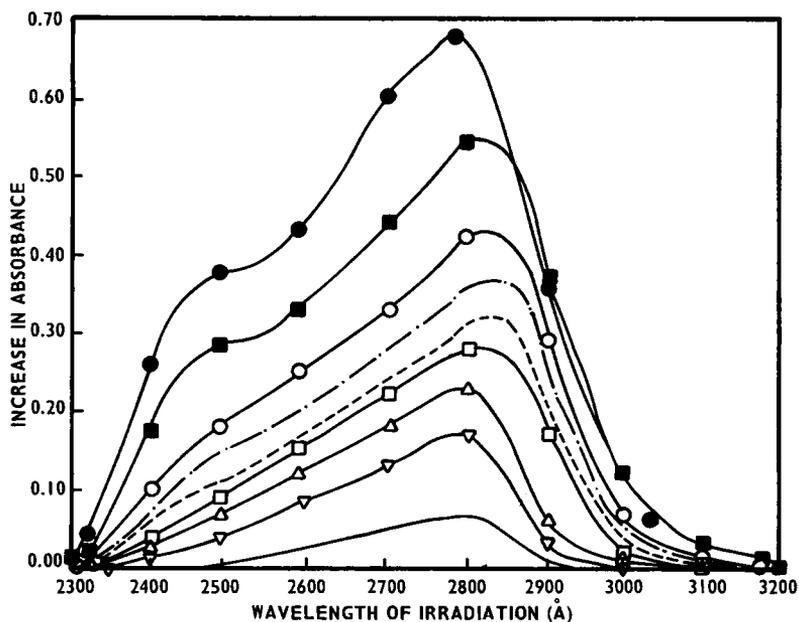


Fig. 3. Activation spectrum of General Electric Lexan polycarbonate solution-cast film (~ 0.1 mil); scan wavelength 3200 \AA . Irradiation times: (—) 5 min, (∇ — ∇) 15 min, (Δ — Δ) 25 min, (\square — \square) 40 min, (---) 1 hr; (-·-) 1.5 hr, (O—O) 2.5 hr, (\blacksquare — \blacksquare) 8.0 hr, (\bullet — \bullet) $22\frac{1}{4}$ hr.

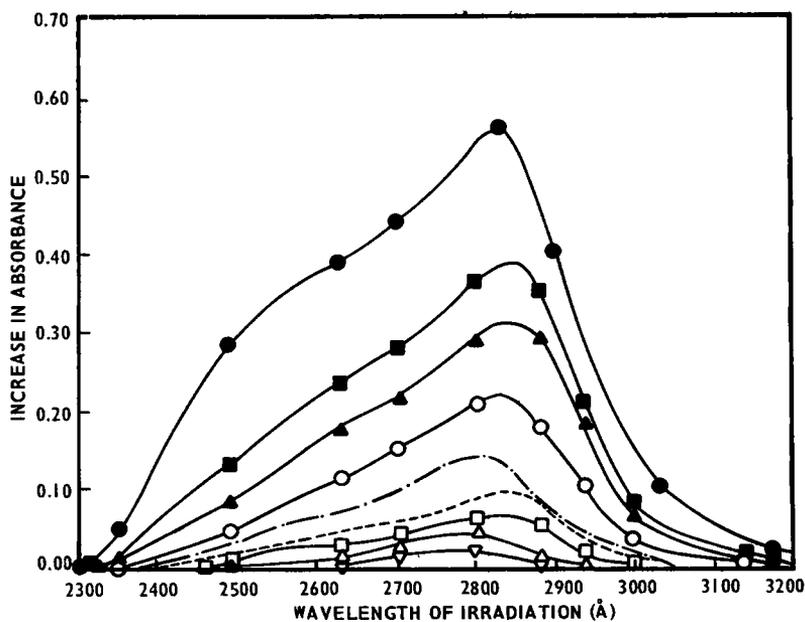


Fig. 4. Activation spectrum of General Electric Lexan polycarbonate solution-cast film (~ 0.1 mil); scan wavelength 3600 \AA . Irradiation times: (∇ — ∇) 15 min, (Δ — Δ) 25 min, (\square — \square) 40 min, (---) 1 hr, (-·-) 1.5 hr, (O—O) 2.5 hr, (\blacktriangle — \blacktriangle) 4.5 hr, (\blacksquare — \blacksquare) 8.0 hr, (\bullet — \bullet) $22\frac{1}{4}$ hr.

crease in absorbance for the polymeric DHB at 3600 Å was only 0.02. This would support the stepwise mechanism proposed by Bellus et al.² Since no increase in absorbance at 4000 Å was observed for the 5- and 15-min irradiation periods, as may be seen from Figure 5, yellowing would appear to be related to the formation of the polymeric DHB. In fact, the shape of the activation spectrum for the 3600 Å scan wavelength resembles quite closely the shape of the spectrum obtained with the 4000 Å scan. This is not surprising, since a dihydroxybenzophenone absorbs at 4000 Å and is slightly yellow.

The main activation peak for polycarbonate was found to be between 2800 and 2900 Å, as may be seen from data given in Figures 3, 4, and 5. The activation peak exhibited a shift to slightly longer wavelengths with increasing irradiation time and a slight short wavelength shift after 22¹/₄ hr of irradiation. The shift of the polymeric PS activation peak is from 2800 to 2830 Å and then from 2830 to 2790 Å, while the polymeric DHB activation peak shifts between 2800 and 2850 Å. The activation peak for yellowing remains constant at 2850 Å up to 22¹/₄ hr when a shift to 2830 Å is noted. These small shifts may be explained by a consideration of the absorption spectra given in Figures 1 and 2. The film rapidly becomes opaque to short wavelength radiation both by an increase in scattering and

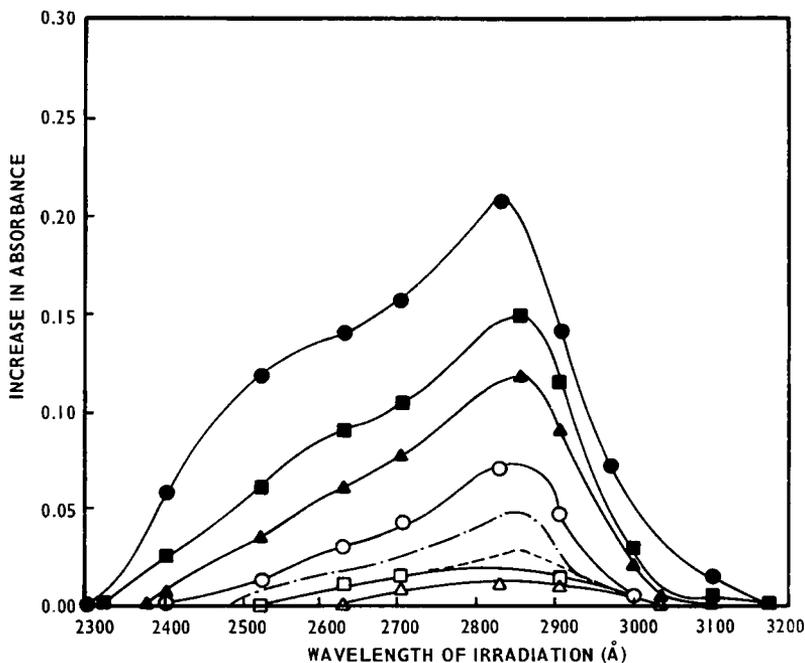


Fig. 5. Activation spectrum of General Electric Lexan polycarbonate solution-cast film (~ 0.1 mil); scan wavelength 4000 Å. Irradiation times: (Δ - Δ) 25 min, (\square - \square) 40 min, (- - -) 1 hr.; (- · -) 1.5 hr, (\circ - \circ) 2.5 hr, (\blacktriangle - \blacktriangle) 4.5 hr, (\blacksquare - \blacksquare) 8.0 hr; (\bullet - \bullet) 22¹/₄ hr.

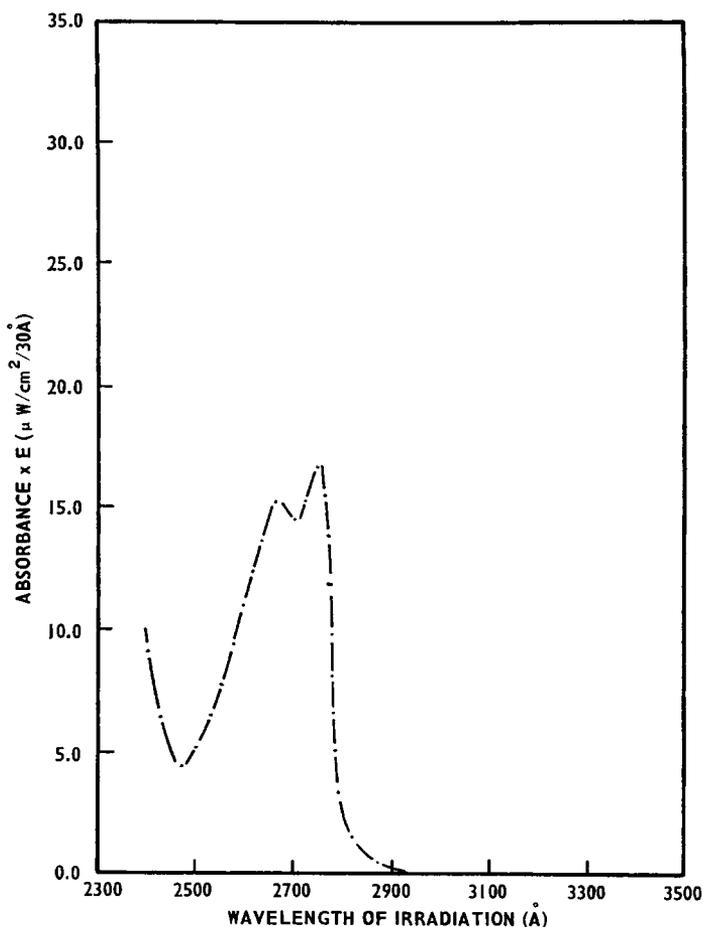


Fig. 6. Calculated activation spectrum of General Electric Lexan polycarbonate solution-cast film (~ 0.1 mil).

by the formation of degradation products with strong short wavelength ultraviolet absorption. Therefore, as the penetration of the short wavelengths is reduced by prolonged irradiation, a slight red shift of the activation peak would be expected. Photodegradation of a polymer in the form of molded, extruded, or solution-cast samples is primarily a surface effect. A General Electric report⁶ notes that when the exposed surface of a weathered sample of polycarbonate is machined to remove the surface skin, all evidence of discoloration is eliminated and the impact properties are identical to unexposed controls. The slight blue shift after $22\frac{1}{4}$ hr may be explained by considering that the activation spectrum with increasing irradiation time represents a composite of all products present in the film. As the concentration of benzophenone increases, the protective influence to long wavelength radiation is increased more relative to increased short wavelength protection, and hence the activation peak will shift

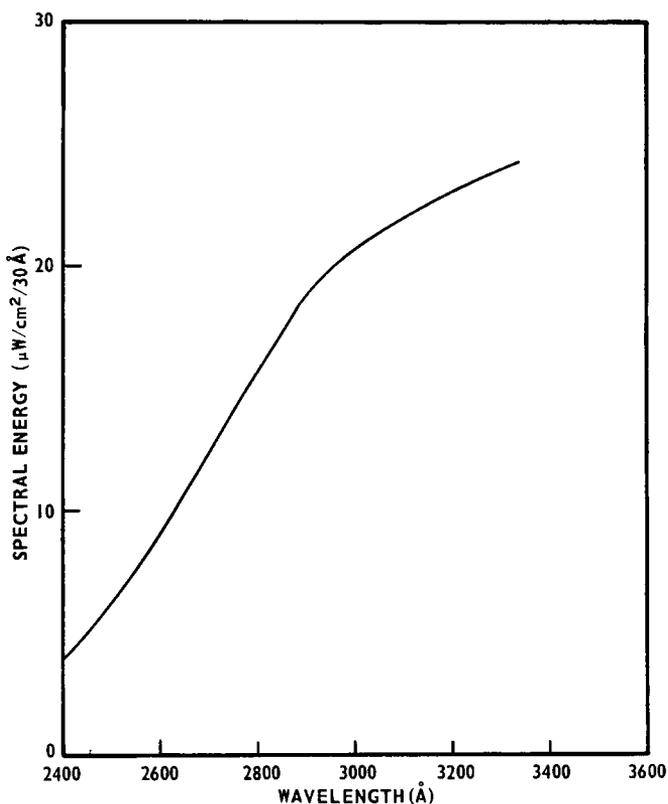


Fig. 7. Spectral energy distribution of a Hanovia 900-W xenon arc (unfiltered).

slightly to shorter wavelengths. The experimental activation spectra also show the formation of a second peak to the short wavelength side of the main activation band.

The magnitude of the change in absorbance at different scan wavelengths must be interpreted with care. Any yellow species formed in the film on irradiation will absorb ultraviolet energy in the region where the polymeric PS absorbs and this, of course, includes polymeric DHB. If we consider that the ϵ at 3600 and 3200 Å for a 2,2'-dihydroxybenzophenone is ca. 12,000 and 11,000, respectively and that the ϵ at 3200 Å for phenyl salicylate is ca. 6000,⁴ it is clear that we may easily overestimate the concentration of polymeric PS formed on irradiation. We may state, however, that at short irradiation times more polymeric PS is formed relative to polymeric DHB and related compounds. With longer irradiation times the situation is more complicated.

For simple mechanisms of photodegradation $A \xrightarrow{h\nu} B$ (photostable), an activation spectrum may be calculated for any irradiating light source and absorbing sample which will closely reproduce the experimental activation spectrum. The activation spectrum for polycarbonate, as shown

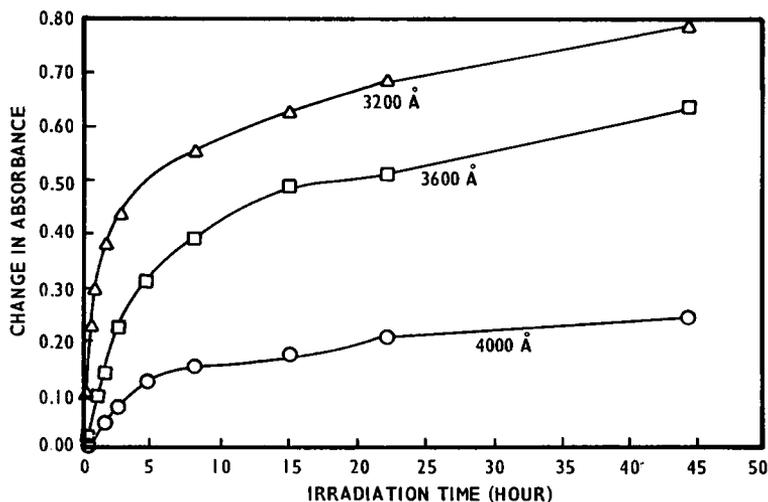


Fig. 8. Extent of photodegradation with irradiation of General Electric Lexan polycarbonate solution-cast film (~ 0.1 mil) as measured at 3200, 3600, and 4000 Å.

in Figure 6, was calculated from the absorption curve of the unirradiated film and the spectral energy distribution of the xenon light source given in Figure 7. The calculation predicts activation peaks for polycarbonate at 2755 and 2665 Å. Experimentally we observed, at short irradiation times, a broad activation peak centered between 2800 and 2900 Å. Initially, one should observe the calculated activation spectrum of polycarbonate but, on extended irradiation when unstable products are formed and degraded, the activation spectrum should evidence such change. If the absorption spectra of the degradation products are different from the absorption spectrum of the parent compound, particularly if the degradation products absorb where the parent material transmits, then one should expect to see differences in activation wavelengths.

The absorption spectra given in Figure 2 show the absorption bands of the polycarbonate degradation products. Degradation products are formed, after 90 min of irradiation, with absorption bands at ca. 3600, ca. 3225, 2800, 2710, 2670, 2650, ca. 2560, and 2500 Å. In order to explain all of these bands, one must consider other degradation products in addition to the polymeric phenyl salicylate and 2,2'-dihydroxybenzophenone particularly to assign the bands at 2800, 2710, and ca. 2560 Å. The present work did not yield sufficient information to permit identification of additional photodegradation products. Model compounds of possible products were not available for study. However, it may be postulated that polycarbonate, through the loss of CO_2 , would degrade to yield polymeric ethers and 2-hydroxybiphenyl compounds. It was considered at one stage in this work that a polymeric phenyl benzoate was formed with subsequent degradation to yield a monohydroxybenzophenone product. This reaction is unknown for the carbonate linkage and therefore cannot be supported

by published results. However, the absorption spectrum of *p*-tolyl benzoate shows structure at 2825, 2730, and 2650 Å, which resembles very closely the absorption spectrum (corrected) of irradiated polycarbonate. In addition, the activation spectrum of a film of *p*-tolyl benzoate in cellulose acetate has a peak at 2860 Å, which falls within the range observed for polycarbonate. The similarity between activation spectra and absorption spectra observed for a film of a *p*-tolyl benzoate in cellulose acetate (before and after irradiation) and irradiated polycarbonate preclude the exclusion of a *p*-tolyl benzoate and the resultant monohydroxybenzophenone as possible reaction products.

Since the 3200- and 3600-Å scans have been taken to represent changes due to two different compounds, it would be expected that with prolonged irradiation the activation peaks at the two scan wavelengths would be different. As has been discussed above, the two scan wavelengths cannot be related to distinct species since the absorbance of the photodegradation products overlap. The effect of "interference" may be seen from Figure 8, which shows the increase in absorbance at 3200, 3600, and 4000 Å as a function of irradiation time. It may be noted that the increase in absorbance at 3200 Å is greater than that at 3600 Å due to the additional absorbance of phenyl salicylate at the shorter wavelength. An interesting feature of this plot is that the increase in yellowing does not parallel the formation of the polymeric DHB.

Extruded Film

The activation spectrum of a 10-mil thick extruded film of Lexan polycarbonate of the same formulation as the ca. 0.1-mil thick solution-cast film is given in Figure 9. It may be noted by comparison with data given in Figures 3 to 5 that the main activation peak of the extruded sample is red shifted by ca. 50 Å. However, the position of the short wavelength shoulder has not been significantly affected. The range of wavelengths causing photodegradation is greater for the extruded film (2300–4300 Å) than for the solution-cast film (2300–3200 Å) and may be attributed to the increase in sample thickness. An increase in sample thickness would have the greatest effect at those wavelengths where the absorbance of the material is low, i.e., to the long wavelength side of ca. 2800 Å. This is supported by the extension of the long wavelength portion of the activation spectrum without a corresponding change at the short wavelengths. The red shift of the activation peak between the two samples may be similarly explained. The increase in absorbance of the extruded sample at the main activation peak for the 3200 Å scan was found to be ca. four times as great as that observed for the solution-cast film, whereas the increase is about two times as great as the solution-cast film absorbance at 3600 and 4000 Å. A very slight decrease in absorbance at 3200 Å may be noted with irradiating wavelengths between 3250 and 3650 Å, with maximum decrease in absorbance at 3430 Å. No such bleaching was found for the solution-cast film due to the thickness and irradiation times employed in the latter investigation.

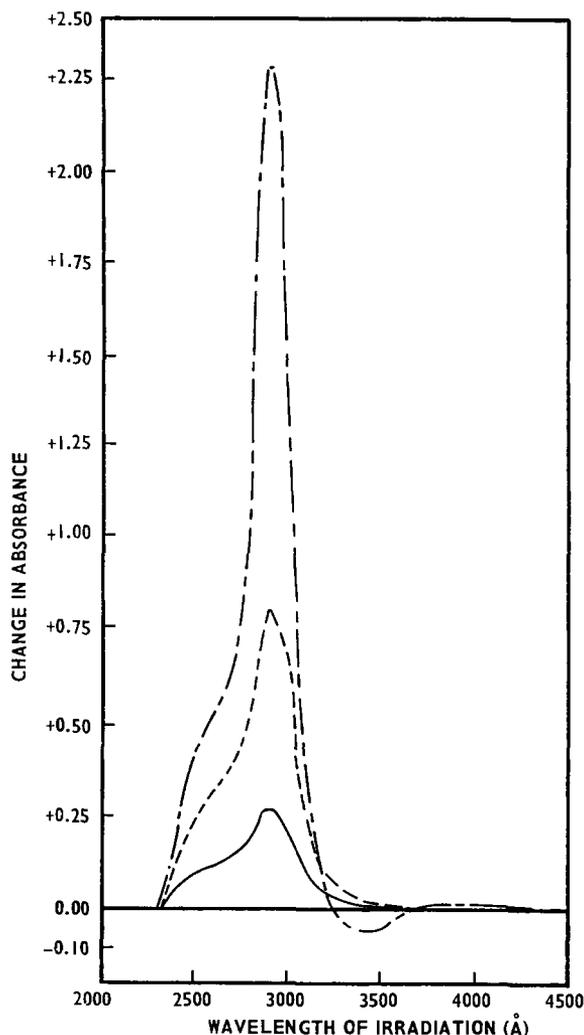


Fig. 9. Activation spectrum of General Electric Lexan polycarbonate extruded film (10 mils) at scan wavelengths of 3200 Å (—), 3600 Å (---), and 4000 Å (-·-).

CONCLUSIONS

Irradiation with ultraviolet light between 2800 and 2900 Å produces maximum photodegradation of polycarbonate as a solution-cast thin film. The effect of increasing film thickness is to red-shift the activation peak and increase the photodegradative effect of long-wavelength ultraviolet radiation. The photodegradation of polycarbonate in this wavelength interval was confirmed to proceed via the photochemical formation of a polymeric phenyl salicylate and the subsequent rearrangement of the salicylate to yield a polymeric dihydroxybenzophenone. The results also indicate that additional degradation products are formed.

The authors are grateful to Mr. J. L. Rodgers and Dr. C. Savides (American Cyanamid Company, Bound Brook, New Jersey) for their many helpful discussions and suggestions.

References

1. R. C. Hirt, N. Z. Searle, and R. G. Schmitt, *SPE Trans.*, **1**, 21 (1961).
2. D. Bellus, P. Hrdlovic, and Z. Manasek, *Polymer Letters*, **4**, 1 (1966).
3. R. C. Hirt and N. Z. Searle, *Wavelength Sensitivity or Activation Spectra of Polymers*, Preprint SPE RETEC, Washington, D.C., 1964.
4. R. G. Schmitt and R. C. Hirt, *WADC Technical Report 59-354*, July 1959.
5. D. Bellus, P. Hrdlovic, and P. Slama, *Coll. Czech. Chem. Comm.*, **33**, 2646, (1968).
6. *General Electric Technical Report CDC423-A*, June 1964.

Received October 28, 1969