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Photochemistry of Bisphenol-A-Based Polycarbonate: Early Detection of Photoproducts by Fluorescence Spectroscopy

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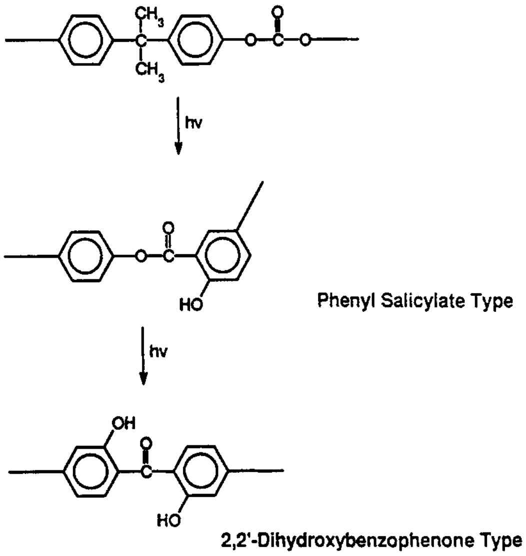
ABSTRACT: The utility of fluorescence spectroscopy in detection of salicylic acid and 2,2′-biphenol type products in the very early stages of photolysis of polycarbonate and its model compounds has been demonstrated. The broad structureless peak around 410 nm produced by photolysis of polycarbonate and model compounds in THF is assigned to emission from a salicylic acid type photoproduct. Formation of salicylic acid groups has been shown to be dependent on the presence of oxygen. The emission with peak maxima around 350–360 nm produced by photolysis of polycarbonate and model compounds in THF (or dichloromethane) is consistent with fluorescence from a 2,2′-biphenol type photoproduct. Salicylic acid and 2,2′-biphenolic products are quite photolabile; hence the need for their early detection during photolysis of polycarbonate.

Introduction

Polycarbonate is an important engineering thermoplastic possessing a variety of useful properties including optical clarity, high impact strength, and high percent elongation. However, upon natural weathering, these and other properties deteriorate rapidly.[1,2] As a result, the photodecomposition of Bisphenol-A-based polycarbonate has been studied by several research groups over the past three decades.[3-23] A review of the literature indicates that a variety of products are formed in the primary photodecomposition of Bisphenol-A-based polycarbonate, i.e., a photo-Fries rearrangement product, a variety of cleavage/expulsion (CO or CO_2)/recombination products, and photooxidation products. The photo-Fries rearrangement process (Scheme I) has been reported to occur upon direct absorption of light by the diaryl carbonate repeat units. Photooxidation has also been reported from photolysis of impurities.[11] Our focus in this paper will be on the detection of the primary photoproducts during the very early stages of photolysis.

Lemaire and co-workers[16,18] have proposed that the primary phenyl salicylate and the 2,2′-dihydroxybenzophenone type photoproducts formed by photo-Fries rearrangements can undergo further photolysis in the presence of oxygen to give acid groups (based on IR absorbance at 1713 cm^{-1}). It has also been suggested that an initial α-cleavage process followed by expulsion of carbon monoxide and carbon dioxide and recombination of resultant radicals can lead to a variety of coupling products[6,7,14-16,20,24,25] (refer to Scheme II). In this paper we report detection of the 2,2′-biphenolic coupling product during the very early stages of photolysis of polycarbonate, in addition to phenyl salicylate and salicylic acid type products, using fluorescence spectroscopy. Our results are in concert with and support the results reported by Lemaire *et al.*[16,18] Identification of these photoproducts is important since it gives us insight into the decomposition mechanism of polycarbonate and leaves little question as to the formation of such species during the very early stages of polycarbonate photolysis. Fluorescent photoproducts are formed even in sunlight as we will briefly describe at the end of the paper. Our results are of particular interest in view of the recent observation by Factor *et al.*[20] of the presence of photo-Fries products upon long-term exposure of polycarbonate to sunlight.

Scheme I. Photo-Fries Rearrangement



Experimental Section

Diphenyl carbonate (99%, Polyscyences) was recrystallized from methanol. Phenyl salicylate (99%, Aldrich) was recrystallized from methanol. Two different samples of polycarbonate (from General Electric) were used during the course of this investigation. The first (designated as sample A) was a FDA grade sample with at least some processing history. The second (sample B) was a Lexan 140 polycarbonate sample with no prior thermal history. Spectral results reported herein did not depend upon the sample which was used. However, for completeness we note that sample A was used to obtain data in Figure 9, while sample B was used to obtain data in the other figures. The bis(phenyl carbonate) of Bisphenol-A was synthesized and purified using the procedure reported by Humphrey and coworkers.[7] Spectral grade dichloromethane (DCM) and tetrahydrofuran (THF) from Burdick & Jackson were used. Polycarbonate films were cast from ca. 10 wt % solution in dichloromethane.

Salicylic acid (99+%), phenol (redistilled, 99+%), diphenyl ether (99%), 2-phenylphenol (99+%), 4,4′-biphenol (99+%, zone refined), and *tert*-butylphenol (99%) obtained from Aldrich were used without further purification. 4-Hydroxybenzoic acid phenyl ester (TCI America) was purified by reprecipitation from water/methanol mixture. Phenyl formate (95%, Lancaster) was vacuum distilled. 2,2′-Biphenol (99%, Aldrich) was purified by vacuum sublimation.

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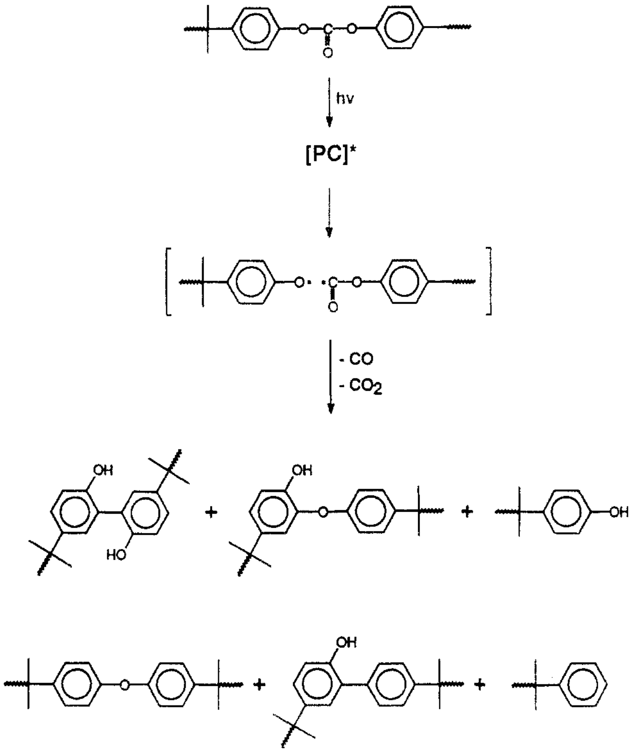
Scheme II. Coupling Products



Photolysis was carried out in air (unless otherwise mentioned) in a Rayonet reactor with 16 21-W lamps having a maximum of ca. 300 nm. The distance between the sample and the lamps is ca. 3 in. UV spectra were obtained on a Perkin-Elmer Lambda 6 UV–vis spectrophotometer, and fluorescence spectra were obtained on a SPEX Fluorolog-2. Chromatographic analysis of the samples was performed on a Hewlett-Packard 5890 gas chromatograph. High-performance liquid chromatographic analysis was performed on a Waters system (Model 6000A solvent delivery pump) with either a UV detector (Lambda Max Model 481, Waters) or fluorescence detector (Model 650 S from Perkin-Elmer).

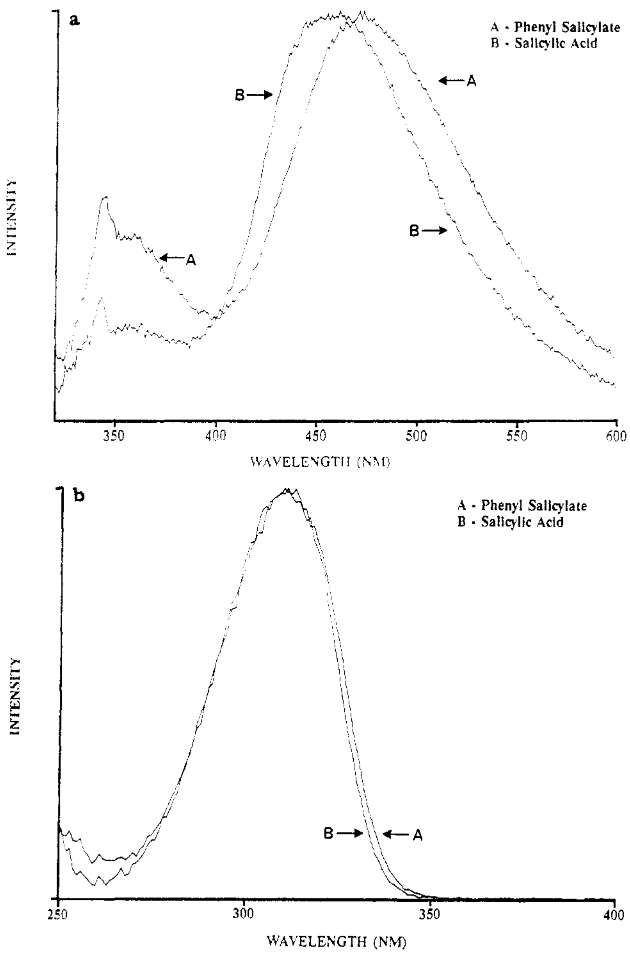


Figure 1. (a) Normalized fluorescence emission spectra (λ_{ex} = 310 nm) of phenyl salicylate (5×10^{-5} M) and salicylic acid (5×10^{-5} M) in DCM. (b) Normalized fluorescence excitation spectra of phenyl salicylate (5×10^{-5} M, λ_{em} = 470 nm) and salicylic acid (5×10^{-5} M, λ_{em} = 460 nm) in DCM.

Results and Discussion

In a previous paper[26] we showed that it was possible to use fluorescence spectroscopy to identify photoproducts during the very early stages of polycarbonate photolysis. We indicated that photoproducts could be identified via characteristic fluorescence emission, according to peaks having maxima at ca. 470–480 nm in dichloromethane. In this paper, we employ fluorescence spectroscopy to identify the formation of biphenolic and salicylic acid type products produced during photolysis of both appropriate model compounds and polycarbonate. The salicylic acid chromophores are formed as a result of the secondary photolysis of phenyl salicylate type photoproducts which themselves are generated in the initial photolysis step. In our previous analysis,[26] we had assigned an emission with maximum around 470 nm produced upon photolysis of both polycarbonate and diphenyl carbonate to a photo-Fries product, produced according to the simple pathway in Scheme I. Interestingly, this original analysis was performed upon samples in dichloromethane, a solvent in which both phenyl salicylate and salicylic acid have similar fluorescence emission and excitation energy maxima (470 nm for phenyl salicylate and 460 nm for salicylic acid). This did not allow for their absolute differentiation (see Figure 1). In the ensuing discussion, we will describe a procedure which allows the detection of salicylic acid as well as phenyl salicylate by fluorescence spectroscopy. By application of this analysis technique to photolyzed solutions of diphenyl carbonate and polycarbonate, we will demonstrate that both products are indeed formed during the early stages of exposure (short photolysis times). By careful extension to polycarbonate films, the production of salicylic acid type products during the initial stages of polycarbonate photolysis will be established. In addition, we will also utilize fluorescence spectroscopy to show that the 2,2′-biphenolic product, as one would expect based on the results in refs 14 and 16, is indeed generated in the very early stages of polycarbonate photolysis. Implications of the detection of the fluorescent photoproducts upon photolysis of polycarbonate films in sunlight will be briefly touched upon in a prelude to a full paper which will describe the photolysis of polycarbonate at wavelengths corresponding to those comprising sunlight.

A. Model Compound Photolysis. Figure 2 shows emission and excitation spectra (λ_{ex} = 310 nm) for diphenyl carbonate in dichloromethane (DCM) and tetrahydrofuran (THF). Diphenyl carbonate does not absorb at wavelengths greater than 280 nm, and hence when excited at 310 nm (before photolysis) no fluorescence is observed in either DCM or THF. Upon photolysis, fluorescence bands with maxima around 350 and 470 nm in DCM and 350 and 410 nm in THF develop upon excitation at 310 nm. Why the large difference between results in DCM and THF: Is it a result of different products being formed in THF and DCM, or do the photoproducts fluoresce at different wavelengths in the two solvents? In Figure 3, the fluorescence spectra of phenyl salicylate and salicylic acid in THF are provided for comparison with the results in

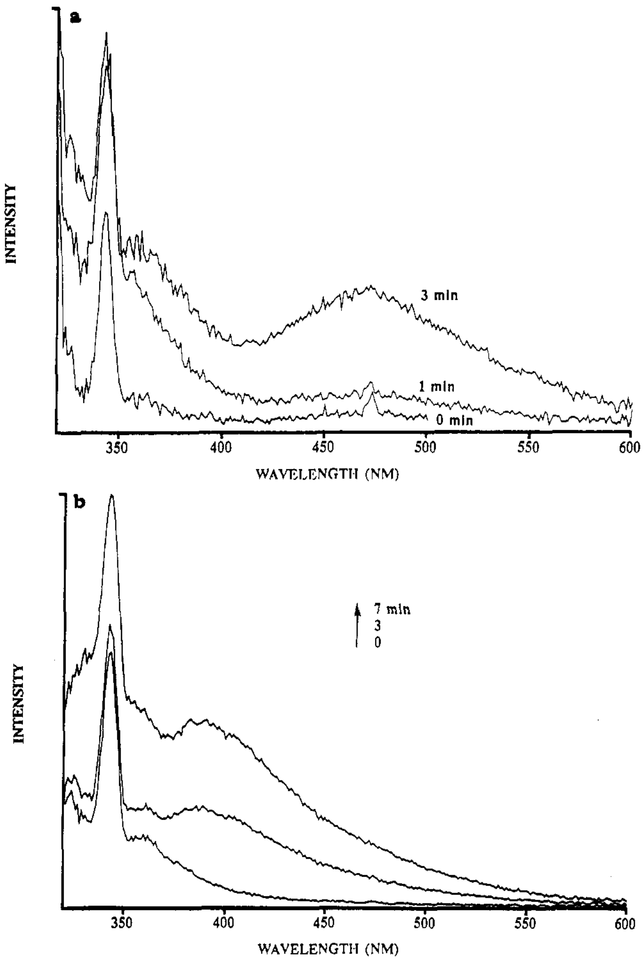


Figure 2. (a) Fluorescence emission spectra (λ_{ex} = 310 nm) of DPC (4.5 × 10^{-3} M) in DCM for 0-, 1-, and 3-min photolysis in a Rayonet reactor with 300-nm lamps.[26] (b) Fluorescence emission spectra (λ_{ex} = 310 nm) of DPC (4.5 × 10^{-3} M) in THF for 0-, 3-, and 7-min photolysis in a Rayonet reactor with 300-nm lamps.

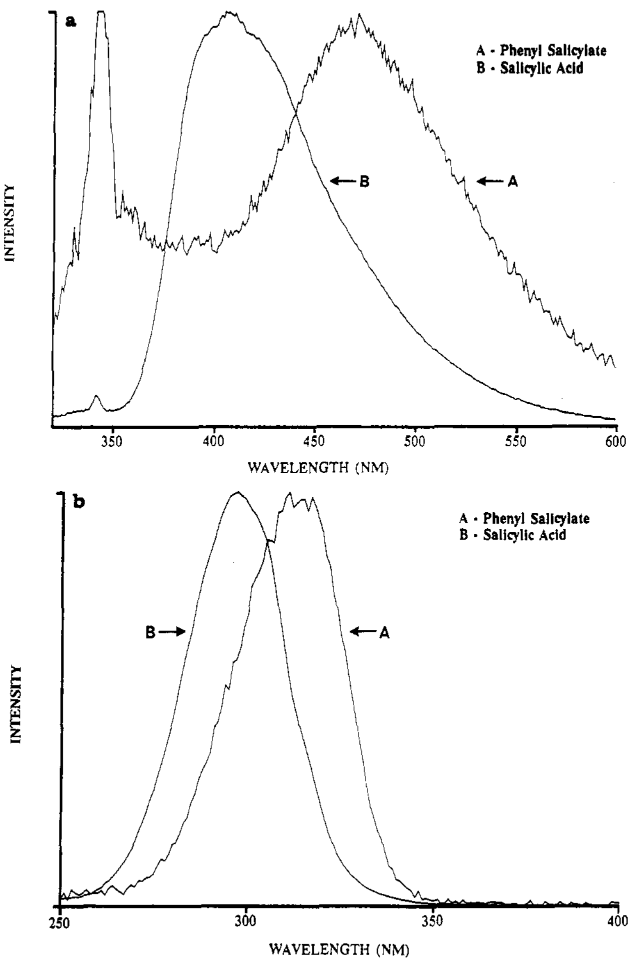


Figure 3. (a) Normalized fluorescence emission spectra (λ_{ex} = 310 nm) of phenyl salicylate (5 × 10^{-5} M) and salicylic acid (5 × 10^{-5} M) in THF. (b) Normalized fluorescence excitation spectra of phenyl salicylate (5 × 10^{-5} M, λ_{em} = 470 nm) and salicylic acid (5 × 10^{-5} M, λ_{em} = 410 nm) in THF.

Figure 1. A cursory examination reveals that while phenyl salicylate shows little difference in the fluorescence emission maxima in DCM (470 nm) and THF (465 nm), salicylic acid has an emission maximum which is markedly blue shifted in THF (410 nm) compared to DCM (460 nm). The blue shift in THF results from a disruption in the internal hydrogen bonding of salicylic acid by the ether functionality of THF.[27] This remarkable blue shift in THF for salicylic acid does not occur for phenyl salicylate. Hence, we have a convenient method for differentiating between emission from salicylic acid and phenyl salicylate. This blue shift for salicylic acid in THF is accompanied by about a 20-fold increase in the fluorescence intensity, hence making fluorescence analysis in THF extremely sensitive for early detection of salicylic acid. By comparison of the photolysis results for diphenyl carbonate in THF (Figure 2b) with the blue-shifted emission for salicylic acid in THF in Figure 3a, one can postulate that indeed photolysis of diphenyl carbonate in THF leads to the eventual formation of salicylic acid, no doubt via the photolysis of phenyl salicylate (the primary photolysis product of diphenyl carbonate). The presence of both phenyl salicylate and salicylic acid upon photolysis of diphenyl carbonate in THF is confirmed by comparison of HPLC retention times of the diphenyl carbonate photolyzed reaction mixture with authentic samples of phenyl salicylate and salicylic acid. We note that HPLC identification of phenyl salicylate and salicylic acid is facilitated by analysis of a photolyzed sample at very short photolysis times before phenyl salicylate and salicylic acid themselves are consumed by photolysis. In other words, the steady-state concentrations of phenyl salicylate and salicylic acid are quite small for photolysis of diphenyl carbonate with a lamp source such as the 300-nm (broad emission centered at 300 nm) Rayonet lamps used in this study.

Before completing our discussion of the method for determination of salicylic acid in photolyzed solutions of diphenyl carbonate, we should point out that identification of the precursor phenyl salicylate can be facilitated by recording excitation spectra of photolyzed THF solutions of DPC at several emission wavelengths. Since the fluorescence of phenyl salicylate is red shifted by ca. 50 nm from salicylic acid, excitation spectra recorded for emission monochromator settings greater than 450 nm should show a larger contribution from the phenyl salicylate component (if present) than excitation spectra obtained corresponding to emission monochromator settings at 410 nm, where the contribution to the total fluorescence intensity is dominated by salicylic acid. The shift expected in the excitation spectrum of the photolyzed DPC solution is a direct result of an ≈10-nm blue shift in the excitation spectrum of pure salicylic acid in THF compared to phenyl salicylate in THF (Figure 3b). Figure 4 shows excitation spectra recorded for a diphenyl carbonate solution in THF photolyzed for 3 min. The blue shift in the excitation spectrum recorded for emission at 400 nm (compared to the spectrum recorded for emission at 470 nm) indicates that both phenyl salicylate and salicylic acid are present: We note that, as described

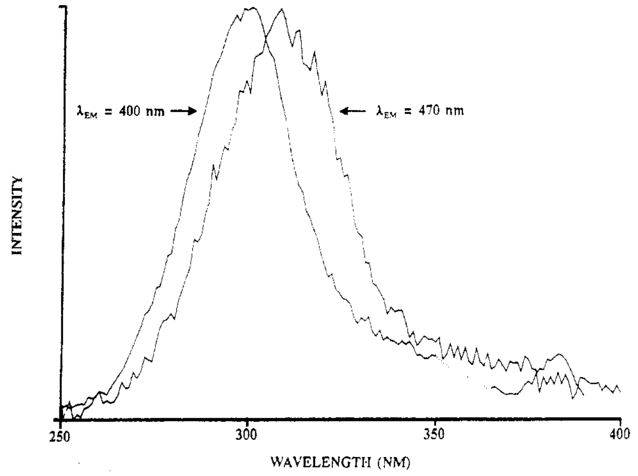


Figure 4. Normalized fluorescence excitation spectra (λ_{em} = 400 and 470 nm) of DPC (4.5×10^{-3} M) in THF photolyzed for 3 min in a Rayonet reactor with 300-nm lamps. A scatter peak around 355 nm has been removed artificially.

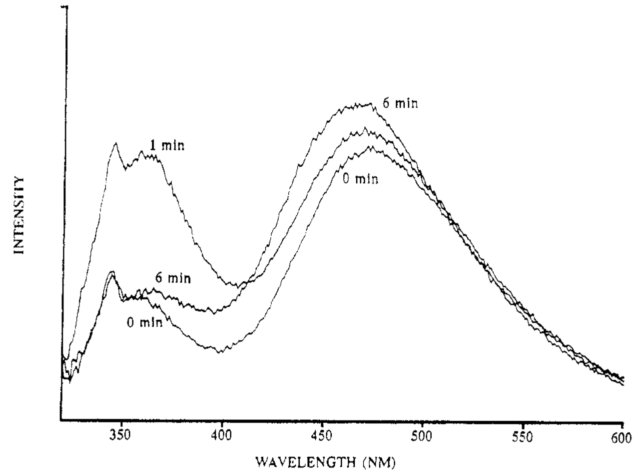


Figure 5. Fluorescence emission spectra (λ_{ex} = 310 nm) of phenyl salicylate (5×10^{-5} M) in DCM for 0-, 1-, and 6-min photolysis in a Rayonet reactor with 300-nm lamps.

earlier, this is exactly the result obtained by HPLC analysis of the photolyzed solution. Incidentally, although not shown herein, independently prepared solutions of phenyl salicylate and salicylic acid exhibited no wavelength dependency for the excitation spectra. Hence, based on a combination of emission and excitation spectra, it is possible to identify the formation of both salicylic acid and phenyl salicylate products formed in the early stages of photolysis of diphenyl carbonate.

To clarify the origin of the salicylic acid and verify that it is indeed formed upon photolysis of the photo-Fries product phenyl salicylate, independently prepared solutions of phenyl salicylate in DCM and THF were subjected to the identical photolysis conditions employed for the diphenyl carbonate photolysis. In both cases, HPLC, GC, and fluorescence analysis (Figures 5 and 6) indicate the formation of salicylic acid after short photolysis times. In THF, as would be expected by examination of the fluorescence from phenyl salicylate and salicylic acid in Figures 1a and 3a, the shift in the fluorescence maximum with photolysis time from 460 to 410 nm is dramatic while in DCM it is rather modest. The large increase in overall fluorescence intensity in THF compared to DCM is a result of the much higher fluorescence quantum yield (ca. 20 times greater) for salicylic acid in THF. The generation of salicylic acid upon photolysis of phenyl salicylate in both protic and nonprotic solvent was reported over two decades ago.[28] Our present analysis not only serves to reiterate this important point but also establishes the utilization of fluorescence spectroscopy as an analysis tool for detection of salicylic acid in the very early stages of phenyl salicylate photolysis. Use of fluorescence as an analysis method will be shown to be an invaluable method for investigation of polycarbonate film photolysis. It is the difference in the fluorescence emission maximum in DCM and THF which will be utilized for identification of salicylic acid type chromophores upon photolysis of polycarbonate films.

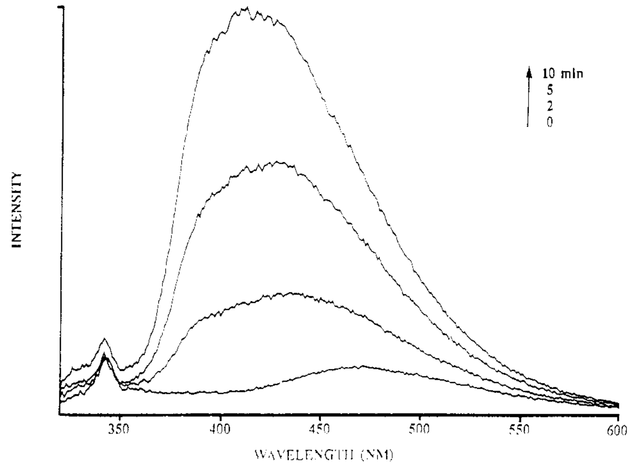
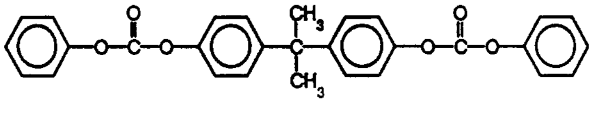


Figure 6. Fluorescence emission spectra (λ_{ex} = 310 nm) of phenyl salicylate (4.9×10^{-5} M) in THF for 0-, 2-, 5-, and 10-min photolysis in a Rayonet reactor with 300 nm lamps.

Before turning to an analysis of polycarbonate film photolysis, we want to consider the photolysis of another model compound for polycarbonate, i.e., the bis(phenyl carbonate) of Bisphenol-A (see structure below). Figure



7a shows the emission spectra of the model recorded at short photolysis times (rayonet reactor, 300-nm lamps) in THF. The emission maximum at 410 nm corresponds to a salicylic acid type product. Figure 7b shows the excitation spectra (λ_{em} = 400 and 470 nm) for the model compound in THF after photolysis at 300 nm for 3 min. The excitation spectra maxima for emission at 400 nm (near salicylic acid maximum) are blue shifted compared to the excitation spectra recorded for emission at 470 nm where the emission is primarily from phenyl salicylate. Hence, we conclude from the results in Figure 7 for the more exacting (compared to DPC) model for polycarbonate that photolysis leads to the formation of salicylic acid in the very early stages of photolysis.

One last consideration must be given attention prior to presenting the fluorescence analysis results for polycarbonate. Figures 2a, 2b, and 7a clearly show the presence of a prominent second peak (well below 400 nm) in the fluorescence spectra of the photolyzed DPC and polycarbonate model compounds. To provide a reasonable explanation for the appearance of this peak at such short photolysis times, a large number of potential photoproducts[6,7,14-16,20,24,25] were screened for their fluorescence spectral characteristics: Table I provides a listing of fluorescence emission and UV–visible absorption maxima in DCM of these compounds. Only 2,2′-biphenol and 4,4′-biphenol have emission maxima above 340 nm. During photolysis of DPC, one would expect formation of all isomers of biphenols, viz., 2,2′-, 4,4′-, and 2,4′-biphenols. However, during photolysis of polycarbonate and the

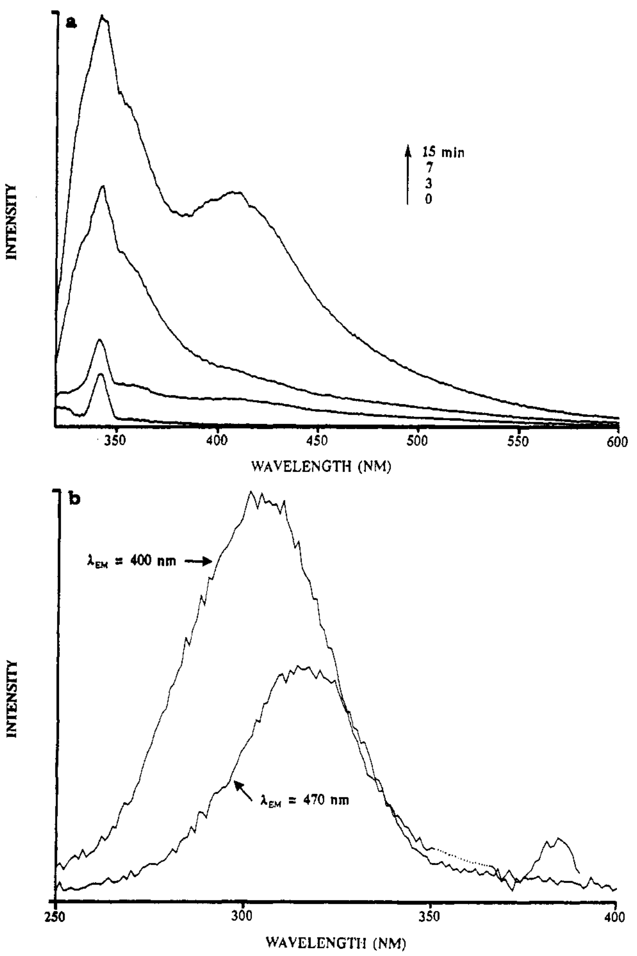


Figure 7. (a) Fluorescence emission spectra (λ_{ex} = 310 nm) of the bis(phenyl carbonate) of Bisphenol-A (5.5 × 10^{-4} M) in THF for 0-, 3-, 7-, and 15-min photolysis in a Rayonet reactor with 300-nm lamps. (b) Fluorescence excitation spectra (λ_{em} = 400 and 470 nm) of the bis(phenyl carbonate) of Bisphenol-A (5.5 × 10^{-4} M) in THF photolyzed for 3 min in a Rayonet reactor with 300-nm lamps. A scatter peak around 355 nm has been removed artificially.

Table I. Fluorescence Emission and UV-Visible Absorption Maxima of Possible Model Photolysis Products Recorded in DCM

compound	$\lambda_{absorption}$, nm (maximum)	$\lambda_{fluorescence}$, nm (maximum)
4-hydroxybenzoic acid phenyl ester (in THF)	261	315–330
phenyl formate	262	302
phenol	271	300
diphenyl ether	272	300
2-phenylphenol	284	333
2,2′-biphenol (in THF)	282	350
4,4′-biphenol (in THF)	265	352
tert-butylphenol	276	305

bis(phenyl carbonate) of Bisphenol-A, since the para positions to the carbonate group are blocked, only the 2,2′-biphenol type product can be formed. The emission spectrum (excitation at 310 nm) of 2,2′-biphenol in THF is shown in Figure 8. The resemblance of the spectrum in Figure 8 for 2,2′-biphenol and the spectrum of the photolyzed model in Figure 7a is striking, suggesting that a 2,2′-biphenolic product, in addition to phenyl salicylate and salicylic acid type products, is produced upon photolysis at short times. [The peak in Figures 2a, 2b, 7a, and 8 at wavelengths slightly less than 350 nm is due to a solvent scattering resulting from excitation at 310 nm: The real maxima of 2,2′-biphenolic compounds in all those spectra are 350 nm or above.] This result is consistent with expulsion of carbon monoxide from the arylformoxyl radical species, generated by the initial α-cleavage of the oxygen–carbonyl carbon bond, and recombination with the corresponding aryloxy group in the solvent cage before diffusion occurs (see Scheme II). Such aryloxy coupling products were indeed suggested by a previous investigation of polycarbonate[14,16] as well as a model system.[6,24] Furthermore, Horspool and Pauson[25] had reported that traces of di-*tert*-butyldiphenol coupling products were obtained upon photolysis of appropriate diaryl carbonate models in solution. We also find evidence via HPLC analysis and comparison with an appropriate authentic sample for the formation of 2,2′-biphenol and 4,4′-biphenol upon photolysis of DPC in DCM or THF at 254 nm. Due to lack of an authentic sample, formation of the 2,4′-biphenol isomer during photolysis of DPC in DCM (or THF) could not be confirmed even though the HPLC analysis exhibited a peak where we would expect 2,4′-biphenol to appear.

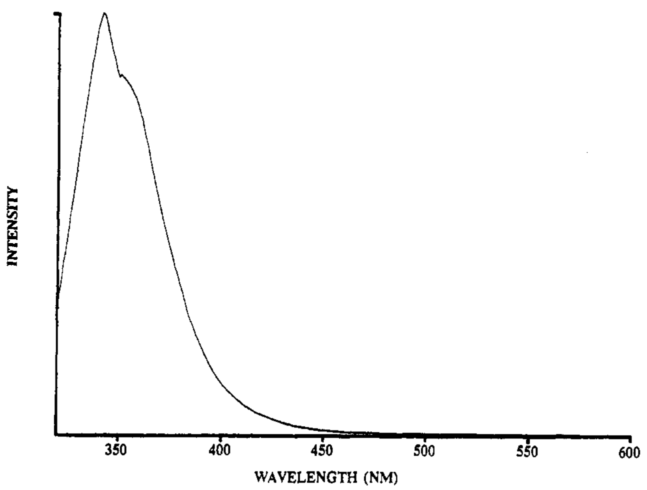


Figure 8. Fluorescence emission spectrum (λ_{ex} = 310 nm) of 2,2′-biphenol (5 × 10^{-5} M) in THF.

It is intuitively obvious that biphenolic coupling products should be formed for polycarbonate photolysis since there is a significant expulsion of carbon monoxide from polycarbonate films upon exposure to light.[4,11,20] Having established a viable tool, i.e., fluorescence spectroscopy, for detection of biphenolic type products, it is now possible to analyze films of polycarbonate photolyzed at very short times for the presence of biphenolic type products, as well as the phenyl salicylate and salicylic acid derivatives already discussed.

B. Polycarbonate Photolysis. Separation and identification of the photoproducts formed during the photolysis of any polymer, including polycarbonate, is extremely difficult. However, comparison of the fluorescence results for the photolysis of the model compounds and the polycarbonate (conducted under the same conditions) can give us a fairly reliable analysis for the types of photoproducts formed. We begin by solution photolysis of polycarbonate before extension to films. We had previously shown that photolysis of polycarbonate in DCM resulted in an increase in the fluorescence emission spectrum with a maximum around 470 nm.[26] This red-shifted fluorescence is due to phenyl salicylate and salicylic acid type photoproducts: The presence of both phenyl salicylate (λ_{max} = 470 nm in DCM) and salicylic acid (λ_{max} = 460 nm in DCM) is difficult to specify by just recording the emission spectrum in DCM as discussed previously in this paper for the model system photolysis. However, by recording the excitation spectra of the photolyzed polycarbonate solution in THF at different wavelengths between 400 and 500 nm, the presence of two species, i.e.,

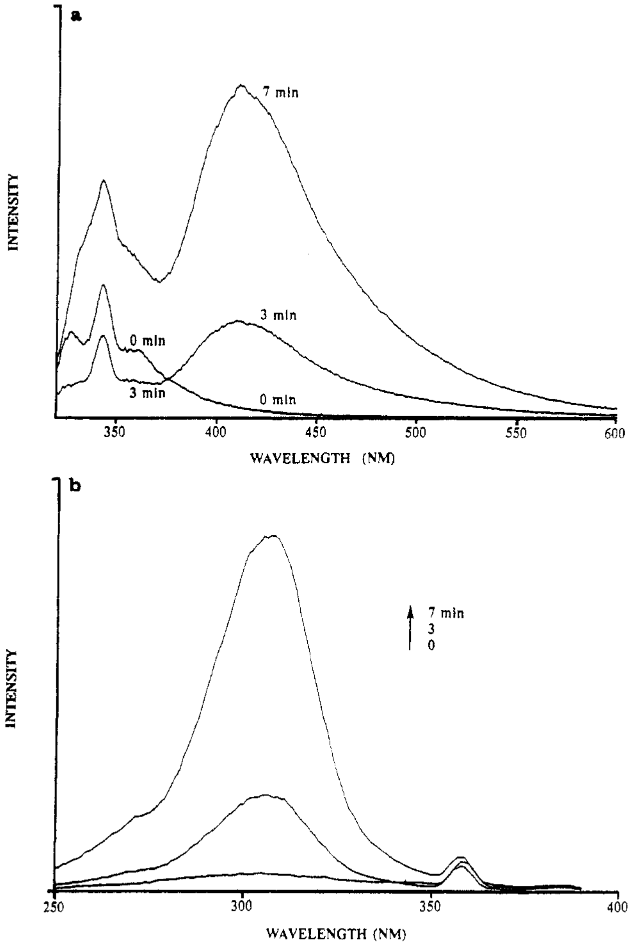


Figure 9. (a) Fluorescence emission spectra (λ_{ex} = 310 nm) of polycarbonate (6.4 × 10^{-4} M) in THF for 0-, 3-, and 7-min photolysis in a Rayonet reactor with 300-nm lamps. (b) Fluorescence excitation spectra (λ_{em} = 400 nm) of polycarbonate (6.4 × 10^{-4} M) in THF for 0-, 3-, and 7-min photolysis in a Rayonet reactor with 300-nm lamps.

phenyl salicylate and salicylic acid, can be inferred. Hence, of particular interest are the excitation and emission spectra (λ_{ex} = 310 nm) for photolyzed polycarbonate in THF (Figure 9). The fluorescence buildup around 410 nm (Figure 9a) is similar to that observed for the photolysis of the BPA-based model in THF (Figure 7a), photolysis of diphenyl carbonate in THF (Figure 2b), and the photolysis of phenyl salicylate in THF (Figure 6): All match the emission maximum for salicylic acid in THF (Figure 3a). The peak maxima for the photolyzed polycarbonate in THF occurring near 300 nm in the excitation spectra (λ_{em} = 410 nm, Figure 9b) are also quite consistent with the formation of a salicylic acid type photoproduct. The peak with maximum between 350 and 360 nm for the photolyzed polycarbonate in THF, by comparison with the spectrum in Figure 8, is indicative of formation of biphenolic type photoproducts at short photolysis times. Excitation spectra (Figure 10) obtained for photolyzed polycarbonate in THF (3-min sample) for emission at 470 nm (phenyl salicylate and salicylic acid type products), 400 nm (salicylic acid type product), and 370 nm (biphenolic type product) show the progressive shift of the excitation maxima to high energies (blue shift) expected for fluorescence corresponding to the presence of multiple chromophoric groups as listed in parentheses.

Extending our analysis to polycarbonate films, Figure 11 shows emission spectra (λ_{ex} = 325 nm) for the polycarbonate film in air before and after photolysis. As for the model compounds and polycarbonate in THF, the fluorescence maxima for the photolyzed film are observed at ca. 360 and 470 nm [note the absence of the solvent scatter peak maximum just less than 350 nm which occurs for the spectra in DCM or THF in Figures 2a, 2b, 7a, 8 and 9a]. The fluorescence buildup around 360 nm is strikingly similar to that for the photolysis of DPC (Figure 2b), the model compound (Figure 7a), and polycarbonate in DCM (not shown) and THF (Figure 9a). The fluorescence buildup around 450–500 nm is broad and could be due to phenyl salicylate and/or salicylic acid type photoproducts. To establish the species responsible for the emission from 450 to 500 nm, photolyzed polycarbonate films were dissolved in DCM and in THF. Parts a and b of Figure 12 show the emission spectra (λ_{ex} = 310 nm) for the photolyzed film dissolved in DCM and THF, respectively. The distinct red shift in the maximum for 470 nm in DCM to 410 nm in THF clearly identifies the presence of a salicylic acid type photoproduct: The increase in fluorescence intensity and shift to 410 nm (with corresponding excitation maximum near 300 nm) are unmistakable. Evidence for phenyl salicylate and biphenolic type products can also be inferred from the excitation spectra for the photolyzed polycarbonate film in THF shown in Figure 13 for emission wavelengths of 470 nm (phenyl salicylate type product), 410 nm (salicylic acid type product), and 360 nm (biphenolic type product).

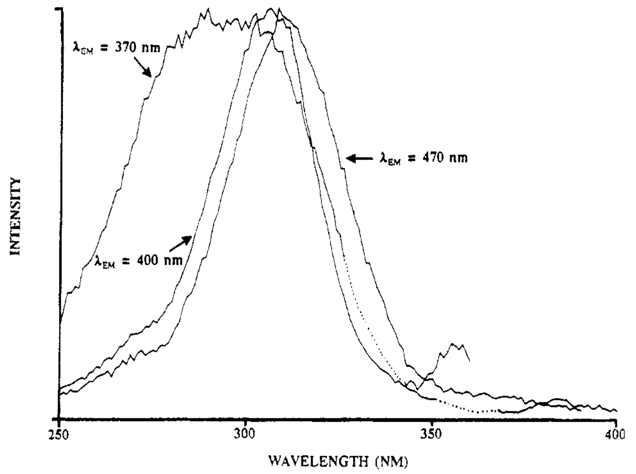


Figure 10. Normalized fluorescence excitation spectra (λ_{em} = 370, 400, and 470 nm) of polycarbonate (6.4 × 10^{-4} M) in THF photolyzed for 3 min in a Rayonet reactor with 300-nm lamps. Scatter peaks around 335 and 355 nm have been removed artificially.

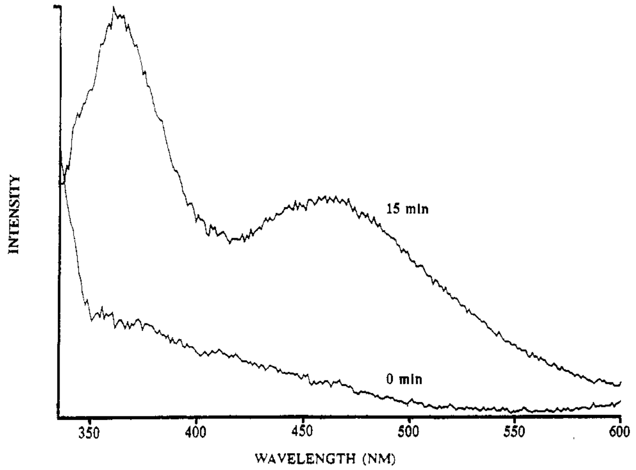


Figure 11. Fluorescence emission spectra (λ_{ex} = 325 nm) of polycarbonate film before and after photolysis for 15 min in a Rayonet reactor with 300-nm lamps.

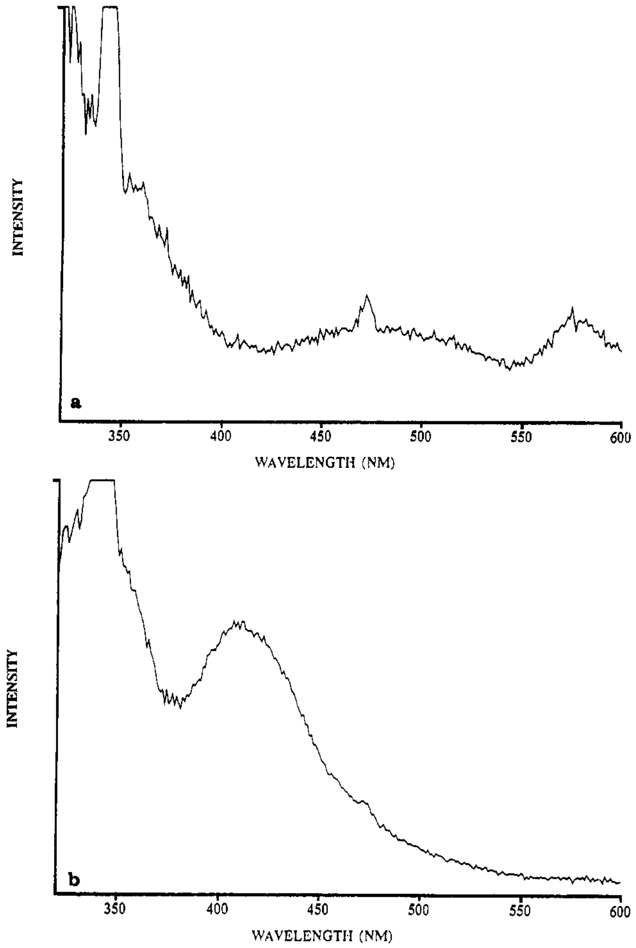


Figure 12. (a) Fluorescence emission spectrum (λ_{ex} = 310 nm) of photolyzed polycarbonate film in DCM (6.5 × 10^{-4} M). Polycarbonate film was photolyzed for 15 min in a Rayonet reactor with 300-nm lamps. (b) Fluorescence emission spectrum (λ_{ex} = 310 nm) of photolyzed polycarbonate film in THF (6.5 × 10^{-4} M). Polycarbonate film was photolyzed for 15 min in a Rayonet reactor with 300-nm lamps.

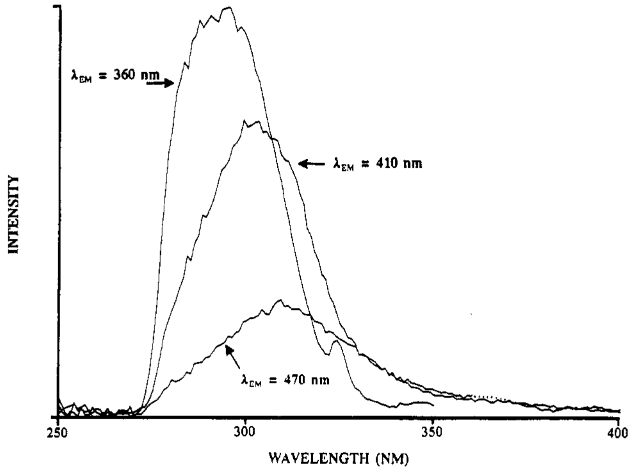


Figure 13. Fluorescence excitation spectra (λ_{em} = 360, 410, and 470 nm) of photolyzed polycarbonate film in THF (6.5 × 10^{-3} M). Polycarbonate film was photolyzed for 1 h in flowing oxygen in a Rayonet reactor with 300-nm lamps. A scatter peak around 365 nm has been removed artificially.

To formulate a viable mechanism for phenyl salicylate photolysis to give salicylic acid, one must presume that oxygen is necessary for the formation of the salicylic acid type product. To verify the effect of oxygen on the formation of the salicylic acid, photolysis of a thin polycarbonate film (cast in nitrogen in a drybox to avoid any residual oxygen in the film) was carried out in vacuum.

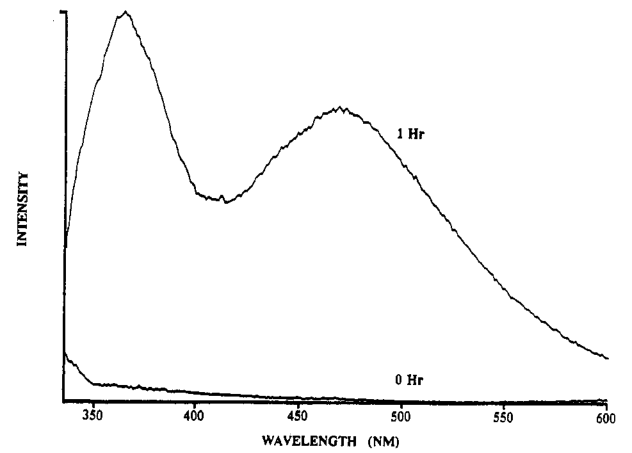


Figure 14. Fluorescence emission spectra (λ_{ex} = 325 nm) of polycarbonate film cast in nitrogen before and after 1-h photolysis in vacuum in a Rayonet reactor with 300-nm lamps.

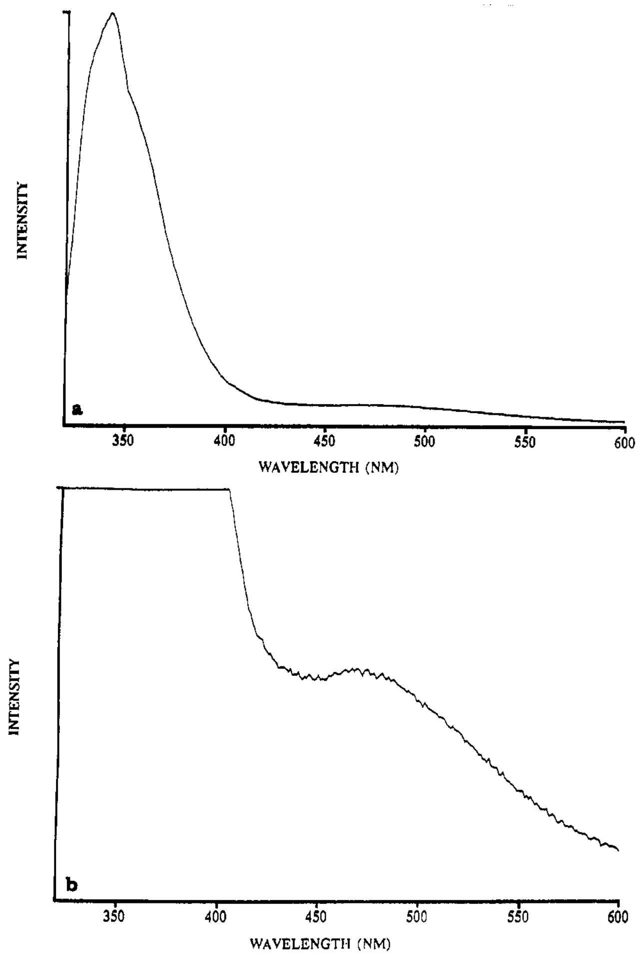


Figure 15. (a) Fluorescence emission spectrum (λ_{ex} = 310 nm) of photolyzed polycarbonate (cast in nitrogen) film in THF (6.5 × 10^{-3} M). The polycarbonate was photolyzed for 1 h in vacuum in a Rayonet reactor with 300-nm lamps. (b) Expanded view of (a).

Figure 14 shows the emission spectra of the nitrogen-cast polycarbonate film before and after photolysis in vacuum: An increase in fluorescence intensity is observed with peak maxima at ~360 and 470 nm. The fluorescence from 450 to 500 nm is due to either a phenyl salicylate type photoproduct, a salicylic acid type photoproduct, or both as was found for photolysis in air. To determine if salicylic acid is present or not, the spectrum of the film (cast in nitrogen, photolyzed in vacuum, and finally dissolved in THF) was recorded in THF (Figure 15a,b): It is obvious that salicylic acid, which fluoresces around 410 nm in THF,

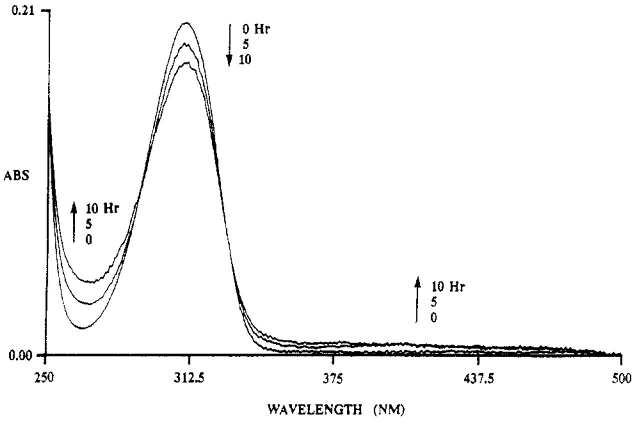


Figure 16. UV–visible spectra of salicylic acid (OD = 0.2 at 310 nm) in DCM for 0-, 5-, and 10-h photolysis at 310 nm (10-nm band-pass, 450-W Xe lamp).

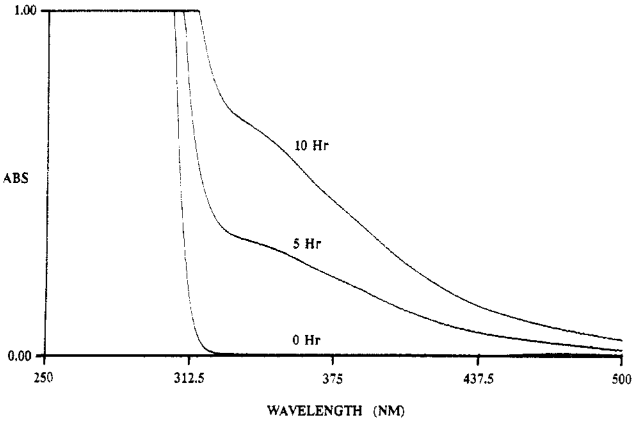


Figure 17. UV–visible spectra of 2,2′-biphenol (OD = 0.2 at 310 nm) in DCM for 0-, 5-, and 10-h photolysis at 310 nm (10-nm band-pass, 450-W Xe lamp).

is not present. In addition to the peak at 360 nm, we observe only a weak, broad fluorescence with a maximum around 460 nm (this is quite clear from the expanded view in Figure 15b) which corresponds to the phenyl salicylate type photoproduct (confirmed by a peak around 310 nm in the excitation spectrum not shown). We conclude that the presence of phenyl salicylate and the lack of salicylic acid (absence of 410-nm emission) in the photolyzed polycarbonate film indicate that oxygen is necessary for the formation of the salicylic acid. This final result is importance since during natural weathering, oxygen is present and salicylic acid would be expected to form.

C. Photolysis of Salicylic Acid and 2,2′-Biphenol. While our results to this point indicate the formation of salicylic acid and 2,2′-biphenolic type products in the very early stages of photolysis of polycarbonate films, as well as appropriate model compounds for the carbonate repeat unit in the backbone, we must still indicate the potential importance of these chromophores to degradation phenomena and color formation in polycarbonate. Figures 16 and 17 show the UV spectra of photolyzed DCM solutions of salicylic acid and 2,2′-biphenol as a function of time. A 450-W xenon lamp/monochromator system with a 10-nm spectral band output centered around 310 nm was employed to photolyze the DCM solutions. Although the initial absorbances at 310 nm were equalized, it should be noted that the spectral overlap of the excitation source (if monochromator bandwidth is taken into account) was greater for salicylic acid than 2,2′-biphenol. In this very rough preliminary analysis of the photolability (with respect to color formation) of the two photoproducts identified herein to form in the early stages of polycarbonate (or diaryl carbonate) photolysis, it seems obvious that both 2,2′-biphenol and salicylic acid are active in color production, with 2,2′-biphenol being the more photolabile. Hence, the early detection of salicylic acid and 2,2′-biphenol in the photolysis of polycarbonate films is important in assessment of the overall discoloration process.

Finally, it should be mentioned that we have found that photolysis of polycarbonate film in sunlight leads to formation of fluorescent photoproducts upon exposure times of only a few days. Thus the present study is important in providing a sound framework for the critical analysis of polycarbonate photolysis in sunlight via fluorescence spectroscopy. In a separate publication, we will expand upon this subject.

Conclusions

In this paper, the fluorescence analysis of polycarbonate and its model compounds in DCM and THF has allowed the study of various aspects of the photolytic decomposition of polycarbonate. Our results are in concert with published literature reports as exemplified in refs 16 and 20 and underscore the importance of early detection and identification of primary photoproducts, which themselves are often photolabile (as pointed out in this paper and the results in refs 14 and 16). Results from our study indicate the following:

1. Fluorescence spectroscopy is a sensitive and a selective technique that can be used to differentiate between phenyl salicylate and salicylic acid type products formed in the very early stages of photolysis of polycarbonate and its model compounds.
2. Fluorescence analysis can be utilized to detect 2,2′-biphenol type products in polycarbonate and its model compounds in the initial stages of photolysis.
3. Oxygen is needed for the formation of salicylic acid type products in photolyzed polycarbonate films.
4. Salicylic acid and 2,2′-biphenol are photolabile and form colored products on photolysis.

The utility of fluorescence as an effective technique for early detection of several photoproducts at the initial stages of the photolysis process is clearly evident. Detection of key products during the early stages of photolysis of polycarbonate in sunlight and at wavelengths greater than 300 nm will be addressed in the next paper in this series.

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