Macromolecules **1994**, *27*, 3773–3781

Photochemistry and Photodegradation of Polycarbonate

Surapol Pankasem, Joseph Kuczynski,[†] and J. Kerry Thomas*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46656

Received January 19, 1994; Revised Manuscript Received April 20, 1994[●]

ABSTRACT: Photophysical and photochemical techniques were used to investigate the photodegradation of Bisphenol A polycarbonate (PC), with diphenyl carbonate as a model compound. UV excitation of these compounds leads to a fluorescence band with a maximum around 300 nm. The triplet state of PC is also observed both by transient absorption and by phosphorescence studies. The PC triplet in dichloromethane solution interacts with oxygen, ferrocene, *trans*-piperylene, and perylene with rate constants of 6.25×10^8, 2.89×10^8, 3.05×10^8, and 5.60×10^8 M^{-1} s^{-1}, respectively. A comparison of the absorption and the fluorescence data of the photointermediates and products of photolysis of diphenyl carbonate to those of polycarbonate indicated that degradation of the polymer, which is enhanced by oxygen, is mainly due to photooxidation rather than to a photo-Fries rearrangement. Generation of singlet oxygen in PC does not lead to degradation, and studies showed that the triplet state of the polymer was not involved in the degradation process. It is suggested that C–C bond scission occurs from the short-lived singlet excited state of polycarbonate.

Introduction

Photostability of polymers is an important factor used to evaluate the qualities of such materials; most polymers tend to lose many of their desirable properties upon exposure to light. Polycarbonates have been a popular choice for many industrial products because of their superior technical properties, which include transparency, tensile strength, impact resistance, and rigidity. However, photodegradation of polycarbonates has been of some concern.[1–8] A number of reports have been filed in relation to the degradation of these polymers; nevertheless most of these reports emphasize only the photo-Fries rearrangement, which involves rearrangement of polymer chains, rather than photooxidation involving chain scission. Until now, the exact mechanism of the degradation process was still in question and required further clarification. The recent work of Hoyle and co-workers[9] and the present study both address the above problem.

It is relevant to study the photophysical and photochemical properties of polycarbonate to elucidate the arguments concerning the photodegradation of polycarbonate. Only a few studies have been reported concerning the photophysics of PC.[10,11] Diphenyl carbonate, one of the monomer units in Bisphenol A polycarbonate, is used as a model compound for the photochemistry and the photodegradation of polycarbonate. This work presents fluorescence and phosphorescence (both steady-state and time-resolved) studies of polycarbonate both in solution and in the solid form. The studies reveal behavior of excited states of PC, which may be involved in the photodegradation process; this work also reports, for the first time, the absorption spectrum of the triplet of PC. The PC triplet may be a crucial intermediate in the degradation, which may involve singlet oxygen. Reactions of the PC triplet with triplet quenchers such as molecular oxygen and ferrocene are also presented to elucidate the degradation process.

Experimental Section

Materials. Bisphenol A polycarbonate, with an average molecular weight of 29 000, was received from Aldrich. Diphenyl carbonate (Aldrich), phenyl salicylate (Aldrich), 2,2′-dihydroxybenzophenone (Aldrich), cyclohexane (HPLC grade, Aldrich), tetrahydrofuran (HPLC grade, Aldrich), and dichloromethane (Fisher) were used as received.

Purified Bisphenol A polycarbonate was generously provided by Prof. C. E. Hoyle from the University of Southern Mississippi.[9]

Sample Preparation. Polycarbonate films were cast from dichloromethane solutions of the polymer. The film was dried in a vaccum oven overnight to remove any residual solvent in the film. In some cases, films were placed under high vacuum for at least 5 h to eliminate oxygen in the film.

Method. Absorption spectra were obtained with a Cary 3 spectrophotometer, and steady-state fluorescence spectra were measured with an SLM spectrofluorometer Model SPF 500C.

Phosphorescence spectra were measured with a Perkin-Elmer MPF-44B spectrofluorometer, which is equipped with a phosphorescence attachment.

Time-resolved fluorescence experiments were performed in the following manner: the samples were excited with a pulsed laser (Lambda-Physik Model EMG 100 Xe–Cl excimer laser) which produces a 308-nm laser phase (40 mJ and FWHM of 6 ns), and the emitted light is observed at 90° after being collected and focused through a series of lenses, passed through an appropriate Corning cutoff filter into a Bausch and Lomb diffraction monochromator, and finally focused onto a Hamamatsu R 1664U multichannel plate. The electrical signal is amplified with a Tektronix 7A29 amplifier (response time = 0.7 ns), then captured with a Tektronix 7912 AD 500-MHz waveform programmable digitizer with a Tektronix 7B10 timebase, and finally transferred to a Zenith Z-200 IBM PC-AT compatible computer.

Transient absorption studies were carried out in a similar manner, with an Oriel 450-W Xe lamp placed directly in line with the sample cell holder and the monochromator. A PRA Model 305 pulser and PRA Model 302 power supply were used to generate pulses of analyzing light with adjustable amplitude and lifetimes up to 500 amp and 10 ms, respectively. The resultant light was collected and focused by two lenses, passed through a monochromator, and then transferred for measurement to an RCA IP 128 photomultiplier tube.

Average molecular weights and molecular weight distributions of polymers were measured by size exclusion chromatography with a Waters HPLC system, which was equipped with a Waters 501 HPLC pump and a Lamba-Max Model 481 LC spectrophotometer. A series of two Ultrastyragel columns (linear) were used along with tetrahydrofuran as an eluent. The calibration was performed with polystyrene primary standards with molecular weights ranging from 2000 to 600 000. The PC secondary standard was then used to correct the numbers with a conversion factor of 0.88.

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* Author to whom correspondence should be addressed.

[†] IBM Corp., Rochester, MN 55901.

[●] Abstract published in *Advance ACS Abstracts*, June 1, 1994.

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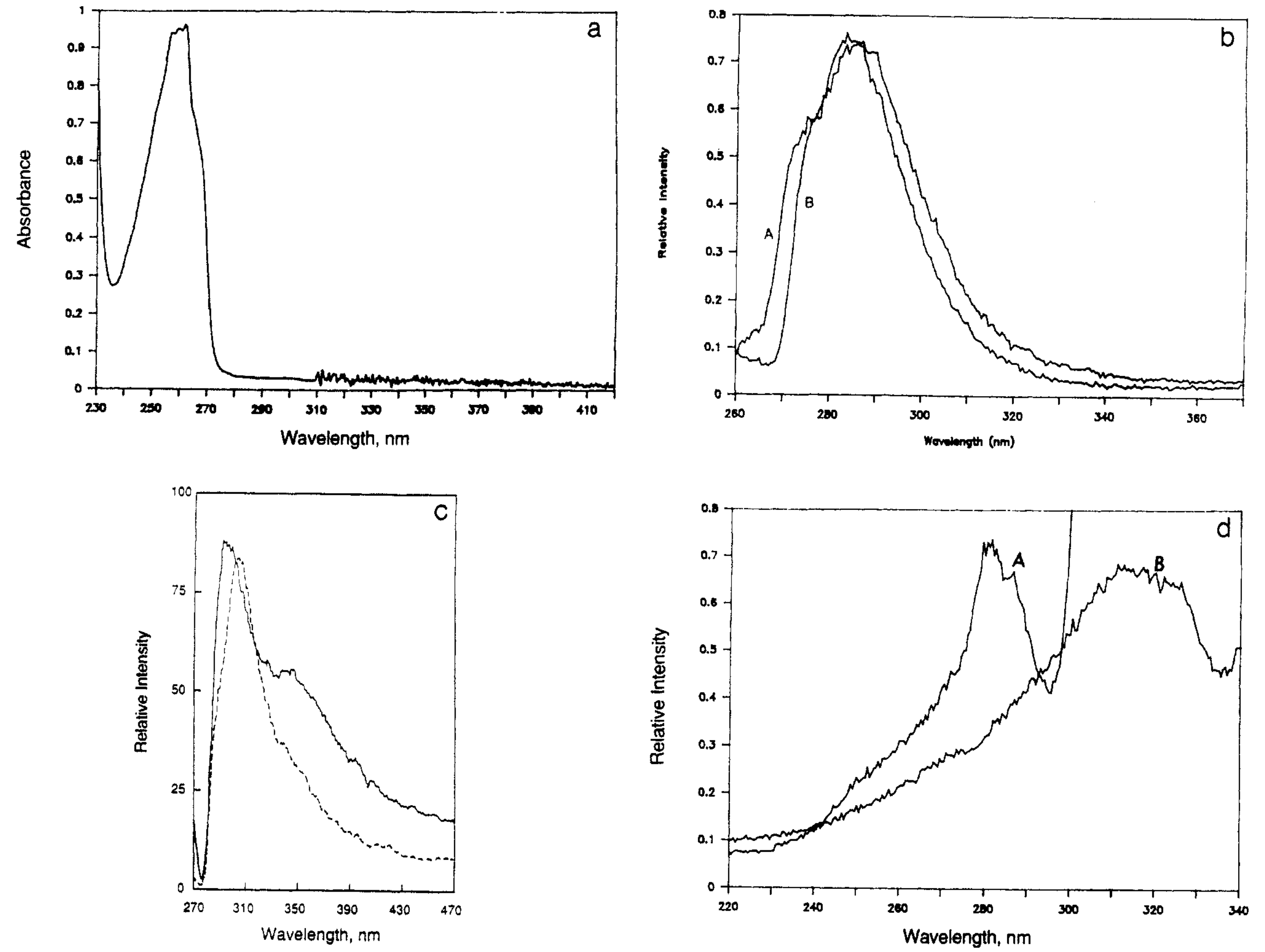


Figure 1. (a) Absorption spectrum of 1 × 10^{-3} M DPC in cyclohexane. (b) Fluorescence spectra of DPC in CH_2Cl_2 with two different concentrations under excitation at 260 nm: (A) 0.1 mM; (B) 10 mM. (c) Fluorescence spectra of polycarbonate films (excited at 265 nm): solid line, spectrum for unpurified PC; dashed line, spectrum for purified PC. (d) Excitation spectra of a polycarbonate film observed at two different emission wavelengths: (A) 310 nm; (B) 360 nm.

Steady-state photolysis experiments were performed with a Rayonet photochemical reactor, which was equipped with different RPR lamps. Most of the photolysis experiments for diphenyl carbonate were performed with RPR 300-nm lamps. Photolysis of polycarbonate was performed under mercury lamps at a flux density of 3.05 × 10^{-6} einstein/s-cm^2 at 253.7 nm.

Results and Discussion

1. Photophysical and Photochemical Studies of Polycarbonate. Photophysical Characterization of Diphenyl Carbonate. Diphenyl carbonate (DPC) is considered to be a monomer unit of polycarbonate, and the photochemistry of DPC should reveal information of direct relevance to the photochemistry of polycarbonate. Photophysical characterization of DPC, which includes absorption and emission spectra, and lifetimes of excited states are used as a basis for understanding the behavior of polycarbonate.

The absorption spectrum of diphenyl carbonate (1 × 10^{-4} M in cyclohexane) is shown in Figure 1a. The spectrum exhibits a structured absorption band with maxima around 260 nm and a shoulder around 270 nm. Excitation of this solution at 260 nm leads to a fluorescence spectrum shown in Figure 1b, which exhibits an emission band with a maximum at 280 nm. However, the fluorescence maximum is shifted to 290 nm (with a small shoulder at 280 nm) if the concentration of the solution increases to 2 × 10^{-2} M. A shift of a fluorescence maximum to a longer wavelength may be a consequence of an interaction of the ground state of DPC and the singlet excited state of DPC, which requires the condition of high concentration.

The lifetime of the singlet excited state of DPC was measured to be 5.46 ns.

Photophysical Properties of Polycarbonate. Studies of the photophysical properties of PC are divided into two categories: solid state and solution studies. Bisphenol A polycarbonate ($\bar{M}_w$ = 29000) as a solid film (thickness = 1.2 μm) exhibits an absorption spectrum with a maximum at 265 nm and a long tail extending to longer wavelengths. Excitation of a PC solid film at 265 nm leads to an emission spectrum shown in Figure 1c (solid line). The spectrum exhibits a structured band with maxima at 292 and 345 and a small peak at 330 nm. The new fluorescence bands (345 and 330 nm), which cannot be seen in DPC samples, may be ascribed either as an excimer emission of the polymer or the emission from another chromophore, i.e., an impurity produced in the processing of the polymer. To answer this question, excitation spectra of the polymer were measured. As shown in Figure 1d, the excitation spectrum observed with the emission set at 310 nm (spectrum A) exhibits a maximum at 280 nm, while the excitation observed at 360 nm (spectrum B) shows a maximum at 312 nm with a shoulder at 324 nm. The results indicate that the fluorescence band at 360 nm arises from a different chromophore. The emission band at 280 nm is due to a π–π* transition involving carbonyl groups in the polymer chains similar to that found in diphenyl carbonate described earlier. The emission at 345 nm may

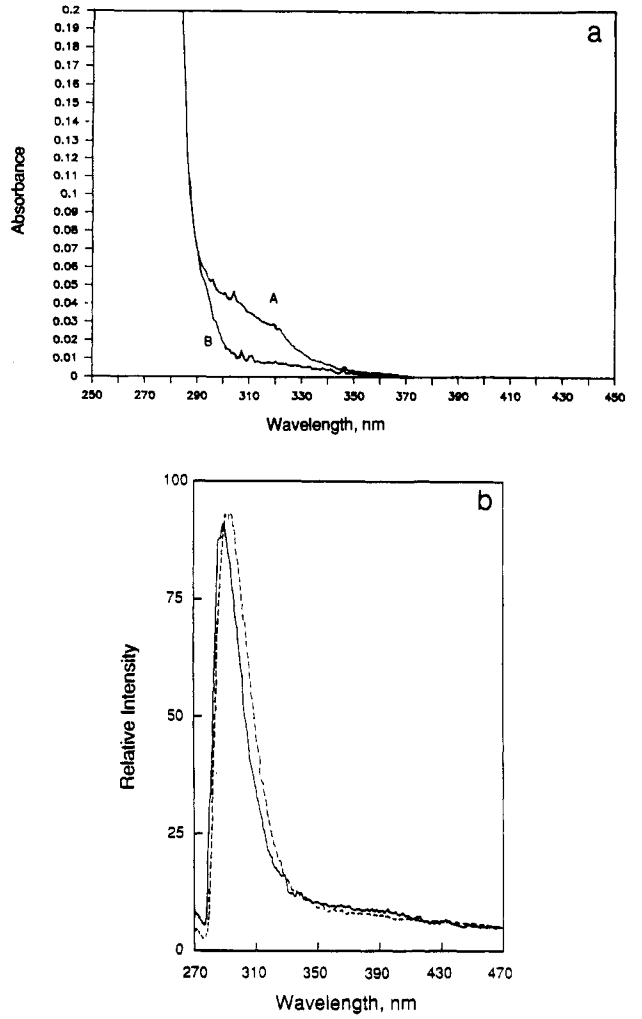


Figure 2. (a) Absorption spectra of two PC solutions (0.7% in CH_2Cl_2): (A) unpurified PC; (B) purified PC. (b) Fluorescence spectra of two PC solutions (10% in CH_2Cl_2): solid line, unpurified PC; dashed line, purified PC.

arise from the transition of an impurity, which has an absorption band at 312 nm.

Studies were initiated to establish the presence of impurities in PC polymer. A sample of purified PC was used in the following studies. The emission spectrum of the purified polymer film exhibits an emission band with a maximum at 305 nm and a small shoulder at 340 nm (Figure 1c, dashed line). These data, i.e., much reduced emission at 345 nm, indicate that the emission at 345 nm in the unpurified polymer is due to an impurity. The shift in the short-wavelength emission band (~300 nm) may be a consequence of molecular weight difference in these two polymers. Further evidence for the impurity in polycarbonate can be obtained from the absorption spectra of these two polymers. Figure 2a shows enlarged absorption spectra of solutions of purified and unpurified polymer in CH_2Cl_2 (0.7%). Compared to the purified polycarbonate (spectrum A), the unpurified sample exhibits a small absorption band with a maximum at 310 nm, due to the impurity described earlier. A small absorption of this band compared to the π–π* transition of the carbonyl group of the polymer chain (260-nm region) indicates that this impurity is present in very small amounts. If the extinction coefficient of the impurity is assumed to be of the same order of magnitude as the π–π* transition of the carbonyl group of polycarbonate, the concentration of the impurity would be 0.1%. However, the nature of the impurity cannot be identified at present.

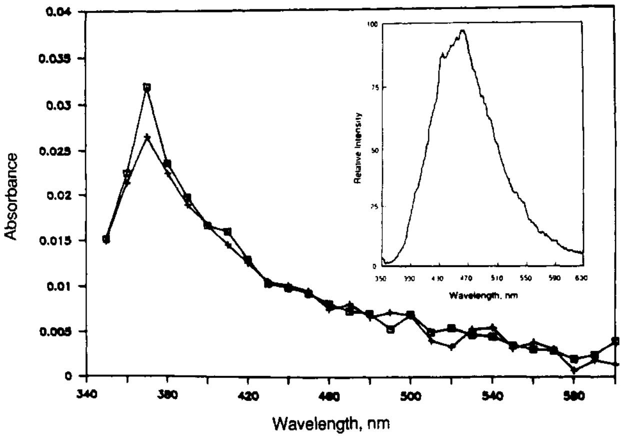


Figure 3. Transient absorption spectra of 10% PC in CH_2Cl_2 (excited at 308 nm): (□) immediately after the pulse; (+) 10 ms after the pulse. Inset: Phosphorescence spectrum of PC film 77 K in vacuum.

The emission spectra of solutions of both purified and unpurified PC in CH_2Cl_2 (1%) are shown in Figure 2b. Only one emission band is observed for each sample with a maximum at 292 and 290 nm, respectively. This supports the conclusion that the impurity exists at very small concentration.

Fluorescence of pure polycarbonate is quenched slightly by oxygen in air because of its short lifetime (<1 ns), the low concentration of oxygen in PC films (0.012 M), and the low oxygen mobility in the solid matrix, which reduces the quenching rate constant.

Transient Absorption Studies of Polycarbonate. Elementary processes involved in the photodegradation of PC may be associated with excited states other than the singlet π–π*. Hence, transient absorption studies of PC are important for determining the mechanism of degradation. The transient absorption spectrum of 10% PC in CH_2Cl_2, on excitation with a 308-nm pulse laser, is shown in Figure 3. The data show a broad spectrum with a pronounced maximum at 370 nm. Both purified and unpurified samples give identical results. It is inferred that the impurity does not play any significant part in the transient absorption studies. Humphrey et al.[10] studied the transient absorption of PC using a pulsed flash lamp as an excitatuion source. They reported a broad transient absorption band with a maximum at 420 nm, which was assigned to the absorption of a phenoxy radical. Gupta et al. monitored the transitory species of PC using a nitrogen laser as the excitation source.[12] They reported that more than one transitory species is produced on excitation of PC. They observed a long-lived species (unidentified lifetime) which was quenched by *trans*-piperylene and a short-lived (lifetime of 0.1 μs) which was not quenched by either oxygen or *trans*-piperylene. The long-lived species was ascribed to a phenoxy radical. The results of the present work show a main transient species with a spectral maximum at 370 nm and a lifetime of 13 μs. This species is quenched by typical triplet quenchers and will be discussed later. These results suggest that the transient observed at 370 nm is not due to the phenoxy radical but to the triplet state of polycarbonate.

Further evidence for the existence of the triplet of PC is the appearance of the phosphorescence of PC, which is shown in Figure 3 (inset). The phosphorescence becomes more intense at lower temperature, i.e., 77 K, both in solution and in the solid film.

Triplet Energy Transfer from PC to Perylene. Triplet–triplet energy transfer from the triplet of PC to the singlet ground state of perylene was studied to confirm

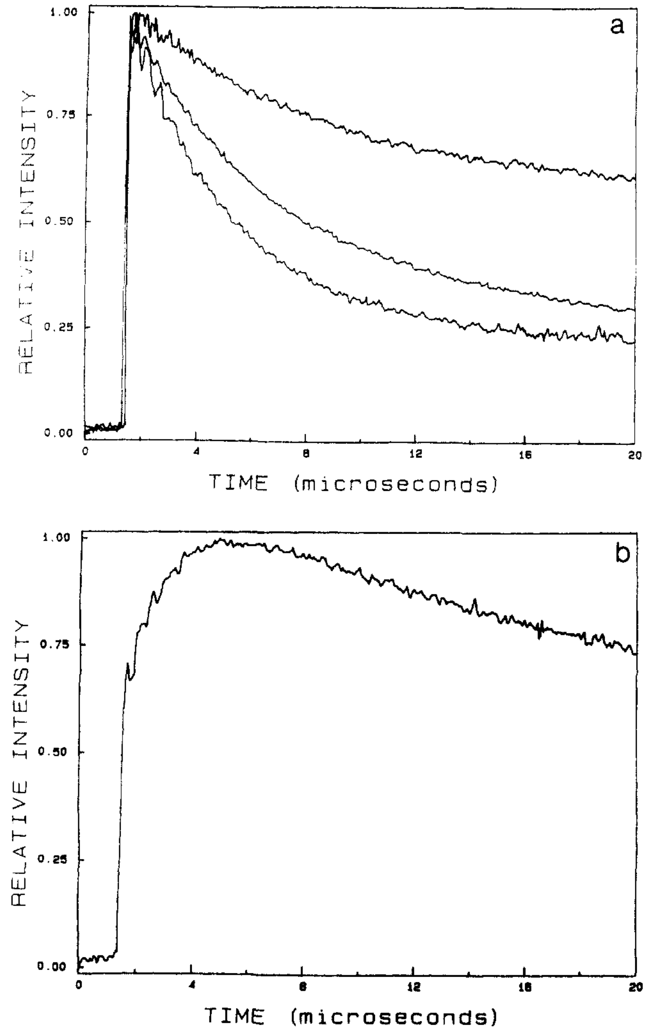


Figure 4. (a) Decay of the triplet of PC (10% in CH_2Cl_2) at various concentrations of perylene (observed at 390 nm): from top to bottom, 0, 0.08, and 0.16 mM, respectively. (b) Transient absorption change observed at 485 nm for 10% PC in CH_2Cl_2 in the presence of 0.16 mM perylene.

that the transient species absorbing at 370 nm is indeed the triplet state of PC. The triplet state of the polymer should be quenched by perylene, and the formation of the perylene triplet should be observed. Figure 4a shows the transient absorption decay of 10% PC in CH_2Cl_2 (observed at 390 nm) with various concentrations of perylene. The data clearly show that the transient species absorbing at 370 nm is quenched by perylene. Furthermore, the transient absorption change observed at 485 nm, which corresponds to the maximum absorption of the triplet of perylene, is shown in Figure 4b, where a growth of the absorption indicates the formation of the triplet of perylene. The growth rate of the absorption at 485 nm also matches the decay rate of the absorption at 370 nm. A quenching rate constant of the triplet of PC by perylene is calculated to be 5.6×10^8 M^{-1} s^{-1}. In Figure 4a, it is noted that decays of the transient at 370 nm are not completely first order. They are in fact composed of two transitory species, one with a lifetime of 10 μs and the other species with a much longer lifetime. The long-lived transient species, which appears to comprise approximately 20% of the relative signal intensity, is not quenched by perylene. This long-lived species may be assigned to the phenoxy radical.[12]

Quenching of PC Triplet by Triplet Quenchers. Additional studies were conducted to show that the species absorbing at 380 nm is indeed the triplet state of PC. These studies involved the reaction between this species and several triplet quenchers such as oxygen, ferrocene, and *trans*-piperylene.

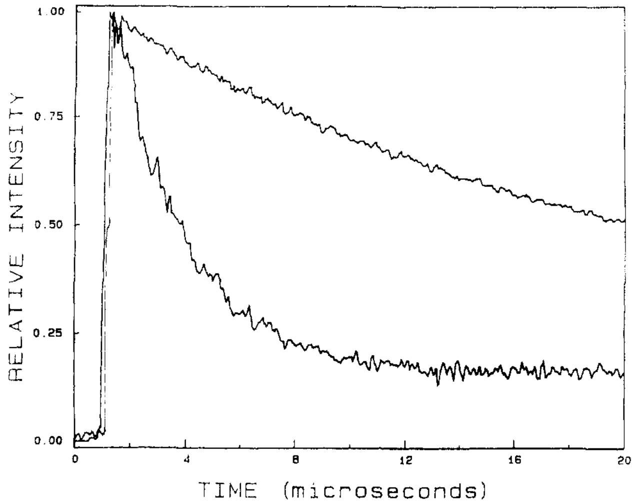


Figure 5. Decays of the triplet of PC (10% in CH_2Cl_2) under N_2 (top) and air (bottom).

Table 1. Quenching Rate Constants of PC Triplet by Various Quenchers

acceptor	k_q, M^{-1} s^{-1}
oxygen	6.25×10^8
ferrocene	2.89×10^8
trans-piperylene	3.05×10^8
perylene	5.60×10^8

Oxygen. Molecular oxygen reacts with most triplet states of organic species. The importance of the interaction with oxygen originates from the fact that PC tends to degrade more severely in the presence of oxygen (see later discussion). Furthermore, a number of studies have reported that singlet oxygen is the key factor for the degradation process. Figure 5 shows decay curves of the triplet of PC in CH_2Cl_2 under nitrogen and air, and from these data a second-order quenching rate constant for oxygen quenching is calculated as 6.25×10^8 M^{-1} s^{-1}.

Ferrocene. Ferrocene is a triplet quencher because its triplet energy is below that of PC,[13] and it has been used as a quencher for a variety of systems such as the triplet and the radical cation of pyrene on γ-alumina.[14] Studies show that the reaction of PC triplet and ferrocene gives a quenching rate constant of 2.89×10^8 M^{-1} s^{-1}.

***trans*-Piperylene (PP).** Earlier work by Gupta et al. described the reaction of the transient PC and PP as a reaction between the phenoxy radical and PP.[12] However, PP is also a well-known triplet quencher.[15] The data in this work clearly show that the transient species interacts with PP, which in turn confirms that the transient species is the triplet of PC. The results indicate a quenching rate constant of 3.05×10^8 M^{-1} s^{-1}.

A comparison of quenching of PC triplet by various quenchers is presented in Table 1.

2. Photodegradation of Polycarbonate. In the previous section, photophysical and photochemical studies of polycarbonate and its model compound (DPC) are reported. The photochemical reactions of polycarbonate may involve various excited states of the polymer. In the past, most attention has been paid to the photo-Fries rearrangement in the polymer rather than to chain scission. This section reports effects of oxygen on the photo-Fries reaction in DPC compared to polycarbonate to evaluate details of photodegradation.

Photolysis of DPC. Figure 6a shows the spectra of 1

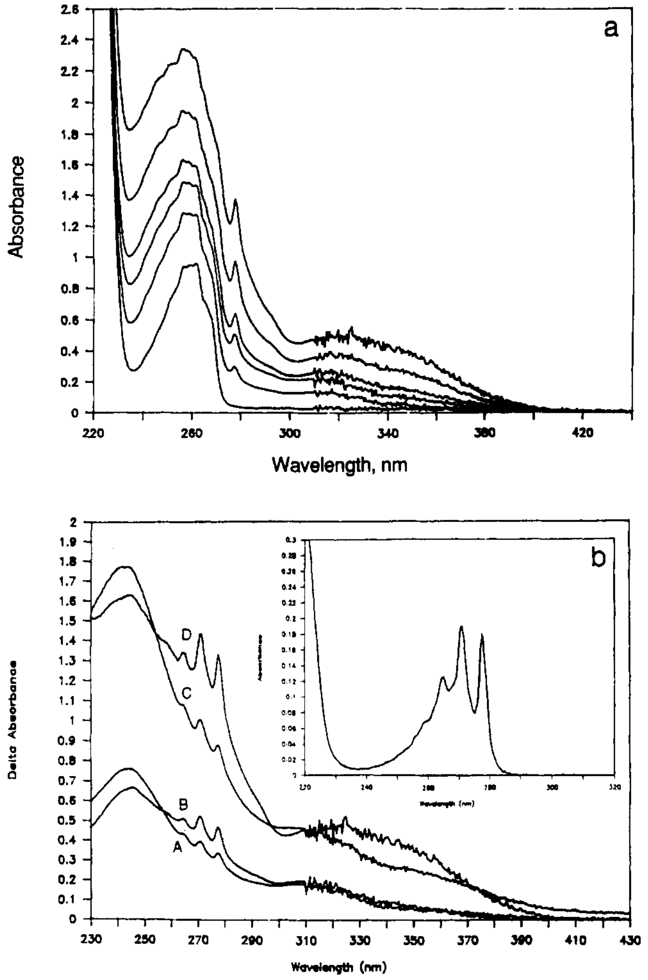


Figure 6. (a) Absorption spectra of 1 mM DPC/cyclohexane (N_2 saturated) as a function of irradiation time (300 nm): from bottom to top, 0, 5, 10, 15, 20, 25, 35, and 40 min. (b) Differential absorption spectra of irradiated DPC/cyclohexane solutions: (A) air, 10 min; (B) N_2, 10 min; (C) air, 40 min; (D) N_2, 40 min. Inset: Absorption spectrum of 1 mM phenol in cyclohexane.

$\times 10^{-3}$ M DPC in cyclohexane solution after various times of photoirradiation. At short irradiation time (10 min), new absorption bands develop at 250, 280, 320, and 355 nm, and the absorption of the sample at 260 nm is greatly intensified due to an overlap of the absorption band of DPC and those of the products.

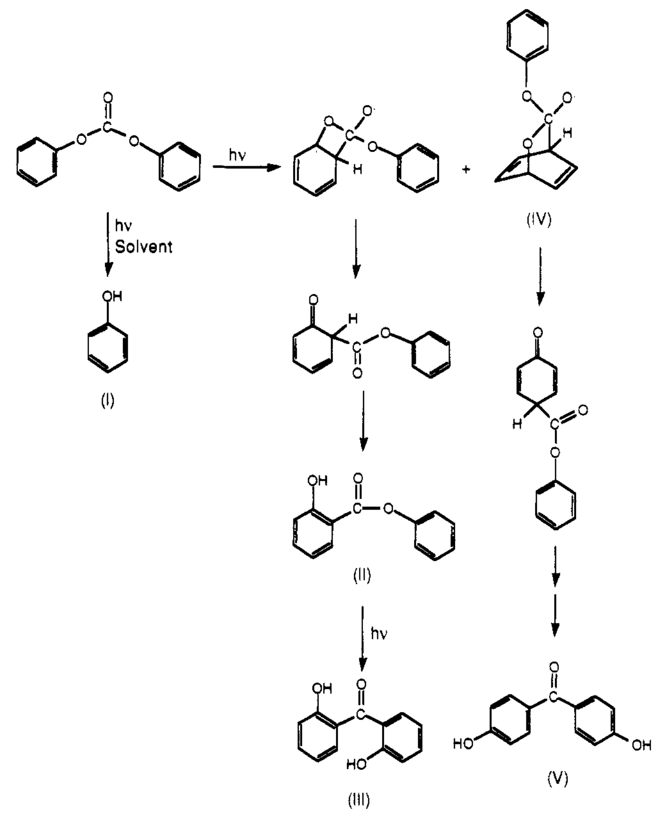
DPC is one of the aryl esters whose photochemical reactions have been extensively studied.[16,17] Two alternative mechanisms have been proposed by various investigators. One is the concerted rearrangement (Scheme 1).

The other mechanism is the nonconcerted cage recombination (Scheme 2) in which the C–O bond of the excited ester breaks up yielding acyl and phenoxy radicals. Combination of these radicals can take place at either the 2 or 4 positions. The recombination would produce acyl cyclohexadienones which eventually tautomerize to hydroxyphenone photoproducts.

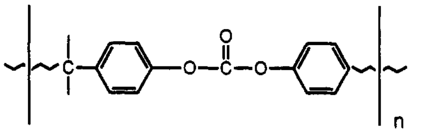
The real mechanism of the photo-Fries reaction has been in debate, and both of these two mechanisms have been supported by a number of investigators. However, works by Hammond and Hercules[16,17] tend to be in favor of the nonconcerted mechanism.

According to Schemes 1 and 2, the main products of photolysis of DPC are phenol (I) and phenyl salicylate (II), which can undergo subsequent reactions leading to formation of 2,2′-dihydroxybenzophenone (III). The product 4,4′-dihydroxybenzophenone (V) is expected to be present in very small amounts due to either the small

Scheme 1



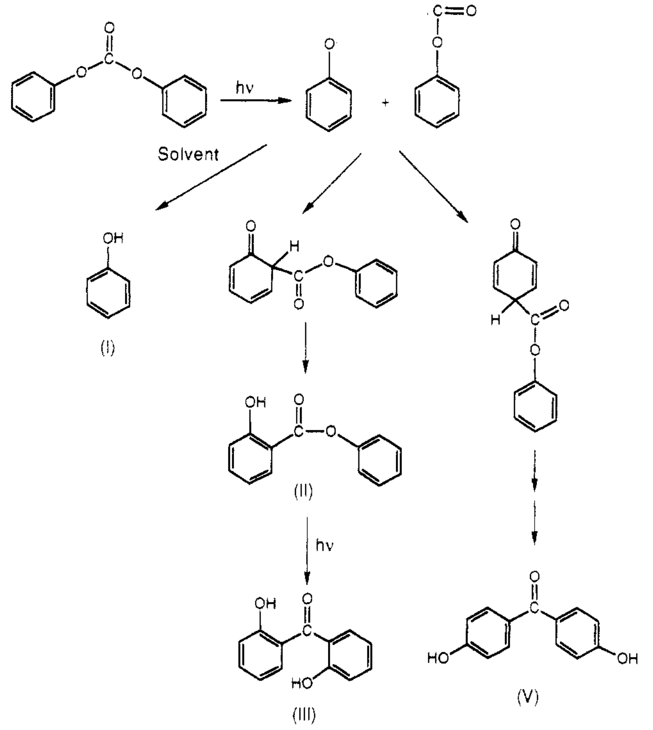
probability of forming intermediate IV with a four-membered bridge over one of the phenyl rings or the unlikeliness of the combination of radicals at these positions. In addition, the structure of Bisphenol A polycarbonate (shown below), where ring positions 4 and 4′ are occupied, does not allow such intermediates to be formed. The combination of radicals at these positions is unlikely also. Therefore, it is not necessary to emphasize this reaction route.



A sharp absorption bnad at 278 nm in Figure 6a is assigned to absorption by phenol. This is more clearly observed via the differential absorption spectra shown in Figure 6b, which exhibit structured absorption bands identical to those of phenol (Figure 6b, inset). The absorption around 250 nm is due to phenyl salicylate and dihydroxybenzophenone, while the absorption at 320 nm is identified as that of phenyl salicylate. Increased irradiation time leads to an increase in absorption at 280 and 360 nm, while the absorption at 320 nm decreases. This is a consequence of a subsequent transformation of phenyl salicylate to dihydroxybenzophenone, which shows an absorption maximum at 360 nm. Figure 7a shows the absorption spectra of phenyl salicylate (A), 2,2′-dihydroxybenzophenone (B), and irradiated phenyl salicylate (C, irradiated 15 min with 300-nm light). These data also confirm that excitation of phenyl salicylate leads to the formation of 2,2′-dihydroxybenzophenone.

In addition to the above absorption data, fluorescence spectral data and product analysis provide further understanding of the processes involved in the photolysis of PC. A photolyzed cyclohexane solution of DPC exhibits a fluorescence spectrum illustrated in Figure 7b (excitation

Scheme 2



wavelength = 320 nm), which exhibits a small band at 350 nm and a broad band with a maximum at 465 nm. The latter emission can be assigned to phenyl salicylate (this is confirmed by measuring an excitation spectrum of this band, which shows a maximum at 320 nm).

Here, the major issue is the effect of oxygen on the photochemical processes involved in Scheme 1. Three conditions were studied where the concentration of oxygen was varied, i.e., nitrogen-, air-, and oxygen-saturated samples.

Figure 8a shows the spectral changes of DPC in air-saturated solution at various irradiation times. It can be seen from this figure that the absorption band at 260 nm increases and tends to shift to the shorter wavelengths compared to data with a nitrogen-saturated sample (Figure 8b). The appearance of a sharp absorption band at 288 nm, which is more pronounced in the nitrogen-saturated sample can be identified as the absorption spectrum of phenol, which is a product of molecular cleavage. The yield of the photo-Fries reaction, which is monitored by the absorption band at 355 nm (dihydroxybenzophenone), is also greater in nitrogen-saturated samples than in the air-saturated samples.

A comparison between air- and oxygen-saturated samples is also instructive. Figure 9a shows spectral changes of DPC under various irradiation conditions. Results similar to the above are obtained, indicating that the yields of molecular cleavage and of the photo-Fries reaction are smaller in oxygen-saturated samples, where the concentration of oxygen is higher.

The results show that oxygen quenches the singlet π–π^* state and consequently reduces the efficiency of the photo-Fries reaction. This is confirmed by the observation that the yields of products (phenol, phenyl salicylate, and dihydroxybenzophenone) decrease with increasing oxygen concentration.

Previous data indicated that the emission band at 465 nm is associated with an intermediate of the photo-Fries reaction. Figure 9a (inset) shows the emission intensity observed at 465 nm (excitation at 320 nm) of two DPC samples (air and oxygen saturation) as a function of irradiation time. The yield of the species which fluoresces at 465 nm in both samples increases at small irradiation times. However, when the irradiation time reaches 35 min, the yield starts to slowly decrease. This confirms that the emission band at 465 nm originates from phenyl salicylate, which is an intermediate of the photo-Fries reaction. At shorter irradiation times, a significant amount of this intermediate is produced, which on continued irradiation undergoes further reaction to give dihydroxybenzophenone, which does not fluoresce.

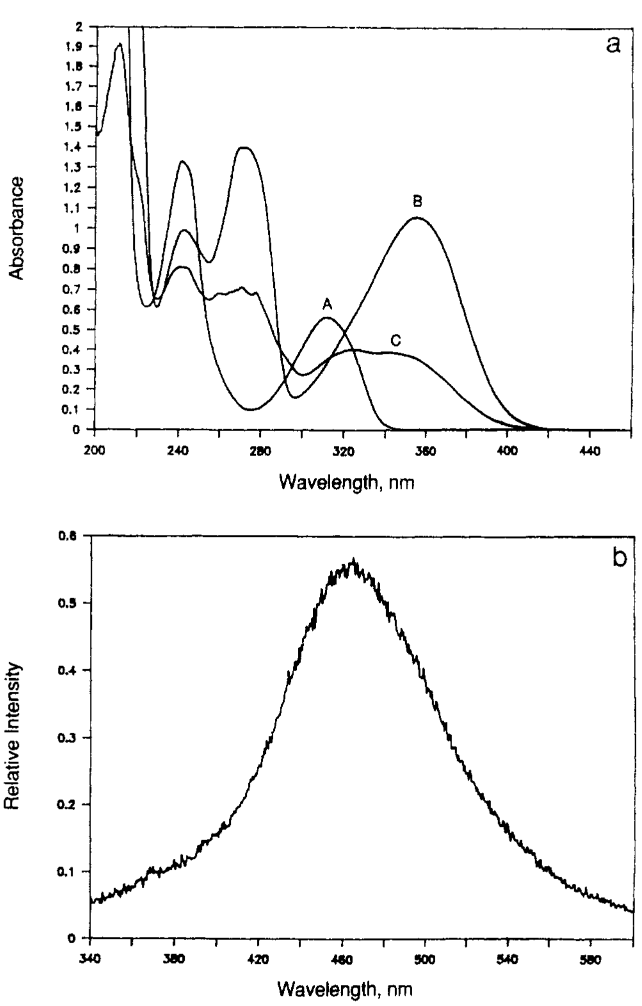


Figure 7. (a) Absorption spectra of intermediates and products of photolysis of DPC: (A) 1 mM phenyl salicylate in cyclohexane; (B) 1 mM 2,2′-dihydroxybenzophenone/cyclohexane; (C) 1 mM phenyl salicylate/cyclohexane after irradiation at 300 nm for 15 min. (b) Fluorescence spectrum of irradiated DPC solution (1 mM DPC/cyclohexane, 300 nm for 40 min, excited at 320 nm).

Table 2 summarizes the spectroscopic parameters for DPC and its photolysis intermediates and products.

Photolysis of Polycarbonate. Most PC photolysis studies were performed on solid films unless otherwise indicated. Photolysis of a PC film with light of 300 nm produces changes in the absorption and emission spectra of the film. Figure 9b shows the absorption spectra of a PC film after various times of irradiation under vacuum. At an early stage of irradiation, an absorption band at 320 nm develops, and as the irradiation continues, an absorption band at 355 nm develops. In comparison to the data for diphenyl carbonate, which is used as a model compound in this case, it can be rationalized that the photo-Fries reaction takes place and leads to formation of polymer chains with phenyl salicylate end groups (maximum absorption at 320 nm). Eventually polymer chains with dihydroxybenzophenone end groups (maximum absorption at 355 nm) are formed.

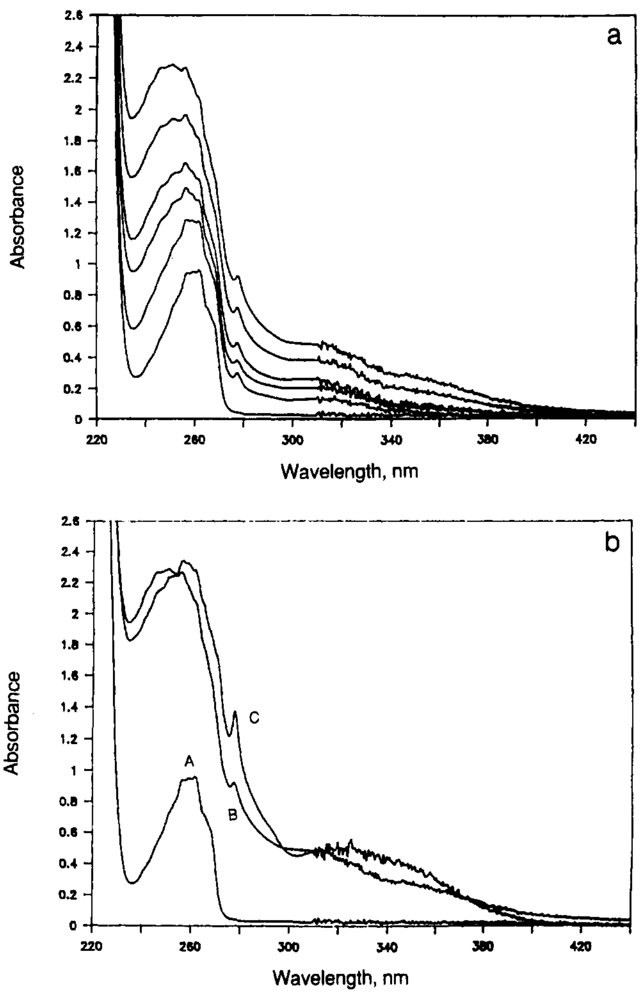


Figure 8. (a) Absorption spectra of 1 mM DPC/cyclohexane (air saturated) as a function of irradiation time (300 nm): from bottom to top, 0, 5, 10, 15, 20, 25, 35, and 40 min. (b) Absorption spectra of 1 mM DPC/cyclohexane: (A) before irradiation; (B) in air after 40 min of irradiation; (C) N_2 saturation after 40 min of 300-nm irradiation.

The emission spectra of the photolyzed polymer also indicate the production of polymer chains with phenyl salicylate groups as an intermediate. This is concluded from the emission band at 465 nm, which first develops and then decreases on extended irradiation.

A growth in the absorption band at 250 nm indicates the existence of chain scission involving the formation of polymer chains with phenolic end groups. The earlier DPC data show evidence that both chain scission, involving phenolic chain formation, and photo-Fries reactions are affected by the presence of oxygen. Oxygen quenches the singlet excited states of PC, which leads to smaller yields for both of these reactions. However, size exclusion chromatography data, which monitor the average molecular weight change of the polymer after irradiation, indicate otherwise. From the SEC chromatograms, the weight-average molecular weight ($\bar{M}_w$) and the number-average molecular weight ($\bar{M}_n$) can be calculated, and they are summarized in Table 3. From the table, it can be seen that degradation of PC (monitored by the decrease of the average molecular weight of PC) is enhanced in the presence of oxygen; i.e., the change of molecular weight is more pronounced in air than in vacuum. The quantum yield of PC degradation in vacuum and in air are calculated to be 0.02 and 0.10, respectively.

To explain the effect of oxygen on the degradation of PC, a few questions have to be answered. First of all, which PC excited state is responsible for the degradation process: the singlet or the triplet? To answer this question, the effect of perylene addition was studied. As demonstrated earlier, perylene is an efficient triplet quencher for PC triplet. From the value of the quenching rate constant, 1 mM perylene should quench the triplet of PC completely, and degradation should be inhibited. How-

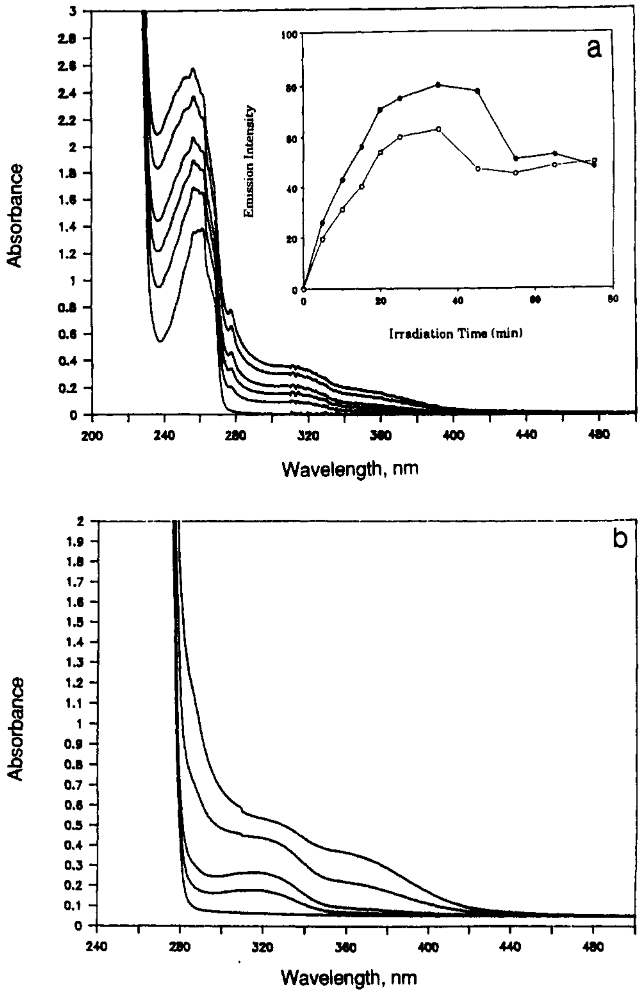


Figure 9. (a) Absorption spectra of 1 mM DPC/cyclohexane (oxygen saturated) as a function of irradiation time (300 nm): from bottom to top, 0, 5, 10, 15, 20, 25, 35, and 40 min. Inset: Fluorescence intensity of 1 mM DPC/cyclohexane as a function of irradiation time: (●) N_2 saturation; (○) air saturation. (b) Absorption spectrum of PC film under vacuum as a function of irradiation time: from bottom to top, 0, 15, 30, 120, and 240 min.

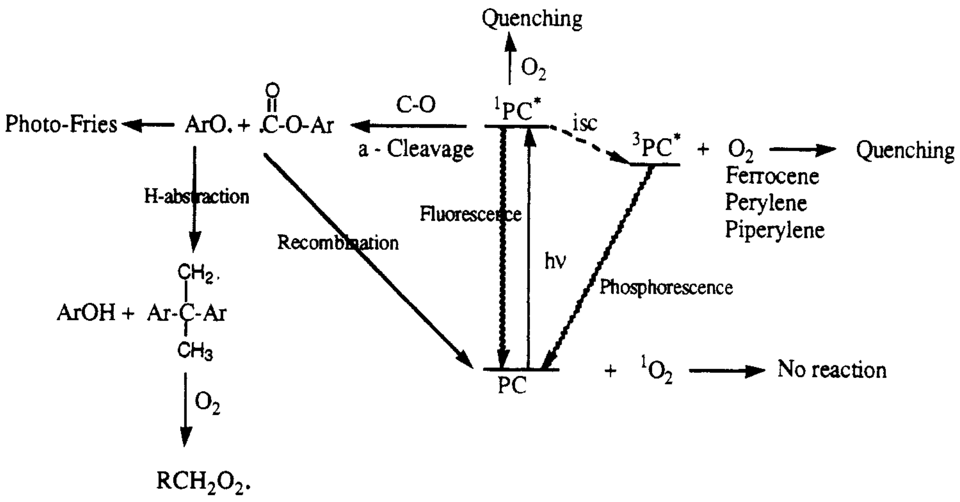
Table 2. Spectroscopic Parameters for DPC and Its Photolysis Intermediates and Products

compound	absorption bands, nm	fluorescence band, nm
DPC	265	280–290
phenol	260, 272, 278	290
phenyl salicylate	245, 315	465
dihydroxybenzophenone	245, 275, 355	no emission

Table 3. Molecular Weight Change of Polycarbonate under Irradiation

	air		vacuum	
irradiation time, min	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$
0	19200	3200	19200	3200
1	18200	2800		
2	15400	2300	17200	2800
4	13220	1600		
6	9700	1100	15800	2300
8	9100	900		
10	8700	820	13400	2000
15	8600	820	12500	1740
20	8600	800	12300	1600

Scheme 3



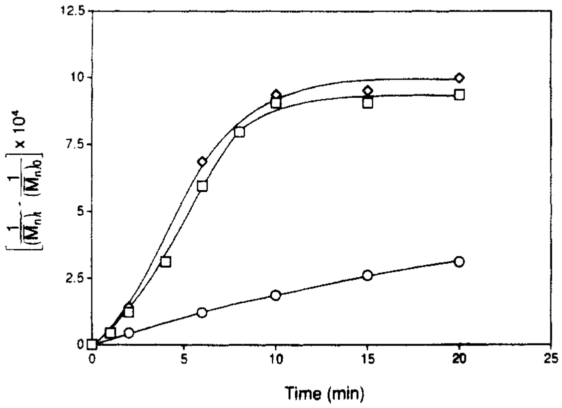


Figure 10. Plots of $1/(\bar{M}_n)_t - 1/(\bar{M}_n)_0$ vs irradiation time at various oxygen concentrations: (○) vacuum; (□) air; (◇) 1 atm of oxygen.

ever, it is found that perylene does not affect the degradation of PC, indicating that the triplet of PC is not primarily involved in the degradation process.

The above data indicate that the triplet state of PC is not responsible for the degradation. The involvement of oxygen may be in secondary processes. Radicals such as phenoxy radicals, which are produced from an α-cleavage, may abstract hydrogen atoms from methyl groups of the polymer backbone. In the presence of oxygen, these radicals react with oxygen to form ROO$^{\bullet}$, which in turn stops the radicals from recombining and enhances degradation.

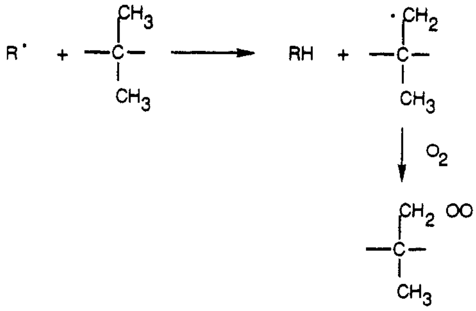


Figure 10 shows a plot of the relative degradation, which was calculated from $1/(\bar{M}_n)_t - 1/(\bar{M}_n)_0$, versus time under various conditions, where $(\bar{M}_n)_t$ is the number-average molecular weight of the polymer at irradiation time t and $(\bar{M}_n)_0$ is the number-average molecular weight of the polymer before irradiation. The plots are relatively linear at small irradiation times with only a hint of upward curvature in the oxygen samples, which indicates that degradation or bond breaking of the polymer comes mainly from the excited state of the polymer itself and not from the photoproducts or the impurities that could interact with the polymer and degrade it. The slight initial upward curvature may indicate a development of a product which also leads to some polymer degradation or to enhanced oxygen reactivity (diffusion) as the polymer degrades.

It is interesting to note that a comparison of the degradation in vacuum, air, and oxygen atmospheres indicates that the degradation in air is more efficient than in vacuum by a factor of 1.5. However, the bond-breaking efficiency in 1 atm of oxygen shows only slight improvement compared to the aerated samples. This indicates that the effect of oxygen degradation is essentially completed at an oxygen concentration defined by 1 atm of air. Oxygen plays two roles in the degradation: it serves as a quencher for the singlet excited state, which inhibits degradation, and as an inhibitor for radical recombination (by reacting with polymer radicals), which enhances degradation. The balance between these two opposing roles appears over various concentrations of oxygen. Under aerated conditions, the quenching of the singlet excited state by oxygen is negligible due to the short lifetime and the low mobility of oxygen in the film. As the oxygen concentration increases, quenching of the singlet becomes a more dominant factor. It is suggested that one mode of decay of the singlet excited state is chain scission, which eventually gives phenol (process I in Scheme 2). The two radicals can recombine, thus eliminating chain breakage. Oxygen interrupts this process and increases C–C bond scission.

Singlet Oxygen Studies in Polycarbonate Films. To see if singlet oxygen plays a role in the degradation of polycarbonate, studies of singlet oxygen in polycarbonate with and without sensitizers were carried out.

Two sensitizers were used for the study, bromopyrene and phenazine. The phosphorescence spectrum of singlet oxygen in PC obtained using these two sensitizers is shown in Figure 11 and exhibits a broad band with a maximum at 1260 nm. No significant difference is found between the spectra taken with either probe, which indicates that the formation of singlet oxygen is independent of the choice of sensitizer. The lifetime of singlet oxygen in PC was measured to be 60.4 μs.

Even though observation of singlet oxygen in other pure polymers has been reported,[18,19] it is noted that under excitation at 308 nm the phosphorescence of singlet oxygen could not be detected in the absence of sensitizer, i.e.,

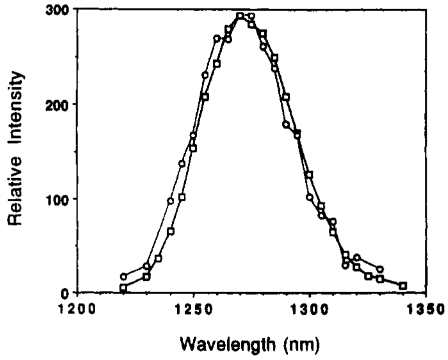


Figure 11. Phosphorescence of singlet oxygen produced in polycarbonate films using two different sensitizers: (□) bromopyrene; (●) phenazine.

pure PC film.

It is also found that under conditions where singlet oxygen is produced (with sensitizers under 308-nm excitation), polycarbonate does not degrade; i.e., no change of molecular weight was observed. This agrees with the data shown earlier that the triplet state is not involved in degradation processes.

Conclusion

Photophysical and photochemical studies of polycarbonate and diphenyl carbonate indicate similarities and differences between the polymer and its model compound. A comparison of the results from the photophysical and photochemical studies of a model compound, diphenyl carbonate, and polycarbonate helps to elucidate the role of oxygen in the photodegradation mechanism. A comparison of the absorption and the fluorescence data of intermediates and products of photolysis of DPC to those of polycarbonate indicates that degradation of the polymer, which is more pronounced in the presence of oxygen, is in fact a consequence of photooxidation rather than a photo-Fries rearrangement. The role of oxygen in PC degradation involves a secondary process where radicals (products of the primary process) abstract hydrogen atoms from methyl groups of the polymer backbone. Excitation of polycarbonate at 308 nm leads to formation of the triplet of the polymer, which reacts efficiently with oxygen, ferrocene, *trans*-piperylene, and perylene with quenching rate constants of 6.25×10^8, 2.89×10^8, 3.05×10^8, and 5.60×10^8 $M^{-1}s^{-1}$, respectively. The triplet of PC is quenched by oxygen, but little singlet oxygen is observed from this process. It is suggested that C–C bond scission occurs from the singlet state and that oxygen prevents radical–radical recombination of the broken ends of the chain, thus enhancing degradation. Deliberate production of singlet oxygen in PC (using sensitizers) does not lead to polymer degradation. Triplet quenching studies show that the triplet state of PC is not involved in the degradation process. These processes are shown in Scheme 3.

Acknowledgment. The authors wish to thank IBM Corp. for support of this work.

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