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Photophysical Investigations of the Interactions of Phospholipids and a Pyrene-Substituted Poly(acrylic acid) in Dilute Solutions

Kartar S. Arora,[†] K.-C. Hwang, and N. J. Turro*

Department of Chemistry, Columbia University, New York, New York 10027.

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ABSTRACT: Fluorescence spectra of a pyrene-substituted poly(acrylic acid) (1) were measured in the presence of dipalmitoylphosphatidylglycerol (DPPG) at pH values of 4 and 7 to investigate the interactions between 1 and phospholipids. These photophysical investigations showed that at pH 4 mixed micelles of 1 and phospholipids were formed with the incorporation of 1 in the hydrophobic core of the mixed micelle. The measurements of fluorescence decay and quenching of fluorescence by nitromethane in solutions of 1 and DPPG also supported this model for the interactions of 1 and phospholipids. These results were in agreement with a calorimetric investigation of the interactions between phospholipids and poly(acrylic acid) derivatives (Tirrell, D. A.; Takigawa, D. Y.; Seki, K. *Ann. N.Y. Acad. Sci.* **1985**, *446*, 237). The effects of head group and temperature on the interactions of 1 and phospholipids were also investigated.

Table I
Definitions and Significance of the Photophysical Parameters of Pyrene Obtained from Emission and Excitation Spectra of 1

symbol	definition	significance
I_M/I_E	ratio of intensities of monomer (0,0) and excimer fluorescence	reflects intrachain interactions of pyrene groups
λ_E	wavelength corresponding to maximum in the excimer emission	environment and orientation of pyrene groups involved in excimer formation affect the value of λ_E
P_M	peak-to-valley ratio for the (0,0) transition in the ^1L_a band in the excitation spectrum viewed at 380 nm	reflects interactions of isolated (non-excimer-forming) pyrene groups
P_E	peak-to-valley ratio for the (0,0) transition in the ^1L_a band in the excitation spectrum viewed at 480 nm	reflects interactions of excimer-forming pyrene groups

Investigations of the interactions of phospholipids and synthetic polymers could be expected to play important roles in the pursuit of scientific knowledge of the structures and functions of biological macromolecules and membranes. These investigations are also of importance for the synthesis of novel functional polymers for reactions in organized media and to mimic the functions of biological molecules. Tirrell and co-workers[1,2] have investigated the interactions of a variety of synthetic polymers and phospholipids in aqueous solutions. Photophysical techniques have been extensively used in the investigations of the structure and functions of synthetic and biological macromolecules.[3] Photophysical properties of the pyrene chromophore covalently bound to poly(acrylic acid) (PAA) have been used by Turro and Arora[4] to investigate the inter- and intrapolymer interactions in dilute aqueous solutions of PAA and complementary polymers. Intrachain interactions of pyrene groups in pyrene-substituted PAA (1) investigated by measurements of fluorescence spectra, fluorescence lifetimes, and quenching of fluorescence were found to be useful probes for inter- and intramolecular interactions in solutions of 1 and complementary polymers. Intramolecular excimer formation in bichromophoric pyrene-substituted compounds has been used to investigate structures and functions of phospho-

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[†] Present address: The Sherwin-Williams Research Center, Chicago, IL 60628.

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Table II
Photophysical Parameters of Pyrene-Substituted Poly(acrylic acid) in Tris Buffer Solutions and in the Presence of Phospholipids[a]

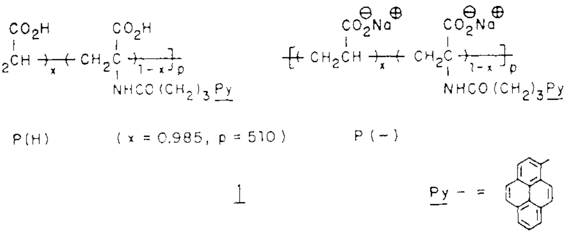
soln comp[b]	temp, °C	I_M/I_E[c]	λ_E, nm	P_M[d]	P_E[e]
P(−)	45	4.33	485	1.94	1.34
P(H)	45	1.62	481	1.70	1.30
P(H):DPPG	45	3.94	474	2.02	1.83
P(−):DPPG	45	2.93	483	1.89	1.50
P(−)	30	4.23	486	1.98	1.32
P(H)	30	1.52	480	1.70	1.29
P(H):DPPG	30	6.22	473	2.08	1.86
P(−):DPPG	30	3.14	483	1.94	1.52

[a] The excitation and emission spectra were recorded on a Perkin-Elmer Model LS-5 luminescence spectrophotometer. [b] A 50 mM Tris buffer solution containing 5×10^{-4} M (repeat units) polymer and 4 mg/10 mL (5×10^{-4} M) of phospholipid was used for measurement. [c] Ratio of intensities of monomer (0,0) and excimer (at λ_E) fluorescence in the emission spectra. Error ±10%. [d] Peak-to-valley ratio for the (0,0) transition in the ^1L_a band in the excitation spectrum viewed at 380 nm. Error ±2%. [e] Peak-to-valley ratio for the (0,0) transition in the ^1L_a band in the excitation spectrum viewed at 480 nm. Error ±2%.

lipids.[5] The photophysical investigations of the interactions of 1 and phospholipids in dilute solutions reported here were carried out to elucidate the nature of interactions of phospholipids and poly(acrylic acid) derivatives[1] and the structures obtained therefrom.

Results and Discussion

Photophysical parameters obtained from the fluorescence emission and excitation spectra of 1 have been used to obtain information about the environment and interactions of pyrene groups in solutions of 1.[4] The definitions and significance of these photophysical parameters are given in Table I. The photophysical parameters of 1 in Tris buffer solutions were obtained at pH 4 and 7 (Table II) since significant changes in the interactions between phospholipids and 1 were expected over this pH range.[1a] A significant amount of carboxylic acid groups in solutions of 1 is expected to be present in an ionized form at pH 7; thus 1 is represented as P(−) above pH 7. The ionization of carboxylic acid groups is expected to be significantly reduced at pH 4; thus 1 is represented as P(H) below pH 4. The interactions of phospholipids and 1 were investigated at 30 and 45 °C to elucidate the effects of temperature. Because of the low concentrations of 1 (>1 mM) used in these experiments, no significant interchain interactions of pyrene groups were expected. This expectation was also confirmed by measurements of I_M/I_E values at different concentrations of 1.[4]



$$-\!\!\left[\left(CH_2\overset{\overset{CO_2H}{|}}{C}H\right)_x\left(CH_2\underset{\underset{NHCO(CH_2)_3\underline{Py}}{|}}{\overset{\overset{CO_2H}{|}}{C}}\right)_{1-x}\right]_p \qquad -\!\!\left[\left(CH_2\overset{\overset{CO_2^{\ominus}Na^{\oplus}}{|}}{C}H\right)_x\left(CH_2\underset{\underset{NHCO(CH_2)_3\underline{Py}}{|}}{\overset{\overset{CO_2^{\ominus}Na^{\oplus}}{|}}{C}}\right)_{1-x}\right]_p$$

P(H) (x = 0.985, p = 510) P (−)

1

Py− =

The I_M/I_E, P_M, and P_E values of P(−) were found to be greater than those of P(H) (Table II) under all conditions investigated. A random distribution of pyrene groups is expected in 1 due to the copolymerization method used in the preparation of 1.[4a] The excimer formation in dilute solutions of 1 should therefore arise from intrachain interactions of pyrene groups which either are present in neighboring positions on the main chain of 1 or are brought closer by coiling of the polymer chain. The low I_M/I_E value of P(H) is attributed to coiled and compact conformations of 1 under low pH conditions. An increase in the charge density along the polymer backbone causes an expansion of the polymer chain and thus reduces hydrophobic intrachain interactions of pyrene groups in 1; however, excimer formation in solutions of P(−) would still result from the presence of pyrene groups in neighboring positions on the main chain of 1 (Figure 1). The higher P_M and P_E values of P(−) in comparison to those of P(H) also imply reduced interactions of pyrene groups in P(−).[6] The λ_E value of P(−) was red-shifted in comparison to that of P(H), which is attributed to changes in the environment and conformations of excimer-forming pyrene groups due to an expanded conformation of P(−). The observed temperature effects on the photophysical parameters of P(H) and P(−) (Table II) are attributed to the effects of temperature on both conformation of 1 and rate parameters of intrachain excimer formation.[7] A detailed investigation of these effects was not attempted here.

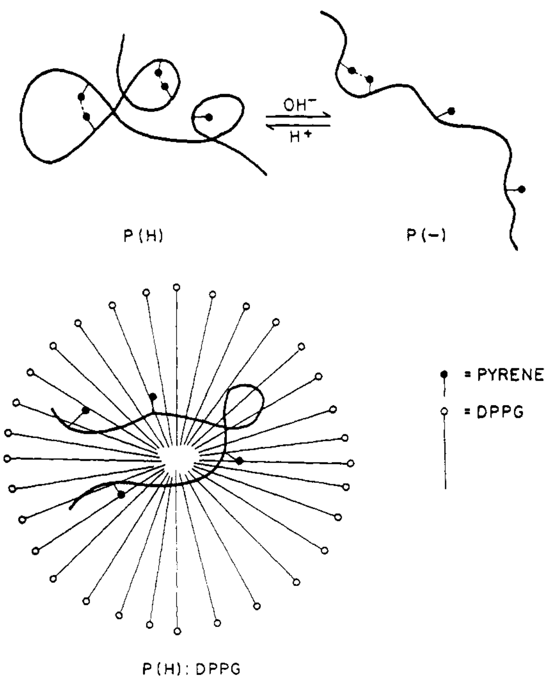


Figure 1. Schematic representation of 1 at pH 4 [P(H)] and pH 7 [P(−)]. The mixed micelles considered to be formed in a solution of 1 and phospholipids at pH 4 are shown for P(H):DPPG.

Photophysical parameters of 1 obtained in the presence of dipalmitoylphosphatidylglycerol (DPPG) at 30 and 45 °C are given in Table II. The I_M/I_E, P_M, and P_E values of P(H) were found to increase in the presence of DPPG at 30 °C as well as 45 °C (Table II). The hydration of phospholipids by ultrasonic irradiation generally produces single-compartment vesicles.[8] However, the Coulombic repulsions between the carboxylate groups in P(−) and the phosphate diester head groups of DPPG might hinder the interactions of P(−) and phospholipids. Thus, the neutralization of carboxylate groups in P(−) favors the interactions of phospholipids and P(H). The formation of mixed micelles of phospholipids and poly(acrylic acid) derivatives has been proposed to account for changes in the thermal transition behavior of phospholipids in the presence of poly(acrylic acid) derivatives at low pH values.[1b] The formation of "mixed micelles" between P(H) and DPPG is considered to cause the observed changes in the photophysical parameters of P(H) in the presence of phospholipids (Figure 1).[9] The intrachain interactions of pyrene groups in P(H) are evidently reduced by interactions of P(H) and phospholipids. The interactions of P(H)

Table III
Lifetime for Pyrene Fluorescence in Solutions of Pyrene-Substituted Poly(acrylic acid)[a]

	monomer fluorescence,[c] ns			excimer fluorescence,[d] ns		
soln comp[b]	τ_1^M	τ_2^M	χ^2	τ_1^E	τ_2^E	χ^2
P(−)	97.4 ± 0.6	27.6 ± 0.2	1.11	47.3 ± 1.8	16.8 ± 1.4	1.40
P(H)	114.5 ± 5.0	33.0 ± 4.6	1.59	51.8 ± 1.0	22.1 ± 1.2	1.17
P(−):DPPG	98.5 ± 2.3	24.3 ± 0.0	1.20	49.2 ± 2.3	21.5 ± 3.7	1.30
P(H):DPPG	117.1 ± 2.0	36.3 ± 0.2	1.32	78.4 ± 1.9	*e*	1.23

[a] Measurements were made with a single-photon-counting instrument and fluorescence lifetime software obtained from PRA, Canada. All measurements were made at 45 °C. [b] Solution composition as given in Table II. [c] Viewed at 378 nm. [d] Viewed at 480 nm. [e] Only one component was obtained from these decay curves (see text).

and DPPG are considered to arise from the hydrophobic interactions of P(H) and lipid chains of phospholipids as well as hydrogen bonding between carboxylic acid groups in P(H) and glycerol head groups of DPPG at low pH values.[1b] Thus, in solutions of P(H):DPPG the pyrene groups are located in the hydrophobic interior of the mixed micelle of P(H) and DPPG. The λ_E values of P(H):DPPG were also blue-shifted, a result consistent with the hydrophobic environment of the pyrene groups in these solutions [cf. λ_E of P(H) and P(−)].

Single photon counting was used to investigate the fluorescence decay behavior of 1 in the presence of DPPG at 45 °C. Fluorescence decay behavior of P(H) and P(−) in Tris buffer solutions was also investigated for comparison with the above results. The observed fluorescence decay curves for pyrene monomer and excimer fluorescence were fitted to equations containing two exponential terms;[10] the results of these deconvolutions are given in Table III. The long-lived component in the decay curve for pyrene monomer fluorescence (τ_1^M) was considered to reflect the lifetime of non-excimer-forming pyrene groups, and that for excimer fluorescence (τ_1^E) was considered to reflect the lifetime of pyrene excimer in 1.[4] The lifetimes of pyrene monomer and excimer fluorescence were found to be increased in P(H) in comparison to those in P(−), which is attributed to a more hydrophobic environment of pyrene groups in P(H). The monomer fluorescence lifetime (τ_1^M) in P(H):DPPG was comparable to that for P(H). No significant changes in excited-state interactions of non-excimer-forming pyrene groups in P(H) are expected due to the presence of P(H) in the hydrophobic core of the "mixed micelle" formed in solutions of P(H):DPPG.

The excimer fluorescence decay curves for P(H):DPPG were found to be different from those of P(H). The decay curves for P(H):DPPG indicated the presence of a growth term whereas no growth term was observed in the excimer fluorescence from P(H). The decay curves for P(H):DPPG could not be fit to a biexponential equation containing a growth and a decay term, which is expected for intramolecular excimer formation.[11] However, the lifetime corresponding to the decay component was obtained by fitting the later part of the excimer fluorescence decay curve to an equation containing one exponential term. The value of τ_1^E obtained in this way was higher than that for P(H) (table III). The excimer formation from pyrene groups in P(H) depends on the intrachain interactions of pyrene groups. These intrachain interactions are reduced by intermolecular interactions of P(H) and DPPG in the mixed micelle of P(H):DPPG, and thus rate constants for formation and decomposition of excimer were affected in P(H):DPPG.

The above proposed model for the interactions of P(H) and phospholipids was also supported by measurement of the rates of quenching of pyrene fluorescence by nitromethane. The Stern–Volmer constant for the quenching of pyrene fluorescence in solutions of 1 was obtained from the plots of I_0/I and concentrations of quencher.[12] [I_0 and I were the intensities of the (0,0) band in the fluorescence spectrum of pyrene in the absence and presence of quencher]. The Stern–Volmer plots for the quenching of pyrene fluorescence from P(H), P(−), P(H):DPPG, and P(−):DPPG were found to be linear. The measurement of fluorescence lifetime in the presence of nitromethane indicated that the quenching was dynamic in nature. The values of K_{SV} (Table IV) and τ_1^M were used to obtain the rate constant for quenching (k_q).[13] The value of k_q for P(H) was reduced in comparison to that for P(−), which is attributed to a coiled conformation of P(H). However, the value of k_q for P(H):DPPG was significantly less than that for P(H). The presence of pyrene groups in the hydrophobic core of the mixed micelle of P(H):DPPG is expected to reduce the quenching of pyrene fluorescence by nitromethane.

Table IV
Quenching of Pyrene Monomer Fluorescence in Solutions of Pyrene-Substituted Poly(acrylic acid) by Nitromethane[a]

soln comp[b]	K_{SV}[c] × 10^{-2}, M^{-1}	k_q[d] × 10^{-9}, $M\ s^{-1}$
P(−)	9.39 ± 0.72	9.64
P(H)	10.04 ± 0.04	8.77
P(−):DPPG	8.07 ± 0.32	8.19
P(H):DPPG	2.99 ± 0.42	2.55

[a] All fluorescence spectra were recorded at 45 °C with a Perkin-Elmer Model LS-5 luminescence spectrophotometer. [b] As given in Table II. [c] Stern–Volmer constant obtained from fluorescence intensity measurements. [d] Rate constant for quenching obtained from K_{SV} and fluorescence lifetime values (cf. Table III).

The photophysical parameters of P(−):DPPG indicated that intrachain interactions of pyrene groups in P(−) were increased by the presence of phospholipids. As mentioned above, the Coulombic repulsion of carboxylate groups in P(−) and phosphodiester head groups in DPPG should hinder the weaker hydrophobic interactions of 1 and phospholipids. The fluorescence lifetimes of pyrene monomer and excimer (Table III) in P(−):DPPG were comparable to those of P(−), indicating a similar environment of pyrene groups in P(−):DPPG. However, the value of k_q for the fluorescence quenching of pyrene in P(−):DPPG was less than that for P(H) and P(−) (Table IV). These results indicate that the conformation of P(−) is affected by the presence of phospholipids at pH 7 but do not provide an unambiguous model for the structures obtained in solutions of P(−) and phospholipids. Tirrell and coworkers[1] have reported that no interactions between poly(acrylic acid) derivatives and phospholipids were observed above critical pH values by calorimetric investigations of the solutions containing phospholipids and PAA derivatives. The critical pH value was proposed to be related to the pK_a value of the PAA derivative and was found to be less than 7 in most cases. It is possible that at pH 7 the ionization of carboxylic groups in P(−) prevents significant interactions of P(−) and phospholipids.[14] However, hydrophobic interactions of excimer-forming pyrene groups (which could be considered as hydrophobic cores in the structure of 1) and lipids are possible under these conditions and therefore the photophysical behavior of P(−) is affected in the presence of DPPG.

A comparison of the photophysical parameters of P(H):DPPG at 30 and 45 °C indicated that intrachain interactions of pyrene groups in P(H) were less at 30 °C than at 45 °C (Table II). The intrachain interactions of pyrene groups in these solutions are expected to be affected by temperature because of the temperature effects on the cooperative motion of lipid chains in phospholipids.[15] The upper transition temperature, which indicates the order-to-disorder transition of lipid chains, has been reported to be 41 °C for DPPG.[16] Therefore, the reduced intrachain interactions of pyrene groups in P(H):DPPG could be attributed to reduced cooperative motion of lipid chains. However, the behavior of solutions containing P(H) and dimyristoylphosphatidylglycerol (DMPG) was found to be similar to that of P(H):DPPG. For example, the I_M/I_E values of P(H):DMPG were 3.78 and 6.00 at 45 and 30 °C, respectively. The upper transition temperature for DMPG has been reported to be 23 °C.[17] Therefore, no signficant changes in intrachain interactions of pyrene groups in P(H):DMPG would be expected between 30 and 45 °C due to cooperative motion of lipid chains. The observed temperature effect is attributed to changes in solvation of P(H) by lipid molecules. Better solvation of P(H) [enhanced interchain interactions of P(H) and lipids] at 30 °C should cause a significant reduction of intrachain interactions of pyrene groups in comparison to those at 45 °C.

Interactions of 1 and dimyristoylphosphatidylcholine (DMPC) and dipalmitoylphosphatidylcholine (DPPC) were also investigated at pH 5 and 7 and at 30 and 45 °C.[18] Investigations of solutions of 1 and DPPC or DMPC at pH 4 were not possible due to precipitation. Photophysical parameters of solutions of 1 and DMPC or DPPC (at pH 5) indicated reduced intrachain interactions of pyrene groups as in the case of P(H):DMPG and P(H):DPPG; that is, an increase in the I_M/I_E, P_M, and P_E values of solutions of 1 and phospholipids was found in comparison to the values of 1 at pH 5. Furthermore, the I_M/I_E, P_M, and P_E values of solutions of 1 and DPPC or DMPC at pH 5 were also greater at 30 °C than those at 45 °C. However, the values of I_M/I_E for solutions containing 1 and phosphatidylcholines were higher than those of phosphatidylglycerol-containing solutions under similar conditions of pH and temperature. For example, at pH 5 and 45 °C, the I_M/I_E value of solutions containing 1 and DPPC was 4.15 whereas that of a solution containing 1 and DPPG was 2.75. The interactions between 1 and choline (dipolar) head group containing phospholipids were favored at high pH values in comparison to those between 1 and glycerol (anionic) head group containing phospholipids. The presence of different head groups did not affect the nature of interactions of P(H) and phospholipids.

When P(H) or P(−) was added to a preformed solution of DPPG,[19] the I_M/I_E value of the resulting solutions was found to be comparable to that of solutions obtained by ultrasonic irradiation of solutions of 1 and DPPG (cf. Table II). Therefore, the interactions of 1 and phospholipids are dependent only on the pH (charge density of 1) of solution, and the formation of "mixed micelles" takes place even when polymer is present outside the vesicles. The interactions of 1 and DPPG were found to be reversible; that is, the I_M/I_E value of a solution containing P(H):DPPG was found to decrease when the pH of the solution was increased to 7.

In conclusion, photophysical investigations of solutions containing 1 and phospholipids suggest that hydrophobic interactions between phospholipids and P(H) lead to the formation of mixed micelles in these solutions at pH 4.

Experimental Section

Preparation and properties of the pyrene-substituted poly(acrylic acid) (1) used in this investigation have been reported earlier.[4] The degree of polymerization of the sample of 1 used in this work was 510 (viscosimetry) and it contained 1.5 mol % of the pyrene chromophore. The samples of phospholipids used in this work were obtained from Sigma Chemical Co. Deionized double-distilled water was used in all measurements.

The solutions of 1 and phospholipids were prepared as follows. A 10.0-mL volume of a dispersion containing 4 mg (5×10^{-4} M) of the phospholipid and 5×10^{-4} M (Repeat units) 1 and 50 mM Tris (Trizma-7, Sigma) buffer was sonicated (Branson Model B-12) at 45–50 °C to obtain a clear solution. The pH of solutions was measured with a Beckman Model 521 pH meter and adjusted by addition of dilute hydrochloric acid/sodium hydroxide. The concentration of 1 in these solutions was checked by measuring the optical density of the solutions at 320 nm (0.10).

Fluorescence emission and excitation spectra were obtained with a Perkin-Elmer Model LS-5 luminescence spectrophotometer equipped with a water-jacketed sample chamber. A Neslab Model RTE-9B constant-temperature circulator bath was used to control the temperature of the sample chamber. Fluorescence lifetimes were determined by using a single-photon-counting (SPC) instrument obtained from Photochemical Research Associates, Canada.[4] All measurements were performed in duplicate and errors refer to one standard deviation.

Spectrophotometric grade nitromethane (Fisher) was used in fluorescence quenching experiments. LS-5 was used in these measurements also. The intensity of the (0,0) band in pyrene fluorescence was used to obtain Stern–Volmer constants.[13]

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Registry No. DPPG, 4537-77-3; DMPG, 61361-72-6; DMPC, 13699-48-4; DPPC, 2644-64-6; CH_3NO_2, 75-52-5.

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(14) This is possible in view of the low concentration of **1** (4 mg/100 mL) used in our experiments in comparison to that used by Tirrell and co-workers (1 mg/mL) in their calorimetric investigations.[1] The low concentration of **1** was required in our experiments in order to avoid interchain interactions of pyrene groups.

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End-Group Effects on the Wavelength Dependence of Laser-Induced Photodegradation in Bisphenol-A Polycarbonate

J. D. Webb* and A. W. Czanderna

Solar Energy Research Institute, Golden, Colorado 80401. Received April 18, 1986

ABSTRACT: Changes in the vibrational spectra of capped and uncapped bisphenol-A polycarbonate films resulting from exposure to pulsed laser radiation at 265, 287, and 308 nm were measured quantitatively by in-situ Fourier transform infrared reflection–absorption spectroscopy. These spectra show molecular weight dependent features which indicate that phenolic end groups in the uncapped polymer, if present in concentrations exceeding the water content of the polymer, are hydrogen bonded to the backbone carbonyl groups. The correspondence of changes in molecular weight to the changes in the vibrational spectra of the exposed films was investigated by size-exclusion chromatography. These results indicate that phenolic end groups sensitize polycarbonate to some photodegradation reactions (such as cross-linking) at 287 and 265 nm, while inhibiting photo-Fries rearrangements. The hydrogen-bonded carbonyl linkages and phenolic end groups are preferentially degraded, especially at 287 nm, where phenolic end group absorption predominates. Absorption (and photoactivity) in highly (>99%) capped polycarbonate is greatly reduced at 287 nm.

Introduction

The photochemistry of bisphenol-A polycarbonate (BPA-PC) has been the subject of a number of investigations since losses of desirable properties such as transparency, tensile strength, impact resistance, and rigidity result from photodegradation when this well-known engineering polymer is used in outdoor applications.[1–3] Since many of these properties are adversely influenced by reactions at the surface of the solid polymer, where solar UV absorption and uptake of oxygen and water are highest, the addition of UV stabilizers and/or antioxidants to the bulk polymer has been generally unsuccessful in extending its outdoor service life to beyond 3 years.[4] Attempts to extend the outdoor service life of polycarbonates by incorporating them into laminates of weatherable, UV-absorbing acrylate and methacrylate polymers have also been unsuccessful, although efforts in this direction continue.[5]

The major parameters influencing outdoor photodegradation of BPA-PC include the wavelength of incident UV radiation, atmospheric oxygen and moisture, and monomer content. Wavelengths as short as 290 ± 2.5 nm may be observed on a continuous basis in the terrestrial solar spectrum,[6,7] and Barker[8] has proposed that intermittent "bursts" of solar radiation at wavelengths as short as 270 nm may penetrate to the earth's surface, based upon measurements of local diurnal variations in the effective thickness of the atmospheric ozone layer.

The first mechanistic interpretations of the photodegradation of BPA-PC were made in terms of photo-Fries rearrangements and chain scission.[9–11] More recent laboratory studies have emphasized the importance of photooxidation and cross-linking reactions in oxygen environments.[12–14] Broad-band UV irradiation or the mercury lines at 254 or 313 nm have been used to initiate photodegradation in these studies. Monochromatic light between 280 and 330 nm with a bandwidth of ±5 nm was used in a recent study of the wavelength dependence of surface photooxidation in BPA-PC.[15] The influence of residual BPA monomer on the photodegradation of BPA-PC was investigated by Pryde,[16] and the role of uncapped phenolic end groups (a processing artifact) in decreasing the thermal[17] and hydrolytic[18] stability of BPA-PC has also been described.

In this work, monochromatic laser UV radiation at 265, 272, 285, 287, and 308 ± 0.01 nm and broad-band UV radiation having various intensity distributions in the range 240–500 nm were used to investigate the wavelength dependence of photodegradation in thin films of capped and uncapped BPA-PC in dry, synthetic air. The technique of Fourier transform infrared reflection–absorption (FTIR-RA) spectroscopy was used to measure photochemically induced changes in the vibrational spectra of the BPA-PC film samples in situ. The advantages of this technique relative to others available and the optimum sample configurations have been described.[19] Changes in the molecular weight distribution of the UV-exposed films were determined by size-exclusion chromatography (SEC). Both FTIR-RA spectroscopy[20] and SEC[10,11] have been utilized to estimate the quantum yields of photoprocesses in BPA-PC.

Experimental Section

Materials and Characterization. BPA-PC polymers I–IV (Table I) were obtained from Polysciences, Inc. and were purified by precipitation from unstabilized, distilled tetrahydrofuran (THF, Burdick and Jackson) into ether or methanol. A general formula for these polymers is given in Table I. Low molecular weight,