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Photophysical and Photochemical Properties of Poly(2-hydroxy-3-allyl-4,4′-dimethoxybenzophenone-*co*-methyl methacrylate): Photochemical Processes in Polymeric Systems. 3

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ABSTRACT: 2-Hydroxy-3-allyl-4,4′-dimethoxybenzophenone (I) has been copolymerized with methyl methacrylate. The copolymer has $\bar{M}_n \simeq 60\,000$ and $\bar{M}_w \simeq 83\,000$ and has been characterized by UV-visible spectroscopy and IR spectroscopy. Optically clear films cast from this copolymer were subjected to ultraviolet irradiation and degradation rates were measured. The structure and rate of decay of the excited state of the polymer-bound benzophenone derivative were investigated by picosecond laser flash spectroscopy. Two transients were observed: the long-lived transient ($\tau > 400$ ps, $\lambda_{max} \simeq 500$ nm) to the first excited triplet and the short-lived transient ($\tau \simeq 10$ ps, $\lambda_{max} \simeq 435$ nm) to the first excited singlet. A mechanism of photodegradation (in air) is presented which is consistent with the data.

The concept that photodegradable polymers may be protected by coating them with a thin transparent film which absorbs ultraviolet light (295–400 nm) present in sunlight at ground level has not yet been fully reduced to practice. Our approach to this problem involves copolymerization of certain allylbenzophenone derivatives with methyl methacrylate so that the resulting copolymer has the following properties: (1) It has chemically bound chromophores which cannot be removed through physical processes. (2) It is protected by benzophenone moieties which when excited do not readily transfer energy to the ester side chain of the acrylic base units or abstract hydrogen from the backbone. It should be recognized that the triplet states of the chromophores and the ester side chain are probably close enough in energy so that endothermic energy transfer is possible, the extent of which will depend on the lifetime of the benzophenone triplet.[1] Since it is well-known that excitation of the side chain in PMMA leads to C–O bond cleavage with high efficiency,[2] photostability of the polymer will depend crucially on the efficiency of energy transfer and, hence, on the benzophenone triplet lifetime. The triplet lifetime similarly controls the efficiency of other chemical processes that it may undergo, such as abstraction of hydrogen or reaction with oxygen, leading to photooxidation and consumption of the chromophore itself and so on. Phosphorescence lifetime measurements by Lamola indicated that the triplet lifetime of 2-hydroxybenzophenone is medium dependent, reaching a few nanoseconds in ethanol at 77 K.[3] It was, therefore, necessary to measure the lifetime of the bound benzophenone triplet and correlate it with the observed rate of photodegradation of the copolymer, since PMMA homopolymer does not interact with photons of wavelengths greater than 295 nm, as established by irradiating PMMA films with Pyrex-filtered radiation from a medium-pressure Hg arc lamp and monitoring molecular weight as a function of exposure period for periods up to 2000 h. The mechanism of photostabilization by 2-hydroxybenzophenone derivatives has been the subject of several investigations, and mechanisms involving a rapid tautomerism of the excited states (between the phenol and the "quinonoid" forms) have been proposed.[4,5] Klopffer[6] proposed that the benzophenone singlet undergoes tautomerism to produce a quinonoid singlet which intersystem crosses rapidly to form the quinonoid triplet which in turn undergoes hydrogen back-transfer to form the phenol triplet. He arrived at a detailed scheme of radiationless transitions in the 2-hydroxybenzophenone system on the basis of emission spectroscopic data and measurement of p*K* values of the ground and excited states. Recently transient absorption measurements on 2-hydroxybenzophenone in aprotic and protic solvents have been reported by Eisenthal[7] and by us.[8] These data indicate that rapid internal conversion of the singlet takes place in aprotic solvents, while weak triplet–triplet absorption is detected in protic solvents such as ethanol.

The preparation of the copolymer involved reconciliation of the vastly different reactivity ratios of the comonomers. The allylbenzophenone used in this study was even more unreactive than vinylbenzophenone commonly used for photostabilization. This comonomer was chosen with the expectation that the resulting copolymer would have a higher efficiency of screening ultraviolet radiation. The copolymer films were compared with the copolymer of methyl methacrylate and Permasorb MA, which is a commercially available 2-hydroxybenzophenone derivative containing vinyl unsaturation. This expectation was fulfilled, as described below. A maximum incorporation of 0.51% of the chromophore was obtained, which means that a film of approximately 0.02-cm thickness is required to achieve 99% attenuation of 360-nm radiation. A copolymer of methyl methacrylate and *n*-butyl methacrylate would be preferable to PMMA as the base medium from processing considerations and polymerization processes. A terpolymer of these two acrylic monomers with I is under investigation.

Experimental Section

I was prepared according to Scheme I. Synthetic procedures will not be described in detail, since they are available in the literature.[9] Compound I (0.5 g), freshly distilled methyl methacrylate (5.0 g), and AIBN (0.1 g) were dissolved in 100 mL of dry Me_2SO/dioxane (1:9 v/v); then the mixture was deaerated with N_2 and maintained at 55 °C for 12 h and then at 80 °C for 24 h. The product was washed with methanol and reprecipitated with methanol from dichloromethane. The product was then exhaustively extracted with methanol in a Soxhlet apparatus until extracts showed no ultraviolet absorption and the UV spectrum of the remaining material (CH_2Cl_2 solution) became constant.

A solution of this copolymer in CH_2Cl_2 was analyzed on a high-performance liquid chromatograph (LC) using four capillary

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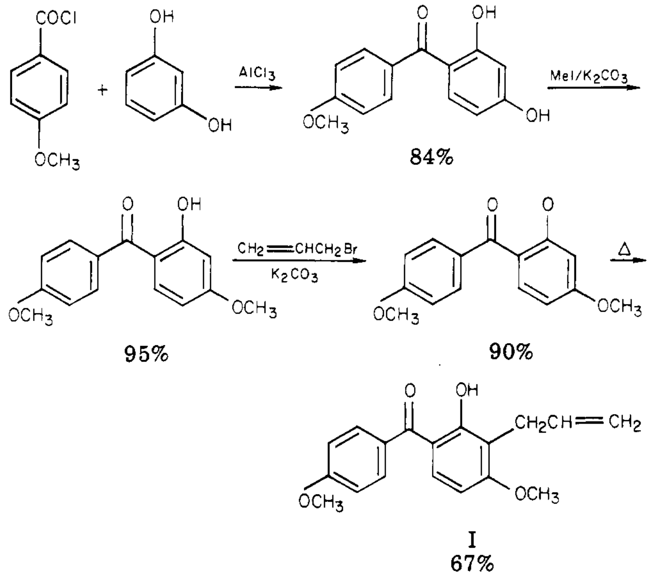
Scheme I



columns packed with μ-Styragel. The refractive index peak matched with the UV (250 nm) peak, indicating that the chains containing the chromophores had the same approximmate distribution as the chains with no chromophores. However, the UV peak gave a lower apparent molecular weight distribution than the refractive index peak, indicating that the chromophore-bearing chains had a lower molecular weight distribution. By following these two distributions simultaneously, it is possible to identify the site of photodegradation in the copolymer. Since incorporation is only about 0.5%, the probability of one chain containing more than one chromophore is quite small, assuming random copolymerization. Hence, the copolymer is almost identical with PMMA in terms of structure and reactivity and is not separated from it either by extraction or by passage through the high-performance LC. We do not expect blocks of I to be formed, since we expect a chain radical ending in I ($R_1\cdot$) to decay mainly through recombination, probably with a chain radical with methyl methacrylate at the end ($R_2\cdot$) or with the initiator radical (P·), since concentrations of $R_2\cdot$ or P· are expected to be much higher than $R_1\cdot$. In a sense, I acts as a polymerization inhibitor making the minimum concentration of initiator need very high. It is expected that much of the low molecular weight product containing a high concentration of initiator end groups (which may be potentially photolabile) is removed through extraction. The copolymer was dissolved in CH_2Cl_2 and cast into optically clear films which were dried to remove solvent. These films were irradiated in a merry-go-round type apparatus with light from a medium-pressure Hg (Hanovia) lamp filtered through 8 mm of Pyrex, which attenuates 99% of the light incident on it at 297 nm. The spectral distribution of this irradiance has been measured and consists of peaks at 302, 313, 366 nm in the ultraviolet region which are absorbed by the sample. In our earlier work on polycarbonate we observed that broad-band photochemistry, especially at the absorption tails, can be considerably different from photochemistry at certain specific wavelengths. Since the objective was to evaluate the photostability of these films in sunlight at ground level (airmass one), we decided to use a broad-band ultraviolet source as described above without further wavelength selection. Test films of approximate thicknesses 4×10^{-3} and 2×10^{-3} cm were used. The light flux absorbed by the sample integrated in time was estimated by using a PMMA film containing the actinometer o-nitrobenzaldehyde, which has approximately the same wavelength response as the test films (Figure 1). Light flux absorbed by the film was calculated by choosing as actinometer film of approximately equal wavelength response and calculating conversion of o-nitrobenzaldehyde to o-nitrobenzoic acid in mg/s. If this is a, then the number of photons absorbed by the test film per second is $(a/151) \times 10^{-3} \times 2.0 \times 6 \times 10^{23}$, where 151 is the molecular weight of o-nitrobenzaldehyde, 2.0 is the reciprocal of the quantum yield of conversion in the actinometer, and 6.0×10^{23} is Avogadro's number. This value was compared with measurements on the lamp and absorbance plot of the actinometer film. Table I gives the number of photons absorbed by the actinometer film estimated radiometrically; this compares with the experimental quantity. In this table, we also include the number of photons absorbed by the copolymer films. Table II gives the total dosages and times of irradiation of the films.

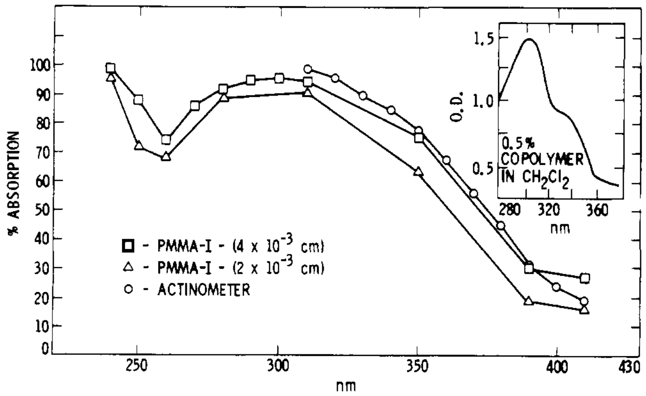


Figure 1. Spectral response of o-nitrobenzaldehyde actinometer.

Table I
Performance of Actinometry on Copolymer Films

wavelength range, nm	actinometer absorption, photons/(cm^2 s)	film absorption, photons/(cm^2 s) $d = 4 \times 10^{-3}$ cm	$d = 2 \times 10^{-3}$ cm
≤293	2.4×10^{13}	9.1×10^{13}	8.9×10^{13}
293-299.6	8.9×10^{13}	3.3×10^{14}	3.3×10^{14}
299.6-307.8	1.0×10^{15}	4.0×10^{15}	3.9×10^{15}
307.8-323.5	7.0×10^{14}	2.8×10^{15}	2.6×10^{15}
323.5-350	1.7×10^{16}	6.3×10^{16}	6.1×10^{16}
350-385.3	5.0×10^{15}	1.9×10^{15}	1.2×10^{16}
total absorption	2.38×10^{16}	8.9×10^{16}	7.9×10^{16}
overall absorp from chem convrsn	2.2×10^{16}		

Table II
Radiation Input to the Copolymer Film

film thickness, $\times 10^{-3}$ cm	time of exposure, h	no. of photons absorbed $\times 10^{20}$ per cm^2
2	0	
4	7	21.7
4	16	49.6
2	77	215.6
2	135	338.0
4	448	1388.8

In terms of AM 1 (airmass one) sunlight, the largest period of exposure corresponds to an outdoor exposure of 1.5 years. This estimate is based on the comparison of absorbed ultraviolet flux during exposure to the Hg lamp relative to expected absorbed UV flux if the copolymer film is exposed to AM 1 sunlight. It has been determined that (a) the quantum yields are wavelength independent in the region 295–366 nm, (b) the UV intensities of the lamp and the sun (AM 1) are too low to cause multiphoton processes, (c) the longer wavelength absorption caused by the presence of vibrational overtones does not contribute to photochemistry, and (d) the quantum yields are light-intensity independent at the intensity levels used in this study. The films were monitored by UV–visible spectroscopy and FT IR spectroscopy as well as by high-performance LC (capillary columns packed with μ-Styragel). A preliminary experiment indicated negligible weight loss on irradiation.

Flash Photolysis. A sample solution was prepared from 0.384 g of a copolymer sample, containing 2.15% of the photostabilizer by weight, by dissolving it in 10 mL of CH_2Cl_2. A solution with a 1-mm path length gave an optical density at 355 nm of ~1.3. This absorption was due entirely to the 4,4′-dimethoxy-2-hydroxybenzophenone chromophore.

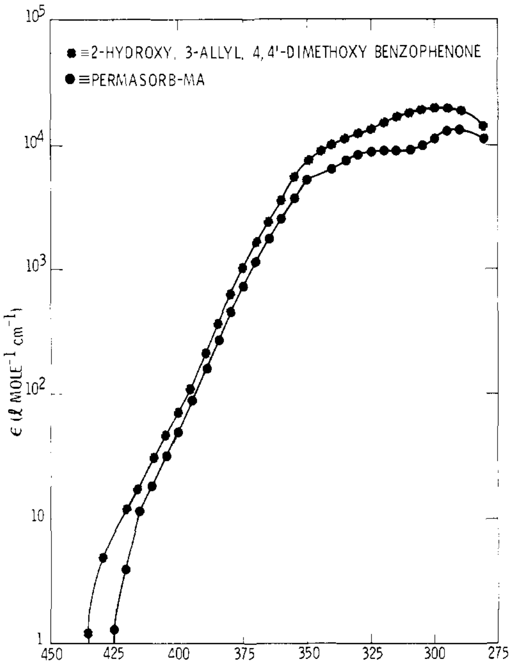


Figure 2. Rate of change of absorbance vs. wavelength for the copolymers of I with MMA and for Permasorb MA and MMA.

A previously described[10] mode-locked Nd^{3+}:glass laser system supplied the spectra. The general technique of obtaining picosecond time-resolved spectra has been previously described.[11-13] A single third-harmonic pulse ($\lambda = 355$ nm, $\Delta t = 8$ ps, $E \simeq 0.5$ mJ) was used for excitation of the sample. The UV pulse was separated from the remaining 1064-nm-fundamental pulse by a dichroic mirror and traveled a fixed-delay optical path to the sample.

The excitation pulse was focused onto a small region of the 1-mm quartz sample cell through a contacted, 0.75-mm aperture. Meanwhile, the 1064-nm pulse traveled along a variable-delay optical path. It was used to generate a visible continuum pulse ($\Delta t \leq 10$ ps) by focusing the 1064-nm-fundamental pulse into a 2-cm cell of either ethanol or D_2O. The remaining 1064-nm intensity was then filtered out and the continuum pulse was diffused with ground glass to partially depolarize it and to remove spatial inhomogeneities. After generation, the continuum probe was split by a 50/50 beam splitter into a reference probe pulse [$I_0(\lambda)$]. Then the sample probe pulse was also focused onto the same aperture at the sample, crossing the excitation pulse at this point with an angle of ~5%.

The intensity vs. wavelength characteristics of $I_0(\lambda)$ and $I(\lambda)$, after the latter probes the excited-sample spectrum, were obtained by focusing both reference and sample probe pulses at different vertical positions of the slit of a 0.3-m spectrograph. The detection system consisted of a Princeton Applied Research optical multichannel analyzer system (OMA2) utilizing an SIT two-dimensional vidicon detector. The detector was used in the linear-response range, and there were no overlaps of sample- and reference-pulse spectra at their respective vertical detector positions.

The delay between the arrival time of the excitation and sample probe pulses could be varied by independently changing the path length that the 1064-nm, continuum generating pulse traversed. The path length giving the delay time of $t = 0$ was determined in separate calibration experiments and corresponded to maximum temporal overlap of the excitation and sample probe pulses at the sample.[1,4] This time was used to determine longer delays by measuring the additional path required, with an accuracy of ~0.3 mm (1 ps). The time-delayed spectra obtained, however, do not represent spectra taken only at the instant of the given delay time but necessarily include a weighted average over the laser pulse duration.

The OMA was programmed to obtain a digitized spectrum of the sample and reference probe pulses for each laser shot. Each 250-point spectrum covered the range ~400-700 nm. An average of the background (i.e., flash lamp) and dark-current counts was automatically subtracted from each shot to determine $I_0(\lambda)$ and $I(\lambda)$. A four-shot average of the ratio $R(\lambda) = I(\lambda)/I_0(\lambda)$, was obtained at *a given delay time without excitation.* Further, a four-shot average of the apparent transient optical density, $\Delta OD(\lambda) = -\log [I(\lambda)/I_0(\lambda)]$, with excitation, was obtained after normalizing to the UV excitation intensity. Finally, the true optical density change, $A(\lambda)$, at each wavelength was obtained by adding the log of the average ratio, $\overline{R(\lambda)}$, to the average, apparent transient optical density $\overline{\Delta OD\ (\lambda)}$. The transient absorption spectra at each delay time reported here are the $A(\lambda)$'s computed from eq 1.

$$A(\lambda) = \Delta OD(\lambda) + \log R(\lambda) \qquad (1)$$

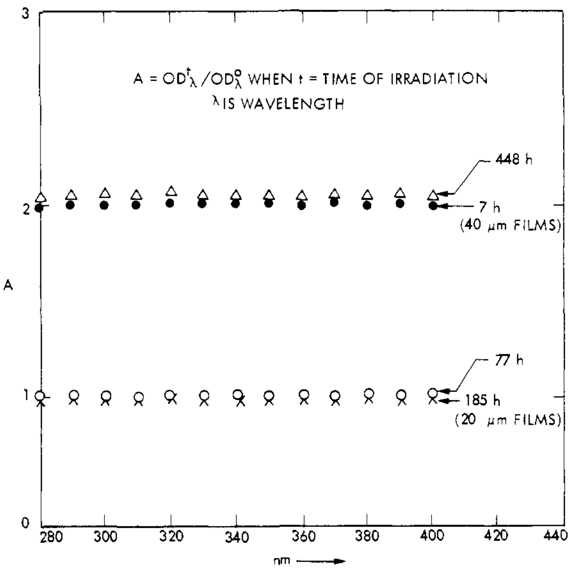


Figure 3. Change of electronic spectra of copolymer films as a function of irradiation period. Exposures of 7 and 448 h were carried out on films 40-μm thick while exposures of 77 and 185 h were carried out on films 20-μm thick.

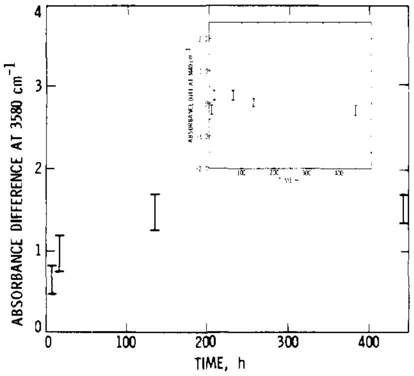


Figure 4. Change in hydroxyl concentration in copolymer films as a function of irradiation period, as measured by monitoring the optical density increase at 3580 cm^{-1}; error bars represent extreme values of 4-6 spectroscopic measurements on the same samples.

Results and Discussion

Figure 2 shows a plot of extinction coefficient vs. wavelength for the copolymers of I with MMA and for Permasorb MA and MMA. Figure 3 is a plot of A vs. wavelength, where $A = OD_\lambda{}^t/OD_\lambda{}^0$ and t is the time of exposure. This plot indicates that there is negligible change in structure of the chromophore due to photodegradation at the two film thicknesses studied. FT IR spectra yield the same results; in other words, our spectroscopic results indicate little change in the structure of the chromophore. Figure 4 shows a difference of plot of hydroxyl absorption at 3580 cm^{-1} vs. time of exposure. The hydroxyl band is broad and cannot be precisely analyzed.

Table III
Molecular Weight Distributions as a Function of Exposure Period

detection mode	time of exposure, h	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
RI	0	46 000	87 000	1.89
UV	0	31 000	69 000	2.21
RI	448	42 000	77 000	1.83
UV	448	34 000	79 000	2.36

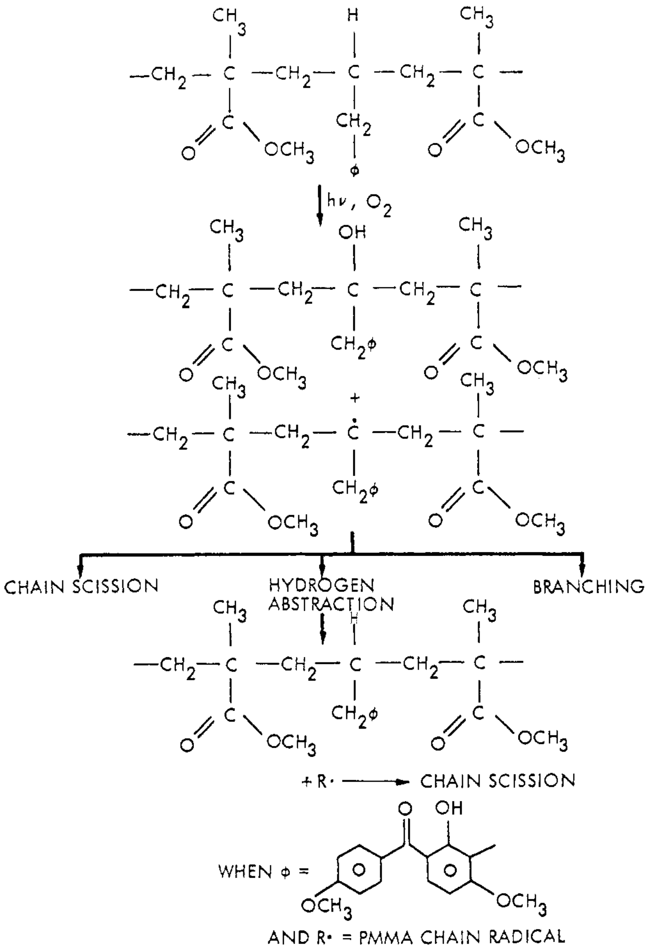
The concentration is quite small, but it would still be sufficient to cause a measurable change in the electronic absorption spectrum if it represented consumption of the chromophore. Hence, we assign it to the MMA segments of the polymer and propose a slow process of photooxidation catalyzed by the chromophore. No methanol is found in high-performance LC analysis performed on the same films. The absence of methanol excludes excitation transfer to the side chain (ester).

Table III gives molecular weight distributions calculated from both refraction index and UV peaks. Refractive index measurements yield a value of 1.8×10^{-8} for the quantum yield of chain scission, assuming that $(\overline{M}_n(t)/\overline{M}_n(0) - 1)C_s = \phi_{cs}P_t$, where ϕ_{cs} is the quantum yield of chain scission, P_t is the number of moles of photons absorbed in time t, and C_s is the number of moles of chains present in the films.

This exceedingly small value is an indication of the extreme photostability of the polymer. There is a simultaneous increase of the molecular weight of the chains bearing chromophores which generate the UV signal. A simple calculation indicates that the probability of occurrence of one or more chromophores in a chain in this system is about 66%, assuming random copolymerization. Hence, using the UV data of Table II, it is possible to calculate the quantum yield of branching for the chains bearing chromophore units. This quantum yield is approximately 1.6×10^{-8}. Considering that the electronic absorption spectrum remains constant (to within 2%) and the chromophore-bearing chains undergo branching while the copolymer as a whole undergoes a net decrease in molecular weight leads to the mechanism proposed in Scheme II for the observed photochemistry. This mechanism identifies the tertiary hydrogens on the chromophore-bearing chains as the primary site of attack by excited oxygen formed via electronic energy transfer from the triplet state of the chromophore. The total concentration of tertiary hydrogens in the copolymer per cm^2 is about 4.2×10^{-8} mol in 1 cm^2 of the 20-μm film. After 448 h of irradiation the number of moles of branch points generated is about 4.8×10^{-9} mol/cm^2 of the film.

The prompt, short-lived transient absorption whose lifetime is estimated to be ~10 ps is presumably due to the first excited singlet of the 2-hydroxy-4,4′-dimethoxybenzophenone chromophore. There is also a definite indication of a long-lived transient absorption (λ_{max} = 475 nm) persisting beyond 480 ps. The optical density observed in this case is similar to that reported by Eisenthal for 2-hydroxybenzophenone at 475 nm at similar time delays. This transient absorption study indicates that internal conversion competes with intersystem crossing in this polymeric chromophore, and triplets which are formed decay in less than 10 ns. Similar conclusions are reached for 2-hydroxybenzophenone, which may be studied in solvents of widely differing protonating and solvating character. These triplets are assumed to be sensitive agents for the observed photooxidative process. Both hydrogen abstraction and energy-transfer processes leading to degradation are expected to be activated and, hence, far less efficient compared with the ultrafast radiationless deactivation process which efficiently depopulates the triplet.

Scheme II



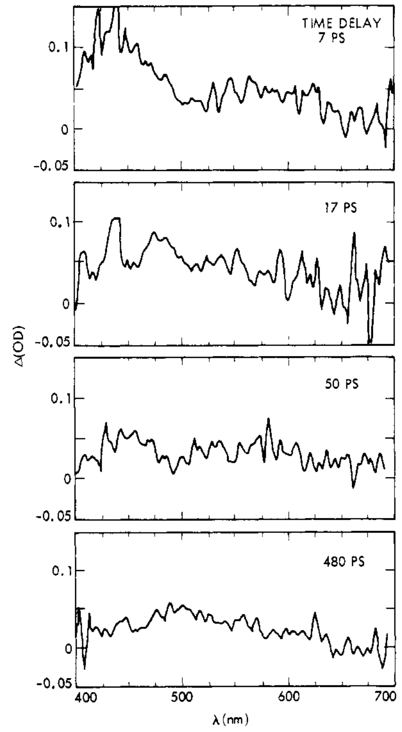


Figure 5. Transient absorption spectra on copolymer I in fluid solution at room temperature by picosecond flash spectroscopy.

Scheme III

$$A \rightarrow A^{1*} \rightarrow A'^{1*} \rightarrow A'^{3*} \rightarrow A' \rightarrow A$$
$$A \rightarrow A^{1*} \rightarrow A'^{1*} \rightarrow A' \rightarrow A$$

The singlet lifetime reported here matches the lifetime of the singlet state of benzophenone;[13] hence, one may assume that the same types of deactivation processes are depopulating the hydroxybenzophenone singlet, which is principally an ultrafast intersystem crossing process, producing triplets with unit efficiency. Scheme III is proposed to interpret these results. In Scheme III A is the benzenoid structure and and A′ is the quinonoid structure. Here we assume that the chromophore exists in only one type of steric conformer, namely, the benzenoid structure with a weak intramolecular hydrogen bond. More precise kinetic studies are needed to resolve this question. If the proton transfer in the triplet manifold is assumed to be fast, then the triplet absorption recorded may, in fact, be the quinonoid triplet. The long-lived transient absorption recorded does not show a prompt rise, concurrent with the singlet decay, and may have an extinction coefficient ($T_n \leftarrow T_1$ absorption) significantly less than that of benzophenone triplets. In an identical experiment, with the same apparatus, the $T_n \leftarrow T_1$ absorption of benzophenone in solution gave a peak OD of ~0.5 at 480 ps, or 10 times that observed in this case. On the other hand, it is possible that the triplet may merely acquire some fractional quinonoid character corresponding to strong hydrogen bonding of the 2-hydroxyl group to the carbonyl group and a quinonoid distortion of the phenyl group. Picosecond flash spectroscopic studies on substituted *s*-triazines reported by Tanaka et al.[14] reveal a different mechanism of deactivation of excited state in that system. They observed intramolecular proton transfer from the singlet, and the singlet tautomer was characterized by its red-shifted emission spectrum. Formation of a metastable ground state was postulated. The uniqueness of stabilizer molecules containing the 2-hydroxybenzophenone nucleus presumably lies in the fact that the singlet state has an ultrafast intersystem crossing channel ($\sim 10^{11}$ s^{-1}) open to it which would effectively compete with radiationless transition mode induced by intramolecular proton transfer, whose rate has been estimated to be 1.2×10^{10} s^{-1} for *s*-triazines by Tanaka et al. Preliminary results of nanosecond flash spectroscopic experiments indicate no long-lived ground-state quinone species in our system. These experiments are being repeated at low temperature, and attempts are being made to chemically trap the ground-state quinone. Quenching experiments with diene quenchers whose triplet energy is in the region 45–50 kcal/mol, so that quinonoid triplets of lower energy can be quenched at a diffusion-controlled rate, are also under way to count the number of triplets formed in the system. A metastable ground-state quinone, if formed in this system, will ultimately control the rate of its photodegradation.

In conclusion, we have described here a stable copolymer containing a 2-hydroxybenzophenone derivative as a pendant group. The stablity of this system is clearly due to the short lifetime of the reactive excited states of the chromophores. This copolymer, therefore, has potential application as a transparent UV-screening agent.

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References and Notes

(1) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, 1965.

(2) A. Gupta, F. D. Tsay, and R. Liang, to be submitted for publication. The quantum yield of product formation was measured under vacuum by irradiating thin films of PMMA with a low-pressure Hg arc.

(3) A. A. Lamola and P. Sharp, *J. Phys. Chem.*, **70**, 2634 (1966).

(4) E. J. O'Connell, *J. Am. Chem. Soc.*, **90**, 6550 (1968); D. N. Shigorin and L. A. Mielszina, *Vysokomol. Soedin.*, *Ser. B*, **9**, 26 (1967).

(5) J. N. Pitts, Jr., H. W. Johnson, and T. Kirwana, *J. Phys. Chem.*, **66**, 2456 (1962); A. M. Trozzolo in "Polymer Stabilization", W. L. Hawkins, Ed., Interscience, New York, 1972, p 159.

(6) W. Klopffer, *J. Polym. Sci.*, *Polym. Symp.*, **No. 57**, 205 (1976).

(7) S. Y. Hon, W. M. Hetherington, G. M. Korenowski, and K. B. Eisenthal, *Chem. Phys. Lett.*, **68**, 282 (1979).

(8) C. Merrit, G. W. Scott, A. Gupta, and A. Yavrouian, *Chem. Phys. Lett.*, **69**, 169 (1980).

(9) D. Tirrell, D. Bailey, C. Pinazzi, and O. Vogl, *Macromolecules*, **11**, 312 (1978), and references therein.

(10) D. E. Damschen, C. D. Merritt, D. L. Perry, G. W. Scott, and L. D. Talley, *J. Phys. Chem.*, **82**, 2268 (1978).

(11) D. Magde and M. W. Windsor, *Chem. Phys. Lett.*, **27**, 31 (1974).

(12) B. I. Greene, R. M. Hochstrasser, and R. B. Weisman, *J. Chem. Phys.*, **70**, 1247 (1979).

(13) R. W. Anderson, Jr., D. E. Damschen, G. W. Scott, and L. D. Talley, *J. Chem. Phys.*, **71**, 1134 (1979).

(14) H. Shizuka, K. Matsui, and I. Tanaka, *J. Phys. Chem.*, **81**, 2243 (1977), and references therein.