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Photochemical Behavior in Copolymers of 2(2-Hydroxy-5-vinylphenyl)2H-benzotriazole and Methyl Methacrylate: Photochemical Processes in Polymeric Systems. 6

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Photochemical Behavior in Copolymers of 2(2-Hydroxy-5-vinylphenyl)2H-benzotriazole and Methyl Methacrylate: Photochemical Processes in Polymeric Systems. 6*

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ABSTRACT

The photochemical behavior of poly[2(2-hydroxy-5-vinylphenyl)2H-benzotriazole)]-co-methyl methacrylate was studied by spectroscopic and analytical techniques; no degradation of this copolymer occurred when the bulk polymer was exposed for several thousand hours of accelerated aging by ultraviolet irradiation. However, by the end of the period, surface deterioration became noticeable. Picosecond flash photolysis on copolymer solutions demonstrated that the lowest energy excited singlet state undergoes rapid internal

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conversion with little or no triplet yield. The observed short singlet lifetime (~25 ps) is undoubtedly responsible for the photostability of this copolymer system. Analysis of the surface exposed to ultraviolet irradiation indicates some photooxidative degradation of the methyl methacrylate portion of the copolymer, but the surface 2(2-hydroxy-5-vinylphenyl)2H-benzotriazoles of the macromolecules remain unchanged.

INTRODUCTION

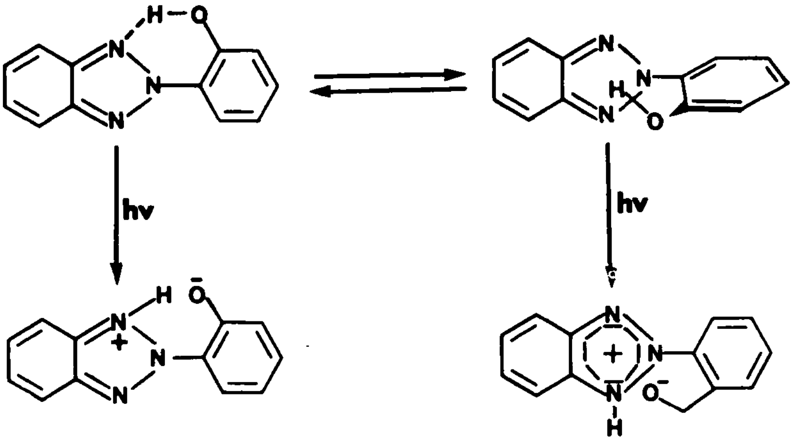
Polymeric ultraviolet stabilizers are useful additives for polymers which are used under light exposure of high ultraviolet content. One such composition is prepared by copolymerization of monomers possessing ultraviolet absorbing chromophores as pendant groups with common acrylic monomers such as styrene or methyl methacrylate. It is important to determine if such copolymers have the required ultraviolet absorption for efficient electronic energy dissipation such that the copolymer remains unchanged under photochemical aging over long periods of time [1, 2]. We have shown in previous reports [3-6] that the critical parameters in determining the photoreactivity of the chromophore are the lifetime and yield of its potentially reactive excited states. The mere presence of low energy excited singlet or triplet states are therefore not prerequisite for enhanced photostability. However, intersystem crossing to excited triplet states from the initial excited singlet states must be avoided or inhibited because triplet states are inherently long lived.

Flash spectroscopic studies [6] on 2-hydroxybenzophenone and a polymeric 2-hydrobenzophenone derivative in nonprotic solvents showed a decay rate of transient absorbance of ~0.1 ps^{-1}. Although in this case the triplet yield is negligible in such solvents, in protic solvents (e.g., ethanol) 2-hydroxybenzophenone has a small but nonzero triplet yield, and a transient triplet-triplet absorbance persists for 400 ps or longer [6-8]. Photodegradation studies of films (below the T_g) of methyl methacrylate copolymers with 4-methacryloxy-2-hydroxybenzophenone [3] showed that a very small but detectable amount of triplet-triplet electronic energy transfer occurs. Hydrogen abstraction by photosensitization occurs at branch points of a polymer backbone, causing a gradual increase in branching and crosslinking which are detected as a change in the molecular weight distribution of the copolymers as aging proceeds.

In previous work we reported studies of 2(2-hydroxy-5-methylphenyl)2H-benzotriazole (2H5M) and other 2(2-hydroxy)2H-benzotriazoles by exciting at 355 nm [9, 10]. This work showed that ground state bleaching recovery is essentially complete after 225 ps (3 half lives) in a nonprotic solvent (dichloromethane). Therefore no significant triplet state quantum yield was observed. However, phosphorescence of 2H5M at 90 K has been reported by Kramer et al. [11].

Fluorescence of 2H5M has been observed at room temperature. The fluorescence yield is quite low (about 2×10^{-5}), and the decay time was found to be ~14 ps in methylcyclohexane, significantly shorter than the ground state bleaching recovery rate (33 ± 5 ps) [9, 10].

Effective ultraviolet stabilizing systems often have ortho hydroxy groups on aromatic rings which hydrogen bond either to a carbonyl oxygen, such as in 2-hydroxybenzophenone, or to a ring nitrogen atom, as in the case of MeHPB. Rapid radiationless transitions in such systems are believed to be facilitated by an intramolecular proton transfer process [9-19]. The electronic absorption spectrum of MeHPB in hydroxylic solvents such as ethanol has an absorption maxima at ~300 nm, similar to the lowest energy band of 2-methoxy and 2-acetoxy derivatives of 2(2-hydroxyphenyl)2H-benzotriazoles [11, 21]. However, the lower energy 340-nm absorption band of 2H5M only exists in a hydrogen-bonded form of 2H5M in which the phenolic ortho hydroxyl groups is H-bonded to a nitrogen atom of the benzotriazole ring; the ratio of the intensities of these two peaks in the absorption spectra of 2H5M at 310 and 340 nm changes by less than 50% upon changing solvents from methylcyclohexane to trifluoroethanol [16]. It is possible that an equilibrium exists between coplanar and noncoplanar hydrogen-bonded forms in the ground state. This equilibrium should be affected by solvent polarity, intermolecular hydrogen bonding, and temperature. Experimentally, the 340-nm absorption peak of 2H5M has the highest extinction coefficient in hydrocarbon solvents [21]. However, M.O. calculations [18] and the x-ray crystal structure [19] indicate that 2H5M has a minimum in its ground state at the planar conformation. Intermediate structures of the ground state and the excited states of 2(2-hydroxyphenyl)2H-benzotriazoles are shown in Scheme 1.



SCHEME 1. Photoexcitation of 2(2-hydroxy-5-vinylphenyl)2H-benzotriazoles.

EXPERIMENTAL

Poly[2(2-hydroxy-5-vinylphenyl)2H-benzotriazole)]-co-(methylmethacrylate)] (poly[2H5V-co-MMA]) was synthesized as described previously [2, 20]. A particular copolymer of poly[2H5V-co-MMA] with a composition of 15 mol% of 2H5V was selected for evaluation. Films of this copolymer were prepared by solvent casting from dichloromethane on Pyrex plates. These films and solutions of the copolymer were subjected to photodegradation by mounting them on the surface of a "merry-go-round" type reactor [22] and exposing them to Pyrex and water filtered ultraviolet from a medium pressure Hg lamp. Actinometry was performed using orthonitrobenzaldehyde as the actionometer. The aging was followed for 3 700 h, at which time the radiation flux which had been absorbed by the copolymer films was a total 5.33 einsteins/cm^2 in the range of 295 to 385 nm.

The photons incident per chromophore molecule ranged up to 4.00 × 10^5. More than 80% of all the radiation was in the given wavelength range (see Table 1). Electronic absorption spectra and infrared spectra [bulk and attenuated total internal reflection (ATR)] were recorded on controls and, as a function of increasing aging times, on aged samples, both in solution and in the films.

Molecular weights and molecular weight distributions of the copolymers (controls and aged samples, both in solution and in films) were determined by GPC measurements carried out on a high performance liquid chromatograph equipped with molecular exclusion-type columns. Surface tension angle measurements were also made as a function of aging on both the exposed and back surfaces of the films.

TABLE 1. Radiation Flux Deposited on Copolymer Films; Greater than 80% of All Radiation was Absorbed in the Given Wavelength Range

Aging time, h	Photon flux, einsteins/cm^2 (295-385 nm)	Photons incident for chromophore molecule
750	1.10	8.00 × 10^4
1 590	1.48	1.85 × 10^5
1 770	2.45	2.55 × 10^5
2 040	2.96	2.65 × 10^5
2 170	3.12	2.70 × 10^5
2 580	3.71	2.19 × 10^5
3 700	5.33	4.00 × 10^5

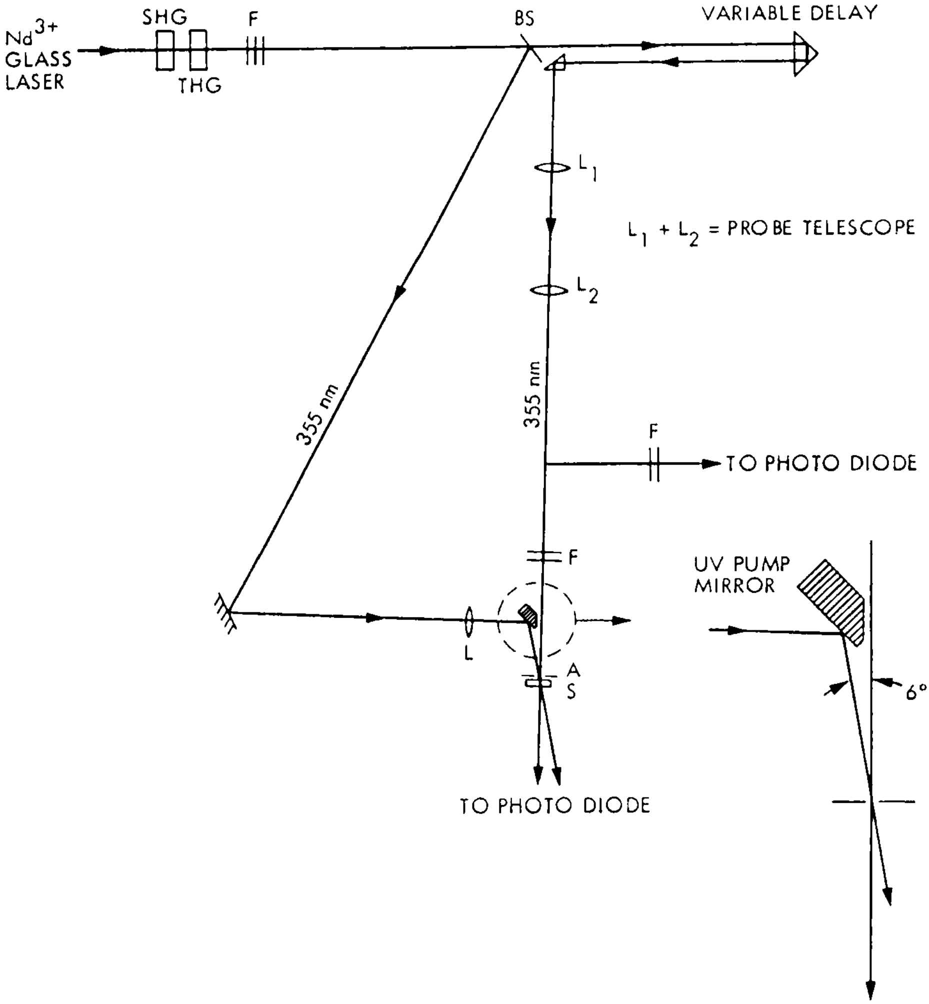


FIG. 1. Schematic of the picosecond flash kinetic set-up for measurement of ground state bleaching recovery rates.

Absorption recovery kinetics of solutions were studied using a single, third harmonic pulse ($\Delta t \approx 10$ ps) at 355 nm from a mode-locked Nd^{3+}:glass laser system (see Fig. 1). Approximately 90% of the UV pulse was used to bleach the ground state absorption of the sample (0.3 mJ/pulse). The remainder of this pulse (probe pulse) followed a variable delay line and was used to monitor changes in sample absorption as a function of time following excitation. Complete experimental details have been published elsewhere [9, 10].

RESULTS AND DISCUSSION

When the copolymer was subjected to accelerated aging in solution, the absorption spectrum of the copolymer remained unchanged. When accelerated aging was carried out in films, there was a slight increase in the absorbance in the 450 to 500 nm regions for extended aging periods. Small changes in the absorption spectrum of aged films were observed which apparently included contributions from increased backscattering; scattering losses were observed in hemispherical transmission spectra.

On the back unexposed surface of copolymer films, no significant change in the surface tension was found (see Table 2). On the exposed surface, however, from 1 770 h on, the surface tension increased, indicating that a change in chemical structure of the surface, probably caused by surface oxidation, had occurred. The increase of surface tension was from about 39 (control) to 60 dyn/cm at an aging time of 2 170 h.

Figure 2 shows the ultraviolet absorption spectra of control and aged samples. The sol fraction of the aged sample (2 500 h) shows an absorption spectrum which is essentially identical to that of the control sample except for a loss of intensity. These spectra demonstrate that the sol fraction of the aged sample is probably not chemically changed insofar as the 2(2-hydroxyphenyl)benzotriazole chromophore is concerned. There is a slight increase in the long wavelength absorption, but that difference is just outside of experimental error. However, since the intensity of the absorption bands is decreased by approximately 20 ± 5%, this could be a measure of the gel content of the

TABLE 2. Surface Tension (γ_c) of Samples Measured as a Function of Aging Time

Aging times, h	Exposed surface, dyn/cm	Back surface, dyn/cm
0	~38	39 ± 3
750	42 ± 2	33 ± 4
1 000	~45	34 ± 5
1 770	~55	32 ± 8
2 040	~59	32 ± 6
2 170	~60	29 ± 4

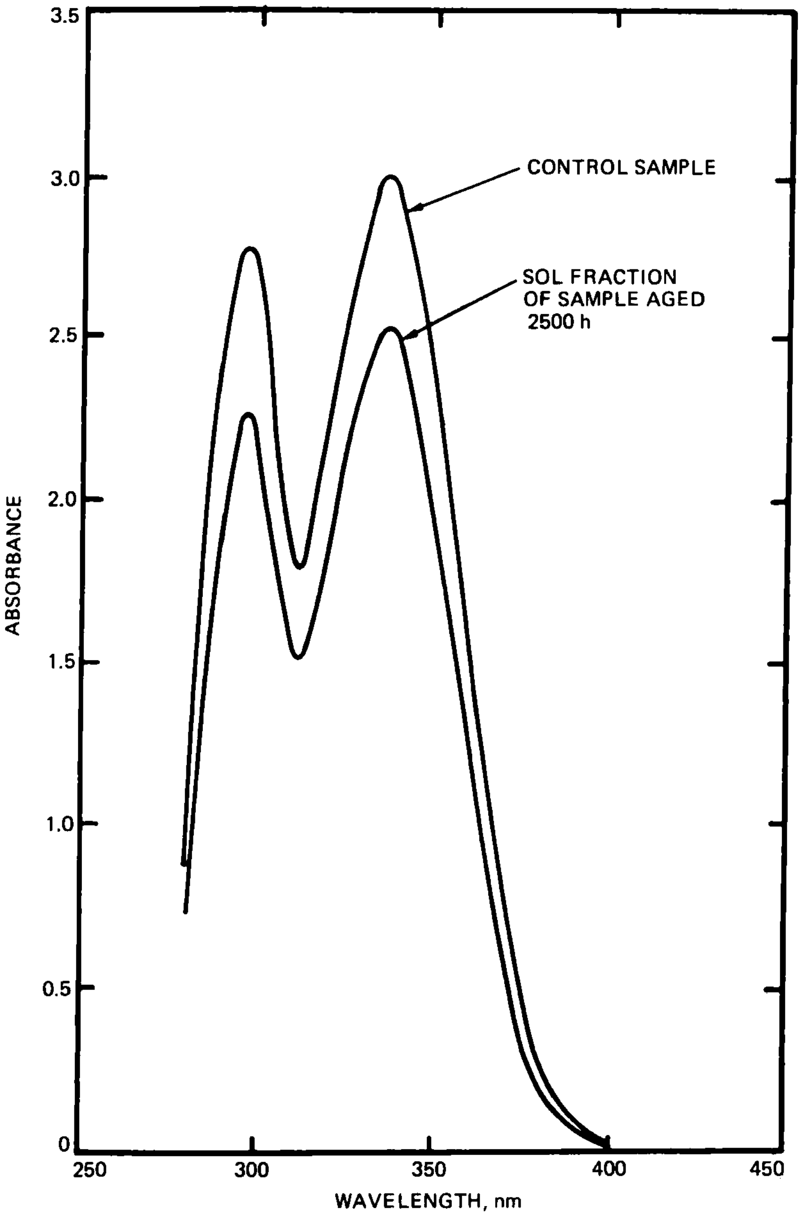


FIG. 2. Electronic absorption spectra of solutions of the copolymer in CH_2Cl_2, 25°C.

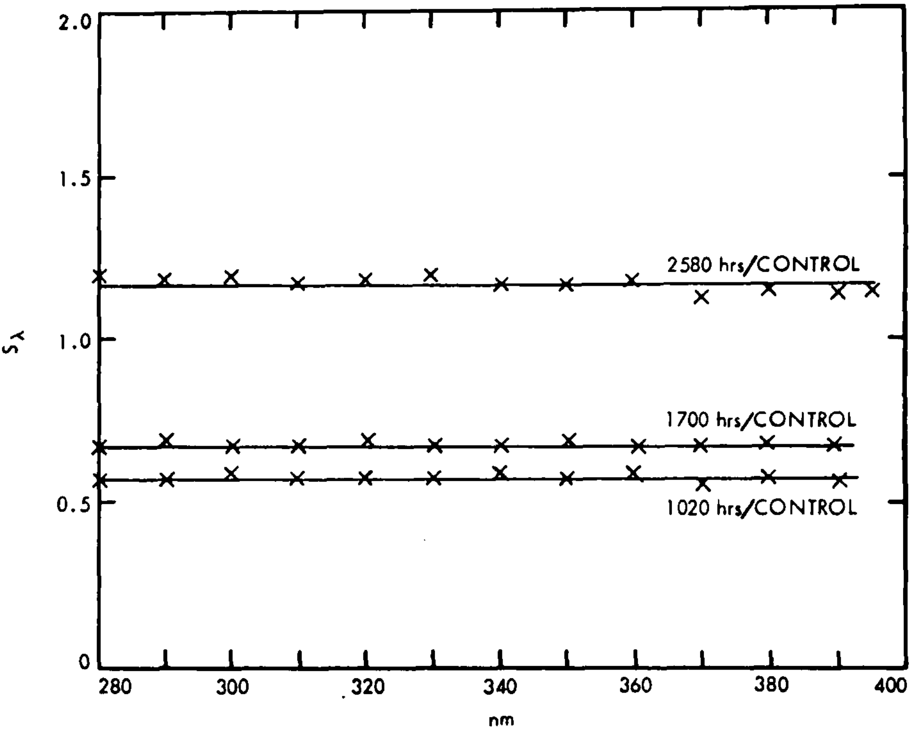


FIG. 3. Ratio of absorbances of solutions of aged samples to those of control samples as a function of wavelength in CH_2Cl_2, 25°C, where $S_\lambda = A_\lambda(\text{sample})/A_\lambda(\text{control})$.

aged sample. Figure 3 shows a plot of the normalized absorbance of the solution aged films relative to the control samples as a function of wavelength. No change with wavelength for a given sample was observed. Figure 4 shows the transmission IR spectra of aged and control samples. Computerized subtraction showed no significant change in peak areas in any of the samples after the spectra were normalized for the film thickness. However, the ATR-IR reflectance spectra (Fig. 5) on the same films show a systematic increase in absorbance in the 3200 cm^{-1} region indicating that hydroxyl groups are being formed on the surface due to photooxidation. The IR peaks due to the chromophore remain approximately unchanged although a change in the C–H peak amplitude can be seen. In agreement with the surface tension angle measurements, the exposed surface apparently undergoes a systematic increase in polarity while its dispersive parameter does not change significantly. The surface energy of the back surface does not undergo significant change.

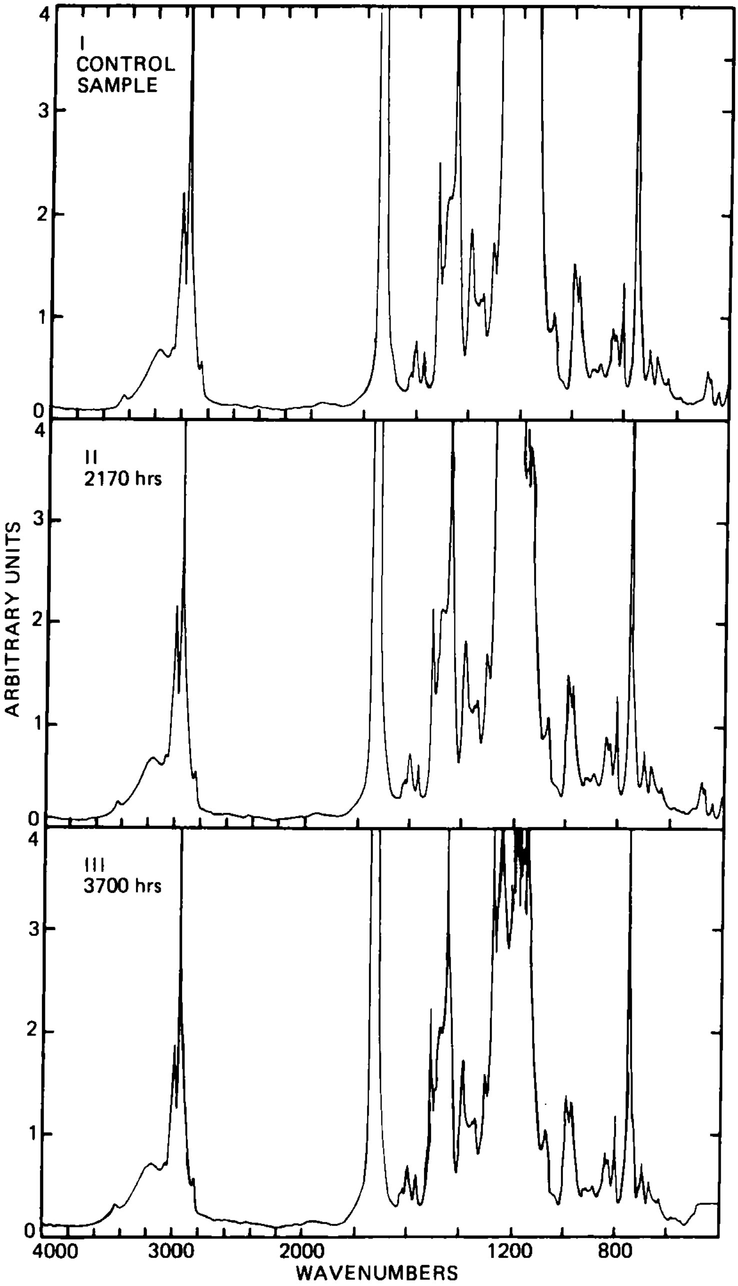


FIG. 4. Transmission IR spectra of the copolymer films.

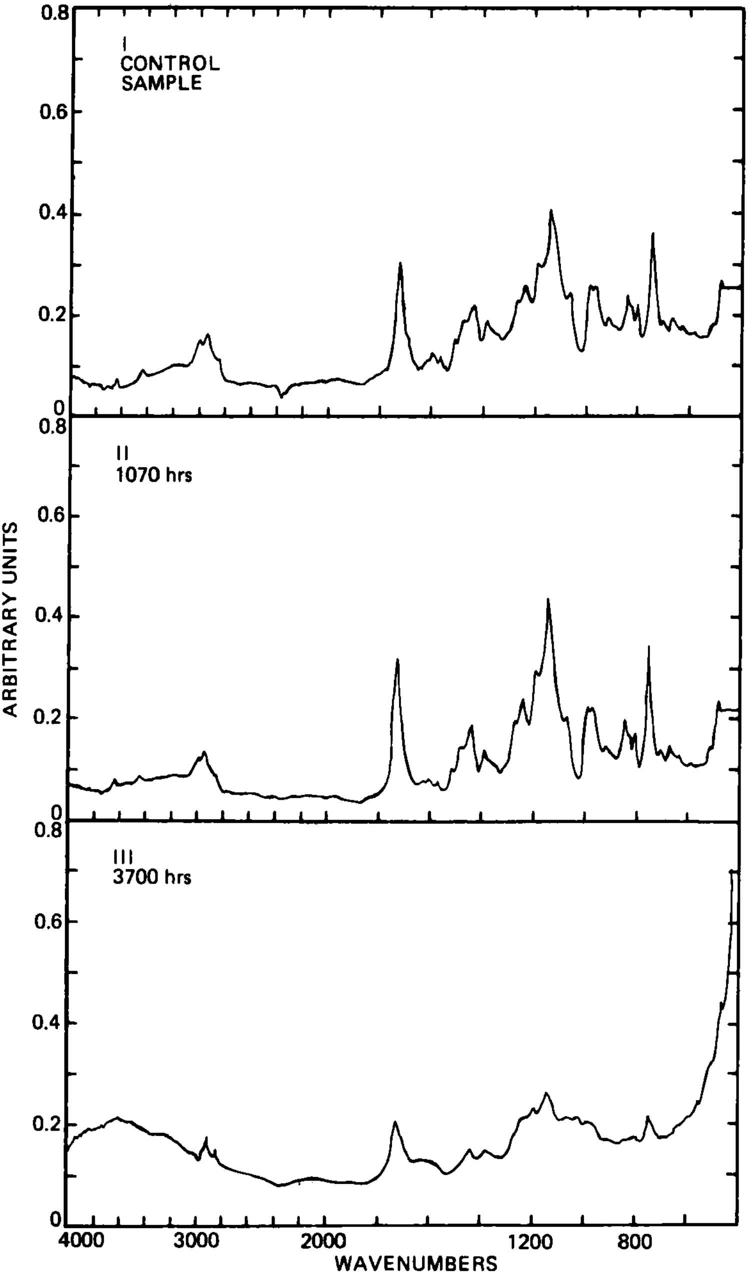


FIG. 5. Reflectance (ATR) IR spectra of the copolymer films.

TABLE 3. Molecular Weight Distribution Data on Aged and Control Samples

Aging time, h	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
0 (Control #1)	93 000	188 000	2.03
750	98 000	202 000	2.05
1 700	75 000	273 000	3.62
2 170[a]	75 000	273 000	3.62
0 (Control #2)	64 000	120 000	1.90
3 700	69 000	171 000	2.49

[a] Gel formation noted. Approximate estimate of gel formation is 20% in the sample aged for 2 170 h and ~30% in the sample aged for 3 700 h.

The molecular weight of the polymer samples was determined as a function of aging time (see Table 3). This distribution for the copolymer samples changed from the $\overline{M}_w/\overline{M}_n$ value of ~2 for the control to values 2.5 and 3.6 (2 samples) following aging. After an aging time of 2 170 h, some gel formation was noted which was estimated to be about 20%; at 3 700 h the gel portion rose to ~30%.

Figure 6 shows a typical kinetics plot of the 355-nm absorption recovery kinetics obtained for the copolymer at room temperature. Table 4 gives ground state bleaching recovery lifetimes measured for this copolymer and on additional model systems. It should be noted, however, that the excited singlet state lifetime of the copolymer must be less than this observed 25-ps recovery time of the ground state absorption. In fact, the fluorescence lifetime is only ~15 ps in the copolymer under similar conditions [10]. This latter value probably measures the internal conversion time of the tautomeric (proton-transferred) form of the copolymer, and hence proton transfer occurs in $\lesssim$10 ps. This extraordinarily high rate of the proton transfer suggests that an incipient, preformed hydrogen bond O–H . . . N is already present in the ground state, regardless of the solvent environment, even in hydroxylic solvents such as alcohols. This result is consistent with the interpretation of the near-UV absorption spectra of these copolymer films, copolymer solutions, and solutions of model compounds, all of which have a strong near-UV absorption band indicative of an intramolecular hydrogen bond [20].

The photodegradation data show that the copolymer of 2H5V and methyl methacrylate is considerably photostable in contrast to the copolymer of MMA and a 2-hydroxybenzophenone derivative on which

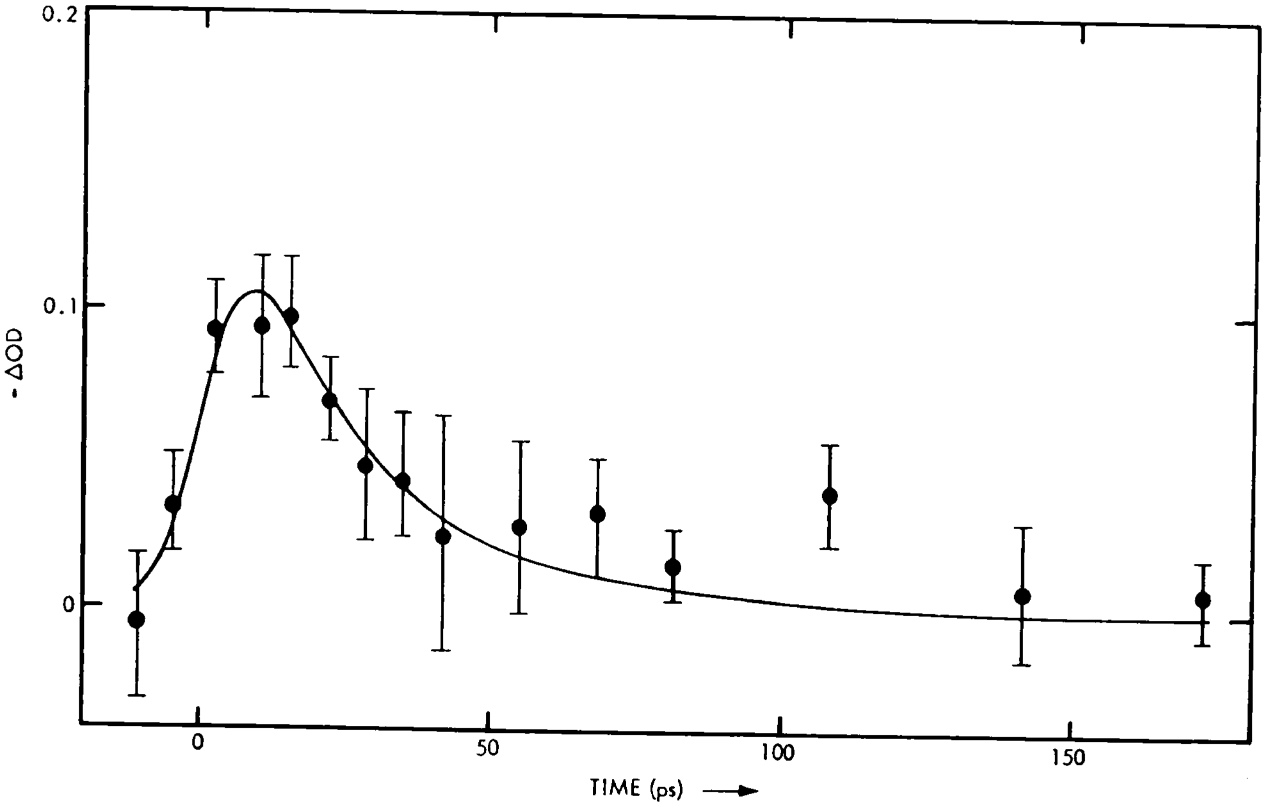


FIG. 6. Typical picosecond flash kinetic data on a solution of the copolymer in CH_2Cl_2. The ground state absorbance bleaching recovery was monitored at 355 nm.

TABLE 4. Ground State Bleaching Recovery Lifetimes Measured at 355 nm of the Copolymer and Model Chromophores at Room Temperature

Sample	Solvent	Ground state bleaching recovery lifetime, ps
Poly[2H5V-co-MMA]	CH_2Cl_2	25 ± 5
2(2-Hydroxy-5-methylphenyl)2H-benzotriazole	Methylcyclohexane	33 ± 5
2(2-Hydroxy-5-methylphenyl)2H-benzotriazole	Ethanol	74 ± 10
2(2-Hydroxy-5-methylphenyl)2H-benzotriazole	n-Hexadecane	33 ± 5
2(2-Deutroxy-5-methylphenyl)2H-benzotriazole	Methylcyclohexane	22 ± 3

we reported earlier [3]. Upon aging for over 3 000 h, the center of the polymer sample is fully protected from photodegradation by the chromophore, but spectroscopic changes appear at the exposed surface which correlate with the development of a polar character at the surface. The exact mechanism of the surface photoreaction is not known. However, it is possible that the methacrylate portion of the copolymer absorbs a small fraction of the short wavelength radiation at the surface without being moderated by the benzotriazole chromophore. Thus photosensitized energy transfer involving hydrogen abstraction or photooxidation may be occurring on the surface. Apparently the center of the polymer sample is protected by the surface chromophores. Photo crosslinking was also observed by the appearance of the formation of a gel fraction in samples aged for both 2 170 and 3 700 h. However, the center of a polymer sample was still unchanged in its chemical composition as established by monitoring its UV and IR spectra. Thus, although surface degradation begins to occur upon accelerated aging, the chromophore of the polymer-bound UV stabilizer protects the interior of the film from photooxidation and photodegradation.

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