a close simulation of the spectrum in dimethylformamide as well, with appropriate detailed changes in absolute chemical shifts and line widths.

It was necessary to assign variable line widths to represent the differing degrees of line broadening from unresolved heptad stereosequences. The given stereosequence assignments are consistent with a bias toward racemic placement, which increased with decreasing temperature (Figure 1). However, m and r could just as easily be interchanged for an adequate simulation with a $P(m)$ value of 0.58. Definitive assignments cannot be obtained without a study of the appropriate model compounds.

The areas predicted by the present simulation deviate most noticeably for the rmmm and mrrm peaks. A better simulation is possible by assuming Markov 1 statistics with $P(m|m) = 0.526$ and $P(r|m) = 0.353$. The quantitative significance of the statistical treatment must remain in doubt, however, owing to the tentative nature of the assignments. An interleaved Bernoulli stereosequence propagation model[6] would perhaps be the most appropriate for the present system, where the probability of one dyad is related to the isomerization of the terminal radical and the probability of the next dyad is related to the addition of a monomer unit.

The absence of crystallinity in PFM[3] is hardly surprising given its degree of stereoirregularity. ^{19}F NMR is an excellent probe of the microstructure, though a detailed understanding of the ordering of the stereosequences according to chemical shift, and the dependence of the ordering and spacing on solvent, remains a challenging problem.

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Photooxidation of Di-*n*-butyl Sulfide Using Sensitizers Immobilized in Polymer Films

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ABSTRACT: The photooxidation of di-*n*-butyl sulfide (Bu_2S) to di-*n*-butyl sulfoxide (Bu_2SO) was investigated in methanol solution by using various dyes as singlet-oxygen sensitizers. The rates of Bu_2SO formation are zero order in [Bu_2S] and in the concentration of dissolved oxygen and thus serve as a measure of sensitizer efficiency. The quantum yields for Bu_2SO formation, using sensitizers dissolved in methanol, were 1.17, 1.31, 0.201, 0.024, 0.0081, 0.0064, and <0.0031 for rose bengal (RB), tris(2,2′-bipyridyl)ruthenium(II) [$Ru(bpy)_3$], saffranine O (SO), rhodamine B, victoria blue B, 1-amino-4-hydroxyanthraquinone, and malachite green, respectively. RB, SO, and $Ru(bpy)_3$ were immobilized in poly(vinyl chloride) [PVC] films and RB was immobilized in cellulose acetate (CA) films. Bu_2S photooxidation quantum yields for the films were 1.2–1.8, 0.019–0.024, 0.026–0.044, and 0.018–0.020 for RB/CA, RB/PVC, $Ru(bpy)_3$/PVC, and SO/PVC, respectively. Photodegradation of immobilized sensitizers to colorless products was also monitored. RB/CA, RB/PVC, SO/PVC, and $Ru(bpy)_3$/PVC films were 50% photodegraded after irradiation for 0.15, 5, 7, and 320 h, respectively. The results indicate that polymer films retard transport of solvent, dissolved oxygen, and/or substrate to sites occupied by the photosensitizer and that there is an attendant decrease in the photooxidation quantum yield relative to that of photosensitizers in solution. Substrate photooxidation and sensitizer photodegradation are parallel processes, probably involving energy transfer from sensitizer to $^3O_2$ in the former case and electron transfer to form sensitizer radical cation and superoxide in the latter.

Molecular oxygen in its first (singlet) electronic excited state ($^1O_2$) undergoes a variety of reactions, including 1,4-cycloaddition to dienes, the "ene" reaction with alkyl-substituted olefins to produce hydroperoxides, 1,2-addition to electron-rich olefins, oxidation of phenols, and oxidation of dialkyl sulfides to dialkyl sulfoxides.[1] These reactions are of interest both because they have useful synthetic applications and because $^1O_2$ has been implicated as the reactive species in photooxidations of biological systems[2] and of synthetic high polymers.[3]

Recently, attention has focused on photosensitized $^1O_2$ reactions employing sensitizers immobilized on various solid supports.[4–15] Immobilized sensitizers offer an advantage over dissolved photosensitizers because they can be employed in solvent systems in which the sensitizer is normally insoluble. Also, immobilization of a sensitizer limits side reactions between sensitizer and oxidizable substrate and facilitates the separation of the photosensitizer from reaction products.

In general, three approaches have been taken in the design of immobilized photosensitizers. In one,[4–6,12] the sensitizer is covalently bound to cross-linked polystyrene beads, via reaction of the sensitizer with chloromethylated polystyrene. A primary advantage of this approach is that the sensitizer is highly resistant to separation from the support material, thus permitting use of the photosensitizer in a wide variety of solvent systems. Although the scope of this approach is unlimited in principle, relatively few photosensitizers can be linked to polymer supports simply and conveniently. Also, absorption and scattering of incident radiation by the polymer beads complicates the use of covalently bound photosensitizers in studies (such as determination of photooxidation quantum yields) in which the intensity of the absorbed radiation must be well-known.

A second approach is immobilization of a photosensitizer by absorption onto a solid support such as silica gel.[8,9,16] This method is convenient, but the sensitizer can be de-

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Table I
Production of Bu_2SO and Disappearance of Bu_2S from Photooxidation of 4.7×10^{-2} M Bu_2S in Methanol with $Ru(bpy)_3$ Sensitizer[a]

time, s	$10^2 \times [Bu_2S]_t$, M	$10^3 \times [Bu_2SO]_t$, M	Bu_2S convrsn,[b] %	$10^5(+d[Bu_2SO]/dt)$, M s^{-1}	$10^5(-d[Bu_2S]/dt)$, M s^{-1}
0	4.70	0.1	0.2		
60	4.41	3.6	7.7	6.00	4.83
120	4.09	6.7	14.2	5.58	5.08
180	3.68	10.1	21.4	5.61	5.67
240	3.39	12.8	27.2	5.33	5.46
360	2.86	18.2	38.7	5.06	5.11
				5.52 ± 0.35[c]	5.23 ± 0.33[c]

[a] Sensitizer concentrations before and after reaction were 8.3×10^{-4} M, identical within experimental uncertainty (±3%). [b] % conversion = $100 \times [Bu_2SO]_t/[Bu_2S]_0$. [c] Average values.

sorbed from the support by polar solvents. Light scattering by the support material is also an inherent difficulty.

A third approach is incorporation of a photosensitizer into a polymer matrix by dissolving the photosensitizer and polymer in a suitable solvent, casting a thin film of the mixture on a glass plate, and allowing the solvent to evaporate.[10,13-15] The number of photosensitizers and polymers that can be employed is large. Moreover, cast films are highly transparent and thus can be used to prepare sensitizer films whose spectral properties are well characterized. This technique has been used to probe the diffusivity and reactivity of $^1O_2$ in polymer matrices[10,11,14,17] and to investigate the relative efficiency and susceptibility to photodegradation of various photosensitizer dyes.[13,15]

Zweig and Henderson[15] immobilized a series of 26 commercially available dyes in cellulose acetate (CA) films and investigated the relative abilities of the dyes to sensitize the photooxidation of a known acceptor (dimethylanthracene) also incorporated into the films. These authors characterized several of the dyes as efficient sensitizers and resistant to photodegradation.

In our laboratory, we have studied several parameters that govern the ability of sensitizers immobilized in polymer films to effect photooxidation of organic substrates in solution. We chose methanol as a representative solvent phase and di-n-butyl sulfide (Bu_2S) as a well-characterized[17-19] $^1O_2$ acceptor. All experiments used monochromatic light of known intensity, thus permitting determination of photooxidation quantum yields. Initially we examined the quantum yields for oxidation of Bu_2S by using various sensitizers dissolved in methanol, employing six dyes studied by Zweig and Henderson and, for comparison, tris(2,2′-bipyridyl)ruthenium(II) fluoroborate [$Ru(bpy)_3$].[20-22] We then immobilized the three most efficient sensitizers in thin films of various polymers for further study. Finally, sensitizers immobilized in poly(vinyl chloride) [PVC] and CA films were investigated with respect to photooxidation quantum yields and rates of sensitizer photodegradation. We examined several parameters of the sensitizer-polymer system that will govern the usefulness of these materials as practical photooxidation sensitizers, including sensitizer efficiency and quantum yield, polymer composition, and rates of transport of oxygen and solvent into the film.

Results and Discussion

Kinetics of Photooxidation of Bu_2S. The photooxidation of Bu_2S is a well-behaved and well-characterized system.[17-19] Bu_2S reacts rapidly with singlet oxygen ($^1O_2$) to form first the persulfoxide, and, on reaction with a second molecule of Bu_2S, two molecules of Bu_2SO. Other processes can compete, and the detailed scheme is shown in Scheme I, where ^1S, $^1S^*$, $^3S^*$ are the sensitizer singlet ground, singlet excited, and triplet excited states, respectively, and $Bu_2S^+OO^-$ is the persulfoxide, believed to be an intermediate in the reaction.

Scheme I

$$^1S + h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^1S^* \qquad (1), (-1)$$

$$^1S^* \xrightarrow{k_2} {}^3S^* \qquad (2)$$

$$^3S^* + {}^3O_2 \xrightarrow{k_3} {}^1S + {}^1O_2 \qquad (3)$$

$$^3S^* \xrightarrow{k_4} {}^1S \qquad (4)$$

$$Bu_2S + {}^1O_2 \xrightarrow{k_5} Bu_2S^+OO^- \qquad (5)$$

$$Bu_2S + Bu_2S^+OO^- \xrightarrow{k_6} 2Bu_2SO \qquad (6)$$

$$Bu_2S + Bu_2S^+OO^- \xrightarrow{k_7} 2Bu_2S + {}^3O_2 \qquad (7)$$

$$Bu_2S^+OO^- \xrightarrow{k_8} Bu_2SO_2 \qquad (8)$$

$$^1O_2 \xrightarrow{k_9} {}^3O_2 \qquad (9)$$

$Bu_2S^+OO^-$ is partitioned among reaction with Bu_2S to yield di-n-butyl sulfoxide (Bu_2SO) (reaction 6), quenching with Bu_2S (reaction 7) to revert to starting material plus $^3O_2$, and reaction 8, yielding di-n-butyl sulfone (Bu_2SO_2). Similarly, the excited sensitizer states are partitioned between decay to ground state (reactions −1 and 4) and either intersystem crossing (reaction 2) or energy transfer to $^3O_2$ (reaction 3). The $^1O_2$ also reacts by parallel pathways, viz., oxidation of Bu_2S to $Bu_2S^+OO^-$ (reaction 5) and decay to $^3O_2$ (reaction 9). The overall kinetic behavior of the photosensitized oxidation will, of course, depend on the relative rates of reactions 1–9. By applying the steady-state approximation to [^3S] and reactions 1–4 we derive eq 10, where ϕ_{O_2} is the quantum yield for production

$$\phi_{O_2} = \frac{d[^1O_2]/dt}{dE/dt} = \frac{k_2k_1[^1S]}{I_a(k_{-1} + k_2)} \frac{k_3[^3O_2]}{k_3[^3O_2] + k_4} \qquad (10)$$

of singlet oxygen, E is the absorbed photon concentration in einstein L^{-1}, and I_a ($=dE/dt$) is the intensity of light absorbed by ^1S. When $k_3[^3O_2] > k_4$,[23] eq 10 reduces to

$$\phi_{O_2} = \frac{k_2k_1[^1S]}{I_a(k_{-1} + k_2)} \qquad (11)$$

In this case, ϕ_{O_2} is independent of the dissolved-oxygen concentration and is a measure of $k_2/(k_{-1} + k_2)$, i.e., the efficiency of intersystem crossing for the sensitizer in question. Application of the steady-state approximation

to the kinetics of Bu_2SO formation gives eq 12, where

$$\phi_{Bu_2SO} = \frac{+d[Bu_2SO]/dt}{dE/dt} = 2\phi_{O_2}\left\{\frac{[Bu_2S]k_5}{[Bu_2S]k_5 + k_9}\right\}\left\{\frac{[Bu_2S]k_6}{[Bu_2S](k_6 + k_7) + k_8}\right\} \quad (12)$$

ϕ_{Bu_2SO} is the quantum yield for Bu_2SO production and ϕ_{O_2} is given by eq 10. The factor of 2 in eq 12 is dictated by the 2:1 stoichiometry of reactions 5 and 6. For diethyl sulfide photooxidation in methanol, Foote and Peters[18] demonstrated that $k_5 \gg k_9$, and that $(k_6 + k_7) \gg k_8$. Therefore, providing that $[Bu_2S]$ remains sufficiently high, eq 12 reduces to

$$\phi_{Bu_2SO} = 2\phi_{O_2}[k_6/(k_6 + k_7)] \quad (13)$$

Under these conditions, the rate of Bu_2SO formation is zero order in both $[^3O_2]$ and $[Bu_2S]$, and Bu_2SO is the only important product. Also, ϕ_{Bu_2SO} is directly proportional to ϕ_{O_2} so ϕ_{Bu_2SO} can be used to calculate the relative efficiencies of various sensitizers.

Experimental Results

To ensure that our photooxidation system was well-behaved, we first studied the kinetics of the photooxidation of 4.7×10^{-2} M Bu_2S, using 8.3×10^{-4} M $Ru(bpy)_3$ dissolved in methanol as the sensitizer and a medium-pressure Hg lamp filtered to pass the 546- and 578-nm emissions. The production of Bu_2SO and the disappearance of Bu_2S were both determined by high-pressure liquid chromatography. The results are shown in Table I (actinometry was not performed in this experiment). The rates for Bu_2S disappearance and Bu_2SO formation are identical, within experimental uncertainty. This demonstrates that Bu_2SO is the major product and that Bu_2SO_2 formation is neglible. Also, Table I shows that the reaction rates are invariant for conversions of Bu_2SO as high as 39%, indicating that the reaction is zero order in Bu_2S. To demonstrate the independence of the reaction on $[^3O_2]$, the photooxidation of 4×10^{-2} M Bu_2S was run in methanol saturated with 1 atm of air and with 1 and 2 atm of oxygen. Rose bengal (RB) was the sensitizer employed, and actinometry was performed so that eq 14 and 15 could be used to calculate quantum yields for Bu_2SO formation

$$\phi_{Bu_2SO} = \frac{+d[Bu_2SO]/dt}{dE/dt} = \frac{+d[Bu_2SO]/dt}{I_a} \quad (14)$$

ϕ_{Bu_2SO} is the quantum yield for production of Bu_2SO, dE/dt refers to the rate of absorption of light (in einstein L^{-1} s^{-1}), and I_a, the absorbed intensity, is calculated from

$$I_a = I_0^{546}(1 - 10^{-A_{546}}) + I_0^{578}(1 - 10^{-A_{578}}) \quad (15)$$

Here, I_a is the total absorbed intensity, I_0^{546} and I_0^{578} are the incident light intensities, and A_{546} and A_{578} are the absorbances of the photosensitizer at 546 and 578 nm, respectively. Data for this series of experiments are summarized in Table II. From the table, it is evident that the values of ϕ_{Bu_2SO} for 1 and 2 atm of oxygen are identical (the average value is $\phi_{Bu_2SO} = 1.08 \pm 0.10$), but the value of ϕ_{Bu_2SO} for 0.2 atm of O_2 is only 0.62. This suggests that the Bu_2S photooxidation is zero order in $[^3O_2]$ if the solution is saturated with at least 1 atm of oxygen. This was the case in all subsequent experiments. We also measured the rates of oxygen consumption and of Bu_2S disappearance for the RB-sensitized photooxidation in methanol and observed a $Bu_2S:O_2$ stoichiometry of 2.08 ± 0.10, as required by reactions 5 and 6.

Table II
Photooxidation of Bu_2S in Air- or Oxygen-Saturated Methanol with Rose Bengal Sensitizer[a]

conditions	$10^2 \times [Bu_2S]_0$, M	$10^5 \times (+d[Bu_2SO]/dt)$, $M\ s^{-1}$	$10^5 I_a$,[b] einstein $L^{-1}\ s^{-1}$	Φ_{Bu_2SO}[c]
air (1 atm)	3.95	4.42	7.06[d]	0.626
oxygen (1 atm)	3.58	8.33	7.06[d]	1.18
oxygen (1 atm)	4.53	11.8	11.0[e]	1.07
oxygen (2 atm)	4.53	10.7	11.0[e]	0.973

[a] RB concentrations before and after reaction were 7.7×10^{-6} M, identical within experimental uncertainty (±3%). [b] I_a calculated from eq 15. [c] Φ_{Bu_2SO} calculated from eq 14. [d] $I_0^{547} = 8.52 \times 10^{-5}$ einstein $L^{-1}\ s^{-1}$. [e] $I_0^{547} = 13.3 \times 10^{-5}$ einstein $L^{-1}\ s^{-1}$.

Table III
Pertinent Spectral Characteristics[a] of Selected Sensitizers

sensitizer	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	ϵ_{546}, M^{-1} cm^{-1}	ϵ_{578}, M^{-1} cm^{-1}
rose bengal (acid red 94)	555	82 000	65 000	11 000
saffranine orange (basic red 2)	528	53 900	28 600	1 260
1-amino-4-hydroxy-anthraquinone (disperse red 15)	522	8 230	7 350	4 420
tris(2,2′-bipyridyl)ruthenium(II) fluoroborate	448	7 000	360	20
malachite green (basic green 4)	620	165 000	20 000	48 000
victoria blue B (basic blue 26)	604	64 000	28 200	56 000
rhodamine B, (basic violet 10)	554	109 100	109 000	9 560

[a] Determined experimentally from UV-visible absorption curves for solutions of accurately known concentrations of sensitizer in CH_3OH.

In summary, the rates and products of the photosensitized Bu_2S oxidation in methanol are in accordance with the mechanism outlined above. Therefore, rates of Bu_2S photooxidation determined under conditions in which I_a is known can be used as valid measures of relative sensitizer efficiency, as defined by eq 11 and 13.

Efficiencies of Photosensitizers in Methanol Solution. Since we were interested in examining the effect of sensitizer efficiencies in $^1O_2$ oxidations, we chose six organic dyes studied by Zweig and Henderson[15] and reexamined their behavior under conditions in which the intensity of absorbed radiation could be determined in a straightforward manner. We also investigated the behavior of $Ru(bpy)_3$ as an example of an inorganic photosensitizer. The sensitizers studied and pertinent spectral data are listed in Table III. Photooxidations with the sensitizers dissolved in methanol were performed by using 5×10^{-2} M Bu_2S as the substrate and 546- and 578-nm emissions of the Hg lamp as the source of illumination. Sensitizer concentrations were adjusted to give an absorbance of 0.50 at 546 nm, the absorbances at 578 nm were calculated from the data in Table III, and absorbed intensities were calculated from eq 15. In each experiment we determined the amount of Bu_2SO formed after 120 s of irradiation, and values of ϕ_{Bu_2SO} were calculated from eq 14.

The data, summarized in Table IV, reveal that the sensitizer efficiencies vary by a factor of >400. This result is in marked contrast to the findings of Zweig and Hen-

Table IV
Rates ($d[Bu_2SO]/dt$) and Quantum Yields (ϕ_{Bu_2SO}) of Bu_2SO Production from Photooxidations of 5.0×10^{-2} M Bu_2S in Methanol with Various Sensitizers

sensitizer[a]	$10^5 \times$ [sensitizer],[b] M	$10^5 I_a$,[c] einstein $L^{-1} s^{-1}$	$10^5 \times (d[Bu_2SO]/dt)$,[d] M s^{-1}	ϕ_{Bu_2SO}[e]
rose bengal (RB)	0.77	7.30	8.58	1.17
tris(2,2'-bipyridyl)ruthenium(II) fluoroborate [$Ru(bpy)_3$]		4.64	6.08	1.31
saffranine O (SO)	1.75	6.37	1.28	0.201
rhodamine B	0.46	6.71	0.163	0.024
victoria blue B	1.77	12.5	0.101	0.0081
1-amino-4-hydroxyanthraquinone	6.8	9.64	0.0620	0.0064
malachite green	2.5	12.8	<0.04[f]	<0.0031

[a] See Table III for sensitizer spectral characteristics. [b] In all cases sensitizer concentrations before and after irradiation were identical, within experimental uncertainty (±3%); concentrations chosen to give $A_{546} = 0.50$. [c] I_a calculated from eq 15; $I_0^{546} = 8.78 \times 10^{-5}$ einstein $L^{-1} s^{-1}$ and $I_0^{578} = 7.29 \times 10^{-5}$ einstein $L^{-1} s^{-1}$. [d] $d[Bu_2SO]/dt = [Bu_2SO]/120$ s, for 120-s irradiation. [e] ϕ_{Bu_2SO} calculated from eq 14. [f] Bu_2SO formation not observed within limits of detectability (5×10^{-5} M Bu_2SO).

derson,[15] who observed all six organic dyes to be of comparable efficiency as photosensitizers. It thus appears that the observed efficiency of immobilized sensitizers is not necessarily an accurate measure of *inherent* efficiency of the sensitizers. As described below, the limiting effect of polymer on mass (i.e., oxygen) transport can affect apparent efficiencies in this manner.

Our values of $\phi_{Bu_2SO} = 1.2$ for RB and $\phi_{Bu_2SO} = 1.3$ for $Ru(bpy)_3$, can be compared to literature values of $2\phi_{O_2} = 1.6$ for RB[1c,24] and $2\phi_{O_2} = 1.7$ for $Ru(bpy)_3$, for generation of $^1O_2$ in methanol. The relative values of $\phi_{Bu_2SO}(RB)/\phi_{Bu_2SO}(Ru(bpy)_3) = 0.90$ and $2\phi_{O_2}(RB)/2\phi_{O_2}(Ru(bpy)_3) = 0.94$ compare favorably, although our absolute values are approximately 25% lower than the values predicted from the efficiency of sensitizer energy transfer to $^3O_2$. Cassagrande et al.[19] also noted that, for the photooxidation of Bu_2S in ethanol sensitized by methylene blue, the value of $\phi_{Bu_2SO} = 0.61$ was significantly lower than the reported[25] value of $2\phi_{O_2} = 1.04$ for methylene blue. These observations are explained by reactions 6 and 7 and eq 13. According to the proposed mechanism for alkyl sulfide oxidation, the intermediate persulfoxide can react with alkyl sulfide to produce 2 mol of sulfoxide, or the persulfoxide can be quenched by sulfide to starting materials and ground-state molecular oxygen. As indicated in eq 13, therefore, the efficiency of Bu_2SO oxidation will differ from the maximum value of $2\phi_{O_2}$ by the factor $k_6/(k_6 + k_7)$. From our data with RB and $Ru(bpy)_3$ as sensitizers, we calculate $k_6/(k_6 + k_7) = 0.76 \pm 0.01$ and $k_6/k_7 = 3.2$ for Bu_2S in methanol. From the results of Cassagrande et al., these values for Bu_2S in ethanol are $k_6/(k_6 + k_7) = 0.59$ and $k_6/k_7 = 1.44$. Both calculations indicate that the oxidation reaction predominates over the quenching reaction, but the differences in the ratio k_6/k_7 are rather large. The reasons for this difference are unclear, although the quenching:oxidation ratio is known to be solvent-dependent.[18]

Photooxidation of Bu_2S Using Sensitizer Films. We chose the three most efficient sensitizers from Table IV—RB, $Ru(bpy)_3$, and saffranine O (SO)—as candidates for further study. We immobilized the sensitizers in thin films made from various polymers (see Experimental Section for details).

Polystyrene films were transparent when undyed but became cloudy when RB was incorporated into the film. When RB/polystyrene films were immersed in methanol, the sensitizer did not leach into the solvent. $Ru(bpy)_3$, however, was leached out of polystyrene films within a few minutes. When RB was incorporated into a poly(butyl methacrylate) film, the color intensity of the dye diminished as the polymer film formed. This indicates acidic impurities in the poly(butyl methacrylate) that become more concentrated as the solvent for the polymer evaporates. When RB/poly(butyl methacrylate) films were immersed in methanol, they became cloudy and shriveled.

Table V
Physical and Spectral Characteristics of Sensitizer Films

	Ru(bpy)/PVC	SO/PVC	RB/PVC	RB/CA
film thickness, cm $\times 10^{-3}$	2.5	2.5	2.5	2.5
absorbance of film at 546 nm (A_0)	0.085	0.24	0.26	0.20
sensitizer concn,[a] M $\times 10^{-3}$	94.0	3.3	1.6	1.2
fraction of 546-nm light absorbed[b]	0.18	0.42	0.45	0.37

[a] A_{546}/ϵ_{546} (2.5×10^{-3} cm), where ϵ_{546} is the sensitizer extinction coefficient at 546 nm (taken from Table III). [b] Fraction absorbed = $1-10^{-A}$.

Sensitizer films made from cellulose acetate (CA) were very smooth and highly transparent. When RB/CA films were immersed in methanol, no leaching of dye into the solvent occurred over several hours. $Ru(bpy)_3$ and SO, however, were completely leached out of CA in minutes.

PVC (actually a vinyl chloride–vinyl acetate copolymer; see experimental details) was the only material investigated that could be used to make satisfactory films containing all three sensitizers. Leaching of the dyes from PVC films was negligible except with very long reaction times. Dry sensitizer/PVC films were stippled, resembling an orange peel. Some blushing (cloudiness) of the films occurred on prolonged irradiation, but this did not affect the efficiencies of the photosensitizer (see Table VI).

On the basis of these limitations, we investigated the rates of photodegradation of the sensitizers and rates of photooxidation of Bu_2S, using RB/CA, RB/PVC, $Ru(bpy)_3$/PVC, and SO/PVC films. Table V lists pertinent data for the four sensitizer films employed.

The sensitizer photodegradation and Bu_2S photooxidation experiments were performed concurrently. Each film was cut into strips, and each strip was immersed in 2 mL of a methanol solution of 5×10^{-2} M Bu_2S in a photolysis tube. The tubes were then irradiated for timed intervals with a Hg lamp filtered to pass only the 546-nm emission. The film was removed after irradiation and the absorbance of the film was determined. At the same time, the concentration of Bu_2S remaining in the tube was quantitated and the rate of Bu_2S photooxidation calculated. Actinometry was performed for these experiments

Table VI
Photooxidation of Bu_2S in Methanol Using Various Photosensitizer Films[a]

sensitizer/film[b]	time, h	ΦBu_2SO[c]
$Ru(bpy)_3$/PVC	0	
	4	0.026
	18	0.044
	48	0.034
SO/PVC	0	
	3	0.018
	6[d]	0.020
RB/PVC	0	
	2	0.019
	4	0.024
	8	0.024
	16[d]	0.057
RB/CA	0	
	0.25	1.2
	0.5	1.8
	1.0	1.4

[a] Experiments performed simultaneously with measurement of rates of photodegradation of sensitizer films. [b] See Table V for details concerning films. [c] $\Phi_{Bu_2SO} \equiv ([\Delta Bu_2S]/\Delta t)I_a^{-1}$; see text. [d] Photooxidations could not be followed to longer times due to leaching of sensitizer from film into methanol.

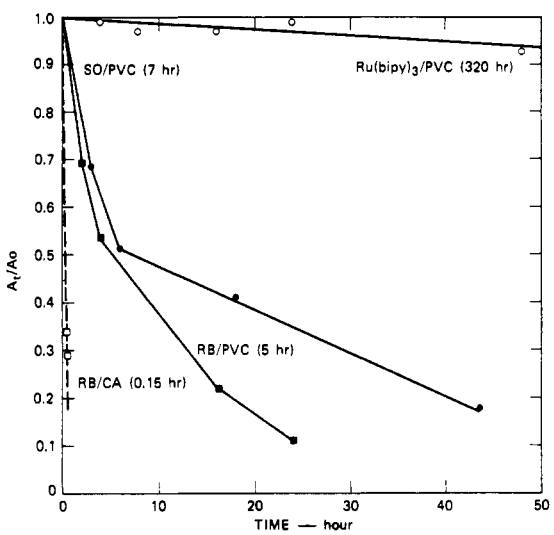

Figure 1. Fraction of sensitizer remaining (A_t/A_0) vs. time for photolysis of Ru(bpy)/PVC (○), SO/PVC (●), RB/PVC (■), and RB/CA (□) films in methanol containing approximately 5×10^{-2} M Bu_2S. Values in parentheses are the times required for A_t/A_0 to reach 0.50.

and values of ϕ_{Bu_2SO} were derived.

The results of the photodegradation experiments are depicted in Figure 1. The ratio of A_t (absorbance of the film after irradiation for time t) to A_0 (initial absorbance of the film) is a measure of the fraction of sensitizer remaining.

It is evident that the four immobilized sensitizers have greatly different susceptibilities to photodegradation. For example, the $Ru(bpy)_3$/PVC film is about 60 times more resistant to photodegradation than the RB/PVC film. The figure also shows that photodegradation rates for a given sensitizer depend on the polymer used for immobilization. The RB/PVC film, for example, is 50% degraded in 5 h, whereas the RB/CA material undergoes a similar degree of fading in about 10 min, a 30-fold difference in bleaching rate. Analogous behavior was noted for the rates of Bu_2S oxidation, summarized in Table VI. The rates of Bu_2S oxidation, $\Delta[Bu_2S]/\Delta t$ were calculated for each time point. Values of ϕ_{Bu_2SO} were calculated from the expression $\phi_{Bu_2SO} = (\Delta[Bu_2S]/\Delta t)I_a^{-1}$. This calculation requires the rate of Bu_2S consumption to equal the rate of Bu_2SO formation, a valid approximation according to the data in Table I. Values of I_a at 546 nm were taken from Figure 1. Since RB and SO were noticeably degrading during the experiments, the I_a values continually decreased. Thus, the calculation of ϕ_{Bu_2SO} above is not rigorously correct, and the quantum yield in each time interval is actually somewhat higher. However, the values of ϕ_{Bu_2SO} so obtained provide good approximations that are useful in evaluating the performance of the sensitizers. As Table VI shows, all three sensitizers immobilized in PVC films exhibited ϕ_{Bu_2SO} values of 0.02 to 0.06. Quantum yields for Bu_2SO formation sensitized by $Ru(bpy)_3$, RB, and SO in solution were 1.3, 1.2, and 0.2, respectively. In contrast, RB/CA films afforded ϕ_{Bu_2S} values of 1.2–1.8, approximately equal to the quantum yields obtained with RB in solution. Since RB/CA films also faded about 30 times faster than did RB/PVC films, it is evident that incorporation of the sensitizers into different films affects photodegradation and photooxidation in parallel.

The best explanation for these observations seems to be that methanol diffuses through the polymer films, carrying along both oxygen and Bu_2S. During passage through the films, $^3O_2$ is converted to $^1O_2$ and reacts with Bu_2S. The transmission rate for methanol through our vinyl chloride–vinyl acetate copolymer is unknown; however, the rate for methanol through PVC[26] is 0.88 (g mil)/(h m^2) and the rate for ethanol through CA[27] is 92 (g mil)/(h m^2). For films 0.5-mil thick and 2 cm^2 in area these rates are equivalent to 2×10^{-9} mol s^{-1} through PVC and 2×10^{-7} mol s^{-1} through CA, both approximately fast enough to account for the rates of oxidation observed with each film and in the correct ratio within a factor of 2. We considered but discarded an alternative explanation, that $^3O_2$ permeated the films, was converted to $^1O_2$, and rediffused into solution to oxidize Bu_2S. Neither the rates of diffusion of $^3O_2$ into these films[38] nor the probable stability of $^1O_2$ in the films[39] was sufficient to account for our measured rates of oxidation.

Finally we consider the matter of sensitizer photodegradation. Recall that RB/CA films were far more susceptible to photobleaching than were RB/PVC films and that Bu_2S photooxidation rates were also higher for RB/CA films. This indicates that sensitizer photodegradation and Bu_2S photooxidation are coupled in some fashion and that O_2 is involved in both processes. A mechanism consistent with this is given by reactions 3a, 3b, and 16

$$^3S^* + {}^3O_2 \rightarrow {}^1S + {}^1O_2 \quad (3a)$$

$$^3S^* + {}^3O_2 \rightarrow S^{+}\cdot + O_2^{-}\cdot \quad (3b)$$

$$S^{+}\cdot \rightarrow \text{colorless products} \quad (16)$$

According to this mechanism, excited-triplet sensitizer reacts with $^3O_2$ either by energy transfer (reaction 3a) to give ground-state sensitizer plus $^1O_2$ or by electron transfer (reaction 3b) to give sensitizer radical cation and superoxide. Subsequent reaction of $S^{+}\cdot$ leads to photobleaching. Similar mechanisms for sensitizer photodegradation have been invoked elsewhere,[2,29] and evidence for the occurrence of reaction 3b for RB[30] and $Ru(bpy)_3$[30,31] has recently appeared. This interpretation also provides an intriguing rationale for the phenomenal stability of $Ru(bpy)_3$ to photodegradation. For this sensitizer, reaction 3b leads to $Ru(bpy)_3^{3+}$. $Ru(bpy)_3^{3+}$ is a strong reducing agent (1.2-V reduction potential in 1 M acid)[32] and could be expected to return to the 2+ oxidation state by reaction with an unspecified reductant rather than undergo subsequent

Table VII
Materials Used for Preparation of Polymer Films

polymer	manufacturer, type	solvent
cellulose acetate	Aldrich, acetyl content 39.8%	90:10 methylene chloride–ethanol (95%)
polystyrene	Dow, Styron 666V	75:25:25 toluene–methyl ethyl ketone–acetone cellosolve
poly(butyl methacrylate)	du Pont, Elvacite 2044	50:45:5 methylene chloride–acetone–ethanol (98%) (Rose Bengal)
poly(vinyl chloride)	Union Carbide, vinyl chloride–vinyl acetate copolymer type (VYHH)	50:40:10 methylene chloride–acetone–ethanol (98%) [$Ru(bpy)_3$]

reactions to yield colorless products.

Conclusions

In the context of a system designed to mediate the photooxidation of organic substrates in solution, the incorporation of sensitizers into solution-cast polymer films provides a ready alternative to covalently bound sensitizers. Using a cast film as support material permits the use of photosensitizers that could not otherwise be employed owing to preparative difficulties. A good example of this is $Ru(bpy)_3$, a highly efficient sensitizer whose stability with respect to photodegradation is far superior to that of typical organic dyes. While preparation of covalently bound $Ru(bpy)_3$ would entail difficult synthetic problems, cast films containing $Ru(bpy)_3$ can be made with ease on as large a scale as desired. Cast sensitizer films are more amenable to investigations in which determination of quantum efficiencies is desired.

There are distinct limitations to the use of the cast sensitizer films, however. Some sensitizer/polymer combinations are suceptible to leaching of the sensitizer into solution. A related limitation is the reduction in photooxidation quantum yield due to retarded transport of solvent, dissolved oxygen, and/or substrate through the polymer film. Unfortunately, films that are highly permeable to solvent are also prone to leaching of the sensitizer into solution. Some compromise between quantum efficiency and resistance to sensitizer leaching will therefore be necessary in the use of cast sensitizer films.

This is not to say that useful cast sensitizer films cannot be found. We consider the $Ru(bpy)_3$/PVC material to be very useful in converting Bu_2S to Bu_2SO. We have extended the utility of the system to photooxidation of neat Bu_2S and find that 90% conversion to Bu_2SO can be obtained within 10 h by using solar radiation and the $Ru(bpy)_3$/PVC film described in this report. Whether or not the cast sensitizer films will have a more general application to organic photooxidation awaits further investigation.

Experimental Section

Materials. General Comments. Di-n-butyl sulfide (Bu_2S) and di-n-butyl sulfone (Bu_2SO_2) from K & K Laboratories were shown by NMR and elemental analyses to be 97% pure. Water appeared to be the only major impurity in each compound, so they were used without further purification. Aldrich supplied 2,3-dimethyl-2-butene, which was used without further purification.

Identities and relative amounts of contaminants in di-n-butyl sulfoxide (Bu_2SO) from K & K Laboratories were determined by high-pressure liquid chromatography, using a refractive index detector, by NMR, and by UV–visible spectroscopy. The purity of the sample was taken into account when determining high-pressure liquid chromatography response factors for analysis of reaction mixtures. All other materials were reagent grade and were used as supplied.

Photosensitizers. The following photosensitizer dyes (color index number in parentheses) were purchased from Matheson Coleman and Bell and used without further purification: rose bengal (45440), saffranine O (50240), rhodamine B (45170), victoria blue B (44045), 1-amino-4-hydroxyanthraquinone (60710), and malachite green (42000). $Ru(bpy)_3$ was prepared from $RuCl_3$ and 2,2′-bipyridine by the procedure described by Sprintschnik et al.[33]

Polymer Films. Sensitizer films were prepared from four different polymers: cellulose acetate, poly(butyl methacrylate), polystyrene, and poly(vinyl chloride). All films were prepared by the solvent-casting technique; the polymer was dissolved in a solvent mixture and cast onto a glass plate with a "doctor's blade", a device that can be set to lay the solution at any desired thickness. Typically, films were prepared as follows. A 10% solution of the polymer was made up, and sensitizer was added to this solution either by dissolving the sensitizer directly in the polymer solution or by mixing in a portion of a saturated solution of the dye. Films were made 2.5×10^{-3} cm thick by spreading 6 g of solution onto a glass plate with the doctor's blade set at 2.0×10^{-2} cm. The polymers, the manufacturers, and the solvents are listed in Table VII.

Apparatus. Photochemical oxidations were performed in 10-mm i.d. × 13-cm o.d. × 100-mm, screw-cap, borosilicate glass tubes (Pyrex 7740) mounted on a merry-go-round photochemical reactor (Ace Glass). The irradiation source was a Hanovia 450-W, medium-pressure Hg lamp contained in a borosilicate immersion well. The distance between the irradiation source and tubes was about 10 cm and the temperature was at the ambient operating temperature of the system, 30 ± 2 °C. Two different sets of filters were used in the experiments. In solution-phase Bu_2S oxidations with dissolved photosensitizers, 12-mm Corning 3-71 sharp-cut yellow filters were employed. These cut off below 440 nm and transmit more than 85% of the 546- and 578-nm Hg lamp emissions. For solution-phase experiments with sensitizer films, 4-mm Corning 4-102 band-pass filters were used. These filters transmit 13% of the 546-nm Hg line and cut off emissions above and below the 546-nm wavelength.

The high-pressure liquid chromatography system (Waters Associates) consisted of a Model 660 solvent programmer, two Model 6000A pumps, and a U6K injector. Two different detectors were used in combination with this system: the Schoeffel Instrument Corp. GM 770 variable-wavelength UV detector and the Waters Associates R401 differential refractometer. Spectrophotometric measurements were performed on a Cary 15 UV–visible recording spectrophotometer and on a Spectronic 20 visible spectrophotometer. Cuvettes 1 cm in path length were used in all cases.

Procedures. Actinometry. Absolute light intensities were determined with a potassium ferrioxalate actinometer.[34,35] After warming up the Hg lamp for 0.5 h, several 3-mL aliquots of aqueous 0.15 M $K_3Fe(C_2O_4)_3$ were exposed to the filtered source for timed periods of 5–20 min. Then, 2-mL aliquots of these exposed solutions were diluted to volume with 0.19 M 1,10-phenanthroline to form a colored complex with Fe^{2+} ions. Comparison of absorbance readings at 510 nm with a Beer's law curve for the phenanthroline complex yields values for Fe^{II} formed during photolysis. The light intensity of the 546-nm Hg line may then be determined from eq 17, where I_0^{546} is the intensity of the

$$I_0^{546} = \left(\frac{V_1 V_3}{V_2}\right)\left(\frac{A_{510}}{l\epsilon_{510}}\right)\frac{1}{\phi_{Fe^{546}}(1 - 10^{-A_{546}})t} \qquad (17)$$

546-nm Hg line incident on the photolysis cell (einstein L^{-1} s^{-1}), V_1 = 3 mL is the volume of $K_3Fe(C_2O_4)$ solution irradiated, V_2 = 2 mL is the volume of aliquot taken for analysis, V_3 = 25 mL is the final volume of phenanthroline solution to which V_2 is diluted, A_{510} is the absorbance of (phenanthroline)iron(II) complex at 510 nm, $\epsilon_{510} = 1.04 \times 10^4$ M^{-1} cm^{-1} is the molar extinction

coefficient at 510 nm for (phenanthroline)iron(II) complex as determined from the Beer's law curve, l = 1 cm is the path length of the cuvette, $\phi_{Fe^{546}}$ = 0.25 is the quantum yield for $K_3Fe(C_2O_4)$ photolysis at 547 nm (see below), A_{546} = 0.015 is the absorbance at 546 nm of 0.15 M $K_3Fe(C_2O_4)$, and t is the photolysis time (s). Because the absorbance and photolysis quantum yield for 0.15 M $K_3Fe(C_2O_4)$ at 578 nm are negligible, it is necessary to calculate the intensity of the 578-nm Hg line from eq 18, where I_0^{578} is the

$$I_0^{578} = I_0^{546}\left(\frac{E_{578}}{E_{540}}\right) = I_0^{546}\left(\frac{20.0}{24.5}\right) \quad (18)$$

intensity of the 578-nm Hg line incident on the photolysis cell (einstein L^{-1} s^{-1}), E_{578} is the rated[36] output of the Hanovia 450-W lamp at 578 nm, and E_{546} is the rated output of the Hanovia 450-W lamp at 546 nm. Since both the absorption coefficient and reported quantum yield for ferrioxalate photolysis at 546 nm ($\phi_{Fe^{546}}$ = 0.15) are small, we checked the system by simultaneously irradiating samples of ferrioxalate and a second chemical actinometer. The second actinometer was the RB-sensitized photooxidation of 2,3-dimethyl-2-butene to 2,3-dimethyl-2-(hydroperoxy)-2-butene (ROOH). This well-characterized[1] photooxidation is similar to a chemical actinometer devised by Demas et al.,[21] except that we substituted RB (which has a higher absorption coefficient at 546 nm) for $Ru(bpy)_3$ as the photosensitizer. The production of ROOH can be readily followed by iodimetric titration in acetic acid–chloroform solvent.[37] Under the conditions employed (0.1 M 2,3-dimethyl-2-butene, 6.2 × 10^{-6} M RB in oxygen-saturated methanol, 546-nm irradiation), all of the $^1O_2$ produced by irradiation of RB is converted to ROOH, and the incident intensity (I_0) can be calculated from eq 19, where (1 −

$$I_0 = \frac{+d[ROOH]/dt}{(1 - 10^{-A_{RB}})\phi_{O_2}} \quad (19)$$

$10^{-A_{RB}}$) = 0.61 is the fraction of light absorbed by the sensitizer and ϕ_{O_2} = 0.8 is the quantum efficiency for the production of $^1O_2$ from RB.[1c,24] An analogous expression (eq 20) can be written for

$$I_0 = \frac{-d[Fe^{3+}]/dt}{(1 - 10^{-A_{546}})\phi_{Fe^{546}}} \quad (20)$$

the ferrioxalate actinometer, where $-d[Fe^{3+}]/dt$ is the rate of ferrioxalate reduction (determined as described above) and (1 − $10^{-A_{546}}$) = 0.034 is the fraction of light absorbed by ferrioxalate. Combining eq 19 and 20 gives

$$\phi_{Fe^{546}} = \frac{-d[Fe^{3+}]/dt}{+d[ROOH]/dt}\{\phi_{O_2}\}\left\{\frac{0.61}{0.034}\right\} \quad (21)$$

For six samples of ferrioxalate irradiated for timed intervals of 600–3000 s, the average value of the rate of ferrioxalate reduction was $-d[Fe^{3+}]/dt = (1.22 \pm 0.05) \times 10^{-7}$ M s^{-1}. For nine samples of 2,3-dimethyl-2-butene irradiated for (0–9) × 10^3 s, the average rate of hydroperoxide production was $+d[ROOH]/dt = (6.98 \pm 0.31) \times 10^{-6}$ M s^{-1}. Substituting these values into eq 21 yields a value of $\phi_{Fe^{546}}$ = 0.25. This value of $\phi_{Fe^{546}}$ was used in conjunction with the ferrioxalate actinometer for all the experiments reported here.

Chromatography. Concentrations of Bu_2S and Bu_2SO were determined by high-pressure liquid chromatography. A 4-mm i.d. × 30 cm reverse phase μ-Bondapak C_{18} column was used. The mobile phase was a CH_3CN/H_2O mixture (70:30). Bu_2S and Bu_2SO were both determined with the UV detector at 220 nm. Standard concentration vs. peak area curves were prepared and used to calculate Bu_2S and Bu_2SO concentrations in reaction mixtures. Bu_2SO_2 exhibits a very weak molar extinction coefficient at 220 nm and could not be detected. Chromatographic peak areas were quantitated with a Spectra-Physics Minigrator digital integrator.

Photooxidation. For photosensitizers and Bu_2S in methanol, solutions of the sensitizers were prepared by using methanol saturated with O_2. In each solution, the concentration of sensitizer was adjusted to give an absorbance of 0.50 at 546 nm in a 1-cm path length cell. Bu_2S was accurately weighed into 25-mL volumetric flasks, and each flask was diluted to volume with a sensitizer solution. The amount of Bu_2S added was chosen to give a solution approximately 5 × 10^{-2} M in sulfide. Next, 2-mL aliquots of solution were transferred to photolysis tubes, and in each tube the volume over the solution was purged with O_2. When prepared in this manner, each tube contained approximately 1 × 10^{-4} mol of Bu_2S in solution, 2.4 × 10^{-6} mol of O_2 in solution, and 2.4 × 10^{-4} mol of gaseous O_2, over the solution. The solutions were irradiated for timed periods, and a syringe was used to withdraw accurately known volumes (10 μL) of solution for analysis. In some experiments, one tube was used for each time point; in others, a single tube with serum stopper was used for several time points.

For photosensitizer films with Bu_2S in methanol, solutions of approximately 5 × 10^{-2} M Bu_2S were prepared as above. Strips of sensitizer films (1.1 × 3 cm) were cut and inserted into photolysis tubes. The tubes were purged with oxygen, and 2 mL of Bu_2S solution was added. A series of tubes was irradiated, and individual tubes were withdrawn at timed intervals. Bu_2S was analyzed by high-pressure liquid chromatography as above. In performing actinometry, it was necessary to correct for the fact that the illuminated surface area of the sensitizer films was less than the illuminated area of the photolysis tubes (including those used for actinometry) by a factor of 0.55. Moreover, during photodegradation of all sensitizer films, a certain amount of film blushing was observed. Since this blushing causes light scattering and high absorbance values, direct absorbance readings on these films were inaccurate. Therefore, we devised a procedure to determine these film absorbances indirectly. Exposed films were weighed and dissolved in 3 mL of methylene chloride, and the absorbance of the methylene chloride solution at 546 nm was measured. Unexposed films, the absorbances of which could be read directly, were handled in the same manner. After normalizing the absorbances on a weight basis, we could determine the exposed film absorbances by using eq 22, where A_t^{film} is the absorbance

$$A_t^{film} = A_0^{film}(A_t^S/A_0^S) \quad (22)$$

of exposed film after time t, A_0^{film} is the absorbance of unexposed film read directly on the spectrophotometer, A_0^S is the absorbance of a 3-mL solution of unexposed film, and A_t^S is the absorbance of a 3-mL solution of exposed film after time t.

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(39) Bourdon et al.[11] and Turro et al.[28] showed that $^1O_2$ can diffuse into polymer films only 500 Å (5×10^{-5} mm) before being quenched.

Photochemistry of Polymers and Copolymers of Phenyl Vinyl Ketone and *o*-Tolyl Vinyl Ketone

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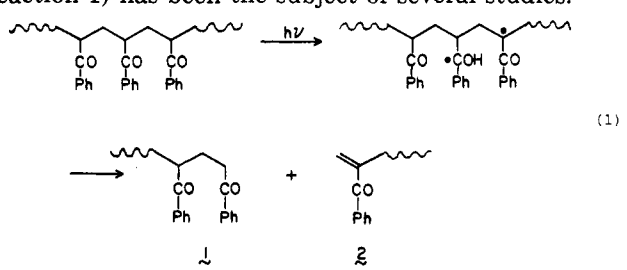
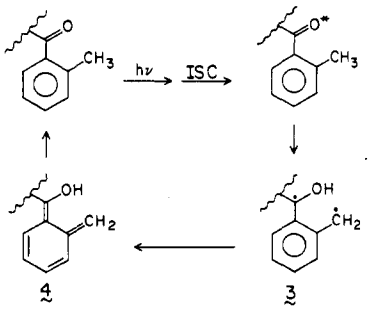
ABSTRACT: Energy migration plays an important role in the photochemistry of polymers containing phenyl vinyl ketone and *o*-tolyl vinyl ketone units. The average "residence time" of the triplet excitation in any given chromophore is in the neighborhood of 30 ps. Triplet lifetimes are estimated as 55 ns for PPVK and 2 ns for PTVK and are intermediate for all the copolymers. Biradical lifetimes are 65 ns for PPVK and 200 ns for PTVK, reflecting the longer lifetime of the biradicals derived from the *o*-methylbenzoyl group. Photoenolization of the *o*-tolyl vinyl ketone moieties provides an energy sink, reducing the degree of photodegration. For example, a copolymer of phenyl vinyl ketone and *o*-tolyl vinyl ketone containing 3% of the latter undergoes only 54% of the degradation undergone by PPVK.

The Norrish type II photofragmentation is an important process in polymer photochemistry.[3,4] The reaction can take place in almost all polymers containing carbonyl groups, including some like polystyrene and polyethylene in which the carbonyl chromophores are incorporated as a result of oxidative processes which are common during polymerization, processing, and purification.[5] Poly(phenyl vinyl ketone), PPVK, is a good model for the Norrish type II process in macromolecules, and its photodegradation (reaction 1) has been the subject of several studies.[4,6–11]



(1)

One way in which the energy can be channeled toward nondegradative processes is by providing an alternative reaction path for the excited carbonyl triplet, such that it will essentially behave as a mode of radiationless deactivation. In a recent preliminary communication[12] from this laboratory we have shown that photoenolizations in high polymers can be used to reduce, or prevent, photodegradation. For example, poly(*o*-tolyl vinyl ketone) is a photostable polymer; we have attributed this stability to the sequence of processes illustrated in reaction 2.



(2)

The behavior of copolymers of phenyl vinyl ketone and *o*-tolyl vinyl ketone, CoPT, can be expected to be controlled by the relative rates of the various possible photoprocesses, as well as by the possibility of energy migra-

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