

Singlet Oxygen as a Reactive Intermediate in the Photodegradation of an Electroluminescent Polymer†

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Abstract: Singlet molecular oxygen ($a^1\Delta_g$) is shown to be a reactive intermediate in the photoinduced oxidative decomposition of the electroluminescent material poly(2,5-bis(5,6-dihydrocholestanoxo)-1,4-phenylenevinylene) [BCHA-PPV] in both liquid solutions and solid films. Upon irradiation of this polymer in CS₂, singlet oxygen is produced by energy transfer from the BCHA-PPV triplet state to ground state oxygen with a quantum yield of ~ 0.025 . Singlet oxygen reacts with BCHA-PPV, resulting in extensive chain scission of the macromolecule. The reaction with singlet oxygen is unique to the polymer; the monomeric analog of this system, stilbene, does not appreciably react with singlet oxygen. Polymer degradation is proposed to proceed via addition of singlet oxygen in a $\pi 2 + \pi 2$ cycloaddition reaction to the double bond that connects phenylene groups in the macromolecule.

Introduction

Electric current induced visible luminescence can be obtained from a variety of conjugated organic polymers.^{1–5} Light-emitting diodes (LEDs) have been constructed by depositing a film of the polymer between two electrodes, one of which is optically transparent. This technology has potential for production of display devices. The usefulness of existing organic polymer-based LEDs is limited, however, by device failure within a time period that can be as short as several minutes. Oxygen-dependent phenomena play a significant role in the LED failure; devices fail faster when operated in the presence of oxygen as opposed to nitrogen.^{6,7} A great deal of evidence suggests that such failure derives, at least in part, from the degradation of the electroluminescent polymer and/or oxidation of the electrodes.⁸ In this paper, we focus on aspects related to the former.

In photoinduced experiments, rather than upon electrical excitation, Yan et al.⁹ examined the effect of oxygen on luminescence from films of poly(1,4-phenylenevinylene) [PPV]. The intensity of this luminescence decreased significantly upon

prolonged irradiation of a film exposed to air, whereas irradiation under nitrogen did not affect the photoluminescence intensity. Furthermore, this decrease in luminescence intensity was shown to correlate with changes observed in the IR spectrum of the PPV; as the luminescence intensity decreased, the concentration of carbonyl groups in the polymer increased, and the concentration of the double bonds that link adjacent phenyl groups decreased. Papadimitrakopoulos et al.¹⁰ subsequently showed that, at early stages of this oxidation, the carbonyls formed are likely to be aromatic aldehydes. These authors also suggested that the decrease in the concentration of bridging double bonds was coincident with macromolecular chain scission. However, a mechanism was not proposed for these photooxygenation reactions, nor was a likely intermediate identified.

Unlike the parent compound PPV, alkoxy-substituted derivatives of PPV are soluble in common organic solvents which facilitates both solution phase measurements and the casting of solid films. Poly(2,5-bis(5,6-dihydrocholestanoxo)-1,4-phenylenevinylene) [BCHA-PPV] is one such derivative that has been identified as a promising material for use in LEDs.^{11,12} We set out to study the oxygen-dependent photophysics and photochemistry of BCHA-PPV. In particular, we were interested to ascertain whether or not singlet molecular oxygen, O₂($a^1\Delta_g$), was an intermediate in the photoinduced degradation of these materials.

In 1982, Gibson and Pochan¹³ suggested that singlet oxygen might be an intermediate in the photoinduced degradation of polyacetylene. Holdcroft^{14,15} has shown that poly(3-alkylthiophenes) can produce singlet oxygen upon irradiation, and that

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singlet oxygen can react with these polymers. With respect to PPV and its derivatives, however, no data pertaining to the possible intermediacy of singlet oxygen in the degradation reactions of such polymers have been published.

In this paper, we document that singlet oxygen is indeed a reactive intermediate in the degradation of BCHA-PPV. Moreover, this chemistry appears to be unique to the polymer; there is no appreciable reaction between singlet oxygen and the monomeric analog for this system, stilbene.

Experimental Section

Details of the techniques and instrumentation we use to monitor oxygen and organic molecule excited states in time-resolved experiments are described elsewhere.^{16–20} Briefly, a Nd:YAG laser was used as the pulsed excitation source. The pulse duration was approximately 5 ns (fwhm) when both the second (532 nm) and third (355 nm) harmonics of the fundamental lasing wavelength were used. The second harmonic was also used to pump a dye laser, thus allowing us to irradiate samples at a variety of wavelengths longer than 532 nm. Additional pulsed laser excitation wavelengths were obtained by stimulated Raman scattering of the Nd:YAG third harmonic with H₂. A 150 W continuous-wave xenon lamp was used as the probe source in the flash absorption experiments. Absorption and luminescence in the visible were detected with a silicon photodiode. The near-infrared phosphorescence of singlet oxygen was monitored with a germanium detector. The instrumentation used in the magnetic field experiments has likewise been described.¹⁷ Gel permeation chromatograms were recorded on a Waters Model 150-C instrument which had a refractive index detector. THF was used as the mobile phase in the GPC experiments. Steady-state fluorescence spectra were recorded on a Perkin-Elmer Model LS-5 instrument. Prolonged photolyses in the photodegradation reactions were performed using a 150 W xenon lamp fitted with Schott cutoff filters. The latter were chosen to pass wavelengths longer than 475 or 435 nm, depending on the experiment.

BCHA-PPV (weight-average MW = 900 000²¹) was obtained from Uniax Corp. and used as received. Benzene, toluene, CCl₄, and CS₂ were obtained from Aldrich (HPLC grade) and used as received. Polystyrene (MW 230 000), zinc(II) octaethylporphine, and the fullerene C₆₀ were likewise obtained from Aldrich and used as received. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was obtained from Aldrich and purified as previously described.¹⁸ Perdeuteriopolystyrene was obtained from Polysciences Inc. Polymer films were cast onto glass plates from benzene solutions.

Results and Discussion

1. Solution-Phase Measurements. The absorption and emission spectra of BCHA-PPV recorded in toluene (Figure 1) were similar to those recorded by Gettinger et al. in *p*-xylene.¹² In a time-resolved experiment, the emission did not broaden the profile of the excitation laser pulse (fwhm \approx 5 ns), indicating that the lifetime of the emitting state is less than \sim 2 ns. This is consistent with BCHA-PPV fluorescence.

a. BCHA-PPV Triplet State. Subsequent to 532 nm pulsed laser excitation of BCHA-PPV in toluene, we recorded the absorption spectrum of a transient species with λ_{max} at \sim 830 nm (Figure 1). At probe wavelengths less than \sim 550 nm, the absorbance change subsequent to pulsed excitation corresponded to a depletion of ground state BCHA-PPV. In a deoxygenated solution, the time-resolved signals at 520 nm (ground state

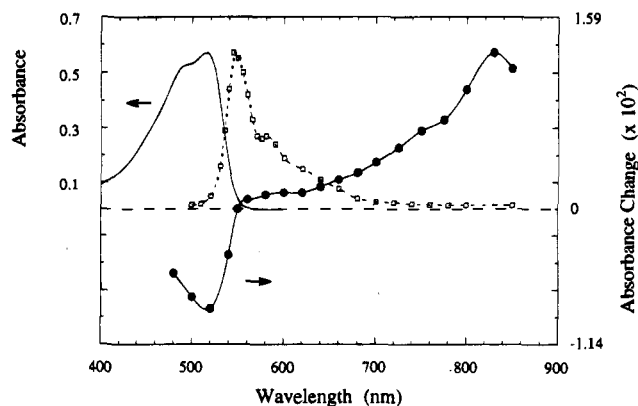


Figure 1. Spectra of BCHA-PPV (2.5 mg/100 mL \approx 2.8×10^{-8} M) recorded in toluene. (a) Difference absorption spectrum of the triplet state recorded subsequent to 532 nm pulsed laser irradiation (filled circles). The data were recorded by extrapolating the time-resolved absorption signals to time 0. In a deoxygenated solution, the triplet signal decay followed first-order kinetics with a lifetime of 150 μ s. (b) Ground state absorption spectrum (solid line). (c) Fluorescence spectrum recorded subsequent to pulsed laser excitation at 416 nm (open squares). Data were recorded in 1 cm cuvettes.

recovery) and 830 nm (transient absorption) were single-exponential with identical time constants of 150 μ s. Thus, the lifetime τ_0 of the transient is 150 μ s. Upon the admission of air to the solution, the transient lifetime was shortened substantially ($\tau \approx$ 455 ns). Dividing measured values of $\tau^{-1} - \tau_0^{-1}$ by 1.4×10^{-3} M, which is the concentration of oxygen in aerated toluene,^{22,23} we determined that the transient was quenched by ground state oxygen ($X^3\Sigma_g^-$) with a rate constant of $(1.6 \pm 0.2) \times 10^9$ M⁻¹ s⁻¹. This rate constant is characteristic for the quenching of organic molecule triplet states by oxygen.²⁴

Leng et al. report that, in neat films, the PPV triplet energy E_T is \sim 135 kJ/mol.²⁵ If BCHA-PPV has a similar triplet energy in solution, then it should be possible to produce the BCHA-PPV triplet state by energy transfer from the triplet state of acridine ($E_T = 190$ kJ/mol²⁶). Upon 355 nm irradiation of acridine in toluene, under conditions in which only a small amount of the incident light was absorbed by BCHA-PPV ($A_{\text{acridine}} = 1.2$ and $A_{\text{BCHA-PPV}} = 0.1$ in a 1 cm cell), we indeed recorded the same flash absorption spectrum as that obtained subsequent to direct irradiation of BCHA-PPV at 532 nm. Furthermore, the rising portion of the time-resolved transient signal, as measured at 830 nm, was single-exponential with a time constant τ that varied with the BCHA-PPV concentration (at [BCHA-PPV] \approx 3.4×10^{-8} M, $\tau = 20$ μ s). Over the range of BCHA-PPV concentrations used in the acridine-sensitized reaction, the rate of transient appearance at 830 nm was (1) identical to the rate of ³acridine decay²⁷ and (2) much slower than the rate of the 830 nm transient appearance subsequent to direct irradiation of BCHA-PPV. Upon direct irradiation of BCHA-PPV, the appearance rate of the transient absorption signal was faster than our instrument response time of 50 ns. (Note that ¹BCHA-PPV, which is the precursor to ³BCHA-PPV in the direct irradiation experiment, has a lifetime $<$ 2 ns, *vide*

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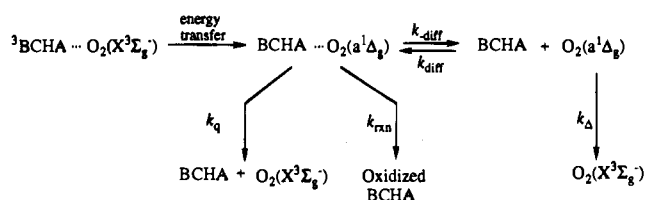
(27) ³Acridine was monitored in a flash absorption experiment at 440 nm. In these experiments, the BCHA-PPV concentration was small enough that absorption by the BCHA-PPV ground state at 440 nm did not perturb the acridine signal.

supra.) Thus, on the basis of the oxygen quenching and energy transfer experiments, we assign the flash absorption spectrum shown in Figure 1 to the BCHA-PPV triplet. Published reports indicate that the PPV triplet state absorbs at ~860–900 nm in solid films.^{25,28,29}

To quantify the BCHA-PPV triplet energy in solution, we attempted to produce the BCHA-PPV triplet using other triplet energy donors. In one experiment, zinc(II) octaethylporphine was used as the triplet sensitizer ($E_T = 170$ kJ/mol²⁶). Upon irradiation of the porphine at 570 nm, the appearance rate of the triplet BCHA-PPV flash absorption signal (1) was again much slower than that observed upon direct irradiation of BCHA-PPV and (2) varied with the BCHA-PPV concentration. These data are, therefore, consistent with energy transfer from the triplet porphine to BCHA-PPV, and $E_T(\text{BCHA-PPV}) < 170$ kJ/mol. In a second experiment, the fullerene C₆₀ was used as the triplet sensitizer ($E_T = 151$ kJ/mol^{30,31}). BCHA-PPV triplet was monitored at 830 nm where the triplet C₆₀ absorbance is comparatively small.^{32,33} Triplet C₆₀ was monitored at 750 nm. The flash absorption data in this case suggested that reversible energy transfer was occurring between the triplet states of BCHA-PPV and C₆₀.^{34,35} Thus, the triplet energy of BCHA-PPV in solution must be ~150 kJ/mol. It is reasonable to expect a lower BCHA-PPV triplet energy in neat, solid films where the high BCHA-PPV concentration along with conformational constraints may influence orbital overlap in the BCHA-PPV π system. The monomeric analog of this polymer, (E)-stilbene, has a triplet energy of 206 kJ/mol.²⁶

If we assume that energy transfer from acridine to BCHA-PPV proceeds with unit efficiency, it is possible to quantify the yield of triplet BCHA-PPV produced upon direct irradiation of the polymer. The acridine triplet state is produced with a quantum efficiency of 0.84³⁶ from a singlet state whose lifetime is sufficiently short (<17 ps)³⁷ as to preclude bimolecular quenching. The fraction F of ³acridine thus produced that is quenched by BCHA-PPV was obtained by measuring the ³acridine lifetime both in the presence (τ) and in the absence (τ_0) of BCHA-PPV; $F = 1 - (\tau/\tau_0)$. In order to trap a fraction of ³acridine that could accurately be quantified (e.g., $F \approx 0.4$), we used comparatively large BCHA-PPV concentrations (~1 $\times 10^{-7}$ M). In the absence of BCHA-PPV, τ_0 was obtained by monitoring ³acridine in a flash absorption experiment at 440 nm. However, because the BCHA-PPV ground state absorbs at 440 nm (Figure 1), it was necessary to obtain τ from the rising portion of the ³BCHA-PPV absorption signal at 830 nm. Assuming energy transfer from ³acridine to BCHA-PPV occurs with unit efficiency, the absorbance of the resultant BCHA-PPV triplet thus reflects a quantum yield of $0.84F$. By using

Scheme 1



this acridine-sensitized BCHA-PPV triplet signal as a standard, we estimate that the BCHA-PPV triplet state is formed with a quantum efficiency of ~0.03 upon direct irradiation of BCHA-PPV at 355 nm.³⁸

We also find that the BCHA-PPV triplet yield upon 532 nm irradiation is a factor of ~1.2 smaller than that obtained upon 355 nm irradiation. These data were obtained by normalizing ³BCHA-PPV absorbance values at a given observation wavelength (e.g., 830 nm) by the number of incident photons absorbed by the BCHA-PPV ground state at 532 and 355 nm, respectively. This dependence of the triplet yield on excitation wavelength also occurs in films of PPV and its derivatives, and will be discussed in greater detail in section 2.

b. Singlet Oxygen. Following 532 nm pulsed laser excitation of BCHA-PPV in aerated CS₂, we observed the time-resolved 1270 nm phosphorescence of singlet oxygen. Under these conditions, flash absorption data indicated that the BCHA-PPV triplet state was being quenched by oxygen. Because the lifetime of the BCHA-PPV singlet state is sufficiently short as to preclude quenching by oxygen (*vide supra*), we suggest that triplet BCHA-PPV is likely to be the sole precursor to singlet oxygen. By comparing the intensity of the BCHA-PPV-sensitized singlet oxygen signal to that obtained subsequent to the irradiation of the fullerene C₆₀, which produces singlet oxygen with unit quantum efficiency in CS₂,³⁹ we estimate that BCHA-PPV produces singlet oxygen with a quantum efficiency of ~0.025. In the previous section we estimated that, upon 532 nm irradiation, the BCHA-PPV triplet state is formed with a yield of $0.03/1.2 = 0.025$. Thus, a singlet oxygen quantum yield of ~0.025 indicates that the formation of singlet oxygen from triplet BCHA-PPV proceeds with approximately unit efficiency.

In self-sensitized, singlet oxygen-mediated reactions, a static quenching channel can account for some of the oxygenated product.^{40–44} With respect to BCHA-PPV, static quenching would refer to reaction between singlet oxygen and BCHA-PPV prior to the dissociation of the initially formed singlet oxygen–BCHA-PPV encounter pair (Scheme 1). In Scheme 1, k_{diff} is the bimolecular rate constant for the diffusion-dependent encounter of two solutes, and k_{-diff} is the unimolecular rate constant for diffusion-dependent dissociation of an encounter pair. We assume that singlet oxygen phosphorescence derives only from free, solvated singlet oxygen molecules [k_A is the sum of solvent-dependent radiative (k_r) and nonradiative (k_{nr}) decay constants]. The observation that the singlet oxygen

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yield, derived from a singlet oxygen phosphorescence measurement, is equivalent to the BCHA-PPV triplet yield indicates that static quenching does not appear to play an important role in this system [i.e., $k_{\text{diff}} > k_q + k_{\text{rxn}}$].

In the absence of quenchers, the lifetime of singlet oxygen in aerated CS_2 is ~ 45 ms.⁴⁵ In a CS_2 solution of BCHA-PPV, the singlet oxygen lifetime is much shorter. As the BCHA-PPV concentration was increased over the range 3.2×10^{-7} to 8.3×10^{-7} M, the singlet oxygen lifetime τ_{Δ} decreased from 707 to 293 μs . Because τ_{Δ} is obtained from a time-resolved singlet oxygen phosphorescence experiment and because we assume that this phosphorescence derives only from the solvated singlet oxygen molecules, these changes in τ_{Δ} reflect a diffusion-dependent dynamic quenching channel. From a plot of τ_{Δ}^{-1} vs [BCHA-PPV], we determined that BCHA-PPV quenches singlet oxygen with a rate constant of $(4.1 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Note that this rate constant was obtained using BCHA-PPV concentration data calculated from the molecular weight of the polymer (900 000). If the rate constant is calculated such as to reflect the molecular weight of each repeat unit in the polymer (875.4), the data yield $k = 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Unlike a low molecular weight solute, the dissolved polymer is not uniformly distributed in the solvent. The probability of interaction between a given singlet oxygen molecule and the active quenching site on the macromolecule thus depends on a number of variables that include, for example, the conformational dynamics of the polymer. As a consequence, an accurate value for this rate constant is likely to be somewhat larger than $4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, thus reflecting several monomeric repeat units in the macromolecule, but certainly not as large as $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The conclusion that the rate constant for singlet oxygen quenching by BCHA-PPV must be less than $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ indicates that this process does not approach the diffusion-controlled limit. For reactions involving a small molecule like oxygen, the diffusion-controlled rate constant is on the order of $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁴⁶ The observation that $k_{\text{diff}} > k_q + k_{\text{rxn}}$, derived from the quantum yield measurements (*vide supra*), is consistent with a reaction that does not approach the diffusion-controlled limit.^{18,47}

c. BCHA-PPV Degradation. Upon prolonged irradiation of BCHA-PPV in aerated solutions of either CS_2 or CCl_4 , the ground state absorption spectrum changed significantly (Figure 2). In particular, the band at ~ 400 – 550 nm decreased in intensity and the λ_{max} of this band shifted to the blue. In deoxygenated solutions, negligible changes in the spectrum were observed upon irradiation for the same period of time. Thus, the reaction which results in the disruption of the BCHA-PPV chromophore is oxygen-dependent.

The irradiation-induced changes observed in the BCHA-PPV ground state absorption spectrum were also reflected in the fluorescence spectrum of BCHA-PPV (Figure 3). Specifically, as the elapsed exposure time to the photolysis source increased, the emission λ_{max} shifted to the blue. This is consistent with the disruption of the BCHA-PPV chromophore.

Irradiation of an aerated solution of BCHA-PPV results in dramatic changes in the BCHA-PPV molecular weight, reflecting extensive scission of the polymer chains at multiple sites. This is illustrated in Figure 4 in which gel permeation chromatograms are shown for both unirradiated and irradiated

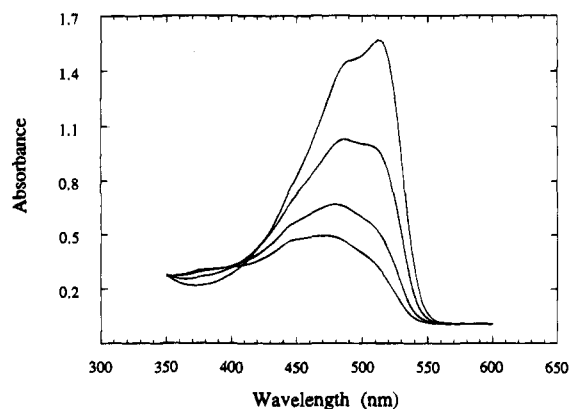


Figure 2. Ground state absorption spectra in a 1 cm cuvette of 3.4 mg/50 mL ($\sim 7.6 \times 10^{-8}$ M) BCHA-PPV in aerated CCl_4 recorded as a function of elapsed photolysis time. BCHA-PPV was irradiated with collimated, broad-band light of wavelength > 475 nm obtained from a 150 W xenon lamp. Data are shown for elapsed photolysis times of 0 (top trace), 1, 2, and 3 min (bottom trace).

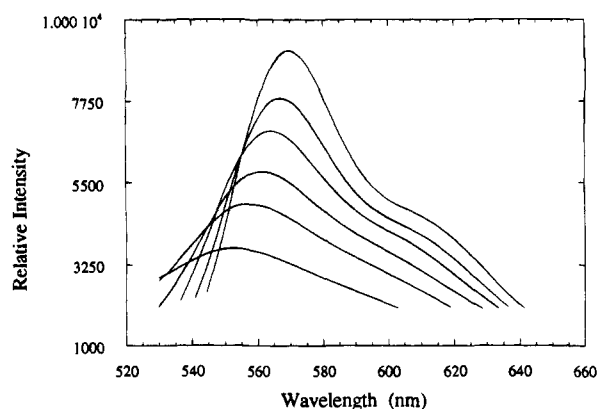


Figure 3. Fluorescence spectra of BCHA-PPV in CS_2 recorded as a function of elapsed photolysis time. The excitation wavelength was 420 nm. BCHA-PPV was irradiated with collimated, broad-band light of wavelength > 475 nm obtained from a 150 W xenon lamp. Data are shown for elapsed photolysis times of 0 (top trace), 1, 2.5, 4.5, 7, and 10 min (bottom trace).

BCHA-PPV. Due to the large molecular weight (900 000) and persistence length¹² of this macromolecule, the GPC peak of the unirradiated material appears at very short retention time. Subsequent to the irradiation of a BCHA-PPV solution for ~ 1 h with broad-band light of wavelength > 435 nm, the peak position observed in the GPC corresponded to $M_w \approx 20$ 000 relative to a polystyrene molecular weight standard. Thus, the GPC data are consistent with both the absorption and emission spectra shown in Figures 2 and 3, and indicate that disruption of the BCHA-PPV chromophore is coincident with macromolecular chain scission.

The results of the following experiments clearly implicate the intermediacy of singlet oxygen in BCHA-PPV photodegradation: (1) The spectral changes observed upon irradiation of aerated BCHA-PPV solutions were reduced by the addition of the well-known⁴⁸ singlet oxygen quencher 1,4-diazabicyclo-[2.2.2]octane (DABCO), as shown in Figure 5. In a flash absorption experiment, we ascertained that DABCO does not quench the BCHA-PPV triplet state. (2) The rate of BCHA-PPV degradation was much faster in CS_2 than in toluene, as shown in Figure 6. These data reflect a singlet oxygen lifetime in CS_2 (~ 45 ms) that is significantly longer than that in toluene (~ 28 μs). In a control study, we ascertained that the BCHA-

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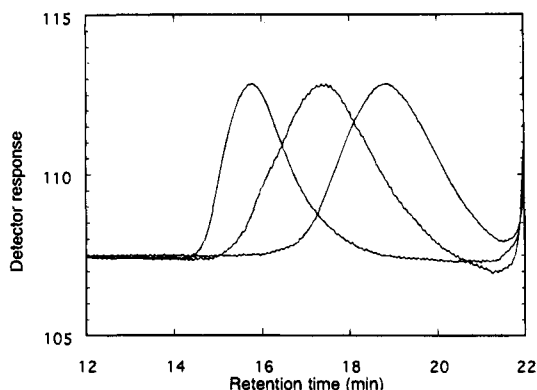


Figure 4. Gel permeation chromatograms of BCHA-PPV recorded as a function of elapsed photolysis time in CS_2 at wavelengths >435 nm (1 mg of BCHA-PPV/2 mL of CS_2): trace 1, unirradiated sample (left); trace 2, 12 min; trace 3, 22 min (right). The successive increase in retention times corresponds to a successive decrease in molecular weight. In order to better show changes in retention time, the chromatograms have been scaled to the same intensity. For all samples examined, including the unirradiated BCHA-PPV, GPC peaks corresponding to very low molecular weight material were observed. These traces are not shown.

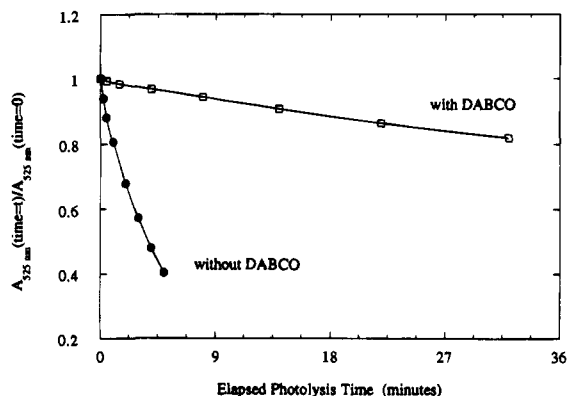


Figure 5. Normalized BCHA-PPV absorbance in CS_2 as a function of elapsed photolysis time. Plotted on the abscissa is the BCHA-PPV absorbance at 525 nm recorded at some elapsed photolysis time t divided by the 525 nm absorbance at time 0. For both systems shown, the absorbance at time 0 was ~ 1.0 ([BCHA-PPV] $\approx 5 \times 10^{-8}$ M ≈ 2.2 mg/50 mL). The DABCO concentration was 1.35×10^{-2} M. BCHA-PPV was irradiated with collimated, broad-band light of wavelength >475 nm obtained from a 150 W xenon lamp.

PPV-sensitized yield of singlet oxygen in CS_2 was the same as that in toluene. (Relative yields were obtained⁴⁹ by comparing the intensities of the time-resolved singlet oxygen phosphorescence signal at time 0 and adjusting for the known effect of solvent on the singlet oxygen radiative lifetime.^{39,50})

If we assume that singlet oxygen is the sole reactive intermediate responsible for BCHA-PPV degradation, then the data from the DABCO and CS_2 /toluene experiments shown in Figures 5 and 6 can be used in Stern–Volmer analyses to yield a rate constant for the quenching of singlet oxygen by BCHA-PPV (see the Appendix). Because we ascertained in the previous section that static quenching does not appear to be

(49) Because the degradation experiments were performed with photolysis wavelengths >475 nm obtained from a xenon lamp, it was necessary to ascertain that the yield of singlet oxygen in these respective solvents was independent of photolysis wavelength. Thus, comparisons of the singlet oxygen phosphorescence intensity were performed for data recorded in CS_2 and toluene at three photolysis wavelengths, 416, 504, and 532 nm.

(50) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 4599–4602.

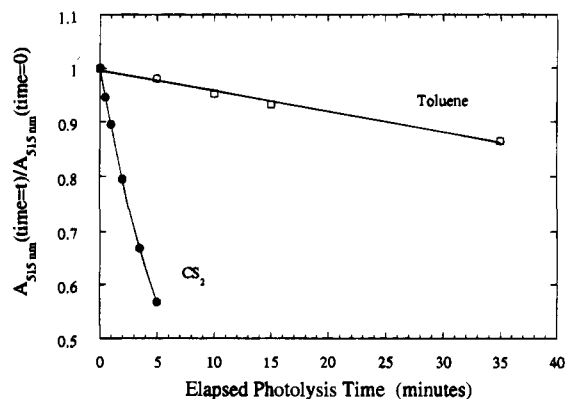


Figure 6. Normalized BCHA-PPV absorbance as a function of elapsed photolysis time in two different solvents. Plotted on the abscissa is the BCHA-PPV absorbance at 515 nm recorded at some elapsed photolysis time t divided by the 515 nm absorbance at time 0. For both systems shown, the absorbance at time 0 was ~ 0.9 ([BCHA-PPV] $\approx 4.4 \times 10^{-8}$ M ≈ 2 mg/50 mL). BCHA-PPV was irradiated with collimated, broad-band light of wavelength >475 nm obtained from a 150 W xenon lamp.

important in this solution-phase photosystem, rate constants thus obtained from the data in Figures 5 and 6 should be identical to those obtained in the singlet oxygen phosphorescence experiment. As outlined in the Appendix, however, the DABCO data yield quenching rate constants of $\sim 1 \times 10^{12}$ $\text{M}^{-1} \text{s}^{-1}$ at [DABCO] = 1.4×10^{-2} M (from Figure 5) and $\sim 2.5 \times 10^{10}$ $\text{M}^{-1} \text{s}^{-1}$ at [DABCO] = 8×10^{-5} M. The CS_2 /toluene data yield $\sim 3.1 \times 10^{10}$ $\text{M}^{-1} \text{s}^{-1}$ for this quenching rate constant. These rate constants are clearly larger than the rate constant obtained by monitoring singlet oxygen phosphorescence (4.1×10^9 $\text{M}^{-1} \text{s}^{-1}$, *vide supra*).

In a control experiment, we ascertained that rate constants obtained from such Stern–Volmer analyses of BCHA-PPV degradation should be reasonably accurate. In this case, rather than monitoring the self-sensitized, singlet oxygen-mediated degradation of BCHA-PPV, C_{60} was used as the singlet oxygen sensitizer. Upon irradiation of C_{60} at wavelengths greater than 590 nm, where BCHA-PPV does not absorb, we analyzed resultant changes in the BCHA-PPV absorbance both in the presence and in the absence of DABCO as outlined in the Appendix and obtained a rate constant for the quenching of singlet oxygen by BCHA-PPV. The rate constant thus obtained (5.5×10^9 $\text{M}^{-1} \text{s}^{-1}$) was similar to that obtained in the singlet oxygen phosphorescence experiment (4.1×10^9 $\text{M}^{-1} \text{s}^{-1}$).

It is important to note in Figure 5 that, even at a comparatively high DABCO concentration, BCHA-PPV nevertheless degrades in a self-sensitized photooxygenation reaction. This observation is consistent with a component of static quenching. Specifically, at an infinitely large DABCO concentration, all the free, solvated singlet oxygen is deactivated by DABCO, and BCHA-PPV oxidation must occur via reaction from the initially formed singlet oxygen–BCHA-PPV encounter pair (i.e., although $k_{\text{diff}} > k_{\text{rxn}} + k_{\text{q}}$ in Scheme 1, k_{rxn} is not negligible). Furthermore, the smaller quenching rate constant obtained upon reducing the DABCO concentration in these degradation reactions is also consistent with a component of static quenching. This latter phenomenon reflects the fact that, because of the static quenching component, increases in DABCO concentration above a certain limit will not inhibit the degradation of BCHA-PPV. As a consequence, “rate constants” thus obtained from degradation experiments for the quenching of singlet oxygen by BCHA-PPV will simply increase with an increase in the DABCO concentration (see eq 6 in the Appendix).

Thus, the rate constants obtained in the DABCO and CS₂/toluene experiments indicate that a static quenching component may indeed play a role in the self-sensitized degradation of BCHA-PPV. However, this component must be small enough as not to significantly influence our quantum yield measurements (*vide supra*). In addition to a small component of static quenching, the DABCO and CS₂/toluene experiments may also indicate that a singlet oxygen reaction is not the only process responsible for changes in the BCHA-PPV absorption profile. Because the rate constants derived from the DABCO and CS₂/toluene data were obtained by monitoring the disappearance of BCHA-PPV, they reflect not only the initial trapping of singlet oxygen but subsequent steps that ultimately result in a change of BCHA-PPV absorbance. Furthermore, because the C₆₀-sensitized BCHA-PPV degradation experiment yielded a quenching rate constant similar to that obtained from the singlet oxygen phosphorescence experiment, these subsequent steps that result in BCHA-PPV degradation appear to be dependent on the absorption of light by BCHA-PPV and/or the primary photo-products of the BCHA-PPV reaction with singlet oxygen. This point is addressed further in section 3.

The BCHA-PPV photodegradation rate was independent of an applied magnetic field (~21 kG). Processes in the oxygen-organic molecule (M) photosystem can be influenced by a magnetic field if the charge-transfer state (M^{•+}O₂^{•-}) plays an intermediary role.¹⁷ This absence of a magnetic field effect is consistent with the proposed intermediacy of singlet oxygen in the photodegradation of BCHA-PPV.

2. Experiments on Solid Films. Data were recorded from (1) neat films of BCHA-PPV and (2) films of BCHA-PPV dissolved in polystyrene (PS), both of which were cast from benzene solutions. The concentration of BCHA-PPV in the PS films was higher than that in solution. In a typical sample ~40 μm thick, [BCHA-PPV] ≈ 2 × 10⁻⁴ M which gave rise to an absorbance in the range 0.1–0.2 at 525 nm. The emission and ground state absorption spectra of BCHA-PPV in these films were similar to those recorded from solutions of BCHA-PPV in toluene.⁵¹

a. BCHA-PPV Triplet State. Upon 532 nm pulsed laser excitation of BCHA-PPV films, a transient absorption spectrum similar to that recorded in liquids was observed (Figure 1). This transient was likewise efficiently quenched by oxygen. In the absence of oxygen, the transient decay in a neat BCHA-PPV film did not follow first-order kinetics. This is a common observation in solid polymers, and may reflect a nonhomogeneous distribution of sites within the solid matrix.⁵² The decay was fit using a biexponential function, and yielded τ₁ = 14.9 μs and τ₂ = 122 μs. In aerated films, the transient decay was first-order with a lifetime of 1 μs. Given the similarity of these data to those recorded in the liquid solutions (*vide supra*), it is likely this flash absorption signal derives principally from a BCHA-PPV triplet-triplet transition. However, published data on PPV films indicate that other species produced upon direct photolysis of the polymer may also absorb in this spectral region.^{25,28,29} Specifically, transitions involving bipolarons (e.g., oxidized radical cations) could be reflected in our flash absorption data. This possibility is further discussed in the next section. The transient we observe at ~830 nm has a compara-

tively long lifetime; thus, it is not likely that we are monitoring "spatially indirect" excitons that have been proposed by Yan et al.⁵³ to exist in these materials.

In a neat BCHA-PPV film, the transient absorbance at 830 nm was ~12 times smaller than that in a liquid. In a polystyrene film, the absorbance was ~5 times smaller than that in a liquid. (The data were normalized for differences in the BCHA-PPV ground state absorbance.) These results are consistent with a BCHA-PPV triplet yield that is smaller in the solids than in a liquid. This phenomenon may reflect the fact that the extent to which the triplet state is produced from the singlet (fluorescent) state in such systems depends on the extent to which rotation can occur about the inter-phenyl double bond; the barrier to rotation in the macromolecule should be larger in the solid than in the liquid.⁵⁴

b. BCHA-PPV Degradation. Upon prolonged irradiation of deoxygenated BCHA-PPV films, negligible changes in the BCHA-PPV absorption spectrum were observed (for a neat film of BCHA-PPV, we estimate a quantum yield for photodegradation under these conditions of 10⁻⁸–10⁻⁹). Upon irradiation of oxygenated (1) neat BCHA-PPV films and (2) films of BCHA-PPV dissolved in PS, the BCHA-PPV absorption spectrum changed in much the same way as it did in solution. Upon 530 nm irradiation of oxygenated PS films containing BCHA-PPV, the rate of change in BCHA-PPV concentration was ~200 times slower than that observed in CCl₄. Upon irradiation of perdeuterio-PS films containing BCHA-PPV, the rate of [BCHA-PPV] change was approximately 5 times faster than that observed in PS. Furthermore, upon the addition of DABCO to a PS film containing BCHA-PPV, the rate of [BCHA-PPV] change was reduced by a factor of 3. These data strongly suggest that irradiation of BCHA-PPV in solid films indeed produces singlet oxygen, and that singlet oxygen is a key intermediate in the photoinduced degradation of BCHA-PPV. The moderate DABCO-dependent reduction in the BCHA-PPV degradation rate was obtained with a large mole ratio of DABCO to BCHA-PPV monomer repeat units (23:1), which is consistent with a pronounced component of static quenching (*vide supra*). Differences in the degradation rate that occur as the polymer is changed from PS to perdeuterio-PS (PS-*d*) reflect differences in the singlet oxygen lifetime (τ_{PS} = 22 μs, τ_{PS-*d*} = 250 μs).^{16,52,55} The comparatively rapid degradation rate observed in CCl₄ likely reflects (a) the relatively long singlet oxygen lifetime in CCl₄ (τ ≈ 73 ms),⁴⁵ (b) larger solute diffusion coefficients in the liquid, and (c) a singlet oxygen quantum yield that may be larger in the liquid than in the solid films.

We indicated that our flash absorption data obtained from neat BCHA-PPV films may reflect both triplet and bipolaron transitions. Leng et al.²⁵ report that as the excitation wavelength is changed from 532 to 355 nm (1) the PPV triplet yield increases by a factor of ~4, (2) the PPV bipolaron yield increases by a factor of ~2, and (3) the PPV singlet yield does not change significantly. Upon irradiation at 355 nm in our system, the BCHA-PPV degradation rate was ~7 times faster than that observed upon 532 nm irradiation (the data were normalized for light intensity and sample absorbance). Upon 355 nm irradiation, however, the BCHA-PPV transient absorbance at 830 nm was only ~2.5 times larger than that observed upon 532 nm irradiation. Several explanations could be provided for the difference between these numbers, including

(51) The absorption spectrum of BCHA-PPV dissolved in CS₂ differs from that for BCHA-PPV dissolved in toluene; BCHA-PPV has an absorption tail in CS₂ that extends out to longer wavelengths. λ_{max} of the BCHA-PPV absorption profile in toluene is 515 nm, whereas λ_{max} in CS₂ is 525 nm. The absorption profile of BCHA-PPV in polystyrene is similar to that in CS₂ with λ_{max} at 525 nm. In a neat film of BCHA-PPV, we record a λ_{max} of 508 nm.

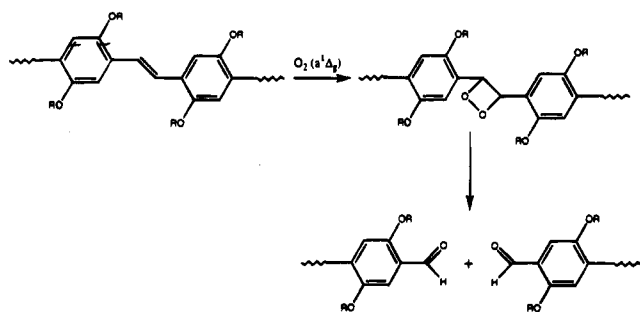
(52) Clough, R. L.; Dillon, M. P.; Iu, K.-K.; Ogilby, P. R. *Macromolecules* **1989**, *22*, 3620–3628.

(53) Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *72*, 1104–1107.

(54) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(55) Ogilby, P. R. *Singlet Oxygen Photophysics*; Wiley: New York, in press.

Scheme 2



the possibilities that (1) in addition to the triplet, another species (e.g., a bipolaron) may contribute to the 830 nm transient absorption in BCHA-PPV films^{25,28,29} and (2) secondary, wavelength-dependent photoinduced reactions may contribute to the degradation of BCHA-PPV (*vide supra*, section 1c). We also ascertained that the BCHA-PPV fluorescence intensity did not change significantly when the pump wavelength was changed from 532 to 355 nm, which is consistent with the expectation that interactions between oxygen and the BCHA-PPV singlet state are not a primary route in the degradation of the polymer.

As in the solution phase, a magnetic field effect was not observed for BCHA-PPV photodegradation under these conditions, suggesting that charge-transfer states are not involved as intermediates in this reaction.

c. Singlet Oxygen. Despite the conclusions reached on the basis of the BCHA-PPV degradation experiments, we were unable to detect singlet oxygen phosphorescence from a neat BCHA-PPV film or from BCHA-PPV in a PS film. The singlet oxygen lifetime in perdeuterio-PS is ~ 11.4 times longer than in PS, thus making detection of singlet oxygen phosphorescence easier in perdeuterated media.^{16,52} Nevertheless, we were also not able to detect BCHA-PPV-sensitized singlet oxygen in perdeuterio-PS. By comparing our levels of noise from the latter experiment with the singlet oxygen phosphorescence intensity produced by energy transfer from C₆₀ in a similar perdeuterio-PS film, we estimate an upper limit of ~ 0.02 for the quantum efficiency of BCHA-PPV-sensitized singlet oxygen production in this solid.

Our inability to spectroscopically detect singlet oxygen in these solid films likely derives from (1) a comparatively small quantum yield of BCHA-PPV-sensitized singlet oxygen and/or (2) efficient static and dynamic quenching of singlet oxygen by BCHA-PPV. With respect to the first point, a small singlet oxygen quantum yield may reflect a small quantum yield of triplet BCHA-PPV. Indeed, our flash absorption data are consistent with a BCHA-PPV triplet yield that is smaller in the solids than in a liquid. With respect to the second point, a static quenching channel that is more pronounced in the solid than in the liquid^{43,44,56} may make spectroscopic detection of singlet oxygen difficult in the solid. Furthermore, given the comparatively high concentration of BCHA-PPV in the solid films, an efficient dynamic quenching reaction could reduce the singlet oxygen lifetime sufficiently to make it difficult to temporally resolve the singlet oxygen phosphorescence signal in a pulsed laser experiment.

3. Degradation Mechanism. Our study indicates that singlet oxygen is an intermediate in the photodegradation of BCHA-PPV. We propose that singlet oxygen adds in a $\pi 2 + \pi 2$ cycloaddition to the double bond which connects phenylene groups in BCHA-PPV (Scheme 2). This reaction yields a

dioxetane which, we then propose, cleaves, resulting in (a) macromolecular chain scission and shortening of π conjugation in BCHA-PPV and (b) the formation of carbonyl fragments. Although the potential monomeric analog for these PPV systems, 1,2-diphenylethene (stilbene), does not appreciably react with singlet oxygen,⁵⁷ electron rich olefins are known to readily yield dioxetanes upon reaction with singlet oxygen.⁵⁸ Thus, we suggest that the increased conjugation of the polymer along with the alkoxy substituents in BCHA-PPV increases the reactivity of the bridging double bond to singlet oxygen.

The mechanism shown in Scheme 2 is consistent with the results of Yan et al.⁹ and Papadimitrakopoulos et al.¹⁰ in which FTIR data show, that during the photoinduced degradation of PPV, a decrease in the absorbance derived from an olefin C–H bending mode correlates with an increase in carbonyl absorption. Papadimitrakopoulos et al.¹⁰ further showed that, at early stages of oxidation, the carbonyl formed is indeed likely to be the aromatic aldehyde. At later stages of oxidation, the carbonyl absorption shifts to the blue which likely indicates secondary reactions to form higher oxidation states (e.g., esters).

Cumpston and Jensen⁵⁹ studied the photooxygenation of BCHA-PPV films cast on Au- and Al-metalized wafers. Upon irradiation of BCHA-PPV in the presence of oxygen, these researchers observe the appearance of a carbonyl absorption band at 1723 cm^{-1} which, like the data of Papadimitrakopoulos et al.,¹⁰ shifts to the blue (1737 cm^{-1}) upon further irradiation. Cumpston and Jensen assign the 1737 cm^{-1} band to the carbonyl absorption of an ester or carboxylic acid. X-ray photoelectron spectroscopic studies support this assignment. Volatile species that apparently result from macromolecular chain scission were trapped and identified as aldehydes. Cumpston and Jensen also conclude that the cholestanoxy side chain is oxidized.

The data of Cumpston and Jensen are consistent with the mechanism we propose in Scheme 2 if it is assumed that secondary photooxidation reactions can oxidize the aromatic aldehydes. Such secondary oxidations may also involve the cholestanoxy side chain. Cumpston and Jensen, however, suggest a different mechanism for BCHA-PPV photooxidation. Although experimental evidence for the intermediacy of singlet oxygen is not provided by these authors, they propose that singlet oxygen likewise adds to the BCHA-PPV to form a dioxetane. It is suggested that the cholestanyl side chain is then oxidized *directly* by the cleaving dioxetane. In this mechanism, the oxygen–oxygen bond of the dioxetane is proposed to cleave to yield a pair of oxygen radicals, one of which subsequently abstracts a hydrogen atom from the cholestanyl side chain. A series of ground state reactions then occur to ultimately oxidize the ether to either an ester or an acid. Clearly, further mechanistic studies need to be performed to elucidate details of the singlet oxygen-mediated BCHA-PPV oxidation.

Upon electrical excitation, BCHA-PPV emits from the same state populated in the photoinduced experiments described herein.¹¹ Therefore, the singlet oxygen precursor (triplet BCHA-PPV) should be formed in an operating LED via intersystem

(57) There are two reports in which it is indicated that the reaction between singlet oxygen and stilbene is slow [(1) Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083–6088. (2) Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275–4277]. The reaction that does occur proceeds via a 2 + 4 cycloaddition between singlet oxygen and stilbene [(1) Matsumoto, M.; Dobashi, S.; Kondo, K. *Tetrahedron Lett.* **1977**, 2329–2332. (2) Boyd, J. D.; Foote, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 6758–6759. (3) Kwon, B.-M.; Foote, C. S.; Khan, S. I. *J. Org. Chem.* **1989**, *54*, 3378–3382]. Thus, although we propose that BCHA-PPV degradation proceeds via a 2 + 2 cycloaddition reaction, we cannot presently exclude the possibility that a 2 + 4 cycloaddition reaction also participates.

(58) Schaap, A. P.; Zaklika, K. A. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 173–242.

(59) Cumpston, B. H.; Jensen, K. F. *Synth. Met.* **1995**, *73*, 195–199.

(56) Ogilby, P. R.; Kristiansen, M.; Mártire, D. O.; Scurlock, R. D.; Taylor, V. L.; Clough, R. L. *Polym. Prepr.* **1993**, *34* (2), 133–134.

crossing from the BCHA-PPV fluorescent state. In an LED, however, excited states of the conjugated polymer are formed via annihilation of the positively and negatively charged polarons (i.e., radical ions) created at the respective electrodes. On the basis of spin statistics, this radical combination is expected to directly yield 75% triplets and 25% singlets.²⁸ As a consequence, the singlet oxygen precursor is expected to be formed in much higher yield upon electrical excitation than under photoinduced conditions. Although other mechanisms likely contribute to the degradation of BCHA-PPV under electroluminescent conditions, singlet oxygen is expected to be an intermediate in the oxygen-dependent failure of these LEDs.

On the basis of these results, we propose several strategies for the stabilization of films containing BCHA-PPV that may prove useful in LEDs: (1) Reduce the reactivity of the substituted PPV toward singlet oxygen by incorporating electron-withdrawing groups on the π system, reducing the number of conjugated phenylene units and/or sterically shielding the π system. (2) Incorporate efficient singlet oxygen quenchers^{18,44} in the luminescent polymer. (3) Incorporate a molecule into the luminescent polymer that can act as a trap for the triplet energy of BCHA-PPV, thus decreasing and/or precluding the BCHA-PPV-sensitized production of singlet oxygen. This trap should have a triplet state energy below the excitation energy of singlet oxygen (i.e., less than ~ 95 kJ/mol).

Conclusions

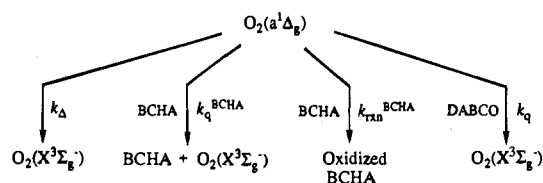
Singlet oxygen is a reactive intermediate in the photooxidative decomposition of BCHA-PPV in both liquid solutions and solid films. This photoinduced reaction results in extensive chain scission of BCHA-PPV. In the solution phase, singlet oxygen is produced by energy transfer to ground state oxygen from the BCHA-PPV triplet state. It is likely that this is also true in solid films. Polymer degradation is proposed to proceed via reaction of singlet oxygen in a $\pi 2 + \pi 2$ cycloaddition to the double bond that connects phenylene groups in the macromolecule. Although the monomeric analog of this system, stilbene, does not appreciably react with singlet oxygen, it is likely that the increased conjugation of the polymer as well as the electron-donating alkoxy substituents increases the reactivity of the bridging double bond in the PPV to singlet oxygen.

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Appendix

Stern-Volmer Analyses of BCHA-PPV Degradation. In the discussion that follows, the acronym BCHA-PPV has been abbreviated to BCHA.

Data from two separate experiments were analyzed to obtain a rate constant for the quenching of singlet oxygen $[O_2(a^1\Delta_g)]$ by BCHA. In both cases, it was assumed that singlet oxygen was the sole photoinduced intermediate responsible for BCHA degradation. The equations shown derive from the following general kinetic scheme:



1. DABCO Experiment. The rate of change in BCHA concentration is shown in eq 1. The time dependence of $[O_2(a^1\Delta_g)]$ is given in eq 2. The subscript 0 indicates the absence

$$d[\text{BCHA}]/dt = k_{\text{rxn}}^{\text{BCHA}}[\text{BCHA}][O_2(a^1\Delta_g)] \quad (1)$$

($a^1\Delta_g$) is given in eq 2. The subscript 0 indicates the absence

$$\begin{aligned}
 (d[O_2(a^1\Delta_g)]/dt)_0 &= I(1 - 10^{-A})\phi_\Delta - \\
 &[k_\Delta + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]] [O_2(a^1\Delta_g)]_0 \quad (2)
 \end{aligned}$$

of DABCO. I denotes the intensity of the photolysis source and $1 - 10^{-A}$ indicates the fraction of incident light absorbed by BCHA whose absorbance is A . ϕ_Δ is the singlet oxygen quantum yield, and k_Δ is the pseudo-first-order rate constant for solvent-induced singlet oxygen deactivation. It is assumed that BCHA will both react with ($k_{\text{rxn}}^{\text{BCHA}}$) and physically quench (k_q^{BCHA}) singlet oxygen.

Invoking the steady-state approximation for singlet oxygen and solving for $[O_2(a^1\Delta_g)]$ yields

$$[O_2(a^1\Delta_g)]_0 = \frac{I(1 - 10^{-A})\phi_\Delta}{k_\Delta + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]} \quad (3)$$

A similar treatment for $[O_2(a^1\Delta_g)]$ in the presence of DABCO yields

$$[O_2(a^1\Delta_g)] = \frac{I(1 - 10^{-A})\phi_\Delta}{k_\Delta + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}] + k_q[\text{DABCO}]} \quad (4)$$

where k_q is the rate constant for quenching of singlet oxygen by DABCO.

By substituting eqs 3 and 4 into eq 1, we obtain

$$\begin{aligned}
 \left(\frac{d[\text{BCHA}]}{dt}\right)_0 &= \\
 \left(\frac{d[\text{BCHA}]}{dt}\right) &= \frac{k_{\text{rxn}}^{\text{BCHA}}[\text{BCHA}] \frac{I(1 - 10^{-A})\phi_\Delta}{k_\Delta + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]}}{k_{\text{rxn}}^{\text{BCHA}}[\text{BCHA}] \frac{I(1 - 10^{-A})\phi_\Delta}{k_\Delta + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}] + k_q[\text{DABCO}]}} \quad (5)
 \end{aligned}$$

If the experiments are performed under conditions in which the initial BCHA concentration is the same, or if data recorded with and without DABCO are corrected for slight differences in $[\text{BCHA}]$, eq 5 reduces to

$$\frac{(d[\text{BCHA}]/dt)_0}{(d[\text{BCHA}]/dt)} = 1 + \frac{k_q[\text{DABCO}]}{k_\Delta + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]} \quad (6)$$

The left-hand side of eq 6 was quantified by taking the slope of the plot shown in Figure 5, using the data obtained at early

irradiation times. We obtained a value of 42.3 for the $d[\text{BCHA}]/dt$ ratio shown with a DABCO concentration of 1.35×10^{-2} M. In a time-resolved singlet oxygen phosphorescence experiment, we independently determined a value of $1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for k_q in CS_2 by monitoring changes in the singlet oxygen decay rate as a function of DABCO concentration. In CS_2 , k_Δ is much smaller than the product $(k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]$.

From this experiment, we obtain a value of $1 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ for $k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}}$.⁶⁰ In an independent experiment in which a lower DABCO concentration was used ($[\text{DABCO}] = 8 \times 10^{-5} \text{ M}$), we obtain a value of $2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for $k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}}$.

2. CS_2 /Toluene Experiment. The approach used to obtain eq 5 can likewise be used to describe BCHA degradation rates in two different solvents.

$$\frac{\left(\frac{d[\text{BCHA}]}{dt}\right)_{\text{CS}_2}}{\left(\frac{d[\text{BCHA}]}{dt}\right)_{\text{tol}}} = \frac{k_{\text{rxn}}^{\text{BCHA}}[\text{BCHA}] \frac{I(1-10^{-A})\phi_\Delta}{k_\Delta^{\text{CS}_2} + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]}}{k_{\text{rxn}}^{\text{BCHA}}[\text{BCHA}] \frac{I(1-10^{-A})\phi_\Delta}{k_\Delta^{\text{tol}} + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]}} \quad (7)$$

As discussed in the text, ϕ_Δ is independent of the solvent change

from CS_2 to toluene. If it is assumed that $k_{\text{rxn}}^{\text{BCHA}}$ likewise does not change significantly with a change in solvent from CS_2 to toluene, then eq 7 can similarly be reduced to yield

$$\frac{(d[\text{BCHA}]/dt)_{\text{CS}_2}}{(d[\text{BCHA}]/dt)_{\text{tol}}} = \frac{k_\Delta^{\text{tol}} + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]}{k_\Delta^{\text{CS}_2} + (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]} \quad (8)$$

In CS_2 , $k_\Delta \ll (k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]$. Thus, eq 8 further reduces to yield

$$\frac{(d[\text{BCHA}]/dt)_{\text{CS}_2}}{(d[\text{BCHA}]/dt)_{\text{tol}}} = \frac{k_\Delta^{\text{tol}}}{(k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}})[\text{BCHA}]} + 1 \quad (9)$$

The left-hand side of eq 9 was quantified using BCHA degradation data recorded in the respective solvents. By taking the slopes of the plots shown in Figure 6, using data at early photolysis time, we obtained a value of 24 for the $d[\text{BCHA}]/dt$ ratio shown. Using the known values of k_Δ^{tol} and $[\text{BCHA}]$, we obtain a value for $k_{\text{rxn}}^{\text{BCHA}} + k_q^{\text{BCHA}}$ of $3.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁶⁰

JA9507731

(60) Reflects a BCHA-PPV molecular weight of 900 000. See the text.