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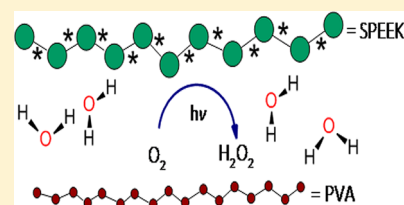
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Photogeneration of H₂O₂ in SPEEK/PVA Aqueous Polymer SolutionsBrian K. Little,[†] PaviElle Lockhart,[†] B. L. Slaten,[‡] and G. Mills^{*,†}[†]Department of Chemistry and Biochemistry and [‡]Department of Consumer Affairs and Design Sciences, Auburn University, Alabama, 36849, United States

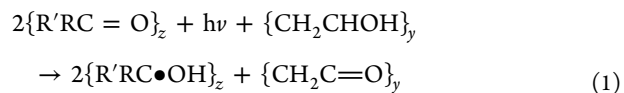
ABSTRACT: Photolysis of air-saturated aqueous solutions containing sulphonated poly(ether etherketone) and poly(vinyl alcohol) results in the generation of hydrogen peroxide. Consumption of oxygen and H₂O₂ formation are initially concurrent processes with a quantum yield of peroxide generation of 0.02 in stirred or unstirred solutions within the range of 7 ≤ pH ≤ 9. The results are rationalized in terms of O₂ reduction by photogenerated α -hydroxy radicals of the polymeric ketone in competition with radical–radical processes that consume the macromolecular reducing agents. Generation of H₂O₂ is controlled by the photochemical transformation that produces the polymer radicals, which is most efficient in neutral and slightly alkaline solutions. Quenching of the excited state of the polyketone by both H₃O⁺ and OH[−] affect the yields of the reducing macromolecular radicals and of H₂O₂. Deprotonation of the α -hydroxy polymeric radicals at pH > 9 accelerate their decay and contribute to suppressing the peroxide yields in basic solutions. Maxima in [H₂O₂] are observed when illuminations are performed with static systems, where O₂ reduction is faster than diffusion of oxygen into the solutions. Under such conditions H₂O₂ can compete with O₂ for the reducing radicals resulting in a consumption of the peroxide.



■ INTRODUCTION

Photoreactive polymers are macromolecular materials that can utilize light as a source of energy to induce chemical reactions. Polymers experiencing light-initiated cross-linking have been extensively studied due to their relevance to photoresists.¹ Photopolymerizations initiated by macromolecular sensitizers are the basis for fast-curing systems.² Macromolecules containing sensitizers that produce singlet oxygen, ¹O₂, have yielded polymeric photooxidizers useful for degrading undesired chemicals,³ and for inactivation of pathogens.⁴ Utilization of benzophenone (BP) as a sensitizer has enabled preparation of polymers able to introduce desired oxygen-containing functionalities into organic compounds.⁵ Furthermore, incorporation of BP onto polystyrene beads yielded solid macromolecular systems able to initiate a variety of photo-reactions.⁶ Blends of poly(vinyl alcohol) (PVA) and the sodium salt of sulfonated poly(ether etherketone) (SPEEK) constitute a different photoreactive polymer system.⁷ Photolysis of the blends with 350 nm photons yields α -hydroxy radicals from SPEEK; optical and EPR data have confirmed the identity of the photoproducts. These observations are rationalized in terms of the known photochemistry of BP.⁸ Illumination of BP produces a triplet (*n*, π^*) excited state able to abstract an H-atom from alcohols, forming an α -hydroxy radical of BP (or benzophenyl ketyl (BPK) radical). Since the concurrently formed α -hydroxy radical of the alcohol can reduce another BP molecule, absorption of one photon can generate up to two BPK radicals.

Radical formation in the polymer system involves a similar process where BP groups of SPEEK act as sensitizers, whereas PVA functions as the H-atom donor and is summarized by the overall reaction:



where SPEEK is represented by $\{R'RC=O\}_z$, $\{CH_2CHOH\}_y$ corresponds to PVA, and $\{CH_2C=O\}_y$ represents an oxidized PVA molecule. For simplicity of notation, the reduced formula $\{R'RC\bullet OH\}_z$ is employed in eq 1 to represent the α -hydroxy radical of SPEEK (or SPEEK \bullet). The meaning of such formula is that, on average, one unpaired electron is present per polymer radical chain. Both PVA and SPEEK are water-soluble, which facilitates preparation of optically transparent films of the blends. Hence, the reactions of photogenerated SPEEK radicals can be studied either in aqueous solutions or using thin films. SPEEK \bullet is a strong reducing agent in solution with an estimated oxidation potential in the range of 1.2–1.4 V.^{7b} An interesting feature of the SPEEK/PVA system is that a fraction of the photogenerated radicals exhibit long lifetimes of about 30–40 min in air-free solutions. They decay via a second-order process involving disproportionation/combination of the radicals with a rate constant in the range of 290–730 M^{−1} s^{−1}. Experiments with α -hydroxy radicals of PVA (PVA \bullet) have also shown a similar behavior except that in this case, the second-order decay constants depended on [radical] with values that were orders of magnitude higher, $k(\text{decay}) \geq 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁹ The slower decay of SPEEK \bullet was rationalized in terms of the high viscosity of the polymer solutions together with the electrostatic repulsions experienced by the negatively

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charged SPEEK chains that inhibit reactive collisions between the macromolecular radicals.^{7b}

SPEEK• was not detected upon illumination of air-saturated SPEEK/PVA aqueous solutions.^{7b} Such outcome seemed logical given that oxygen reduction by SPEEK• is thermodynamically favorable as the redox potential of the $\text{O}_2/\bullet\text{O}_2^-$ couple amounts to -0.33 V at $\text{pH} = 7$.¹⁰ An efficient reduction of O_2 by SPEEK• was anticipated due to the fast reactions of typical α -hydroxy radicals, such as $(\text{CH}_3)_2\text{C}\bullet\text{OH}$ and $\text{PVA}\bullet$, with oxygen in water.^{9,11} In contrast, SPEEK radicals survive for tens of min when generated via photolysis of SPEEK/PVA films in the presence of air.^{7a} Under such conditions SPEEK• reacts with oxygen with an apparent first-order rate constant of $1 \times 10^{-3}\text{ s}^{-1}$ probably due to the low O_2 mobility in PVA,¹² which is the solvent in the films. The solution reaction of PVA radicals with O_2 ultimately yields $\text{HO}_2\bullet$ or $\bullet\text{O}_2^-$ depending on pH ;^{9,13} both of the latter radicals form H_2O_2 through disproportionation processes.¹⁰ Thus, formation of H_2O_2 was anticipated to occur upon photogenerating SPEEK• in the presence of oxygen. Support for such expectation is provided by earlier studies that reported reduction of O_2 to H_2O_2 when aqueous solutions of BP, or derivatives of the ketone, were photolyzed in the presence of several H-atom donors including PVA.^{14–16}

Formation of H_2O_2 by illumination of SPEEK/PVA films in the presence of air was deemed interesting since the peroxide is known to enhance the heterogeneous photodegradation of organophosphorus compounds.¹⁷ In fact, recent investigations have demonstrated that methods based on the reactivity of H_2O_2 are highly effective for the decontamination of several chemical warfare agents.¹⁸ Considering the reactivity of hydrogen peroxide, chemicals adsorbed on SPEEK/PVA films may experience a combined attack of SPEEK• and of H_2O_2 given the long lifetime of the polymer radicals in the macromolecular matrices.^{7a} Such possibility is attractive since a combination of reducing radicals and H_2O_2 results in the complete degradation of very inert compounds, such as halocarbons, presumably via a synergistic action of both reactive chemicals.¹⁹ Also, polymer films containing chemically bonded BP molecules have been reported to develop antibacterial properties under illumination that were attributed to the photochemical formation of BPK radicals and H_2O_2 .²⁰

Reactive clothing able to chemically inactivate toxic compounds and pathogens are of considerable interest as protective barriers.²¹ An example of such materials are “self-cleaning fabrics” containing enzymes capable of degrading organophosphorus compounds.²² Another approach utilized photoactive TiO_2 particles to initiate the light-induced degradation of undesirable materials adsorbed on fabrics.²³ Films of SPEEK/PVA were anticipated to exhibit properties relevant for the realization of “self-cleaning surfaces”, with the photogenerated reactive radicals and peroxide acting as agents for the degradation of undesired materials present on the solid surface. Studies were, therefore, performed to evaluate the performance of SPEEK/PVA blends as sensitizers for the generation of hydrogen peroxide. Reported here are kinetic data pertaining to the formation of H_2O_2 in illuminated aqueous solutions containing SPEEK and PVA. Such investigations were initially preferred since quantification of $[\text{H}_2\text{O}_2]$ in solution is straightforward, and also because liquid phase reactions are less constrained by diffusion restrictions that are significant in the solid state. Furthermore, mechanistic knowledge gained from solution experiments was anticipated to aid understanding the H_2O_2 photogeneration in polymer films

that is currently being explored. An important finding is that the photoprocesses experienced by SPEEK controlled the kinetics of H_2O_2 formation, not the chemistry of the radical intermediates.

EXPERIMENTAL SECTION

PVA, 99+% hydrolyzed with an average molar mass of $8.9\text{--}9.8 \times 10^4\text{ g/mol}$ as well as ammonium molybdate (VI) tetrahydrate were obtained from Aldrich. Poly(ether etherketone) (PEEK) with an average molar mass of $4.5 \times 10^4\text{ g/mol}$ was a gift from Victrex and served as a precursor of the sodium salt of SPEEK. Hydrogen peroxide (30% v/v) was acquired from Fisher Scientific, and potassium hydrogen phthalate was from EM Science. All solutions were prepared with purified water obtained from an ion-exchange resin deionizer (US filter service). Preparation procedures of the polymer solutions were described before;⁷ in most cases, the photolyzed solutions consisted of 0.018 M SPEEK and 0.36 M PVA (both molarities are expressed in terms of the monomer units), which yielded the most efficient photoreductions in previous experiments. Illuminations were conducted using Milton Roy #33-17-80 optical test tubes flattened on the bottom since they were able to withstand the low temperature (77 K) of the degassing process.^{7b} Unless otherwise stated, the SPEEK/PVA solutions were saturated first with a desired gas followed by sealing the optical tubes with rubber septa; samples for analysis were extracted using gastight syringes (Hamilton). For anaerobic experiments, a freeze–pump–thaw method was utilized to eliminate air from SPEEK/PVA solutions; the vessels were backfilled with Ar to maintain a pressure of one atmosphere.

Irradiations were carried out inside a Rayonet 100 circular illuminator that generated photons with $\lambda = 350 \pm 15\text{ nm}$ by means of 16 RPR-3500A lamps; the light intensity (I_0) was determined using the Aberchrome 540 actinometer.²⁴ In most cases, the solutions were not stirred during illumination to simulate the conditions relevant to experiments with polymer films. Every photochemical experiment was performed at least twice and for the desired exposure time without interruptions, followed by retrieval of samples for chemical analysis. Uniform exposure of the optical tubes was achieved by positioning them at the center and midheight of the cavity inside the Rayonet, where the temperature was constant at $29\text{ }^\circ\text{C}$. All other measurements were conducted at room temperature ($23\text{ }^\circ\text{C}$). $[\text{H}^+]$ determinations employed a Radiometer PHM95 pH/ion meter equipped with an Accumet pH electrode. Oxygen consumption was followed using a Hansatech Oxygraph instrument equipped with a S1 Electrode Disc (Clark polarographic sensor); calibrations were conducted using nonilluminated SPEEK/PVA samples. The instrument is provided with a cover to suppress diffusion of air into the vessel containing the polarographic sensor. Sealing this container with a septum increased the internal air pressure, thereby changing the amount of O_2 dissolved in solution. For this reason, the vessel was only covered during determinations, resulting in minor and slow air leaks. Therefore, the lowest oxygen reading was taken to represent the $[\text{O}_2]$ present in solution during photolysis. Polarographic analysis of $[\text{O}_2]$ was performed under slow stirring ($\sim 100\text{ rpm}$), which had no effect in the transport of oxygen into the solutions. Optical data were collected on a Shimadzu UV–vis 2501PC spectrophotometer. The spectrophotometric molybdenum–triiodide method served to quantify the generated H_2O_2 .²⁵ In the employed procedure, an aqueous solution containing KI, $(\text{NH}_4)_2\text{MoO}_4$,

and NaOH was mixed (in equal volumes) with a potassium biphthalate solution inside 1 cm quartz optical cells under stirring, followed by addition of a small aliquot of photolyzed sample and deionized water to yield a total volume of 3 mL. Quantifications of $[H_2O_2]$ via the I_3^- procedure exhibited a typical error of <10% in water, but deviations of 30% were observed in SPEEK/PVA solutions.

RESULTS AND DISCUSSION

Exposure to 350 nm photons of an air-free SPEEK/PVA solution was performed first as a control experiment. Illumination yielded an optical signal with a wavelength of maximum absorbance (λ_{max}) of 565 nm that decayed slowly over several tens of min. Similar observations have been reported before and are typical of the photochemical generation of SPEEK radicals.⁷ Once the decay of SPEEK• was completed, the irradiated solution was tested for the formation of peroxides using the I_3^- method. As anticipated, triiodide was not detected when illuminations were performed in the absence of O_2 . On the other hand, an instantaneous decay of the radical signal at $\lambda_{max} = 565$ nm was noticed when a degassed solution was exposed to air after photolysis. Furthermore, the optical signal of SPEEK• was not observed upon photolysis of air-saturated solutions containing PVA and SPEEK. These findings provide evidence that the photogenerated radical reacted fast with oxygen. Addition of solutions photolyzed in the presence of air to the iodide-molybdate reagent turned the resulting mixtures yellow due to the formation of I_3^- ions; shown in Figure 1 are

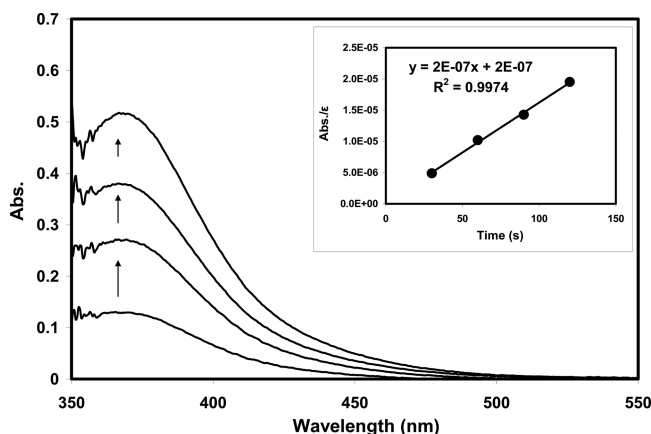


Figure 1. Optical spectra obtained after analysis with the iodide-molybdate method on air-saturated solutions at pH = 7 containing 0.018 M SPEEK and 0.36 M PVA photolyzed in closed systems; illuminated solutions were diluted by a factor of 6 during the peroxide assay. Bottom to top: samples irradiated with 350 nm light, $I_0 = 4.9 \times 10^{-5} \text{ M}(\text{h}\nu)/\text{s}$, for 30 s, 60 s, 90 and 120 s. Inset: plot of absorbance at 370 nm divided by ϵ as a function of irradiation time.

the corresponding optical spectra. An absorbance centered at $\lambda_{max} = 370$ nm was noticed that increased in intensity as illumination progressed. This signal is shifted to longer wavelengths as compared with the I_3^- absorption maximum in water of 350 nm.²⁵ Red-shifts of the triiodide spectrum and decreases in the ϵ value are known to occur in concentrated aqueous solutions of alcohols.²⁶ Experiments were, therefore, conducted to test a possible effect of SPEEK and PVA on the optical signal of I_3^- . In agreement with earlier observations,^{25,26} generation of I_3^- in water yielded a spectrum exhibiting a maximum at 350 nm whereas a λ_{max} of 370 nm resulted when

triiodide ions were produced in SPEEK/PVA solutions. Consequently, the data depicted in Figure 1 clearly demonstrated that peroxides were formed upon photolysis of solutions of the polymers in the presence of air.

Although H_2O_2 reacts fast with I^- , organic peroxides oxidize iodide much slower resulting in a delayed formation of I_3^- .²⁵ No slow formation of the optical signal from I_3^- was noticed, meaning that H_2O_2 was the main peroxide formed upon illumination of SPEEK/PVA solutions. As shown in the inset of Figure 1 the absorbance at 370 nm increased linearly with time for short illumination periods. Thus, the slopes of such plots were utilized to evaluate the initial rate (r_i) of H_2O_2 formation, where $r_i = \text{slope}/\epsilon(I_3^-)$ and $\epsilon(I_3^-)$ = extinction coefficient of I_3^- at λ_{max} . Repeated attempts to determine the extinction coefficient of I_3^- in the polymer solutions yielded results equal to, or lower by 30%, than the value measured in water, $\epsilon = 2.64 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ($\pm 4\%$).^{25,26} Given such erratic results all calculations of $[H_2O_2]$ in polymer solutions used the ϵ value obtained in H_2O . This method underestimated the initial rates used to characterize the kinetics of the H_2O_2 photogeneration. Since r_i values were employed to evaluate the initial quantum yields of H_2O_2 formation ($\phi_i(H_2O_2) = r_i/I_0$), the reported efficiencies represent lower limits.

Depicted in Figure 2 are kinetic data collected at short times when air-saturated SPEEK/PVA solutions were exposed to

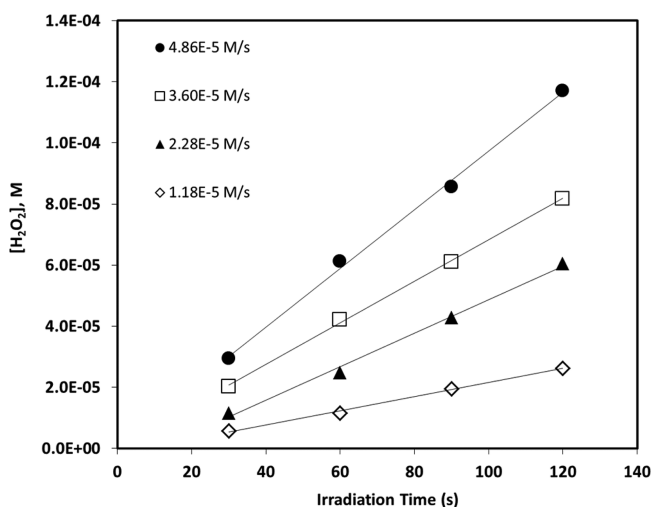


Figure 2. Plots of $[H_2O_2]$ versus irradiation time at different light intensities obtained from photolysis with 350 nm light of air-saturated solutions containing 0.018 M SPEEK and 0.36 M PVA at pH = 7 in a closed system.

different light intensities. In all cases, $[H_2O_2]$ increased linearly with time and a plot of r_i vs I_0 also yielded a straight line with $y = 2.1 \times 10^{-2} x - 3 \times 10^{-8}$, $r^2 = 0.99$. These findings mean that the photon intensity controlled the speed of H_2O_2 generation with the reaction rate being first-order with respect to I_0 . Consequently, the quantum efficiencies were anticipated to be independent of I_0 , which was confirmed by the fairly constant $\phi_i(H_2O_2)$ values at all light intensities depicted in Figure 3, with an average efficiency of 0.02. Evaluation of the efficiency of H_2O_2 formation from the data of Figure 1 yields $\phi_i(H_2O_2) = 0.024$, which is consistent with the results of Figure 3 within experimental error. Subsequent efforts aimed at relating the kinetics of the H_2O_2 generation with that of the O_2 reduction. Initial trials explored the O_2 consumption process via placing

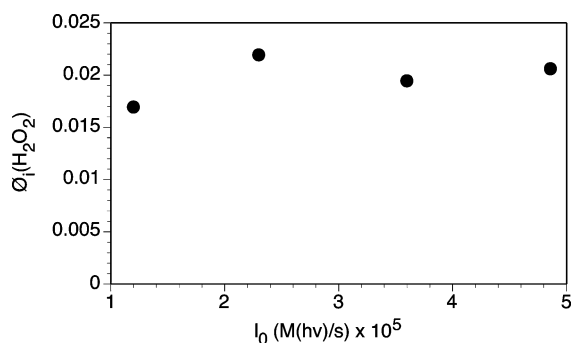


Figure 3. Dependence of $\phi_1(\text{H}_2\text{O}_2)$ on light intensity for air-saturated solutions at pH = 7 containing 0.018 M SPEEK and 0.36 M PVA irradiated with 350 nm photons in closed systems.

the polarographic vessel containing a SPEEK/PVA solution inside the Rayonet followed by photolysis. Determination of I_0 was not possible because the polarographic sensor was incompatible with the solvent of the actinometer. The polarographic data displayed in Figure 4 shows that the initial

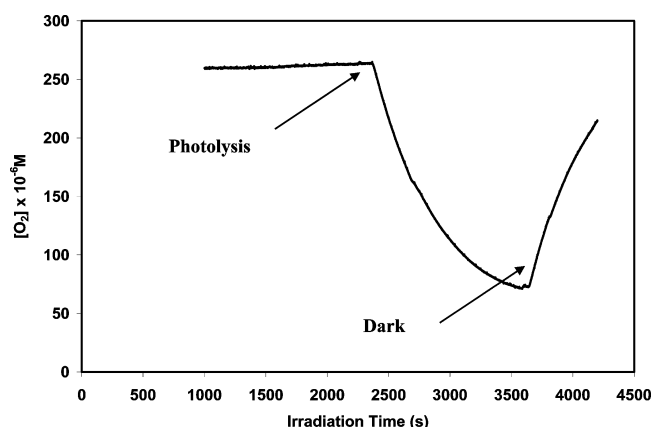


Figure 4. Evolution of $[\text{O}_2]$ during an experiment in which the polarographic cell containing 1 mL of an air-saturated solution with 0.018 M SPEEK and 0.36 M PVA at pH = 7 was placed inside the Rayonet and irradiated continuously with 350 nm photons.

$[\text{O}_2]$ for neutral SPEEK/PVA solutions was of 0.26 (± 0.01) mM, coinciding with the known oxygen solubility in air-saturated H_2O .²⁷ O_2 consumption started synchronously with the light exposure and proceeded initially linearly with time, followed thereafter by a nonlinear process. The oxygen concentration increased again several seconds after illumination was terminated.

Experiments were then performed to establish the relationship between the rates of H_2O_2 formation and of O_2 consumption. Photolyses were carried out using tubes open to air in order to correlate the results with the data of Figure 4. For this purpose, two aliquots of the photolyzed sample were analyzed in parallel for $[\text{O}_2]$ and $[\text{H}_2\text{O}_2]$. The vessel containing the polarographic sensor was filled with SPEEK/PVA solutions immediately after illumination and closed with the cover. Figure 5 depicts the resulting data showing that H_2O_2 formed with an initial rate of $r_i = 1 \times 10^{-6}$ M/s, whereas the r_i value for O_2 consumption was 6×10^{-7} M/s. In addition, both $[\text{H}_2\text{O}_2]$ and $[\text{O}_2]$ reached a value close to half of the initial oxygen concentration in about 190 s of photolysis. These findings indicate that initially O_2 reduction and H_2O_2 generation took

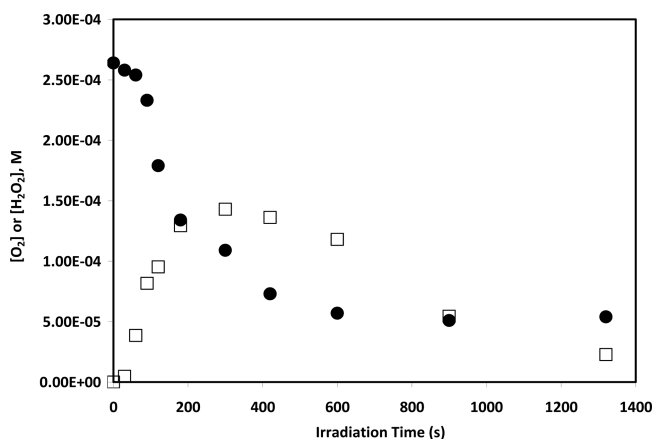


Figure 5. Plot of the concentrations of O_2 (●) and H_2O_2 (□) as a function of irradiation time. The aqueous air-saturated solutions containing 0.36 M PVA and 0.018 M SPEEK at pH = 7 were illuminated in an open vessel with 350 nm light.

place in a synchronous fashion and confirmed that no stable organic peroxides existed as intermediates. According to Figure 5, the rates of both processes declined after 200 s, and a maximum in $[\text{H}_2\text{O}_2]$ was reached at about 300 s, followed by a subsequent decrease in peroxide concentration. This decline in $[\text{H}_2\text{O}_2]$ was not a consequence of peroxide disproportionation, which is a very slow process in neutral solutions at room temperature.²⁸

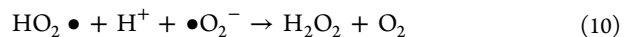
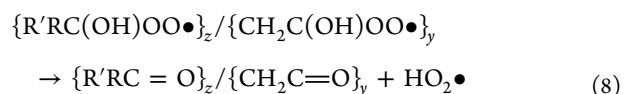
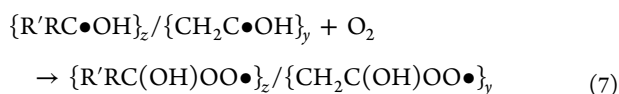
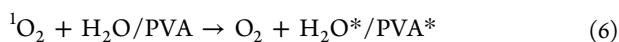
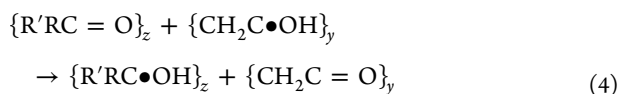
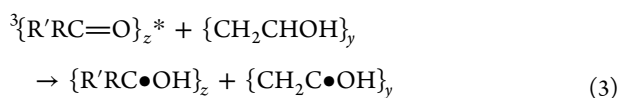
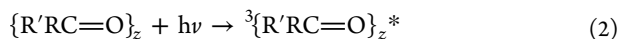
Comparison of the data shown in Figure 5 with that of Figure 4 seems to indicate a delay of about 70 s in the O_2 reduction for photolyzed solutions that were transferred to the polarographic vessel. This phenomenon originated mostly due to the small leaks of air into the polarographic vessel mentioned earlier. In addition, O_2 diffusion into the samples during the transfer process may have also contributed to the initial slow oxygen consumption noticed in Figure 5. The $[\text{O}_2]$ increases observed after termination of photolysis in Figure 4 lend support to this explanation. Diffusion of air into the polarographic vessel can also account for the apparent slower decrease in $[\text{O}_2]$ as compared with the increase in $[\text{H}_2\text{O}_2]$ (Figure 5). Considering the experimental constraints, the data of Figure 5 strongly suggests that O_2 consumption and H_2O_2 formation occurred with the same initial rates. An analogous relationship between the initial reaction rates of O_2 consumption and H_2O_2 generation was found at short reaction times during the oxidation of PVA via photolysis of benzophenone-3,3'-disulfonate in oxygen-saturated water.¹⁵ Further comparison of Figures 4 and 5 reveals that in both cases consumption of oxygen ceased to be a linear function of time once the $[\text{O}_2]$ remaining in solution reached 68% of the initial concentration. This trend, together with the occurrence of the $[\text{H}_2\text{O}_2]$ maximum shown in Figure 5, suggested that photolysis of unstirred SPEEK/PVA solutions yielded gradients in $[\text{O}_2]$; such hypothesis will be discussed below.

Oxygen molecules deactivate the triplet (n, π^*) excited state of BP generating singlet oxygen with a high quantum yield ($\phi(^1\text{O}_2)$) in nonaqueous solvents.²⁹ However, only low quantum yields of singlet oxygen formation ($\phi(^1\text{O}_2) \leq 0.015$) have been reported in water when 4-hydroxybenzophenone and BP-derivatized polymers of *N*-isopropylacrylamide served as sensitizers.⁵ Low $\phi(^1\text{O}_2)$ values are expected because energy transfer from singlet oxygen to H_2O occurs within a few microseconds due to the large pseudo-first-

order deactivation rate constant of $k_d = 5 \times 10^5 \text{ s}^{-1}$ in air-saturated water.³⁰ In analogy to BP, O_2 was anticipated to quench the triplet excited state of SPEEK, $^3\{\text{R}'\text{RC}=\text{O}\}_z^*$, with generation of $^1\text{O}_2$. Singlet oxygen produced by sensitizing groups present in macromolecular chains is believed to initiate solid-state polymer photodegradations that form peroxides.³¹ Such processes are not feasible in SPEEK/PVA solutions given that $^1\text{O}_2$ reacts with alcohols only via fast deactivation ($1 \times 10^4 \leq k_d \leq 4 \times 10^5 \text{ s}^{-1}$).³⁰ An analogous conclusion was reached when the oxygen photoreduction by BP was studied in water/acetone nitrile mixtures containing 2-propanol as a H-atom donor.¹⁶

Nevertheless, efforts were made to ascertain whether $^1\text{O}_2$ formed during photolysis of the polyketone in order to corroborate that oxygen was able to quench the SPEEK triplet excited state. Detection of $^1\text{O}_2$ in aqueous solutions is feasible via the reaction of singlet oxygen with I^- to form triiodide ions.³² Because high concentration of I^- ions are present during irradiation, the oxidation reaction of iodide ions can compete with the water-induced $^1\text{O}_2$ inactivation. This method is different from the procedure used to quantify $[\text{H}_2\text{O}_2]$,²⁵ in which I^- was added to SPEEK/PVA solutions once photolysis was terminated, that is, long after the decay of $^1\text{O}_2$. However, only qualitative data were expected from this method, as I^- is an effective quencher of the BP triplet excited state with a quenching constant of $k_q = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.³³ Given that ketones are suspected to quench $^1\text{O}_2$,²⁹ a lower [SPEEK] was used to avoid a similar quenching process induced by the polyketone. Thus, illuminations were performed with air-saturated solutions containing 0.2 M KI, $1.6 \times 10^{-4} \text{ M}$ $(\text{NH}_4)_2\text{MoO}_4$, $4 \times 10^{-4} \text{ M}$ SPEEK, and phosphate buffer to maintain a constant pH of 6. The irradiations resulted in a linear increase of $[\text{I}_3^-]$ as a function of time with a formation rate of $1.4 \times 10^{-6} \text{ M/min}$ at $I_0 = 3.1 \times 10^{-5} \text{ M(h}\nu\text{)/s}$. Having in mind that no H_2O_2 formed during photolysis of SPEEK in the absence of PVA, the data implies that the quantum yield of $^1\text{O}_2$ formation equals 8×10^{-4} . Despite their qualitative nature, these findings imply that O_2 is indeed able to quench the triplet state of SPEEK.

The results presented thus far can be rationalized in terms of a modified version of the mechanism proposed earlier for the photoreduction of metal ions in degassed SPEEK/PVA solutions,^{7b} which consists of the following steps:



To simplify the notation, $\{\text{CH}_2\text{C}\bullet\text{OH}\}_y$ was employed to represent the α -hydroxy radical of PVA, and the meaning of this formula is that, on average, one unpaired electron is present per polymer radical chain. H-atom abstraction from PVA yields α - (70%) as well as β - (30%) hydroxy radicals; while both species react with O_2 , only the former is known to be a strong reducing agent.¹³ Hence, for simplicity, only reactions of the former PVA radical were considered to contribute to the H_2O_2 generation, whereas β -hydroxy radicals were most probably involved in the secondary reaction channel leading to chain scission of the polyol.¹⁵ The α -hydroxy radical of PVA is expected to reduce SPEEK via step 4, which should be favored by the high concentration of SPEEK carbonyl groups present in the solutions. As in the case of α -hydroxy radicals derived from simple alcohols,¹¹ $\text{PVA}\bullet$ reacts with O_2 via formation of a peroxy radical. This intermediate decays subsequently through elimination of either $\text{HO}_2\bullet$ ($k = 700 \text{ s}^{-1}$), or of $\bullet\text{O}_2^-$ via a base-catalyzed process.⁹ Similar reactions are expected to occur for the α -hydroxy radical of SPEEK. For this reason, steps 7 and 8 represent the contributions of both $\text{PVA}\bullet$ and $\text{SPEEK}\bullet$ to the O_2 reduction in the SPEEK/PVA system. Disproportionation reactions involving $\text{HO}_2\bullet$ and/or $\bullet\text{O}_2^-$ produce H_2O_2 , but step 10 is the fastest of such processes and is aided by the deprotonation ($\text{p}K_a = 4.8$) of the perhydroxyl radical, step 9.¹⁰ Reaction 10 is frequently used to summarize the disproportionations of $\text{HO}_2\bullet$ and $\bullet\text{O}_2^-$ and was employed in the mechanism for the same purpose.

Included in the mechanism are the competing quenching reactions of the SPEEK (n, π^*) triplet state by PVA and O_2 , steps 3 and 5, respectively. Although rate constants for steps 3 and 5 are not known, the values for the analogous reactions of the triplet excited state of BP can be employed to perform a rough assessment of the predominant quenching process experienced by $^3\{\text{R}'\text{RC}=\text{O}\}_z^*$. The rate constant for chemical quenching of $^3\text{BP}^*$ by 2-propanol amounts to $k_q = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$;¹⁶ utilization of this value for step 3 seems reasonable considering that the ability of PVA to donate H-atoms to the triplet excited state of BP is comparable to that of isopropanol.³⁴ Quenching of $^3\text{BP}^*$ by O_2 in water takes place with $k_q = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$,³⁵ which together with $[\text{O}_2] = 2.6 \times 10^{-4} \text{ M}$ and $[\text{PVA}] = 0.38 \text{ M}$ yield pseudo-first-order rate constants for steps 3 and 5 of $k_3' = 7.2 \times 10^5 \text{ s}^{-1}$ and $k_5' = 1 \times 10^5 \text{ s}^{-1}$. These estimates suggest that only about 20% of the SPEEK triplet states were deactivated by oxygen. Another way to assess the impact of step 5 is via comparison of the data shown in Figure 5 with previous results on the photoreduction of Ag^+ and Cu^{2+} in air-free SPEEK/PVA solutions.^{7b} Both metal ions are efficient quenchers of the SPEEK triplet state with $k_q \geq 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which decreases the efficiency of polymer radical formation via step 3. Hence, the photoreductions are initially slow since relatively high metal ion concentrations favor efficient quenching of $^3\{\text{R}'\text{RC}=\text{O}\}_z^*$. As the photoreactions progress the quantum yields for reduction increase due to the quenching processes becoming less efficient with decreasing metal ion concentrations. In contrast, the data

of Figure 5 show that reduction of O_2 was most efficient initially, when $[O_2]$ was high, and that the reaction rate decreased at longer times as the oxygen concentration dropped. A reasonable conclusion from this analysis is that step 5 was not a controlling event in the photochemistry of air-saturated SPEEK/PVA systems.

Illustrated in Figure 6 is a comparison of $\phi_i(H_2O_2)$ and of the initial quantum yield of SPEEK radical formation,

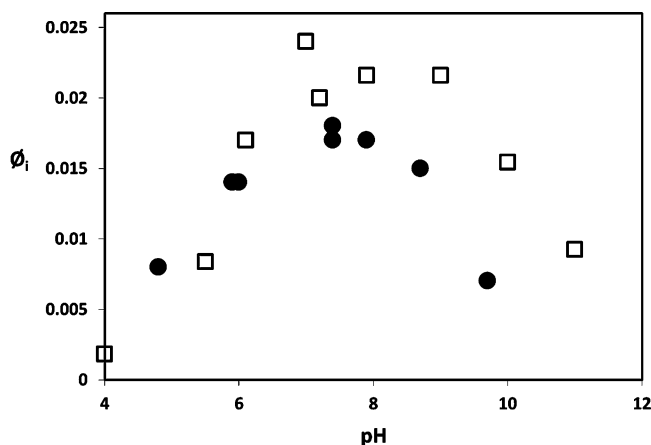
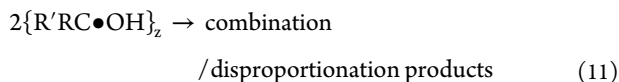


Figure 6. Dependence of $\phi_i(H_2O_2)$ (□) and $\phi_i(SPEEK\bullet)$ (●) on the solution pH. Determinations of $\phi_i(H_2O_2)$ were carried using air-saturated solutions containing 0.018 M SPEEK and 0.36 M PVA in unstirred closed systems. Values of $\phi_i(SPEEK\bullet)$ were obtained from similar solutions that were degassed. Photolysis with 350 nm light, $I_0 = 5.3 \times 10^{-5} \text{ M(h}\nu\text{)/s}$.

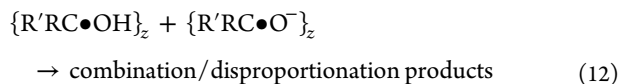
$\phi_i(SPEEK\bullet)$, at different pH values. Essentially the same quantum yields were obtained when the pH was adjusted with $HClO_4$ and $NaOH$, or using buffers (1 mM). Values of $\phi_i(SPEEK\bullet)$ were determined optically as in a previous study using air-free unstirred solutions to prevent the accelerating effect that stirring induces on the radical decay via dimerization/disproportionation.^{7b} As mentioned previously, the $\phi_i(SPEEK\bullet)$ values determined under steady-state conditions are a measure of the amount of radicals that survived at the end of the photolysis the radical–radical reaction



and represent only lower limits of the true quantum yields. Photogeneration of $SPEEK\bullet$ was most efficient in the pH range of 7–8, and the resulting quantum yields agreed, within experimental error, with the earlier value (0.02) for neutral solutions. Radical formation in the acidic range turned progressively less effective as $[H_3O^+]$ increased. Such a trend is not surprising since H_3O^+ ions are efficient quenchers of triplet excited BP via energy transfer ($k_q = 3.8\text{--}6.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).^{35,36} Physical quenching of the SPEEK triplet excited state by hydronium ions reduces the probability of radical formation via step 3, which explains the decrease of $\phi_i(SPEEK\bullet)$ with increasing $[H_3O^+]$. A similar but more pronounced decrease in $\phi_i(SPEEK\bullet)$ is also noticed in Figure 6 at $pH > 8$. Hydroxide ions also quench $^3BP^*$ but with a rate constant of only $4.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$,³³ meaning that an analogous quenching of $^3\{R'RC=O\}_z^*$ by OH^- may have contributed to the decreasing trend of $\phi_i(SPEEK\bullet)$ at high pH values. However,

the fact that k_q is 100 times lower for OH^- than for H_3O^+ seems at odds with the steeper decrease in radical yield determined for basic solutions.

Further optical determinations revealed a more complex behavior of the SPEEK radical in alkaline solutions. For instance, photolysis for 1 min of solutions with $6 \leq pH \leq 8$ yielded a fairly constant SPEEK \bullet absorption with $\lambda_{max} = 565 \text{ nm}$ similar to that reported before.^{7b} Increasing the $[OH^-]$ decreased the signal intensity and at $pH = 9.7$ the absorption broadened into wavelengths longer than 600 nm. In addition, the second-order decay at 565 nm proceeded with a rate constant 6 times higher than the one determined for step 11 in neutral solutions. At $pH = 12.3$ only a very weak and broad absorption centered at about 660 nm was detected. Earlier studies showed that the BPK radical of benzophenone deprotonates in basic solution with $pK_a = 9.2$, yielding a radical anion that exhibits an absorption maximum between 600 and 630 nm.^{37,38} Additional findings were that in solutions containing high alcohol concentrations, the rate constant for the dimerization of a neutral radical with an anionic radical is about 30 times higher as compared to combination of uncharged radicals.^{35,39} No such differences exist in water where both dimerization reactions occur with similar high rate constants.³⁵ These observations suggest that deprotonation of $\{R'RC\bullet OH\}_z$ to form $\{R'RC\bullet O^-\}_z$ occurred in SPEEK/PVA solutions at $pH > 9$. Efforts to determine the pK_a of SPEEK \bullet were unsuccessful due to the fast decay and low intensity of the optical signals. Deprotonation of SPEEK \bullet implies that at $pH > 9$ the speedy decay of the optical signals originated from



and that, as for BP solutions containing alcohols, this reaction was faster than step 11. Consequently, quenching of $^3\{R'RC=O\}_z^*$ by OH^- together with step 12 contributed to the sharp lowering of $\phi_i(SPEEK\bullet)$ illustrated in Figure 6 for basic solutions. A further conclusion is that the high PVA concentration employed in the present study influenced the dimerization of the neutral SPEEK radicals in a way analogous to the one observed for BP solutions containing alcohols.

Figure 6 shows that the dependence of $\phi_i(H_2O_2)$ on solution pH is similar to that of $\phi_i(SPEEK\bullet)$ particularly in the acidic range. Such resemblance is not surprising given that SPEEK \bullet is a precursor of H_2O_2 . However, according to the above mechanism, $HO_2\bullet/\bullet O_2^-$ are the direct precursors of H_2O_2 and undergo disproportionations to form the peroxide. Step 10 is the fastest disproportionation reaching a maximum rate at the pK_a for $HO_2\bullet$.¹⁰ Inspection of Figure 6 reveals that H_2O_2 generation was most efficient at $pH > 4.8$, meaning that peroxide formation in SPEEK/PVA solutions was not governed by the reaction kinetics of the peroxy radicals. This analysis supports the notion that the photochemical process generating the SPEEK \bullet radicals controlled the rate of H_2O_2 formation. Therefore, factors that affected radical formation influenced the peroxide generation in a similar way. An example is quenching of the SPEEK triplet excited state by hydronium ions, which lowered the efficiency of SPEEK \bullet formation and, consequently, decreased $\phi_i(H_2O_2)$ in acid solutions. Analysis of the data shown in Figure 6 reveals that $\phi_i(H_2O_2) \geq \phi_i(SPEEK\bullet)$, a result that seems puzzling since the mechanism requires two SPEEK radicals for the reduction of a O_2 molecule to H_2O_2 . Because the $\phi_i(SPEEK\bullet)$ values are only lower limits of the

true quantum yields, a more realistic assessment of the efficiency of H_2O_2 photogeneration can be obtained by means of the quantum yield for the formation of SPEEK triplet excited states, $\phi(^3\{\text{SPEEK}\}^*)$. According to the mechanism, each SPEEK triplet state generates two reducing radicals, predicting a maximum H_2O_2 quantum yield equal to $\phi(^3\{\text{SPEEK}\}^*)$. The $\phi_i(\text{H}_2\text{O}_2)$ maxima shown in Figure 6 averaged 0.022, whereas values of $\phi(^3\{\text{SPEEK}\}^*)$ of 0.04 and 0.056 were obtained in neutral solutions.^{7b} Hence, about 40–55% of the photogenerated reducing radicals were able to react with O_2 , while Cu^{2+} and Ag^+ ions managed to scavenge about 70–80% of the SPEEK• species.^{7b} The most probable reason is that radical combination via step 11 is able to compete with step 7 and limit the formation efficiency of the precursors of H_2O_2 .

As shown in Figure 6, $\phi_i(\text{SPEEK}\bullet)$ decreased at $\text{pH} > 8$, whereas a similar trend was noticed for $\phi_i(\text{H}_2\text{O}_2)$ only at $\text{pH} > 9$. The high $\phi_i(\text{H}_2\text{O}_2)$ values at $7 \leq \text{pH} \leq 9$ indicate that reaction of neutral SPEEK radicals with O_2 via step 7 was able to compete with step 11. A possible interpretation for the data obtained at higher $[\text{OH}^-]$ is that scavenging of $\{\text{R}'\text{RC}\bullet\text{O}^-\}_z$ by oxygen was less able to compete with step 12 when the extent of SPEEK• ionization increased. However, deprotonation of α -hydroxy radicals from simple alcohols yields radical anions exhibiting higher oxidation potentials (by ≈ 0.6 V) than their conjugates.⁴⁰ This means that $\{\text{R}'\text{RC}\bullet\text{O}^-\}_z$ is anticipated to be a stronger reductant than $\{\text{R}'\text{RC}\bullet\text{OH}\}_z$, which is unlikely to decrease the efficiency of the O_2 reduction. The stability of H_2O_2 is known to decrease when the pH increases above 10.⁴¹ Thus, the occurrence of peroxide decomposition together with quenching of the SPEEK triplet state by hydroxide ions and fast radical consumption via step 12 are all contributors to the lower H_2O_2 yields found in alkaline solutions.

The earlier discussion of Figure 5 mentioned some findings that seemed intriguing, including the peculiar progression of $[\text{H}_2\text{O}_2]$ during illumination. Efforts were therefore made to further characterize the evolution of $[\text{H}_2\text{O}_2]$, and results obtained from photolysis of solutions that were either open or close to air are presented in Figure 7. Both systems yielded very similar profiles of $[\text{H}_2\text{O}_2]$ versus time and the same r_i values of H_2O_2 formation. Maxima in $[\text{H}_2\text{O}_2]$ (or $[\text{H}_2\text{O}_2]_{\text{max}}$), resembling the data of Figure 5 were noticed in both cases,

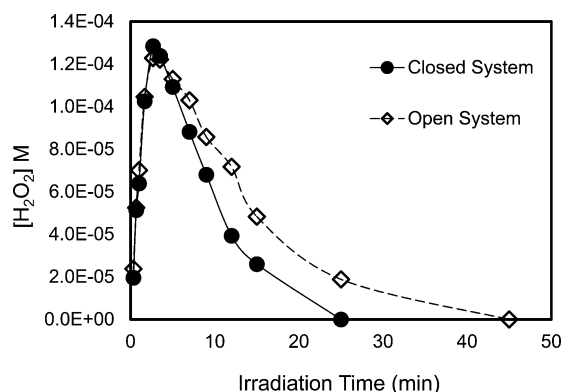


Figure 7. Plot of $[\text{H}_2\text{O}_2]$ versus irradiation time determined using air-saturated aqueous solutions in closed and opened vessels containing 0.018 M SPEEK and 0.36 M PVA at $\text{pH} = 7$. Illumination with 350 nm photons in a closed system (●) and open system (◇), $I_0 = 4.2 \times 10^{-5} \text{ M}(\text{h}\nu)/\text{s}$. Lines between data points are not fits, but are present as a guide.

followed by peroxide consumption with initial rates about 10 times lower than the r_i values. A simple explanation that accounts for these observations is that consumption of O_2 via step 7 was faster than diffusion of oxygen from the gas phase into solution. Replenishment of consumed O_2 was also possible in closed systems given that a small headspace (of about 0.5 mL) existed between the septa and the solutions. According to this explanation, light acted in a way similar to partial degassing of the solutions; the simultaneous decline in $[\text{O}_2]$ coupled with an increasing $[\text{H}_2\text{O}_2]$ eventually enabled the peroxide to compete with oxygen for the photogenerated SPEEK radicals. Under these conditions the reduction of H_2O_2 to water was able to occur in parallel with the formation of the peroxide via steps 7 to 10. Results from additional experiments supported this explanation, including data from an illumination that employed a lower light intensity. In that experiment $[\text{H}_2\text{O}_2]_{\text{max}}$ was detected at longer times than in Figure 7, and the peroxide was not completely consumed during extended photolysis. Further experiments that mimicked those of Figure 7 employed either a solution open to air or a closed system saturated with pure O_2 that were vigorously stirred throughout the illuminations. No $[\text{H}_2\text{O}_2]$ maxima were observed: the peroxide formed with the same r_i as in the experiments of Figure 7 and $[\text{H}_2\text{O}_2]$ continued to increase up to concentrations of $(1.7\text{--}3) \times 10^{-4} \text{ M}$, remaining then constant upon further irradiation. The time profile of $[\text{H}_2\text{O}_2]$ in these experiments was very similar to the one observed during the photolysis of benzophenone-3,3'-disulfonate in oxygen-saturated solutions of PVA.¹⁵ Thus, the occurrence of maxima in $[\text{H}_2\text{O}_2]$ was averted by the action of stirring, which efficiently replenished any consumed O_2 .

Examination of the results depicted in Figures 5 and 7 reveals that the maxima took place at a time when $[\text{H}_2\text{O}_2] \approx [\text{O}_2]$. Occurrence of a maximum implies that the rates of peroxide formation and consumption were equal. Given that the former is close to the rate of oxygen reduction, then $\text{rate}(\text{O}_2 \text{ reduction}) = \text{rate}(\text{H}_2\text{O}_2 \text{ reduction})$, leading to $k(\text{O}_2 \text{ reduction}) = k(\text{H}_2\text{O}_2 \text{ reduction})$. These rate constants pertain the reactions of SPEEK• with O_2 and H_2O_2 since the polyketone radical is the main species involved in the H_2O_2 formation and consumption. The relevant rate constants are not known for SPEEK• but for $(\text{CH}_3)_2\text{C}\bullet\text{OH}$ they are $k(\text{O}_2) = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k(\text{H}_2\text{O}_2) = 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$;¹¹ similar values have been reported for $\text{H}_2\text{C}\bullet\text{OH}$. Obviously, the large difference between the rate constants is incompatible with the predictions derived from such a simple analysis. O_2 reacts with radicals of PVA• and with the radical derived from the anionic form of poly(acrylic acid) (PAA) with rate constants of $5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively.⁴² Although the rate constants for the reaction of the polymer radicals with hydrogen peroxide are unavailable, values similar to those for the reactions of H_2O_2 with $(\text{CH}_3)_2\text{C}\bullet\text{OH}$ and $\text{H}_2\text{C}\bullet\text{OH}$ are anticipated. On the basis of such considerations, the equality of rates of O_2 and peroxide consumptions during $[\text{H}_2\text{O}_2]_{\text{max}}$ implies that the reduction of peroxide was able to compete with the reduction of oxygen only when $[\text{O}_2] < 1 \times 10^{-6} \text{ M}$. Because much larger oxygen concentrations were detected at the times of the maxima according to Figures 5 and 7, a possible explanation is that localized $[\text{O}_2]$ gradients generated during illumination made possible the scavenging of SPEEK• by H_2O_2 .

An analogous idea served to rationalize the 3 times higher rate constant for the reaction of oxygen with the neutral PAA

radical as compared with the value for the radical of the deprotonated polymer.⁴² Polyelectrolytes decrease the solubility of gases in H₂O, but the “salting-out” effect of the ionic macromolecules is less pronounced than those of simple electrolytes.⁴³ Even if salting-out of O₂ by SPEEK was as effective as the effect induced by NaCl,⁴⁴ the [SPEEK] needed to decrease [O₂] to the μ M level would surpass by orders of magnitude the polyelectrolyte concentration employed in the present study. However, polyelectrolytes are known to form aggregates in solution that are considered to be precursors of gelation.⁴⁵ Aggregates of SPEEK are anticipated to contain PVA chains given that the high concentration of the polyol will inevitably lead to entanglement of the polymer chains. Hence, excitation of SPEEK chains located in the aggregates also yields H₂O₂ via the mechanism represented by steps 2 to 10. Consumption of O₂ under illumination is expected to be fast in the aggregates because of the close proximity between oxygen molecules and photogenerated radicals. Replenishment of consumed O₂ via diffusion from the surrounding solution into the aggregates is slow in static systems. Similarly, migration of photogenerated H₂O₂ from the aggregates into the solution is also anticipated to occur slowly under such conditions. Both effects lead to an efficient consumption of the peroxide, which is absent in stirred systems due to a fast exchange of O₂ and H₂O₂ between solution and polymer aggregates. Given that the extent of aggregation is not known, a reasonable scenario is that individual chains of SPEEK as well as aggregates participate in the H₂O₂ formation, with the latter being the main contributors to peroxide consumption. Obviously, rationalization of the evolution of [H₂O₂] under extended exposures requires a more complex mechanism to account for both peroxide generation and consumption. Experimental results that support such a mechanism will be presented in a subsequent report.

Illumination of BP in H₂O/CH₃CN mixtures containing 2-propanol resulted in quantum yields of O₂ consumption that increased with rising [alcohol].¹⁶ In the presence of 0.3 M 2-propanol, the quantum efficiency amounted to 0.2, which is about 10 times higher than the yields obtained in SPEEK solutions containing an equivalent amount of PVA. Previously, the limited efficiency of SPEEK/PVA systems to induce reductions of electron acceptors was attributed to the lower quantum yield of ³{SPEEK}* as compared with that of the triplet excited state of BP, that is equal to 1.^{7a,8} An alternative possibility involves the combination reaction between SPEEK• and PVA• as a factor that limits the yield of reducing radicals. Such reaction is expected to be less efficient in the solid state than in fluids, whereas ϕ_i (SPEEK•) was found to remain unchanged in films and solutions. However, the presence of polymer aggregates in SPEEK/PVA solutions would make the differences between fluid and solid states less noticeable. Experiments with cross-linked SPEEK/PVA films currently underway are anticipated to provide further insight into the factors that limit the efficiency of the photoreactions given that radical diffusion is severely restricted in such systems.

CONCLUSIONS

The results gathered in the present investigation demonstrate that H₂O₂ is generated in photolyzed solutions of SPEEK/PVA that contain air. Formation of the peroxide occurs in a synchronous fashion with the consumption of oxygen. The kinetic data are consistent with a mechanism in which the rate-determining step is the photochemical process that generates the polymeric SPEEK radicals. Formation of ¹O₂ via quenching

of ³{R'RC=O}_z* by oxygen was shown to be a minor reaction channel. Nevertheless, photogeneration of singlet oxygen could confer SPEEK/PVA systems with an ability to inactivate bacteria in a fashion similar to that of cationic conjugated polyelectrolytes.⁴ As found in earlier studies involving BP radicals,^{35,39} the presence of an alcohol in the solutions (in this case, PVA) accelerates the combination/disproportionation process involving SPEEK• and the deprotonated form of this radical. This process contributes to the decreases in quantum yields of peroxide formation detected at pH > 9. Rates of peroxide generation are highest in neutral to slightly alkaline solutions, suggesting that efficient formation of H₂O₂ via photolysis of SPEEK/PVA films is feasible. The decay of H₂O₂ that takes place at longer irradiation times in unstirred solutions is not expected to occur on the surface of SPEEK/PVA films due to the high and constant [O₂] present in that region but may limit the efficiency of peroxide formation within the solid polymer matrices.

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Notes

The authors declare no competing financial interest.

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