Singlet Oxygen Formation in a Solid Organic Polymer upon Irradiation of the Oxygen-Polymer Charge-Transfer Band

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ABSTRACT: Singlet molecular oxygen ($^1\Delta_gO_2$) phosphorescence has been observed at 1270 nm in a time-resolved experiment subsequent to pulsed UV laser photolysis of the oxygen ($^3\Sigma_g^-O_2$)-polymer charge-transfer (CT) absorption band of solid polystyrene samples. These data indicate that the polymer-oxygen CT potential surface (polymer$^{\bullet+}O_2^{\bullet-}$) is coupled to the potential surface of the polymer-$^1\Delta_gO_2$ complex. Continued photolysis into the CT absorption band results in the formation of products that act as $^1\Delta_gO_2$ photosensitizers, thus providing a second, independent channel for $^1\Delta_gO_2$ formation. By monitoring the time-resolved $^1\Delta_gO_2$ phosphorescence, we are able to distinguish between $^1\Delta_gO_2$ produced in a photosensitized reaction and $^1\Delta_gO_2$ produced from the oxygen-polymer CT state. Unless rigorous steps are taken in the preparation and subsequent handling of the polymer sample, a substantial portion of the $^1\Delta_gO_2$ produced upon UV irradiation of the oxygenated polymer originates from a photosensitized process. $^1\Delta_gO_2$ has also been observed subsequent to UV photolysis of the oxygen-polymer CT band in a poly(dimethylsiloxane) oil and rubber. The polymer data are supported by independent time-resolved studies of $^1\Delta_gO_2$ phosphorescence in a low molecular weight 130 K organic glass. Our results provide direct experimental support for a mechanism of light-induced $^1\Delta_gO_2$ formation in a bulk polymer that obviates the necessity of invoking a photosensitizer. Thus, we conclude that, no matter how clean or impurity-free a particular solid polyolefin can be prepared, it is still possible to produce $^1\Delta_gO_2$ upon irradiation. These data should be useful in understanding events that initiate polymer photodegradation.

Introduction

Exposure of many organic liquids to molecular oxygen ($^3\Sigma_g^-O_2$) yields a ground-state complex that can absorb light to produce a charge-transfer (CT) state.[1] At oxygen pressures of approximately 1 atm, this transition appears as a structureless red-shift in the absorption onset of the organic molecule. The oxygen-organic molecule CT absorption has also been recorded in several solid organic polymers [polyethylene,[2] polypropylene,[3] poly(4-methyl-1-pentene),[4] and polystyrene[5-7]]. In polystyrene at high ambient oxygen pressures (~20-150 bar), this absorption is quite prominent and appears as a band with $\lambda_{max} \sim 275$ nm.[5,6]

Theoretical studies have indicated that the CT state, which is usually represented as an excited-state complex with radical cation and radical anion character ($M^{\bullet+}O_2^{\bullet-}$), will interact, often substantially, with other excited electronic states of the oxygen-organic molecule (M) complex.[1,8,9] We have recently obtained experimental evidence that UV irradiation of the oxygen ($^3\Sigma_g^-O_2$)-organic molecule CT absorption bands of certain liquid monomeric hydrocarbons, ethers, and alcohols can result in the formation of singlet molecular oxygen ($^1\Delta_gO_2$).[10,11] The available data also suggest that, in certain polar solvents, the CT complex is in equilibrium with the solvated organic radical cation ($M^{\bullet+}$) and the superoxide ion ($O_2^{\bullet-}$).[11] Thus, photolysis of the CT band can result in the formation of two independent and reactive forms of molecular oxygen ($^1\Delta_gO_2$ and $O_2^{\bullet-}$).

The photodegradation of polymers in commercial applications is an extremely important problem, and the complex photochemical and photophysical processes by which these materials react in the presence of oxygen and light have not been resolved.[12-16] This is particularly true of the initiation stages of the photooxidation process. A potentially important part of this process on which we now focus concerns the role of both $^1\Delta_gO_2$ and the CT state in the degradation of polymers. In monomeric organic liquids, it appears from the existing literature that, subsequent to CT band irradiation, a variety of different chemical reaction channels can yield oxidation products.[17-22] The relative importance of each channel is substrate dependent, and the reaction can proceed either within the caged radical ion pair ($M^{\bullet+}O_2^{\bullet-}$) or with solvated radical ions or $^1\Delta_gO_2$ as intermediates. In polystyrene and polystyrene model compounds, it is frequently concluded that excitation to the CT state results in the formation of a hydroperoxide as a primary product.[7,20,21,23-28] Alkyl and aryl hydroperoxides can serve as both photochemical and thermal precursors (via further free-radical-mediated chain branching oxidation schemes) of some of the products ultimately isolated in studies of polystyrene oxidative degradation (e.g., alcohols, ketones, alkenes, peroxyesters, ethers, etc.).[21,22,25,26,29] Furthermore, changes in polymer macroscopic properties characteristic of material degradation are mediated by the decomposition of peroxides in the polymer.[30] The more fundamental question is the source of the initial peroxides.

Even though singlet oxygen ($^1\Delta_gO_2$) has often been cited as a possible intermediate in the photooxidation of some polymers, its exact role remains to be clearly elucidated.[12-16,31] In addressing this problem, there are two key issues that need to be further resolved. The first concerns the mechanism by which $^1\Delta_gO_2$ may directly react with the polymer. One $^1\Delta_gO_2$ reaction channel that could readily contribute to the decomposition of many polymers is the *ene* reaction with olefins to form hydroperoxides.[14,31,32] Some polymers (e.g., polybutadi-

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ene) contain high concentrations of double bonds along the backbone at regular intervals. In many other polymers, double bonds could also be available for reaction with $^1\Delta_gO_2$ after having been formed either during polymerization (for example, at the end of the macromolecule in a radical termination reaction) or in the course of preliminary degradation reactions.[29,31] Other mechanistic possibilities have been suggested that have not been widely verified or accepted. These include the direct reaction of $^1\Delta_gO_2$ (1) with phenyl rings in polystyrene[25,28,33] (or in an appropriate analogue, such as benzene[34]) and (2) with saturated hydrocarbons.[16,35]

The second key issue that needs to be resolved concerning $^1\Delta_gO_2$ participation in polymer photodegradation is the means by which $^1\Delta_gO_2$ is generated. This is the focus of our current work. In polymers that inherently contain certain chromophores (e.g., carbonyl groups or aromatic rings), $^1\Delta_gO_2$ could readily be formed in a standard photosensitized process.[31] In many other systems, however, the method by which $^1\Delta_gO_2$ could be produced is unclear. Indeed, the nature of the light-absorbing chromophore, for any photodegradation scheme one might postulate, is not resolved in the case of many important polymer types (such as polyolefins). In polymers that lack inherent chromophores, trace impurities have been postulated as potential photosensitizers. Some examples of impurities and anomalous macromolecular structures that have been suggested include (1) carbonyl groups on chain backbones whose origin can be attributed to the presence of oxygen or carbon monoxide in the polymerization mixture,[15,16,31] (2) oxidation products (carbonyl groups, aromatic hydrocarbons) that can arise during processing of the material,[15,16,31,36a] and (3) aromatic hydrocarbons that might originate from the atmosphere (due to the burning of hydrocarbon fuels, for example).[16] Important pieces of negative evidence for these photosensitized $^1\Delta_gO_2$ oxidation scenarios, however, include (1) the lack of correlation between the rate of photooxygenation and the concentration of intentionally introduced carbonyl groups in polyethylene[16,37] and (2) the suppression of photoinduced free-radical formation in polyolefins doped with aromatic hydrocarbons.[15] Another method by which $^1\Delta_gO_2$ could possibly be produced in bulk polymers that has been postulated[38] but not experimentally evaluated is that $^1\Delta_gO_2$ might originate directly from the oxygen–polymer CT state.

We recently completed a detailed spectroscopic study of $^1\Delta_gO_2$ kinetics in a variety of *photosensitized* solid organic polymer systems.[39,40] The data exhibit unique characteristics that allow one to distinguish $^1\Delta_gO_2$ kinetics in a solid, rigid polymer matrix from the kinetics in an analogous liquid-phase photosensitized system. For the present study, we set out to show that $^1\Delta_gO_2$ could also be produced from the oxygen–polymer CT state and thus obviate the necessity of invoking a photosensitizer as the sole source of $^1\Delta_gO_2$ upon irradiation of a polymer matrix. This paper describes a detailed investigation of that photoinduced process. In order to provide support for this solid-phase polymer study, we also report on the time-resolved $^1\Delta_gO_2$ phosphorescence in an appropriate analogue: a low-temperature, low molecular weight organic glass.

Experimental Section

Instrumentation. The general features of our time-resolved $^1\Delta_gO_2$ phosphorescence detection system and flash absorption apparatus have been discussed elsewhere.[11,41,42] For the near-IR $^1\Delta_gO_2$ experiments reported here, a 5-mm diameter germanium p–n junction detector (Germanium Power Devices Corp.), cooled to 77 K, was used as the detector. The time response of our system for these studies (1.7 μs) was chosen to provide an optimal $^1\Delta_gO_2$ signal to noise ratio and yet preclude the necessity of deconvoluting a detector response function from our data. Pulsed laser photolysis wavelengths used in this study were obtained by taking either the third (355 nm) or the fourth (266 nm) harmonics of a Nd:YAG laser or by stimulated Raman scattering with these two wavelengths in H_2 gas.[11] Spectroscopic measurements were made on the 130 K 1-phenylbutane samples by using a variable-temperature refrigeration apparatus, which has been described elsewhere.[40,43] Absorption spectra were recorded on a Beckman DU-40 UV–vis spectrophotometer interfaced to an IBM personal computer.

Sample Preparation. Polystyrene samples were prepared by two independent methods: free-radical polymerization of styrene monomer and hot-pressing of polystyrene powder. Details of our approach in the first case have already been published.[40] In the second case, polystyrene powder (Pressure Chemical, MW = 223 000, M_w/M_n = 1.06) was pressed in vacuo in a mold at 180 °C for approximately 0.5 h. Optically transparent samples were obtained in both cases. The poly(dimethylsiloxane) rubber was prepared by combining vinyl-terminated poly(dimethylsiloxane) [Sylgard 100, McGhan-Nusil, DP = 100], an (Si–H)-bearing dimethylsiloxane cross-linking agent, and 6 ppm of a chloroplatinum catalyst. The mixture was allowed to stand at 25 °C for 48 h and then at 100 °C for 18 h. Solid samples were cut to the desired size with a razor blade. The poly(dimethylsiloxane) oil (obtained from Petrarch, Inc.; viscosity of 1000 centistokes) was washed several times with methanol to remove any impurities. Residual methanol was removed by bubbling the oil with nitrogen gas prior to oxygenation. The absence of methanol in the final sample was verified by IR spectroscopy. 1-Phenylbutane (Aldrich) was distilled from sodium immediately before use. A mixture of N_2 and O_2 gas was bubbled through the liquid prior to the preparation of the low-temperature glass. The N_2/O_2 ratio was varied as experiments were repeated. The oxygen concentration in the solid polymers was controlled by allowing the samples to reach equilibrium with an ambient atmosphere (630 Torr) containing a specific partial pressure of O_2 and N_2. A vacuum manifold equipped with a capacitance manometer (MKS Instruments) and needle valves to control the introduction of O_2 and N_2 was used for this purpose.

Results and Discussion

Absorption Spectra. Absorption spectra of polystyrene and poly(dimethylsiloxane) recorded under both nitrogen and oxygen saturated conditions are shown in Figures 1 and 2, respectively. The oxygen-dependent CT band is visible in each spectrum. In the polystyrene spectra, an "apparent" absorption extends out into the visible region of the spectrum. This absorption is much more pronounced in the solid polystyrene samples than in the concentrated solution of polystyrene in benzene. Similar observations in both polystyrene and polyethylene have been examined in detail by Partridge[36] and were attributed to a combination of both surface scattering and Rayleigh scattering in the bulk of the material. Indeed, we found that when the polystyrene was dissolved in either tetrahydrofuran or diglyme, whose refractive indices ($n_D{}^{20}$ = 1.407 and 1.410, respectively) differ from that of polystyrene ($n_D{}^{20}$ = 1.59–1.60),[44] the intensity of the apparent absorption tail remained prominent and had a wavelength dependence similar to that observed for the solid glass. When polystyrene was dissolved in either toluene or benzene ($n_D{}^{20}$ = 1.497 and 1.501, respectively), whose refractive indices more closely match that of polystyrene, however, the intensity of this tail "absorption" decreased substantially (Figure 1). Further evidence that the "absorption" tail in the polystyrene samples is due to light scattering is that, while the tail intensity increased with an increase in the concentration of dissolved polystyrene, the change did not depend linearly on the concentration changes (under conditions where the sample

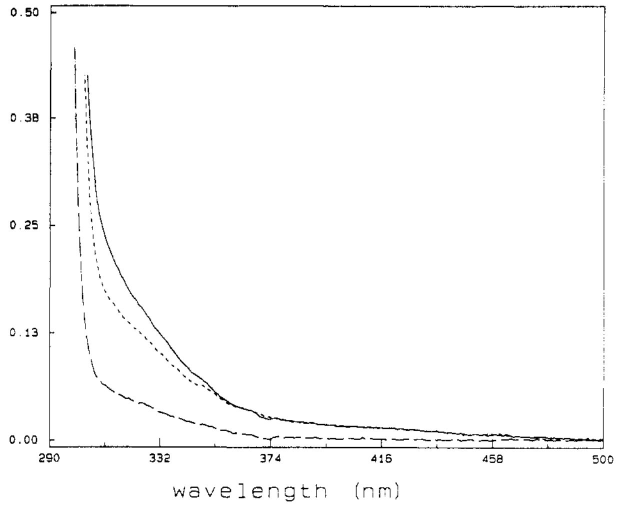

Figure 1. Absorption spectrum of polystyrene glass (—) equilibrated with 630 Torr of oxygen (0.5 cm path length). Absorption spectrum of the same sample (- - -) equilibrated with 630 Torr of nitrogen. Absorption spectrum of a concentrated solution of polystyrene (– • –) in benzene under nitrogen saturated conditions (1 cm path length). The "apparent" absorption that extends out toward the visible region of the spectrum in the solid samples is assigned to a combination of both surface scattering and Rayleigh scattering in the bulk of the material (see text). The data have been normalized to an absorbance value of zero at 500 nm. All of these particular data were recorded from polystyrene samples prepared by free-radical bulk polymerization of styrene at 100 °C.

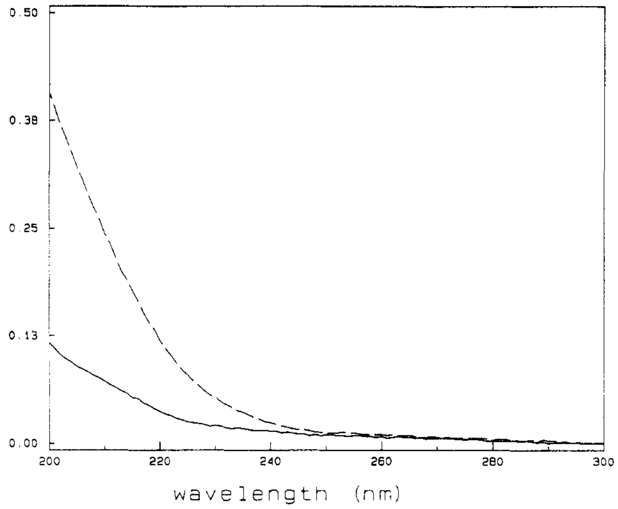

Figure 2. Absorption spectrum of a poly(dimethylsiloxane) oil (viscosity = 1000 centistokes, 1.0 cm path length) recorded under both oxygen (– • –) and nitrogen (—) saturated conditions (630 Torr).

optical density did not exceed 0.05). This indicates that the phenomenon can indeed be attributed to multiple scattering in the sample rather than to direct absorption by either an impurity or the polymer itself. Changes in the sample "absorbance" recorded as a function of changes in the acceptance angle of light incident on the UV/vis absorption spectrometer detector also support the light scattering interpretation.

The assignment of this "apparent" absorption tail in polystyrene to scattering losses is important for two reasons: (1) We are able to select a wavelength for pulsed laser photolysis and remain confident that, in properly prepared samples (vide infra), the CT band is selectively irradiated and irradiation into a polymer absorption band (e.g., $\pi^* \leftarrow \pi$) is precluded. (2) We can now monitor samples with different preparation and handling histories for

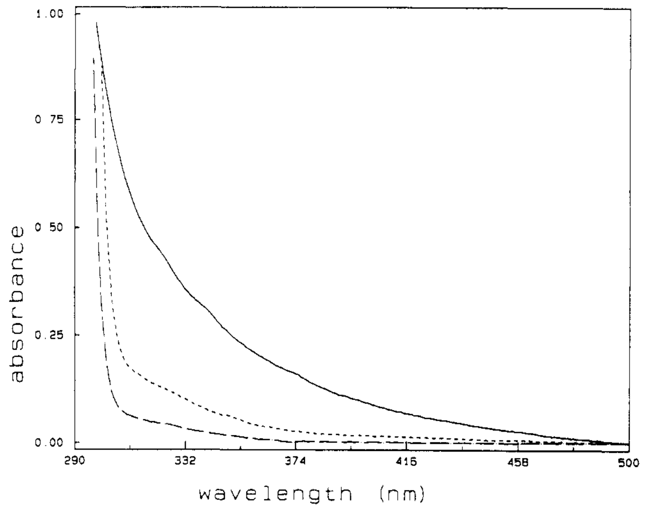

Figure 3. Absorption spectra of nitrogen saturated polystyrene glasses. Spectrum of a sample prepared by hot-pressing polystyrene powder in a mold at 180 °C (—). Spectrum of a sample prepared by bulk free radical polymerization of styrene at 100 °C (- - -). The glass prepared by free-radical polymerization was dissolved in benzene, and its spectrum was recorded (– • –). The data have been normalized to an absorbance value of zero at 500 nm.[45]

impurities that can sensitize the production of $^1\Delta_gO_2$. For example, samples prepared by hot-pressing purified polystyrene powder in a mold at 180 °C routinely gave rise to an absorption that was not present initially in either the powdered material or in solid samples prepared by the free-radical bulk polymerization of styrene at 100 °C (Figure 3).[45] Our time-resolved $^1\Delta_gO_2$ phosphorescence data (vide infra) indicate that the compound responsible for this absorption in the molded samples can sensitize the formation of $^1\Delta_gO_2$.

Time-Resolved $^1\Delta_gO_2$ Phosphorescence Data. Pulsed UV laser photolysis into the oxygen CT absorption band of solid polystyrene gave rise to luminescence at 1270 nm that could be assigned to $^1\Delta_gO_2$ phosphorescence.[10,11,41-43] [For each different polymer system examined (i.e., both hot-pressed and bulk polymerized), this near IR luminescence was not observed from samples in equilibrium with an ambient atmosphere of nitrogen.] The characteristics of this time-resolved $^1\Delta_gO_2$ phosphorescence had a strong dependence on the method of sample preparation (Figure 4). Polystyrene samples prepared by hot-pressing polystyrene powder gave rise to time-resolved $^1\Delta_gO_2$ phosphorescence whose rates of appearance and disappearance (non-single exponential) were slower than those obtained from a bulk polymerized polystyrene sample and were analogous to those observed for the photosensitized production of $^1\Delta_gO_2$ in solid dye-doped polystyrene.[39,40] We have shown that the rate of $^1\Delta_gO_2$ phosphorescence appearance and disappearance, subsequent to pulsed laser excitation of a sensitizer, is much slower in the polystyrene glass than in a liquid phase analogue (e.g., toluene or ethyl benzene).[40] Since the time-resolved $^1\Delta_gO_2$ phosphorescence data in a photosensitized reaction are a convolution of the intrinsic decay rate of $^1\Delta_gO_2$ and the decay rate of the $^1\Delta_gO_2$ precursor and since triplet oxygen ($^3\Sigma_g^-O_2$) diffusion to quench the precursor is slower in the polymer glass than in the liquid, the observed (or manifest[40]) $^1\Delta_gO_2$ phosphorescence will have slower rates of appearance and disappearance in the solid glass. Thus, we suggest that, in our pressed polystyrene samples, a thermally produced impurity is acting as a $^1\Delta_gO_2$ sensitizer. In support of this interpretation, an additional, more distinct, absorp-

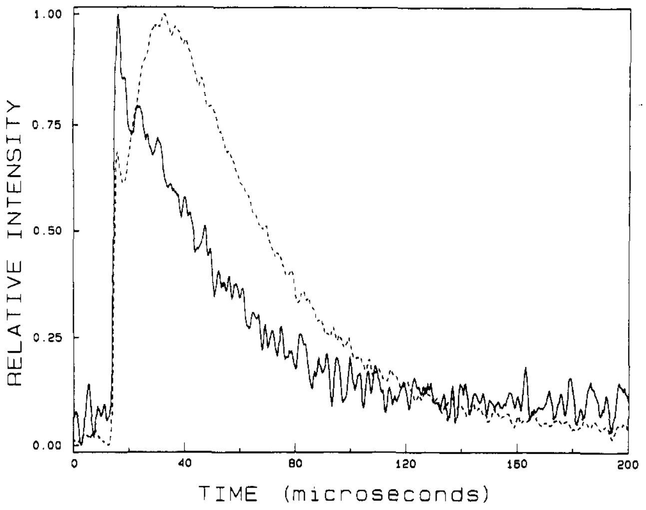

Figure 4. Time-resolved $^1\Delta_gO_2$ phosphorescence recorded from polystyrene glasses subsequent to pulsed laser photolysis of the CT band at 309 nm. In the data (- - -) recorded from a sample prepared by hot-pressing polystyrene powder at 180 °C, the rates of phosphorescence appearance and disappearance were analogous to those recorded for the phenazine-sensitized production of $^1\Delta_gO_2$ in polystyrene.[39,40] In the data (—) recorded from a sample prepared by free-radical bulk polymerization of styrene at 100 °C, the rates of phosphorescence appearance and disappearance were much faster. The raw data have been normalized to yield signals of the same intensity. Because of a slower $^1\Delta_gO_2$ risetime in the hot-pressed sample, a background spike that can be attributed to scattered laser light becomes more apparent.

tion tail was observed in the pressed samples superimposed on the "apparent absorption" tail due to light scattering (Figure 3).[45] In addition, in a flash absorption experiment (pulsed excitation at 309 nm), we were able to record the absorption spectrum of what could be the triplet state of this impurity/$^1\Delta_gO_2$ sensitizer. (The absorbance progressively decreased from a large value at ~420 nm and approached zero at ~700 nm.) Both the intensity and the lifetime[46] of this transient absorption signal were smaller in an aerated sample than in a nitrogen-saturated sample, as expected for a species acting as a $^1\Delta_gO_2$ sensitizer.

In contrast to the data recorded from the pressed polystyrene sample, data recorded from a polystyrene sample prepared at a lower temperature in a free-radical bulk polymerization of styrene did not show the additional distinct tail in the ground-state absorption spectrum (Figure 3) and did not show a flash absorption signal. The time-resolved $^1\Delta_gO_2$ phosphorescence from this latter polystyrene sample had a detector-response-limited risetime (1.7 μs) and a single exponential decay (Figure 4). We suggest that, following initial population of the $^3(\text{polymer}^{\bullet+}\ O_2{}^{\bullet-})$ state, the process of coupling to the $(^1_0\text{polymer}\cdots{}^1\Delta_gO_2)$ potential surface and subsequent dissociation to free $^1\Delta_gO_2$ will be much faster than events that result in $^1\Delta_gO_2$ production in a process sensitized by an impurity solute.[47] Consequently, in glassy polymers such as polystyrene, where diffusion coefficients can be quite small, the production of $^1\Delta_gO_2$ in a photosensitized process is easily distinguished from $^1\Delta_gO_2$ production from the oxygen–polymer CT state simply on the basis of the $^1\Delta_gO_2$ phosphorescence risetime subsequent to pulsed laser irradiation.

In a time-resolved experiment, when the rate of $^1\Delta_gO_2$ production is fast relative to the rate of $^1\Delta_gO_2$ deactivation by the surrounding medium, it is not necessary to deconvolute the $^1\Delta_gO_2$ precursor decay function from the manifest $^1\Delta_gO_2$ phosphorescence data in order to obtain an intrinsic $^1\Delta_gO_2$ lifetime.[40] Therefore, our ability to detect time-resolved $^1\Delta_gO_2$ phosphorescence subsequent to CT excitation in a solid polymer provides a novel and independent method by which $^1\Delta_gO_2$ lifetimes can be determined. The $^1\Delta_gO_2$ lifetime directly observed subsequent to pulsed photolysis (2.4 mJ/pulse, 341 nm) of the polystyrene CT band ($\tau_\Delta = 22 \pm 2$ μs) is equivalent to the lifetime we obtained (through deconvolution) from a photosensitized reaction in solid polystyrene samples specifically doped with a sensitizer dye molecule ($\tau_\Delta \sim 22$ μs).[40] Thus, the present $^1\Delta_gO_2$ lifetime measurements validate both our earlier results and the model used to deconvolute the $^1\Delta_gO_2$ precursor decay in a photosensitized process.[40] These polystyrene data are approximately equivalent to those recorded in photosensitized processes in liquid analogues [toluene ($\tau_\Delta = 29 \pm 1$ μs) and ethyl benzene (26 ± 1 μs)] and consequently also support our earlier suggestion that, to a first-order approximation, a solid-phase matrix exerts control over the intrinsic rate of $^1\Delta_gO_2$ deactivation in a way similar to that in liquid systems.[48]

We were also able to detect weak $^1\Delta_gO_2$ phosphorescence subsequent to pulsed UV irradiation of the CT band in poly(dimethylsiloxane). In this medium, however, since the oxygen diffusion coefficient is sufficiently large, we are unable to distinguish between the photosensitized production of $^1\Delta_gO_2$ and the production of $^1\Delta_gO_2$ from the CT state on the basis of the time-resolved $^1\Delta_gO_2$ phosphorescence risetime. In all cases examined (both rubbers and oils), the rate of $^1\Delta_gO_2$ phosphorescence appearance was limited by our detector response time (1.7 μs). Upon 239 nm, 0.25 mJ/pulse photolysis of the CT band, the $^1\Delta_gO_2$ phosphorescence had a single exponential decay with a lifetime of 46 ± 1 μs. Data recorded from photosensitized reactions in poly(dimethylsiloxane) oils and rubbers yield a $^1\Delta_gO_2$ lifetime of 51 ± 1 μs.[52] This slight difference in $^1\Delta_gO_2$ lifetimes is in keeping with results we obtained from other liquid solvent systems in which the $^1\Delta_gO_2$ lifetime can be shorter subsequent to pulsed irradiation into the CT absorption band.[11] This phenomenon is discussed in greater detail below.

Oxygen Concentration Dependence of the Time-Resolved $^1\Delta_gO_2$ Data. In the photosensitized production of $^1\Delta_gO_2$, the rate of sensitizer deactivation, and consequently the rate of $^1\Delta_gO_2$ formation, will be dependent on the equilibrium concentration of ground-state oxygen ($^3\Sigma_g{}^-$-O_2) in the system.[41] At higher $^3\Sigma_g{}^-$-O_2 concentrations, the $^3\Sigma_g{}^-$-O_2-sensitizer encounter probability will be higher, and the rates of sensitizer deactivation and $^1\Delta_gO_2$ formation will be greater. The *intrinsic* rate of $^1\Delta_gO_2$ deactivation, however, is independent of $^3\Sigma_g{}^-$-O_2 concentration in both organic liquids and solid polymer systems.[40] Therefore, in a time-resolved photosensitized process in polymer glasses, where the *manifest* $^1\Delta_gO_2$ phosphorescence data are determined by the convolution of a relatively slow sensitizer decay function and the *intrinsic* $^1\Delta_gO_2$ decay function, an increase in the equilibrium $^3\Sigma_g{}^-$-O_2 concentration results in faster rates of $^1\Delta_gO_2$ phosphorescence appearance and disappearance.[40]

Pulsed UV laser photolysis of polystyrene samples prepared by hot-pressing of polystyrene powder gave rise to time-resolved $^1\Delta_gO_2$ phosphorescence that was $^3\Sigma_g{}^-$-O_2 concentration dependent. At higher equilibrium $^3\Sigma_g{}^-$-O_2 concentrations,[53] the rates of phosphorescence appearance and disappearance were faster than the corresponding rates at lower $^3\Sigma_g{}^-$-O_2 concentrations (e.g., the rates at 630 Torr of $^3\Sigma_g{}^-$-O_2 were approximately 1.5 times those of 130 Torr of $^3\Sigma_g{}^-$-O_2). These data are in keeping with the suggestion that the process of sample molding resulted in thermally produced impurities that can sensitize the production of ${}^1\Delta_gO_2$. In contrast, the polystyrene samples prepared at a lower temperature by bulk free-radical polymerization of styrene yielded time-resolved ${}^1\Delta_gO_2$ phosphorescence that was independent of ${}^3\Sigma_g{}^-O_2$ concentration. Over the range of ${}^3\Sigma_g{}^-O_2$ concentrations examined,[53] the appearance rate of ${}^1\Delta_gO_2$ phosphorescence was always limited by the time response of our detection system (1.7 μs). This result is consistent with the formation of ${}^1\Delta_gO_2$ from the CT state.[11] The decay of ${}^1\Delta_gO_2$ phosphorescence in these latter samples always followed first-order kinetics with a lifetime of 22 ± 2 μs.

Photolysis Wavelength and Laser Energy Dependence of the ${}^1\Delta_gO_2$ Phosphorescence Data. In an attempt to further confirm our assignment of the CT state as the ${}^1\Delta_gO_2$ precursor in our polystyrene samples, we examined the ${}^1\Delta_gO_2$ phosphorescence intensity as a function of the pulsed UV laser photolysis wavelength.[54] The intensity of ${}^1\Delta_gO_2$ phosphorescence decreased as the photolysis wavelength was successively changed from 309 nm to 341 nm to 355 nm, corresponding to the successive decrease in the optical density of the CT absorption band. (All of the ${}^1\Delta_gO_2$ intensities were normalized for the number of photons in the excitation pulse.) At 299 nm, where most of the incident laser light is directly absorbed by the polymer itself, the ${}^1\Delta_gO_2$ phosphorescence intensity was ~5% of the intensity at 309 nm, where the CT band absorbance is quite large relative to the polystyrene absorbance. On the basis of this latter observation, it appears that the polymer itself is not an efficient sensitizer of ${}^1\Delta_gO_2$ under our conditions, which is indeed expected for an organic molecule (polymer) with such a high triplet energy.[55] Furthermore, at a photolysis wavelength that should be sufficiently red shifted to preclude single photon excitation to a polystyrene excited state (355 nm),[36b] the ${}^1\Delta_gO_2$ phosphorescence intensity was linearly dependent on the laser energy. We can thus exclude from consideration a multiphoton process to form an excited state of polystyrene with the subsequent sensitized production of ${}^1\Delta_gO_2$.

In our study of liquid solutions,[11] we found that, at high incident laser energies or at wavelengths where the CT band absorption cross section is large, the lifetime of ${}^1\Delta_gO_2$ produced by CT band irradiation was consistently shorter than the ${}^1\Delta_gO_2$ lifetime determined under comparable photosensitized conditions in the same solvent. At the limit of low laser energy or where the CT absorption cross section is small, however, these independently determined ${}^1\Delta_gO_2$ lifetimes become equivalent. We suggested that irradiation into the CT band also creates a species capable of quenching ${}^1\Delta_gO_2$ (e.g., peroxy radical and/or $O_2{}^{\bullet-}$).[11] Thus, under conditions where the number of incident photons absorbed by the sample is large, both this species and ${}^1\Delta_gO_2$ would be formed in greater yields, resulting in an increased probability for bimolecular encounter and $\tau_\Delta{}^{CT} < \tau_\Delta{}^{sens}$. The species that quenches ${}^1\Delta_gO_2$ under these circumstances may also contribute to the overall photooxidative degradation of the organic material.[17-20]

In contrast to our data in liquids, for ${}^1\Delta_gO_2$ produced subsequent to CT irradiation in solid polystyrene, the ${}^1\Delta_gO_2$ lifetime was independent of both laser energy and wavelength. At the different photolysis wavelengths accessible in this study (vide supra), changes in τ_Δ did not exceed the error limits for a single τ_Δ determination (τ_Δ = 22 ± 2 μs). Similarly, over the range of 0.35–6.0 mJ/pulse at 355 nm, we were unable to observe τ_Δ values other than 22 ± 2 μs. These unique polymer data may be partially due to a combination of CT absorption cross sections and incident laser energies that are sufficiently small. It is also likely that, in this solid polymer, diffusion of ${}^1\Delta_gO_2$ to a site in the matrix that contains a photoinduced ${}^1\Delta_gO_2$ quencher (e.g., peroxy radical that results from a different oxygen–polymer CT state) is precluded within the ${}^1\Delta_gO_2$ lifetime. Only in liquids (or rubbers, vide supra), where diffusion coefficients are much larger, will the encounter probability between ${}^1\Delta_gO_2$ and a transient quencher be large enough to shorten τ_Δ subsequent to CT band photolysis.

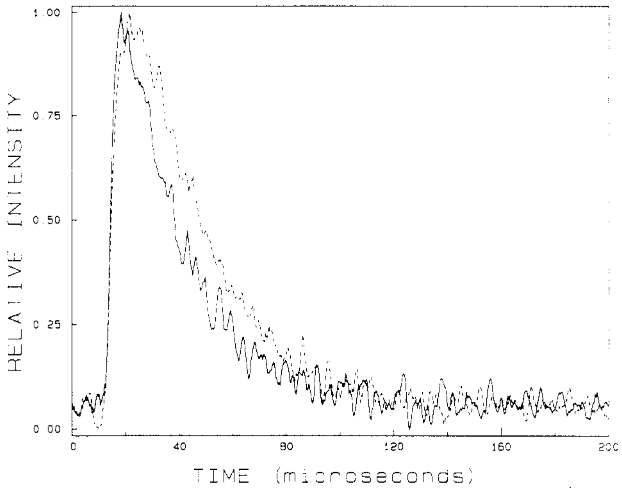

Figure 5. Time-resolved ${}^1\Delta_gO_2$ phosphorescence recorded from polystyrene glasses subsequent to laser irradiation of the CT band at 341 nm. The data (—) recorded from a freshly prepared sample that had not previously been irradiated had faster rates of both appearance and disappearance than the data (- - -) recorded from the same sample subsequent to three separate 30-min periods of photolysis (341 nm, 2.6 mJ/pulse). Between photolysis sessions, the sample was allowed to stand under 630 Torr of oxygen for 4 days (25 °C, ambient lighting).

Photolytic and Thermal Creation of ${}^1\Delta_gO_2$ Sensitizers. As we have already discussed, polystyrene samples prepared by our lower temperature, bulk free-radical polymerization technique showed no evidence of impurities that could act as ${}^1\Delta_gO_2$ sensitizers. However, the concentration of such impurities increased subsequent to three separate 30-min periods of photolysis with a pulsed laser (at 341 nm and 2.6 mJ/pulse) into the CT band. Between photolysis sessions, the sample was allowed to stand at 25 °C under 630 Torr of oxygen for 4 days. The creation of these impurities is evident both in the successively slower rates of ${}^1\Delta_gO_2$ phosphorescence appearance and disappearance in a time-resolved experiment (Figure 5) and in the appearance of a new band in the absorption spectrum of polystyrene (as in the spectrum of the pressed polystyrene shown in Figure 3).

1-Phenylbutane Glass Studies. Time-resolved ${}^1\Delta_gO_2$ phosphorescence was recorded from frozen (130 K) samples of 1-phenylbutane, which form a glass under these conditions. To our knowledge, this is the first direct observation of ${}^1\Delta_gO_2$ phosphorescence within a solid, low molecular weight organic medium, and the data from this system provide a useful check for our interpretations of the bulk polystyrene results. In aerated liquid samples of 1-phenylbutane at 295 K, the risetime of the ${}^1\Delta_gO_2$ phosphorescence subsequent to pulsed laser photolysis of either a ${}^1\Delta_gO_2$ sensitizer or the solvent–oxygen CT band is limited by the response time of the detector used in this particular study (1.7 μs). At the limit of low laser energy, the ${}^1\Delta_gO_2$ lifetime in the photosensitized 295 K process

(τ_Δ^{sens} = 25 ± 1 μs) was equivalent to that obtained subsequent to CT band irradiation. These results are consistent with data we reported earlier in independent studies of liquids (vide supra).[11,41] In an aerated 130 K glass of 1-phenylbutane containing the $^1\Delta_gO_2$ sensitizer acridine, the rise and decay rates of $^1\Delta_gO_2$ phosphorescence [$\tau_{1/2}$(rise) ~ 11 μs; $\tau_{1/2}$(decay) ~ 125 μs; non-single exponential] were dramatically slower than the values obtained in the liquid state and were analogous to rates of rise and decay observed (a) subsequent to pulsed photolysis of a sensitizer dye molecule specifically incorporated in a solid matrix of polystyrene[40] and (b) subsequent to pulsed UV irradiation of the pressed polystyrene glass containing the impurity/$^1\Delta_gO_2$ sensitizer (Figure 4). In contrast to the sensitized process, the risetime of $^1\Delta_gO_2$ phosphorescence subsequent to pulsed laser photolysis into the CT band in a pure sample of 130 K 1-phenylbutane was much faster and was limited by our detector response time (1.7 μs). These latter data are analogous to those recorded from impurity-free bulk polymerized polystyrene samples subsequent to CT band photolysis (vide supra). The $^1\Delta_gO_2$ phosphorescence decay following CT band irradiation in the pure 1-phenylbutane 130 K sample was single exponential with a lifetime of 35 ± 5 μs (unfortunately, the $^1\Delta_gO_2$ signal:noise level was sufficiently poor to preclude a more accurate determination of the lifetime). As the temperature of a 1-phenylbutane sample was decreased over the range 295–130 K, the $^1\Delta_gO_2$ lifetime obtained subsequent to CT irradiation progressively increased from 25 ± 1 μs to 35 ± 5 μs. These data are in keeping with the very slight temperature effect previously reported for the intrinsic $^1\Delta_gO_2$ lifetime.[40,43,56] Moreover, a sharp change in τ_Δ did not occur at the 1-phenylbutane glass transition temperature (~180 K).

Conclusions

We have shown that irradiation into the polymer–oxygen charge-transfer (CT) absorption band of polystyrene creates singlet molecular oxygen ($^1\Delta_gO_2$). By examining the time-resolved $^1\Delta_gO_2$ phosphorescence subsequent to pulsed laser photolysis in a polymer glass, we are able to distinguish $^1\Delta_gO_2$ created in a photosensitized process from $^1\Delta_gO_2$ created by dissociation of the polymer–oxygen CT state. In the latter case, the intrinsic $^1\Delta_gO_2$ lifetime (τ_Δ) is directly obtained without deconvoluting a $^1\Delta_gO_2$ precursor decay function from the manifest phosphorescence data, and we have obtained a value of τ_Δ = 22 ± 2 μs for polystyrene using this technique. The present lifetime data agree with our earlier independent results[40] obtained in photosensitized (dye-doped) polystyrene systems and thus validate the deconvolution model invoked in that study. We have shown that $^1\Delta_gO_2$ formation in solid polystyrene can proceed by two independent pathways (photosensitization and CT state dissociation) and that the relative importance of these pathways explicitly depends on the polymer sample history and method of preparation. Furthermore, we have shown that the yield of $^1\Delta_gO_2$ from a photosensitized process increases with progressive irradiation into the polymer–oxygen CT band. Most importantly, we are able to conclude that, even if a sample is prepared to exclude impurities that can act as $^1\Delta_gO_2$ photosensitizers, $^1\Delta_gO_2$ will still be photolytically produced by irradiation of the oxygen ($^3\Sigma_g^-O_2$)–polymer CT absorption band. The results reported here are expected to be useful in understanding the primary events of both photoinduced[13–16] and radiation-induced[57] oxidative degradation of polymers.[58]

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(45) The absorption spectrum differences shown in Figure 3 for the solid polystyrene samples that were prepared by two different techniques carried over into the spectra recorded when these samples were dissolved in benzene, indicating inherent differences in light absorbing chromophores in the two materials. In addition, the solid sample prepared by hot-pressing polystyrene scattered more light than did the bulk free-radical-polymerized sample. Thus, normalizing the data to an absorbance of zero at 500 nm gives rise to an apparent intersection between the two absorption curves at approximately 305 nm.

(46) The transient did not decay with simple first-order kinetics (see ref 40 for a discussion of this phenomenon). A biexponential fitting function adequately represented the data. One component of decay appeared to be independent of oxygen concentration and had a lifetime of ~170 μs. The lifetime of the second component decreased from 870 to 20 μs upon aeration of a deoxygenated sample.

(47) In $^1_0$polymer, the subscript denotes the ground electronic state. Superscripts denote spin multiplicities.

(48) To a good approximation, the lifetime of $^1\Delta_gO_2$ in solution can be related to the number and kind of C–H bonds present in the host medium[43,49,50] because C–H bonds (and O–H bonds, when present) are excellent sinks for the $^1\Delta_gO_2$ excitation energy in a process of electronic-to-vibrational energy transfer.[43,51] The *concentration* and type of C–H bonds in toluene and ethyl benzene liquids is approximately equivalent to that in polystyrene. To the extent that these solvents are indeed appropriate liquid phase analogues for solid polystyrene with respect to $^1\Delta_gO_2$ dynamics, it appears that the $^1\Delta_gO_2$ lifetime we measure in polystyrene ($\tau_\Delta = 22 \pm 2$ μs) may be slightly shorter than those measured in the liquids [$\tau_\Delta = 29 \pm 1$ μs (toluene) and 26 ± 1 μs [ethylbenzene]). These subtle differences could be due to a variety of factors, including $^1\Delta_gO_2$ quenchers unique to the polymer[40] or cage/reencounter effects more pronounced than those found in the liquids. This question is currently under investigation.

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(53) Polymer samples were equilibrated with ambient oxygen partial pressures ranging from 100 to 630 Torr. We have already discussed in detail why, over this pressure range and under our conditions, $^1\Delta_gO_2$ cannot originate through direct excitation of either $^3\Sigma_g^-O_2$ or $(^3\Sigma_g^-O_2)_2$.[11]

(54) In our earlier study on liquid samples,[11] we determined a $^1\Delta_gO_2$ quantum yield from the CT state (ϕ_Δ^{CT}) of approximately 0.2. Unfortunately, we have not yet been able to establish a ϕ_Δ standard in the solid polymers to serve as a reference in $^1\Delta_gO_2$ intensity measurements. At present, our efforts are limited by the inefficiency of triplet state sensitizer quenching by $^3\Sigma_g^-O_2$ in the glassy polymers.[40] Nevertheless, the $^1\Delta_gO_2$ intensity measurements made in polystyrene subsequent to CT excitation suggest that ϕ_Δ^{CT} (polystyrene) is not drastically different from ϕ_Δ^{CT} (liquid benzene).[11]

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(58) Our results are also expected to be useful in understanding events that result in the reported acceleration of polymerization reactions subsequent to irradiation of monomer-$^3\Sigma_g^-O_2$ CT absorption bands.[59]

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Registry No. O_2, 7782-44-7; (polystyrene)·O_2, 39839-71-9; 1-phenylbutane, 104-51-8.

Photodecoupling of Cross-Links in Polymeric Gels

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ABSTRACT: Poly(butyl methacrylate) gels with photolabile cross-linked acyloxime units were prepared. The acyloxime moieties are scissioned on exposure to UV radiation, the cross-links decouple, and the solid material is thereby solubilized. The quantum yield of cross-link decoupling is about $\Phi = 0.03$. The physicochemical consequences of cross-link decoupling are investigated.

Introduction

While the phenomenon of photo-cross-linking has been investigated in detail,[1,2] the inverse phenomenon, namely the opening of cross-links by the action of radiation has received but little attention.[3] Yet the photodecoupling of cross-links is both of fundamental and potentially of practical interest. Photodecoupling of cross-links makes it possible to convert a three-dimensional network into an ensemble of linear chains by approaching the gel point of the system from the direction of higher cross-link densities. Apart from its inherent significance as a test for some aspects of gelation theory, photodecoupling may have interesting applications in lithography and in other imaging technologies. In fact, positive resists based on

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