Behavior of Singlet Molecular Oxygen ($^1\Delta_gO_2$) in a Polymer Matrix: Effects of Temperature, Matrix Rigidity, and Molecular Composition

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ABSTRACT: Singlet molecular oxygen ($^1\Delta_gO_2$) has been created, by energy transfer, from a triplet-state photosensitizer in a variety of solid organic polymers. In independent time-resolved experiments, the phosphorescence of $^1\Delta_gO_2$ and the absorbance of the sensitizer triplet state were monitored as a function of the sample temperature, matrix rigidity, and molecular composition. In more glassy samples, the time-dependent behavior of the $^1\Delta_gO_2$ phosphorescence signal is strikingly different from that observed in liquid analogues, exhibiting long decay times with non-first-order kinetics. As the polymer matrix is made less glassy, however, either by an increase in temperature or by using copolymers or low molecular weight additives, the $^1\Delta_gO_2$ phosphorescence signal appearance and disappearance rates increase, approaching rates observed in liquid solvent analogues. At this limit, the $^1\Delta_gO_2$ decay follows first-order kinetics. The triplet sensitizer flash absorption data indicate that, in the glassy organic polymers, the time-dependent behavior of the $^1\Delta_gO_2$ phosphorescence signal principally reflects that of its precursor. Deconvolution of the sensitizer decay from the experimentally observed (or *manifest*) $^1\Delta_gO_2$ phosphorescence signal yields *intrinsic* $^1\Delta_gO_2$ lifetimes which, to a first-order determination, are independent of temperature and matrix rigidity and are approximately equivalent in magnitude to those recorded in liquid-phase analogues. In this convolution integral, it is necessary to incorporate a model in which the $^1\Delta_gO_2$ sensitizer exists in a distribution of nonequivalent sites in the polymer matrix. Data obtained from a perdeuterated polymer give an *intrinsic* $^1\Delta_gO_2$ lifetime that is an order of magnitude longer compared with that obtained from a perprotiated analogue and indicate that a solid-phase matrix exerts control over the intrinsic rate of $^1\Delta_gO_2$ deactivation in a way very similar to that in liquid-phase systems.

Introduction

Singlet molecular oxygen ($^1\Delta_gO_2$), generated in liquid solutions and also in the gas phase, has been extensively studied during the past several decades.[1,2] Oxygen is also quite soluble in most solid organic polymers, and there has been considerable interest in investigating the behavior of $^1\Delta_gO_2$ in polymer systems.[3-5] Besides being of fundamental mechanistic interest, an understanding of $^1\Delta_gO_2$ behavior in solid macromolecular matrices is potentially relevant to the important problem of polymer photooxidative degradation. This topic has been the subject of considerable discussion and debate[3-5] and warrants further investigation.

We recently reported[6,7] that singlet molecular oxygen phosphorescence ($^3\Sigma_g^-O_2 \leftarrow {}^1\Delta_gO_2$, 1270 nm) can be detected, in a time-resolved photosensitized experiment, from a solid poly(methyl methacrylate) (PMMA) glass. This experimental probe affords a method by which the photophysics and photochemistry of $^1\Delta_gO_2$ can be directly studied in macromolecular systems. The time-resolved near-IR $^1\Delta_gO_2$ phosphorescence signals observed in 25 °C PMMA are strikingly different from those observed in liquid phase organic solvents[8-10] and are characterized by several features:[6] (1) The rates of both signal appearance and disappearance in air-saturated samples are approximately 1 order of magnitude less than those in a liquid phase analogue, methyl propionate, for which the $^1\Delta_gO_2$ lifetime (τ_Δ) is ~38 µs. (2) A substantial deviation from first-order decay kinetics is observed in the PMMA glass. This is not a common observation in liquid solvents, although there are special circumstances in which the $^1\Delta_gO_2$ decay can deviate from first-order kinetics.[11] The $^1\Delta_gO_2$ decay in methyl propionate follows first-order kinetics. (3) The rates of $^1\Delta_gO_2$ signal appearance and disappearance in PMMA increase with an increase in the ambient oxygen partial pressure. The rate of $^1\Delta_gO_2$ phosphorescence signal decay in common liquid solvents is independent of the ambient oxygen partial pressure at atmospheric pressures.[12]

In an attempt to identify specific features of this photophysical system that could give rise to such large differences in the observed $^1\Delta_gO_2$ phosphorescence signal, we set out to examine the triplet photosensitized production of $^1\Delta_gO_2$ (1) in several polymers over a temperature range (~150 °C) that includes the glass transition temperature (T_g), (2) in acrylate polymers of very similar atomic composition in which the glassy nature of the matrix was systematically changed by means of copolymers or low molecular weight diluents, (3) in styrene polymers in which the atomic composition was varied by deuteration, and (4) in polymers at equilibrium with different ambient oxygen partial pressures. In each case, $^1\Delta_gO_2$ was monitored by its time-resolved near-IR phosphorescence, and the sensitizer triplet state was monitored in a flash absorption experiment. The results of these studies are presented in this paper.

Experimental Section

Instrumentation. The instrumentation and approach used to detect the time-resolved, near-IR phosphorescence of $^1\Delta_gO_2$ and to perform triplet-state absorption studies are described elsewhere.[9,10,13,14] For experiments in which $^1\Delta_gO_2$ phosphorescence and the sensitizer triplet state absorption were both monitored, the excitation/detection system used the three axes of a Cartesian coordinate system: the polymer sample containing the $^1\Delta_gO_2$ sensitizer was irradiated with a pulsed laser along the Z-axis (1–3 mJ/pulse at 355 nm), $^1\Delta_gO_2$ phosphorescence was detected along the Y-axis, and the sensitizer triplet state was probed along the X-axis. With this system, independent data sets could be recorded without moving the sample. The triplet states of acridine and phenazine were monitored at 440 nm.[15] All time-resolved signals used for analysis and shown in the figures were an average ob-

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tained from either 32 or 64 independent laser pulses. Polymer samples were allowed to equilibrate with air (or other oxygen: nitrogen ratios, created using a Matheson Model 7352 flow meter/gas proportioner[9]) at atmospheric pressures[16] for approximately 2 weeks prior to use.

In order to raise the polymer temperature above 25 °C, the samples were bathed in a stream of heated air as the spectroscopic measurements were being made. Data were recorded 10 min after each incremental change in the air stream temperature, which was monitored by a Keithley Model 869 platinum resistance thermometer. Samples were cooled below 25 °C by using a variable-temperature refrigeration apparatus similar to one used previously for solution-phase samples.[17,18] Because the sample temperature is controlled by a bath of nitrogen gas, it is important to use this device only at temperatures where gas diffusion within the polymer is found to be slow enough (vide infra) as not to alter the sample oxygen concentration during the time period required to achieve temperature equilibrium and record the data.

Polymerization of Methyl Methacrylate (MMA) Samples. MMA (Aldrich, gold label) was distilled under vacuum just prior to use. Polymerization was carried out in glass ampules with 2,2'-azobis(2,4-dimethylvaleronitrile) as the radical initiator. In a typical preparation, 1.8 mg of the azo compound and 0.25 mg of phenazine were dissolved in 10 g of MMA. This results in a sensitizer concentration of $\sim 1.4 \times 10^{-4}$ M. The solution was subjected to three freeze–thaw degassing cycles, after which the ampules were sealed and placed in a 50 °C oil bath. The samples were removed after 8 h and slowly shaken. After standing undisturbed at 50 °C for an additional 16 h, the temperature was increased to 100 °C, and the samples were allowed to stand in the bath an additional 24 h. The resulting polymer rod was cut into ~5-mm-thick disks, and opposing sides of each disk were cut off to give two parallel faces. The flat surfaces of the glassy disks were polished to high optical clarity with diamond-paste polishing wheels.

For other polymerizations, a selected amount of ethyl acrylate, dimethyl adipate, or diphenyl ether was weighed out into the initial mixture prior to polymerization. Ethyl acrylate (Aldrich) was distilled under vacuum just prior to use. Highly rubbery samples could be readily cut by hand with a razor blade.

Polymerization of Styrene Samples. Styrene (Aldrich, gold label) and styrene-d_8 (Aldrich, 98% isotopic purity) were distilled under vacuum just prior to use. A mixture of monomer, sensitizer, and radical initiator was degassed and subjected to the same polymerization and polishing steps as for the PMMA described above.

Materials. 1,12-Benzoperylene (K&K Laboratories) was recrystallized twice from ethanol. Acridine and phenazine (Aldrich) were recrystallized three times from ethanol/water. Dimethyl adipate and diphenyl ether (both from Aldrich, 99+%) were used as received. 2,2'-Azobis(2,4-dimethylvaleronitrile) (Du Pont) was purified by dissolution in methanol at 25 °C to prepare a saturated solution, which was then cooled to -15 °C to induce crystallization.

Results

Temperature Studies. Time-resolved $^1\Delta_gO_2$ phosphorescence signals from PMMA and poly(styrene) (PS) were recorded as a function of sample temperature. Typical data are given in Figure 1. The following observations were made: (1) As the temperature was increased and ultimately carried through T_g (PMMA $T_g \sim 100$ °C; PS $T_g \sim 95$ °C),[19,20] the rates of $^1\Delta_gO_2$ signal appearance and disappearance likewise increased gradually (Figure 1b). This is represented graphically, in Figure 2, in a plot of the $^1\Delta_gO_2$ signal decay half-life[21] as a function of temperature. (2) At low temperatures, where the rates of the $^1\Delta_gO_2$ signal disappearance were slowest, the decay did not obey first-order kinetics. As the temperature was increased, however, the observed signal gradually approached the limit at which the entire decay could be expressed by a single exponential function. At this limit ($T \geq T_g$), the signal lifetime corresponded approximately to those determined in liquid-phase PMMA and PS analogues, methyl propionate ($\tau_\Delta = 38 \pm 2$ μs) and ethyl benzene ($\tau_\Delta = 26 \pm 1$ μs), respectively (Figure 2).[22] The $^1\Delta_gO_2$ decay in PS approached this liquid-phase limit at temperatures well below those required for PMMA. Consequently, at 25 °C, the $^1\Delta_gO_2$ decay in PS was only modestly different from that observed in ethyl benzene (Figure 2A); whereas, the $^1\Delta_gO_2$ signal decay rate in PMMA was an order of magnitude less than that in methyl propionate and did not follow first-order kinetics (Figure 2B). (3) The trends observed upon heating the sample through T_g (points 1 and 2, above) appeared, in reverse, as the sample was cooled back to ~25 °C. However, in the cooling cycle, the rates of $^1\Delta_gO_2$ signal appearance and disappearance and the signal intensity were substantially smaller than those recorded at the same temperature during the heating cycle (as seen, for example, in Figure 1A for data recorded at 22 °C both before and after (dotted line) a PMMA sample had been heated). Upon exposure of this same sample to the atmosphere at 22 °C for approximately 2 weeks, we were able to reproduce the time-resolved $^1\Delta_gO_2$ signal recorded at 22 °C prior to heating.

Flash absorption measurements of both the acridine and phenazine triplet state in aerated, 25 °C PMMA samples

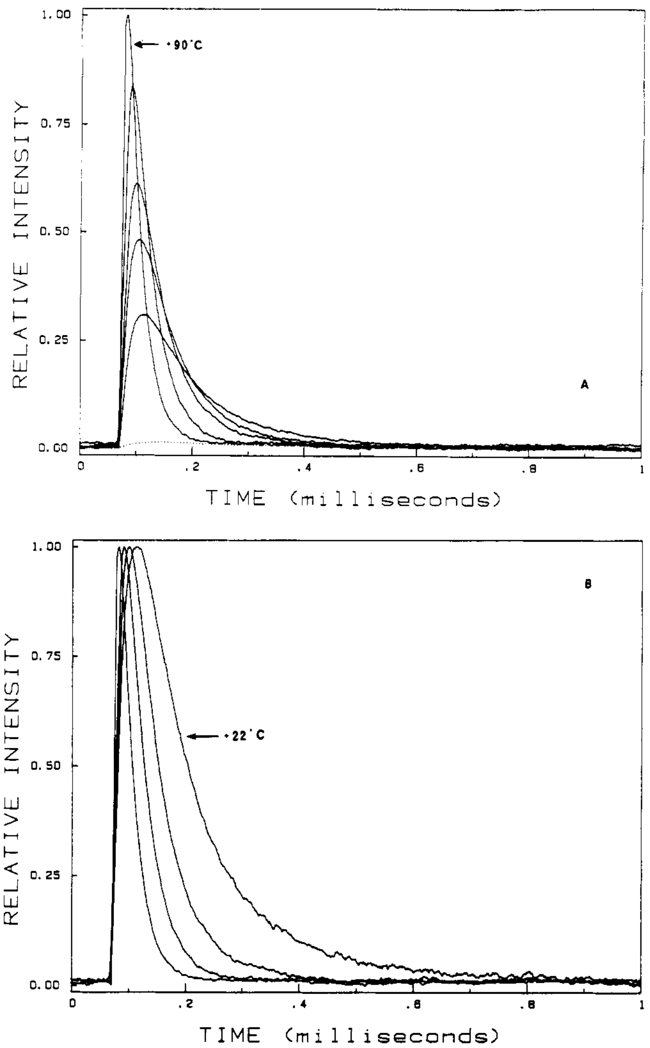


Figure 1. Time-resolved $^1\Delta_gO_2$ phosphorescence signal in PMMA recorded at temperatures above +22 °C. The $^1\Delta_gO_2$ sensitizer was acridine (1.7×10^{-4} M). (a) The temperature was incrementally raised (22 °C, 33 °C, 42 °C, 60 °C, 90 °C). After the data at 90 °C were recorded, the sample was cooled to 22 °C and the signal rerecorded (dotted line). (b) The 22, 42, 60, and 90 °C data presented in Figure 1a have been rescaled to make all signal amplitudes equivalent. In each panel, data recorded at other temperatures are not shown in order to relieve congestion.

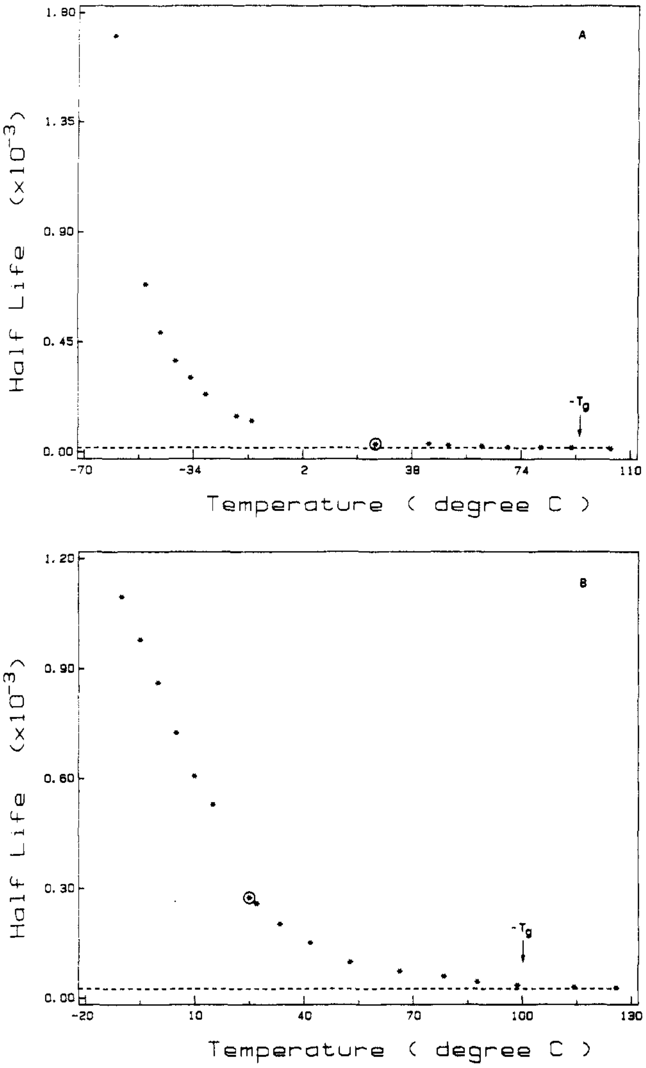


Figure 2. Half-life for the manifest $^1\Delta_gO_2$ phosphorescence decay (in microseconds) as a function of the polymer temperature. Data were recorded as the sample temperature was incremented. The glass transition temperatures (T_g) are indicated. The circled data point was recorded at 25 °C. (A) PS containing 1,12-benzoperylene (3.6×10^{-4} M). The dashed line indicates the $^1\Delta_gO_2$ half-life at 25 °C in a liquid PS analogue, ethylbenzene ($\tau_{1/2}$ = 18 μs, τ_Δ = 26 ± 1 μs, with anthracene as sensitizer).[22] (B) PMMA containing phenazine (1.7×10^{-4} M). The dashed line indicates the $^1\Delta_gO_2$ half-life at 25 °C in a liquid PMMA analogue, methyl propionate ($\tau_{1/2}$ = 27 μs, τ_Δ = 38 ± 2 μs, with anthracene as sensitizer).[22]

revealed that the triplet sensitizer decay does not follow first-order kinetics and that the triplet decay half-life is approximately equivalent to that recorded for $^1\Delta_gO_2$ phosphorescence (Figure 3). As the sample temperature was incrementally raised to ~115 °C, the rate of triplet sensitizer deactivation incrementally increased (Figure 3B), and the signal decay approached the limit of a single exponential function with a lifetime comparable to that observed in a liquid solution. The signal recorded at 25 °C, after heating a PMMA sample through T_g and subsequent cooling, decayed substantially slower than that at 25 °C prior to heating (Figure 3B). After exposure of this sample to the atmosphere at 25 °C for 2 weeks, we reproduced the triplet decay signal recorded prior to heating. The temperature dependence of the sensitizer triplet absorption signal in PS was analogous to that observed in PMMA. As in the case of the $^1\Delta_gO_2$ signals, however, the sensitizer signals in PS approached the liquid-phase limit at temperatures well below those required for the PMMA sample.

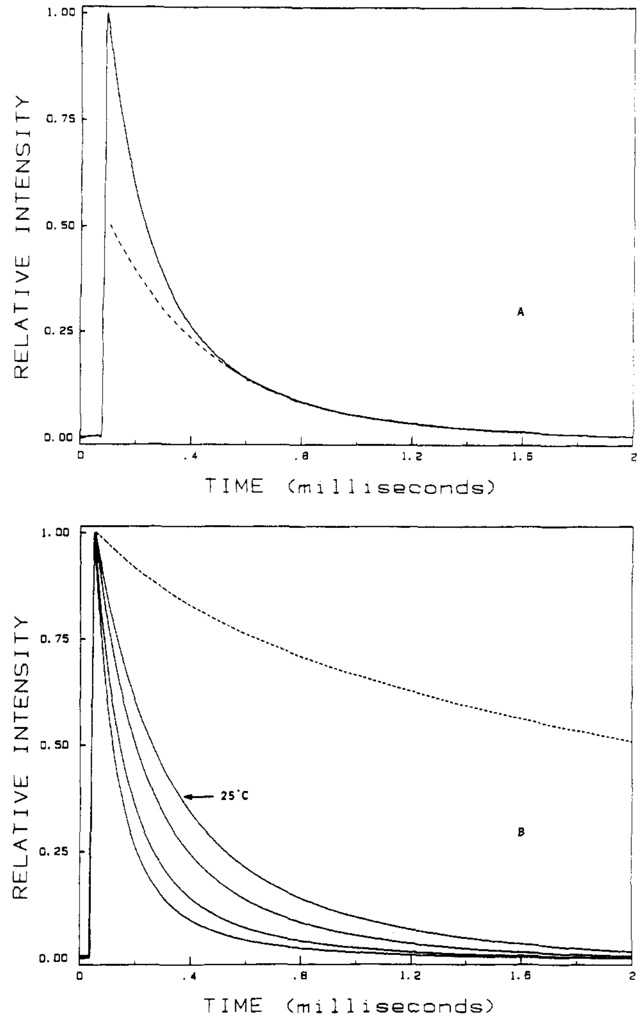
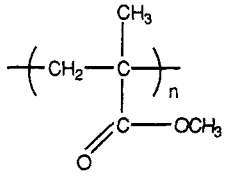


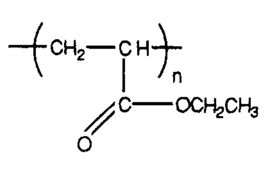
Figure 3. Time-resolved triplet–triplet absorption signals of acridine in an aerated PMMA sample. (A) The signal obtained at 25 °C. The dashed line is a single exponential function and indicates the extent to which the triplet decay deviates from first-order kinetics. (B) The signal obtained at four different temperatures (25 °C, 31 °C, 41 °C, 50 °C). The dashed line represents the triplet absorption signal recorded at 25 °C after the polymer sample had been heated through T_g and subsequently cooled. Data have been rescaled such that signal amplitudes are equivalent.

Oxygen Partial Pressure Studies. Time-resolved $^1\Delta_gO_2$ phosphorescence signals and phenazine triplet state absorption signals were recorded from 25 °C PMMA samples that had been equilibrated with different ambient oxygen partial pressures. As the oxygen partial pressure was increased, (1) the $^1\Delta_gO_2$ signal intensity increased, (2) the $^1\Delta_gO_2$ signal appearance and disappearance rates increased, and (3) the decay rate of the triplet-state sensitizer increased.

Copolymer Studies. Copolymers of methyl methacrylate (MMA) and ethyl acrylate (EA) were prepared. These two compounds, and the resulting polymers (PMMA and PEA, respectively), are structural isomers that differ only in the location of a methyl group. On the basis of solution-phase results, the $^1\Delta_gO_2$ lifetime is expected to be inversely proportional to the number of C–H bonds in the



PMMA



PEA

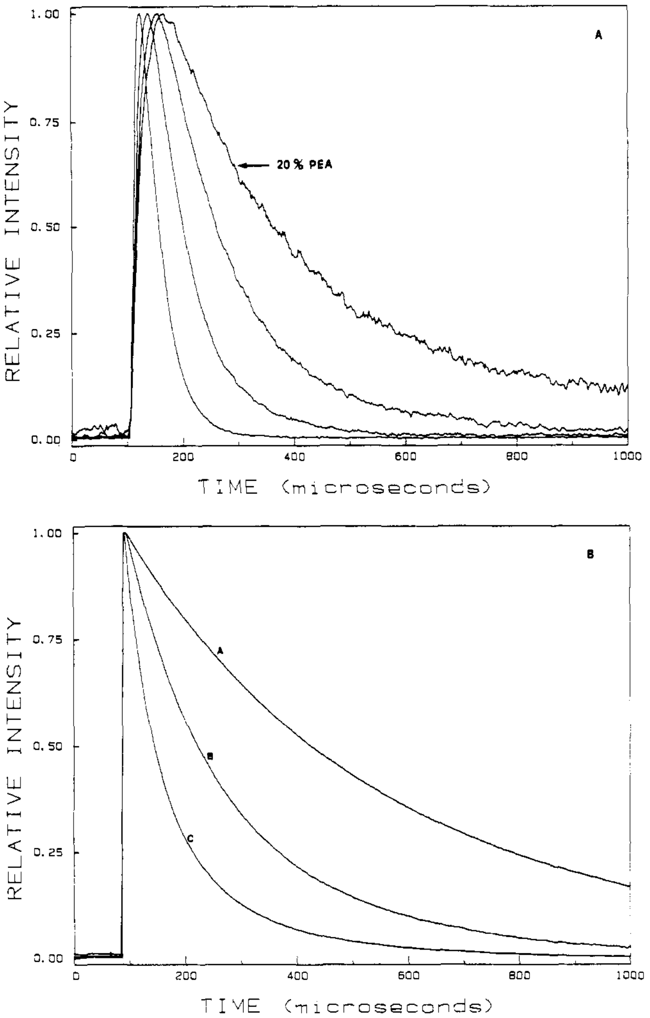


Figure 4. (A) Time-resolved $^1\Delta_gO_2$ phosphorescence signal as a function of percent ethyl acrylate content in aerated PMMA–PEA copolymers containing 1.4×10^{-4} M phenazine. The data have been rescaled to make all peak signal amplitudes equivalent. Signals correspond to the following PEA:PMMA ratios: 70:30, 40:60, 30:70, 20:80. (B) Time-resolved phenazine triplet absorption signal from the PMMA–PEA copolymers. Traces (scaled to make all signal amplitudes equivalent) correspond to the following PMMA:PEA ratios: (A) 100:0, (B) 80:20; (C) 60:40.

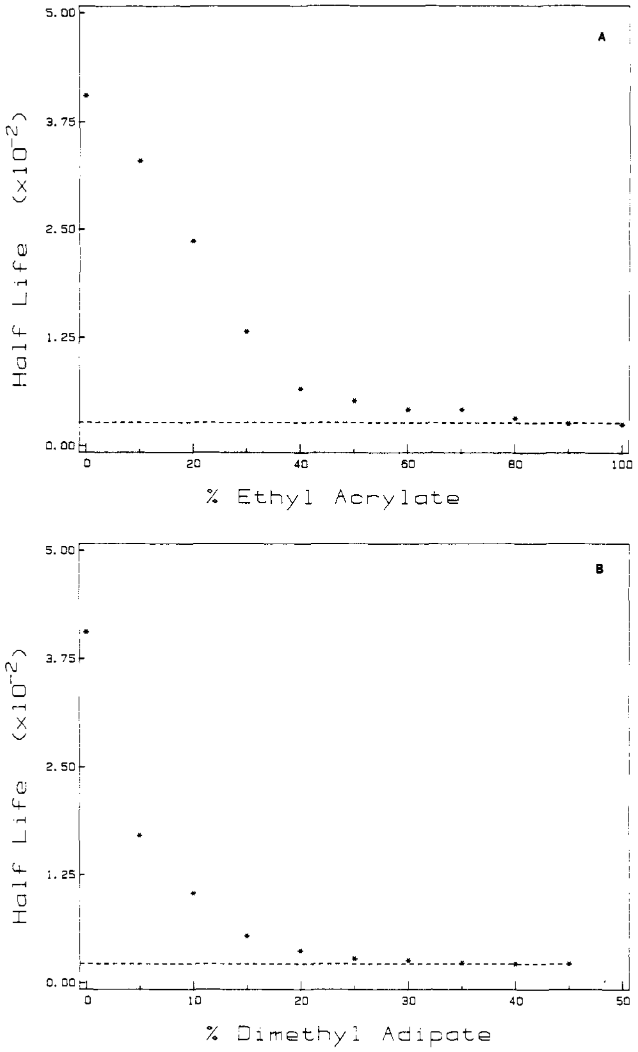


Figure 5. (A) Manifest singlet oxygen ($^1\Delta_gO_2$) signal decay half-life (in microseconds) as a function of percent ethyl acrylate in the PMMA–PEA copolymers. The dashed line represents the $^1\Delta_gO_2$ half-life in a liquid ester analogue, methyl propionate ($\tau_{1/2}$ = 27 μs; τ_Δ = 38 ± 2 μs). (B) Manifest singlet oxygen ($^1\Delta_gO_2$) signal decay half-life (in microseconds) in PMMA samples, as a function of percent dimethyl adipate dissolved in the matrix. The dashed line represents the $^1\Delta_gO_2$ half-life in a liquid solution of dimethyl adipate ($\tau_{1/2}$ = 22 μs; τ_Δ = 32 ± 2 μs). Analogous data were recorded for the solute diphenyl ether in PMMA.

host matrix.[8] In these two polymers, the concentration of sp^3 C–H bonds is identical. However, the two polymers exhibit very different physical properties. A matrix comprised of PMMA is rigid and glassy; whereas, a matrix of PEA is elastic (i.e., rubbery and malleable). Copolymers of MMA and EA exhibit properties ranging between the two extremes.

Time-resolved $^1\Delta_gO_2$ phosphorescence signals and phenazine triplet state absorption signals were recorded from 25 °C PMMA–PEA copolymers prepared with differing amounts of EA. As the percentage of EA in the copolymer increased and the sample became less glassy, (1) the rates of $^1\Delta_gO_2$ signal appearance and disappearance increased, (2) the $^1\Delta_gO_2$ decay kinetics approached first order, and (3) the rate of triplet sensitizer decay increased and also approached the first-order limit (Figures 4 and 5a). Thus, trends in the isothermal copolymer data complement those in the temperature-dependent PMMA data (vide supra).

Low Molecular Weight Diluent Studies. PMMA samples were prepared containing varying amounts of a low molecular weight organic compound dissolved in the polymer, which caused plasticization of the matrix.[23] Time-resolved $^1\Delta_gO_2$ phosphorescence signals and phenazine triplet-state absorption signals were recorded from 25 °C samples containing differing amounts of either dimethyl adipate or diphenyl ether. As the percentage of the diluent molecule incorporated into the PMMA matrix increased and the sample became less glassy, trends in the time-resolved data analogous to those found in both the temperature and copolymer studies were recorded (Figure 5B).

Polymer Deuteration Study. Time-resolved $^1\Delta_gO_2$ phosphorescence signals and phenazine triplet state absorption signals were recorded from both poly(styrene) and perdeuteriopoly(styrene) samples at 25 °C (Figure 6). Although the triplet state decay rates were approximately equal in the two matrices, the rates of $^1\Delta_gO_2$ signal appearance and disappearance were each substantially slower in the perdeuterated matrix.

Discussion

(A) The Rate Constant for Intrinsic $^1\Delta_gO_2$ Decay in a Solid Polymer. In a photosensitized reaction, the time-dependent behavior of the experimentally observed (or *manifest*) $^1\Delta_gO_2$ phosphorescence signal is necessarily a convolution of the *intrinsic* $^1\Delta_gO_2$ decay function and the decay function of the immediate precursor to $^1\Delta_gO_2$, the

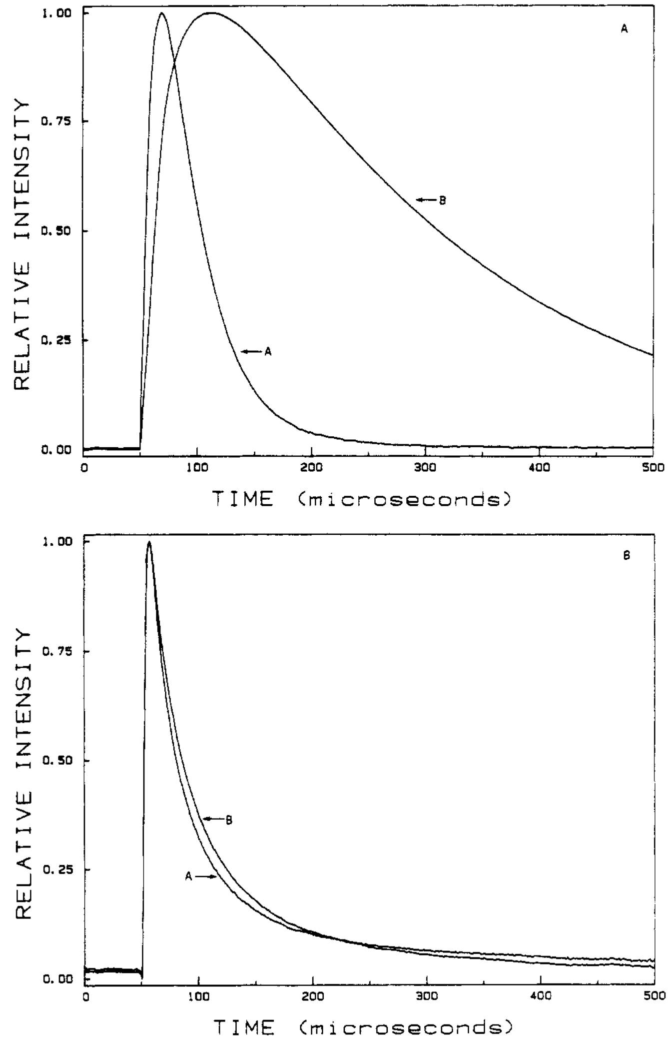


Figure 6. (A) Time-resolved $^1\Delta_gO_2$ phosphorescence signal from aerated samples of (A) poly(styrene) containing 1.6 × 10^{-4} M phenazine and (B) perdeuteriopoly(styrene) containing 1.1 × 10^{-4} M phenazine. (B) Time-resolved phenazine triplet absorption signals from the same air-equilibrated samples.

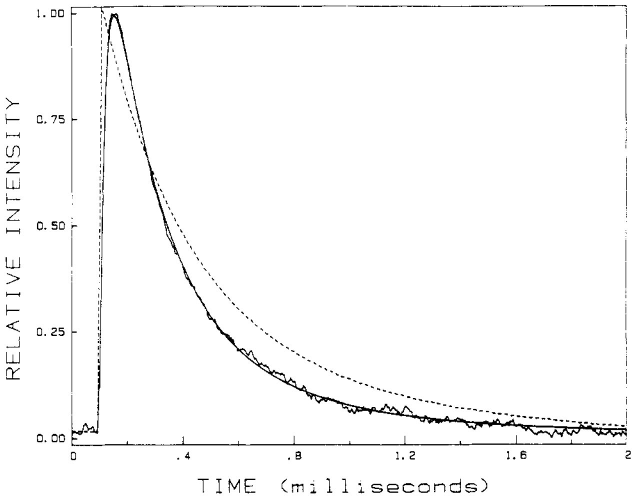


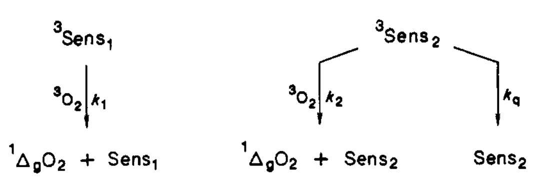
Figure 7. Examples of the triplet flash absorption signal (- - -) and the manifest $^1\Delta_gO_2$ phosphorescence signal (—) in a 25 °C PMMA sample 1.7 × 10^{-4} M in phenazine. An iterative solution for the convolution of an intrinsic $^1\Delta_gO_2$ decay function and the sensitizer decay function, incorporating the Geacintov model (see text), yields the fitting function shown as the solid line on the $^1\Delta_gO_2$ data. Note the apparent "crossover point" between the triplet absorption signal and the $^1\Delta_gO_2$ signal.

excited-state sensitizer. For aerated liquid solutions, the decay rate of the $^1\Delta_gO_2$ precursor is substantially faster than that of $^1\Delta_gO_2$ itself.[9,10] Consequently, this convolution results in a $^1\Delta_gO_2$ phosphorescence signal appearance rate which corresponds to the intrinsic rate of $^1\Delta_gO_2$ formation, which, in turn, is equivalent to the total rate of $^1\Delta_gO_2$ precursor decay.[9,10] Under these same conditions, the rate of $^1\Delta_gO_2$ signal disappearance solely reflects the intrinsic process of $^1\Delta_gO_2$ deactivation. The application of simple fitting functions to the rising and falling portions of the manifest $^1\Delta_gO_2$ phosphorescence signal, therefore, yield accurate kinetic information about $^1\Delta_gO_2$ in the liquid, solution phase.[8-10,13] If the relative decay rates of both $^1\Delta_gO_2$ and the sensitizer in a glassy polymer were the same as they are in liquids (i.e., if the rate of sensitizer decay exceeded that for $^1\Delta_gO_2$), then the time-resolved $^1\Delta_gO_2$ phosphorescence signals recorded in our present experiments would indicate that $^1\Delta_gO_2$ (1) has a much longer intrinsic lifetime in a glass than in an appropriate liquid analogue and (2) does not follow first-order decay kinetics. However, in the glassy polymers, the rate of $^1\Delta_gO_2$ precursor deactivation, as measured in the flash absorption experiments of the sensitizer triplet state, corresponds approximately to the manifest $^1\Delta_gO_2$ phosphorescence signal decay rate. Furthermore, temperature, copolymer and low molecular weight diluent dependent changes in the manifest $^1\Delta_gO_2$ phosphorescence signal roughly correlate with changes in the triplet absorption signal. Therefore, unlike data in the liquid phase, we conclude that the decay of the manifest $^1\Delta_gO_2$ phosphorescence signal in solid polymers principally reflects the decay kinetics of the $^1\Delta_gO_2$ precursor, thereby indicating that the intrinsic rate of $^1\Delta_gO_2$ decay is greater than that of the sensitizer. Consequently, information about intrinsic $^1\Delta_gO_2$ kinetics in a polymer glass can only be obtained by deconvoluting the time-dependent behavior of the $^1\Delta_gO_2$ precursor from the manifest $^1\Delta_gO_2$ phosphorescence signal.[24]

The polymer systems under study are simplified if an appropriate sensitizer can be chosen such that $^1\Delta_gO_2$ originates, by energy transfer, from only one sensitizer excited state. Acridine and phenazine are ideal in that the triplet state is the sole $^1\Delta_gO_2$ precursor.[25] Consequently, if the sensitizer triplet state decay is accurately quantified under the conditions in which the $^1\Delta_gO_2$ phosphorescence signal is monitored, it should be possible to use the triplet decay kinetics to analyze the manifest $^1\Delta_gO_2$ signal and isolate a rate constant for the intrinsic $^1\Delta_gO_2$ decay. The decays of triplet acridine and phenazine in a polymer glass do not follow first-order kinetics (Figure 3A). There is extensive documentation in the literature of non-first-order triplet-state decay kinetics for dye molecules dissolved in a solid polymer host.[15,28,30] Although a variety of interpretations have been presented for this observation, we have focused on one specific model in the analysis of our data (vide infra).

In Figure 7, a time-resolved $^1\Delta_gO_2$ phosphorescence signal and a flash absorption signal of the $^1\Delta_gO_2$ sensitizer are presented together. When the data are scaled to the same amplitude, it is clear that the relationship between the observed triplet decay signal and the $^1\Delta_gO_2$ signal is not the same as that expected from the simple convolution of two exponentially decaying functions (the triplet sensitizer decay and the *intrinsic* $^1\Delta_gO_2$ decay).[31,32] Specifically, in Figure 7, there is an apparent "crossover" in the triplet absorption signal and the $^1\Delta_gO_2$ signal. We suggest that the data in Figure 7 can be interpreted within the context of a model presented by Geacintov et al.[30] In analyzing the effect of oxygen on the phosphorescence of a solute dissolved in a solid organic polymer, Geacintov

Scheme I



and co-workers suggested that not all solute molecules may be equally accessible to quenching by oxygen ($^3\Sigma_g^-O_2$). It has been suggested that this phenomenon may be due to a polymer microviscosity that is inhomogeneous.[15,28,30] Similar conclusions have independently been drawn from studies in which dye molecules were deposited in Langmuir–Blodgett films[33] and in which dye molecules were complexed with cyclodextrins.[34,35] Under our conditions, a sum of two independent exponential decay functions accurately represents the triplet absorption data. Therefore, to interpret the results in Figure 7, using Geacintov's model, it is sufficient to represent the triplet-state deactivation as the sum of two independent components (Scheme I). More complex schemes having more numereous components and rate constants could also be presented (giving rise, at the limit, to an infinite sum of exponential decay functions). These latter schemes are also a valid approach to representing the distribution of nonequivalent triplet sensitizer sites in the polymer matrix but would only complicate the task of illustrating our point. $^3Sens_1$ and $^3Sens_2$ are distinguished by a difference in the magnitude of the oxygen quenching channel (i.e., $k_1[^3O_2] > k_2[^3O_2]$). The rate constant k_q may represent either a unimolecular or a bimolecular process that competes with $^3\Sigma_g^-O_2$-induced deactivation of the triplet sensitizer.

On the basis of Scheme I, expressions for the time dependence of both the triplet sensitizer and $^1\Delta_gO_2$ can be derived. As defined in our example, since one of the pathways for triplet sensitizer deactivation does not result in the formation of $^1\Delta_gO_2$, these two expressions will be distinguished, in part, by the relative magnitude of multiplicative preexponential constants. Specifically, when compared to terms in the function for the triplet decay, the corresponding terms in the time-dependent expression for the $^1\Delta_gO_2$ signal will be influenced by a factor that depends on the constants k_1, k_2, and k_q. This can result in an apparent "crossover point" in the observed triplet decay signal and the manifest $^1\Delta_gO_2$ signal. By incorporating the Geacintov model into our deconvolution routine, we are able to accurately fit the manifest time-dependent $^1\Delta_gO_2$ phosphorescence signal (Figure 7). In performing the convolution routine, the rate constants for sensitizer decay obtained from the flash absorption experiment were used as fixed parameters. The preexponential factors (vide supra) and the intrinsic, first-order rate constant for $^1\Delta_gO_2$ decay (k_d) were variables, the magnitudes of which were determined iteratively. Since a reasonable fit to the data in Figure 7 is obtained, we suggest that to a good approximation, the intrinsic decay of $^1\Delta_gO_2$ in this particular polymer sample indeed follows first-order kinetics.[36]

The intrinsic $^1\Delta_gO_2$ lifetimes ($\tau_\Delta = 1/k_d$) thus obtained in the glassy polymers are on the same order as those in liquid-phase analogues. At laser energies and sensitizer concentrations that approximate those used in the polymer experiment, τ_Δ in methyl propionate is ~38 μs. τ_Δ in 25 °C PMMA ranged from ~20 to 25 μs. At 25 °C, τ_Δ in ethyl benzene and PS are ~26 μs and ~17–21 μs, respectively. The fact that $^1\Delta_gO_2$ lifetimes in the polymer appear to be somewhat shorter than in liquid solution may be due, all or in part, to quenchers or processes unique to the polymer matrix (e.g., reencounter with the parent sensitizer and quenching by sample impurities such as unreacted monomer and/or trapped radicals).[40] As the temperature was incremented, τ_Δ in PMMA decreased from a value of ~23 μs at 25 °C to ~16 μs at 80 °C. A less pronounced decrease in τ_Δ was observed as the temperature of a methyl propionate solution was raised to ~80 °C.[22] At this juncture, we cannot categorically attribute this small decrease in τ_Δ in the polymer to a change in the intrinsic rate of $^1\Delta_gO_2$ decay with temperature. Rather, these lifetime changes might be due, for example, to an increase in the magnitude of diffusion coefficients (vide infra) and a corresponding increase in the encounter frequency with a quencher(s). Similarly, to a first-order determination, the intrinsic $^1\Delta_gO_2$ lifetime is independent of the polymer matrix rigidity as established in our copolymer and low molecular weight diluent experiments. Further studies on these issues are in progress.

(B) The Effect of Temperature and Matrix Rigidity on the Manifest $^1\Delta_gO_2$ Phosphorescence Signal. We have indicated that temperature and matrix rigidity dependent changes in the manifest $^1\Delta_gO_2$ phosphorescence signal principally reflect changes in the decay kinetics of the $^1\Delta_gO_2$ precursor, the triplet-state sensitizer. Ground-state oxygen ($^3\Sigma_g^-O_2$) is an excellent quencher of organic triplets.[9,10] Thus, any change in the photophysical system that results in a lower $^3\Sigma_g^-O_2$–sensitizer encounter frequency will result in a longer triplet sensitizer lifetime and, because of the convolution integral discussed above, slower rates of manifest $^1\Delta_gO_2$ signal appearance and disappearance. For the experiments reported in this paper, changes in the $^3\Sigma_g^-O_2$–sensitizer encounter frequency are principally defined by changes in both the $^3\Sigma_g^-O_2$ diffusion coefficient and the $^3\Sigma_g^-O_2$ concentration.

(i) Changes in the Equilibrium Polymer Oxygen Concentration. The effect of $^3\Sigma_g^-O_2$ concentration on $^1\Delta_gO_2$ kinetics in liquid-phase photosensitized reactions has been discussed previously.[9,10,12] Since the lifetime of a triplet state $^1\Delta_gO_2$ precursor in liquids is much shorter than the intrinsic $^1\Delta_gO_2$ lifetime, an increase in $^3\Sigma_g^-O_2$ concentration results in a corresponding increase in the appearance rate of the manifest $^1\Delta_gO_2$ phosphorescence signal.[9,10] The decay rate of the $^1\Delta_gO_2$ phosphorescence signal, however, is independent of $^3\Sigma_g^-O_2$ concentration for a variety of organic liquids at atmospheric pressure.[41] In glassy polymers, however, where the $^1\Delta_gO_2$ precursor lifetime is substantially longer, changes in the sample equilibrium $^3\Sigma_g^-O_2$ concentration change the manifest $^1\Delta_gO_2$ signal appearance *and* disappearance rates as a consequence of the convolution integral discussed above. Also, as the polymer equilibrium $^3\Sigma_g^-O_2$ concentration is increased, the absolute number of sensitizer molecules quenched by $^3\Sigma_g^-O_2$ increases, resulting in a rise in the $^1\Delta_gO_2$ signal intensity.

Upon heating our samples through T_g, we degas the polymer.[39] Time-resolved $^1\Delta_gO_2$ phosphorescence (Figure 1) and triplet absorption (Figure 3) data reflect this change: In samples that have been heated, $^1\Delta_gO_2$ signal intensities at a given temperature are smaller, and $^1\Delta_gO_2$ rise and decay rates, as well as triplet decay rates, are substantially slower. Because the oxygen diffusion coefficient ($D_{25°C}$) in PS is ~60 times larger than in PMMA,[44-47] PS regains its 25 °C equilibrium $^3\Sigma_g^-O_2$ concentration faster than PMMA, and the time required to record $^1\Delta_gO_2$ signals identical in all aspects with those recorded prior to heating is much less for the PS samples.[48]

(ii) Changes in the Oxygen Diffusion Coefficient. In solid organic polymers, the oxygen diffusion coefficient can be as much as 4 orders of magnitude smaller than that in a corresponding liquid.[49] Gas diffusion in polymers is a thermally activated process that involves the movement of polymer segments.[47,53,54] Macromolecular flexibility is affected, in part, by the strength of attractive interactions between adjacent polymer chains (i.e., dipole–dipole or hydrogen-bonding interactions) and the ease of rotation about bonds comprising the chain, as determined by the macromolecular structure. The same molecular features that affect the diffusion coefficient are reflected in macroscopic properties: (1) In a related species of polymers, T_g generally shows an inverse correlation with the diffusion coefficient,[47,55] (2) methyl group substitution along the macromolecular chain is known to result both in a sterically controlled increase in the sample rigidity[56] and a decrease in diffusion coefficients,[47,55] and (3) introduction of a low molecular weight solute molecule in the matrix can decrease attractive interactions between macromolecular chains, enhancing solute diffusion and decreasing matrix rigidity.[47,55]

Therefore, changes in either the matrix rigidity or temperature alter the $^3\Sigma_g^-O_2$ diffusion coefficient and, thereby, affect the $^3\Sigma_g^-O_2$–sensitizer encounter frequency. Thus, on the basis of the convolution integral discussed above, the manifest $^1\Delta_gO_2$ signal appearance and disappearance rates decrease as the polymer sample is made more rigid or as the temperature is lowered, reflecting a decrease in the oxygen diffusion coefficient (Figures 1–5).[57] A clear example of the influence of the oxygen diffusion coefficient on the manifest $^1\Delta_gO_2$ kinetics is provided by data from 25 °C PS and PMMA samples (circled data points in Figure 2; $D_{25\,°C}{}^{PS} \sim 60D_{25\,°C}{}^{PMMA}$).[44–47]

On the basis of our discussion, Arrhenius plots of the triplet sensitizer decay constants should yield apparent activation parameters that reflect the combined processes of $^3\Sigma_g^-O_2$ diffusion and $^3\Sigma_g^-O_2$-induced sensitizer deactivation.[58] For both PS and PMMA, from ~25 to ~75 °C, plots of ln k versus $1/T$ are not linear, exhibiting negative curvature at high temperatures. Similar curvature has been observed previously for other solute photophysical parameters in polymer matrices (e.g., phosphorescence)[54,59–61] and for parameters characteristic of the organic polymer itself (i.e., mechanical and dielectric properties)[62,63] and has been attributed to different kinds of polymer motion that become more favorable as the temperature is raised.[54,59–64] Because the magnitude of the oxygen diffusion coefficient should depend on the nature of these macromolecular motions, it is not surprising that curvature is observed in an Arrhenius plot of our triplet decay data. In PS, this curvature may also be due, in part, to sample degassing resulting in a smaller relative contribution from the $^3\Sigma_g^-O_2$-induced sensitizer deactivation channel at higher temperatures. For a PMMA sample that had been heated from 25 to 50 °C in 1 h, however, the change in $^3\Sigma_g^-O_2$ concentration was less than 10%, as estimated from the $^1\Delta_gO_2$ signal intensity after the sample had been recooled to 25 °C. Therefore, activation energies determined from Arrhenius plots at low temperatures in PMMA, where the data are more nearly linear, should not be influenced substantially by $^3\Sigma_g^-O_2$ concentration changes.

For PMMA, an activation energy of ~7.5 kcal mol^{-1} was obtained from both components of triplet sensitizer decay. Our data are in keeping with those reported in studies of phosphorescence quenching[51,54,59] and luminescence depolarization.[60,61] We have also determined apparent activation entropies ($\Delta S^‡$) of ~−30 eu from these data, which is reasonable if the decay process is dominated by the quenching step in which $^3\Sigma_g^-O_2$ must assume a specific orientation with respect to the sensitizer molecule.[58] This value of $\Delta S^‡$ is comparable with those determined for solution-phase $^1\Delta_gO_2$ quenching reactions, which similarly are expected to have ordered transition states.[65,66] Activation entropies that have been determined for polymer viscoelastic relaxations themselves tend to be positive.[64]

(C) Changes in the Matrix Atomic Composition: Effects of Perdeuteration on Manifest and Intrinsic $^1\Delta_gO_2$ Lifetimes. In the previous sections, we discussed experiments in which the $^3\Sigma_g^-O_2$–sensitizer encounter frequency could be systematically controlled by changing both the $^3\Sigma_g^-O_2$ concentration and the $^3\Sigma_g^-O_2$ diffusion coefficient. In these experiments, the overall matrix atomic and molecular composition were held as nearly constant as possible, and changes found in the manifest $^1\Delta_gO_2$ phosphorescence signal were shown to reflect changes in the $^1\Delta_gO_2$ precursor kinetics. We next wished to study the effect on $^1\Delta_gO_2$ kinetics of varying the atomic composition of the solid macromolecular matrix, while holding variables that are known to influence the $^3\Sigma_g^-O_2$–sensitizer encounter frequency (e.g., matrix rigidity and morphology) as nearly constant as possible.

It has been observed that in liquids, $^1\Delta_gO_2$ has a much longer intrinsic lifetime in solvents that are perdeuterated than in the appropriate protiated analogue.[8] This phenomenon is believed to be principally due to the relative inefficiency of a C-D or O-D bond to act as a sink for the $^1\Delta_gO_2$ excitation energy in a nonradiative deactivation process, which is the principal $^1\Delta_gO_2$ decay channel in the liquid phase.[13,18] Upon deuteration of a host polymer matrix, substantial changes are not expected in the triplet sensitizer decay rate[67] or in the physical properties of the polymer matrix.[68] Thus, such a system meets the desired experimental criteria established above. Data obtained for poly(styrene) and perdeuteriopoly(styrene) are shown in Figure 6. Indeed, the triplet sensitizer decay rate is independent of matrix deuteration (Figure 6B), whereas the manifest $^1\Delta_gO_2$ signal rates of appearance and disappearance are substantially slower in the perdeuterated matrix (Figure 6A). Deconvolution of the triplet sensitizer decay function from the manifest $^1\Delta_gO_2$ signal yields an intrinsic $^1\Delta_gO_2$ lifetime in perdeuteriopoly(styrene) of ~250 μs. Under comparable experimental conditions, the $^1\Delta_gO_2$ lifetime that we measure in liquid toluene-d_8 is 285 ±15 μs. We conclude that the *intrinsic* lifetime of $^1\Delta_gO_2$ in these polymers is controlled, to a first-order determination, by the same host structural parameters as in the liquid phase. In addition, the fact that we can successfully fit manifest $^1\Delta_gO_2$ phosphorescence signals from samples in which the intrinsic lifetime varies over a wide range gives us added confidence that our model, embodied by the convolution integral discussed in section A, adequately represents the photophysics of the oxygen–organic molecule system in solid polymers.

Conclusions

Singlet molecular oxygen ($^1\Delta_gO_2$) has been created by triplet photosensitization in a variety of solid organic polymers. In time-resolved experiments, the phosphorescence of $^1\Delta_gO_2$ and the absorbance of the triplet state sensitizer have been jointly examined as a function of the polymer temperature, matrix rigidity, matrix composition, and sample oxygen ($^3\Sigma_g^-O_2$) concentration. In glassy samples, and at low temperatures, the time-dependent behavior of the experimentally observed (or *manifest*) $^1\Delta_gO_2$ phosphorescence signal is quite different from that observed in liquid analogues, exhibiting long decay times with non-first-order kinetics. As the polymer matrix is made less glassy, however, either by an increase in temperature or through the use of copolymers or low molecular weight solutes, the manifest $^1\Delta_gO_2$ signal appearance and disappearance rates increase and approach rates observed in liquid analogues. We have attributed these changes in the $^1\Delta_gO_2$ phosphorescence signal to changes in the $^1\Delta_gO_2$ precursor decay kinetics which, in turn, depend principally on the $^3\Sigma_g^-O_2$–sensitizer encounter frequency. We have shown that in order to obtain information on *intrinsic* $^1\Delta_gO_2$ lifetimes in glassy polymer matrices, the $^1\Delta_gO_2$ sensitizer decay function must be deconvoluted from the manifest $^1\Delta_gO_2$ phosphorescence signal. Furthermore, we have shown that the convolution integral used must incorporate the concept of nonequivalent sensitizer sites within the polymer matrix. By using this approach, we have determined that *intrinsic* $^1\Delta_gO_2$ lifetimes in glassy polymer matrices are approximately equivalent to those determined in analogous liquids. Thus, $^1\Delta_gO_2$ has an "existence time" in solid polymers that is determined by its precursor lifetime and that can be quite long, despite a relatively short intrinsic $^1\Delta_gO_2$ lifetime. From studies utilizing a perdeuterated glassy polymer matrix, we conclude that the photophysics of $^1\Delta_gO_2$ quenching in the solid phase is controlled by the same molecular structural parameters as in the liquid phase. In ongoing studies, we are making use of the insights gained in this work, and of the model embodied by the convolution integral, to examine the effects of other factors, including reactive functional groups, added quenchers, and different macromolecular structures on $^1\Delta_gO_2$ lifetimes in solid polymer systems.

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Registry No. PMMA, 9011-14-7; PS, 9003-53-6; (MMA)(EA) (copolymer), 9010-88-2; PEA, 9003-32-1; O_2, 7782-44-7; 1,12-benzoperylene, 191-24-2; phenazine, 92-82-0; acridine, 260-94-6.

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(41) The rate constant for $^3\Sigma_g^-O_2$ quenching of $^1\Delta_gO_2$ in the gas phase is $\sim 1.9 \pm 0.5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}.[42] Transformation to solution phase units yields 1.1×10^3 s^{-1} M^{-1}. In a series of solution-phase experiments, we have obtained evidence which suggests that 1.1×10^3 s^{-1} M^{-1} is indeed a reasonable upper limit for the quenching rate constant. Specifically, first-order kinetics were obtained with *oxygen concentration independent* lifetimes when $^1\Delta_gO_2$ decay was monitored in both aerated ($[O_2] \simeq 1.3 \times 10^{-3}$ M) and oxygenated ($[O_2] \simeq 8 \times 10^{-3}$ M) solutions[16,43] of CD_3CN and C_6D_6. [$\tau_\Delta(CD_3CN) = 1.5 \pm 0.1$ ms and $\tau_\Delta(C_6D_6) = 770 \pm 30$ μs.] The rate constant for $^1\Delta_gO_2$ decay can be expressed as the sum of a pseudo-first-order solvent-dependent term[18] and an $^3\Sigma_g^-O_2$ quenching term ($\tau_\Delta{}^{-1} = k_0 + k_q[^3\Sigma_g^-O_2]$). At these oxygen concentrations, our results indicate that the product $k_q[^3\Sigma_g^-O_2]$ is is still too small to influence k_0 when $k_0 \simeq (1.5 \text{ ms})^{-1}$. Recent results of Schmidt and Brauer[12] indicate that k_q may, in fact, be substantially smaller than 1.1×10^3 s^{-1} M^{-1}. In their study, $^1\Delta_gO_2$ decay in CS_2 ($\tau_\Delta \simeq 34$ ms) was found to be oxygen concentration independent. In solvents where $\tau_\Delta \geq 500$ μs, τ_Δ is often limited by other $^1\Delta_gO_2$ quenchers, e.g., the $^1\Delta_gO_2$ sensitizer itself or photolytically created species.[18] Our CD_3CN data were recorded at very low laser energy (0.7 mJ/pulse^{-1} at 355 nm), using a low sensitizer concentration (7×10^{-5} M phenazine). The τ_Δ obtained is larger than those previously reported[8] and, therefore, is likely a more accurate representation of intrinsic solvent-induced quenching in CD_3CN.

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A Lattice Model of the Isotropic Phase to Mesophase Transition of Polymers with Semiflexible Backbone and Flexible Side Chains

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ABSTRACT: The transition temperatures of semiflexible polymers with flexible side chains from an ordered (liquid crystalline) state to the disordered (isotropic) state are calculated based on a lattice model. In order to account for the flexibility of the backbone, a modification of the original approach by Flory is developed. The transition temperatures of a series of poly(3-*n*-alkyl-4-hydroxybenzoate)s are calculated by using this approach. The results agree well with experimental data.

Introduction

The statistical thermodynamics of solutions of stiff chain molecules has been the subject of many investigations.[1–4,16] Although different models were proposed, most of them led to the conclusion that the dominant factor controlling the transition from the isotropic to the liquid crystalline phase is entropical in nature and is determined by the sizes and shapes of the macromolecules.

One of the most used models is the lattice model.[5,6] Although often critically discussed,[20] it has survived because it is very helpful for the calculation of the configurational partition functions of molecules under the con-

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