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# Quenching of Singlet Oxygen in Solid Organic Polymers

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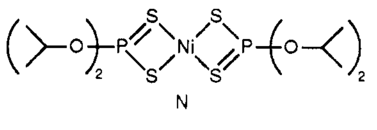
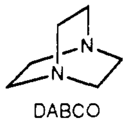
ABSTRACT: The quenching of singlet molecular oxygen (${}^1\Delta_gO_2$) by 1,4-diazabicyclo[2.2.2]octane (DABCO), triphenylamine (TPA), and nickel(II) bis[diisopropyl dithiophosphate] (N) was studied in solid polystyrene (PS) and poly(methyl methacrylate) (PMMA). Quenching rate constants ($k_q$) were determined by monitoring the time-resolved ${}^1\Delta_gO_2$ phosphorescence as a function of quencher concentration in photosensitized experiments. For the efficient quencher N and the moderately efficient quencher DABCO, the rate constants determined in the polymers are smaller than those determined in liquid-phase analogs [$k_q$(PMMA) < $k_q$(PS) < $k_q$(liquid)]. Moreover, the solids have a "leveling effect" on the N and DABCO rate constants, minimizing differences in $k_q$ that are quite pronounced in the liquid. These observations track a decrease in the oxygen diffusion coefficient [$D_O$(PMMA) < $D_O$(PS) < $D_O$(liquid)] and are consistent with a quenching process in the polymer that is principally controlled by solute diffusion to form the ${}^1\Delta_gO_2$–quencher encounter pair. For the poorer quencher TPA, however, where the rate of quenching is determined more by events in the ${}^1\Delta_gO_2$–quencher encounter pair than by solute diffusion, $k_q$(PMMA) > $k_q$(PS) > $k_q$(liquid). These data are consistent with an increase in the number of collisions between the quencher and ${}^1\Delta_gO_2$ in the more rigid solvent cage of the solid polymer. Because differences between $k_q$(polymer) and $k_q$(liquid) will vary greatly as a function of the quencher efficiency, published attempts to define the role of ${}^1\Delta_gO_2$ in a mechanism of polymer degradation may need reinterpretation; specifically, the common practice of comparing values of $k_q$(liquid) with parameters that reflect photodegradation in quencher-doped polymers may be misleading.

## Introduction

The lowest excited electronic state of molecular oxygen, singlet molecular oxygen (${}^1\Delta_gO_2$), can be formed by a variety of methods in gases, liquids, and solid organic polymers.[1-3] The photophysics and photochemistry of ${}^1\Delta_gO_2$ systems have been extensively studied, partly because ${}^1\Delta_gO_2$ is known to participate in the oxygenation of many organic molecules.[4-6] This may be relevant to the important problem of polymer photooxidative degradation.[6b,c] Thus, under conditions where polymer longevity is desired, it may be beneficial to dissolve a ${}^1\Delta_gO_2$ quencher into the material. On the other hand, if a photolabile polymer is needed (e.g., in a degradable plastic bottle), it may be useful to exclude specifically solutes that deactivate ${}^1\Delta_gO_2$. Unfortunately, despite often extensive efforts in the past several decades,[6b,c] very little is known about the kinetics of ${}^1\Delta_gO_2$ quenching in solid organic polymers. This is due, in part, to the limitations imposed by the indirect experimental methods utilized in these complex systems, thus making accurate quantitative assessment difficult. Using a variety of direct spectroscopic techniques, particularly the time-resolved phosphorescence of ${}^1\Delta_gO_2$, we therefore set out to examine the behavior of three ${}^1\Delta_gO_2$ quenchers, 1,4-diazabicyclo[2.2.2]octane (DABCO), nickel(II) bis[diisopropyl dithiophosphate] (N), and triphenylamine (TPA) in both polystyrene (PS) and poly(methyl methacrylate) (PMMA). Although a minor fraction of the N, DABCO, and TPA present in a given system may irreversibly react with ${}^1\Delta_gO_2$, these molecules are principally physical quenchers of ${}^1\Delta_gO_2$.



N



DABCO

Reactions between two solutes in an inert solvent can be represented as proceeding via the intermediacy of a reversibly formed encounter pair.[7a] This is shown schematically in eq 1 for the deactivation of ${}^1\Delta_gO_2$ by a physical quencher (Q). $k_{\rm diff}$ is the rate constant for diffusion-dependent encounter pair formation from separated ${}^1\Delta_gO_2$ and Q.

$$ {}^1\Delta_gO_2 + Q \underset{k_{-\rm diff}}{\overset{k_{\rm diff}}{\rightleftarrows}} {}^1[{}^1\Delta_gO_2\cdots Q] \xrightarrow{k_{\rm isc}} {}^3[{}^3\Sigma_g^-O_2\cdots Q] \rightarrow {}^3\Sigma_g^-O_2 + Q \quad (1)$$

Events within the ${}^1\Delta_gO_2$–Q encounter pair would subsequently result in intersystem crossing ($k_{\rm isc}$) to yield the ground triplet state of oxygen (${}^3\Sigma_g^-O_2$). Similar schemes have previously been used to describe both the physical and chemical quenching of ${}^1\Delta_gO_2$ in liquid solvents.[7b,c]

On the basis of the kinetic scheme in eq 1, providing that the concentration of the encounter pair is small and assuming a steady state, the overall quenching rate constant that would be obtained experimentally is[7a]

$$k_q = \frac{k_{\rm diff}k_{\rm isc}}{k_{-\rm diff} + k_{\rm isc}} \quad (2)$$

and the observed first-order rate constant for ${}^1\Delta_gO_2$ decay in the presence of the quencher is

$$k_{\rm obs} = k_O + k_q[Q] \quad (3)$$

where $1/k_O$ is the intrinsic lifetime of ${}^1\Delta_gO_2$ ($\tau_O$) in the absence of Q.

Given eq 2, two limiting conditions can be identified for the overall deactivation of ${}^1\Delta_gO_2$:[7] (1) when $k_{\rm isc} \gg k_{-\rm diff}$, ${}^1\Delta_gO_2$ quenching will be determined by solute diffusion to form the encounter pair and (2) when $k_{-\rm diff} \gg k_{\rm isc}$, events that occur within the encounter pair will determine the reaction rate. In the former, diffusion-controlled limit, the overall quenching rate constant (eq 2) reduces to

$$k_q = k_{\rm diff} \quad (4)$$

This limit would be characterized by the behavior of very

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efficient $^1\Delta_gO_2$ quenchers. In the latter, so-called reaction[7b] or preequilibrium[7c] limit, the quenching rate constant is

$$k_q = \frac{k_{diff}}{k_{-diff}} k_{isc} = K_p k_{isc} \qquad (5)$$

$K_p$ is the equilibrium constant for $^1\Delta_gO_2$–Q pair formation. The behavior of less efficient or poor $^1\Delta_gO_2$ quenchers is characteristic of this limit.

In the present study, we examine the deactivation of $^1\Delta_gO_2$ in solid bulk polymers where changes in matrix rigidity could significantly influence the reaction kinetics for a variety of quenchers added to the host medium as a solute.

## Experimental Section

The instrumentation and approach used to detect the time-resolved phosphorescence of $^1\Delta_gO_2$ and to perform flash absorption studies at a variety of temperatures are described elsewhere.[8-11] Likewise, our method of bulk free radical polymerization used to prepare solid samples of PS and PMMA with added solutes has been presented.[11] For the present experiments, radical inhibitors were removed from the monomers prior to polymerization by column chromatography with columns marketed by Aldrich specifically for this purpose (Model 30, 631–2 for methyl methacrylate and Model 30, 632–0 for styrene). Molecular weights and polydispersities were determined by using a Maxima Model 820 GPC. Samples prepared by our bulk polymerization technique[11] had molecular weights ($M_w$ = 2.2 × $10^6$ for PMMA and 1.0 × $10^6$ for PS) and polydispersities ($M_w/M_N$ = 2.7 for PMMA and 3.1 for PS) that were independent of quencher concentration. The PS in the mixed PS/toluene study was used as received from Aldrich ($M_w$ = 250 000).

Phenazine (Aldrich) and 2′-acetonaphthone (methyl 2-naphthyl ketone; Aldrich) were recrystallized from ethanol/water. The Rose Bengal derivative (Rose Bengal ethyl ester tetrabutylammonium salt) was prepared by using the method of Lamberts and Neckers.[12] DABCO (Aldrich) was recrystallized from acetone, sublimed, and then stored under nitrogen. N (Custom Chemicals, Livermore, CA), TPA (Aldrich, 98%), tetraphenylporphine (Porphyrin Products, Inc.), and Tinuvin 770 [bis(2,2,6,6-tetramethyl-4-piperidinyl) decanedioate; Ciba-Geigy] were used as received. Toluene and methyl propionate (HPLC grade, Aldrich) were used as received.

## Results and Discussion

**I. Liquids.** $^1\Delta_gO_2$ was produced subsequent to pulsed laser photolysis of a sensitizer (phenazine) in liquid analogs of PS and PMMA: toluene and methyl propionate, respectively. In each case, the time-resolved $^1\Delta_gO_2$ phosphorescence was monitored as a function of added quencher concentration. Because the events that result in $^1\Delta_gO_2$ production in these systems (photolysis, sensitizer intersystem crossing, energy transfer to $^3\Sigma_g^-O_2$) are fast relative to the deactivation of $^1\Delta_gO_2$, the kinetics of $^1\Delta_gO_2$ decay can be obtained directly from examination of the *falling* portion of the time-resolved $^1\Delta_gO_2$ phosphorescence signal.[8,9] A first-order fit to the data yields an observed $^1\Delta_gO_2$ lifetime ($\tau_{obs} = 1/k_{obs}$) which, in turn, can be used to obtain a bimolecular quenching rate constant ($k_q$) for an added solute Q according to eq 3. Representative data for two quenchers are shown in Figure 1. The $k_q$ values thus obtained are listed in Table I. Our results are consistent with published data.[13] Furthermore, values of $k_O$, obtained from the $y$-intercept in plots of eq 3, agree with independently determined values of the $^1\Delta_gO_2$ lifetime in toluene and methyl propionate (29 ± 1 and 39 ± 1 μs, respectively).[10,11]

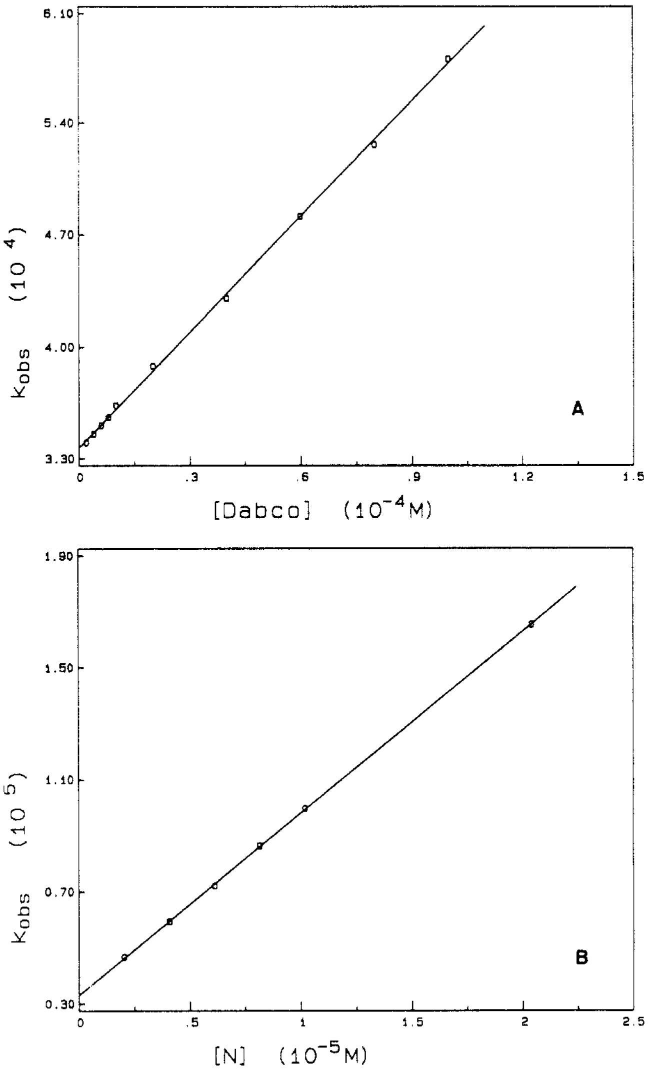


**Figure 1.** Plots of $k_{obs}$ vs quencher concentration (eq 3) in toluene. The quencher was (A) DABCO and (B) N.

**Table I**
**Rate Constants ($k_q$) for Quenching of Singlet Oxygen by DABCO, N, and TPA[a]**

| solvent | $T$ (°C) | quencher | $k_q$ ($s^{-1}$ $M^{-1}$) | $k_q$(N)/ $k_q$(DABCO) |
|---|---|---|---|---|
| toluene | 20 | N | (6.5 ± 0.1) × $10^9$ | 27 ± 1 |
| | | DABCO | (2.4 ± 0.1) × $10^8$ | |
| | | TPA | (1.6 ± 0.1) × $10^5$ [b] | |
| polystyrene | 44 | N | (4.3 ± 0.2) × $10^8$ | 3.9 ± 0.5 |
| | | DABCO | (1.1 ± 0.1) × $10^8$ | |
| | 20 | N | (2.0 ± 0.1) × $10^8$ | 2.2 ± 0.4 |
| | | DABCO | (9 ± 1) × $10^7$ | |
| | | TPA | (3.0 ± 0.4) × $10^5$ [c] | |
| methyl propionate | 20 | N | (6.4 ± 0.1) × $10^9$ | 26 ± 1 |
| | | DABCO | (2.5 ± 0.1) × $10^8$ | |
| poly(methyl methacrylate) | 20 | N | (1.4 ± 0.2) × $10^7$ [d] | 4 ± 1 |
| | | DABCO | (3.5 ± 0.4) × $10^6$ | |
| | | TPA | (6.2 ± 0.5) × $10^5$ [e] | |

[a] Data were compiled from independent experiments in which phenazine [(1–2) × $10^{-4}$ M] and 2′-acetonaphthone [(1–2) × $10^{-2}$ M] were used as sensitizers (except as indicated). [b] Phenazine and the Rose Bengal derivative (2.5 × $10^{-5}$ M) were used as sensitizers. [c] The Rose Bengal derivative (9 × $10^{-5}$ M) was the sensitizer. [d] Tetraphenylporphine (8 × $10^{-4}$ M) and phenazine were the sensitizers. [e] Tetraphenylporphine (8 × $10^{-4}$ M) was the sensitizer.

It is clear from our data that, in toluene and methyl propionate, $k_q$ values for both DABCO and N are independent of solvent. N is an excellent $^1\Delta_gO_2$ quencher with a $k_q$ that approaches the diffusion-controlled limit in a liquid solvent (~3 × $10^{10}$ $s^{-1}$ $M^{-1}$ at 20 °C for reactions between oxygen and a large polyatomic organic molecule).[14] N quenches $^1\Delta_gO_2$ ~27 times more effectively than does

DABCO, whereas TPA is ~4 × $10^4$ times less effective than N and is thus a relatively poor $^1\Delta_gO_2$ quencher. The absolute magnitude of $k_q$(TPA) indicates that the quenching process in this case is almost entirely defined by events in the $^1\Delta_gO_2$–Q encounter pair (i.e., preequilibrium limit).

**II. Solid Polymers.** In solid polymers, where solute diffusion coefficients are smaller than in analogous liquids, the encounter frequency between a triplet sensitizer and $^3\Sigma_g^-O_2$ is comparatively low, resulting in a slower rate of $^1\Delta_gO_2$ formation. In earlier work, we have established that, in air-saturated PS and PMMA samples, the rate of $^1\Delta_gO_2$ formation subsequent to pulsed photolysis of a sensitizer is substantially slower than the decay rate of $^1\Delta_gO_2$.[3,11] Thus, in order to obtain a value for either $k_{obs}$ or $k_O$ (eq 3), it is necessary to deconvolute the decay kinetics of the $^1\Delta_gO_2$ precursor from the experimentally observed (or manifest[11]) time-resolved $^1\Delta_gO_2$ phosphorescence signal.[11] The former data are readily obtained in a flash absorption experiment in which the sensitizer triplet state is monitored. (The sensitizers we have chosen to use have a singlet-state lifetime that is sufficiently short as to preclude quenching by $^3\Sigma_g^-O_2$. Thus, the triplet-state sensitizer is the sole $^1\Delta_gO_2$ precursor.)

PS and PMMA samples were prepared with different concentrations of the $^1\Delta_gO_2$ quenchers DABCO, TPA, and N. In all cases, we were able to observe $^1\Delta_gO_2$ quenching, which became more pronounced as the quencher concentration increased. Furthermore, in a series of triplet-triplet absorption experiments, we ascertained that the decay kinetics of the $^1\Delta_gO_2$ precursor were *not* affected by the addition of DABCO, TPA, or N in aerated samples (Figure 2A).[15] Under conditions where the manifest time-resolved $^1\Delta_gO_2$ phosphorescence signal is a convolution of a slow triplet decay function and a much faster intrinsic $^1\Delta_gO_2$ decay function, quencher-induced changes in the latter will be reflected on both the rising *and* falling portions of the $^1\Delta_gO_2$ signal.[11] Specifically, as the quencher concentration is increased, the rates of $^1\Delta_gO_2$ phosphorescence appearance and disappearance likewise increase, corresponding to an increase in $k_{obs}$ (Figure 2B).

In an early series of experiments, phenazine was used as the $^1\Delta_gO_2$ sensitizer. Although we were able to obtain values of $k_q$ from this system, using eq 3 (Table I), the phenazine was photolabile.[16] Thus, we repeated all experiments, using 2′-acetonaphthone, for example, as the $^1\Delta_gO_2$ sensitizer. In this case, where the sensitizer was photostable, identical values of $k_q$ were obtained (within our error limits), indicating that the photochemistry unique to the phenazine system did not influence data on quencher deactivation of $^1\Delta_gO_2$. As with the aforementioned flash absorption results, in which the triplet sensitizer decay was independent of added quencher, these results also suggest that our data are not a result of unique quencher–sensitizer association phenomena in the polymers.

Values of $k_q$ were also obtained by using the Stern–Volmer approach (eq 6) in which the *intensity* of the time-resolved $^1\Delta_gO_2$ phosphorescence was monitored both in the absence ($I^\circ$) and presence ($I$) of various quencher concentrations.[18]

$$\frac{I^\circ}{I} = 1 + k_q\tau_O[Q] \qquad (6)$$

The Stern–Volmer slopes thus obtained were divided by $\tau_O$, which was, in turn, obtained either by our deconvolution technique[11] or subsequent to photolysis of the polymer–oxygen charge-transfer absorption band.[3] In the latter, deconvolution of the $^1\Delta_gO_2$ precursor decay kinetics from the manifest $^1\Delta_gO_2$ phosphorescence signal is not required because $^1\Delta_gO_2$ is formed very rapidly in these systems. In all cases, the resultant $k_q$ values were identical (within experimental error) to those determined by using eq 3. It is particularly important to note that, with the exception of the method by which $\tau_O$ is obtained, the techniques used to apply eq 6 do not rely on time-dependent data. Therefore, these latter results corroborate and validate our kinetic model in which we deconvolute the decay rate of the $^1\Delta_gO_2$ precursor from the manifest $^1\Delta_gO_2$ phosphorescence signal (eq 3).[11]

For all quenchers in the solid polymers, plots of $k_{obs}$ vs [Q] were linear over a large quencher concentration range (Figures 3 and 4). For the more efficient quencher N and moderately efficient quencher DABCO, the $k_q$ values thus determined were smaller than those in the analogous liquids (Table I). Furthermore, $k_q$(N)/$k_q$(DABCO) ratios are much smaller in the polymer (i.e., in 20 °C PS, N is only 2 times more effective than DABCO as a $^1\Delta_gO_2$ quencher, whereas in the liquid, N is ~27 times more effective). Thus, for quenching rate constants of this magnitude, the polymer appears to have a "leveling effect." This latter, general observation has been previously reported in studies of $^1\Delta_gO_2$ quenching using indirect methods.[19,20] For the poorer quencher TPA, however, the converse was observed; $k_q$(TPA) values for the polymers were *larger* than that determined in a liquid.

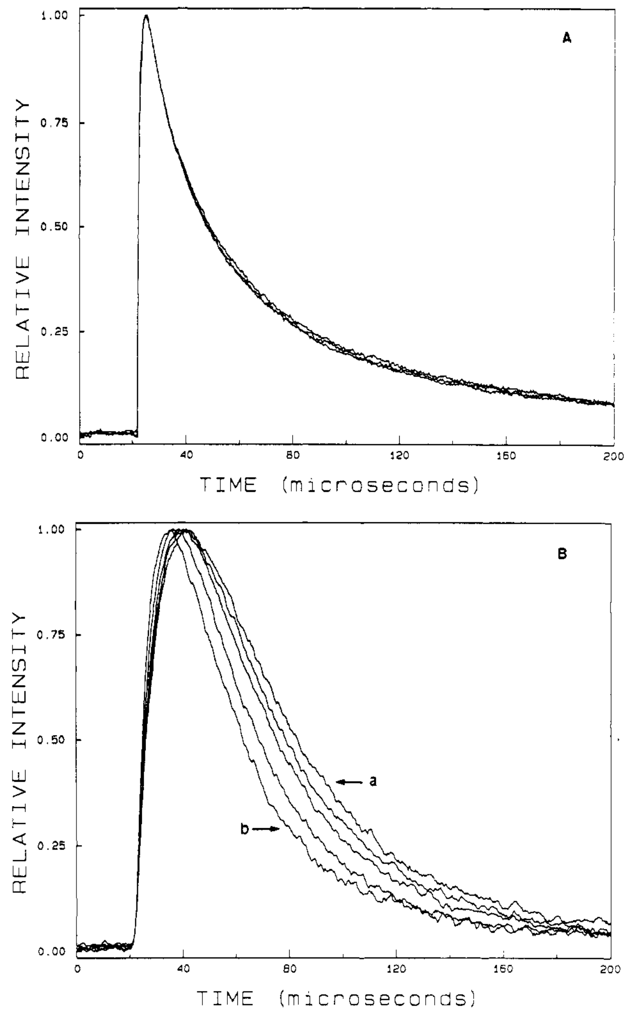


**Figure 2.** (A) Triplet–triplet absorption signals for 2′-acetonaphthone in air-saturated PS as a function of DABCO concentration. The data from three different experiments are shown: no added DABCO, 2.6 × $10^{-4}$ M DABCO, and 1 × $10^{-3}$ M DABCO. (B) Time-resolved $^1\Delta_gO_2$ phosphorescence signals recorded from the system described above. Data from five different experiments are shown in which the DABCO concentration was incremented from 0 (trace a) to 1 × $10^{-3}$ M (trace b).

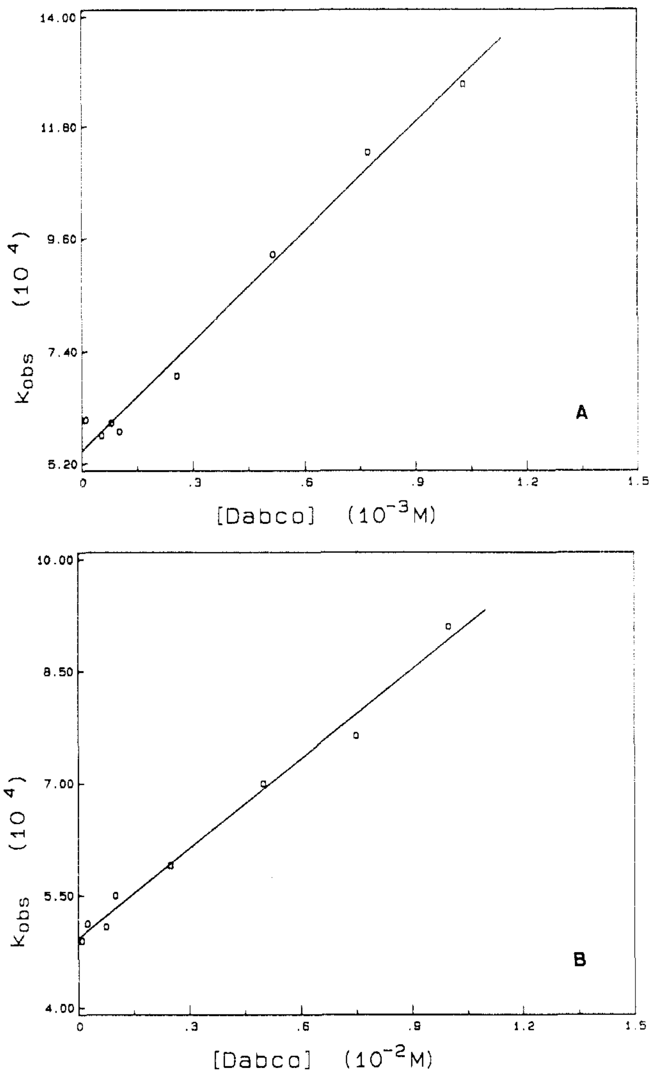


**Figure 3.** Plots of $k_{obs}$ vs DABCO concentration (eq 3): (A) in PS with 2′-acetonaphthone as the sensitizer and (B) in PMMA with phenazine as the sensitizer.

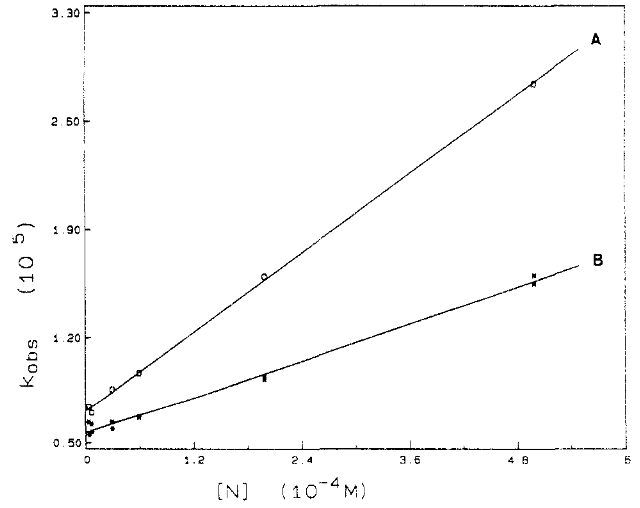


**Figure 4.** Plots of $k_{obs}$ vs N concentration (eq 1) in PS. Data recorded at 44 °C (line A) yield a larger $k_q$ value than data recorded at 20 °C (line B). Data points used to yield the linear least squares fit B were recorded both before and after heating the polymer sample, indicating a reversible process. The increase in $k_O$ ($y$-intercept) with temperature is consistent with published data on the intrinsic $^1\Delta_gO_2$ lifetime.[3]

**Table II**
**Approximate Rate Constant "Reduction Factors" as a Function of Changes in the Host Solvent**[a]

| | experimental data | | | |
|---|---|---|---|---|
| solvent change | $k_q$(N) | $k_q$(DABCO) | $k_q$(TPA) | calcd[b] $k_{diff}$ |
| liquid to PS | 33 | 3 | 0.5 | 350–450 |
| PS to PMMA | 14 | 26 | 0.5 | 10–30 |

[a] Reduction factors were obtained by taking the ratio of the indicated 20 °C rate constants, e.g., $k_q$(liquid)/$k_q$(PS). [b] Rate constant for a diffusion-controlled reaction calculated using eq 7.

**Table III**
**Rate Constants ($k_q$)[a] for Quenching of Singlet Oxygen by DABCO in Toluene/PS Mixtures of Different Viscosity**[b]

| solvent | $k_q$ ($s^{-1}$ $M^{-1}$) × $10^{-8}$ |
|---|---|
| toluene | 2.35 ± 0.09 |
| 2.5 g of PS/100 mL of toluene | 2.46 ± 0.10 |
| 5.0 g of PS/100 mL of toluene | 2.45 ± 0.06 |
| 15 g of PS/100 mL of toluene | 1.87 ± 0.08 |
| PS (44 °C) | 1.1 ± 0.1 |
| PS | 0.9 ± 0.1 |

[a] All data were recorded at 20 °C unless otherwise indicated. [b] Reference 22.

For the efficient quencher N, where $k_q$(liquid) approaches the limit of ~3 × $10^{10}$ $s^{-1}$ $M^{-1}$ (vide supra),[14] we expect that the rate-limiting step for $^1\Delta_gO_2$ quenching in liquids will be determined principally by solute diffusion. Thus, in the transitions from liquid to PS to PMMA, the decrease in $k_q$ values is consistent with a successive decrease in solute diffusion coefficients[21] and a corresponding decrease in the $^1\Delta_gO_2$–quencher encounter frequency. This point is further illustrated by the concentrations of N necessary to achieve any noticeable $^1\Delta_gO_2$ quenching: ~$10^{-6}$ M in liquids, ~1–5 × $10^{-4}$ M in PS, and ~2 × $10^{-3}$ M in PMMA.

In the liquids, DABCO is ~27 times less efficient than N as a $^1\Delta_gO_2$ quencher. Thus, unlike N where solute diffusion is the principal rate-limiting factor, events in the $^1\Delta_gO_2$–DABCO encounter pair are expected to play a comparatively larger role in determining $k_q$. In fact, Gorman et al.[7c] have shown that, in liquid toluene at 20 °C, $k_q$(DABCO) is fully characteristic of a quenching process at the preequilibrium limit (positive Arrhenius slope, negative activation enthalpy for the overall quenching process). Therefore, successive decreases in sample temperature[7c] or increases in solvent viscosity[22] are expected to reduce $k_{-diff}$ and result in an *increase* of $k_q$ until the overall quenching process becomes diffusion limited ($k_{isc} \gg k_{-diff}$), beyond which point $k_q$ will decrease in magnitude, tracking changes in $k_{diff}$. Since the transition from 20 °C liquid toluene to 20 °C solid PS results in a ~3.0-fold *decrease* in $k_q$(DABCO) (Table II), we suggest that the transition from the preequilibrium regime to the diffusion-controlled regime for DABCO quenching occurs at a viscosity intermediate between the liquid and solid. Within our experimental error limits, however, we are unable to discern an initial *increase* in the value of $k_q$(DABCO) for mixed toluene/PS solvents as the concentration of PS in toluene is increased and the solvent becomes more viscous (Table III). Nevertheless, a very clear example of this phenomenon (the expected *increase* in $k_q$ with an increase in solvent viscosity for a quenching process in the preequilibrium regime) is provided by our TPA data and is discussed further below.

If both the "leveling effect" and change in $k_q$ values described above are indeed due to a decrease in solute diffusion coefficients, and if $k_q$(N) and $k_q$(DABCO) in PS are characteristic of diffusion-limited processes, then data recorded from PS at a slightly elevated temperature should give $k_q$(N)/$k_q$(DABCO) ratios that more closely resemble the liquid-phase data. Since solute diffusion is a thermally activated process,[11,23] even small temperature changes should be manifested as an increase in the Q–$^1\Delta_gO_2$ encounter frequency. Indeed, by raising the polymer sample temperature by ~20 °C (thus keeping the system well below $T_g$), quenching rate constants for N and DABCO increase, and the "leveling effect" of the polymer is less pronounced (Figure 4 and Tables I and III).

Changes in the magnitude of the bimolecular rate constant for a diffusion-controlled reaction ($k_{diff}$) can be equated to changes in solute diffusion coefficients using the Smoluchowski relationship (eq 7):[7a,14,24,25]

$$k_{diff} = \frac{4\pi N}{1000}(r_O + r_Q)(D_O + D_Q) \qquad (7)$$

where $N$ is Avogadro's number and $(r_O + r_Q)$ is the critical reaction distance expressed in terms of the radii of oxygen and the quencher, respectively. $D_O$ and $D_Q$ are the corresponding solute diffusion coefficients.[26]

The same procedure used to determine the diffusion-limited rate constant for *encounter* between two reactants (eq 7) can be used to obtain the maximum rate of unimolecular *dissociation* out of a solvent cage.[25b]

$$k_{-diff} = \frac{3(D_O + D_Q)}{(r_O + r_Q)^2} \qquad (8)$$

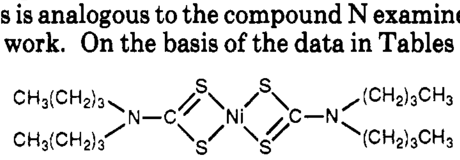
In this case, as the host medium becomes more viscous and diffusion coefficients decrease, $k_{-diff}$ decreases and the number of Q and $^1\Delta_gO_2$ encounters within the solvent cage correspondingly increases. This phenomenon will of course be manifested in the magnitude of $k_q$ when $^1\Delta_gO_2$ quenching is determined by events in the encounter pair (e.g., at the preequilibrium limit, eq 5).

Using eq 7 with $D$ values available from the literature,[21] we estimate that $k_{diff}$ should decrease by a factor of ~400 as the host medium is changed from toluene to PS (Table II). Experimental data reported in Table I indicate that, for this change in solvents, the quenching rate constant for N decreases by a factor of ~33, that for DABCO by a factor of ~3, and that for TPA by a factor of ~0.5 (Table II). Since the quenching of $^1\Delta_gO_2$ by N, DABCO, and TPA in liquids is not limited by diffusion (i.e., $k_q < k_{diff}$), the latter "reduction factors" are indeed expected to be smaller than that determined with the Smoluchowski equation.[25a] Nevertheless, $k_q$(N) in toluene is only ~5 times less than $k_{diff}$ (~$3 \times 10^{10}$ s$^{-1}$ M$^{-1}$)[14] and thus should scale differently with a viscosity change in the host medium than $k_q$ values for the poorer quenchers DABCO and TPA, which are dependent more on $k_{isc}$. Using $D$ values for the solid polymers,[21] we similarly estimate that $k_{diff}$ should decrease by a factor of ~10–30 as the medium is changed from PS to PMMA. The N and DABCO "reduction factors" for this change in solvents are equivalent within our experimental error (14 and 26, respectively) and fall in this range, indicating that these quenching reactions are now indeed fully limited by diffusion. Thus, for these particular molecules, an increase in solvent viscosity causes a change in the rate-limiting step for the quenching of $^1\Delta_gO_2$. Specifically, in the solid state where solute diffusion is slow, the rate of $^1\Delta_gO_2$ deactivation by the relatively efficient quenchers N and DABCO will be determined more by the rate of solute encounter rather than by events that happen in the oxygen-quencher caged pair (i.e., $k_{isc} \gg k_{-diff}$). At this limit, the Smoluchowski equation can be used to adequately predict changes in $k_q$. Of course, the observed "leveling effect" is entirely consistent, indeed expected, within the context of these arguments.

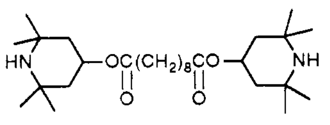
For the poor $^1\Delta_gO_2$ quencher TPA, $k_q$(liquid) is ~$2 \times 10^5$ times smaller than the diffusion controlled rate constant of ~$3 \times 10^{10}$ s$^{-1}$ M$^{-1}$. Thus, the rate of $^1\Delta_gO_2$ quenching in solution is determined by events that occur in the TPA–$^1\Delta_gO_2$ encounter pair. PS is apparently not viscous enough to cause diffusion-dependent encounter between TPA and oxygen to be rate limiting, and the key rate-determining events still occur in the caged complex. Thus, the relatively large decrease in rate constants observed for N and DABCO in the transition from a liquid to a solid solvent system are not seen for TPA. The solid polymer, however, does afford a more inflexible cage. As a result, more TPA–$^1\Delta_gO_2$ collisions will occur in the solid prior to cage escape than will occur in a liquid (eq 8). Consequently, we expect to find an *increase* in $k_q$(TPA) as the medium is changed from toluene to PS (i.e., reduction factor <1.0 (Table II)). This point is further illustrated as the solvent system is changed from PS to PMMA which corresponds to an approximate 10–30-fold decrease in $D_O$. In this case, the data clearly show that $k_q$(TPA) *increases* once again with the increase in solvent viscosity, as expected for a quenching process in the preequilibrium regime.

In their study of $^1\Delta_gO_2$ quenching in polymers, Turro et al.[20] also reported rate constant "reduction factors" for the change from a liquid solvent to solid PS. Unfortunately, their $k_q$(polymer) values were determined by using an indirect technique and reflect a rather large error.[28] This inaccuracy results in reported reduction factors that, in some cases, are too large. For example, 2,5-diphenylfuran (DPF) has a $k_q$(liquid) of ~$8 \times 10^7$ s$^{-1}$ M$^{-1}$,[13] and thus is a slightly poorer $^1\Delta_gO_2$ quencher than DABCO, i.e., the DPF quenching process is closer to the preequilibrium limit than that for DABCO. Thus, on the basis of our discussion above and data in Table II, a transition from liquid to 20 °C PS should yield a DPF reduction factor <3. Of course, if the PS temperature is greater than 20 °C, an even smaller reduction factor is expected. Therefore, the DPF reduction factor of 102 reported by Turro et al. for the change from a liquid solvent to 47 °C PS is clearly too large.

Our results may be helpful in selecting additives for use as stabilizers if $^1\Delta_gO_2$ is believed to play a role in the degradation of a material. For example, a molecule especially designed to be an excellent $^1\Delta_gO_2$ quencher in the liquid phase may be no better as a quencher in a solid polymer than a common, easily prepared and inexpensive molecule. The commercial stabilizer nickel(II) bis(di-*n*-butyl dithiocarbamate) [NBC, DuPont][30] has a $^1\Delta_gO_2$ quenching rate constant of ~$4 \times 10^9$ s$^{-1}$ M$^{-1}$ in solution[31] and thus is analogous to the compound N examined in the present work. On the basis of the data in Tables I and II, this rather exotic compound is expected to be a much less efficient $^1\Delta_gO_2$ quencher in a solid polymer. Conversely, a poor $^1\Delta_gO_2$ quencher in the liquid phase may, in fact, be a more effective quencher in a solid polymer. Tinuvin 770 is a Ciba-Geigy stabilizer used industrially.[32]



NBC



Tinuvin 770

In liquids, we find that it is a very poor $^1\Delta_gO_2$ quencher [$k_q$(toluene) = $(4.2 \pm 0.3) \times 10^4$ s$^{-1}$ M$^{-1}$].[33] However, like TPA, Tinuvin 770 is expected to be a more effective $^1\Delta_gO_2$

quencher in the rigid environment of a solid polymer.[33c] Of course, polymer stabilizers are selected for industrial use on the basis of a variety of different properties and not primarily on their ability to quench $^1\Delta_gO_2$. Depending on the application, an efficient stabilizer may act as a UV filter, a radical trap, or a catalyst to promote decomposition of potentially harmful intermediates.

Our results should be useful in interpreting published studies in which an attempt has been made to define the role of $^1\Delta_gO_2$ in a mechanism of polymer degradation.[6,35–38] Specifically, our data indicate that comparisons between values of $k_q$(liquid) and a parameter that reflects photostability (e.g., embrittlement times) for quencher-doped polymers may be misleading. Because differences between $k_q$(liquid) and $k_q$(polymer) can be large and depend on the absolute magnitude of $k_q$, it is imperative that $k_q$(polymer) be used to interpret longevity data from quencher-doped polymers.

## Conclusions

We have examined the quenching of $^1\Delta_gO_2$ by three molecules, nickel(II) bis[diisopropyl dithiophosphate] (N), 1,4-diazabicyclo[2.2.2]octane (DABCO), and triphenylamine (TPA), in solid polystyrene and poly(methyl methacrylate) and compared our data to those obtained in liquid analogs of the polymers. We find that the bimolecular quenching rate constants ($k_q$) for the relatively efficient quenchers N and DABCO are smaller in the solid media. Moreover, the solids have a "leveling effect" on the N and DABCO quenching rate constants, minimizing differences in $k_q$ that are quite pronounced in the liquids. The N and DABCO data are consistent with a quenching process in the solids that is principally controlled by solute diffusion to form the $^1\Delta_gO_2$–Q encounter pair. For the poor $^1\Delta_gO_2$ quencher TPA, however, the rate of quenching is always determined by events that occur in the $^1\Delta_gO_2$–TPA encounter pair. When compared to a liquid, the solid polymer offers a more inflexible solvent cage for the encounter pair and will thus lead to more $^1\Delta_gO_2$–TPA collisions prior to cage escape. Consequently, at this limit where $k_q$(liquid) is less than approximately $5 \times 10^5$ s$^{-1}$ M$^{-1}$, an *increase* in the rate constant for $^1\Delta_gO_2$ quenching is expected on going from a liquid to a solid polymer. These results can influence the criterion by which additives are selected for use as polymer stabilizers. We have recently extended our $^1\Delta_gO_2$ quenching studies in polymers to include molecules that chemically react with $^1\Delta_gO_2$. These data will be reported in a future communication.[39]

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## References and Notes

(1) Rosenthal, I. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. I, pp 13–38.

(2) (a) Scurlock, R. D.; Ogilby, P. R. *J. Am. Chem. Soc.* **1988**, *110*, 640–641. (b) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1989**, *93*, 5493–5500.

(3) Ogilby, P. R.; Kristiansen, M.; Clough, R. L. *Macromolecules* **1990**, *23*, 2698–2704.

(4) Frimer, A. A., Ed. *Singlet Oxygen*; CRC Press: Boca Raton, FL, 1985; Vols. 1–4, and references cited therein.

(5) Wasserman, H. H., Murray, R. W., Eds. *Singlet Oxygen*; Academic Press: New York, 1979, and references cited therein.

(6) (a) Ranby, B.; Rabek, J. F. *Singlet Oxygen: Reactions with Organic Compounds and Polymers*; Wiley: New York, 1978, and references cited therein. (b) Ranby, B.; Rabek, J. F. *Photodegradation, Photooxidation, and Photostabilization of Polymers*; Wiley: New York, 1975. (c) Rabek, J. F. In ref 4, Vol. IV, pp 1–90, and references cited therein.

(7) (a) Rice, S. A. Diffusion-Limited Reactions. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Compton, R. G., Eds.; Elsevier: New York, 1985; Vol. 25. (b) Stevens, B. *Acc. Chem. Res.* **1973**, *6*, 90–96. (c) Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 8053–8059.

(8) (a) Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1987**, *91*, 1611–1617. (b) Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1988**, *92*, 5854.

(9) Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1988**, *92*, 4662–4666.

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

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

(12) Lamberts, J. J. M.; Neckers, D. C. *Tetrahedron* **1985**, *41*, 2183–2190.

(13) Wilkinson, F.; Brummer, J. G. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809–999.

(14) Ware, W. R. *J. Phys. Chem.* **1962**, *66*, 455–458.

(15) Rates of triplet state decay in nitrogen-saturated samples were over 1 order of magnitude slower than those in air-saturated samples, a result that is consistent with quenching by oxygen. The data in Figure 2A also indicate that the added quencher does not plasticize the sample, and therefore does not change the rate of sensitizer quenching by oxygen. As in our previous studies,[11] the triplet-state decay did not follow first-order kinetics even in aerated samples. These data are expected under conditions where the sensitizer molecules occupy a distribution of nonequivalent sites in the polymer matrix.

(16) Phenazine is an aromatic heterocycle that we have used extensively as a photosensitizer in our liquid-phase studies. It has a short singlet-state lifetime, a high intersystem crossing quantum efficiency, and a high quantum yield of $^1\Delta_gO_2$ production. Although phenazine (and the similar molecule acridine) are photochemically reactive under certain conditions,[17] we find them to be quite stable in both toluene and methyl propionate under the conditions we use to record $^1\Delta_gO_2$ data. This includes experiments in which DABCO or N are added as cosolutes. In aerated solid polymers, however, particularly PS, photolysis of phenazine results in changes in the (1) ground-state absorption spectrum, (2) flash absorption spectrum, and (3) decay kinetics of the transients that give rise to the flash absorption spectrum. These observations are more pronounced in the presence of DABCO and in the absence of oxygen. Furthermore, microcrystalline regions begin to appear in phenazine-doped PS samples that have been allowed to sit in a dark drawer for several weeks at 20 °C. We encountered none of these problems with 2′-acetonaphthone in an air-saturated polymer. We are presently unable to provide a definitive explanation for the phenomena described above.

(17) (a) Whitten, D. G.; Lee, Y. J. *J. Am. Chem. Soc.* **1971**, *93*, 961–966. (b) Davis, G. A.; Gresser, J. D.; Carapellucci, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 2179–2182. (c) Iwaoka, T.; Niizuma, S.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2786–2795.

(18) Time-resolved $^1\Delta_gO_2$ phosphorescence signals obtained under conditions of identical sensitizer concentration and photolysis laser power were integrated to yield values of $I$ and $I°$.

(19) Bystritskaya, Y. V.; Karpukhin, O. N. *Vysokomol. Soyod.* **1976**, *A18*, 1963–1970.

(20) (a) Turro, N. J.; Chow, M.-F.; Blaustein, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 7110–7112. (b) Turro, N. J.; Chow, M.-F.; Blaustein, M. A. *J. Phys. Chem.* **1981**, *85*, 3014–3018.

(21) $D_Q$(liquid) $\sim 2 \times 10^{-5}$ cm$^2$ s$^{-1}$. In the solid polymers, quencher diffusion is negligible relative to diffusion of the smaller, more mobile oxygen molecule. Literature values of $D_O$ can differ from each other by as much as 1 order of magnitude.[11] Even with such a large error, the data clearly indicate that diffusion coefficients decrease as the solvent is changed from a liquid to PS to PMMA, respectively. The numerical factors that we cite and/or use for relative changes in $D_O$ were obtained by taking an average of literature data: $D_O$(liquid) $\sim 5 \times 10^{-5}$ cm$^2$ s$^{-1}$; $D_O$(PS) $\sim 2 \times 10^{-7}$ cm$^2$ s$^{-1}$; $D_O$(PMMA) $\sim 1 \times 10^{-8}$ cm$^2$ s$^{-1}$.

(22) Our use of the word "viscosity" can potentially be misleading since viscosity represents a macroscopic phenomenon. The events described in this report depend on the local environment (microviscosity) of $^1\Delta_gO_2$ and the quenchers.

(23) (a) Stannett, V. In *Diffusion in Polymers*; Crank, J., Park, G. S., Eds.; Academic Press: London, 1968; pp 41–73. (b) Hopfen-

berg, H. B.; Stannett, V. In *The Physics of Glassy Polymers*; Haward, R. N., Ed.; John Wiley: New York, 1973; pp 504–547.

(24) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, 1985; pp 56–58.

(25) (a) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper and Row, Inc.: New York, 1987; pp 212–217. (b) Gardiner, W. C. *Rates and Mechanisms of Chemical Reactions*; W. A. Benjamin, Inc.: Menlo Park, 1972; pp 165–170. (c) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*; Dover: New York, 1963; pp 59–62.

(26) Equation 7 is the time-independent Smoluchowski expression. In the period immediately after initiation of the reaction, the Smoluchowski rate coefficient is much larger than that shown in eq 7 and is time-dependent due to a transient $^1\Delta_gO_2$ concentration around the quencher that is in excess of the ultimate steady-state $^1\Delta_2O_2$ concentration gradient found at longer times. The time-dependent Smoluchowski rate coefficient is[7a,27]

$$k(t) = \frac{4\pi N}{1000}(r_O + \mathrm{r_Q})(D_O + \mathrm{D_Q})\left[1 + \frac{(r_O + r_Q)}{\{\pi(D_O + D_Q)t\}^{1/2}}\right] \qquad (7a)$$

and the maximum value can by approximated by[27]

$$k_{q,\max} = \frac{4\pi N}{1000}(r_O + r_Q)(D_O + D_Q)\left[1 + \frac{(r_O + r_Q)}{\{2(D_O + D_Q)\tau_O\}^{1/2}}\right] \qquad (7b)$$

for a quenching process that has no appreciable electrostatic interactions.Under our conditons, the correction factor given in eq 7b represents a change of ~5–10% in the magnitude of eq 7.

(27) (a) Yquerabide, J.; Dillon, M. A.; Burton, M. *J. Chem. Phys.* **1964**, *40*, 3040–3052. (b) Mullin, C. R.; Dillon, M. A.; Burton, M. *J. Chem. Phys.* **1964**, *40*, 3053–3058.

(28) Factors which, in part, contribute to the errors in the $k_q$(polymer) values reported by Turro[20] are inaccurate values of the $^1\Delta_gO_2$ lifetime used in the data analysis. Specifically, Turro used $\tau_O$ values of 135 and 430 μs for PS and PMMA, respectively. We have shown, however, using direct, time-resolved spectroscopic techniques that more accurate $\tau_O$ values are ~20 and 22 μs for PS and PMMA, respectively.[3,11,29]

(29) Ogilby, P. R.; Dillon, M. P.; Gao, Y.-P.; Iu, K.-K.; Kristiansen, M.; Taylor, V. L.; Clough, R. L. *Adv. Chem. Ser.*, in press.

(30) Reference 6b, p 404.

(31) Monroe, B. M. In ref 4, Vol. I, pp 177–224.

(32) Klemchuk, P. P. In *Oxidation Inhibition in Organic Materials*; Pospisil, J., Klemchuk, P. P., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. I, pp 11–32.

(33) (a) In the polar solvent acetonitrile, we determined $k_q$(Tinuvin) = $(3.5 \pm 0.2) \times 10^5$ $s^{-1}$ $M^{-1}$. This value is approximately 1 order of magnitude larger than that obtained in toluene. Our acetonitrile data are consistent with those from a recent indirect study in which $k_q(CHCl_3) = 2 \times 10^5$ $s^{-1}$ $M^{-1}$ was reported for Tinuvin 770.[33b] The observed increase in $k_q$ with solvent polarity is consistent with a quenching process facilitated by an increase in the amount of charge-transfer character ($Q^{\bullet +}O_2^{\bullet -}$) in the quencher–oxygen encounter pair. This phenomenon is discussed in greater detail elsewhere.[34] (b) Pan, J.-Q. *Polym. Deg. Stab.* **1991**, *32*, 219–229. (c) It is likely that Tinuvin 770 quenches $^1\Delta_gO_2$ by a combination of physical and chemical mechanisms.[33d] This does not alter the arguments presented. (d) Grassie, N.; Scott, G. *Polymer Degradation and Stabilization*; Cambridge University Press: Cambridge, 1985; pp 161–162.

(34) Kristiansen, M.; Scurlock, R. D.; Iu, K.-K.; Ogilby, P. R. *J. Phys. Chem.* **1991**, *95*, 5190–5197.

(35) Carlsson, D. J.; Suprunchuk, T.; Wiles, D. M. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 61–65.

(36) (a) Allen, N. S.; Chirinos-Padron, A.; Appleyard, J. H. *Polym. Deg. Stab.* **1984**, *6*, 31–45. (b) Allen, N. S.; Chirinos-Padron, A.; Appleyard, J. H. *Polym. Deg. Stab.* **1984**, *6*, 149–176.

(37) McKellar, J. F.; Allen, N. S. *Photochemistry of Man-Made Polymers*; Applied Science Publishers, Ltd.: London, 1979; p 235.

(38) Chirinos-Padron, A. J. *J. Photochem. Photobiol., A.* **1989**, *49*, 1–39.

(39) Clough, R. L.; Taylor, V. L.; Ogilby, P. R. Manuscript in preparation.

**Registry No.** PS (homopolymer), 9003-53-6; PMMA (homopolymer), 9011-14-7; DABCO, 280-57-9; N, 30111-46-7; TPA, 603-34-9; $PhCH_3$, 108-88-3; $MeOC(O)CH_2CH_3$, 554-12-1; $O_2$, 7782-44-7; phenazine, 92-82-0; 2′-acetonaphthone, 93-08-3; tetraphenylporphine, 917-23-7; Tinuvin 770, 52829-07-9.