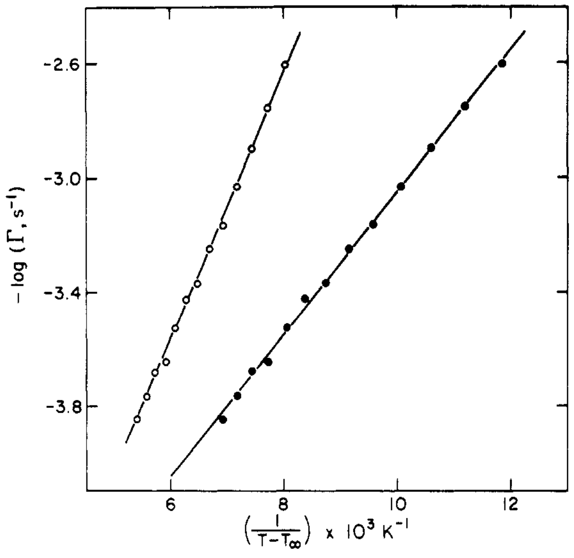

Figure 7. Experimental decay rates correlated with eq 3 for T_∞ = 168.6 K with slope B = 1080 K (○) and for T_∞ = 208.6 K with slope B = 576 K (●). The slopes are obtained by a least-squares fit.

temperature study can be used to distinguish which of the two species has the dominating effect on the mutual diffusion coefficient.

Conclusion

We have observed by photon correlation the q^2-dependent diffusion mode previously reported on mixtures of polystyrene and poly(methylphenylsiloxane) mixtures. For polystyrene molecular weights of 10 200, 12 200 and 17 500, which are substantially larger than the PMPS solvent molecular weight 2 600, the infinite dilution limit $D°$ of the diffusion coefficient extracted from the initial decay of the correlation appears to follow a Stokes–Einstein diffusion mechanism with a molecular weight dependence close to $M^{-0.5}$. In the very small concentration regime of polystyrene studied here, the estimated contribution from the temperature-dependent component of the thermodynamic interaction term is very small and the values of $D/D°$ remain unchanged within experimental error from their values at 50 °C to their values at 65 °C. Since both D and $D°$ vary substantially with temperature but their ratio does not, we have monitored primarily the decrease of the tracer diffusion of polystyrene with concentration. The "hydrodynamic interaction" parameter k describing this decrease appears to have a stronger dependence on molecular weight in this polymeric solvent than the one expected in a small-molecule Θ solvent, possibly due to the entropic component of χ. The temperature dependence of the initial decay rate of the correlation obeys an Arrhenius law at temperature far away from the coexistence curve of the mixture; deviations occur as the coexistence curve and the glass transition temperature are approached. A Vogel-type equation can correlate the temperature dependence of the relaxation time related to the diffusion (Γ^{-1} s) over the entire temperature range studied rather well, but very different sets of parameters appear to give an equally good fit to the experimental data.

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Photophysical Studies of Molecular Mobility in Polymer Films. 1. Oxygen Mobility in Polymer Films Monitored by Quenching of the Triplet–Triplet Absorption of Bromopyrene

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ABSTRACT: Oxygen mobility in several polymer films has been monitored by measuring oxygen quenching of the excited triplet state of film-incorporated bromopyrene observed via its triplet–triplet (T_1–T_n) absorption. Cross-linking did not impose any restriction on oxygen movement in the SU8 epoxy film below the glass transition temperature, and the oxygen quenching rate increases markedly with temperature in an uncured epoxy film; the effect is relatively small in a completely cross-linked film. A significant effect of polymer chain structure on the oxygen quenching rate was observed and a possible mechanism discussed. The quenching rate constants in these polymers increase in the order poly(dimethylsiloxane) ≫ polystyrene > poly(ethyl methacrylate) ≳ cellulose acetate ~ poly(vinyl acetate) > epoxy SU8 film ≳ poly(ethylene terephthalate) (Mylar). The quenching rate constants are much higher than that expected from the bulk macroviscosity of the film and are of the order 10^6–10^9 M^{-1} s^{-1}. Both nitrogen and oxygen plasticize the glassy SU8 film and increase the effectiveness of oxygen quenching; the observed pressure effect is in agreement with the "dual-mode" theory.

Introduction

The molecular motion of low molecular weight solutes in polymer films is of fundamental importance for both kinetic theory and technology. In the technological field an understanding of movement in polymer films has been vital in recent years with the development of a wide variety of packaging films, surface protective coatings, and drug delivering membrane systems. The mobility of oxygen in

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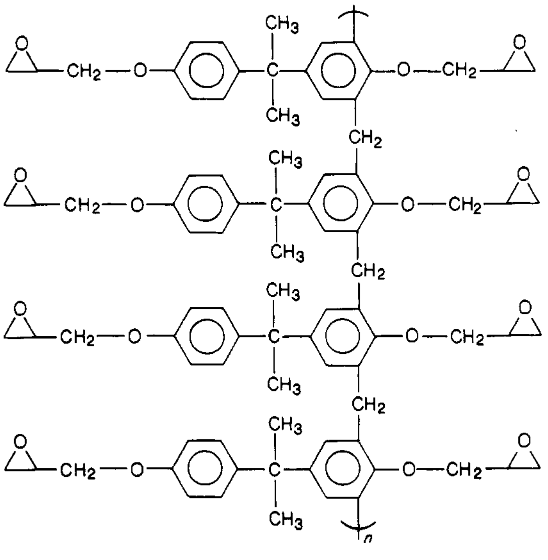
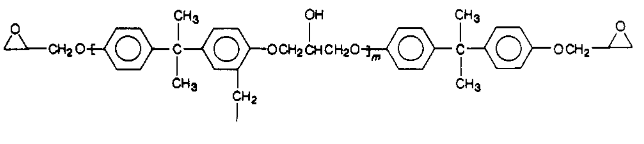
polymer matrices is often the controlling factor during photooxidative degradation and photoprocessing of such materials. The diffusion or movement of oxygen and other small gas molecules is rapid compared with that of the polymer chains and side groups, and the rate of permeation of small molecules is controlled entirely by the matrix. A study of oxygen mobility in polymer films is expected to provide valuable information about the motion and properties of the chains and side groups of the polymer matrix.

Experimental methods for the measurement of the permeability and diffusion of oxygen and other gases have been described previously.[1-3] Most techniques are based on direct measurements of the net flux of material through a polymer film, e.g., the time-lag method. A few indirect methods have also been reported, such as oxygen quenching of fluorescence[4,5] or phosphorescence.[6-9] However, there are severe limitations in the above methods due to the short lifetime of fluorescence or the low quantum yield of spin-forbidden phosphorescence. The method used in the present work monitors the oxygen mobility by measuring oxygen quenching of the excited triplet state of film-incorporated bromopyrene observed via its triplet–triplet (T_1–T_n) absorption. In the absorption spectrum, transitions from the lowest excited triplet state, T_1, to higher excited triplet states, T_n, are spin-allowed and intense.[10-12] The significance of the present studies lies in the convenience of the laser flash photolysis method which is suitable for both elastomeric and glassy polymers. Due to the long lifetime and high quantum yield of excited triplet and the ease of observation[13,14] the oxygen mobility in a wide variety of polymers can be measured. The effects of the experimental conditions and the polymer structures on oxygen mobility and quenching rates are discussed.

Experimental Section

Chemicals. SU8, an epoxy resin (structure as indicated below), was obtained from Interez, Inc., either as a powder or a 70–75 wt % solid solution in methyl isobutyl ketone (molecular weight 5000–7000). The molecular weight increases via polymerization of the octa-functional polymer unit. However, NMR and IR studies show considerable OH functionality in the polymer. Hence, polymerization along the molecule may also occur as shown below.





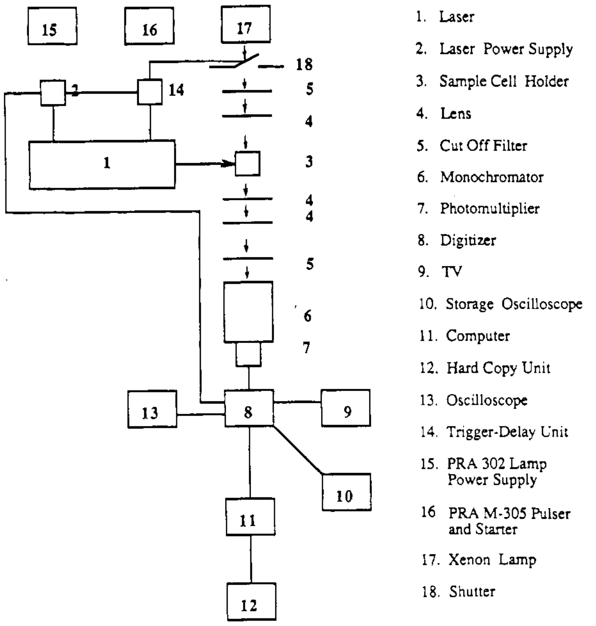


Figure 1. Schematic diagram for laser flash photolysis: (→) light pathway; (—) electrical signal pathway.

Polystyrene of molecular weight 3 × 10^5 and other polymer materials were used as received from Aldrich Chemical Co. or Polyscience, Inc. Poly(ethylene terephthalate) (Mylar, D grade) was supplied by Du Pont in film form. Poly(dimethylsiloxane) and GE UVE 1014 were kindly supplied by General Electric Co. Prepurified nitrogen and oxygen were obtained from Mittler Supply, Inc. Pyrene (Aldrich) and 1-bromopyrene (Alfa) were recrystallized 3 times from methanol. Tris(2,2′-bipyridine)ruthenium(II) chloride (Ru(II), G. Fredrick Smith) was recrystallized twice from deionized water. Perylene (Aldrich), anthracene (Fisher), and 2-naphthalenesulfonic acid sodium salt (Eastman) were used without further purification.

Sample Preparation. Luminescent probes were incorporated into the epoxy resins and other polymers by dissolving both materials in methyl ethyl ketone, toluene, or other convenient organic solvents. Each sample was vortex mixed and cast down onto a Mylar substrate film by using a standard coating rod. After 1 day of air drying, the residual solvent was baked off in a vacuum oven. For an epoxy resin, the usual condition for solvent removal was 40–50 °C for 8 h, unless stated otherwise, and for polystyrene 110 °C for 2 h.

The cured epoxy resin films were made by the following procedure: SU8 films were prepared on Mylar as above, except for those films containing 10 wt % triarylsulfonium salt (General Electric UVE 1014) as photoinitiator. For the sulfonium salt samples, the initiator was added to the SU8 prior to coating the resin on the Mylar substrate. The films were then cured to different degrees by an initial 15-min exposure of 200–400 mJ/cm^2 at 300 nm in a Rayonet photochemical reactor; this was followed by baking at 50–120 °C for 10 min. IR spectra of the films showed that the starting material when exposed to 400 mJ/cm^2 followed by a 120 °C bake was completely cross-linked or cured: the stretching bands of the epoxy ring (860, 910, and 970 cm^{-1}) completely disappear due to the release of epoxy ring strain.[15] Mylar film of 0.003-cm thickness, for the measurement of oxygen quenching, was dipped and equilibrated in a concentrated methanol solution of bromopyrene, until the concentration of bromopyrene in the film, monitored by UV absorption spectrophotometry, reached the order of 10^{-3} M ($\sim 10^{-6}$ mol·g^{-1}); the sample was then washed with methanol, or ethanol, and dried.

Measurements. Steady-state luminescence experiments were carried out by using a Perkin-Elmer MPF 44B spectrofluorimeter equipped with a phosphorescence attachment. Laser photolysis studies employed a Lambda-Physic EMB 100 nitrogen laser (337 nm). Figure 1 shows a diagrammatic sketch of a transient absorption measurement utilizing a Tektronix computer assembly. In T_1–T_n absorption spectroscopy, a 450-W xenon arc lamp is set directly in line with the sample cell holder and monochromator, as an analyzing light source. A trigger unit, which is connected with the xenon lamp, opens the shutter in the front of the xenon lamp. The laser is fired approximately 1, 10, or 100 μs following the lamp trigger to produce the transient species. A tektronix 7704 oscilloscope with a 7D12 M2 sample/hold module records the initial analyzing light intensity, I_0, prior to the laser pulse. The transient species absorbs a fraction of the incident analyzing light then subsequently decays. The absorbance of excited triplet states after time t (at a specific wavelength, e.g., 425 nm for bromopyrene in SU8) can be calculated by $A = \log [I_0/(I_0 - \mathrm{d}v)]$ where dv is the absorbed light intensity by the triplet species. As the concentration of the absorbing triplet state, $[T_1]$, is proportional to the T_1–T_n absorbance value from Beer's law, the observed decay rate constants of excited triplet states, k_{obsd}, can be obtained from the slope of a plot of $\ln \{\log [I_0/(I_0 - \mathrm{d}v)]\}$ versus t.

The quenching rate constant, k_q, is related to an overall observed rate constant by the Stern–Volmer relationship $k_{\mathrm{obsd}} = k_0 + k_q[O_2]$, where k_{obsd} and k_0 are the first-order decay rate constants in the presence and absence of quencher, respectively. If Henry's law is accepted, $[O_2] = SP_{O_2}$, then the slope of the plot of k_{obsd} versus P_{O_2}, the pressure of oxygen in centimeters of mercury gives a product k_qS, where S is the solubility of oxygen in the system (M cmHg^{-1}).

The sample films were mounted at a 45° angle in the cell holder, for both steady-state and laser photolysis experiments, to minimize light scatter from the sample and substrate. Measurements were taken at 20 °C unless stated otherwise.

Complete oxygen diffusion onto or out of epoxy films of thickness about 100 μm requires about 1 h, while polystyrene requires 15 min. Each measurement was taken after equilibrium was reached.

Results and Discussion

Oxygen Quenching of Excited Singlet and Triplet States in SU8. The fluorescence of pyrene, perylene, and 2-naphthalenesulfonic acid sodium salt and the phosphorescence of Ru(II) in SU8 epoxy resin were not quenched by oxygen at 1 atm over the film. This indicates that the diffusion rate of oxygen in the film is low and that k_q is smaller than 10^8–10^7 M^{-1} s^{-1}. This is estimated from the Stern–Volmer equation, $k_{\mathrm{obsd}} = k_0 + k_q[O_2]$. If the concentration of oxygen in the glassy film is $\sim 10^{-3}$ M (typical value for films) and k_0, the natural decay of the excited probe, is $\sim 10^6$ s^{-1}, i.e., the reciprocal of the lifetime of the longest lived probe Ru(II), and as quenching is not observed (k_{obsd}/k_0 is <1.05), then k_q cannot be faster than 5×10^7 M^{-1} s^{-1}.

Oxygen quenching of the excited triplet states, which exhibit lifetimes of the order of several milliseconds to seconds, does occur and is dynamic in character. The mechanism is as follows: $(\mathrm{Py}_{T_1})^* + O_2 \rightarrow \mathrm{Py} + O_2(^1\Delta_2)$.[10,12] Similar data for the quenching rate were obtained by using anthracene and bromopyrene via laser photolysis and by observation of the T_1–T_n absorption. Bromopyrene was chosen as the main triplet probe in the present work due to its photochemical stability during repetitive laser photolysis, whereas anthracene undergoes photooxidation and/or photodimerization.[16] Furthermore, the linear first-order decay of excited triplet bromopyrene and the large molar extinction coefficient of T_1–T_n are desirable properties for the experiment. Figure 2 displays the transient absorption spectra of bromopyrene in the laser flash photolysis of SU8 epoxy film. The band at 425 nm is attributed to the T_1–T_n triplet to triplet absorption[17] and is dominant. The slower decay of the excited triplet in SU8, compared to that in liquid hydrocarbons, is indicative of the rigid environment of bromopyrene in the solid film, thus decreasing the probability of deactivation of the excited triplet via nonradiative and quenching processes.

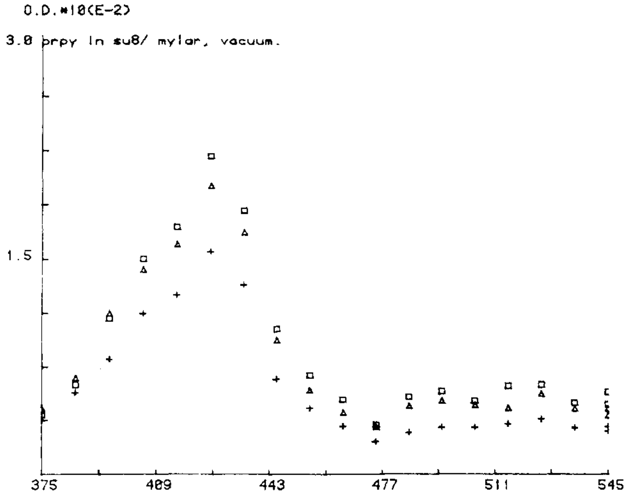


Figure 2. Transient absorption spectra of 4×10^{-6} mol g^{-1} bromopyrene in SU8 film: (□) immediately after laser pulse; (△) 200 μs after laser pulse; (+) 600 μs after laser pulse.

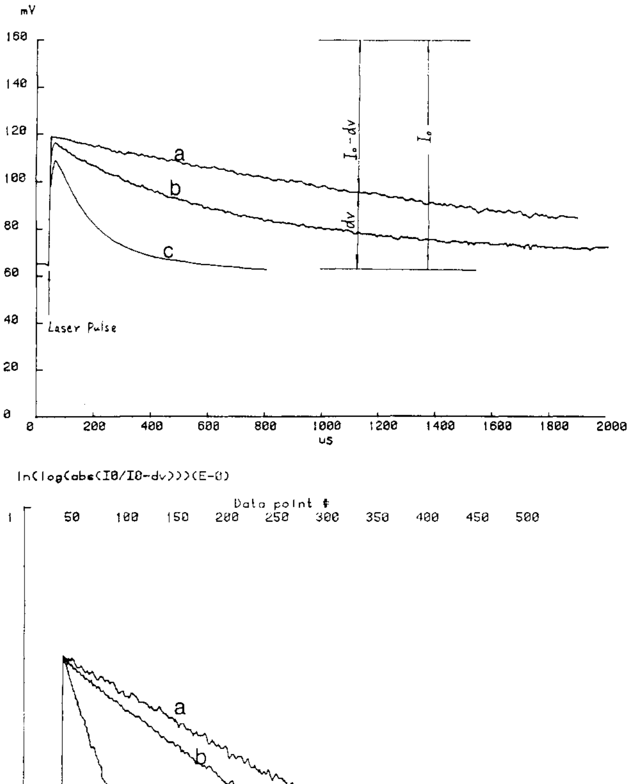


Figure 3. (A) Decay curve of excited triplet bromopyrene in SU8 film, under (a) nitrogen, (b) air, and (c) oxygen. Note: Absorbance of excited triplet = $\log [I_0/(I_0 - \mathrm{d}\nu)]$. The value I_0 and dv in curve a is shown in the figure. (B) First-order decay curve of excited bromopyrene in SU8 film, under (a) nitrogen, (b) air, and (c) oxygen; $\ln \{\log [I_0/(I_0 - \mathrm{d}v)]\}$ versus t.

The time profiles of the triplet state of bromopyrene (monitored at $\lambda = 425$ nm, T_1–T_n band) in SU8 under vacuum, air, and O_2 are shown in Figure 3A. An increasing rate of decay is observed with increasing oxygen concentration, and the quenching is completely dynamic in character. Figure 3B shows the first-order plots of the decay curves from Figure 3A, from which decay rates for the excited triplet state of bromopyrene can be extracted. The observed overall decay rates, k_{obsd}, at a particular

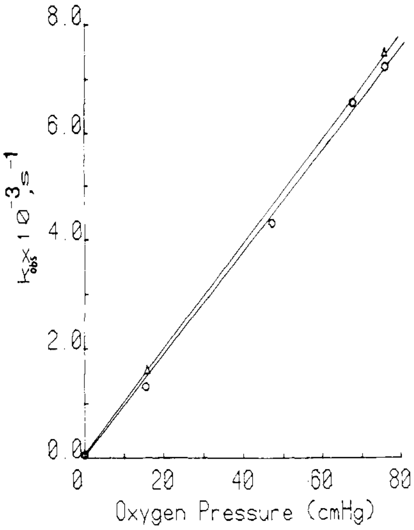


Figure 4. Stern-Volmer kinetic data plot of excited triplet bromopyrene: k_{obsd}, observed decay rate constant versus oxygen pressure: (○) in SU-8 film, dried at 40-50 °C, 8 h; (△) in SU-8 film, dried 1 h at 100 °C following 30-40 °C, 8 h. Note: 15 cmHg oxygen is taken under air condition, zero cmHg either under vacuum or nitrogen.

Table I
Effect of Drying Method on the Oxygen Quenching Rate in SU8

T, °C	$10^{-2}k_qS$, s^{-1} $cmHg^{-1}$ [a]
<40, 24 h	0.88
40-50, ~8 h	0.84
100, 1 h; followed by 30-40, dried 8 h	0.80
dried at ambient conditions, 7 days	0.69

[a] [Bromopyrene] = 6 × 10^{-6} mol g^{-1}.

oxygen pressure are plotted in Figure 4 where the slope of the line gives the second-order rate data for the quenching reaction of the excited triplet bromopyrene with oxygen. The rate data are expressed as k_qS where k_q is the quenching rate constant and S the solubility of oxygen in the film. Identical results were obtained with SU8 films cast either on glass slides or on Mylar film. However, the subsequent cutting of SU8 on Mylar to a required shape is much easier than that with SU8 on glass. Due to its convenience, Mylar was used as a substrate film for laser photolysis experiments. The thickness of the SU8 film does not affect the quenching rate constants measured in pulse studies, but the film thickness does affect the total equilibration time of O_2 within the sample. The thicker films require longer equilibration times for complete oxygen diffusion into the film, and films over 0.005 cm in thickness are not suitable for measurement.

Experimental data show that the oxygen quenching rate is independent of the bromopyrene concentration (0.5-6 × 10^{-6} mol g^{-1}). However, in order to achieve good, noise-free signals, the concentration of bromopyrene used should be greater than 2 × 10^{-6} mol g^{-1}.

The effect of various drying methods and of film cross-linking on the quenching rate of excited triplet bromopyrene by oxygen is given in Table I. Various vacuum-bake methods for drying the films yielded similar results, except the completely ambient dried sample without baking, which gave a 10% lower quenching rate. This indicates that the oxygen quenching is related in some degree to the process of solvent evaporation from the film. Ambient drying of the film is slow and any defects, such as pinholes, made in the film due to solvent evaporation are decreased in this case.

Table II
Effect of Cross-Linking of SU8 on the Quenching Rate

T, °C (measure)	$10^{-2}k_qS$, s^{-1} $cmHg^{-1}$ uncured[a]	cured[b]
20	0.83	0.84
45	4.2	2.1
60	8.8	3.2

[a] T_g ~ 36 °C. [b] Completely cross-linked sample, T_g > 190 °C.

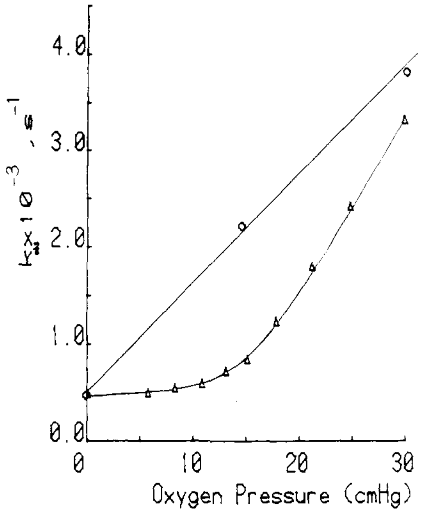


Figure 5. Effect of nitrogen on the plot of k_{obsd} of excited triplet bromopyrene versus oxygen pressure: (△) pure oxygen quenching; (○) total pressure of oxygen and nitrogen = 1 atm. Note: SU8 film was dried at 40-50 °C, 8 h.

Samples with different degrees of cross-linking (see Experimental Section), even the completely crosslinked sample, yielded similar quenching rates at 20 °C (Table II). The lack of restriction imposed cross-linked polymer chains on the oxygen mobility at room temperatre indicates that the mobility of small molecules is independent of segmental motion of the polymer chains. Below the glass transition temperature, SU8 is glassy and segmental chain motion is restricted; however, thermal motion of the methyl groups is not restricted in this condition either in uncured or cured epoxy films. Hence, it is suggested that the slow diffusion of oxygen at room temperature is controlled to some degree by the motion of the SU8 methyl groups. At temperatures above the T_g of uncured SU8, free movement of the polymer chain segments accelerates the movement of oxygen in the SU8 film; the effect is comparatively small in the completely cross-linked film. The phase-transition temperature of the cross-linked sample is over 190 °C. The cross-linked polymer chains impart restriction on mobility of oxygen at high temperatures as shown in Table II. This table indicates that k_qS is increased markedly with temperature in the uncured film but only exhibits a relatively small increase in a completely cross-linked film. Measurements become difficult at high temperature due to a marked decrease in quantum yield of excited triplets. Quenching with larger molecules than oxygen is needed for further studies on the effect of cross-link density on molecular movement in SU8 polymer films.

Abnormal Gas Pressure Effects. Figure 5 shows quenching data for triplet bromopyrene in SU8 at various oxygen pressures below 30 cmHg. The quenching efficiency increases with increasing oxygen pressure. However, addition of an initial high nitrogen pressure to low oxygen pressures markedly increases the efficiency of quenching. It is suggested that the gases plasticize the film. This is

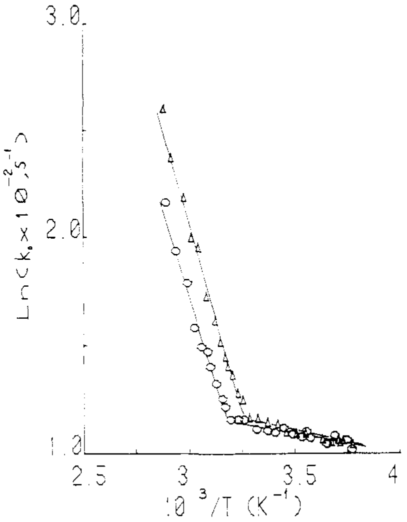


Figure 6. Arrhenius curves for excited triplet natural decay, k_0, of 4 × 10^{-3} M bromopyrene in SU8 film: (O) under vacuum, T_g = 43 °C; (Δ) under 1 atm nitrogen, T_g = 36 °C. Note: the transition temperature under 1 atm of nitrogen corresponds to the T_g measured via differential scanning calorimetry (DSC).

Table III
Comparison of Oxygen Quenching in SU8 with That in Polystyrene

polymer	$10^{-2}k_qS$, s^{-1} $cmHg^{-1}$	k_q, M^{-1} s^{-1}	D_{O_2}, cm^2 s^{-1}	$k_{q(calcd)}$,[a] M^{-1} s^{-1}
polystyrene	51.1	1.7 × 10^8	3.3 × 10^{-7}	1.5 × 10^8
SU8	0.84	5.0 × 10^6	1.0 × 10^{-8}	4.5 × 10^6

[a] $k_{q(calcd)}$ is calculated from steady-state experimental data and the diffusion coefficient, D_{O_2} (see text).

further illustrated by the variation of the natural decay rate constant of excited triplet bromopyrene with temperature. Figure 6 shows the natural decay data plotted in the Arrhenius form. This plot exhibits two linear portions which intersect at a temperature corresponding to the glass transition which is related to segmental motion of the polymer chain. An initial high pressure of nitrogen lowers the glass transition temperature, T_g, fro m 43 °C in vacuum to 36 °c in 1 atm of nitrogen. The polymer, plasticized by nitrogen, promotes nonradiative deactivation of the excited triplet, leading to a lower phase transition temperature.

It is suggested that gases plasticize the SU8 film, leading to an increase in oxygen mobility and solubility, due to an increase in the free volume of the film. The data correspond to the reported "dual-mode" theory, a nonlinear dependence of solubility on the gas pressure below T_g and at low pressure. The present data provide a fruitful method for further studies of the dual-mode theory.[18]

Polystyrene Films. Table III compares oxygen quenching data of the excited triplet bromopyrene in SU8 and polystyrene films. The concentration of oxygen in polystyrene at 1 atm is taken from the literature at 3 × 10^{-3} M[19] but is not available in SU8 (in present studies it is estimated as ~1.3 × 10^{-3} M by using gas chromatography and polystyrene as a standard). The oxygen quenching rate constant, k_q, is about 30 times larger in polystyrene compared to that in SU8 epoxy film. This indicates that the ease of oxygen movement in polystyrene films is much greater than that in SU8 films. The larger oxygen mobility in polystyrene is due to the thermal motion of benzene rings below T_g, which creates more free volume than the motion of the smaller methyl groups in SU8. The low oxygen mobility of SU8 may also be associated with the more polar and rigid structure of SU8 compared to polystyrene. This is borne out by other spectroscopic studies. Figure 7 shows the pyrene fluorescence in SU8 which exhibits a ratio of peak 3 to peak 1, I_3/I_1, of 0.72 compared to 1.1 in polystyrene. The fluorescence lifetime τ_f is shorter in SU8 (232 ns) than in polystyrene (286 ns). This indicates a more polar environment in SU8 compared to that in polystyrene.[14] Intramolecular hydrogen bonding is observed in SU8 film, as a strong band at 3500 cm^{-1} in the IR spectrum, and the band frequency is independent of the thickness of the film.[16] It is suggested that hydrogen bonding of SU8 places a restriction on the movement of oxygen in this film.

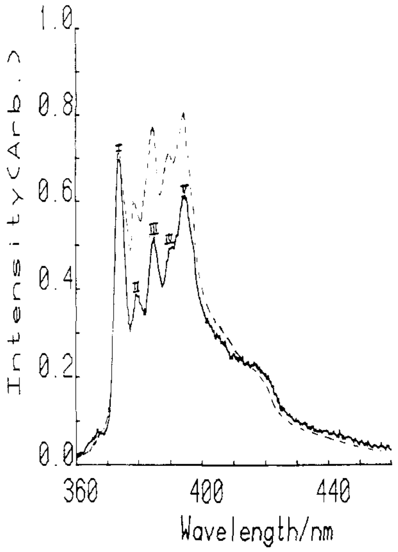


Figure 7. Fluorescence spectrum of 4 × 10^{-1} M pyrene in SU8 (—) and in polystyrene (---) film. Note: in SU8, I_3/I_1 = 0.72, τ_f = 232 ns; in polystyrene, I_3/I_1 = 1.1, τ_f = 286 ns.

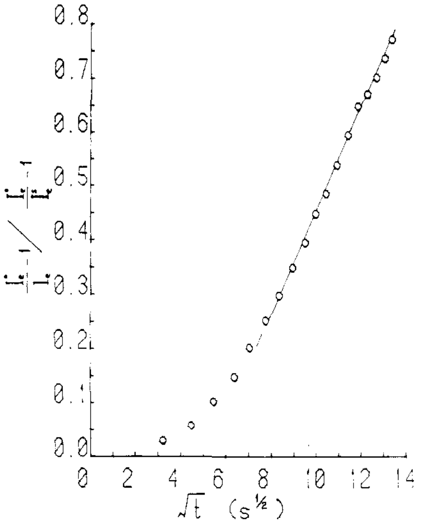


Figure 8. Plot of $((I_e^0/I_e) - 1)/((I_e^0/I_e^s) - 1)$ versus $t^{1/2}$ in SU8 under 1 atm of air.

Pulsed Studies and Steady-State Studies. The diffusion rate constant of oxygen in a film, D_{O_2}, may be obtained from steady-state oxygen quenching of phosphorescence of bromopyrene in the film. The diffusion of a molecule in a film is defined by the equation[5]

$$\left(\frac{I_e^0}{I_e}-1\right)\Big/\left(\frac{I_e^0}{I_e^s}-1\right)=\frac{4}{L}\left(\frac{D_{O_2}t}{\pi}\right)^{1/2}$$

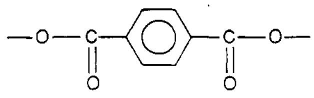
where I_e^0 represents the luminescence intensity in the absence of oxygen, I_e and I_e^s are the luminescence intensity in the presence of oxygen at time t and after saturation equilibrium, D_{O_2} is the diffusion coefficient of oxygen in the film, and L is the thickness of the film. Figure 8 shows a plot of

$$\left(\frac{I_e^0}{I_e}-1\right)\Big/\left(\frac{I_e^0}{I_e^s}-1\right) \text{ versus } t^{1/2}$$

in SU8 film. There is an induction period before the linear portion of the curve is established. This induction period has been related to a nontypical polymer structure in the surface layers of the polymer and also considered as an important feature of case II sorption, due to the swelling of the glassy polymer by penetrant which plasticizes the glass.[20] Since the quenching rate is measured after final equilibration of the oxygen diffusion processes, it is reasonable to use the slope of the linear portion of curve after the induction period. The value of D_{O_2} measured in polystyrene is 3.3×10^{-7} cm^2 s^{-1}, which is in agreement with other reported measurements of 3.1×10^{-7} cm^2 s^{-1}.[19] The D_{O_2} in SU8 is 1.0×10^{-8} cm^2 s^{-1}.

For a diffusion-controlled dynamic quenching process, we can write $k_{\text{diff}} = 4\pi NDR_{AB}/1000$, where k_{diff} is the rate constant from the laser flash photolysis experiment, D is the sum of the diffusion coefficients of reactants (aromatic compound and oxygen), and R_{AB} represents their interaction radius. In the above process, the quenching probability per encounter in assumed as 1. For the oxygen quenching of excited triplet bromopyrene in a glassy polymer, R_{AB} is ~6 Å[21] and the diffusion rate constant of oxygen in the above films, D_{O_2}, can be used as D, as the diffusion rate of the aromatic compound is small compared to that of oxygen. Therefore, $k_{q(\text{calcd})} = 4.53 \times 10^{14}\ D_{O_2}$. The calculated k_q's for polystyrene and SU8 from steady-state measurement are also listed in Table III. The agreement of steady-state experiments and laser photolysis T_1–T_n measurements illustrates that the results of both methods are satisfactory for the monitoring of oxygen mobility in the film. However, the experimental conditions for the steady-state measurement is critical and depends on the film thickness and sample geometry. The laser flash photolysis technique does not require the above conditions and is a more convenient photophysical method.

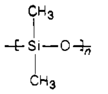
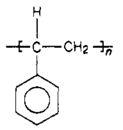
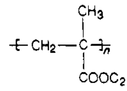
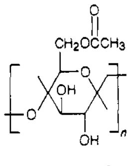
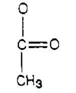
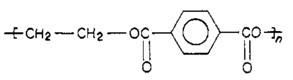
Oxygen quenching rate constants of excited triplet bromopyrene at 20 °C in several polymers, together with their structures, are listed in Table IV. At 20 °C, which is below the glass transition temperature of all the polymers, except for poly(dimethylsiloxane), the polymers are in the glassy state. From the data of k_q, it can be seen that the major factor that affects the oxygen mobility below T_g is the chemical structure of the polymers. There is no relationship of O_2 mobility and the glass transition temperature, T_g. For example, the T_g of polystyrene is ~100 °C, which is higher than that of SU8, while the T_g of poly(vinyl acetate) is ~28 °C, which is lower than that of SU8, however, the oxygen quenching rate constants in these two polymer films are faster than in SU8. The size of the side functional group, polarity, and hydrogen bonding are suggested as major factors that affect solute mobility. For example, hydrogen bonding in cellulose acetate, poly(vinyli acetate), and SU8 leads to small quenching rate constants, while the absence of side groups, e.g., $-CH_3$, $-C_6H_5$, $-O_2CCH_o$, etc., and the presence of the rigid group



$$-O-\underset{\substack{\| \\ O}}{C}-C_6H_4-\underset{\substack{\| \\ O}}{C}-O-$$

leads to the lowest oxygen quenching rate in Mylar, Table IV. The oxygen quenching rate in poly(dimethylsiloxane) is very fast and close to that in a hydrocarbon solvent, such as benzene. It is related to the high chain flexibility around the –Si–O– bond at 20 °C, a temperature above the glass transition and melting point temperatures, and is also due to the weak intermolecular interaction or loose packing of the chains as indicated by the low density.[4] Although the macroviscosity of poly(dimethylsiloxane) is 10^5 orders of magnitude higher than in hydrocarbon solvents, the microviscosity of the polymer, as ascertained by O_2 studies, might be similar to that in a hydrocarbon solvent. The oxygen quenching rate constants in all the polymers are much higher than expected from the bulk viscosities of the films. Further studies of film viscosity effects on oxygen mobility are under way in our laboratory.

Table IV
Oxygen Quenching Rates in Several Polymers

polymer	structure	k_q (20 °C), M^{-1} s^{-1}
poly(dimethylsiloxane)		9.5×10^9
poly(styrene)		1.7×10^8
poly(ethyl methacrylate)		4.6×10^7
cellulose acetate		3.0×10^7
poly(vinyl acetate)		2.6×10^7
SU8 epoxy	see Experimental Section	5.0×10^6
poly(ethylene terephthalate) (Mylar)		3.3×10^6

Summary

Laser photolysis T_1–T_n absorption provides a novel photophysical method for monitoring oxygen mobility in both glassy and elastomeric polymers. The primary requirement on the polymer material to be studied is that bromopyrene probe molecules must be soluble in it. It is possible to use this method to monitor the diffusion processes of other molecules that can quench the excited triplet of bromopyrene.

The oxygen quenching rate presented in this work indicated that the oxygen mobility in polymers below T_g is related to the chemical structure of the polymer, especially the size of side groups, the presence of hydrogen bonding, and also the presence of polar stiffening groups.

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Registry No. Poly(ethylene terephthalate), 25038-59-9; poly(styrene), 9003-53-6; poly(ethyl methacrylate), 9003-42-3; cellulose acetate, 9004-35-7; poly(vinyl acetate), 9003-20-7; SU8,

64112-84-1; 1-bromopyrene, 1714-29-0.

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Excimer Formation of a Naphthalene Diisocyanate Based Polyurethane in Solution

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ABSTRACT: Naphthylcarbamates are shown to form excimers that are stabilized by hydrogen bonding inherent in the participating species. Substitution of a methyl group on the central nitrogen atom of the carbamate moiety severely limits excimer formation. A polyurethane based on 1,5-naphthalene diisocyanate forms intramolecular excimers in dilute solutions of both good and poor solvents; however, excimer formation is significantly enhanced in poor solvents, where intramolecular contact between naphthylcarbamate groups is favored. The photophysics of excimer formation in the polyurethane is interpreted on the basis of an "isolated monomer" scheme. By measurement of the excimer to monomer intensity ratio in pure and mixed solvent systems, the solubility parameter of the polymer is estimated to be between 21 and 22 × 10^3 $(\mathrm{J/m^3})^{1/2}$.

Introduction

Excimers are defined as excited-state complexes between two equivalent species, one of which is in the excited state prior to formation of the complex. Excimers have lower excited-state energies than the monomeric chromophores of which they are comprised and consequently are characterized by a red-shifted emission. Their lifetimes may be longer or shorter than the monomer species from whence they are derived.

Since their discovery in polymeric systems, excimers have continued to be a topic of significant activity. Several excellent reviews of excimer formation in polymer solutions and films have been published in recent years.[1-3] In most of the reports of excimer formation in polymer systems to date, the excimers are comprised of fluorescent species attached as pendant chromophores to the polymer backbone. These polymers are capable of forming excimers between nearest and nonnearest neighbors. In contrast to the large number of reports of excimers formed from pendant fluorescent groups, there are only a few reports of excimers formed between interactive chromophores that are spaced periodically at large distances from each other in the same polymer backbone.[4-11] In addition, there are also some reports of excimer formation between interactive chromophores located at polymer chain ends.[12-14]

We recently reported that polyurethanes based on 1,5-naphthalene diisocyanate form intramolecular excimers between two naphthylcarbamate groups located in the same polymer chain.[10,11] By comparison of the fluorescence decay parameters with model naphthyl carbamates, it was suggested that an "isolated monomer" scheme could account for the complex photophysics of these naphthyl-containing polyurethanes. The extent of excimer formation was found to be related to the intrinsic viscosity of the dilute polymer solutions.[10] In this paper, our earlier work is expanded, and complete details of the effect of solvent on the photophysics of a 1,5-naphthalene diisocyanate based polyurethane is presented. In particular, the ratio of excimer to monomer emission is used to predict the polymer solubility parameter. Additionally, by utilization of model compound studies, it is found that the strong degree of excimer formation between naphthyl carbamate chromophores can be attributed, at least in part, to a hydrogen-bonding effect between participating chromophores.

Experimental Section

Materials. Dichloromethane, 1,2-dichloroethane, *N,N'*-dimethylformamide (DMF), cyclohexane, and benzene were purchased from Burdick and Jackson and used without further purification. Xylene (Baker), toluene (Baker), ethylbenzene (Gold Label, Aldrich), 1-butanol (Aldrich), 1,2-propanediol (Aldrich), 1,4-butanediol (Aldrich), and 2,3-butanediol (Aldrich), were used as received. Propylbenzene (Aldrich) was distilled prior to use. Deionized water was used.

Equipment. Steady-state emission spectra were recorded on a Perkin-Elmer 650-10S fluorescence spectrophotometer. UV spectra were obtained on a Perkin-Elmer 320 UV spectrophotometer. Fluorescence decay curves were obtained on a single-photon-counting apparatus from Photochemical Research Associates. All samples were thoroughly purged with nitrogen prior to fluorescence measurements. The data were analyzed by a

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