Studies of Oxygen Diffusion in Poly(styrene-*co*-1-naphthyl methacrylate) by Phosphorescence Quenching

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ABSTRACT: Measurements of oxygen diffusion in naphthalene-labeled polystyrene films were made at cryogenic temperatures by observations of the kinetics of quenching of naphthalene phosphorescence. Values of the diffusion coefficient D ranged from 3.3×10^{-11} to 2.8×10^{-7} cm^2 s^{-1} at −104 and +23 °C, respectively. The activation energy for diffusion was 7.1 kcal mol^{-1}, which is similar to that observed above room temperature. Static measurements employing the Stern–Volmer equation to determine k_q gave comparable values only if $k_q = k_D/9$. Theoretical and experimental justifications for this relation are discussed.

Introduction

Experiments involving the diffusion of small gas molecules into polymers have been used to investigate the microrheological properties of plastics both above and below their glass transition temperatures.[1–5] A phosphorescence technique utilized by Hormats and Unterleitner[1] and by Shaw[2] for determining the diffusivity of oxygen in cylindrical samples of poly(methyl methacrylate) has been modified in the present work for the case of a nonstationary state of flow in one dimension in a solid plane film of polystyrene. Oxygen is an efficient quencher of phosphorescence. By monitoring variations in the phosphorescence emission (I_p) from a small amount of naphthyl methacrylate copolymerized with styrene, one can relate changes in I_p to the diffusion of oxygen in the polymer.

Numerous experiments have shown that the diffusion of low molecular weight gases through polymer membranes obeys Fick's law of diffusion, a familiar form of which is given for the one-dimensional case by eq 1 where C is the

$$\partial c/\partial t = D(\partial^2 C/\partial \xi^2) \qquad (1)$$

concentration of the diffusant, D is the diffusion coefficient of gas moving in direction ξ, and t is time. In deriving solutions for eq 1 the reasonable assumption is made that Henry's law is valid so that C is proportional to the partial pressure of oxygen surrounding the sample.

While previous studies of diffusion have been restricted to temperatures above 0 °C, the present work shows that the diffusivity of oxygen in polystyrene changes by 4 orders of magnitude over the temperature range +24 to −104 °C. Throughout this range, the diffusion constant for oxygen shows a linear Arrhenius dependence on temperature. These new data present an extended basis for discussion of the role of micro-Brownian motions in gas transport through glassy polymers.

Experimental Section

Materials. Poly(styrene-*co*-naphthyl methacrylate) (PS–NMA), 1.25 g of naphthyl methacrylate, and 0.10 g of decanoyl peroxide were combined with 24.75 mL of freshly dried and distilled styrene (Eastman). Bulk polymerization was carried out in vacuo at 70 °C to 37% conversion (7 h). The polymer was reprecipitated six times from benzene into methanol and then Soxhlet extracted with cyclohexane for 2 days. After drying for 48 h in a vacuum oven at 60 °C, viscometry in benzene (30 °C) gave a molecular weight of 146 000. UV absorption showed the sample to contain ca. 5 mol % naphthyl methacrylate units. The diffusivity of oxygen in the polystyrene is not likely to be affected by the nature or relatively low concentration of the phosphor used in this study.[2]

Oxygen (Canox; minimum 99.6% purity) was used for most experiments after it was demonstrated that the results obtained were indistinguishable from those using the high-purity gas (Matheson; research grade).

Film Preparation. Thin polymer films were prepared by coating a 1–10% solution of polymer dissolved in spectral-grade benzene (Fisher) on a carefully cleaned and polished aluminum plate. Slow, undisturbed evaporation of the solvent deposited films of thickness 2–280 μm which adhered well to the aluminum surface. Thin films (2–20 μm) were used for the low-temperature diffusion studies since crazing in thicker films led to anomalously high diffusion coefficients. The coated plate was then transferred to the cooling probe of a liquid-nitrogen cryostat. Samples were routinely degassed on a greaseless vacuum system at 4×10^{-5} Torr from 2–4 days. During this time the film was heated at 120 °C to remove residual solvent and dissolved gases. Film thicknesses were determined from the area of the films and their mass and density.

Procedure. A cryostat was constructed which would be accommodated in the phosphorescence accessory of a Hitachi Perkin-Elmer MPF-2A spectrophotometer. The design is shown in Figure 1, and the sample configuration is shown in Figure 2. Phosphorescence was gathered from the film at an angle of 25° to the excitation beam. Prompt signals due to fluorescence and scattered light were eliminated by a chopper rotating at 40 Hz. With the excitation and emission monochromators fixed at 313 and 520 nm, respectively and the output from the photomultiplier displayed on a chart recorder, variations in the intensity of phosphorescence, I_p, with time could be determined.

The sample temperature could be adjusted by means of a resistance heater, but better control was obtained by cooling to temperatures determined by pure solvent–liquid nitrogen slushes. The temperature of the film was controlled by a 3-mil copper–constantan thermocouple fixed to the back of the aluminum plate at a point approximately in the center of the incident beam. A second thermocouple, shown in Figure 2, was fixed directly to the film (out of the path of the excitation beam) by allowing the tip of the thermocouple containing a tiny bean of solvent-softened polymer to fuse with the film surface. Under cryogenic conditions, the temperatures recorded from the film surface were consistently 5–7 °C warmer than those indicated from the back of the plate. For the diffusion experiments an average of the two readings was taken as the film temperature. Generally it was not possible to reproduce experiments at precisely the same temperature, owing to the dependence of the temperature on the amount of gas admitted to the cryostat chamber. Films were thoroughly degassed before each diffusion experiment.

Diffusion Coefficients. Provided that the absorbance of the film at the wavelength of excitation is less than 0.1, as is the case in these experiments, the intensity of phosphorescence

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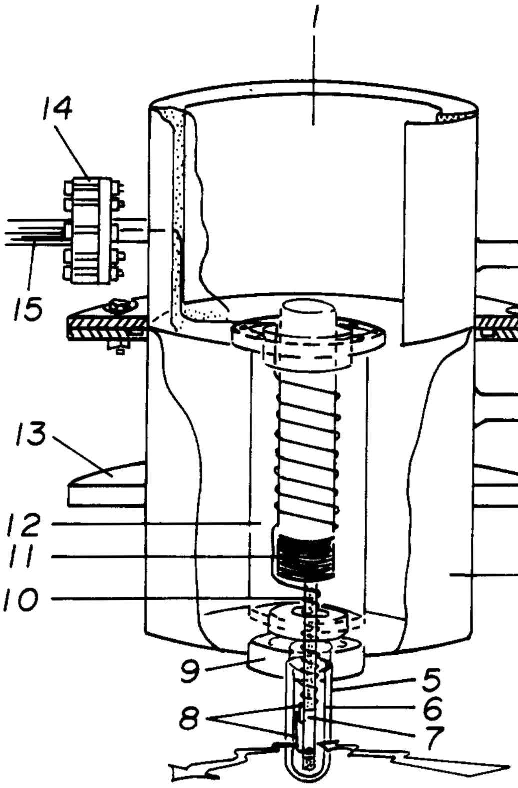


Figure 1. Apparatus for cryogenic luminescence studies: (1) liquid-nitrogen reservoir; (2) brass flange coupling inner cryostat chamber with high-vacuum system; (3) brass flange coupling outer cryostat chamber with high-vacuum system; (4) outer cryostat shroud; (5) outer quartz tube; (6) inner quartz tube; (7) specimen polymer film on aluminum plate; (8) thermocouples; (9) grooved brass ring for positioning cryostat in phosphoroscope; (10) copper cooling probe; (11) cupron resistance heater; (12) inner cryostat shroud; (13) cryostat supporting ring; (14) Plexiglas electrical feed-through; (15) bundle of thermocouple and heater filaments.

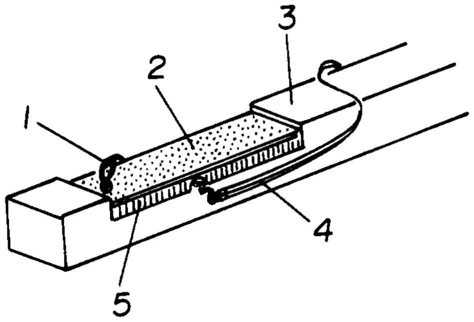


Figure 2. Method of accommodating polymer film on copper cooling probe: (1) thermocouple terminating in bead of solvent-softened polymer; (2) polymer film; (3) copper cooling probe; (4) thermocouple; (5) aluminum plate.

reaching the photomultiplier can be approximated by the relation

$$I_p = B\phi_p I_0 \epsilon c_p l \tag{2}$$

where B is an instrumental factor assumed constant for these experiments, ϕ_p is the quantum yield for phosphorescence, I_0 is the source intensity, ϵ and c_p are the molar absorptivity and concentration of phosphor, respectively, and l is the film thickness. The time dependence of phosphorescence quenching can be related to the rate at which oxygen diffuses through the film, as phosphorescence quenching monitors internally the progress of oxygen through the polymer medium. Losses of intensity may be interpreted as due to a decrease in the number of emitting species from some initial concentration $c_0(\xi,t)$ at position ξ and time t, prior to oxygen diffusion, to some value $c(\xi,t)$ during diffusion. Viewed alternatively, reductions in luminescence intensity can be imagined as arising from an emitting triplet population depleted by diffusion out of the film. Since in reality there is no material loss of phosphor (the probe is chemically attached to the chain) a "diffusional loss" of emitter would be characterized, in the appropriate frame of reference, by the diffusivity of oxygen. Proceeding on this basis, a solution to Fick's diffusion equation, by analogy[6] with the linear flow of heat in a solid bounded by parallel planes, $\xi = 0$ and $\xi = l$, yields for the time variation of oxygen concentration in the film

$$c = lc_0 + l\left(\frac{c_2}{2} - c_0\right)\left(1 - \sum_{m=0}^{\infty}\frac{1}{(2m+1)^2} \times \exp\left[\frac{-Dt(2m+1)^2\pi^2}{l^2}\right]\right) \tag{3}$$

where c_0 is the concentration of oxygen in the film at $t = 0$ and c_2 is the initial concentration of oxygen at the front face corresponding to the equilibrium solubility and the partial pressure to which it is exposed

$$c_2 = Sp_{O_2} \tag{4}$$

where S is the solubility coefficient for oxygen in the polymer film. This particular solution of the diffusion equation is valid only as long as the concentration of oxygen at the back face of the film (c_1) is equal to c_0. This can be tested experimentally by use of the relation

$$t_b = l^2/6D \tag{5}$$

where t_b is the time at which the diffusion gas will appear at the back surface of the film. Measurements at times longer than this will occur under a smaller concentration gradient and would be expected to show a decreased average rate of diffusion, unless the oxygen is removed from the back surface in some manner.

In order to calculate diffusion constants from quenching data, it is necessary to assume that each oxygen molecule quenches a constant fraction f of the excited naphthalene triplets and that therefore the concentration of emitting sites will be inversely proportional to $1 + fp_{O_2}$. In that case one can show[7] that the intensity of phosphorescence will be given by

$$I_p(t) = B\phi_p I_0 \epsilon f c_p\left(\frac{8l}{\pi^2}\right)\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-Dt\pi^2(2n+1)^2}{l^2}\right] \tag{6}$$

Because the series converges rapidly for times only slightly larger than zero, the first term of the summation was used to determine D. The intensity of phosphorescence at any given time after diffusion is therefore

$$I_p(t) = B' \exp[-Dt\pi^2/l^2] \tag{7}$$

where the constants preceding the summation of eq 6 have been absorbed into B'. The diffusion constant is calculated by regression analysis of the slope of $\ln I_p(t)$ vs time. The diffusion constant D is obtained from the slope of this line and should not depend on the value of B' provided it is constant in time.

Results and Discussion

With the cryostat isolated from the diffusion pump, the phosphorescing sample was exposed to a predetermined amount of oxygen. The immediate and exponential decrease in I_p with time was followed by monitoring the 520-nm emission on a strip-chart recorder.

Following equilibration at selected temperatures, triplet lifetimes were determined by observing the decay of the 520-nm phosphorescence in vacuo. The signal from the phosphorescence amplifier was fed into a Tektronix 7402N oscilloscope, and the trace was photographed and analyzed according to first-order kinetics. Between 77 and 95 K in vacuo, decay curves were exponential. Above 95 K a short-lived component contributed some initial nonexponential curvature. The fast-decaying component(s) accounted for about 3% of the emission at 95 K and about 20% at room temperature. All lifetimes were calculated from the

Table I
Triplet Lifetimes as a Function of Temperature for PS-NMA[a]

temp, K	triplet lifetime,[b] s	temp, K	triplet lifetime,[b] s
92.5	1.73	238	1.10
149	1.65	250	0.85
172	1.52	270	0.74
185	1.49	278	0.51
208	1.22	296	0.37

[a] Film, 4 × 10^{-5} Torr. [b] Between 90 and 150 K triplet lifetimes were constant.

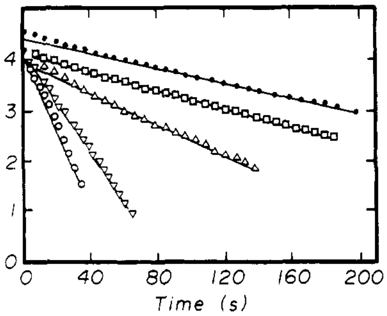


Figure 3. Semilogarithmic plot of phosphorescence intensity vs time after exposure of PS-NMA films to oxygen. Film thickness (cm) and temperature (°C), respectively: (●) 1.7 × 10^{-3}, -67.3; (□) 2.0 × 10^{-4}, -104; (△) 4.8 × 10^{-4}, -82.2; (▽) 8.0 × 10^{-4}, -62.0; (○) 8.0 × 10^{-4}, -50.0.

Table II
Diffusion Coefficients of Oxygen in Glassy Poly(styrene-*co*-naphthyl methacrylate) at Various Temperatures

temp, °C	film thickness, cm	D, ±12% cm^2/s
23.2 ± 0.1	1.6 × 10^{-3}	2.8 × 10^{-7}
22.4 ± 0.1	2.7 × 10^{-2}	2.8 × 10^{-7}
3.0 ± 1.0	1.6 × 10^{-3}	1.1 × 10^{-7}
-50.0 ± 2.0	7.6 × 10^{-4}	3.9 × 10^{-9}
-62.0 ± 1.0	7.6 × 10^{-4}	2.8 × 10^{-9}
-67.3 ± 2.0	1.6 × 10^{-3}	1.7 × 10^{-9}
-82.2 ± 0.5	4.6 × 10^{-4}	3.0 × 10^{-10}
-104.0 ± 2.0	1.9 × 10^{-4}	3.3 × 10^{-11}

linear portions of the curves and are summarized in Table I.

Figure 3 shows semilog plots of I_p as a function of time of films of various thicknesses at a variety of temperatures and oxygen partial pressures. The curves do not extrapolate to a common intercept at $t = 0$ because I_p depends both on film thickness and temperature. Curvature at small times is attributable in part to early truncation of the series eq 6. In part it may be due to a bimodal sorption process of the type proposed by Vieth et al.[8] or due to contributions arising from Knudsen-type flow[9] in microchannels established by sample inhomogeneities. The diffusion coefficients listed in Table II were calculated from a least-squares fit to the linear region of each curve. Diffusivities were found to be independent of oxygen pressure external to the film over the range 0.50-760 Torr, confirming the validity of Fick's law and Henry's law.

Williams and Stannett[10] calculated a diffusivity of 1.1 × 10^{-7} cm^2 s^{-1} for oxygen in polystyrene at 25 °C. Weir[11] found the diffusion coefficient in anionically prepared polystyrene to decrease asymptotically with increasing molecular weight from 2.75 × 10^{-7} ($\bar{M}_n$ = 2.03 × 10^3) to 1.2 × 10^{-7} ($\bar{M}_n$ = 7.36 × 10^4), also at 25 °C. Nowakowska and co-workers[12] calculated a value of 3.1 × 10^{-7} cm^2 s^{-1} at room temperature. Classical diffusion measurements have given values of 3.6 and 4.6 × 10^{-7} cm^2 s^{-1}.[13] Our values of 2.8 × 10^{-7} cm^2 s^{-1} at 23 °C appear to compare favorably with these, but we are unaware of any published data regarding the diffusivity below 0 °C.

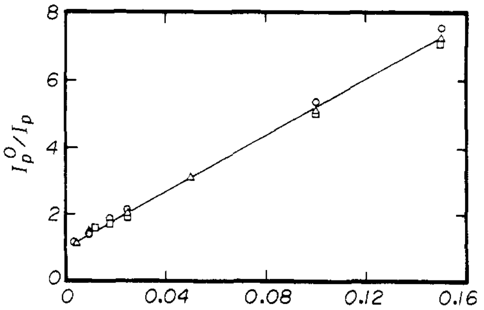


Figure 4. Stern-Volmer quenching by oxygen of PS-NMA phosphorescence at room temperature. Results of three experiments on a PS-NMA film 8-μm thick.

An alternative method of determining diffusion constants in solid polymers[14] involves the use of the Stern-Volmer relation

$$I_p^0/I_p = 1 + k_q S p_{O_2} \tau_T^0 \qquad (8)$$

where I_p^0 and τ_T^0 are the phosphorescence intensity and lifetime of triplet NMA in vacuo, respectively, S is the solubility of oxygen in polystyrene, and p_{O_2} is the partial pressure of oxygen. This is a static experiment where the film is allowed to reach equilibrium with a particular concentration of oxygen, and the intensity of the phosphorescence emission is recorded. If quenching occurs at every collision, then k_q will be equal to the collision rate k_D which is usually related to the diffusion constant D through the Smoluchowski equation

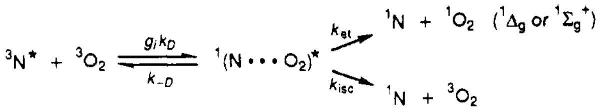
$$D = 1000 k_D / 4\pi N R \qquad (9)$$

which establishes the proportionality between diffusivity and the diffusion-controlled rate constant for quenching. In this equation, N is Avogadro's number and R is the interaction radius (10 ± 3 Å)[15] for the quenching of excited triplet planar aromatic hydrocarbons. Figure 4 shows the results of three quenching experiments on a PS-NMA film 8-μm thick. The slope of the least-squares fit to the line is 0.0434 μm^{-1}. Since τ_T^0 at room temperature is 0.37 s, a value of k_q = (2.9 ± 0.6) × 10^7 M^{-1} s^{-1} is calculated. Usually it is not possible to equate the value of k_q determined in this way with the diffusion-controlled rate constant k_D. This is because quenching seldom occurs at every collision between oxygen (or other quenchers) and the excited triplet chromophore.

The mechanism of quenching of triplet aromatic molecules by oxygen has been investigated extensively. Formally the quenching of phosphorescence by ground-state molecular oxygen can be represented by

$$^3\mathrm{N}^* + {}^3\mathrm{O}_2 \xrightarrow{k_q} {}^1\mathrm{N} + {}^1\mathrm{O}_2 \qquad (10)$$

The quenching constant k_q depends on a number of molecular parameters which collectively determine that the probability of quenching of triplet aromatics on collision with oxygen will be less than unity.[16,17] The quenching kinetics can be analyzed according to the following reaction sequence:



$$^3\mathrm{N}^* + {}^3\mathrm{O}_2 \underset{k_{-D}}{\overset{g_i k_D}{\rightleftharpoons}} {}^1(\mathrm{N}\cdots\mathrm{O}_2)^* \begin{cases} \xrightarrow{k_{et}} {}^1\mathrm{N} + {}^1\mathrm{O}_2\ ({}^1\Delta_g \text{ or } {}^1\Sigma_g^+) \\ \xrightarrow{k_{isc}} {}^1\mathrm{N} + {}^3\mathrm{O}_2 \end{cases} \qquad (11)$$

In the plastic film where the NMA is considered to be fixed in the matrix, the quencher diffuses toward NMA at a rate k_D, where k_D is the total diffusion-controlled rate constant. The term g_i represents a spin statistical factor ($^1/_9$, $^3/_9$, or $^5/_9$) weighting a particular channel to the collision complex $(\mathrm{N}\cdots\mathrm{O}_2)^*$ which has singlet–triplet–quintet character (i = 1, 3, or 5). The rate constant for unimolecular dissociation of the intermediate is k_D, while k_{et} is the rate constant for energy transfer from the complex to a final state in which singlet oxygen is generated. Quenching by enhanced intersystem crossing to the ground-state $^1\mathrm{N}$ is described by k_{isc}. Since there are no spin- and energy-allowed product states for the quintet intermediate, k_q can be expressed in terms of these rate constants as

$$k_\mathrm{q} = \frac{k_D}{9}\left[\frac{k_{\mathrm{et}}}{k_{\mathrm{et}} + k_{-D}} + 3\left(\frac{k_{\mathrm{isc}}}{k_{\mathrm{isc}} + k_{-D}}\right)\right] = \frac{k_D}{9}[P_1 + 3P_3] \tag{12}$$

In fluid solution at room temperature, aromatic hydrocarbons whose triplet energies (E_T) lie in the range 10 000–15 000 cm^{-1} [12] are quenched at a rate $k_\mathrm{q} = k_\mathrm{D}/9$. For these aromatics, $k_{\mathrm{et}} \gg k_{-D} \gg k_{\mathrm{isc}}$ and energy transfer to oxygen ($P_1 \cong 1$) is the major $^3\mathrm{N}^*$ quenching mechanism. Quenching by enhanced intersystem crossing (k_{isc}) was found to be relatively unimportant,[16] as predicted theoretically.[18] There is evidence,[16,19] however, that solvent polarity and viscosity may affect the overall rate constant for oxygen quenching. Young and Brewer[20] found that k_{isc} became competitive with k_{-D} for quenching of triplet dyes (11 000 $< E_\mathrm{T} <$ 15 000 cm^{-1}) dissolved in water or viscous ethylene glycol. Both energy transfer and enhanced intersystem crossing were the suggested modes of triplet quenching in the two solvent systems. The results indicated a value of k_q closer to $4k_D/9$, consistent with $P_1 = P_3 = 1$.

Aromatic molecules with $E_\mathrm{T} >$ 15 000 cm^{-1} are apparently quenched at rates inversely proportional to E_T in fluid solutions[16,17] and solid polystyrene matrices.[21-23] According to these authors, k_q for high triplet energy compounds is given by

$$k_\mathrm{q} = (k_D/9)P_1 \tag{13}$$

where P_1 is less than unity and determined largely by diminishing Franck–Condon factors, although variations in electronic matrix elements may also contribute.[16,21,22] On this basis, a triplet energy of 20 325 cm^{-1} for NMA would suggest a lower value of P_1 than for aromatics such as anthracene and pyrene, which are closer to unity.

Benson and Geacintov[22,23] have determined a value of P_1 for naphthalene in polystyrene of 0.23 ± 0.03. Using a value of the solubility of oxygen in polystyrene of 3.1×10^{-3} mol L^{-1} atm^{-1}, one can calculate a value of k_q from their data of 2.3×10^7 L mol^{-1} s^{-1}, in excellent agreement with our experimental value of 2.9×10^7 L mol^{-1} s^{-1}.

Applying the value of $P_1 = 0.23$ to our system in eq 13 would give

$$k_\mathrm{q} = k_D/39 \tag{14}$$

Converting our measured diffusion constant at 23 °C to the collisional rate constant k_D via eq 9 gives a value of $k_D = 2.1 \times 10^8$ L mol^{-1} s^{-1}, which leads to a predicted value of k_q of 5.3×10^6 L mol^{-1} s^{-1} which does not agree with the experimental data of both Benson and Geacintov and our own static quenching studies.

The parameter P is defined by

$$P = \frac{k_{\mathrm{et}}/k_{-D}}{1 + (k_{\mathrm{et}}/k_{-D})} \tag{15}$$

In solid polystyrene matrices, the diffusion constant and hence k_{-D} for oxygen is about 30 times smaller than it is in fluid solution, whereas the rate constant k_{et} seems unlikely to be affected. Under these circumstances it might be expected that P would be nearly unity, in which case the relation between k_D and k_q from eq 14 would be

$$k_\mathrm{q} \doteq k_D/9 \tag{16}$$

Using this relation the value of k_q calculated from the experimentally measured diffusion constant (2.8×10^{-7} cm^2 s^{-1}) is 2.3×10^7 L mol^{-1} s^{-1}, in excellent agreement with our experimental value of 2.8×10^7 L mol^{-1} s^{-1} and Benson and Geacintov's value of 2.3×10^7 L mol^{-1} s^{-1}. Although eq 16 should be tested in many other polymer matrices, it is tempting to suggest that it be generally used for experiments of this type, particularly when the measured diffusion constant is on the order of 10^{-7} cm^2 s^{-1} or less.

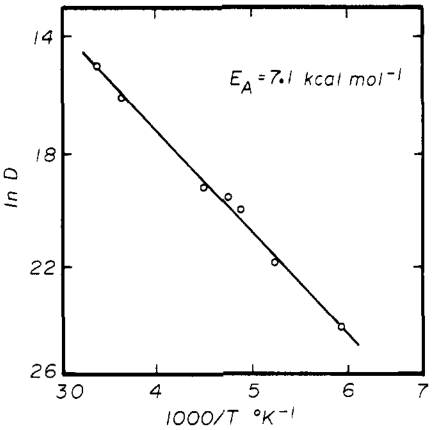


Figure 5. Arrhenius plot for oxygen diffusion in PS.

These results suggest that the Stern–Volmer method can be used, as suggested by Jones,[15] to estimate diffusion constants in polymers, provided that eq 16 is used to calculate k_D from the experimental value of k_q.

Nowakowska et al.[12] have reported a value for D_{O_2} in polystyrene of 3.1×10^{-7} cm^2 s^{-1} at 20 °C, in excellent agreement with our own value. These data are obtained from diffusion measurements in which the concentration of O_2 was measured by UV spectroscopy. From naphthalene fluorescence quenching by O_2, where quenching was assumed to occur at every collision, one can calculate a value by the Stern–Volmer method of 5.3×10^{-7} cm^2 s^{-1} for D_{O_2} in polystyrene, which is in reasonable agreement with other determinations.

Temperature Coefficients. Figure 5 shows the Arrhenius behavior of the diffusion coefficient over the temperature range +23 to −104 °C. The data listed in Table II were plotted according to the expression

$$D = D_0 \exp[-E_\mathrm{D}/RT] \tag{17}$$

The value of 7.1 kcal mol^{-1} determined for activated diffusion of O_2 in polystyrene compares well with the activation energy of 8–10 kcal mol^{-1} for diffusion of small, nonreacting gases through most polymers below the glass transition.[9] For comparison, Williams and Stannett[10] calculated an activation energy of 8.3 kcal mol^{-1} for O_2 diffusion through glassy polystyrene for temperatures above 25 °C. The fact that ln D varies linearly with $1/T$ for our polymer suggests that the molecular motions controlling the diffusion of oxygen through the solid polymer matrix do not change over the temperature range −104 to +23 °C.

It is concluded from these studies that, although the effects of oxygen permeation in plastic films can be observed both kinetically and in the steady state, the former measurements are more readily converted into diffusion constants since there is no need to determine the relation between k_D, the rate constant for collision, and k_q, the rate constant for quenching. If, however, this relation is known, or can be calculated, then reasonable estimates of the diffusion constant can be made from steady-state phosphorescence data provided that the solubility of the penetrant is known. The phosphorescence technique allows measurements of extremely low diffusion constants ($\sim 10^{-11}$ cm^2 s^{-1}) which would be difficult to determine by other procedures.

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