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Activation Barriers for Oxygen Diffusion in Polystyrene and Polycarbonate Glasses: Effects of Low Molecular Weight Additives

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ABSTRACT: A recently developed spectroscopic technique was used to determine oxygen diffusion coefficients, D, as a function of temperature in polystyrene and polycarbonate films. The data were quantified by using an Arrhenius expression with the following variables: (a) a diffusion activation barrier, E_{act}, and (b) a diffusion coefficient, D_0, that represents the condition of "barrier-free" gas transport. From the perspective that diffusion depends on free volume, the parameters E_{act} and D_0 are interpreted to reflect dynamic and static elements of free volume in the polymer matrix. The addition of low molecular weight solutes to these amorphous glasses can alter the oxygen diffusion coefficient by affecting the dynamic and/or static free volume of the material. These effects are manifested in the parameters E_{act} and D_0. Depending on the temperature, the additive may either inhibit or facilitate oxygen diffusion relative to diffusion in the unperturbed, additive-free material. Data are reported for films containing dimethyl phthalate, diphenyl phthalate, cholestane, and molecular nitrogen as additives.

Introduction

Studies of oxygen diffusion in solid amorphous organic polymers are important from both fundamental and practical perspectives. The oxygen diffusion coefficient is a useful parameter for those interested in packaging materials, protective coatings, membranes for gas separation, and polymer oxidative degradation. From a fundamental viewpoint, such studies should yield a better understanding of the often subtle (1) interactions between oxygen and the polymer and (2) inter- and intrachain dynamics of the macromolecule. Because these latter phenomena manifest basic principles, data thus obtained should be useful in attempts to develop a molecular perspective for a variety of other systems.

Models based on the concept of "free volume" have thus far proven effective in understanding gas mobility in glassy polymers.[1-9] From this perspective, gas diffusion is perceived to depend on the presence of spaces in the polymer matrix through which the diffusing molecule can move. We can expand this concept by recognizing that, over a specific temperature range and in a given period of time, these spaces will be either dynamic or static. The former derive from ephemeral cavities created by thermally accessible conformational changes and segmental motions of the macromolecule. In defining a static cavity, we envision spaces in the matrix whose volume is essentially independent of the thermally accessible motions of the macromolecule. A similar distinction between types of free volume is presented by Kaelble[10] in which the terms "hole" and "interstitial" free volume are used. When summed over the entire polymer sample, these dynamic and static spaces define an overall volume characteristic of a particular material at a given temperature. Indeed, the concept of free volume is an attempt to express in one parameter the many structural, steric, and dynamic parameters that influence a polymer property such as gas mobility.[7]

The notion that a dissolved gas molecule can exist within a cavity in the polymer matrix is a defining feature of the dual-mode sorption model.[11-13] In liquids and rubbers, gas sorption behaves according to Henry's law, in which the mole fraction (or concentration) of a dissolved gas depends linearly on the partial pressure of that gas in the atmosphere surrounding the sample. In amorphous glasses, however, isothermal gas sorption does not often behave according to Henry's law, and a second pressure-dependent term is commonly added to the Henry's law term in order to account for this deviation. This additional "Langmuir" term is included to describe a proposed population of gas molecules sorbed in the matrix cavities of the more rigid glassy material. Although exchange between the Henry domain of molecularly dissolved gas and the Langmuir domain of encapsulated gas is likely to be facile, two separate diffusion coefficients can nevertheless be defined within the context of this model. Thus, the macroscopically observed diffusion coefficient, D, should reflect contributions of mass transport within the Henry (D_H) and Langmuir (D_L) domains, respectively.[12]

The molecular events that control gas diffusion in a polymer are thermally activated.[1,8,14-17] Specifically, over limited temperature ranges, the diffusion coefficient, D, behaves according to eq 1.

$$D = D_0 \exp\left(\frac{-E_{act}}{RT}\right) \qquad (1)$$

This expression is analogous to the Arrhenius equation. The exponential term thus represents the fraction of diffusing molecules able to surmount a diffusion activation barrier, E_{act}, at the temperature T. The magnitude of this exponential term ranges from 1.0 at large T to 0 at low T. The activation barrier E_{act} is believed to derive principally from characteristic motions of the macromolecule in a given temperture domain. Thus, E_{act} is likely to manifest events that define the dynamic free volume of a material. These events may include, for example, the rotation of a pendant phenyl group or "breathing" modes of macromolecular chain segments. If $\ln D$ varies linearly with $1/T$ over a given temperature range, it is typically concluded that the type of polymer motions and interactions that control gas mobility do not change within this temperature domain. E_{act} can be obtained from the slope in a plot of $\ln D$ vs $1/T$.

In a plot of $\ln D$ *vs* $1/T$, the pre-exponential factor D_0 can be obtained by extrapolating to $1/T = 0$. At such

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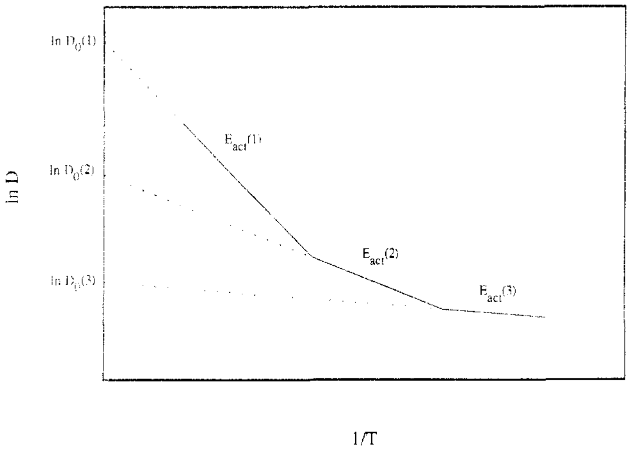

Figure 1. Arrhenius plot for oxygen diffusion that might be observed over a temperature range in which several polymer transitions occur. In a specific temperature domain where ln D depends linearly on $1/T$, only certain polymer motions are thermally accessible. These motions define specific dynamic and static free volumes and are reflected as specific values of E_{act} and D_0.

infinitely high temperatures, gas transport can be considered "barrier-free" [i.e., $\exp(-E_{act}/RT) = 1.0$]. This condition corresponds to an "imaginary" state of the material because the polymer will clearly not remain an amorphous glass at these temperatures. We simply envision a state of the polymer under conditions where all the diffusing molecules are able to surmount the activation barrier E_{act} characteristic of a given temperature domain. From this perspective, D_0 will reflect the static free volume of the matrix for the temperature domain defined by the ln D *vs* $1/T$ plot.

When transition state theory is applied to this problem, terms in eq 1 take on additional meaning.[1] E_{act} will correspond to an activation enthalpy $\Delta H^\ddagger$ for diffusion. D_0 will be a function of the activation entropy $\Delta S^\ddagger$ and a term λ that defines the distance between equilibrium positions for the diffusing molecule in the matrix (eq 2).

$$D_0 = e\lambda^2 \frac{kT}{h} e^{\Delta S^\ddagger/R} \qquad (2)$$

From this perspective, the pre-exponential factor D_0 contains variables that reflect both static (λ) and dynamic ($\Delta S^\ddagger$) elements of free volume. The dependence of D_0 on temperature in eq 2, however, indicates that transition state theory may not provide a totally accurate model with which the data can be interpreted. Because plots of ln D *vs* $1/T$ are indeed reasonably linear over temperature ranges that can be as large as 80–100 °C (*vide infra*), it is likely that at least the temperature dependence of D_0 as shown in eq 2 is incorrect.

Elements that define a given D_0 and E_{act} clearly pertain only to a specific temperature domain in a glassy polymer. This point is illustrated in Figure 1, where different values of E_{act} and D_0 reflect different polymer motions that sequentially become accessible as the temperature is raised. Successive increases in E_{act} and D_0 that correspond to successively higher temperature domains reflect polymer motions that incorporate increasingly larger segments of the macromolecule. These changes in accessible polymer motions that come with a large change in temperature are often accompanied by noticeable morphological changes in the polymer (e.g., glass to rubber transition). Activation barriers for oxygen diffusion obtained from data such as those represented in Figure 1 can be compared to barriers for macromolecular motion independently obtained from temperature-dependent NMR or dielectric/mechanical relaxation studies.[17-26] Therefore, a measure of the diffusion coefficient as a function of temperature is certainly more informative than data recorded at a single temperature.

The incorporation of a low molecular weight solute in a solid polymer often perturbs molecular phenomena that influence gas diffusion.[6,13,14,27] This perturbation may involve (1) a simple filling of voids in the matrix and/or (2) a change in the intra- and intermolecular interactions of the macromolecule, which in turn could influence specific polymer motions. The transport properties of gas molecules sorbed in the Henry domain are thus expected to respond to these changes differently from those of gasses sorbed in the Langmuir domain.[13] Furthermore, the additive may act either to facilitate or inhibit gas diffusion relative to diffusion in the unperturbed, additive-free material. The addition of these low molecular weight solutes to the polymer is also often manifested in other properties of the material. For example, some additives, called plasticizers, can facilitate segmental motion of the macromolecule and make a rigid polymer more flexible.[28] On the basis of the preceding discussion, the addition of a plasticizer is thus expected to yield a larger gas diffusion coefficient. Conversely, an antiplasticizer hinders certain motions of the polymer and is thus expected to yield both a more rigid material and a smaller gas diffusion coefficient.[6,27,29,30] Although the motions affected by the antiplasticizer may involve large segments of the macromolecule, it appears that the influence of antiplasticizers derives principally from a suppression of more localized motions that occur below the glass transition temperature.[27]

In an attempt to better understand the molecular events that control oxygen diffusion, we set out to quantify the extent to which a low molecular weight additive could change the activation barrier for oxygen diffusion. The data were recorded by using a previously described technique[31] in which oxygen sorption into a polymer film is spectroscopically monitored. The effects of adding low molecular weight solutes to polystyrene and polycarbonate glasses were studied.

Experimental Section

The methods by which we quantify oxygen diffusion coefficients and prepare polymer films have been previously described in detail.[31] In the present work, polystyrene films were prepared from benzene solutions by spin-casting. Polycarbonate films were prepared by first dissolving the polymer and the additive(s) (e.g., sensitizer) in CH_2Cl_2 to yield a homogeneous mixture. The CH_2Cl_2 was then removed, *in vacuo*, and the resultant solid was pressed between heated platens. Except when noted otherwise, all of the experiments were initiated by abruptly exposing the degassed polymer sample to an ambient atmosphere containing only oxygen at 30 Torr.

Polystyrene from three different sources was used: (I) Aldrich Chemical Co., average molecular weight = 280 000 (catalog #18,242-7) and 239 700 (catalog #18,243-5); (II) Pressure Chemical Co., average molecular weight = 50 000; and (III) Polysciences, Inc., average molecular weight = 90 000 (catalog #00867) and 650 000 (catalog #16239).

The polystyrene was purified by first dissolving it in CH_2Cl_2. The material was then precipitated and washed with acetone and ethanol. The polymers were dried by placing them in an evacuated dessicator for 2 weeks.

Poly(bisphenol A carbonate), MW = 32 000–36 000, was obtained from Polysciences, Inc. (catalog #00962), and used as received. Dimethyl phthalate (DMP), diphenyl phthalate (DPP), and cholestane were obtained from Aldrich and used as received. The singlet oxygen photosensitizer *meso*-tetraphenylporphine (Porphyrin Products, Inc.) was used as received.

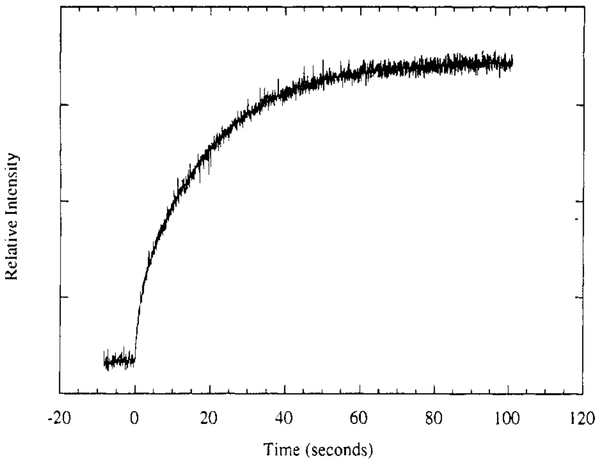

Figure 2. $O_2(a^1\Delta_g)$ phosphorescence intensity from a polycarbonate film as a function of the elapsed exposure time to an oxygen atmosphere of 30 Torr. The sample was a 31-μm-thick free-standing film. The fitting function, which is barely visible through the data, was obtained by incorporating eq 3 into a nonlinear least squares routine.

Results and Discussion

As described in an earlier publication,[31] the technique we use to quantify oxygen diffusion relies on a spectroscopic probe in which the 1270 nm phosphorescence of singlet oxygen is monitored $[O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)]$. Singlet oxygen is produced from ground-state oxygen by energy transfer from a photosensitizer dissolved in the polymer.

$$\text{Sens} \xrightarrow{h\nu} \text{Sens}^* \xrightarrow{O_2(X^3\Sigma_g^-)} O_2(a^1\Delta_g) + \text{Sens}$$

Thus, upon exposure of a degassed polymer film to oxygen, the intensity of singlet oxygen phosphorescence increases as the concentration of $O_2(X^3\Sigma_g^-)$ in the polymer increases (Figure 2). Although the proportionality constant that relates the photosensitized $O_2(a^1\Delta_g)$ phosphorescence intensity to the amount (M) of sorbed oxygen can be determined in independent control experiments, it is not necessary with this technique to explicitly know the solubility of oxygen in the polymer. Data such as those in Figure 2 behave according to eq 3, where the amount of $O_2(X^3\Sigma_g^-)$ that has entered the film at time t (M_t), normalized by the amount at time = ∞ (M_∞), is expressed as a function of the film thickness, l, and the diffusion coefficient, D.[31,32] The diffusion coefficient, D obtained

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right) \quad (3)$$

from an iterative fit of the data to eq 3 for films of known thickness, l, are independent of (1) the concentration of photosensitizer over the range ~(0.1–1.5) × 10^{-3} M and (2) the polymer film thickness over the range ~15–90 μm.

It is important to note several points about this technique. First, this approach monitors oxygen sorption *into* the polymer rather than oxygen permeation *through* the film. Thus, it is not susceptible to errors that can arise from pinholes in the material. Secondly, the data directly yield the diffusion coefficient D. It is not necessary to calculate D from the permeability coefficient P and gas solubility S ($P = DS$).

1. **Effect of Polymer Molecular Weight.** In 1975, Weir quantified the effect of polystyrene molecular weight on the oxygen diffusion coefficient.[34] He reported that, above a MW of ~50 000, D is independent of the polystyrene molecular weight. Below a molecular weight of ~50 000, D increases as the MW decreases. According to Weir, the latter phenomenon most likely reflects the larger number of macromolecule chain end groups typically associated with a low molecular weight polymer, which, in turn, contributes to an increase in the polymer free volume. By using our technique, we likewise measured D for polystyrene samples over a molecular weight range of 50 000–650 000. The data, shown in Table 1, are consistent with Weir's results and indicate that, at a molecular weight greater than ~200 000, D^{PS} does not extensively vary with molecular weight. Data recorded from high molecular weight 25 °C polystyrene (PS) yield $D^{PS} = (2.3 \pm 0.3) \times 10^{-7}$ cm^2 s^{-1}. This result compares well with what is available in the literature.[15,16,35-37] Polystyrene with a molecular weight of 280 000 was used in the experiments discussed below.

Table 1. Oxygen Diffusion Coefficients (D) as a Function of Polystyrene Molecular Weight (MW)[a]

MW	D (×10^7)	MW	D (×10^7)
50 000	4.3 ± 0.4	280 000	2.3 ± 0.2
90 000	2.7 ± 0.3	650 000	2.1 ± 0.2
239 700	2.3 ± 0.2		

[a] Data were recorded at 25 °C. Values of D have the units cm^2 s^{-1}.

Table 2. Oxygen Diffusion Coefficients (D) in 25 °C Polycarbonate Containing an Additive[a]

dimethyl phthalate (DMP)		diphenyl phthalate (DPP)	
% DMP	D (×10^8)	% DPP	D (×10^8)
0	5.5	0	5.5
3.3	3.9	1.0	4.6[b]
4.9	3.3[b]	2.9	4.0
6.2	3.7	4.8	3.9
9.0	3.5	9.1	2.9
17.1	2.4		

[a] The amount of additive dissolved in the polymer is expressed as a weight percent. Values of D have the units cm^2 s^{-1}. Errors are ±10% of the value indicated. [b] Diffusion coefficients were also determined as a function of temperature for these samples. See Table 7.

The effect of polycarbonate molecular weight on the oxygen diffusion coefficient was not examined. For the polycarbonate (PC) used in this study (MW = 32 000–36 000), data recorded from 25 °C samples yield $D^{PC} = (5.5 \pm 0.5) \times 10^{-8}$ cm^2 s^{-1}. This result likewise compares well with published data.[38]

2. **Effect of Additives.** Oxygen diffusion coefficients were measured at 25 °C under conditions in which a low molecular weight additive was dissolved in the polymer. Additives chosen in this study were diphenyl phthalate (DPP), dimethyl phthalate (DMP), and cholestane (Ch). DPP and DMP were chosen because the effects of these and similar phthalates on other polymer properties have been studied, particularly in polycarbonate.[29,39,40] Cholestane was chosen on the basis of some independent work done in our laboratories.[41] In a slightly different experiment, the effect on oxygen diffusion of adding molecular nitrogen to the ambient atmosphere surrounding the polymer sample was also studied. The data are shown in Tables 2–5.

a. **DPP, DMP, and Ch.** The data in Table 2 indicate that upon the addition of as little as ~1–3% (by weight) of either DMP or DPP to polycarbonate, the oxygen diffusion coefficient decreases. D^{PC} continues to decrease as the amount of solute added to polycarbonate is increased. The data in Table 3 indicate that, upon the addition of a similarly small amount of either DMP, DPP, or Ch to polystyrene, the oxygen diffusion coefficient

Table 3. Oxygen Diffusion Coefficients (D) in 25 °C Polystyrene Containing an Additive[a]

dimethyl phthalate (DMP)		diphenyl phthalate (DPP)		cholestane (Ch)	
% DMP	D (x10^7)	% DPP	D (x10^7)	% Ch	D (x10^7)
0	2.3	0	2.3	0	2.3
2.7	1.4	1.0	1.4[b]	0.4	2.3
5.3	1.8	2.9	1.6	0.7	2.4
7.2	1.5[b]	9.1	1.4	1.4	2.4
11.6	1.3			2.2	2.2
13.7	1.3			3.9	1.5
16.7	1.5			6.8	1.5
20.0	1.3				
21.3	1.1				
23.1	1.5				
24.8	1.5				

[a] The amount of additive dissolved in the polymer is expressed as a weight percent. Values of D have the units cm^2 s^{-1}. Errors on D are ±10% of the value indicated. [b] Diffusion coefficients were also determined as a function of temperature for these samples. See Table 6.

decreases by a factor of ~1.6. Unlike the polycarbonate data, however, further changes in D^{PS} do not occur as the amount of added solute is increased. Furthermore, in both polystyrene and polycarbonate, the $O_2(a^1\Delta_g)$ phosphorescence intensity for a sample in equilibrium with the surrounding atmosphere (i.e., at time = ∞ in Figure 2) decreased as the amount of added solute increased. This latter phenomenon ultimately limited our ability to quantify D in ~50 μm films containing large amounts of additive.

These data are characteristic of the antiplasticization phenomenon.[6,27] Indeed, phthalates are well-known antiplasticizers when added in these amounts to polycarbonate, as reflected in other properties of the material (e.g., hardness).[29,39,40] Two separate features of the antiplasticization phenomenon are manifested in our data: (1) The decrease in the equilibrium $O_2(a^1\Delta_g)$ phosphorescence intensity with added solute corresponds to a decrease in oxygen solubility in the polymer.[42] (2) The decrease in the rate at which this equilibrium condition is achieved with added solute corresponds to a decrease in D. It is important to note that solubility is a thermodynamic term and should not be confused with the kinetic terms which are reflected in D.

In both polycarbonate and polystyrene, D does not depend linearly on the amount of added solute over the range ~0–20 weight percent of additive. On the basis of work published by Maeda and Paul as well as Zhou and Stern,[6,13] we suggest that these data are nevertheless consistent with the free-volume and dual-mode sorption models. Specifically, Maeda and Paul[6] have shown that the change in polymer free volume with added solute does not necessarily behave in an ideal and linear manner. Rather, deviations from ideal behavior in the volume of mixing of such binary systems are reflected in the free volume, which in turn should similarly be reflected in the gas transport properties of the doped polymer.

b. Molecular Nitrogen. The data in Tables 4 and 5 indicate that the addition of a small amount of nitrogen gas to the atmosphere surrounding the polymer sample results in a larger oxygen diffusion coefficient. This nitrogen-induced increase in D is observed in both polystyrene and polycarbonate. Thomas et al. recorded a similar phenomenon in an epoxy resin.[15] Our study indicates that the change in D occurs at a comparatively low nitrogen partial pressure and that further increases in the amount of added nitrogen do not influence the data.

Table 4. Oxygen Diffusion Coefficients (D) in 25 °C Polystyrene under Various Partial Pressures of Nitrogen[a]

p_{nitrogen} (Torr)	D (x10^7)	p_{nitrogen} (Torr)	D (x10^7)
0	2.3 ± 0.2	290	3.8 ± 0.4
30	3.0 ± 0.3	350	3.8 ± 0.4
110	3.6 ± 0.4[b]		

[a] The data were recorded at an oxygen partial pressure of 30 Torr. Values of D have the units cm^2 s^{-1}. [b] The diffusion coefficient was also determined as a function of temperature under these conditions. See Table 6.

Table 5. Oxygen Diffusion Coefficients (D) in 25 °C Polycarbonate under Various Partial Pressures of Nitrogen[a]

p_{nitrogen} (Torr)	D (x10^8)	p_{nitrogen} (Torr)	D (x10^8)
0	5.5 ± 0.5	200	6.8 ± 0.7
44	6.7 ± 0.7[b]	300	6.8 ± 0.7
130	6.8 ± 0.7		

[a] The data were recorded at an oxygen partial pressure of 22 Torr. Values of D have the units cm^2 s^{-1}. [b] Using a different sample, the diffusion coefficient was also determined as a function of temperature under these approximate conditions. See Table 7.

In 25 °C polystyrene and polycarbonate, the nitrogen diffusion coefficient is ~3 times smaller than the oxygen diffusion coefficient.[7,38] Thus, upon exposure of a degassed film to a mixture of oxygen and nitrogen, the rate of nitrogen incorporation into the film will be slower than the rate of oxygen incorporation. Nevertheless, nitrogen will be present in the film, particularly in the area near the film surface, while oxygen is still being incorporated. As a consequence, the observed increase in the oxygen diffusion coefficient could indeed be due to nitrogen dissolved in the film.

Oxygen diffusion coefficients in polycarbonate and poly(methyl methacrylate) [PMMA] depend on the ambient oxygen pressure over the range ~50–1000 Torr.[44,45] Thus, it appears that the mobility of oxygen in a polymer can be promoted by the presence of other oxygen molecules. Similarly, CO_2 diffusion coefficients in PMMA and PMMA blends depend on the CO_2 pressure to which the polymer sample is exposed.[46] By extension, our data indicate that the increase in mobility of one gas molecule can also be induced by a different small gas molecule. Specifically, it appears that nitrogen can facilitate oxygen diffusion in both polycarbonate and polystyrene, perhaps by acting as a plasticizer.

In both polycarbonate and polystyrene, the change in D with added nitrogen is analogous to that observed, for example, in the polystyrene/DMP case discussed above. Specifically, after an initial change in D with a small amount of additive, further changes are not observed as the amount of added solute is increased. Thus, these data may likewise reflect nonideal changes in free volume for the binary mixed solvent system of nitrogen dissolved in the polymer. However, a more definitive interpretation of these data, particularly with respect to the *increase* in the diffusion coefficient, can only be somewhat speculative without additional experimental data.

3. Effect of Temperature on Additive-Free Polymers. a. Polystyrene. Oxygen diffusion coefficients were determined as a function of temperature for a polystyrene film containing only the singlet oxygen photosensitizer (Table 6). A plot of ln D *vs* $1/T$ was linear over the temperature range −5 to 85 °C and yielded an activation barrier for diffusion of 29.7 ± 0.8 kJ/mol and a pre-exponential factor D_0 of $(3.2 \pm 0.6) \times 10^{-2}$ cm^2 s^{-1} (Figure 3). A correlation coefficient of 0.996 was obtained from the linear fit to these data. These data are consistent

Table 6. Oxygen Diffusion Coefficients (*D*) at Various Temperatures and the Corresponding Diffusion Activation Energy (E_{act}) for Polystyrene Films with and without Additives[a]

T (°C)	D (x10^7)	D^{DMP} (x10^7)	D^{DPP} (x10^7)	$D^{Nitrogen}$ (x10^7)
-5	0.5			
10	0.9			1.7
15	1.1		1.0	2.1
20	1.4		1.2	2.5
25	2.3	1.4	1.4	3.5
30	2.4	1.8		3.8
35	3.0	2.4	2.1	
40	3.4	2.8	2.7	
45	4.4	3.8		
50	4.9	4.5		
55	5.9	5.6		
60	6.5	6.4		
65	7.6	8.0		
70	8.6	11[c]		
75	9.7	16[c]		
80	12	21[c]		
85	15			
90	29[b]			
E_{act}[d]	29.7 ± 0.8	36.3 ± 0.7	29.3 ± 1.6	30.1 ± 2.5

[a] DMP: The polystyrene film contained 7.2% (by weight) of dimethyl phthalate. DPP: The polystyrene film contained 1.0% (by weight) of diphenyl phthalate. Nitrogen: Measured at a nitrogen partial pressure of 110 Torr. *D* units are $cm^2 s^{-1}$. [b] These data were excluded from the Arrhenius plot. See the text. [c] These data were not used to calculated E_{act}.[48] [d] The errors reported are the standard deviation obtained for the slope of the Arrhenius plot. Units are kJ mol^{-1}.

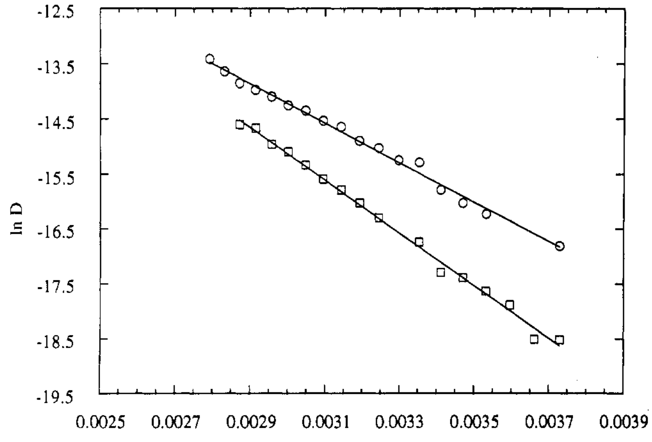

Figure 3. Plots of ln *D* as a function of $1/T$ for oxygen diffusion coefficients, *D*, determined in polystyrene (circles) and polycarbonate (squares).

Table 7. Oxygen Diffusion Coefficients (*D*) at Various Temperatures and the Corresponding Diffusion Activation Energy (E_{act}) for Polycarbonate Films with and without Additives[a]

T (°C)	D (x10^8)	D^{DMP} (x10^8)	D^{DPP} (x10^8)	$D^{Nitrogen}$ (x10^8)
-5	0.91			
0	0.92			
5	1.7			
10	2.2			
15	2.8		2.9	4.1
17			3.0	
20	3.1		3.6	
25	5.4	3.3	4.6	8.8
30			6.4	
35	8.4	5.8	9.7	15
40	11		12	
45	14	10	15	25
50	17		19	
55	22	16	26	40
60	28		31	
65	32		37	73
70	43			
75	46			100
E_{act}[b]	40.2 ± 0.8	43.1 ± 0.8	43.1 ± 0.8	44.4 ± 0.8

[a] DMP: The polycarbonate film contained 4.9% (by weight) of dimethyl phthalate. DPP: The polycarbonate film contained 1.0% (by weight) of diphenyl phthalate. Nitrogen: Measured at a nitrogen partial pressure of 41 Torr and an oxygen pressure of 25 Torr. *D* units are $cm^2 s^{-1}$. [b] The errors reported are the standard deviation obtained for the slope of the Arrhenius plot. Units are kJ mol^{-1}.

with those recently published by Guillet and Andrews.[16] At temperatures greater than 85 °C, the increase in *D* with each incremental increase in temperature is much larger than that observed over the range -5 to 85 °C. At these higher temperatures, the polymer is evolving from a glass to a rubber, and this transition to a more fluid medium is reflected in values of *D*. The glass transition temperature (T_g) of polystyrene is ~95 °C.[47]

Independent data obtained from NMR and mechanical/dielectric relaxation measurements of polystyrene in the temperature range -5 to 85 °C indicate that rotation of the pendant phenyl group is the principal characteristic motion of the macromolecule. Reported values for the activation energy of this process are ~38 kJ/mol.[18,19] Because of the general agreement between the activation barriers for oxygen diffusion and phenyl group rotation, we suggest that at these temperatures phenyl group rotation may indeed create the dynamic cavities in polystyrene that control gas transport. On the basis of phosphorescence quenching data, Guillet and co-workers have likewise made the connection between oxygen diffusion and rotation of the pendant phenyl group in polystyrene.[17]

b. Polycarbonate. Oxygen diffusion coefficients were determined as a function of temperature for a polycarbonate film containing only the singlet oxygen photosensitizer (Table 7). A plot of ln *D* *vs* $1/T$ was linear over the temperature range -5 to 75 °C and yielded an activation barrier for diffusion of 40.2 ± 0.8 kJ mol^{-1} and a pre-exponential factor D_0 of 0.5 ± 0.4 $cm^2 s^{-1}$ (Figure 3). A correlation coefficient of 0.998 was obtained from the linear fit to these data. These data are larger than those published by Paul et al.,[38] who report E_{act} = 30.0 kJ/mol and $D_0 = 7.13 \times 10^{-3}$ $cm^2 s^{-1}$, respectively. It should be noted, however, that Paul's data were obtained from solubility and permeability measurements made at only four temperatures.

Independent data obtained from NMR and mechanical relaxation measurements indicate that rotation of the phenyl group in the polycarbonate backbone, along with attendant local segmental conformational changes, is the principal characteristic motion of the macromolecule over the temperature range -5 to 75 °C. Activation energies for this process obtained from mechanical measurements (~54 kJ/mol)[16,18] are slightly higher than those obtained from NMR line width analyses (~38-50 kJ/mol).[22,24-26] The latter data are certainly consistent with the activation barrier of 40.2 ± 0.8 kJ/mol we obtain for oxygen diffusion. As in the case of polystyrene, we thus suggest that at these temperatures, phenyl group rotation may indeed be the principal motion that creates the dynamic cavities that control gas transport in the polycarbonate matrix.

4. Effect of Temperature on Polymers That Contain an Additive. a. DMP and DPP. Oxygen diffusion coefficients were determined as a function of temperature for polycarbonate and polystyrene films containing the additives DMP and DPP (Tables 6 and 7). Plots of ln *D* *vs* $1/T$ were linear with correlation coefficients that

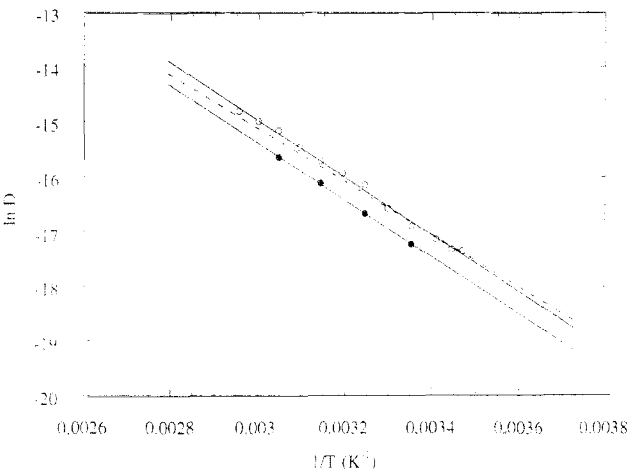

Figure 4. Plots of ln D as a function of $1/T$ for oxygen diffusion coefficients, D, determined in polycarbonate containing 4.9% DMP (filled circles) and 1.0% DPP (open circles). The solid lines are linear least squares fits to the data. The dashed line is the linear least squares fitting function for additive-free polycarbonate. The data from which this line is derived are shown in Figure 3.

exceeded 0.995 (Figures 4 and 5). Diffusion activation energies obtained from these plots are presented in Tables 6 and 7.

In polycarbonate, temperature-dependent studies were performed on a sample that contained 4.9% DMP and one that contained 1.0% DPP. Data obtained from these samples at 25 °C indicate that the additive acts as an antiplasticizer, causing a decrease in the diffusion coefficient relative to that observed in the additive-free material (*vide supra*, Table 2). The diffusion activation barriers obtained for these samples appear to be consistent with this perspective. Specifically, values of E_{act} for DMP- and DPP-containing polycarbonate are ~3 kJ/mol *larger* than E_{act} for the additive-free material. However, care must be exercised in describing the phenomenon of antiplasticization or plasticization in terms of the parameters E_{act}, D, and D_0. This point is elaborated below.

In Figure 4, the ln D *vs* $1/T$ plots for additive-free and doped polycarbonate are presented. The linear fitting functions have been extended to better illustrate our discussion. As expected from the data in Table 7, slopes of the DMP and DPP data are parallel and both are steeper than the ln D *vs* $1/T$ slope for additive-free polycarbonate. The DPP line, however, clearly intersects the line derived from the additive-free material. At temperatures higher than ~30 °C, DPP at this concentration results in a *larger* diffusion coefficient relative to that obtained from neat polycarbonate. At temperatures lower than ~30 °C, DPP at this concentration results in a *smaller* diffusion coefficient relative to that obtained from neat polycarbonate. The slope derived from the DMP data does not intersect that from the additive-free material over this temperature range. Thus, over the entire temperature range examined, DMP at this concentration results in smaller diffusion coefficients relative to those obtained from the additive-free polycarbonate.

Our description and use of the terms plasticizer and antiplasticizer change when we focus on E_{act} rather than individual values of D. For both the DMP- and DPP-doped polycarbonate samples, E_{act} is larger than that for the additive-free material. These results may reflect an additive-dependent perturbation that impedes local or segmental motion of the macromolecule. As such, the additive would be called an antiplasticizer over the entire temperature domain for which the plot of ln D *vs* $1/T$ is linear. We rather believe, however, that the results reflect the same phenomenon represented in Figure 1. Specifically, upon incorporation of the additive into polycarbonate, motions that involve comparatively larger segments of the macromolecule become accessible. This is tantamount to a phase transition induced by an increase in temperature as might be observed in going from a glass to a rubber. Because the polymer motions made accessible by the additive are less localized and may include a greater contribution from the macromolecule backbone, for example, E_{act} increases. From this viewpoint, the polycarbonate data in Figure 4 reflect the general phenomenon of plasticization, not antiplasticization.

The data in Figure 4 yield values of D_0 for the doped polycarbonates that are *larger* than D_0 for the additive-free material ($D_0^{PC\text{-}DMP}$ = 1.1 cm^2 s^{-1}, $D_0^{PC\text{-}DPP}$ = 1.9 cm^2 s^{-1}, D_0^{PC} = 0.5 cm^2 s^{-1}). Within the context of the model described in the Introduction, these D_0 values reflect additive-dependent differences in both static (λ) and dynamic ($\Delta S^{\ddagger}$) properties of the polymers for the temperature range ~15–65 °C. These results could reflect a phenomenon whereby the additives fill inherent static cavities and, in turn, cause the jump length λ between equilibrium positions to increase relative to that found in the additive-free polycarbonate. This perspective would be consistent with that in which the additive increases E_{act} by virtue of a local restriction of accessible motions and, as such, would be called an antiplasticizer. As already discussed, however, we take a different view. We rather believe that the additive-dependent increase in D_0 reflects the general phenomenon of plasticization. Thus, by allowing motions that involve extended segments of the polymer to become accessible, (1) E_{act} increases and (2) both the jump length, λ, and the activation entropy, $\Delta S^{\ddagger}$, increase. The latter, in turn, are reflected through eq 2 in a larger D_0.

In polystyrene, temperature-dependent studies were performed on a sample that contained 7.2% DMP and on one that contained 1.0% DPP. Data obtained from these samples at 25 °C indicate that the additive causes a decrease in the diffusion coefficient relative to that observed in the additive-free material (*vide supra*, Table 3). The Arrhenius plot for the DMP-doped material yields E_{act} = 36.3 kJ mol^{-1} and D_0 = 0.3 cm^2 s^{-1}, both of which are larger than those obtained from additive-free polystyrene (Table 6, Figure 5).[48] On the basis of the preceding discussion on the polycarbonate data, we suggest that these results are consistent with DMP acting as a plasticizer in polystyrene. The line corresponding to the slope of the DMP-doped data clearly intersects the line derived from the slope of additive-free polystyrene. At temperatures greater than ~50 °C, DMP at this concentration results in a *larger* diffusion coefficient relative to that obtained from the additive-free material. At temperatures less than ~50 °C, however, DMP at this concentration results in a *smaller* diffusion coefficient relative to that obtained from the additive-free material.

Data obtained from polystyrene doped with 1.0% DPP yield an activation barrier for diffusion that does not differ significantly from that obtained from the additive-free material (Table 6). This result is not consistent with that obtained in polycarbonate, where the DPP-doped material yielded an activation barrier similar to that obtained from the DMP-doped material. Despite the apparent insensitivity of E_{act} to this additive in polystyrene, DPP in this amount nevertheless effectively acts as an antiplasticizer in this temperature domain. This is illustrated in Figure 5 as a line that is parallel but shifted downward relative to the line derived from the slope of the additive-free

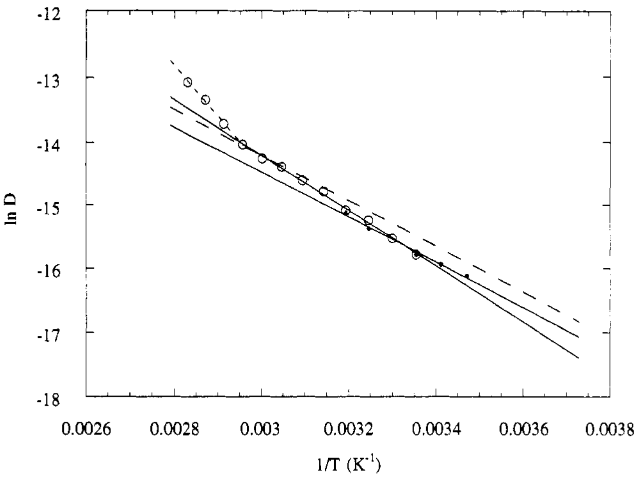

Figure 5. Plots of ln D as a function of $1/T$ for oxygen diffusion coefficients, D, determined in polystyrene containing 7.2% DMP (open circles) and 1.0% DPP (filled circles). The long-dashed line is the linear least squares fitting function for additive-free polystyrene. The data from which this line is derived are shown in Figure 3. The solid lines are linear least-squares fits to the data recorded from the doped polymers. For the DMP-doped material, this line derives from data obtained over the temperature range 25–65 °C. The short-dashed line is a linear least-squares fit to the data for the DMP-doped material over the range 65–80 °C. See discussion in ref 48.

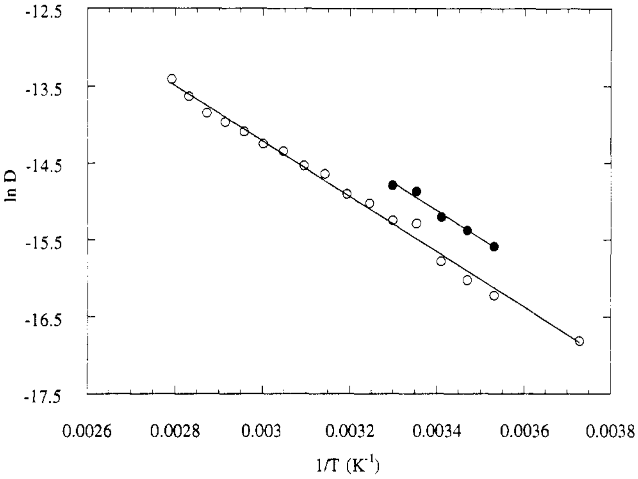

Figure 6. Plots of ln D as a function of $1/T$ for oxygen diffusion coefficients, D, determined in polystyrene. Data shown as filled circles were recorded under conditions in which the polymer film was exposed to an ambient atmosphere containing 30 Torr of oxygen and 110 Torr of nitrogen. Data shown as open circles were recorded under conditions in which the ambient atmosphere contained only oxygen at 30 Torr.

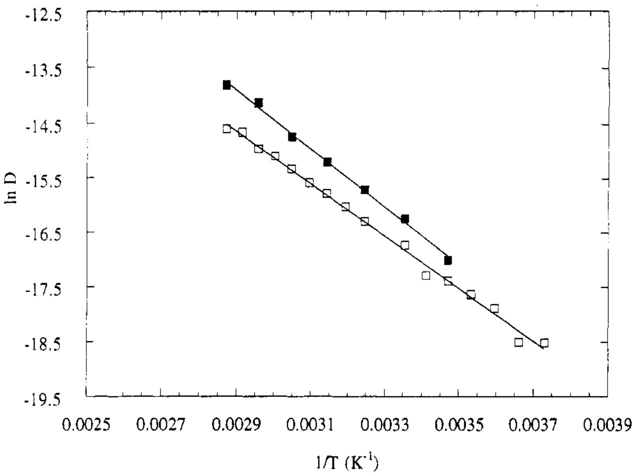

Figure 7. Plots of ln D as a function of $1/T$ for oxygen diffusion coefficients, D, determined in polycarbonate. Data shown as filled squares were recorded under conditions in which the polymer film was exposed to an ambient atmosphere containing 25 Torr of oxygen and 41 Torr of nitrogen. Data shown as open squares were recorded under conditions in which the ambient atmosphere contained only oxygen at 30 Torr.

material (i.e., $D_0^{PS\text{-}DPP} = 0.022$ cm^2 s^{-1} < $D_0^{PS} = 0.032$ cm^2 s^{-1}). At present, we are unable to provide an explanation for this phenomenon.

b. Molecular Nitrogen. Oxygen diffusion coefficients were determined as a function of temperature for polycarbonate and polystyrene films under conditions in which molecular nitrogen was a copenetrant (Tables 6 and 7). Plots of ln D *vs* $1/T$ were linear with correlation coefficients of 0.99 (Figures 6 and 7). Diffusion activation energies obtained from these plots are presented in Tables 6 and 7.

In polystyrene, oxygen diffusion coefficients obtained in the presence of nitrogen are clearly larger than those obtained in the absence of nitrogen over the entire temperature range examined (Figure 6). The activation energies obtained from these data, however, are essentially equal. Thus, in this temperature domain, it appears that the presence of nitrogen in the matrix does not substantially influence intrinsic motions of the polymer that define the dynamic free volume. Although the Arrhenius slope for the nitrogen-doped polystyrene is equivalent to that obtained from the nitrogen-free material, extrapolation to an infinitely high temperature yields D_0 values for oxygen diffusion that depend on the presence of nitrogen ($D_0^{nitrogen} = 0.065$ cm^2 s^{-1} > $D_0 = 0.032$ cm^2 s^{-1}). Thus, nitrogen perturbs the system in such a way as to increase the static component, λ, and/or the activation entropy, ΔS^*, for oxygen diffusion. As discussed previously with respect to the additives DMP and DPP, dissolved nitrogen may fill static voids and thus increase λ. Concurrently, the random thermal motion of dissolved nitrogen may also cause an increase in the available degrees of freedom for both oxygen and polystyrene and thus appear as an increase in ΔS^*. Further experimentation is certainly needed, however, to provide a more definitive interpretation of this phenomenon.

In polycarbonate, oxygen diffusion coefficients obtained in the presence of nitrogen are likewise larger than those obtained in the absence of nitrogen over the entire temperature range examined (Figure 7). In this case, the Arrhenius plot of the N_2-doped material yields $E_{act} = 44.4$ kJ mol^{-1} and $D_0 = 4.6$ cm^2 s^{-1}, both of which are larger than corresponding values obtained in the absence of nitrogen. Thus, the phenomenon of plasticization by nitrogen, as reflected in the oxygen diffusion coefficient, is more clearly manifested in polycarbonate than in polystyrene.

Conclusions

Our limited temperature ranges, the temperature dependence of the oxygen diffusion coefficient can be quantified by using an Arrhenius expression in which the following parameters are defined: (a) a diffusion activation barrier, E_{act}, and (b) a diffusion coefficient, D_0, for the "imaginary" condition of barrier-free gas transport. These parameters are interpreted to reflect dynamic and static elements of polymer free volume for the temperature domain over which the plot of ln D *vs* $1/T$ is linear.

Data recorded from amorphous polystyrene and polycarbonate glasses indicate that the incorporation of a low molecular weight additive in the polymer matrix can either inhibit or facilitate oxygen diffusion relative to diffusion in the unperturbed, additive-free material. Furthermore, addition to the polymer of as little as 1% (by weight) of a solute can cause a comparatively large change in the oxygen diffusion coefficient.

The addition of a low molecular weight solute to amorphous polystyrene and polycarbonate glasses can alter the oxygen diffusion coefficient by affecting the dynamic and/or static free volume of the material. These effects, in turn, are manifested in the parameters E_{act} and D_0. It is suggested that, when classifying the additive as either a plasticizer or antiplasticizer, it is more appropriate to consider E_{act} and D_0 rather than individual values of D. The basis for this suggestion derives from the observation that, at a given concentration, the additive may at one temperature cause an increase in D relative to that found in the additive-free material; whereas, at a different temperature, the additive may cause a decrease in D relative to that found in the additive-free material. Despite these apparently different behaviors, the perturbation caused by the additive on a molecular level nevertheless remains the same over the entire temperature range for which the plot of $\ln D$ *vs* $1/T$ is linear. These observations should be useful to those interested, for example, in the construction of polymer membranes as gas barriers.

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References and Notes

(1) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*, 1st Edition, McGraw-Hill, New York, 1941; pp 477 and following.

(2) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164–1169.

(3) Kumins, C. A.; Kwei, T. K. In *Diffusion in Polymers*, Crank, J.; Park, G. S., Eds.; Academic Press: London **1968**; pp 107–140.

(4) Rogers, C. E. In *Polymer Permeability*, Comyn, J., Ed.; Elsevier: London, **1985**; pp 11–73.

(5) Wen, W.-Y. *Chem. Soc. Rev.* **1993**, 117–126.

(6) Maeda, Y.; Paul, D. R. *J. Polym. Sci., B, Polym. Phys.* **1987**, *25*, 1005–1016.

(7) Puleo, A. C.; Muruganandam, N.; Paul, D. R. *J. Polym. Sci., B, Polym. Phys.* **1989**, *27*, 2385–2406.

(8) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci.: Polym. Phys. Ed.* **1977**, *15*, 403–416.

(9) Stern, S. A.; Trohalaki, S. *ACS Symp. Ser.* **1990**, *423*, 22–59.

(10) Kaelble, D. H. in *Rheology*, Eirich, F. R., Ed.; Academic Press: New York, 1969; Vol. 5, pp 223–296.

(11) Koros, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 981–992.

(12) Paul, D. R. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 294–302.

(13) Zhou, S.; Stern, S. A. *J. Polym. Sci, B, Polym. Phys.* **1989**, *27*, 205–222.

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

(15) Chu, D. Y.; Thomas, J. K.; Kuczynski, J. *Macromolecules* **1988**, *21*, 2094–2100.

(16) Guillet, J. E.; Andrews, M. *Macromolecules* **1992**, *25*, 2752–2756.

(17) Somersall, A. C.; Dan, E.; Guillet, J. E. *Macromolecules* **1974**, *7*, 233–244.

(18) Yano, O.; Wada, Y. *J. Polym. Sci. A-2*, **1971**, *9*, 669–686.

(19) Connor, T. M. *J. Polym. Sci., A-2* **1970**, *8*, 191–205.

(20) Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54–64.

(21) Jho, J. Y.; Yee, A. F. *Macromolecules* **1991**, *24*, 1905–1913.

(22) Henrichs, P. M.; Nicely, V. A. *Macromolecules* **1991**, *24*, 2506–2513.

(23) Kim, C. K.; Aguilar-Vega, M.; Paul, D. R. *J. Polym. Sci., B: Polym. Phys.* **1992**, *30*, 1131–1142.

(24) Walton, J. H.; Lizak, M. J.; Conradi, M. S.; Gullion, T.; Schaefer, J. *Macromolecules* **1990**, *23*, 416–422.

(25) O'Gara, J. F.; Jones, A. A.; Hung, C.-C.; Inglefield, P. T. *Macromolecules* **1985**, *18*, 1117–1123.

(26) Roy, A. K.; Jones, A. A.; Inglefield, P. T. *Macromolecules* **1986**, *19*, 1356–1362.

(27) Maeda, Y.; Paul, D. R. *J. Membr. Sci.* **1987**, *30*, 1–9.

(28) Stevens, M. P. *Polymer Chemistry*, 2nd ed.; Oxford: New York, 1990; pp 137–140.

(29) Jackson, W. J.; Caldwell, J. R. *J. Appl. Polym. Sci.* **1967**, *11*, 211–226.

(30) Jackson, W. J.; Caldwell, J. R. *J. Appl. Polym. Sci.* **1967**, *11*, 227–244.

(31) Gao, Y.; Ogilby, P. R. *Macromolecules* **1992**, *25*, 4962–4966.

(32) Under our conditions, this solution to Fick's second law for one-dimensional diffusion does not apply to approximately the first 3% of the data recorded. At these early times, M_t/M_∞ is expressed in terms of an error function.[33] Equation 3 is applicable for the remaining ~97% of the data recorded at "later" times. Note in Figure 2 that data are recorded until an equilibrium between the film and the ambient atmosphere is achieved. When analyzing our data with eq 3, the summation is typically only carried out from $n = 0$ to $n = 5$.

(33) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford, 1975; pp 47–49.

(34) Weir, N. A., *J. Macromol. Sci., Phys.* **1975**, *B11*, 553–563.

(35) Nowakowska, M.; Najbar, J.; Waligora, B. *Eur. Polym. J.* **1976**, *12*, 387–391.

(36) Yasuda, H.; Stannett, V. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; p III-229–III-240.

(37) Timpe, H.-J.; Basse, B.; Muller, F. W.; Muller, C., *Eur. Polym. J.* **1987**, *23*, 967–971.

(38) Muruganandam, N.; Koros, W. J.; Paul, D. R., *J. Polym. Sci., B.* **1987**, *25*, 1999–2026.

(39) Belfiore, L. A.; Henrichs, P. M.; Massa, D. J.; Zumbulyadis, N.; Rothwell, W. P.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1744–1753.

(40) Roy, A. K.; Ingelfield, P. T.; Shibata, J. H.; Jones, A. A. *Macromolecules* **1987**, *20*, 1434–1437.

(41) Ogilby, P. R.; Dillon, M. P.; Gao, Y.; Iu, K.-K.; Kristiansen, M.; Taylor, V. L.; Clough, R. L. *Adv. Chem. Ser.* **1993**, *236*, 573–598.

(42) Given our experimental technique, it is possible that the decrease in the equilibrium $O_2(a^1\Delta_g)$ phosphorescence intensity could derive from the decrease in values of D. Specifically, a decrease in the oxygen diffusion coefficient will likely yield a smaller bimolecular rate constant for oxygen quenching of the sensitizer triplet state. As a consequence, if the intrinsic lifetime of the sensitizer triplet state is sufficiently short, it is possible that a smaller fraction of triplet states will be removed by oxygen quenching in a medium where D is smaller. Data we have recorded in independent studies, however, indicate that the intensity data reported herein likely reflect a change in the solubility of oxygen rather than the change in D.[43]

(43) Scurlock, R. D.; Martire, D. O.; Ogilby, P. R.; Taylor, V. L.; Clough, R. L. *Macromolecules* **1994**, *27*, 4787–4794.

(44) Barker, R. E. *J. Polym. Sci.*, **1962**, *58*, 553–570.

(45) Unfortunately, our experimental approach to quantify D precludes the use of oxygen pressures in excess of approximately 30 Torr. [At high oxygen pressures, the oxygen concentration in the polymer is sufficient to quench all of the triplet state sensitizers. In this saturated domain, the $O_2(a^1\Delta_g)$ phosphorescence intensity is independent of oxygen concentration and cannot be used to obtain D.][31] Nevertheless, over the limited oxygen pressure range of 12–30 Torr, we are able to observe a slight change in D. This change, however, does not exceed our reported error limits and thus cannot be taken as significant (e.g., in polycarbonate, D increases from 5.1×10^{-8} to 5.5×10^{-8} $cm^2\ s^{-1}$ over this pressure range).

(46) Chiou, J. S.; Paul, D. R. *J. Appl. Polym. Sci.* **1986**, *32*, 2897–2918.

(47) Rudd, J. F. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; 2nd ed.; Wiley: New York, 1975; pp V-59–V-62.

(48) Upon examination of the $\ln D$ *vs* $1/T$ plot for the DMP-doped polystyrene (Figure 5), it appears that a transition occurs at about 70 °C in which a different set of polymer motions becomes accessible. The solid line shown in Figure 5 for the DMP-doped data was obtained from a linear fit of $\ln D$ *vs* $1/T$ for data over the range 25–65 °C. Data recorded at 70, 75, and 80 °C were not included. Data recorded at these latter temperatures clearly yield a larger E_{act} and D_0, as indicated by the short-dashed line in Figure 5.