A New Technique To Quantify Oxygen Diffusion in Polymer Films

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ABSTRACT: Diffusion coefficients for oxygen in polymer films are quickly and accurately obtained by using a near-infrared luminescence spectrometer. The spectroscopic technique described herein uses the 1270-nm phosphorescence of singlet molecular oxygen ($^1\Delta_gO_2 \rightarrow {}^3\Sigma_g^-O_2$) to directly monitor oxygen sorption into polymer films (15–80 μm thick) of small area (~1 cm × 1 cm). The approach is illustrated by using films of polystyrene for which a 25 °C diffusion coefficient of (2.3 ± 0.3) × 10^{-7} cm^2/s is obtained.

Introduction

The solubility and mobility of gases in solid organic polymers is an exciting topic from both a fundamental and a practical perspective. The transport behavior of molecular oxygen is particularly important to those interested in membranes for gas separation, packaging materials, protective coatings, and polymer oxidative degradation. A complete discussion of the mechanism for gas mobility in organic polymers requires an understanding of the inter- and intrachain dynamics of the macromolecule as well as specific gas–polymer interactions. The latter may be relatively more important in the particular case of oxygen, which is known to exhibit unique gas–solvent phenomena.[1-4] The large number of research publications on gas, and more specifically oxygen, transport is a testimony of the importance of this topic. Several reviews provide a historical perspective and summarize the vast literature.[5-11]

Although gas transport in polymers has been a focus of scientific investigation for many years, the experimental methods used to quantify gas permeation, sorption, and diffusion have not changed substantially over the past several decades. Felder and Huvard[9] and Crank and Park[11] have reviewed many of the "classic" techniques still being used extensively, and with great success, by research groups currently active in the field.[12,13] In these studies, either gravimetric (change in sample weight), barometric (change in ambient gas pressure), or volumetric (change in ambient gas volume) measurements are made to quantify (1) gas sorption into, or desorption out of, a polymer sample or (2) gas permeation through a polymer membrane.[9,11] Current state-of-the-art and many commercial instruments often rely on modern thermal conductivity, coulometric, or ionization based detectors, for example, to monitor gases that have passed through the membrane under study. All of the techniques mentioned above, however, can require (1) a great deal of time for accurate data acquistion or (2) polymer samples that either have a large area or are relatively thick. The latter, for example, may be important in sorption experiments where the changes in mass may be difficult to measure accurately for small samples. Furthermore, data from permeation measurements can be influenced by "pinholes" that may be present in the sample film. Although the mathematics for accurate reduction and analysis of the resultant data can be complicated, the extensive discussions by both Crank[14] and Carslaw and Jaeger[15] no longer make this facet of a gas transport study the limiting step.

Molecular oxygen is an excellent quencher of singlet and triplet excited states of organic molecules. Thus, the fluorescence, phosphorescence, and triplet absorption intensities (and associated decay kinetics) of an organic molecule dissolved in a solid organic polymer will change as a degassed or nitrogen-saturated sample incorporates oxygen from an ambient oxygen atmosphere. This photophysical approach to quantify oxygen sorption into an organic polymer has been used to determine oxygen diffusion coefficients.[16-22] In a novel approach to quantify oxygen permeation through a polymer membrane, Petrak[23a] and Holland et al.[23b] independently constructed an oxygen "chemical detector" by monitoring the sensitized photooxygenation of a molecule dissolved in a separate film deposited between the membrane under study and an oxygen-impermeable substrate. In this method, quenching of the excited-state photosensitizer in the detector layer by the available ground-state oxygen ($^3\Sigma_g^-O_2$) produces singlet oxygen ($^1\Delta_gO_2$), which in turn reacts with an oxygen acceptor such as 1,3-diphenylisobenzofuran (DPBF). Changes in the DPBF absorbance were used to determine the oxygen flux through the polymer membrane into the detector layer and hence obtain the permeability coefficient.

We have been able to detect the time-resolved near-infrared phosphorescence of singlet molecular oxygen ($^1\Delta_gO_2 \rightarrow {}^3\Sigma_g^-O_2$; 7880 cm^{-1}, 1270 nm) in solid organic polymers subsequent to (a) irradiation of a photosensitizer dissolved in the polymer matrix[24,25] and (b) photolysis into the polymer–oxygen charge-transfer (CT) absorption band of sensitizer-free materials.[25,26] We thus have a direct spectroscopic probe for the presence of molecular oxygen in polymeric media. Although our data in these studies reflect both the solubility and mobility of oxygen in the polymer, we have heretofore not made an attempt to quantify oxygen diffusion explicitly. In the present paper, we introduce and describe a technique that uses the phosphorescence of $^1\Delta_gO_2$ to obtain oxygen diffusion coefficients easily and quickly in small, readily prepared samples. The approach is illustrated with films of polystyrene.

Experimental Section

A. Instrumentation. A steady-state near-infrared spectrometer was constructed to monitor $^1\Delta_gO_2$ phosphorescence from polymer films (either free-standing or cast onto an oxygen-impermeable substrate; vide infra). A schematic diagram of the instrument is shown in Figure 1. A Photon Technology International 150-W horizontal-burn Xe lamp was the excitation source. A large portion of the infrared and near-infrared component of the lamp output was removed with a filter of circulated water and a UV/vis-reflecting, IR-transmitting mirror

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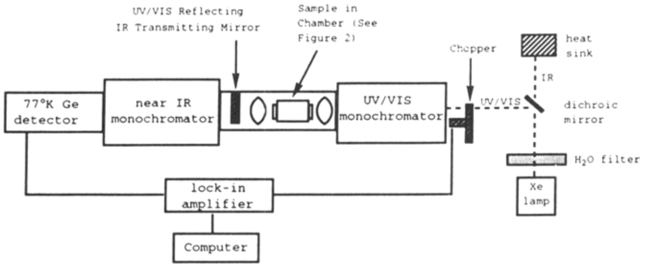
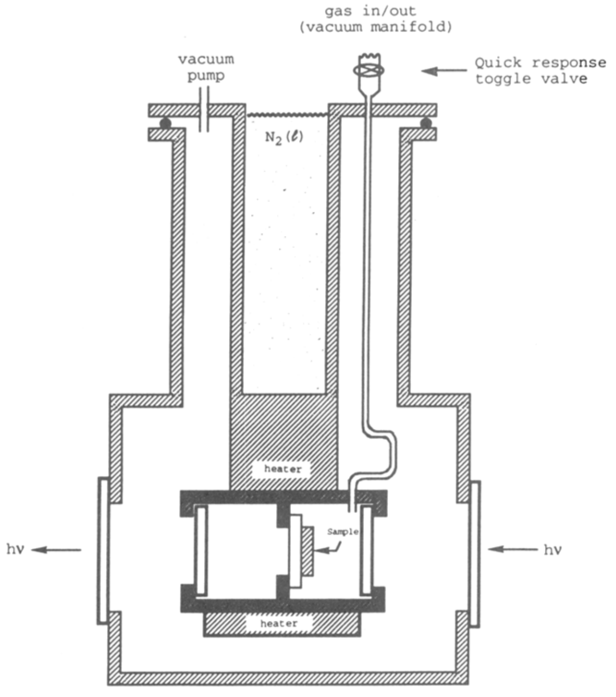


Figure 1. Schematic diagram of the spectrometer used to monitor $^1\Delta_gO_2$ phosphorescence in polymer films.



Schematic representation of polymer sample chamber

Figure 2. Schematic representation of the variable-temperature, controlled-atmosphere polymer sample chamber.

(CVI Corp.). Either an Oriel Model 77250 monochromator or band-pass filters were used to select the appropriate wavelength for sample irradiation, and the resultant beam was focused into the sample chamber (Figure 2; vide infra). The beam waist at the sample was ~3 mm (thus, large-area films are not necessary). The near-IR phosphorescence of $^1\Delta_gO_2$ was isolated by first using a visible-reflecting, near-IR-transmitting mirror (Melles Griot, Inc.) in combination with a Schott RG 850 filter to remove a large portion of the (1) residual photolysis light transmitted by the sample and (2) sensitizer fluorescence. Final wavelength selection was achieved with either (1) a Photon Technology International Model 01-001FAST monochromator (0.25 m, *f* 2.6) with a 600 lines/mm grating blazed at 1250 nm or (2) a combination of a silicon window with an antireflective coating for 1270 nm (CVI Corp.) and an interference filter with a band-pass centered at 1270 nm (Barr Associates, 70% transmittance, fwhm = 50 nm). Near-IR signal intensities were monitored with a North Coast Model EO817L 77 K germanium detector. A Standford Research Systems Model SR510 lock-in amplifier interfaced to an IBM personal computer was used for signal processing. The Xe lamp output was mechnically chopped at the lock-in reference frequency. The time response of our detector/amplifier/digitizer system for a given set of low-pass *RC* filters on both the lock-in amplifier and detector was measured by using a Vincent Associates UniBlitz shutter whose closed-to-open transit time was 1.5 ms. Under the conditions used in this study, the system response (~50 ms) was much faster than the time required for (1) oxygen incorporation into the polymer samples and (2) gas entry into the sample chamber (vide infra).

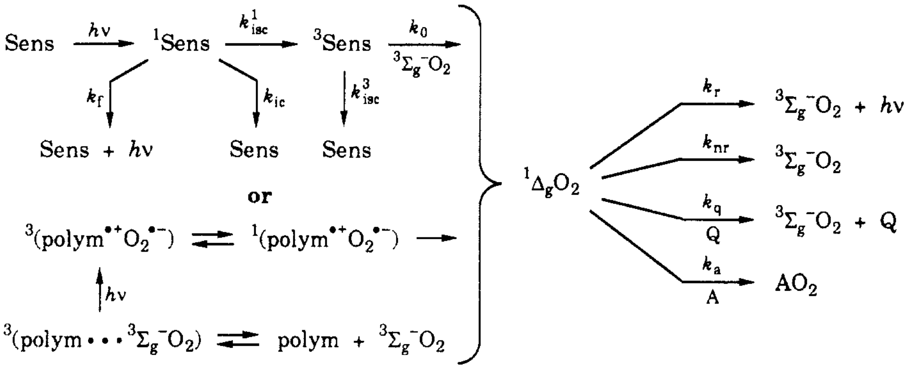
The design of our sample chamber requires that we detect $^1\Delta_gO_2$ phosphorescence along the axis of excitation rather than perpendicular to the axis. The entire system, represented schematically in Figure 2, consists of a modified Specac Model 21000 vacuum-jacketed variable-temperature cell compartment and a Model 20620 polymer film holder that allows facile and rapid exchange of the gas surrounding the polymer sample. Heating elements embedded in the sample holder are controlled by a Specac Model 20100 temperature controller. The volume surrounding the polymer in the sample holder is connected to the top of the cryostat assembly by two 1.3-mm-i.d. stainless steel tubes. These gas-transfer tubes have several features that facilitate gas–wall collisions and thus minimize the temperature difference between the equilibrated polymer sample and the gas introduced abruptly into the chamber: (1) 180° bends were put into the lower portion of the tubes which are at the same temperature as the sample holder and (2) the gas entry ports into the sample chamber consist of convoluted grooves cut into the block housing itself. These features do not adversely affect the time necessary to change the atmosphere around the polymer sample (vide infra). Outside the cryostat assembly, the 1.3-mm-i.d. gas-transfer tubes were connected to a 3.2-mm-i.d. stainless steel tube, which in turn was connected to a vacuum manifold. Specific O_2/N_2 gas mixtures were prepared in the latter, and pressures were determined with a capacitance manometer (MKS Baratron, range 1000 Torr). The atmosphere surrounding the polymer sample was rapidly changed by establishing a pressure differential across a quick-response toggle-operated bellows valve located at the top of the cryostat. Thus, opening the valve allowed one to either remove gas from or add gas to the sample chamber. The volume of the sample chamber (i.e., below the toggle valve) was small compared to that of the vacuum manifold. Absorption spectra were recorded on a Beckman Model DU-40 spectrometer.

B. Sample Preparation. For these early studies in which our principal interest is to demonstrate the experimental technique, we used polystyrene pellets from Aldrich Chemical Co. to prepare our polymer films (catalog no. 18,242-7). Information supplied with this material indicates that it has an average molecular weight of 280 000, $T_g = 100$ °C, and $d = 1.047$. Future studies will use more rigorously characterized materials.

Polystyrene films were prepared by two methods. In the first, a known amount of the sensitizer (*meso*-tetraphenylporphine (TPP); Porphyrin Products, Inc.) was added to a known amount of the polymer pellets. An arbitrary amount of benzene was then added, and the resultant mixture was kept in the dark with periodic stirring until both the sensitizer and polymer were completely dissolved, yielding a homogeneous solution. Polymer films were then cast from this mixture onto an optical flat by using a Headway Research, Inc., photoresist spinner. Residual benzene was removed from the film by placing the sample in an evacuated desiccator for at least 48 h. This technique was used to prepare films ~5–15 μm thick. Free-standing films (~30–80 μm thick) were prepared by again dissolving known amounts of the sensitizer and polymer in an arbitrary amount of benzene. The solvent was removed in vacuo, and the resultant solid was pressed either at 130 °C (2 metric ton load) or 240 °C (1 metric ton load) by using a Specac Model 15620 constant-thickness film maker in a Carver hydraulic press fitted with heated platens (Specac Model 15515). A typical preparation involved 5 min of heating, followed by 3 min of pressing at the same temperature, after which the film maker was transferred to a water-cooled chamber. The resultant film was removed and placed in the sample chamber shown in Figure 2. Although these films were prepared by using calibrated spacers of known thicknesses provided with the Specac film maker, a more accurate thickness value, and that used in calculations to determine the diffusion coefficient, was independently determined by using the techniques described below. The concentration of the sensitizer in the films ((0.2–1.0) × 10^{-3} M) was calculated by using the specified density of the polystyrene and the masses of both sensitizer and polymer initially used. A homogeneous distribution of the sensitizer in the polymer was assumed. Because diffusion coefficients obtained from our samples (vide infra) were independent of (1) film thickness, (2) the method by which the films were prepared, and (3) storage time in an evacuated or nitrogen-purged desiccator (range of ~48 h to 1 month), we believe all of the benzene used in sample preparation was removed.

Film thicknesses were determined by several techniques.[27]

Scheme I



$$\Phi_p = \Phi_{^1\Delta_gO_2} \frac{k_r}{k_r + k_{nr} + k_q[Q] + k_a[A]} \qquad (1)$$

$$I_\Delta = \gamma\Phi_p \qquad (2)$$

(1) The absorption spectrum of the sensitizer dissolved in the polymer film at a known concentration was recorded. The Beer–Lambert law was used to calculate the sample path length from the absorbance at λ_{max}. The extinction coefficient for the sensitizer in the polymer[29] was independently determined from polystyrene samples with path lengths that could be accurately measured with a micrometer (e.g., 1-2 mm).[24-26]

(2) A sample of known area was weighed. The volume, and hence thickness, of the sample was calculated by using the specified density of polystyrene.

For a given sample, the thicknesses obtained by these techniques did not differ by more than 5%.

Results and Discussion

In the present work, where our principal interest is to introduce this general approach to quantify oxygen diffusion coefficients, we have focused on the photosensitized production of $^1\Delta_gO_2$ in polymer films. The photolytic production of $^1\Delta_gO_2$ in sensitizer-free materials provides unique experimental challenges[2,3,26] and will be discussed in a separate report.

We were indeed able to observe $^1\Delta_gO_2$ phosphorescence from a sensitizer-doped, oxygen-saturated polymer film by using the apparatus described above. The emission maximum was centered at 1270 nm, which is in agreement with previous $^1\Delta_gO_2$ assignments.[24a,30-32] In the absence of oxygen, the 1270-nm luminescence was correspondingly absent. In the absence of the polymer sample, the luminescence signal was not observed from the cell containing 700 Torr of oxygen. When oxygen was abruptly introduced into the atmosphere surrounding the polymer sample, the phosphorescence signal intensity slowly increased, reaching a steady-state level dependent on the film thickness and ambient oxygen partial pressure (Figure 3). These data are consistent with those obtained in our previous studies in which we showed that the 1270-nm phosphorescence originates from $^1\Delta_gO_2$ generated throughout the polymer sample, not just at the surface.[24-26,33]

In an independent control experiment, we ascertained that the rate of gas entry into the sample cell was fast when compared to the appearance rate of the $^1\Delta_gO_2$ signal. A mixture of Br_2 and N_2 gases was prepared in the vacuum manifold such that the total pressure differential across the quick-release toggle valve (Figure 2) was identical to that in a given oxygen/polymer experiment. The rate of Br_2 entry into the evacuated sample chamber was monitored by following the change in absorbance at 410 nm (Br_2 λ_{max}). These data are also shown in Figure 3. Since the root mean square speed of O_2 will be ~2.2 times greater than that of the heavier Br_2 under identical temperature and pressure conditions,[34] we conclude from data such as those in Figure 3 that we are able to quickly introduce oxygen into the ambient environment of the sample (for the data shown in Figure 3, oxygen entry into the sample chamber is complete within approximately 200 ms, whereas the $^1\Delta_gO_2$ phosphorescence signal increases over a period of approximately 20 s). We thus conclude that the intensity increase in the $^1\Delta_gO_2$ phosphorescence signal shown in Figure 3 is a result of oxygen sorption into the polymer film.

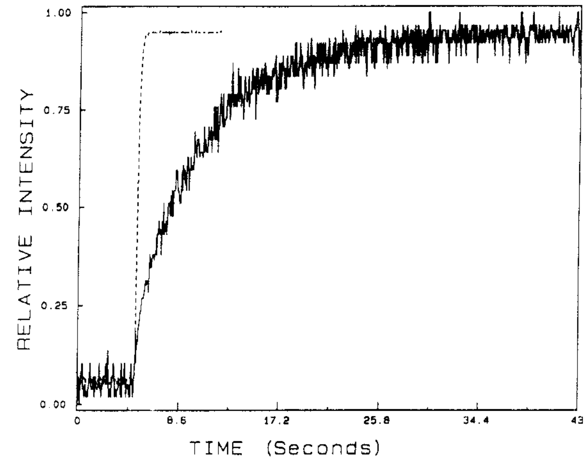


Figure 3. (a) (Solid line) $^1\Delta_gO_2$ phosphorescence intensity as a function of elapsed exposure time to an oxygen atmosphere of 50 Torr. The phosphorescence intensity increases upon exposure of a degassed 44-μm-thick free-standing polystyrene film to oxygen. (b) (Dashed line) Change in absorbance due to the admission of Br_2 gas into the sample cell. The pressure differential across the quick-release toggle valve (Figure 2) was identical to that for the oxygen data shown.

The quantum yield of $^1\Delta_gO_2$ phosphorescence (Φ_p), which is directly proportional to the intensity, I_Δ, of the 1270-nm signal,[35] can be expressed in terms of the events shown in Scheme I.

Singlet oxygen can be produced (with an efficiency of $\Phi_{^1\Delta_gO_2}$) either by energy transfer to $^3\Sigma_g^-O_2$ from a photosensitizer or by photolysis into the polymer–oxygen charge-transfer absorption band of a sensitizer-free material. In condensed phases, only a small fraction of the $^1\Delta_gO_2$ produced decays radiatively (k_r); nonradiative (k_{nr}) channels dominate the deactivation process.[36] The latter may be enhanced by the presence of a physical quencher (Q) of $^1\Delta_gO_2$. In addition, $^1\Delta_gO_2$ can be removed from the system by reaction (k_a) either with the polymer itself[37] or with another solute,[38,39] which may be present, for example, as an impurity. This process will, of course, reduce the amount of $^3\Sigma_g^-O_2$ in the system. Although the presence

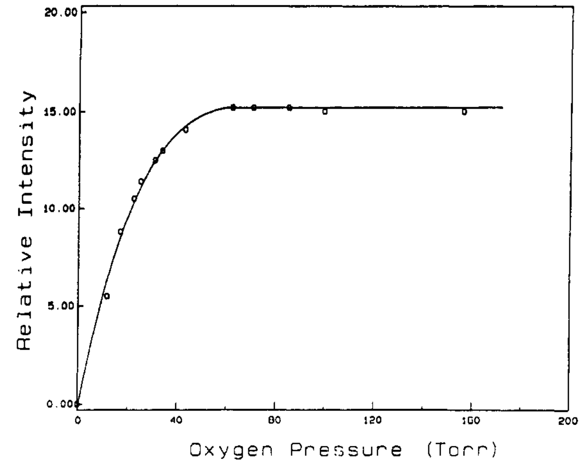


Figure 4. Intensity of ${}^1\Delta_gO_2$ phosphorescence from a TPP-doped polystyrene sample as a function of the ambient oxygen pressure. Each point was recorded after the sample had reached equilibrium with the surrounding atmosphere.

of a physical quencher (Q) or reactive acceptor (A) will lower the intensity of phosphorescence, it will not adversely influence an attempt to quantify oxygen diffusion if (i) the quenchers/acceptors are homogeneously distributed throughout the sample, (ii) the change in acceptor concentration is small or negligible over the time period required for oxygen incorporation into the film, or (iii) the reaction to form AO_2 does not alter the polymer morphology yielding diffusion/permeation coefficients that are not constant over the period of oxygen incorporation.

In a photosensitized process, $\Phi_{{}^1\Delta_gO_2}$ can depend strongly on the equilibrium ground-state (${}^3\Sigma_g{}^-$) oxygen concentration.[3] This is shown in Scheme I and eq 3, where an oxygen-independent ^{3}Sens decay channel (k^3_{isc}) competes with ${}^1\Delta_gO_2$ formation ($k_Q[{}^3\Sigma_g{}^-O_2]$). (For the sake of simplicity, we present the case where all ${}^3\Sigma_g{}^-O_2$–^{3}Sens collisions result in ${}^1\Delta_gO_2$.)

$$\Phi_{{}^1\Delta_gO_2} = \Phi_{{}^3\mathrm{Sens}} \frac{k_Q[{}^3\Sigma_g{}^-O_2]}{k_Q[{}^3\Sigma_g{}^-O_2] + k^3_{\mathrm{isc}}} \tag{3}$$

Thus, $\Phi_{{}^1\Delta_gO_2}$ (and consequently Φ_p and I_Δ) will not depend linearly on $[{}^3\Sigma_g{}^-O_2]$ over a wide range of oxygen concentrations as oxygen is incorporated into a previously degassed sample. This is documented by the data in Figure 4 in which ${}^1\Delta_gO_2$ phosphorescence intensities from a TPP-doped polystyrene sample in equilibrium with the surrounding atmosphere are plotted as a function of the ambient oxygen pressure.[40] We have obtained analogous curves for a variety of sensitizers in liquid solvents.[3] Therefore, to use ${}^1\Delta_gO_2$ phosphorescence data such as those shown in Figure 3 to quantify oxygen diffusion, either the factor relating $\Phi_{{}^1\Delta_gO_2}$ to $[{}^3\Sigma_g{}^-O_2]$ must be constant over a given $[{}^3\Sigma_g{}^-O_2]$ range or the changes in this factor must be known explicitly. For the photosensitized production of ${}^1\Delta_gO_2$, these stipulations can be met in the following ways: (i) The initial and final ambient oxygen pressures to which the polymer sample is exposed must fall on a linear region of a plot such as that in Figure 4. (ii) The function relating I_Δ to $[{}^3\Sigma_g{}^-O_2]$ can be obtained directly from a plot such as Figure 4, and appropriate weighting factors can be used to normalize raw data for the corresponding change in ambient oxygen pressures.

Of course, the entire problem of a nonlinear relationship between I_Δ and $[{}^3\Sigma_g{}^-O_2]$ is obviated when ${}^1\Delta_gO_2$ is produced in a sensitizer-free material by photolysis into the oxygen–polymer charge-transfer absorption band.[2,3,26] (Upon photolysis into the CT band of polymers at temperatures below T_g, a plot of I_Δ vs ambient oxygen pressure (e.g., Figure 4) may not be linear due to the "Langmuir contribution" to the gas solubility.[7])

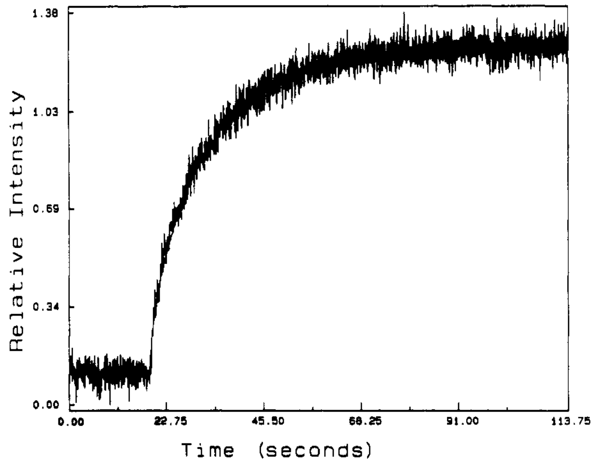


Figure 5. ${}^1\Delta_gO_2$ phosphorescence intensity as a function of elapsed exposure time to an oxygen atmosphere of 30 Torr. The sample was a 55-μm-thick free-standing film containing 3×10^{-4} M TPP. The fitting function was obtained by incorporating eq 5 into a nonlinear least squares routine.

Data such as those in Figure 3 can be analyzed by using well-established mathematical expressions[14] to yield the oxygen diffusion coefficient. Specifically, Fick's second law for one-dimensional diffusion (eq 4) can be solved for either a free-standing polymer film or a film cast onto an oxygen-impermeable substrate (e.g., a quartz optical flat). For each case, the solutions are identical

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{4}$$

where C = oxygen concentration, t = time, D = diffusion coefficient, and x = distance coordinate normal to plane face.

We also assume (1) for a given ambient oxygen pressure (p_{O_2}), there will be a constant concentration (C_0) of gas at, or just within, the film surface (i.e., Henry's law is obeyed) and (2) D is constant. Specifically, D is independent of the oxygen concentration.

For a free-standing film of thickness $2l$ or a cast film of thickness l, the solution[14] to eq 4 yields an expression for the total amount of oxygen that has entered the film at time t (M_t) normalized by the amount at $t = \infty$ (M_∞). The latter represents the amount of oxygen in the film when the film is at equilibrium with the ambient environment.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right\} \tag{5}$$

Equation 5 accurately represents our experimental data, and we have incorporated this expression into a standard nonlinear least squares fitting routine through which values of D can be obtained (Figure 5).

Our polystyrene data yield D_{O_2}(25 °C) = $(2.3 \pm 0.3) \times 10^{-7}$ cm²/s. The indicated error reflects the average deviation from the mean for independent measurements made on samples (1) that had thicknesses that ranged from 15 to 80 μm, (2) that were both free-standing and cast onto a quartz optical flat, and (3) that contained different concentrations of the sensitizer TPP. It is also important to recall that these samples were prepared by different techniques and under different conditions. In Table I, we compare our value for D_{O_2} with those obtained by using the methods described in the Introduction. On the whole, the agreement is quite good.

Table I
Diffusion Coefficient[a] of Oxygen in Solid Polystyrene at 25 °C

this work	lit. values	ref
$(2.3 \pm 0.3) \times 10^{-7}$	3.3×10^{-7}	22
	$(3.1 \pm 0.3) \times 10^{-7}$	19
	1.1×10^{-7}	5b, 21, 44
	$(1-2) \times 10^{-8}$	43
	1.1×10^{-8}	20

[a] In cm^2/s.

Conclusions

We have described a spectroscopic technique with which oxygen diffusion coefficients can be quickly obtained for readily prepared polymer films (~15–80 μm thick) of small area (~1 cm × 1 cm). Because this technique depends on oxygen sorption *into* the polymer and not on detecting the amount of oxygen that permeates *through* the material, we are not susceptible to errors that can arise from "pinholes" in the sample film. The approach was illustrated for 25 °C polystyrene. Having established this technique as a rapid and accurate method of quantifying oxygen mobility, we are now poised to systematically participate in the effort to correlate molecular phenomena and structure with the macroscopic property of oxygen permeability.

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(27) Because uncertainty in the film thickness (l) greatly influences the error in the diffusion coefficient (D), [D is a function of l^2 (eq 5)], it is important to determine l accurately. In future experiments, l will also be determined by recording optical interference fringes from cast films.[28] This technique will certainly be important in sensitizer-free films where $^1\Delta_gO_2$ is produced by photolysis into the oxygen–polymer CT band.
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Registry No. O_2, 7782-44-7; $(PhCH{=}CH_2)_x$ (homopolymer), 9003-53-6.