A Method for Measuring Oxygen Diffusion and Oxygen Permeation in Polymer Films Based on Fluorescence Quenching

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A Method for Measuring Oxygen Diffusion and Oxygen Permeation in Polymer Films Based on Fluorescence Quenching

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We describe a new and simple technique based on luminescence quenching for measuring oxygen diffusion and oxygen permeation in free-standing polymer films and in viscous liquid polymers. The polymer film acts as a membrane to separate the source of oxygen from a small receiving volume containing an oxygen sensor. The sensor is made of a resin containing a phosphorescent dye sensitive to oxygen quenching. The measured film is either laminated on the sensor (film−sensor) or separated from it with a spacer (film−spacer−sensor). At time $t = 0$, the film equilibrated in atmospheric air is flushed with pure oxygen and the time profile of the decay of the phosphorescence emission from the sensor is monitored. The Stern−Volmer equation for luminescence quenching is combined with Fick's law for diffusion to derive the mathematical expressions describing each of our experiments. By means of this method, we measured the diffusion coefficient and permeability with a good accuracy in various free-standing polymers films such as polystyrene and poly(ethylene terephthalate). We also measure the oxygen diffusion coefficient in un-cross-linked polyisobutylene as an example of a viscous liquid polymer.

The solubility of a gas in a polymer, and its diffusivity, are properties that one needs to know for many applications including the preparation of polymer foams and the development of gas barrier materials and gas separation membranes and for novel technologies such as "phosphorescence barometry", where polymer films are used as air pressure profile sensors.[1−5] The parameters of interest for the gas in the polymer are its diffusion coefficient (D), its solubility (S), and its permeability ($P_p = DS$).[1] For many gases, D and P_p values are commonly obtained from sorption or time lag measurements. In the sorption technique, the film is initially evacuated and pressurized with the diffusing gas in a chamber of a fixed volume. The quantity of gas sorbed in the film is monitored either by the drop in the pressure of the chamber or by a gravimetric measurement.[1,3] In the time-lag technique, the film is initially positioned between two chambers, which are then evacuated. A constant pressure of gas is introduced into one of the chambers while one monitors the increase of pressure in the adjacent chamber by means of a pressure gauge.[1−4] With advances in pressure transducer technology, it has become possible to measure accurately extremely low gas pressure values.[2] Thermal conductivity can also be used to detect the permeating gas.[13]

There are a number of shortcomings with this method. This technique requires homogeneous free-standing films of uniform thickness with areas ranging from 3 to 25 cm². It is often not convenient to prepare large films with such controlled properties. The precision in this technique is determined by the ratio S/V, where S is the area of the film through which diffusion occurs and V is the receiving volume where the penetrant gas is detected. The ideal instrument should have an extremely small receiving volume, which is difficult to achieve in the traditional method due to the restrictions induced by the detector dimensions. Most instruments have a value of S/V less than 10 cm²/mL. In addition, this technique is ineffective for liquid polymers. One can convert liquid polymers to free-standing elastomeric films through the introduction of cross-links. In this case, the presence of cross-links can affect the permeability properties of the polymer.[12]

For the specific case of oxygen diffusion in polymer films, one can imagine taking advantage of the powerful fluorescence- and phosphorescence-quenching capabilities of O_2 as the basis for designing a methodology for determining its D, S, and P_p values in a broad variety of polymer films. While a number of attempts toward this goal have been reported in the literature, there has been no development of a useful and general analytical method based upon luminescence quenching for determining oxygen diffusion and permeability in polymers.[7−12]

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The development of phosphorescence barometry as a tool for aviation design has placed new impetus on understanding the connection between oxygen diffusion and fluorescence quenching in polymer films.[5,7] In this technique, an aviation model is coated with a thin polymer film (micrometers) containing a dye with a long-lived excited state (microseconds). The model is illuminated in a wind tunnel and monitored by a digital TV camera. Sites of high air pressure on the model lead to a higher local concentration of O_2 in the film, resulting in enhanced quenching. Bright areas in the digital image correspond to low air pressure and darker areas correspond to higher pressure. Image analysis provides the air pressure profile across the model.

Previous studies in our laboratory have modeled this process, using fluorescence and phosphorescence quenching as a means of measuring oxygen diffusion in polymer films.[11,12] In these experiments, the dye is dissolved (or can be chemically bound) to the polymer of interest. A flat film mounted on a substrate is placed in a controlled-atmosphere sample holder, which is placed in the sample chamber of a fluorescence spectrometer. In a "diffuse-in" experiment, the film is first equilibrated with nitrogen and then at $t = 0$ is exposed to an atmosphere of air or oxygen. One monitors the time profile of the decrease of emission intensity of the dye in the film as O_2 diffuses into the polymer. In a "diffuse-out" experiment, the film is first equilibrated with air (or oxygen) and then at $t = 0$ is rapidly flushed with an inert gas to remove all of the air or oxygen from the surrounding atmosphere. One monitors the time profile of the increase of emission intensity of the dye in the film as O_2 diffuses out of the film. The diffusion coefficient and permeability are determined from analysis of the trace of the dye emission intensity vs time.

While this technique works well for polymers in which one can prepare flat thin films containing a uniformly distributed dye, it lacks generality. It will not work for polymers in which the dyes will not dissolve or tend to aggregate. One anticipates serious problems for semicrystalline polymers. For many applications, the dependence of oxygen diffusion and permeability on sample processing history and sample aging is important. These features would be destroyed upon introducing a dye into the film. The technique appears also to be limited to polymers that dissolve in common solvents and from which films can be prepared by casting. These are serious shortcomings, and to overcome them, one has to recreate some of the features of a traditional gas diffusion experiment, replacing a traditional detector with a luminescence detector.

In this paper, we describe a general method to measure oxygen diffusion and oxygen permeation in polymer films without pre-mixing the dye with the polymer. The polymer film to be studied acts as membrane to separate the source of air or oxygen from a small receiving volume containing an oxygen sensor. The oxygen sensor is made of a thin film (1−2 μm) of high O_2 permeability resin containing a phosphorescent dye, coated on a quartz or Pyrex substrate. The film is positioned onto the sensor in two different ways: film-on-sensor or film−spacer−sensor. In the film-on-sensor method, the receiving volume is essentially zero. In the film−spacer−sensor method, the receiving volume is small, but finite. At time $t = 0$, the film, equilibrated with atmospheric air, is flushed with pure oxygen and the time profile of the decay of fluorescence emission from the sensor layer is monitored. We
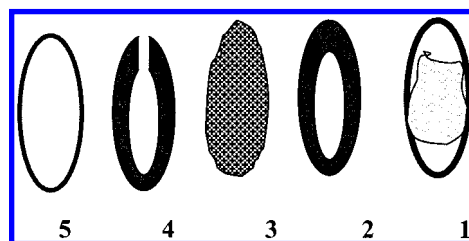

Figure 1. Assembly of the gas diffusion device. (**1**) The sensor is made of a Pyrex disk (25-mm diameter), coated with the PDMS resin containing the Pt dye. (**2**) The washer is made of Teflon with a central diameter of 18 mm, exterior diameter of 25 mm, and thicknesses varying from 0.5 to 4.35 mm. (**3**) The film to be measured. (**4**) A metal washer with central diameter of 18 mm, exterior diameter of 20 mm, and thickness of 5 mm. This washer has two small holes for the inflow and outflow of gases. (**5**) A Pyrex disk 25 mm in diameter.

combine Fick's law with the Stern−Volmer equation for luminescence quenching to derive the mathematical expressions describing each of our experiments. The diffusion coefficient and permeability are determined from the comparison of the theoretical equations and the experimental decays.

We find that the film-on-sensor geometry allows one to determine the diffusion coefficient of O_2 with a good accuracy in either a free-standing film or in a viscous liquid polymer. In this geometry, the experiment is not sensitive to oxygen permeability. The film−spacer−sensor geometry provides a measure of both the permeability and diffusivity of oxygen, but is much more accurate for determining the permeability. In this geometry, one cannot examine polymers that can flow.

This technique has several advantages compared to the traditional polymer membrane method. First, the area of film used for the gas diffusion measurement can be reduced to the dimensions of the light spot (1−2 mm), minimizing the possibility of inhomogeneities and thickness variation in the film. Second, the parameter S/V defining the sensitivity of the measurement can be chosen from 0 to infinity. Third, this method allows the measure of the diffusion coefficient in viscous polymer liquids.

We tested this methodology with various polymer films, including commercially available polyethylene films and Teflon films that differ significantly in O_2 diffusivity and permeability properties. We compare these results to those reported in the literature and comment on some of the limitations of the method. We complete the study by describing the measurement of oxygen diffusion in an un-cross-linked polyisobutylene (PIB) sample as an example of a measurement on a viscoelastic polymer fluid.

EXPERIMENTAL SECTION

Device for the Gas Diffusion Measurement. The device employed (see Figure 1) consists of two chambers separated by the film to be tested, enclosed in a metal box. The first chamber "the receiving chamber" is made of a Pyrex disk coated with the sensor resin (1) and separated from the film to be tested by a series of spacers (2) (film−spacer−sensor) in order to control the volume of the chamber and the area of the gas diffusion. The spacers, with thicknesses of 0.51, 0.8, 1.66, 2.85, and 4.35 mm, consist of Teflon washers with a central diameter of 10 mm and an exterior diameter of 25 mm. In other experiments (film-on-sensor), no spacer was used. The films were put in direct contact with the silicone sensor layer, leading to an extremely small
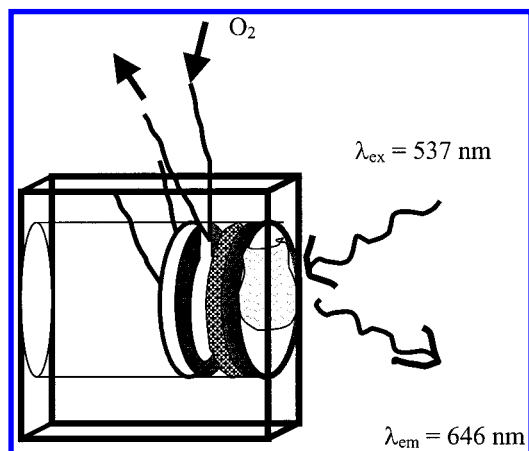
Figure 2. The device for gas diffusion described in Figure 1, assembled in a metal box and positioned in the front-face configuration in the fluorescence spectrometer. The Pyrex disk containing the sensor faces the excitation light beam. The size of the light beam is reduced to a spot smaller than the size of the sensor.

receiving chamber. Polyisobutylene (Aldrich, M = 200 000) was used as both an adhesive and a sealant to attach the film to be examined to the spacer and the glass support for the sensor.

The second chamber, the "reservoir chamber", is constructed from a Pyrex disk (25 mm), separated from the diffusion chamber by a washer with an interior diameter of 10 mm, an exterior diameter of 25 mm, and a thickness of 5 mm. Two needles were inserted into the reservoir chamber for the inflow and outflow of air or oxygen. The entire device was then mounted on a sample holder and positioned in the sample chamber of a fluorescence spectrometer (Figure 2).

The sensor for the gas diffusion measurement consists of a phosphorescent dye, platinum octaethylporphine (PtOEP, Porphyrin Products Inc., Logan, UT) dissolved in a polymer resin (Genesee, Flint, MI, GP197 siloxane resin). The resin is supplied as a dilute solution (3.88 wt %) of polymer in a mixed organic solvent. The dye PtOEP (0.3 mg) was dissolved in the GP197 resin solution (10 mL) at room temperature by stirring the solution for 2 h. This solution was then diluted with cyclohexane to a polymer concentration of 1 g/L. A few drops of this solution were spread on a Pyrex disk (25 mm diameter) and then dried at room temperature for 1 h. This polymer was then cured for 24 h at 120 °C, resulting in a tough elastomeric film with a thickness less than 2 μm. We note that, for such a thin film, the results we obtain are independent of the shape of the film and any irregularities in its thickness.

Fluorescence Measurements. A SPEX Fluorog 2 fluorescence spectrometer equipped with a DMA 3000 data module was used in this study. The fluorescence intensity was monitored in the time scan mode with λ_{ex} = 537 nm and λ_{em} = 646 nm. All the experiments were carried out at room temperature 23 °C. We start our experiment by positioning the diffusion cell (Figures 1 and 2) in the sample chamber of the spectrometer in the front face configuration, facing the sensor to the excitation light beam. The size of the excitation beam light is then reduced to less than the size of the sensor film (2−3 mm) and the device is rotated slightly, moved upward or backward, to maximize the response of the sensor.

Table 1. Properties of the Polymer Films

films	thickness, μm	irregularity in the thickness, %
Teflon 1	12	±10
Teflon 2	125	2
PET	111	2
polystyrene 1	110	5
polystyrene 2	250	5
polyethylene (0.92), low density	75	±10
	130	±5

Before starting the measurement, the films are equilibrated with atmospheric air for a few hours in the chamber. Pure oxygen is then injected through one needle in the reservoir chamber while the other needle vents the gas to the atmospheric air. In the case where the applied oxygen pressure is close to the atmospheric pressure, 1.04 atm, the real pressure in the chamber is very close to 1 atm of pure oxygen. From control experiments, we know that only few seconds are necessary for such a small chamber to be filled with pure oxygen. The starting time is then negligible compared to the measurement time.

Films Used in the Gas Diffusion Measurement. A series of films with different permeabilities were used to test the technique of gas diffusion measurement. The first series of samples were Teflon films (Dupont, sold under the trade name Teflon FEP) with thicknesses of the 12.5 and 125 μm (Table 1). The transparency of these films varies from clear for the 12.5-μm film to turbid for the 125-μm film. The second type of sample was a poly(ethylene terephthalate) (PET) film (ICI Melinex) with a uniform thickness of 0.11 mm. The third series of films were prepared in our laboratory from polystyrene (Aldrich, M_w = 280,000) and linear low-density polyethylene (PE) (Dupont, M_w = 210 000, ρ = 0.92). These films were prepared by molding the granular polymer in a Carver press at 140 °C under a pressure of 5 metric tonnes for 10 min. The samples were compression molded between two PET films coated with silicone oil in order to control the surface smoothness of the samples and to make it easy to remove them from the mold. The samples were then cooled to room temperature over 20 min. The cooling rate is important, particularly for PE, because it controls the crystallization rate. A reproducible cooling protocol is critical for obtaining reproducible gas diffusion results. The characteristics of these samples are listed in Table 1. These films were then cut into 25-mm-diameter disks from areas of the film free of any defects or bubbles.

PIB liquid (Polysciences, M_w = 1350) was used to test our method for studying gas diffusion in a viscous fluid. A film of fluid of PIB was spread directly on the sensor and pressed against a PET film coated with silicone to smooth the surface. The film was then cooled with liquid nitrogen, and the PET film was removed without affecting the surface. The resulting film has a relatively uniform thickness of 0.15 mm. The film was then left at room temperature for 1 h prior to the measurement.

RESULTS AND DISCUSSION
Design and Fabrication of the Sample Chamber. In this section, we consider the features involved in the design and construction of a sample cell for measurement of oxygen diffusion

across thin polymer films with detection based upon luminescence quenching. The cell consists of four parts: a reservoir chamber where air or oxygen can be introduced, a polymer membrane, a receiving chamber into which the oxygen diffuses, and a film containing a phosphorescent dye that senses the presence of oxygen in this chamber. Drawings illustrating the cell and its operation are presented in Figures 1 and 2, and details about its construction are given in the Experimental Section above.

At the heart of the measurement are the receiving chamber and its sensor. In sample-on-sensor measurements, the receiving chamber has an effective volume close to zero because the film to be tested is placed in direct contact with the sensor film. As we will see below, this sample geometry provides accurate values of the diffusion coefficient for oxygen across the polymer film to be tested but does not provide reliable values of the oxygen permeability. In film−spacer−sensor experiments, a spacer is introduced to separate the polymer film from the sensor film to create a receiving volume for the oxygen that diffuses through the film. By choosing spacers of different thicknesses, the size of the receiving volume can be controlled over a wide range. (In a traditional membrane diffusion apparatus, the surface-to-volume ratio (S/V) is normally less than 10 cm^2/ mL).

The cell fits in the sample chamber of a commercial fluorescence spectrometer. One monitors the change in intensity over time of the emission of a dye in the sensor layer. The sensor layer itself consists of a phosphorescent dye dissolved in a polymer resin, which is mounted on a quartz plate. The thin polymer film containing the dye sits inside the receiving chamber. The dye is excited through the quartz disk, and emission from the dye is monitored in the reflectance ("front-face") mode. This resin satisfies two important conditions of the experiment, transparency at the excitation and emission wavelengths of the dye and high permeability to oxygen. The sensitivity of the sensor film to the oxygen pressure can be controlled by choosing a resin of appropriate permeability to oxygen and a dye with an appropriate lifetime. Here we employ a phosphorescent dye, because the long lifetime of the excited state enhances its sensitivity to quenching by small amounts of oxygen.

The control of the gas leakage from the chamber is a very important technical issue because of the long measurement time, which can be an entire day in some cases. Thus, it is necessary to seal the spacer to the glass and to the film to be examined with an adhesive that has a very low permeability to oxygen. We have found that polyisobutylene (M_w = 200 000) is an effective material for this purpose, both for its adhesive property and its low gas permeability. No leakage of air through the device could be observed over a time period of a few days

Sensor Characterization. The spectroscopic properties of the dye and the gas permeability of the Genesse GP197 resin were studied in previous work in our laboratory.[11] The unquenched lifetime of the PtOEP dye in the GP197 resin was found to be in the range of τ° = 100 μs. The diffusion coefficient of oxygen in the GP197 resin measured by fluorescence quenching was found to be 5.7 × 10^{-7} cm^2/s, and its solubility was calculated from these measurements to be 4.2 × 10^{-4} M/atm.

The sensor must meet two additional important criteria. First, the sensor must have a fast response to the change in the external
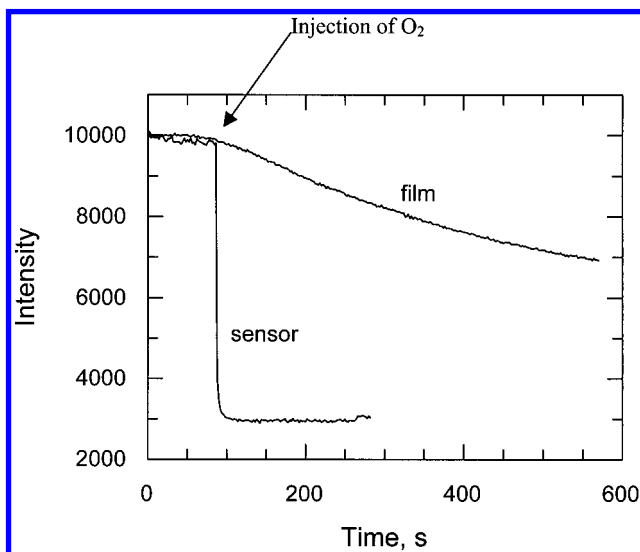
Figure 3. Decay of emission of the sensor itself compared to the decay of emission of the sensor limited by oxygen diffusion through a film of Teflon (125 μm). λ_{ex} = 573, λ_{em} = 646 nm. The response time of the sensor is negligible compared to the response of any of our samples.

oxygen pressure. The response of our sensor, a thin film (<2 μm) with a high oxygen permeability, is less than 2 s (Figure 3), which is negligible compared to the time of any of the experiments reported here. Second, the sensor response must be linear with the variation in the oxygen pressure. The linearity of the sensor response was tested by exposing the sensor film to an oxygen-free atmosphere (pure nitrogen) and two partial pressures of O$_2$ (air and pure O$_2$ at 1 atm). The effect of these different atmospheres on the dye luminescence intensity was measured, and the data from these three experiments were plotted in the Stern−Volmer form,

$$I_o/I - 1 = k\tau^\circ[O_2] = k\tau^\circ S_s P_{O_2} \qquad (1)$$

where I_o and I are, respectively, the phosphorescence intensities for pure nitrogen and for different oxygen pressures. S_s is the solubility of O$_2$ in the sensor resin, and τ° is the unquenched lifetime of the dye. Figure 4 shows that ($I_o/I-1$) exhibits a linear response when plotted vs the partial pressure of oxygen, indicating that the Stern−Volmer law applies to our system over this range of oxygen pressures. We note that there is a very small negative curvature for high pressure (~1 atm of pure oxygen). This curvature is reproducible for this resin even in samples with a different history. In most of the cases we consider, the change in pressure within the receiving chamber is always very small (0.1 times the initial pressure).

Gas Diffusion. After the sample in the diffusion cell is equilibrated with atmospheric air, pure oxygen is flushed into the reservoir chamber. The luminescence intensity measured simultaneously is plotted vs time in the Stern−Volmer form as shown in Figure 5. This typical decay shows two main features: that (I_{air}/I) is constant for a short time and then it exhibits a linear increase at longer times. The shape of this curve is similar to that observed in traditional dynamic gas diffusion experiments.[1−4] The lag time θ is the time necessary for the film to reach its steady-state
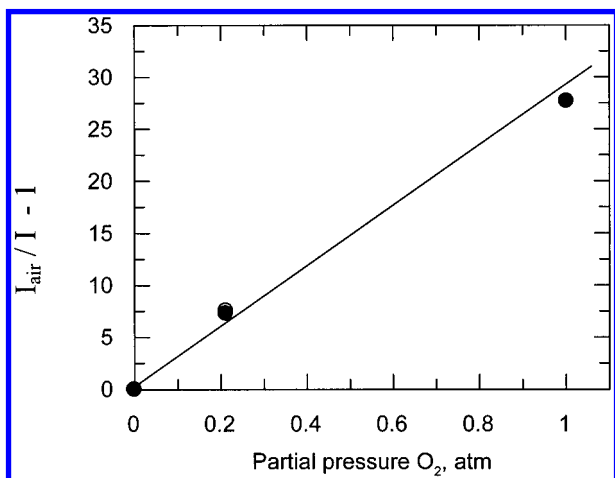
Figure 4. Stern−Volmer representation of the luminescence intensity of the sensor equilibrated with pure nitrogen, air, and pure oxygen. $\lambda_{ex} = 573$, $\lambda_{em} = 646$ nm.
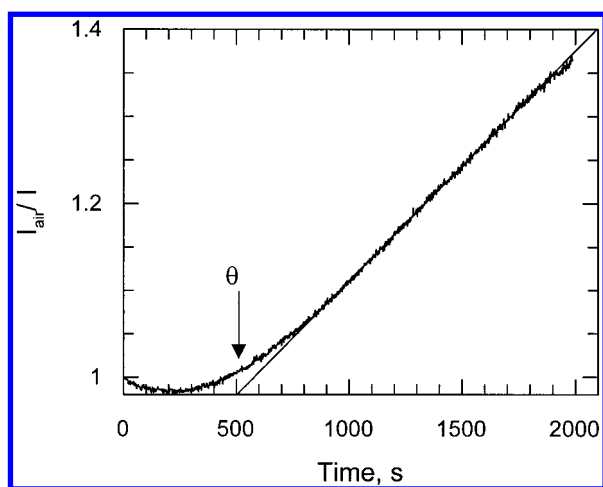

Figure 5. Change in sensor luminescence intensity accompanying oxygen diffusion through a polystyrene film (0.24 mm). $\lambda_{ex} = 573$, $\lambda_{em} = 646$ nm. The intensity values are plotted as (I_{air}/I) vs time. The diffusivity is determined from the lag time θ, and the permeability can be calculated from the slope of the linear part of the signal at $t > 3\theta$. This profile is typical for gas diffusion through a polymer film.

concentration profile between the two chambers. The linearity in the second part of the response reflects the steady-state flux of oxygen across the film between the two chambers.

Theoretical Considerations. The diffusion of gas through a polymer material is described by Fick's law, which in one dimension is written in the form

$$\partial C/\partial t = D(\partial^2 C/\partial^2 x) \tag{2}$$

where $C(x,t)$ is the local concentration at the position x at time t and D is the diffusion coefficient of the gas in the material. The solution to this equation depends on the boundary conditions at the edges of the film. In our case, the concentration of gas in the film in contact with the receiving chamber $C(0,t)$ is always constant and proportional to the oxygen pressure in this chamber P_{O_2} (1 atm)

$$C(0,t) = S_f P_{O_2} \tag{3}$$

where S_f is the solubility of the gas in the film. The tricky part of this problem is the determination of the concentration at the second edge of the film $C(L,t)$. In the case where the diffusion chamber is sufficiently large, the change in the pressure in this chamber is small. The concentration of gas at this edge of the film can be considered to be constant and equal to

$$C(L,t) \sim C(L,0) = S_f P_{air} \tag{4}$$

where P_{air} is the partial pressure of the oxygen in the atmospheric air (0.21 atm). Fick's equation can then be solved under our conditions by changing the variable from $C(x,t)$ to $\delta C(x,t)$

$$C(x,t) = \delta C(x,t) + C(L,0) \tag{5}$$

$$\partial \delta C/\partial t = D(\partial^2 \delta C/\partial^2 x) \tag{6}$$

$$\delta C(0,t) = S_f(P_{O_2} - P_{air}) \tag{7}$$

$$\delta C(L,t) \sim 0 \tag{8}$$

Under these conditions, the problem becomes similar to that described previously.[14] The pressure of oxygen that accumulates in the diffusion chamber $P(t)$, over the time scale of the experiment, is calculated from equations 2−8 to yield

$$P(t) = \frac{S}{VL}(P_{O_2} - P_{air})S_f\left(Dt - \frac{L^2}{6} + ...\right) + P_{air} \tag{9}$$

where S is the surface area of the diffusion, V is the receiving volume, and L is the film thickness. Equation 9 contains an additional term, describing the convergence of the system to the steady-state limit, which is assumed to be negligible for $t > 2L^2/(6D)$. For all times, eq 9 holds true for the values of $P(t) - P_{air}$ that are negligible compared to the pressure in the reservoir chamber P_{O_2}. The response of the sensor to the increases in oxygen pressure is described by the combination of eq 9 and the Stern−Volmer equation for the sensor,

$$I_o/I - 1 = k[O_2] = kS_s P(t) \tag{10}$$

where S_s is the solubility of the oxygen in the sensor. The parameter kS_s is determined from the difference in the luminescence intensity upon exposure of the sensor film to an atmosphere of nitrogen and air.

$$I_{air}/I - 1 = (1 - I_{air}/I_o)\frac{P(t) - P_{air}}{P_{air}} \tag{11}$$

$$I_{air}/I - 1 = (1 - I_{air}/I_o)\frac{S}{VL}S_f\left(Dt - \frac{L^2}{6} + ...\right)\left(\frac{P_{O_2} - P_{air}}{P_{air}}\right) \tag{12}$$

For our sensor film, $(1 - I_{air}/I_o)$ is estimated to be 0.84 and $(P_{O_2} - P_{air})/P_{air}$ is equal to 3.76. The shape of the theoretical decay (I_{air}/I) vs time (Figure 6) is very close to the experimental one.

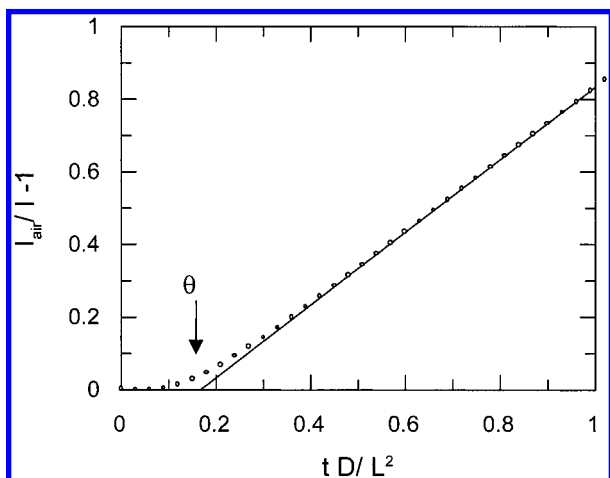(14) Crank, J. *The Mathematics of Diffusion*; 2nd ed.; Oxford University Press: Oxford, 1975.

Figure 6. Theoretical values of $(I_{air}/I - 1)$ calculated from eq 12 and plotted vs normalized time, tD/L^2. (D, diffusion coefficient; L, film thickness). The shape of this decay curve is similar to the experimental curve in Figure 5.

The crossover occurs at $\theta = L^2/(6D)$ giving an estimate of the diffusion coefficient D without any geometrical correction. The linear part of the decay is proportional to the permeability of the gas through the film P_p

$$P_p = S_f D \qquad (13)$$

Method of Analysis. The permeability (P_p) is determined from the slope of the linear part of the I_{air}/I vs time curve, and the diffusivity (D) is determined from the extrapolation of this line to $y = 0$ on the time axis. To ensure that the steady-state regime is reached, the linear part of the decay is fitted starting from 3 times the lag time θ. This method for the determination of D and P_p is based on the assumption that the diffusion chamber is infinite in volume. In the case of an extremely small chamber, the previous equations do not apply and the measured values of permeability and the diffusivity must be corrected. Paul and Dibenedetto[15] have treated the problem of diffusion in a finite volume and derived equations to correct the measured values of D and P_p. They defined a parameter η as

$$\eta = 1.01 \times 10^5 (T/273) S_f\, SL/V = 1.01 \times 10^5 (T/273) S_f\, L/h \qquad (14)$$

where S_f has the dimensions of $(cm^3(STP)/cm^2/Pa)$, T is the temperature (K), and h (cm) and L (cm) are, respectively, the thicknesses of the spacer (in our system) and the film. If the measured value of the diffusivity and permeability are D_c, and P_c, the corrected values D and P_p are calculated as

$$\alpha = L/h \qquad (15a)$$

$$S_f = \frac{P_c/D_c}{1 + 0.38\alpha P_c/D_c} \qquad (15b)$$

(15) Paul, D. R.; DiBenedetto, A. T. *J. Polym. Sci., Part C* **1965**, *10*, 17.

$$P_p = P_c(1 + 0.69\alpha S_f) \qquad (15c)$$

$$D = D_c(1 + 0.29\alpha S_f) \qquad (15d)$$

In all of our experiments, we chose the thickness of the washer (h) to give a very small η values ($0.01-0.05$), leading to the direct determination of D and P_p values. The precision in the determination of the diffusivity depends on the flatness of the linear plot of the decay. To increase the precision in the determination of D, a very thin washer ($h = 0.51$ mm) is used in the receiving chamber. However, for such a thin separator, a considerable error arises in the determination of the receiving volume. This error does not affect the determination of D, which is in principle independent of the experimental conditions, since η is small. On the other hand, the determination of P_p is sensitive to the errors in the receiving volume V. Consequently, a thicker washer (>1 mm) is used for a more precise determination of P_p.

Diffusion Coefficient Measurements. The diffusion coefficient of oxygen through the polymer film (D) is calculated from the delay time in the diffusion process θ, $D = L^2/(6\theta)$. Experimentally, θ is estimated from the extrapolated intersection of the linear part of the I_{air}/I plot with the x axis. In the case where the receiving volume is sufficiently large, the linear part of the decay has a small slope. This "flatness" can lead to uncertainty in the estimation of the lag time θ. To improve the precision in D, we repeated the experiment with a very small receiving volume made of a washer with a thickness $h = 0.51$ mm leading to a surface-to-volume ratio of 19.6 cm^2/mL. Table 2 shows the diffusion coefficient measured in a series of films at room temperature (23 °C) by using our technique. These D values are compared to values in the literature obtained by different methods.

The diffusion coefficient of oxygen in polystyrene calculated from the trace in Figure 5 is 1.84×10^{-7} cm^2/s. When this experiment is repeated on the same film we find $D = (1.90 \pm 0.05) \times 10^{-7}$ and $(1.9 \pm 0.1) \times 10^{-7}$ cm^2/s when a series of experiments are carried out on films of different thicknesses. Wang and Ogilby[10] used a spectroscopic technique to study the oxygen diffusion in polystyrene and found values ranging between 2×10^{-7} and 4×10^{-7} cm^2/s, depending on the temperature and the pressure of oxygen and nitrogen.

We obtain the diffusion coefficient of O_2 in PET films with great accuracy and precision because the lag time θ is large. We find $D = 4.07 \times 10^{-9}$ cm^2/s ($\pm 2\%$). This precision is due to the large ratio of surface-to-volume, 19.6 cm^2/cm^3. This value is similar to the reported value of 4.5×10^{-9} cm^2/s.[18] Recent studies on highly drawn films[16] using a dynamic diffusion technique led to a value of the diffusion coefficient at 25 °C in the range 4.0×10^{-9} cm^2/s. This study also found that the dynamic diffusion measurement did not give good reproducibility of the diffusion coefficient, even when repeated on the same sample. The fluorescence-quenching method described here gives the highest precision for samples with low oxygen diffusivity.

Permeability Measurements. The permeability P_p is calculated from the slope of the long-time linear part of the decay curves as shown in Figure 5. Note that the film-on-sensor geometry

(16) Slee, J. A.; Orchard, G. A. J.; Bower, D. I.; Ward, I. M. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 71.

(17) Koros, W.; Wang, J.; Felder, R. *J. Polym. Sci.* **1981**, *26*, 2805.

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Table 2. O₂ Diffusion Coefficients in Various Polymer Films

films	L,[a] μm	D (10^{-7} cm²/s) calcd[b]	lit.
Teflon	125	1.69 ± 0.04	1.84 [17]
PET	111	0.0407 ± 0.0008	0.045 [16,18]
polystyrene	250	1.90 ± 0.05	2−4
polyethylene ($d = 0.92$)	0.185	0.7	4.6 [19]

[a] Film thickness. [b] Calculated from the lag time θ.
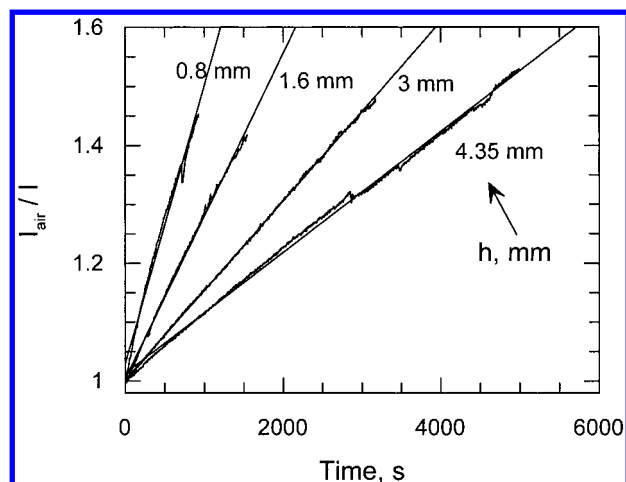
Figure 7. Plot of (I_{air}/I) vs time for the luminescence intensity measured during oxygen diffusion through a Teflon film (12 μm) for different surface-to-volume ratios in the receiving chamber. In this geometry, S/V is equal to h^{-1}.

Figure 8. Rate of oxygen permeation through a Teflon film, calculated from the slopes of the lines in Figure 7, and plotted vs the surface-to-volume ratio of the receiving chamber. The rate has the dimension of (cm³(STP)/day). The permeability is calculated from the slope of each line. Note that the data corresponding to a very small receiving volume have a large error.

Table 3. O₂ Permeability in Various Polymer Films

films	L[a], μm	P_p[b]	lit. P_p[b]
Teflon 1	12	1.71 ± 5%	3.64 (25 °C)[17]
Teflon 2	125	1.83 ± 5%	
polystyrene	110	1.8 ± 5%	at 25 °C, from[20] 1.35 to 1.85
polyethylene (1)	185	1.5	2.2 (at 25 °C)
polyethylene (2)	75	1.6	

[a] Film thickness. [b] Permeability, 10^{13} cm³(STP) cm/ (cm² s Pa),

cannot be used to measure this permeability because the volume of the diffusion chamber is unknown. Instead we use washers of known thickness to create diffusion chambers of known volume. The critical ratio of the diffusion surface to the chamber volume, S/V, is equal in our system to the inverse of the washer thickness. Equation 12 predicts that the flux of gas through the film reaching the sensor is proportional to this ratio. We tested this prediction and display the results in Figure 7. We observe that the slope of the I_{air}/I plot is proportional to the spacer thickness for spacers ranging from 0.8 to 4.35 mm. In Figure 8 we show that the measured rate of oxygen transport through the film of Teflon 1 (12.5 μm) is proportional to the ratio S/V. The slope of the linear part of the curve is the flux, which is constant and independent of the geometry of the system. The permeability P_p is then calculated from the flux. There is considerable uncertainty in the permeability determination for very thin spacers, where there is a significant error in the calculation of the volume of the diffusion chamber. This is due to the technical difficulty of controlling the flatness of a flexible film positioned on a thin spacer of 10-mm interior diameter. One can resolve this problem by supporting this film by a spacer with a smaller interior diameter or by using a thin disk bearing many small holes, such as the support used in the conventional method.

Here we should point out that if the volume of the diffusion chamber is big enough, and the sensor is sufficiently sensitive, a single measurement would be sufficient to give a reliable value for the permeability. On the o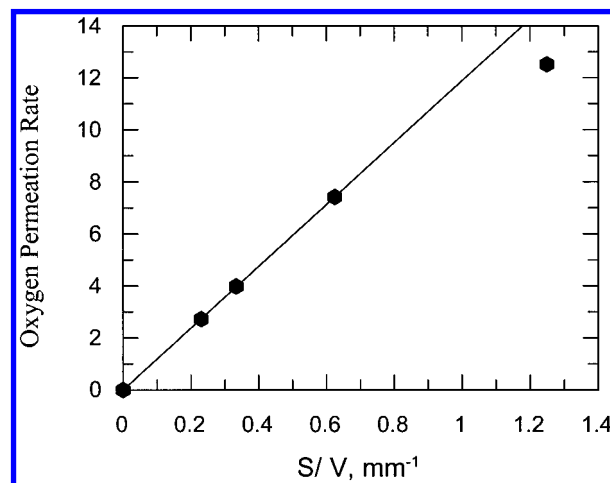ther hand, results obtained from an extremely small receiving volume correspond to large values of η and need to be corrected as described above.

In all cases, the linearity of the rate vs S/V was tested in order to reduce the error in the determination of the permeability. The slope of the curve in the plot of I_{air}/I vs S/V gives the permeability with great precision. It is clear that one experiment can determine the permeability if the volume of the receiving chamber is big enough and the error in calculating its volume is negligible. Table 3 presents a list of the permeability values calculated for various films: Teflon, polystyrene, and linear low-density polyethylene.

Since polystyrene is an amorphous polymer, there are no complications due to the sample crystallinity. These films are useful samples for testing this method of measurement. Earlier studies have reported a rather large scatter in the permeability values for P_p ranging from 1.35×10^{-13} to 18×10^{-13} cm³(STP) cm/ (cm² s Pa). Recently Burmester et al.[20] found that this scatter may be due to experimental error and found that the actual values of the permeability vary from 1.35×10^{-13} to 1.85×10^{-13} cm³(STP) cm/(cm² s Pa) according to the sample history. We have found that at room temperature (23 °C) the permeability is equal to $1.8 ± 5\% \times10^{-13}$ cm³(STP) cm/(cm² s Pa) for samples prepared by our melt pressing and cooling protocol. Our values are in the same range as that found by Burmester.

A linear low-density polyethylene ($d = 0.92$) film sample was also used to test the efficiency of this technique for measuring

(19) Michaels, A. S.; Bixler, H. J. *J. Polym. Sci.* **1961**, *50*, 413.
(20) Burmester, F.; Manial, T. A.; Mchattie, J. S.; Wessling, R. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 414.
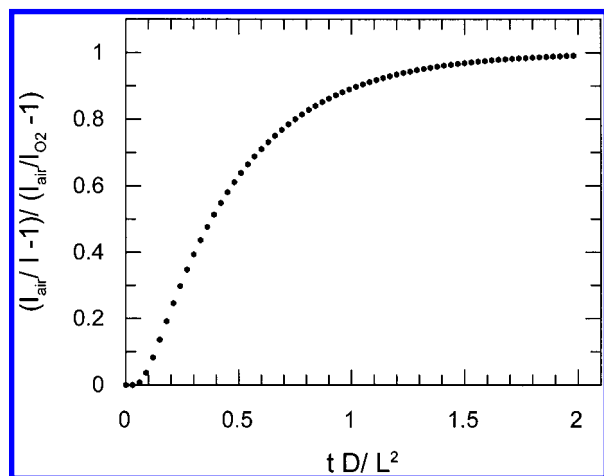
Figure 9. Theoretical values of $(I_{air}/I - 1)/(I_{air}/I_{O_2} - 1)$ described by eq 17, calculated numerically, plotted vs the normalized time (tD/L^2).

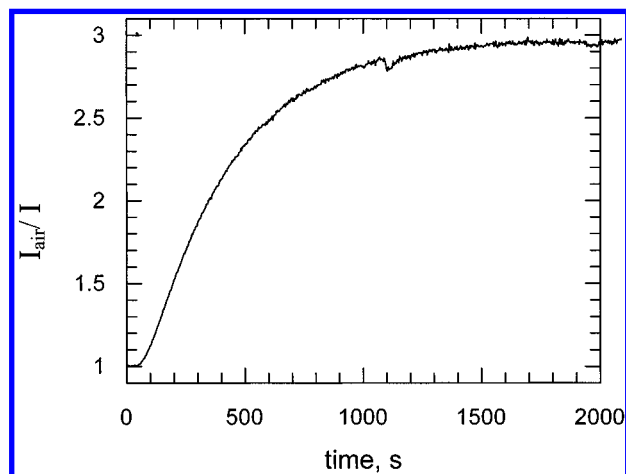**Figure 10.** Plot of (I_{air}/I) vs time for the luminescence intensity measured during the diffusion of oxygen through a polyisobutylene film (0.15 mm). $\lambda_{ex} = 573$, $\lambda_{em} = 646$ nm. This decay curve is similar to the theoretical curve shown in Figure 9.

oxygen permeability. Here we found a value of the permeability equal to 1.55×10^{-13} cm³(STP) cm/(cm² s Pa), which is in the same range of the values reported in the literature[19] 2.2×10^{13} cm³(STP) cm/ (cm² s Pa) at 25 °C.

For the Teflon EFP, we have found a value of 1.71×10^{-13} cm³(STP) cm/(cm² s Pa) for the Teflon 1 film (12 μm) and 1.83×10^{13} cm³(STP) cm/(cm² s Pa) for the Teflon 2 film (125 μm). These values are very reproducible, within 4%. Compared to the values reported in the literature[17] (3.64×10^{-13} cm³(STP) cm/ (cm² s Pa)) our values are smaller. We should point out that when we used our method to study the diffusion of N_2 in air into a N_2 atmosphere in the receiving chamber, we obtained permeability values of 3.75×10^{-13} cm³(STP) cm/(cm² s Pa), similar to those reported in the literature.

Measuring the Diffusivity of Oxygen in Fluid Samples. In the sample-on-sensor geometry, one eliminates the empty volume between the sample and the sensor. This can be achieved if either the sensor or the film is a viscous fluid. Thus, this method could be used to measure the diffusivity of oxygen in fluid materials, where the sample cannot be positioned as a film between two chambers in the geometry film−spacer−sensor. To simplify this system, the sensor should act only as a detector and not as a
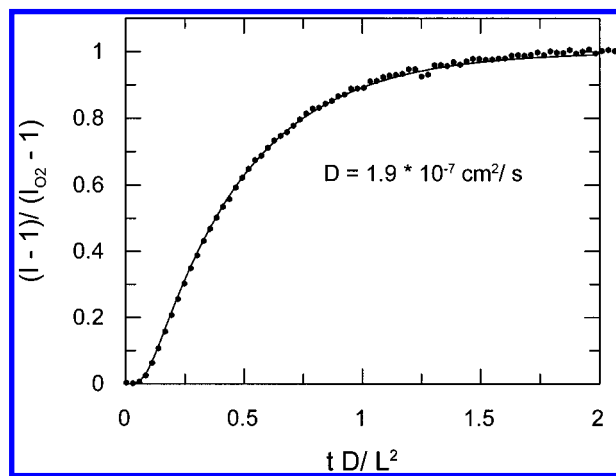
Figure 11. Superposition of the experimental decay shown in Figure 10 on the theoretical curve of Figure 9. The best fit is obtained for a diffusion coefficient $D = 1.9 \times 10^{-7}$ cm²/s.

receiving volume. Consequently, the thickness of the sensor should be negligible compared to the thickness of the measured film. In such a case, the gas is equilibrated in the sensor instantly since its permeability is high. The solution of Fick's law under these conditions was reported previously.[4] Here we are interested in the concentration of the diffusing gas at the film−sensor interface.

$$\frac{P(L,t) - P_{air}}{(P_{O_2} - P_{air})} = 1 - \frac{4}{\pi}\sum\frac{(-1)^n}{(2n+1)}\exp\left(\frac{-D(2n+1)^2\pi^2t}{4L^2}\right)$$

$$(16)$$

By combining (16) with the Stern−Volmer equation, the luminescence intensity can be written as

$$\left(\frac{I_{air}}{I} - 1\right) =$$

$$\left(\frac{I_{air}}{I_{O_2}} - 1\right)\left(1 - \frac{4}{\pi}\sum\frac{(-1)^n}{(2n+1)}\exp\left(\frac{-D(2n+1)^2\pi^2t}{4L^2}\right)\right) \quad (17)$$

Figure 9 presents a plot of values of $(I_{air}/I - 1)$ calculated from eq 17 vs the normalized time $t \times (D/L^2)$. The intensity is constant for short times and then it increases rapidly, before saturating at longer time.

An example is given in Figure 10 for a relatively thin film of PIB (0.15 mm). Preparation of a flat, smooth film of a viscous polymer fluid requires some skill. The specific procedure we use is described in the Experimental Section above. When the intensities are plotted as shown in Figure 10, they give the same general shape as the theoretical curve (see also Figure 9). The superposition of the experimental and the theoretical curves is achieved for a D value of 1.9×10^{-7} cm²/s (Figure 11). This value compares to a literature values of 0.81×10^{-7} cm²/s obtained in a cross-linked PIB film.[21]

CONCLUSION

The phosphorescence-quenching technique for measuring the diffusivity and the permeability of oxygen in polymer films has various advantages compared to the traditional method:

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(a) The area of film used for the gas diffusion can be reduced to the dimension of the light spot (1−2 mm), minimizing the possibility of inhomogenities and thickness variation in the film.

(b) The surface-to-volume ratio (S/V) can be chosen from 0 to large values since the detector is very thin (micrometer size). As a consequence, we can use a variety of different spacers to control the S/V ratio. In many experiments reported here, a 0.51-mm-thick spacer was used. This gave a S/V value of 19.6 cm^2/mL. We can envisage using a 0.1-mm spacer to obtain S/V on the order of 100.

(c) This method allows one to measure the diffusion coefficient of oxygen in a viscous polymer liquid. Normally, to measure D and P_P for low-T_g polymers, one has to first cross-link the polymer so that it can form a free-standing film. The method we describe allows us to examine the un-cross-linked polymer. In this way, one can examine how the presence of cross-links affects gas diffusion in these polymers.