

Permeability of Oxygen Through Polymers. I. A Novel Spectrophotometric Method

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Synopsis

A novel method for the measurement of oxygen permeability through polymer membranes is described. It is based on monitoring the sensitized photo-oxygenation of a singlet oxygen acceptor in a detector layer sandwiched between a support and the polymer layer under test. The detector layer contains a sensitizer which on irradiation produces singlet excited oxygen from the ground-state oxygen available. The singlet oxygen reacts with an oxygen acceptor, the disappearance of which can be followed by spectrophotometry. In the photostationary state, changes in the acceptor absorbance are directly related to the overall flux of oxygen through the polymer membrane. It can be shown that the permeation coefficient P of oxygen is proportional to the rate of change in acceptor absorbance and to the inverse of the oxygen concentration in the surrounding atmosphere. It is given by the expression

$$P = \frac{1}{10^3 \epsilon \Delta C} \cdot \frac{\Delta D l}{\Delta t}$$

where ϵ is the molar extinction coefficient, ΔC is the difference in the oxygen concentration on the two sides of the polymer membrane, ΔD is the change in optical density during the time interval Δt , and l is the thickness of the polymer membrane. The method is comparatively simple and rapid and provides data for polymers that are difficult to study by more conventional methods. Oxygen permeabilities were measured for a group of water-soluble polymers.

INTRODUCTION

In many applications it is of interest to know the oxygen permeability of a polymeric material. Conventional methods for the determination of gas permeabilities are often inadequate when low-level permeabilities are measured. The preparation of a self-supporting membrane able to withstand the pressure fluctuation of a manometric procedure can be difficult, and it is not always easy to establish a satisfactory seal between the membrane and the cell. Sorption techniques may yield uncertain values when the amount of permeant sorbed by a polymer sample is very small. A comprehensive account of the methods for measuring permeabilities already exists.¹

We have now found a spectrophotometric method that eliminates many of these disadvantages. It is based on measuring the flux of oxygen by monitoring its reaction in the singlet excited state with a suitable oxygen acceptor.

METHOD

The experimental arrangement consists of a thin *detector* layer coated on a transparent support and overcoated with a thick polymeric membrane (Fig. 1).

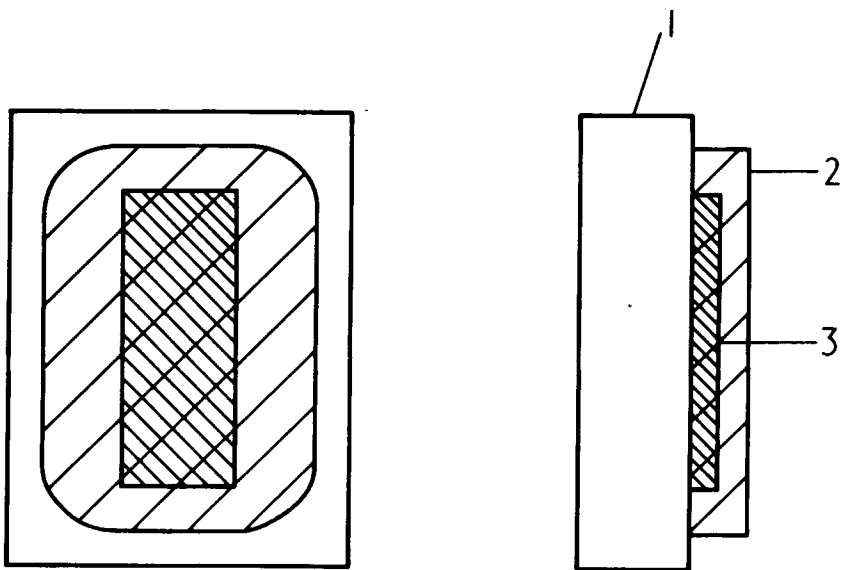


Fig. 1. The sample: (1) support; (2) polymeric membrane; (3) detector layer.

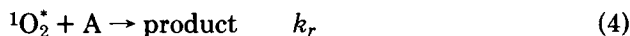
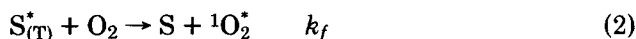
The detector layer contains a sensitizing dye (in our case Rose Bengal) which on irradiation produces singlet excited oxygen from the ground-state oxygen available² and a singlet oxygen acceptor (in our case diphenylisobenzofuran, DPBF).³ Rose Bengal is known to be an efficient singlet oxygen producer and has been reported to give a singlet-oxygen yield of 0.76 in air-saturated methanol.² Rose Bengal itself is not subject to photo-oxygenation, and also it absorbs at lower frequency than DPBF, thus permitting selective excitation. DPBF undergoes a rapid and irreversible reaction with singlet oxygen, and its disappearance can easily be followed photometrically. It is known to interact with $^1\text{O}_2^*$ primarily via a chemical reaction with little physical quenching occurring^{3,4,8} (for example, in methanol, the reaction between $^1\text{O}_2^*$ and DPBF is about 10^5 faster than solvent quenching of $^1\text{O}_2^*$).

The support (e.g., glass, quartz) must be transparent at the λ_{max} of the acceptor.

For the success of the experiment it is important that no mixing takes place between the components of the detector layer and the polymer membrane. Consequently, when water-soluble polymer membranes are studied, a water-insoluble acceptor (DPBF) is used, and the water-soluble sensitizer (Rose Bengal) is rendered hydrophobic by attaching it to a water-insoluble polymer [e.g., poly(benzylvinyl chloride)]. This does not change significantly its ability to produce a singlet oxygen. The quantum yield for the formation of singlet oxygen with polymer-bound Rose Bengal in a heterogeneous sensitization reaction was reported¹⁰ to be 0.43. A hydrophobic binder of relatively high oxygen permeability (e.g., polystyrene) can also be added to the detector layer. The polymeric membrane is cast over the detector layer in such a way that the latter is well sealed between the membrane and the support as shown in Figure 1.

The kinetics of acceptor disappearance will now be described with reference to the mechanism of singlet oxygen formation.^{5,6} On irradiation of the sample, the sensitizer is eventually promoted to its triplet state. The triplet excited dye

reacts with ground-state oxygen to give singlet excited oxygen, which then is intercepted by the acceptor. The following scheme describes this reaction sequence:



In the photostationary state, i.e., when the concentration of ${}^1O_2^*$ is constant, the rate of disappearance of acceptor is given by the expression

$$-\frac{d[A]}{dt} = \frac{k_f[S^*][O_2][A]}{\beta + [A]} \quad (5)$$

where $\beta = k_d/k_r$. For DPBF³ the value of β is much smaller than $[A]$, i.e., there is enough acceptor present to capture all the singlet oxygen produced in the detector layer. In that case eq. (5) is simplified to

$$-\frac{dA}{dt} = k_f[S^*][O_2] \quad (6)$$

$[S^*]$ being constant.

When there is an unlimited supply of oxygen, the value of $[O_2]$ remains constant and the rate of disappearance of acceptor measures this constant oxygen concentration. If, however, the supply of oxygen to the detector layer is limited, a diffusional steady state will eventually be reached where removal of oxygen by reaction (4) is balanced by the available oxygen supply. In that case, *the rate of disappearance of acceptor measures the flux of oxygen through the polymer membrane.*

The amount of acceptor n_A in the detector layer is related to the optical density D :

$$n_A = \frac{DL}{10^3\epsilon} \quad (7)$$

where ϵ is molar extinction coefficient, and L is the area of the detector layer.

The flux of oxygen/cm² through the membrane is therefore given by the expression

$$J \equiv \frac{d n_A}{dt L} = \frac{\Delta D}{\Delta t} \frac{10^{-3}}{\epsilon} \quad (8)$$

The permeation coefficient P is defined as the flux under unit concentration gradient:

$$J = P \frac{\Delta C}{l} \quad (9)$$

where ΔC is the difference in concentration across the layer of thickness l .

P may be expressed in terms of the measurable quantities of our experiment by the final equation

$$P = \frac{l}{10^3\epsilon \Delta C} \frac{\Delta D}{\Delta t} \quad (10)$$

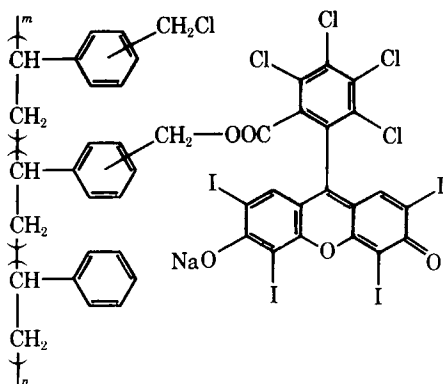
If Δt is expressed in seconds, the permeation coefficient P is obtained⁹ in units of cm^2/sec .

EXPERIMENTAL

Preparation of Polymer-Supported Rose Bengal

Poly(styrene)₂₀-*co*-benzylvinyl chloride (2.24 g, 10^{-3} mol) was reacted with Rose Bengal (1.02 g, 10^{-3} mol) in DMF (100 ml) at 100°C for 3 days. The product was isolated by precipitating into water and the solid was filtered off, thoroughly washed with water, and dried at 40°C under vacuum. A bright purple polymer, fully soluble in CHCl_3 and dioxan and insoluble in water, was obtained. Found: I, 2.94%. This suggests that about one in eight of the original polymer $-\text{CH}_2\text{Cl}$ groups had reacted.

Alternatively, poly(benzylvinyl chloride) (5.04 g, 3.3×10^{-2} mol) was reacted with Rose Bengal (1.02 g, 1×10^{-3} mol) in DMF (150 ml) at 100°C for 60 hr, the reaction mixture was precipitated into water and the solid was filtered off, dried, and then extracted with CHCl_3 to give a small quantity (about 0.5 g) of a dark-red polymer. Found: I, 10.80%. This corresponds to about one Cl in 18 of the starting polymer reacting with the dye. The molar absorptivity of this polymer-supported Rose Bengal was approximately 1500.



Polymer-supported Rose Bengal

The detector layer was prepared by coating, onto a surface-modified glass plate, a solution containing 0.1 g poly(styrene-*co*-benzylvinyl chloride)-supported Rose Bengal; approx. 0.01 g diphenylisobenzofuran (DPBF) (or enough for the dye layer to have a DPBF absorbance of 1.0–1.8); 0.2 g polystyrene; and 10 ml CHCl_3 .

The detector layer was dried in air and its thickness was estimated as follows: a set of detector layers of various thickness on glass was prepared and the thickness was measured with an optical interferometer. A plot of Rose Bengal absorbance versus thickness then served as a calibration graph for estimating the thickness of the detector layer from its optical density. The detector layer thickness varied from 1 to $5 \mu\text{m}$.

The surface of the glass (Chance Propper Ltd., Micro Slides, $76 \times 25 \text{ mm}^2$, 1.2/1.5 mm thick) was modified by reacting it first with hexamethyldisilazane

in CHCl_3 . The polymers of the test layer were cast from their aqueous solutions over the detector layer and dried in air for not less than 48 hours. The thickness of the test layer was measured with a micrometer.

The changes in the DPBF absorbance at $\lambda_{\text{max}} = 422 \text{ nm}$ under constant irradiation were determined. A 150-W tungsten/halogen lamp, supplied from a stabilized power pack (output voltage variations $< \pm 0.1\%$) was used as an irradiation source. The light intensity of the source did not vary by more than $\pm 0.3\%$ over a 60-min period. The light was passed through an achromatic doublet lens of +108 mm focal length and through a Wratten No. 12 filter (cut off at 520 nm) before it reached the sample. A heat-absorbing glass filter was placed between the lamp and the sample to keep the sample at near-ambient temperature.

Typical experimental results are represented graphically in Figure 2. The rate of DPBF disappearance was expressed as the slope m of the linear section of the curve. The permeability of polymers to oxygen was expressed as the permeation coefficient P .

RESULTS AND DISCUSSION

Results obtained with a group of water-soluble polymers are shown in Figure 2. There we have plotted D of the acceptor in the detector layer as a function of irradiation time. With the detector layer alone, the acceptor disappears quickly, and at a constant rate, since an ample supply of oxygen is available, see eq. (6). With a polymeric overcoat (i.e., in the sandwich arrangement shown in Fig. 1) the initial rapid decrease of absorbance is followed by a gradual change; eventually, a constant rate of decrease in absorbance is established. It can be seen in Figure 2 that the slope m of the linear part of the curves varies widely with polymer membranes used.

The value of the slope m for the detector layer itself is at least 10^2 orders of magnitude greater (Fig. 2, curve 1) than the slope for any of the sandwich structures (Fig. 2, curves 2 to 6). It means that in the steady state, oxygen is supplied to the detector layer at a rate at least 10^2 times lower than the rate of oxygen consumption. Therefore, the concentration of oxygen in the detector layer is negligible compared to the concentration of oxygen on the outside of the

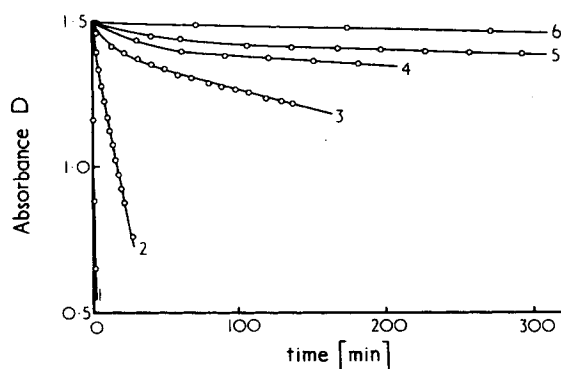


Fig. 2. Change in D_{DPBF} vs time on irradiation of the sandwich structure samples containing the detector layer and (1) no other polymer, (2) poly(styrene-co-benzylvinyltriethylammonium chloride), (3) poly(styrene-co-N-benzyltrimethylpropylammonium chloride maleimide), (4) poly(1-vinylimidazole), (5) poly(vinyl alcohol) (Elvanol 70-05), and (6) carboxymethylcellulose (Hercules 7LF).

polymer membrane, and ΔC simply equals the ambient oxygen concentration.

Values of the permeation coefficient P were calculated according to eq. 11 using $\epsilon_{\text{DPBF}} = 1.88 \times 10^4 \text{ l/mol cm}$ and $\Delta C = 9.4 \times 10^{-6} \text{ mol/cm}^3$ (air). In that case, eq. (10) becomes

$$P = 5.66 \times 10^{-3} \frac{\Delta D}{\Delta t} l \quad (11)$$

The values of m and P obtained in this way for various polymers are collected in Table I.

Many composite units of the permeability coefficient have appeared in the literature,¹¹ and direct comparison of values expressed in different units is often difficult. However, from Table I it can be seen that permeation coefficients of an expected order of magnitude^{11,12} are obtained. Also the relative permea-

TABLE I
Values of m and P for Various Polymers

Polymer	$l, \mu\text{m}$	$m, \text{sec}^{-1} \times 10^6$	$P, (\text{cm}^2/\text{sec}) \times 10^{10}$	$P_{\text{av}} \times 10^{10}$	σn
Detector layer	4 ± 1	$10\,700.00^{\text{a}}$ ± 992			
“Sandwich” structures: carboxymethylcellulose ^b	55	1.22	0.338		
Poly(vinyl alcohol) ^c	73	1.72	0.636	0.63	0.01
	59	1.94	0.617		
Poly(1-vinylimidazole) ^d	75	4.17	1.76	1.78	0.02
		4.44	1.77		
	52	6.22	1.80		
		6.11	1.79		
Poly(1-vinylimidazole-co-3-benzyl-1-vinylimidazolium chloride)	28	17.7	2.80	2.75	0.15
		18.0	2.90		
	26	17.1	2.50		
	33	14.4	2.69		
		15.6	2.87		
Poly(styrene-co-N-benzyltrimethylpropylammonium chloride maleimide)	65	28.9	10.2	10.15	0.05
	70	25.6	10.1		
Poly(styrene-co-benzylvinyltriethylammonium chloride)	140	402	324	310	34
	130	487	357		
	126	407	290		
	125	373	267		
Poly(1-vinylimidazolium chloride-co-3-benzyl-1-vinylimidazolium chloride)	90	6.78	3.45	3.32	0.11
	92	5.61	3.32		
	96	4.33	3.18		
Polyacrylamide	68	2.44	0.95	0.925	0.025
		2.33	0.90		

^a An average of 10 determinations.

^b Hercules 7LF.

^c Elvanol 70-05.

^d MW $\approx 40,000$ as determined by light scattering.

bilities observed agree with the qualitative features of the structure/permeability correlation proposed for the polymers by Salame.¹³

The results also show that the method is sensitive; a flux of oxygen of 10^{-10} mol can be detected with confidence when DPBF is used. The reproducibility of the method is also good; the standard deviation σ_n in permeation coefficient P is usually well below 10%. The method offers several advantages over the more conventional techniques. Sample preparation is easy since self-supporting membranes are not required; complications arising from the use of clamps and supporting grids are eliminated. Experiments may easily be conducted at constant temperature and humidity and with a predetermined oxygen concentration. The method can be used readily to study the effect of various chemical changes (e.g., chemical modifications, crosslinking) on the oxygen permeability of polymers.

With small modifications the technique can be used for the determination of diffusion coefficients by a time lag method. Further work on this will be reported at a later date.

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