Determination of Diffusion Coefficient of Oxygen into Polymers by Using Electron Spin Resonance Spectroscopy. I. Poly(methyl Methacrylate)

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Synopsis

A simple technique has been proposed for the measurement of the diffusion coefficient of oxygen into polymeric spheres. The technique is based on the scavenging of radicals produced by high energy radiation by oxygen. The diffusion coefficient of oxygen determined for poly(methyl methacrylate) has shown an inverse dependency on the dose received. Diffusion coefficient determined for low doses ($D = 3.4 \times 10^{-8}$ cm^2/s) as well as that determined after extrapolation to zero dose ($D_0 = 3.7 \times 10^{-8}$ cm^2/s) are in excellent agreement with the values reported in the literature.

INTRODUCTION

Most of the photophysical and chemical reactions taking place in polymers occur as a result of mass diffusion of reactants. A knowledge of the diffusion coefficient of these reactants into polymeric systems is of prime importance in the developments of materials of desired properties. Oxygen is one of the most important reactants to be considered in the diffusion phenomenon. The control of the diffusion of oxygen is of particular importance in the design of polymeric membranes for separation processes in production of films for packaging industry, and in the developments of biocompatible materials.

The usual procedures used to measure the diffusion coefficients of gases through polymeric systems are based upon measurements of the amount of gas which permeates a given area of polymer in a given time. In addition to this direct method of determination, depending upon the properties of the gases being investigated there are also indirect methods based on the quenching or bleaching action of these gases on the molecular probes imbedded uniformly in the polymer.

Shaw was able to determine the diffusion coefficient of oxygen into poly(methyl methacrylate) (PMMA) by the quenching of phosphorescence of the phenanthrene added into polymer.[1] Barker, on the other hand, had utilized the bleaching action of oxygen on color centers produced by electron beam irradiation of polycarbonate and PMMA by following optically the

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moving boundary.[2] MacCallum and Rudkin[3] studied the quenching of fluorescence of naphthalene in PMMA by oxygen in thin films after displacement of nitrogen atmosphere over the sample by oxygen. Every technique mentioned above carries some inherent advantages and disadvantages.

In this study we have utilized the radical scavenging of oxygen to monitor its diffusion into PMMA. The depletion rate of radicals produced in spherical PMMA samples irradiated in vacuum with gamma rays upon contact with air was investigated by electron spin resonance (ESR) spectroscopy. By following the rate of decrease of original ESR signal intensities with contact time and by using equations developed for diffusion of gases into spherical particles, the diffusion coefficient of oxygen into PMMA was determined.

THEORY

When polymers are irradiated with high energy radiations such as electron beams or gamma rays, free radicals are produced uniformly in the system considered. The chemical structure and the quantity of these radicalic species can be easily investigated by ESR spectroscopy. Depending on the chemical and physical environment, the radicals produced in polymeric backbones show quite characteristic ESR signals. When a polymer irradiated in vacuum is exposed to oxygen or air, the shape of the original ESR signal starts to change rapidly and an asymmetric signal due to formation of peroxidic radicals develop. These reactions can be written as

$$R \xrightarrow{\text{irradiation}} R \cdot \tag{1}$$

$$R \cdot + O_2 \xrightarrow{k_{\text{obs}}} RO_2 \tag{2}$$
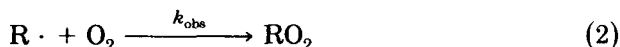
where R represents any group or atom on the polymeric backbone, $R \cdot$ is the free radical produced by irradiation, and RO_2 is the peroxide radical. k_{obs} in the second equation is the observed rate constant of the reaction. The active radical sites are trapping the penentrant oxygen molecules according to eq. (2). Before being trapped, oxygen molecules must first diffuse to the reactive sites. The diffusion and reaction processes of oxygen can be written explicitly in the following form:

$$R \cdot + O_2 \underset{k_d}{\overset{k_{\text{diff}}}{\rightleftharpoons}} [R \cdot O_2] \xrightarrow{k_r} RO_2 \tag{3}$$
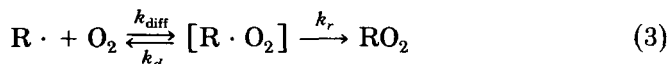
where $[R \cdot O_2]$ represents an intermediate structure, k_{diff}, the coefficient of diffusion process, and k_d, the dissociation of the intermediate back into reacting species. k_r is the reaction rate constant for the fast step. The reaction rate between a radical and scavenger oxygen molecule is very fast as compared to the slow rate of diffusion. Therefore, we can assume that the transfer of oxygen to reactive sites which is represented by the first step in eq. (3) is very slow and the reaction giving RO_2 is a very fast one. The observed reaction rate constant k_{obs} can be expressed in terms of the constants given in eq. (3) in the following form[4]:

$$k_{\text{obs}} = \frac{k_r * k_{\text{diff}}}{k_r + k_{d.}} \tag{4}$$

It can be assumed that $k_r \gg k_d$; therefore, eq. (4) can be rearranged to

$$k_{\text{obs}} = k_{\text{diff}} \qquad (5)$$

This is always the case when a reaction is diffusion-controlled. Therefore, the determination of the rate constant for the formation of peroxide radicals will directly give the diffusion coefficient of oxygen into polymer considered.

DIFFUSION IN SPHERICAL SYSTEMS

When Fick's second law of diffusion is applied to spherical systems and solved by assuming a constant diffusion coefficient, the following equation is obtained[5]:

$$\frac{C}{C_0} = 1 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \cdot \sin \frac{n\pi r}{a} \cdot \exp(-Dn^2\pi^2 t/a^2) \qquad (6)$$

where a is the radius of the sphere, D, the diffusion coefficient, and C_0 and C are the concentration of the diffusant at time zero and t, respectively. r corresponds to the radial distance at which C is measured. We can replace the concentration terms directly with the amount of diffusant by using eq. (7).

$$M = \int_v C\, dV \qquad (7)$$

when eq. (7) is considered for a spherical volume element and substituted in eq. (6), the following solution is obtained[5]:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2) \qquad (8)$$

where M_t and M_∞ represent the amounts of diffusant entering the spheres at time t and infinity, respectively.

Equation (8) can be used in several ways for the determination of D, the diffusion constant. One of the most straightforward ways of using eq. (8) is the expansion and rearrangement of this equation for the half-time of sorption process. Half-time $t_{1/2}$ is the time required for the uptake of half the amount of diffusant, sorbed at equilibrium. Therefore, when $1/2$ is substituted in eq. (8), the following simple relation is obtained for spherical systems[6]:

$$t_{1/2} = 0.0717a^2/D \qquad (9)$$

If the truncation of eq. (8) has been made not on the second but on the third term, the coefficient of a^2/D in eq. (9) changes only by 0.1%. Therefore, the error introduced by taking only the first two terms of expanded form of eq. (8) is not significant.

One can also obtain equations similar to eq. (9) by not taking the half-time values but other fractional life-times such as $t_{1/4}$ and $t_{3/4}$. The expressions to

be obtained will have the following forms:

$$t_{1/4} = 0.0414a^2/D \tag{10}$$

$$t_{3/4} = 0.1414a^2/D \tag{11}$$

Depending on the availability and reliability of data one can use either eq. (9), (10), or (11) to determine D, the diffusion coefficient. In the present study, eq. (9) is preferred, as will be explained in a later section.

When the half-time values for various average size polymer spheres are determined, a plot of $t_{1/2}$ vs. a^2 will directly give the corresponding diffusion coefficient. In order to determine the $t_{1/2}$ values, one needs to construct M_t/M_∞ vs. t curves. In the present technique it is possible to obtain either the decrease of ESR signal intensities of radicals with time, or the increase of ESR signal intensities of peroxide radical. It is therefore necessary to find a direct relation between the measured quantity (signal intensity) and the ratio M_t/M_∞. Before expressing the M_t/M_∞ ratio in terms of radical concentrations which are directly followed as intensities of ESR signals, we assume that the generation of radicals within the polymeric spheres is completely uniform. We further assume that a single oxygen molecule is responsible for the scavenging of a radical and the diffusion of oxygen takes place radially from the surface into the center of spheres as concentric spherical segments. We can therefore write the following[6]:

$$M_t/M_\infty = 1 - R_t/R_0 \tag{12}$$

where R_0 and R_t are the primary radical concentrations initially at $t = 0$ and upon exposure to oxygen after a time t, respectively. The difference $R_0 - R_t$ merely shows the amount of radicals scavenged by oxygen in a given time t. Equation (12) relates directly the amount of oxygen diffused into polymer with the concentration of radicals remaining R_t in this systemn. M_t/M_∞ vs. time curves can be constructed by following the changes in the ESR signal intensities of the irradiated polymers which are a direct measure of radical concentrations with exposure time to oxygen. From such a plot, time corresponding to $M_t/M_\infty = 1/2$ will give the half-time, which can be further used to find D, the diffusion constant according to eq. (9).

EXPERIMENTAL

Poly(methyl methacrylate) samples used in this study were commercial samples with viscosity average molecular weight of 23,000. Fine spherical polymer samples were first screened into separate groups having average diameters of 56, 63, 71, 90, 105, and 125 μm. The PMMA samples with a definite average diameter were placed in glass ampoules than connected to vacuum line of 10^{-4} torr, and flame-sealed. The samples kept in vacuum were irradiated in a Gammacell 220 type ^{60}Co gamma irradiator at room temperature at a dose rate of 0.15 Mrad/h. After removing the paramagnetic centers produced in the pyrex glass by carefully heating the inverted ends of the tubes, they were placed in the cavity of the ESR spectrometer.
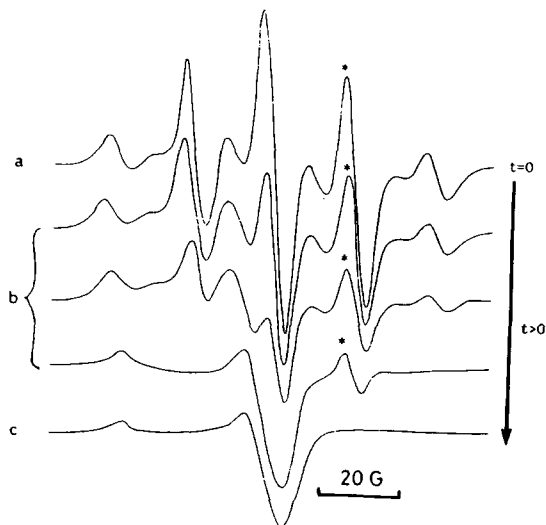
Fig. 1. (a) ESR spectrum of PMMA irradiated in vacuum. (b) The change of the spectrum after exposure to air. (c) Spectrum of peroxy radical.

The ESR spectra of samples irradiated in vacuum and after contacted with oxygen were taken with a Varian E-9 type X-band spectrometer. The spectra were taken and recorded at room temperature. The microwave power was kept to stay at 1 mW throughout the study.

RESULTS AND DISCUSSION

When poly(alkyl methacrylate)s are irradiated with UV light, electron beams, or gamma rays, a characteristic nine-line ESR spectrum is obtained. ESR spectrum of PMMA sample irradiated in vacuum and given in Figure 1 exhibits the typical isotropic nine-line hyperfine structure consisting of five- and four-line components. When the samples irradiated in vacuum were exposed to air, however, the intensity of the spectrum started to decrease and after a relatively short time its line shape changed into the asymmetric peroxy radical line. It can be concluded therefore that the observed peroxyradicals in the irradiated PMMA originate from the radicals giving rise to the nine-line spectrum. The change in the shape and intensity of the spectrum was followed for a period of 5 min. During this time interval, no change was observed in the spectrum of the samples kept in vacuum. This observation shows that there is no appreciable self-decay of radicals that would interfere with the decay due to scavenging of oxygen. Since intensity is a direct measure of the amount of the radicals responsible for the observed lines, the change in the intensities of certain lines can be used to monitor the rate of diffusion of oxygen into the polymer samples.

In Figure 1 the spectrum of the final product peroxide is given together with the spectrum of the freshly irradiated PMMA. As can be seen from this figure, some of the lines of PMMA spectrum overlap with those belonging to peroxide. In the selection of a certain line therefore, one has to consider those that are not interfering. In the present study the line represented by an
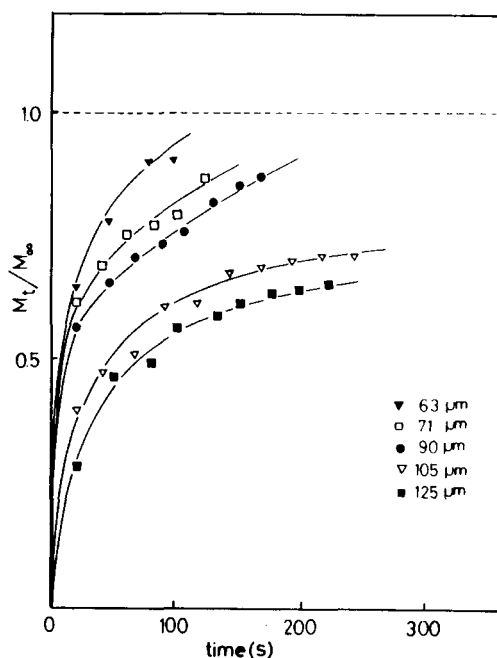
Fig. 2. The change of M_t/M_∞ ratio with time for PMMA spheres of various sizes (μm) irradiated with gamma rays to 0.037 MRad dose: (▼) 63; (□) 71; (●) 90; (▽) 105; (■) 125.

asterisk (*) in Figure 1 does not overlap the lines of peroxy radicals, and the rate of change of the intensity of this line is followed upon exposure to air.

Irradiation of PMMA to high radiation doses results with large reductions in molecular weight. In order not to affect the original molecular weight of the polymer samples appreciably, they were irradiated to relatively low doses. Irradiations to very low doses, however, are impractical due to the limitations in the precision of the instrument used. Spherical PMMAs with various sizes were irradiated to 0.300, 0.150, and 0.037 Mrad doses. R_t/R_0 values were directly determined as the ratios of the height of the peak with the asterisk at the time t to that of the same peak at $t = 0$. By using eq. (12) R_t/R_0 values were converted into M_t/M_∞ values. M_t/M_∞ values thus found were plotted against time, and the results obtained are shown in Figures 2–4. The curves given in these figures pertain to PMMA spheres with various sizes. From these figures, the half-time $t_{1/2}$ values were easily determined as the times corresponding to $M_t/M_\infty = 1/2$ value. One could also determine the times corresponding to $M_t/M_\infty = 1/4$ or $3/4$ and use eqs. (10) and (11) in order to calculate the diffusion coefficient. In the present study, however, there are not enough data points available corresponding to the $M_t/M_\infty = 3/4$ case, and prediction of times for $M_t/M_\infty = 1/4$ cannot be made reliably. These difficulties can be easily seen from the curves given in Figures 2–4. Therefore, $t_{1/2}$ values thus obtained for a given irradiation dose were plotted against the a^2 values according to eq. (9). For the three radiation dose values, three lines with different slopes are obtained, as shown in Figure 5. The slopes of these lines are equal to $0.0717/D$. The diffusion coefficients calculated from slopes
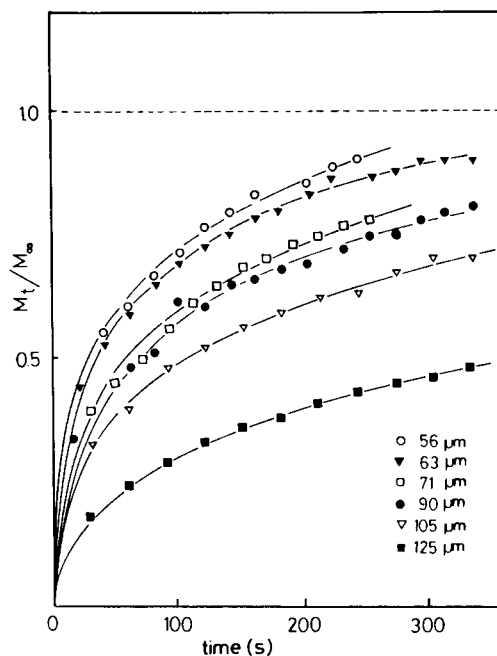
Fig. 3. The change of M_t/M_∞ ratio with time for PMMA spheres of various sizes (μm) irradiated with gamma rays to 0.15 MRad dose: (○) 56; (▼) 63; (□) 71; (●) 90; (▽) 105; (■) 125.
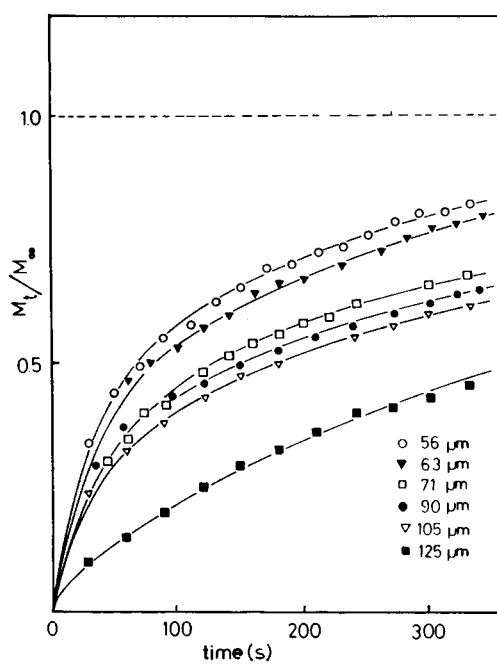

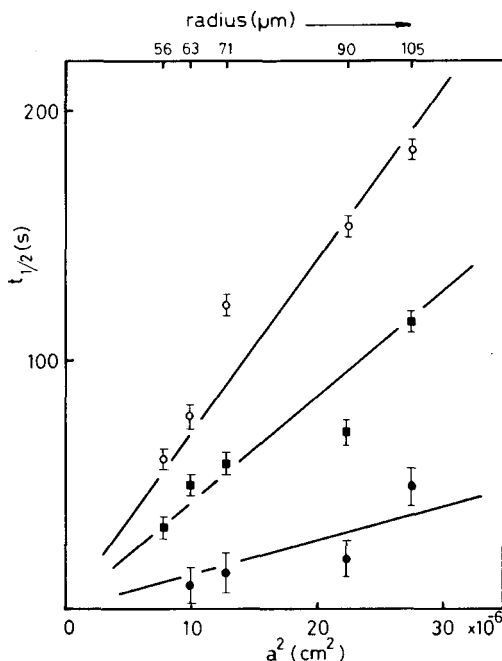Fig. 4. The change of M_t/M_∞ ratio with time for PMMA spheres of various sizes (μm) irradiated with gamma rays to 0.30 MRad dose: (○) 56; (▼) 63; (○) 71; (●) 90; (▽) 105; (■) 125.

Fig. 5. The plot of the half-time $t_{1/2}$ values against square of the radii of PMMA spheres irradiated to ($\bullet$) 0.037, ($\blacksquare$) 0.15, and ($\circ$) 0.30 MRad doses.

are listed in Table I. The values determined are dependent on dose, and they decrease with the absorbed dose. This dependence can be explained in two ways. First of all the proposed method of determination of D is based on irradiation of polymers. Irradiation of polymers by high energy radiation leads either to crosslinking and/or chain scission reactions. In either case the original structure and molecular weights of the polymers being irradiated will be altered. The greater the dose received, the greater will be this alteration. It is therefore preferable to work with as small doses as possible, and it is not surprising to find changing diffusion coefficients as the dose received by the samples is increased. The decrease in D value with increasing dose can be explained by an increase in the radical population. It has been determined in our previous studies related with the radiolysis of poly(alkyl methacrylate)s[7] that the so-called propagating radical concentration increases steadily with dose.

TABLE I

Dependence of Diffusion Coefficients of Oxygen into PMMA
on the Dose Received

Dose received (Mrad)	Diffusion coefficient $(cm^2/s \times 10^8)$
0.300	1.2
0.150	1.8
0.037	3.4

It has already been pointed out in the Theory section that oxygen molecules diffuse and attach themselves to these radicalic sites forming peroxide radicals. The concentration of peroxide radicals will therefore increase with increasing irradiation dose. Every peroxide structure, however, may behave as a barrier towards the penetration of oxygen further into the center of the polymer sphere, making the diffusion of oxygen more and more difficult. This may account for the observed dependency of diffusion coefficient of oxygen on dose in the system studied. Although the order of magnitude of the D values given here are of the same order with the values reported in the literature, it is possible to obtain a more accurate result by extrapolation to zero dose. The D value obtained for the samples irradiated to lowest dose, 0.0037 Mrad, namely 3.4×10^{-8} cm^2/s and the extrapolated value 3.7×10^{-8} cm^2/s agree very well with the 3.8×10^{-8} cm^2/s value of MacCallum and Rudkin[3] and with that of Higashide et al.,[8] namely, 3.3×10^{-8} cm^2/s.

This study shows that by using ESR technique and following the rate of decrease of the intensities of the lines of some radicals previously produced by irradiation with gamma rays in polymeric spheres upon exposures to air, it is possible to determine the diffusion coefficient of oxygen easily. This technique can be satisfactorily applied to any polymeric system provided that ESR signal lines of the irradiated polymer do not completely overlap those of the peroxide radical signal. In addition to the simplicity of this method, it provides also the advantages of working at quite low temperatures. Although in the mathematical interpretation of diffusion theory we have used the half-time method, it is also possible to use the diffusion equation (8) directly and determine the diffusion coefficient. The shapes of the curves given in Figures 2–4 agree very well with theory. When it was tried to fit these curves with eq. (8), a correlation coefficient of 0.99 was obtained. This approach is the subject of our work related with the determination of diffusion coefficient of oxygen into poly(vinyl acetate), and it is the second part of this study, which will be published separately.

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