

Determination of Diffusion Coefficient of Oxygen into Polymers by Using Electron Spin Resonance Spectroscopy. II. Poly(vinyl acetate)

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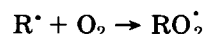
SYNOPSIS

Electron spin resonance spectroscopy has been used to follow the kinetics of radical decay during postirradiation oxidation of poly(vinyl acetate). The oxygen uptake of γ -irradiated spherical poly(vinyl acetate) has been determined from changes in the intensity of the ESR signal. The diffusion coefficient (D) of oxygen determined by this technique showed an inverse relation with dose. The value of the diffusion coefficient of oxygen obtained in this study, after correcting for dose and size effects is $4.5 \times 10^{-8} \text{ cm}^2/\text{s}$, and is in very good agreement with the literature value of $D = 5.1 \times 10^{-8} \text{ cm}^2/\text{s}$.

INTRODUCTION

When polymers are irradiated with ionizing radiation free radicals are generated as intermediate species. The decay of these radicals depends on the crystallinity of the polymer, temperature, and presence or absence of oxygen or other gases that may scavenge the radicals. For the qualitative and quantitative identification of radical species, electron spin resonance (ESR) spectroscopy has become the standard method.

When vacuum irradiated polymers are exposed to air (postirradiation oxidation) the radicals trapped in the material are transformed into peroxy radicals by the addition of molecular oxygen to the free radicals:



As a consequence of this reaction the ESR signal arising from R^{\cdot} starts to lose its intensity and change its shape, and furthermore is replaced by a peroxy signal. This effect can be used as a tool to measure

the oxygen uptake of irradiated material. In previous work from this laboratory we were able to determine the diffusion coefficient of oxygen into poly(methyl methacrylate) (PMMA) by following the postirradiation oxidation of PMMA spheres.¹ In the present work this approach is extended to poly(vinyl acetate) (PVAc), for the purpose of determining the diffusion coefficient of oxygen into this polymer.

THEORY

The solution of Fick's second law of diffusion in spherical systems gives²

$$M_t/M_{\infty} = 1 - 6/\pi^2 \sum 1/n^2 \exp(-Dn^2\pi^2t/a^2) \quad (1)$$

Where M_t and M_{∞} represent the amount of diffusant entering the spheres with radius a , at times t and infinity, respectively. D is the coefficient of diffusion of diffusant— O_2 in the present case. We have related the M values with the radical concentrations in the following way.^{1,3}

$$M_t/M_{\infty} = 1 - R_t/R_0 \quad (2)$$

where R_0 and R_t are the primary radical concentrations initially at $t = 0$ and upon exposure to air after

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a time t , respectively. Substitution of eq. (2) into eq. (1) gives

$$R_t/R_0 = 6/\pi^2 \sum 1/n^2 \exp(-Dn^2\pi^2t/a^2) \quad (3)$$

Equation (3) can be utilized in several ways for the determination of D , the diffusion coefficient. In our previous work with PMMA, the above equation was expanded and rearranged to find a relation between the half-time of the sorption process, $t_{1/2}$, the radius of polymeric spheres a , and D , namely:

$$t_{1/2} = 0.0717a^2/D \quad (4)$$

In the present work, instead of using eq. (4), a different approach was followed. We already know that in the expansion of the exponential term under the summation sign in eq. (3), the contribution of higher values of n ($n > 1$) can be neglected.³ By combining the R_0 value with $6/\pi^2$ and considering the $n = 1$ case, equation (3) can be rewritten as

$$R_t = R_0' \exp(-D\pi^2t/a^2) \quad (5)$$

The above equation forms the theoretical basis for determining D in this study. By following the relative change in the radical concentration with time, i.e. R_t/R_0 of γ -irradiated poly(vinyl acetate) spheres with known radii, a , it is possible to fit the above equation to experimental data and determine D , the diffusion coefficient of oxygen. The same quantity can also be found from the slope of a plot of $\ln R_t/R_0$ versus time.

EXPERIMENTAL

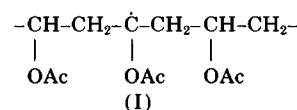
A poly(vinyl acetate) sample in the form of beads obtained from BDH Chemicals Ltd. had viscosity average molecular weight of 60,000. The beads were screened into groups with mean diameters of 200, 300, and 425 μm . We were not, however, able to obtain the size distribution of spheres for a given size. To remove the gases or moisture dissolved or adsorbed superficially on the beads they were kept in a vacuum oven overnight at 40°C. The samples placed in pyrex ESR tubes of 3 mm diameter were evacuated to 10^{-4} torr and flame sealed. The samples kept under vacuum were irradiated in a Gammacell 220 type ^{60}Co γ -irradiator at room temperature at a dose rate of 1.5 kGy/h.

The paramagnetic centers produced in the pyrex glass were removed by carefully heating the inverted ends of the tubes and they were later placed in the

cavity of the ESR spectrometer. The ESR spectra of samples irradiated under vacuum, and after contact 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 at 1 mW throughout the study.

RESULTS AND DISCUSSION

Poly(vinyl acetate) is known to undergo crosslinking when exposed to high energy radiation in the absence of air.⁴ The radicals trapped in vacuum-irradiated PVAc give rise to a triplet ESR signal which was believed to be due to the following structure⁵⁻⁷



The characteristic triplet ESR spectrum of the above structure is also observed in this study and is shown in Figure 1. When the vacuum-irradiated samples were exposed to air, the intensity of the signal started to decrease and after a relatively short time (a few minutes) its line shape changed into the asymmetric peroxy radical line, the spectrum given at the bottom of Figure 1. In order to check whether the decrease in the intensity of spectrum could be due to self-decay of radicals, the intensity and the shape of the signals were followed while the samples were still under vacuum. No change was observed either in the intensity or in the shape of the signals for about 10 min. The observed decrease in radical concentration was solely due to the interaction of diffused oxygen molecules with the macroradicals.

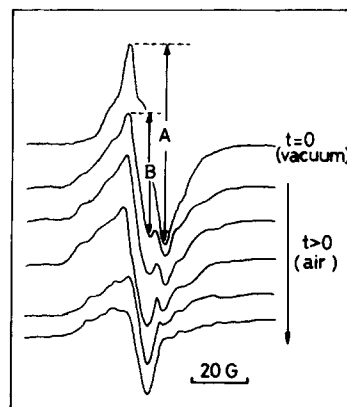


Figure 1 ESR spectra of PVAc irradiated in vacuum and exposed to air.

Unlike the case of PMMA, the spectrum due to PVAc macroradical appears in the same region of the magnetic field as that of peroxy radical. In other words there are no distinct spectral lines which are not overlapping with those of asymmetric peroxy radical. This may seem to complicate the kinetics of the decay process. However, even from this overlapped spectra it is possible to trace the decrease in the signal intensity. As indicated in Figure 1, the shoulder appearing upon contact with oxygen and shown with an arrow at position B represents peroxy radical. The relative intensity shown by A decreases with time. The line intensity at B can be taken as an indicator of the development of peroxy radicals, whereas that observed at A is a measure of the decay of macroradicals reacting with oxygen. We can therefore follow the rate of decrease of line intensity of A in order to determine the diffusion coefficient of oxygen into this polymer.

The PVAc samples used in this work were irradiated to relatively low doses (7.5, 30, and 60 kGy) in order not to cause substantial changes in the molecular weight and structure of the virgin polymer. The doses given to the samples were well below the gelation dose⁸ of 100 kGy which eliminates the

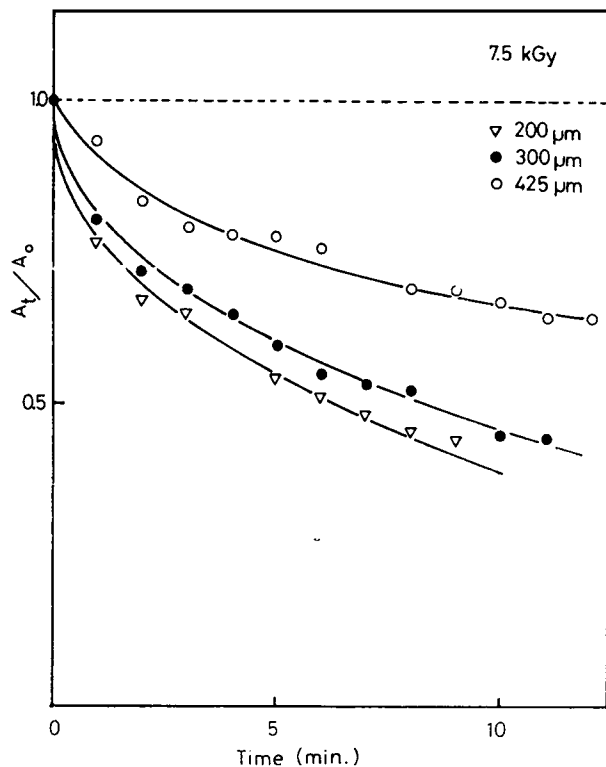


Figure 2 The change of A_t/A_0 ratio with time for PVAc spheres irradiated to 7.5 kGy.

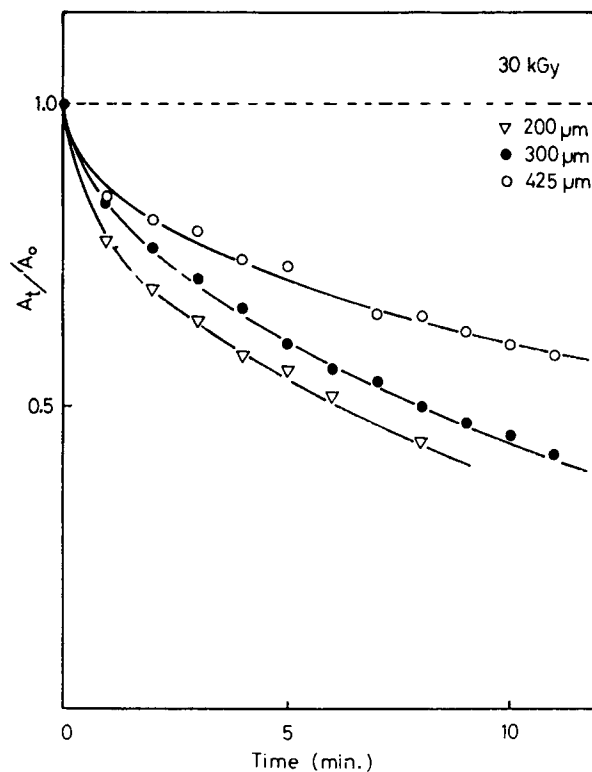


Figure 3 The change of A_t/A_0 ratio with time for PVAc spheres irradiated to 30 kGy.

problems that may arise from the formation of an extensive network of polymeric chains. For the samples irradiated to doses lower than 7.5 kGy, the transformation of macroradical (I) into peroxy radical took place so rapidly that no reliable data could be obtained. There is therefore an optimum range of doses to be given to polymers in the present method.

The intensity of the line denoted by A in Figure 1 depends directly on the concentration of radicals giving rise to this signal. In eq. (3) however, R_0 and R_t values correspond to the number of radicals per unit weight of polymer. The determination of absolute concentrations of spins in ESR studies is rather difficult. The substitution of A_t/A_0 for R_t/R_0 can be safely done without introducing any error, where A_0 and A_t are simply the heights of the signal observed at A initially and at time t . In Figures 2-4, A_t/A_0 values determined from the ESR spectra of PVAc beads irradiated to various doses were plotted against time of contact with air. The curves fitted to the data points in these figures were used to determine the diffusion coefficient of oxygen by a simple iterative procedure. Values of D corresponding to the best fit ($r^2, 0.98$) of eq. (5) with the curves

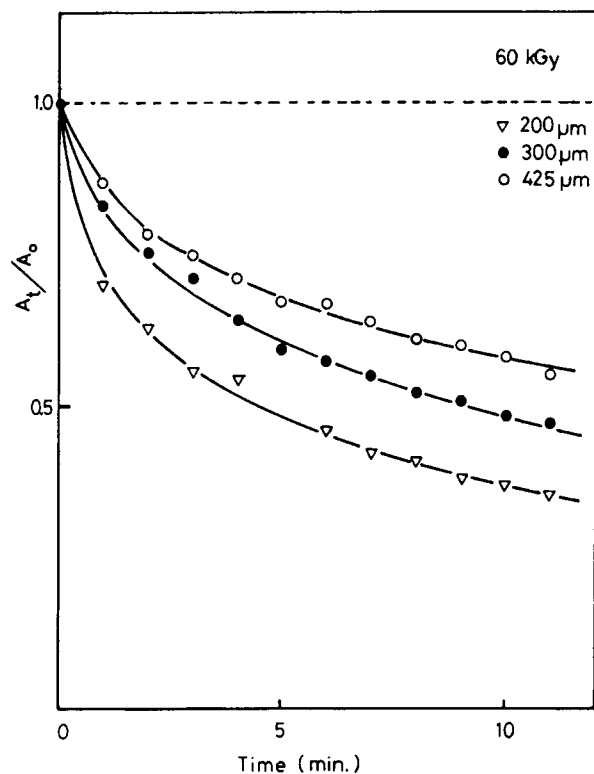


Figure 4 The change of A_t/A_0 ratio with time for PVAc spheres irradiated to 60 kGy.

in Figures 2–4 were calculated and are listed in Table I.

The D values listed in Table I show two general trends. First, the diffusion coefficient of oxygen decreases with increasing dose irrespective of the size of the spheres. Second, as the size of the spheres increase the D value also increases at every given dose.

The dependence of D on the given dose, as determined by this method, can be expected, and its decrease with increasing dose can be explained. The determination of D for oxygen by the present method is based on the attachment of O_2 molecules to the radicals. As the given dose is increased the radical population increases and the concentration of peroxy structures in the polymeric spheres increase. Although their concentration on a molar basis is rather low, the higher the population of peroxy structures in a given volume of polymer, the more difficult may become the radial diffusion of O_2 further into the spheres. There is probably one further and important effect of radiation on the diffusion of oxygen into PVAc. As was mentioned in the introduction, PVAc undergoes crosslinking mainly when irradiated with γ -rays in vacuum. The larger the dose given, the higher becomes the extent of cross-

Table I Diffusion Coefficient (D , $\times 10^8$, cm^2/s) of Oxygen into PVAc—Dependence on the Dose Received and Size of the Spheres

Diameter (μm)	Dose (kGy)			
	7.5	30	60	0.0 ^a
200	1.59	1.55	1.28	1.67
300	2.48	2.20	1.68	2.62
425	2.90	2.86	2.35	3.10

^a Extrapolated.

linking, and since crosslinking reduces the chain mobility, this will cause a decrease in the transport of oxygen by restricting the motion of polymer segments. We observed a similar inverse effect of chain stiffness on the diffusion rate of oxygen in PVAc when we investigated the effect of temperature on D . Since this is going to be the subject of another paper it will be sufficient to say that below T_g (c.24°C) the diffusion coefficient of oxygen shows a considerable decrease. In order to eliminate the effect of dose on the D values reported in Table I, they are therefore extrapolated to zero dose and corresponding values, D_0 are also listed in the last column of the same table.

Concerning the dependence of D on the size of the PVAc spheres, we were unfortunately not able to obtain spheres with sizes smaller or larger than those listed in Table I, neither could we get the size distribution of the beads. Even from the present data however, we can say that as the size of the spheres increases, the extent of increase in D values gets smaller. The spheres used in this work were of relatively large sizes and we can therefore extrapolate

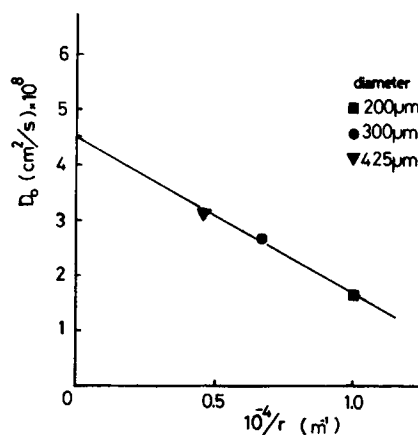


Figure 5 The dependence of diffusion coefficient of oxygen on the size of the PVAc spheres.

the radius of the spheres to infinity and eliminate this effect. In other words if D_0 values obtained after extrapolation to zero dose are plotted against $1/r$, r being the radius, a final extrapolation to $r = \infty$, or $1/r = 0$ will give the value of the diffusion coefficient of oxygen corrected for dose and size effects. This last extrapolation is given in Figure 5 and the value thus obtained is $D = 4.5 \times 10^{-8} \text{ cm}^2/\text{s}$. This value is in very good accordance with the value reported in the literature,⁹ namely, $D = 5.1 \times 10^{-8} \text{ cm}^2/\text{s}$.

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