

## The Effect of Photodegradation of Polystyrene on its Permeability Characteristics

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### Synopsis

The diffusion ( $D$ ) and permeability ( $P$ ) coefficients for  $^{14}\text{CO}_2$  in polystyrene films which had been irradiated by short-wave ultraviolet (253.7 nm) radiation under vacuum and in oxygen were determined in the temperature range of 20° to 55°C. Both  $D$  and  $P$  decreased with increasing exposure, the vacuum-irradiated sample showing significantly greater decreases, presumably on account of a larger extent of crosslinking which was possible in the absence of oxidation. A good correlation was observed between crosslinking and decreasing  $P$  and  $D$  values. The solubility coefficients for all irradiated samples increase with increasing dose. Activation energies for diffusion increase with increasing irradiation, particularly for the vacuum-irradiated samples. Reductions in  $P$  and  $D$  values are interpreted in terms of free-volume decreases due to crosslinking and other modifications, while the increasing activation energies are attributed to the increasing energy requirements for creation of free volume in modified polymers.

### INTRODUCTION

Numerous investigations have been made of the effects of  $\gamma$ -radiation on the permeability characteristics of polymer membranes, and the subject has been reviewed by Rogers.<sup>1</sup> Large-scale modifications of chemical structures and morphologies of the polymers (e.g., increased crosslinking and crystallinity)<sup>2</sup> result from their exposure to  $\gamma$ -radiation, and it has been shown that these effects are generally reflected in decreased permeabilities and diffusion coefficients of gases through the membranes.

Exposure of polymers to ultraviolet radiation also results in increased crosslinking in many cases and in chemical modification, if oxygen is present during irradiation, the extents of these effects being much less than those produced during the corresponding  $\gamma$ -irradiations.

Little is known about the possible effects of polymer modification by UV irradiation on the permeability characteristics of films, despite the implications of decreased diffusion rates on mechanisms and rates of photo- and photo-oxidative reactions of polymer films.

In this investigation, the gas transport characteristics of polystyrene films modified by exposure to UV radiation under high vacuum and in presence of oxygen were determined. The choice of polystyrene was influenced by two factors: (a) the effects of UV radiation on polystyrene both under vacuum and in oxygen are fairly well understood, and (b) atactic polystyrene is amorphous and

remains so after UV irradiation, hence the complications associated with the radiation of polyethylene, in which it is impossible to distinguish between effects due to crosslinking and those due to changes in crystallinity, are avoided.

CO<sub>2</sub> was chosen as the diffusant since it appears not to react chemically (as O<sub>2</sub> would) with the irradiated films.

## EXPERIMENTAL

### Materials

Atactic polystyrene was prepared by thermal polymerization of purified monomer at 70°C under high vacuum (10<sup>-5</sup> mm Hg) conditions. It was subsequently purified by repeated precipitation and characterized by viscometry and membrane osmometry. Details of preparation and characterization have been previously described.<sup>3</sup> The sample had a  $\bar{M}_n$  value of  $2.4 \times 10^6$  and a ratio of viscosity-to-number-average molecules weights  $\bar{M}_v/\bar{M}_n = 1.73$ .

Carbon dioxide (instrument grade) was obtained from Matheson; and labeled <sup>14</sup>CO<sub>2</sub>, from the Radiochemical Center, U.K.

### Apparatus

Diffusion coefficients of <sup>14</sup>CO<sub>2</sub> were obtained by the time-lag method and by sorption studies. The diffusion cell, illustrated in Figure 1, consists of two stainless steel rings with machined depressions which accommodate the film and its support—a stainless steel grid—which is fixed by screws to the upper ring. The joints in the cell are sealed with Viton O-rings. The upper ring has a quartz

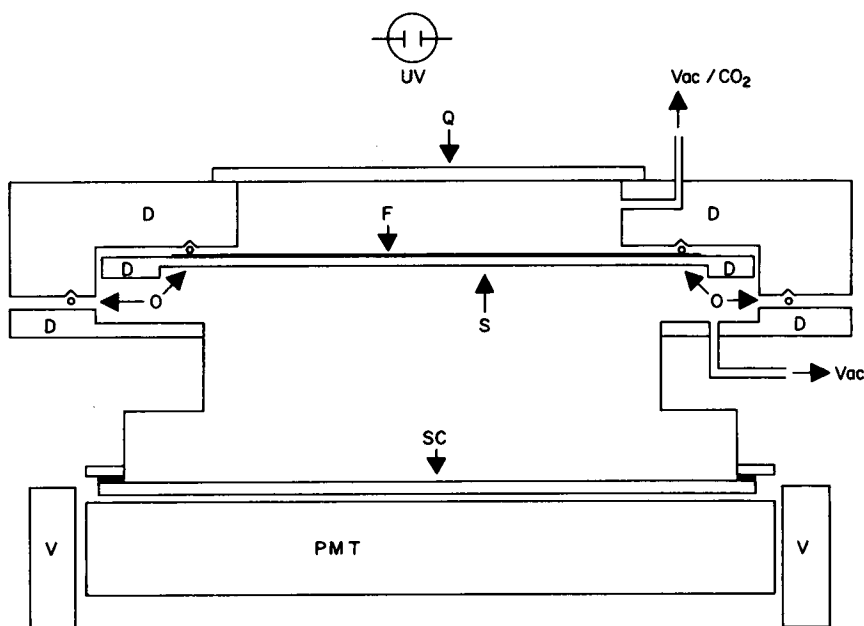


Fig. 1. Schematic diagram of diffusion cell and gas counting equipment: UV, ultraviolet lamp; Vac/CO<sub>2</sub>, to high vacuum and to CO<sub>2</sub> supply; D, stainless steel discs; F, film; S, support for film; SC, scintillator; PMT, photomultiplier tube; V, shielding; Q, quartz plate.

plate mounted on it, and this permits UV irradiation of the films within the diffusion cell. The advantage of this system is that the films could be irradiated under high vacuum while mounted in the cell, and the need to transfer an irradiated film from a high vacuum environment (and inevitably expose it to  $O_2$ ) to the diffusion cell was eliminated. Consequently, complications due to oxidation were minimized. The lower ring is connected to a gas scintillation counting cell (volume = 6 cm<sup>3</sup>) which consists of a glass flange with an anthracene-coated glass disc attached to it. The disc is coupled to the face of a low-noise lead-shielded photomultiplier tube by silicone oil, and the tube is connected to standard scintillation counting equipment. Both rings are connected independently to a high-vacuum system ( $10^{-5}$  mm Hg), and the upper ring is also connected to a supply of  $^{14}CO_2$ , the pressure of which is maintained by a Toepler pump.<sup>4</sup> The cell was thermostatted at  $25^\circ \pm 0.2^\circ C$ .

Sorption studies were carried out using the standard method,<sup>5</sup> by suspending a film from a quartz spring which was mounted in a thermostatted ( $25^\circ \pm 0.2^\circ C$ ) quartz tube which permitted the irradiation of the film in situ.

### Film Preparation

Films were obtained by casting (4% w/v) solutions of polystyrene in methylene dichloride onto clean mercury surfaces. Before use, the films were dried under high vacuum ( $10^{-5}$  mm Hg) at  $60^\circ C$  for at least 50 hr. Thicknesses were determined by weighing and measuring film areas and using a density of 1.054 g/cm<sup>3</sup>. The film thickness used throughout this work was 0.01 mm since it has been shown that absorbance of short-wave and UV radiation (253.7 nm) is almost complete across a film of such thickness.<sup>6</sup>

### Gas Scintillation Counting

$^{14}CO_2$  was supplied in high activity in break-seal tubes from which it was removed in an all-glass gas-handling system and subsequently diluted with pure  $CO_2$ . In order to calibrate the gas counting cell,  $^{14}CO_2$  of known activity was admitted and the pressure determined by connecting the cell to a McLeod gauge and, for higher pressures, to a U-tube monometer. The counting equipment was then adjusted for optimum  $^{14}C$  counting efficiency and maximum signal-background ratio. Figure 2 shows the linear dependence of observed count rate of  $^{14}CO_2$  pressure, and this is maintained to a pressure of at least 150 mm Hg of  $^{14}CO_2$ . The overall counting efficiency was found to be 58%, and the equipment is sufficiently sensitive to detect pressure differences of  $2 \times 10^{-3}$  mm Hg when moderately active  $^{14}CO_2$  (0.1 mCi/mM) is used. (The above pressure difference could be indicated with an accuracy of  $\pm 1.5\%$ .) In addition, the use of  $^{14}CO_2$  with this order of activity ensures that the pressure on the "low pressure" side of the membrane is sufficiently low for the Daynes equation<sup>5</sup> to be valid.

### Procedure

#### *Diffusion Experiments*

Films were mounted in the cell and degassed at  $10^{-5}$  mm Hg.  $^{14}CO_2$  was then admitted and a constant pressure maintained on the "high pressure" side of the film. In order to avoid complications from the pressure dependence of the dif-

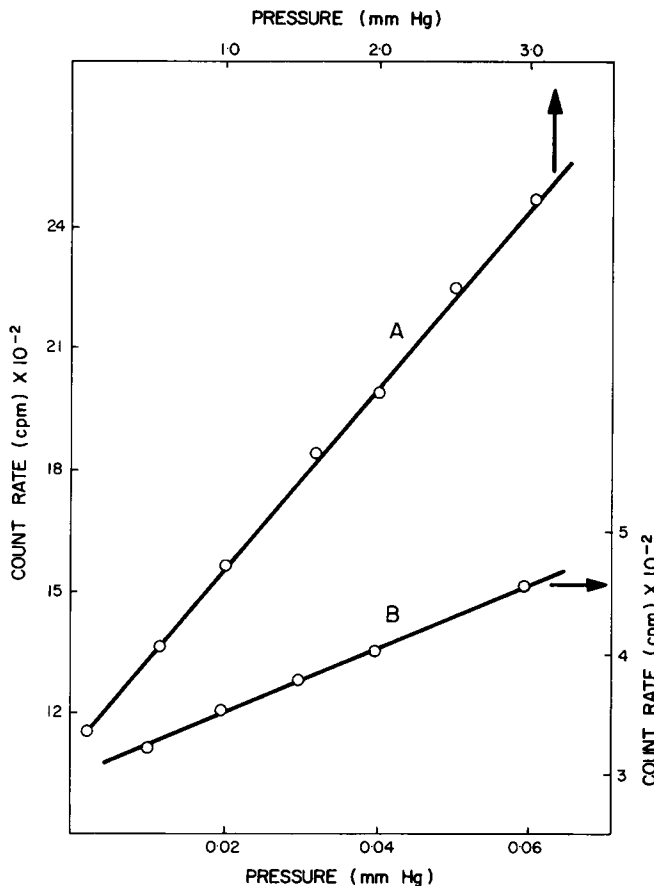


Fig. 2. Calibration of scintillation counter for  $^{14}\text{CO}_2$ . Count rate as a function of pressure: x-axis, pressure of  $^{14}\text{CO}_2$  (mm Hg); y-axis, count rate (counts per minute).

fusion coefficient, the high pressure was maintained at values greater than 150 mm Hg, in which region no such dependence has been observed.<sup>7</sup>

The progress of the transport of  $^{14}\text{CO}_2$  through the film and the time lag were indicated by the scintillation counter. The diffusion coefficient  $D$  was obtained by application of the Daynes equation,<sup>5</sup> i.e.,

$$D = \frac{l^2}{6\theta}$$

where  $\theta$  is the time lag and  $l$  the film thickness. Permeability coefficients were obtained in the normal manner from the steady-state region of the pressure-time plots.

The procedure was identical for irradiated films, except that after degassing, the film was irradiated under vacuum or in presence of oxygen for the required time and further degassed before diffusion measurements were made. The UV source used was a 100-W low-pressure Hg arc which produced predominantly 253.7 mm quanta incident on the films was  $1.2 \times 10^{-9} \text{E cm}^{-2} \text{sec}^{-1}$  as determined by ferrioxalate actinometry.<sup>8</sup>

*Sorption Studies*

These were carried out by the standard method<sup>5</sup> using 0.02-mm-thick films (15 cm<sup>2</sup> area). The quartz spring had a sensitivity of  $8.4 \times 10^{-2}$  cm/mg. Films to be irradiated in either vacuum or in presence of oxygen were previously degassed, irradiated, further degassed, and exposed to <sup>14</sup>CO<sub>2</sub> for sorption studies. Diffusion constants  $D$  were obtained from weight change using the equation describing sorption kinetics,<sup>9</sup>

$$\frac{q}{q_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp[-\{(2n+1)\pi/l\}^2 Dt]}{(2n+1)^2}$$

in which  $q$  and  $q_{\infty}$  are amounts of gas taken up at time  $t$  and at saturation; respectively;  $l$  is the film thickness; and  $n$  is an integer.

**RESULTS**

The validity of the time-lag data obtained by the present tracer technique was investigated, the diffusion coefficient  $D$  for <sup>14</sup>CO<sub>2</sub> at 25°C and the activation energy  $E_D$  for diffusion being determined. Values of  $D$  and  $E_D$  obtained were  $0.744 \times 10^{-7}$  cm<sup>2</sup>/sec and 8.9 kcal/mole, respectively, both in good agreement with previous data.<sup>5,10</sup> The general accuracy of the time-lag technique for determining the diffusion and permeability coefficients (for 95% confidence limits) was  $\pm 7\%$ . Since the solubilities were derived from these quantities, they were subject to correspondingly greater errors.

Figure 3 shows the effect of UV irradiation under high vacuum on the value of  $D$  obtained by the two methods. It can be seen that there is good agreement between the two sets of data, and also that relatively small radiation doses significantly alter the permeability characteristics of polystyrene films.

At longer exposure times, the  $D$  values decrease more rapidly, presumably on account of the large scale nonuniform crosslinking that occurs after such exposures, the surface of the film being much more highly crosslinked than the bulk. It has been shown<sup>11</sup> in the case of polyethylene that application of diffusion theory is valid only when essentially uniform and random crosslinking occurs. It is obvious that these conditions are met only in the early stage of the irradiation of polystyrene, and the present studies were restricted to these periods.

Figure 4 shows the effect on the diffusion coefficient of irradiation of the film in oxygen. Initially, the behavior is similar to that shown in Figure 3; however, longer exposures appear to result in a progressive rather than an accelerating decrease in  $D$ .

Similar results were obtained for the oxygen pressure ( $PO_2$ ) range  $100 \leq PO_2 \leq 700$  mm Hg but at lower pressures, particularly below 50 mm Hg curves similar to that shown in Figure 3 were obtained. The curve for 50 mm Hg oxygen pressure is also shown in Figure 4.

Permeability coefficients for films exposed to UV under vacuum and the presence of oxygen are shown in Figure 5, and it can be seen that the effects of radiation are similar to those observed for diffusion coefficients, however, the extent of the effect, particularly when oxygen is present, appears to be less.

The solubility coefficient ( $S$ ) for <sup>14</sup>CO<sub>2</sub> in polystyrene, derived from the data in Figures 4 and 5 ( $S = P/D$ ), is shown in Figure 6 as a function of time of irradiation in both vacuum and in presence of oxygen. It can be seen that under both

TABLE I  
Effect of UV Irradiation on Arrhenius Parameters for Diffusion of  $^{14}\text{CO}_2$  in Polystyrene

Irradiation time, min	Atmosphere	$D_0$ , $\text{cm}^2/\text{sec}$	$E$ , kcal/mole
0	oxygen	0.23	8.9
30	oxygen	0.26	9.1
60	oxygen	0.29	9.5
120	oxygen	0.34	9.9
180	oxygen	0.37	10.4
30	vacuum	0.29	9.1
60	vacuum	0.38	9.6
90	vacuum	0.54	10.4
120	vacuum	0.72	11.8

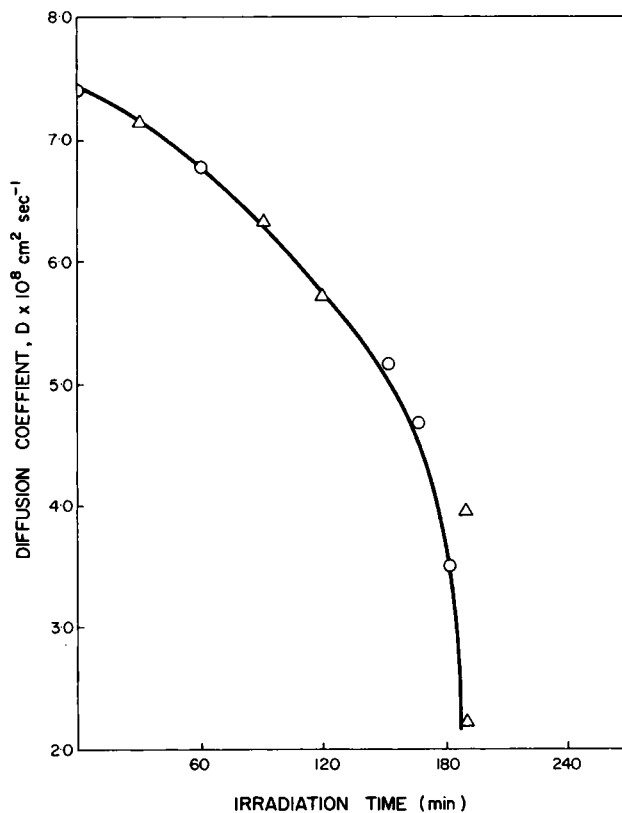


Fig. 3. Diffusion coefficients for  $^{14}\text{CO}_2$  in vacuum-irradiated polystyrene at  $25^\circ\text{C}$ : ( $\Delta$ ) time-lag data; ( $\circ$ ) sorption data; x-axis, irradiation time (min); y-axis, diffusion coefficient  $D \times 10^8 \text{ cm}^2/\text{sec}$ .

conditions of irradiation, the solubility of the gas increases in a similar fashion. While an increasing  $S$  value for irradiation in oxygen compensates to some extent for the decreasing  $D$  value, presumably because of greater interaction of  $\text{CO}_2$  with the polar groups introduced as a result of oxidation, the rate of increase in  $S$  for the vacuum-irradiated sample does not sufficiently compensate for the rapidly

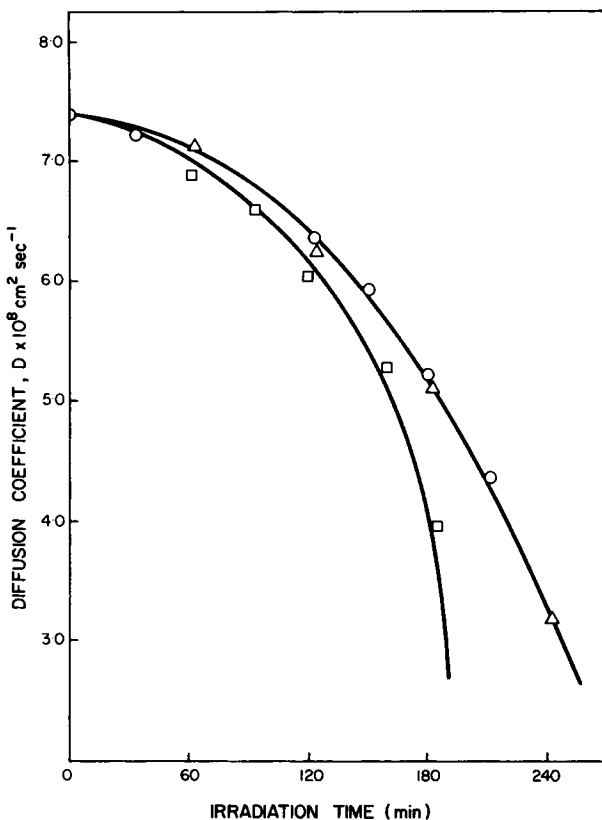


Fig. 4. Diffusion coefficients for  $^{14}\text{CO}_2$  in polystyrene irradiated in oxygen (600 mm Hg) at  $25^\circ\text{C}$ : ( $\Delta$ ) time-lag data; (O) sorption data; ( $\square$ ) irradiation in oxygen, 50 mm Hg; x-axis, irradiation time (min); y-axis, diffusion coefficient,  $D \times 10^8 \text{ cm}^2/\text{sec}$ .

decreasing value of  $D$ , hence the permeability of the vacuum-irradiated sample tends to decrease more rapidly with increasing dose.

The Arrhenius plots for diffusion coefficients for films (with irradiation times less than 2.5 hr) gave linear relationships. However, higher doses, particularly under vacuum, produce complex plots which were not analyzed. The temperature dependence of  $D$  can thus be described by

$$D = D_0 \exp(-E_D/RT)$$

in which  $D_0$  is the preexponential factor and  $E_D$  is the activation energy for diffusion.

Table I summarizes relevant data. It can be seen that activation energies for diffusion in both films increase with increasing dose; the effect is discussed later.

Crosslinking of polymers can be studied by following insolubilization as a function of radiation dose using the Charlesby method.<sup>12</sup> Assuming simultaneous crosslinking and chain scission and an initial random molecular weight distribution (both conditions being met in this case) the weight of soluble fraction  $S$ , after absorbance of UV radiation of intensity  $I_0$ , is related to the dose by the equation<sup>13</sup>

$$S + S^{1/2} = \frac{\alpha}{\beta} + \frac{1}{P_0\beta I_0 t} \quad (1)$$

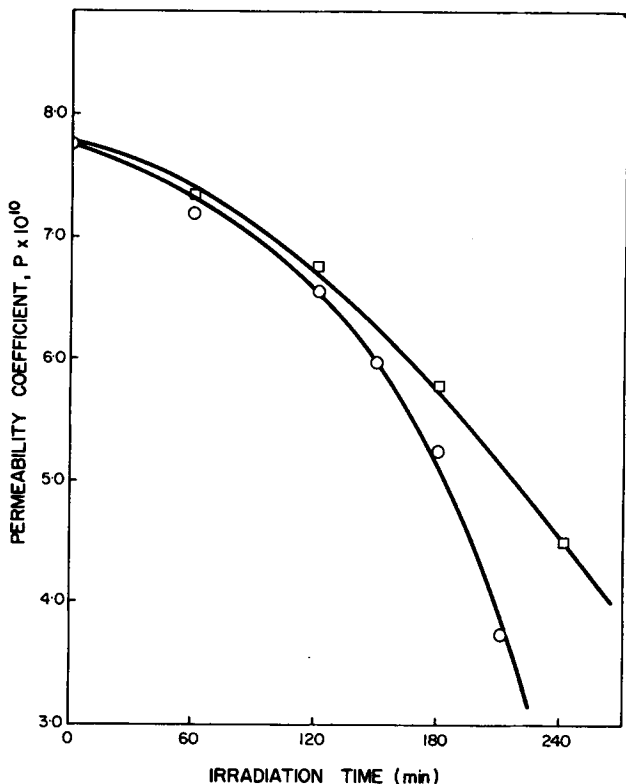


Fig. 5. Permeability coefficients  $P$ , in units of  $\text{cm}^3(\text{S.T.P.})\text{cm}/\text{cm}^2\text{-sec-cm Hg}$ , for  $^{14}\text{CO}_2$  in polystyrene at  $25^\circ\text{C}$ : ( $\square$ ) irradiation in oxygen, 600 mm Hg; ( $\circ$ ) irradiation under vacuum; x-axis, irradiation time (min); y-axis, permeability coefficient  $P \times 10^{10}\text{cm}^3(\text{S.T.P.})\text{cm}/\text{cm}^2\text{-sec-cm Hg}$ .

in which  $P_0$  is the initial chain length,  $t$  is the exposure time, and  $\alpha$  and  $\beta$  are constants proportional to the probabilities of chain scission and crosslinking, respectively.

Figure 7 shows Charlesby plots for irradiation of the polymer in oxygen and under vacuum. It can be seen that the extent of crosslinking is significantly less when oxygen is present and that there is a good correlation between isolubilization due to crosslinking and decreasing permeability and diffusion constants.

The deviation of the vacuum irradiated sample from eq. (1) after about 2.5 hr of irradiation (presumably due to enhanced crosslinking) resembles the behavior shown in Figures 3 and 5.

## DISCUSSION

It has been shown that UV (253.7 nm) irradiation of polystyrene both under vacuum and in the presence of oxygen results in the formation of conjugated C—C double bond sequences in the backbone and in the production of radicals on the  $\alpha$ -carbon atoms, these radicals subsequently reacting to form crosslinks and, if oxygen is present, to produce oxygenated products such as ketones.<sup>14</sup>

The results shown in Figures 3, 4, and 5 show that both permeability ( $P$ ) and diffusion ( $D$ ) coefficients for polystyrene films decrease with increasing exposure



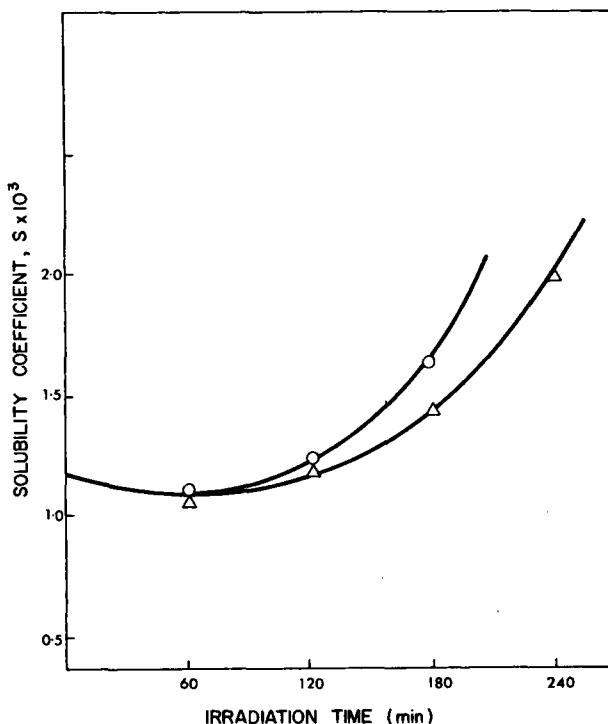


Fig. 6. Solubility coefficient in units of  $\text{cm}^3(\text{S.T.P.})/\text{cm}^3\text{cm Hg}$  for  $^{14}\text{CO}_2$  in polystyrene at  $25^\circ\text{C}$ : (O) irradiation under vacuum; ( $\Delta$ ) irradiation in oxygen, 600 mm Hg; x-axis, irradiation time (min); y-axis, solubility coefficient  $S \times 10^3 \text{cm}^3(\text{S.T.P.})/\text{cm}^3\text{-cm Hg}$ .

to UV radiation; and from Figure 7, it can be seen that insolubilization associated with crosslinking follows the same general pattern. Thus, crosslinking, which has been shown to influence  $P$  and  $D$  values,<sup>5</sup> would appear to be responsible for the observed reductions in  $P$  and  $D$ .

The difference between vacuum-irradiated films and those irradiated in the presence of oxygen can be qualitatively accounted for as follows: (a) oxidation of the polymer (radical +  $\text{O}_2$ ) competes with crosslinking, oxygen molecules acting as efficient scavengers for polymer radicals, with consequent reduction in crosslinking probability; (b) subsequent photodecomposition of the oxygenated products can result in chain scission, and the effect of this on values of  $P$  and  $D$  would be opposite to that of crosslinking.<sup>5</sup>

The effect of oxygen pressure during irradiation on  $D$  values is related to (a) above. At low oxygen concentrations, crosslinking competes more favorably with oxidation; however, as the oxygen concentration is increased, the competition is reversed until a saturation situation is produced in which an excess of oxygen has access to a high proportion of all radicals formed.

Diffusion in polymers may be explained in terms of the free-volume theory,<sup>15</sup> the diffusion coefficient  $D$  being related to the probability  $P(v^*)$  of finding a hole of critical volume  $v^*$  or greater, as follows:

$$D \propto P(v^*)$$

$$P(v^*) = \int_{v^*}^{\infty} P(v)dv \quad (2)$$

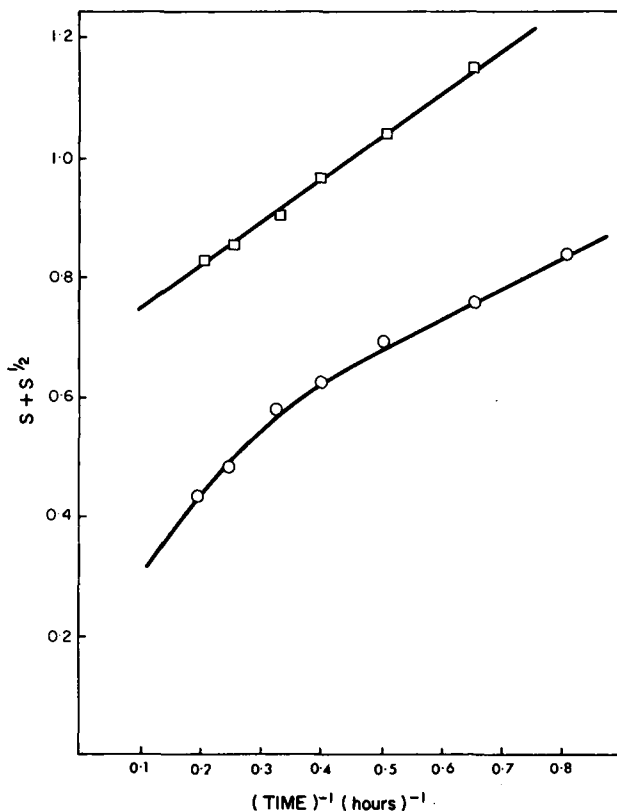


Fig. 7. Charlesby plots of soluble fractions vs. reciprocal exposure times to UV radiation: (○) high vacuum; (□) in presence of oxygen, 600 mm Hg; x-axis; (time)<sup>-1</sup> (hr)<sup>-1</sup>; y-axis,  $S + S^{1/2}$ .

$P(v)$  being the volume distribution function. Evaluation of eq. (2)<sup>15</sup> gives

$$D = A \exp(-\gamma v^*/v_f) \quad (3)$$

where  $A$  and  $\gamma$  are constants and  $v_f$  is the average free volume;  $v_f$  is related to temperature  $T$  as follows:

$$v_f = (v_f)_g + \alpha(T - T_g) \quad (4)$$

where  $\alpha$  is related to the thermal expansion coefficient,  $T_g$  is the glass transition temperature, and  $(v_f)_g$  the free volume associated with  $T_g$ . The effect of polymer modification (crosslinking, oxidation, and formation of unsaturation) on  $D$  may be explained by reference to eqs. (3) and (4). Crosslinking, incorporation of polar side groups on chains, and main-chain double bonds increase  $T_g$  by decreasing chain flexibility and increasing cohesive energy and perhaps also decrease  $(v_f)_g$ . Thus, the average free volume  $v_f$  in degraded polymers will decrease, and since  $v^*$  is essentially a function of the size of the diffusant, the reduction in  $D$  values with increasing modification can be inferred from eq. (3). (Alternatively, the probability of having critical volume  $v^*$  available  $P(v^*)$  will decrease with degradation.)

Table I shows the gradual increase in Arrhenius parameters  $D_0$  and  $E_D$  for increasing extents of degradation. These can be quantitatively understood by reference to the transition state theory formulation of  $D$ ,<sup>16</sup> i.e.,

$$D = e\lambda^2 \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H/RT} \text{ cm}^2/\text{sec.} \quad (5)$$

$\Delta H$  can be substituted by  $E_D$ , since volume changes are small;  $\lambda$  is the average jump distance, and  $\Delta S^\ddagger$  is the entropy of activation; other symbols have their usual meaning. The increasing  $E_D$  values can be explained on the basis of larger energy requirements for the creation of the necessary free volume for gas molecules to pass through the crosslinked and other more rigid polymers. The polar groups incorporated in the oxidized polymer increase the cohesive energy with a similar effect on  $E_D$ . From the Arrhenius equation and (5) above,

$$D_0 = e\lambda^2 \frac{kT}{h} e^{\Delta S^\ddagger/R}. \quad (6)$$

The increasing  $D_0$  values may be accounted for as follows. Although the jump distance  $\lambda$  is frequently (and arbitrarily) associated with the molecular diameter of the diffusant and regarded as a constant, it is possible that as the polymer becomes crosslinked and otherwise modified and the accessibility of the diffusant to the polymer decreases, the average jump distance has to be increased, with a consequent increase in  $D_0$ .  $D_0$  will, however, be relatively more sensitive to changes in the exponential term, and increasing  $D_0$  values could be attributed to increasing entropies of activation, the comparative order in the transition state of the undergraded polymer becoming increasingly unattainable as the polymer becomes modified.

The results demonstrate that care must be exercised in interpreting the kinetics of photoreactions of polystyrene, e.g., the liberation of  $\text{CO}_2$ , a photo-oxidation product, could become a diffusion-controlled process after small extents of oxidation.

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### References

1. C. E. Roger, *Physics and Chemistry of the Organic Solid State*, Vol. 2, D. Fox, Ed. Interscience, New York, 1965.
2. P. J. F. Kanitz and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **14**, 2739 (1970).
3. J. B. Lawrence and N. A. Weir, *J. Polym. Sci.*, **11**, 105 (1973).
4. R. M. Barrer and G. Skirrow, *J. Polym. Sci.*, **3**, 549 (1948).
5. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968.
6. N. Grassie and N. A. Weir, *J. Appl. Polym. Sci.*, **9**, 963 (1965).
7. H. H. G. Jellinek, *J. Phys. Chem.*, **74**, 1049 (1970).
8. G. C. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, **A235**, 518 (1956).
9. P. Meares, *Polymers: Structure and Bulk Properties*, D. Van Nostrand, London, 1965, Chap. 12.
10. B. Takeda and B. Yamagushi, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **62**, 1897 (1959).
11. H. J. Bixler, A. S. Michaels, and M. Salame, *J. Polym. Sci. A*, **1**, 895 (1963).
12. A. Charlesby, *Atomic Radiation of Polymers*, Pergamon Press, Oxford, 1960.

13. N. A. Weir, *J. Appl. Polym. Sci.*, **17**, 401 (1973).
14. N. Grassie and N. A. Weir, *J. Appl. Polym. Sci.*, **9**, 975 (1965).
15. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
16. S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, New York, 1941.

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