

# Permeation of Gases through Modified Polymer Films.

## V. Permeation and Diffusion of Helium, Nitrogen, Methane, Ethane, and Propane through $\gamma$ -Ray Crosslinked Polyethylene

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### Synopsis

The permeation and diffusion of helium, nitrogen, methane, ethane, and propane through  $\gamma$ -irradiated polyethylene films were investigated. These studies were carried out with two objectives in mind: (1) to determine the effect of crosslinking by  $\gamma$  irradiation on permeability and diffusivity using the gas molecules as molecular probes; and (2) to study the plasticizing effects of the low hydrocarbons on the polyethylene film. The  $\gamma$ -ray-induced crosslinking efficiency of polyethylene was investigated in the following irradiation atmospheres: vacuum, acetylene, and nitrogen-acetylene mixtures. Results showed that irradiation in acetylene decreased the crosslinking efficiency while an acetylene-nitrogen atmosphere increased the efficiency compared to irradiation in vacuum. Both the permeation constants and the diffusion coefficients were found to decrease with increasing irradiation dose while the activation energies increased. The permeation constants of the organic gases through polyethylene increased with molecular diameter while the diffusion coefficients decreased. This increase in permeability was attributed to an increase in the solubility due to solubilization of the membrane by the penetrant. For example, the molecular diameter of propane is 4.397 Å compared with 2.807 Å for methane; however, propane permeated the polyethylene film at a rate twice that of methane. Nitrogen and methane have approximately the same molecular diameters—2.7085 and 2.807 Å, respectively—but owing to the plasticizing effect of methane, it permeated the film at a rate three times greater than that of nitrogen. It is interesting to note that the stronger the plasticizing ability of the penetrant, the greater the effect of the irradiation dose. The permeability of propane decreased by 40.7%, while the permeability of helium decreased by 6.4% after an irradiation dose of 50 Mrad.

### INTRODUCTION

Although data on the permeability and separation properties of polymers are abundant, there is a lack of information available for modified polymer films. In recent studies conducted in this laboratory, Huang and Kanitz<sup>1</sup> investigated the permeation of nitrogen, oxygen, and carbon dioxide gases through a series of polyethylene-styrene graft copolymer films prepared by  $\gamma$ -ray irradiation. Kanitz and Huang<sup>2,3</sup> studied the permeation, diffusion, and separation of nitrogen and methane gases in a series of air and vacuum irradiated polyethylene and Teflon FEP films. They found that the irradiation in air reduced the crosslinking density as compared to the vacuum irradiated samples. The selectivity of the Teflon FEP film increased with the irradiation dose, but this was achieved at the expense of a decrease in the permeation rate. The effect of grafting styrene and acrylonitrile onto polyethylene and Teflon FEP film by

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$\gamma$ -ray irradiation on the gas permeation and separation of nitrogen and methane were also studied in detail.<sup>4</sup> Since the previous investigations in this laboratory were concerned with the permanent gases and methane, it was decided to investigate the diffusion solubility and permeation characteristics of the organic molecules, methane, ethane, and propane and compare the results to those of the permanent gases, nitrogen and helium. A continuing area of research in this laboratory has been the study of various methods of treating polymer membranes by physical or chemical means in order to improve their transport properties to various gases. In this study, polyethylene films were irradiated in vacuum, acetylene, and acetylene-nitrogen mixtures in order to study the changes induced in the crosslinking efficiency and the transport properties with both the irradiation dose and irradiation atmospheres.

If the diffusion and solubility coefficients are not functions of concentration, Barrer<sup>5</sup> and Daynes<sup>6</sup> have shown that the diffusivity, solubility, and permeability may be obtained by using the unsteady-state or time-lag method. Siegel and Coughlin<sup>7</sup> have illustrated that large errors in the diffusivity can result from the application of the time-lag method even if the experimental data exhibit a good fit to a straight line. Meares<sup>8</sup> postulates that below the glass transition temperature one mode of sorption leads to gas molecules which are not mobile and do not participate in the diffusion step, whereas the other mode gives a mobile species (dissolved gas). He concludes that the time-lag method only measures the amount of mobile molecules while equilibrium-sorption measures both, thus giving larger solubility coefficients. Barrie and Machin<sup>9</sup> found that when the diffusivity is concentration dependent, the variation of the time-lag method with concentration is always smaller than that of the diffusivity with concentration. Therefore, discrepancies arise when comparing steady-state and time-lag data. Barrer<sup>10</sup> extended Eyring's activated complex theory to explain the exponential dependence of the diffusion coefficient on the temperature. He considered the activation energy for diffusion to be the energy required for the penetrant molecules to form holes against the cohesive energy of the surrounding chains. Paul and DiBeneditto<sup>11</sup> went further to consider the forces that act to prevent holes from being formed and found that those forces were not constant but varied with hole size. Li, Long, and Henley<sup>12</sup> found that the activation energies for permeation and diffusion are independent of temperature, while other workers<sup>2,13,14</sup> maintain that apparent activation energy for diffusion decreases with increasing temperature. Kumins and Roteman<sup>14</sup> have shown that for small-sized gas molecules, the activation energies for permeation and diffusion are independent of temperature for the range of 25–50°C. Brandt<sup>15</sup> has developed an expression for the activation energy of small molecules diffusing in polymers in terms of the intermolecular and intramolecular interactions and the number of degrees of freedom involved in the molecular process. The observed lack of dependence of the activation energy of gaseous diffusion on the polymer density indicates that there is little or no straining of amorphous segments at high polymer densities.<sup>16</sup> Michaels and Bixler<sup>17</sup> stated that the stresses imposed upon the amorphous phase by crystallization are of insufficient magnitude to create significant changes in the thermodynamic properties. Michaels and Parker<sup>18</sup> have studied a complete series of polyethylenes with respect to both mode of polymerization and range of crystallinities. They have proposed that two impedance factors are operating to reduce the diffusion constants in semicrystalline polyethylene.

Small and subtle differences in penetrant geometry can result in large differences in transport constants. The solubility of the penetrant (increases with an increase in molecular diameter) is governed by its polarity, or its cohesive-energy density, and the similarity of these quantities with that of the polymer film.<sup>19</sup> The permeability has been shown to be affected strongly by the solubility of the gas in the polymer.<sup>20,21</sup> Li and Long<sup>22</sup> found that the permeation rates of organic gases through polyolefin films were higher than that of inorganic gases of the same molecular weight. Van Amerongen<sup>23</sup> demonstrated that the differences in permeability of natural rubber to different gases are caused not only by differences in diffusion rates but also by differences in solubilities. The solubility effect generally far exceeds the diffusion effect on permeation with the possible exception of small and simple gas molecules.<sup>20,21,23</sup> Owing to the lack of data on the effective diameters of molecules during diffusion, a precise relationship between molecular diameters and diffusivity has not been developed.<sup>24,25</sup> It has been shown that the diffusivity generally decreases<sup>17,23,25,26</sup> and the activation energy for diffusion increases<sup>23,27-29</sup> as the molecular weight or the volume and shape of the penetrant increases. Cyclization and branching of the penetrant causes a decrease in the diffusion coefficient because of an increase in cross-sectional area.<sup>16,24,30</sup> An olefin such as ethylene, however, diffuses more rapidly than ethane, the double bonds making the dimensions of the penetrant more favorable for diffusion. Comparing the permeations of carbon dioxide and nitrous oxide,<sup>20</sup> it is interesting to note that although both gases have the same molecular weight and similar molecular forms, the permeability of nitrous oxide varied with pressure while carbon dioxide did not over the range of pressures investigated (1-11 atm). Moreover, nitrous oxide has a much higher permeability than carbon dioxide at any one pressure. Pilar<sup>31</sup> observed that the permeation rates of oxygen and nitrogen through polyethylene increased with relative partial pressures of *n*-hexane. Robeson<sup>32</sup> noted that the permeability of ethane and butane increased with increasing butane concentration in the feed. This effect was attributed to the plasticizing effect of sorbed butane, whose equilibrium concentration in the film is an order of magnitude greater than ethane.

Polyethylene is a polymer of the crosslinking type with a scission-to-crosslinking ratio of approximately 0.35.<sup>33,34</sup> The crosslinking of polyethylene has been shown to be totally dose dependent while independent of the dose rate.<sup>34-36</sup> Charlesby, von Arnim, and Callaghan<sup>37</sup> found that the crosslinking taking place is approximately the same in both the amorphous and crystalline regions of polyethylene. Stannett and co-workers<sup>38</sup> have reported no changes in the permeability of gases and vapors in  $\gamma$ -irradiated polyethylene up to an irradiation dose of 10 Mrad. At higher doses they found that the permeability of the film decreased to approximately half of that normally measured for the unirradiated film. Several workers<sup>23,39-41</sup> have found that both the permeability and diffusion coefficients decreased with increasing degree of crosslinking. The solubility, however, is little affected, except at very high degrees of crosslinking.<sup>40,42</sup> It has been shown that the decrease in the diffusion coefficient is approximately linear with crosslink density at low degrees of crosslinking.<sup>23</sup> At higher crosslink densities the decrease is nonlinear.<sup>40</sup> Rogers<sup>26</sup> states that the rate of decrease of the diffusion coefficient becomes more pronounced as the size and shape of the penetrant molecule increases. Okada and Amemiya<sup>43</sup> compared  $\gamma$ -irradi-

ation-induced crosslinking of polyethylene in various gaseous atmospheres to irradiation in a vacuum. They found that  $N_2O$  accelerated the crosslinking,  $H_2$  and  $CO$  had no effect, and the remaining gases depressed crosslinking in the following order  $NO_2 > O_2 > NH_3 \geq SO_2 \geq Cl_2$ . Odian and Bernstein<sup>44</sup> studied the effect of numerous polyfunctional monomers on the crosslinking efficiency and found allyl methacrylate and allyl acrylate to increase the crosslinking density the most. They found that the crosslinking was directly dependent on allyl methacrylate concentration with the effect of leveling off rapidly at 3% monomer.<sup>35</sup> They also stated that the majority of the monomer was reacted immediately to form a low molecular weight polymer. Hagiwara, et al.<sup>45</sup> have reported that acetylene compounds greatly enhance the crosslinking ability of methyl methacrylate.

## EXPERIMENTAL

### Permeation and Diffusion Experiments

#### *Apparatus*

A modification of the permeation apparatus designed and built by Huang and Kanitz<sup>1</sup> was used to measure the permeation and diffusion coefficients simultaneously. The design of the apparatus was based on the high vacuum technique originally introduced by Barrer with modifications to the film holder as suggested by Huld. The experimental procedure has been described in detail in a previous article in this series.<sup>1</sup> Experimental runs were carried out in the temperature range of 25–50°C and pressure ranges of 100–300 torr.

### Preparation of Modified Films

#### *Material Specifications*

Polyethylene film was supplied by Canadian Industries Ltd. Films 5 and 10 mil thick were made by the blown tubular process. Its specifications were shown in Table I. Reagents were xylene (0.05% water) from Fisher Scientific Co., and *N*-phenyl-2-Napthtylamine, Fisher Scientific Co.

#### *Radiation Facility*

The polyethylene films were modified by  $\gamma$ -ray irradiation in a Gammacell 220 <sup>60</sup>Co unit designed and built by the Commercial Products Division, Atomic Energy of Canada Ltd. The intensity of the source during the period of use varied from 0.6195 to 0.6128 Mrad/hr. Irradiation of the samples was carried out at 35°C.

#### *Sample Preparation*

Polyethylene films were placed inside constricted Pyrex ampoules where they were outgassed at a pressure of  $10^{-4}$  torr for 2 hr. The ampoules were then filled with acetylene or nitrogen-acetylene mixture to atmospheric pressure, or evacuated to vacuum, immersed in liquid nitrogen, and sealed off at the con-

TABLE I  
Film and Gas Specifications

Films			
Thickness, in.	Melt index, g/10 min	Density, g/cm <sup>3</sup>	Additives
0.005	2.0	0.9203 ± 0.0003	None
0.010	2.0	0.9203 ± 0.0003	None
Gases			
Gas	Supplier	Grade	Purity
Helium	Linde	High purity	99.995%
Nitrogen	Linde	Cylinder dry grade	99.95%
Methane	Matheson	C.P. grade	99.0% min
Ethane	Matheson	C.P. grade	99.0% min
Propane	Matheson	C.P. grade	99.0% min
Acetylene	Union Carbide	High purity	99.5%

striction. The samples were stored for 24 hr before irradiation in the Gammacell 220 unit. After irradiation, the samples were stored under vacuum ( $10^{-1}$  torr) until placed in the permeation cell.

### Characterization of Modified Polymers

#### *Gel Experiments*

On removal from the Gammacell, the films were placed in a vacuum oven at 50°C for 24 hr to remove any sorbed components. These samples (approximately 0.6 g) were weighed and placed in extractor Soxhlets where they were extracted with xylene containing 0.1% *N*-phenyl-2-naphthylamine as an antioxidant at 100°C for six days. The samples were then vacuum dried at 50°C for 24 hr, weighed, and the percent gel calculated using the following relationship:

$$\% \text{ gel} = (W_2/W_1) \times 100$$

where  $W_1$  is the weight of the polymer sample before extraction and  $W_2$  is the weight of the nonextractable fraction.

TABLE II  
Change of Activation Energy of Permeation with Penetrant Nature and Irradiation Dose<sup>a</sup>

Test gas	Activation energy of permeation, $E_p$			
	Irradiation dose, mrad:	0	20	50
He		6.217	6.607	6.721
N <sub>2</sub>		6.732	7.190	7.478
CH <sub>4</sub>		9.623	9.732	9.821
C <sub>2</sub> H <sub>6</sub>		9.802	10.37	10.97
C <sub>3</sub> H <sub>8</sub>		10.82	11.49	12.01

<sup>a</sup> Units of  $E_p$  kcal/mole.

*Infrared Analysis*

Infrared spectra were determined by means of a Perkin-Elmer Infrared model 337 spectrophotometer. The analyses were obtained directly from film samples of the modified films.

**EXPERIMENTAL RESULTS****Irradiated Films**

Crosslinked polyethylene films were produced by  $\gamma$ -ray irradiation from a  $^{60}\text{Co}$  source. The following three irradiation atmospheres were studied to determine their effect on the crosslinking efficiency: vacuum, acetylene (atmosphere), and acetylene-nitrogen. The effect of varying the amount of acetylene in the acetylene-nitrogen mixture was studied using a fixed irradiation dose of 2.75 Mrad. The crosslinking efficiency was observed to level out in the region of 15% acetylene (partial pressure) in the mixture. A 12.5% acetylene mixture was then chosen for further study. These results are shown in Figures 1 and 2, respectively. Owing to the problem in duplicating a particular mixture with the equipment in the laboratory, another set of runs was executed using a pure acetylene atmosphere (1 atm. pressure). The results of this run were compared to a vacuum run as shown in Figure 3. An interesting observation was that an acetylene-nitrogen atmosphere enhanced the amount of crosslinking (compared to vacuum), while the pure acetylene atmosphere lowered the crosslinking efficiency.

The  $\gamma$ -ray irradiation chemistry of polyethylene, acetylene, and acetylene-nitrogen mixtures were studied in an attempt to explain the difference in crosslinking efficiencies. This is illustrated in Figures 4, 5, and 6, respectively. In addition, infrared spectra (Figs. 7 and 8) and gas chromatography of the postirradiation gases were used to further study these effects.

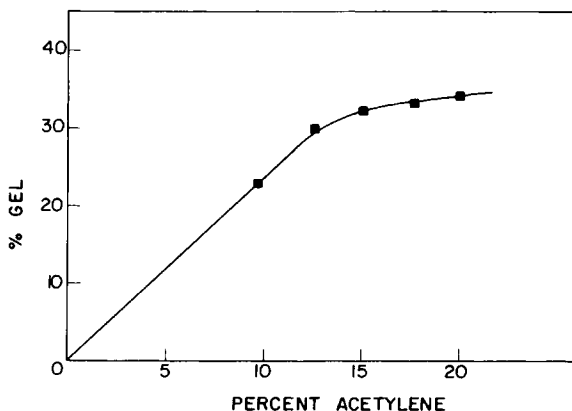


Fig. 1. Effect of irradiation atmosphere on crosslinking efficiency of polyethylene. Samples crosslinked in  $\text{C}_2\text{H}_2\text{-N}_2$  atmosphere. Total dose for each 2.75 Mrad.

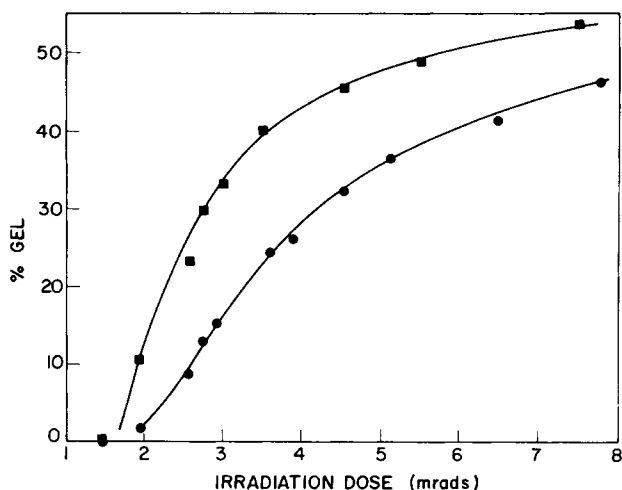


Fig. 2. Effect of irradiation dose on crosslinking polyethylene. ●, crosslinked in vacuum; ■, crosslinked in 12.5% C<sub>2</sub>H<sub>2</sub> (in C<sub>2</sub>H<sub>2</sub>-N<sub>2</sub> mixture).

### Gas Permeation, Diffusion, and Solubility Results

The reproducibility of the permeation data was studied by passing methane through four different film samples. The results are plotted in Figure 9. The effect of the irradiation atmosphere on methane permeability was studied and is shown in Figure 10. The gas permeabilities of unirradiated and acetylene atmosphere-irradiated polyethylene film to helium, nitrogen, methane, ethane, and propane were studied for the film temperature range of 24–50°C (Figs. 11–13). The permeability temperature dependence was found to obey the following form:

$$P = P_0 \exp(-E_p/RT)$$

and the activation energy for the permeation increased with both the irradiation dose and molecular diameter (Table II).

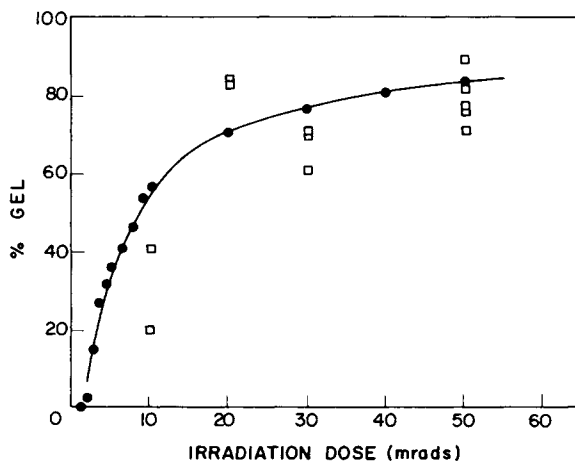
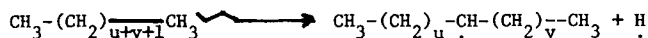


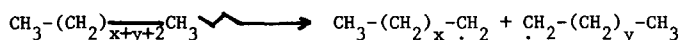
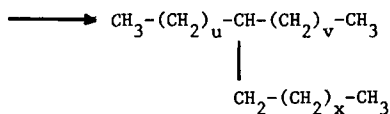
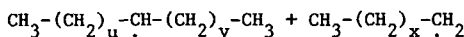
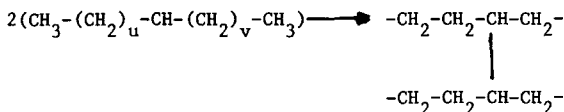
Fig. 3. Effect of irradiation dose on crosslinking of polyethylene. ●, crosslinked in vacuum; □, crosslinked in pure C<sub>2</sub>H<sub>2</sub> (1 atm).

A. Free Radical Formation

(1) Free Radical Formation on backbone



(2) Chain Fracture

B. Branching ReactionC. Crosslinking ReactionFig. 4.  $\gamma$ -ray irradiation of polyethylene.

The permeability of the penetrant in a polymer is a function of the diffusivity and the solubility. Therefore, these two quantities were studied in order to give a better understanding of the effects of temperature, irradiation dose, and molecular diameter on the transport properties of the film. The effects of these variables on the diffusion coefficients of the test gases are shown in Figure 14. The diffusivity decreases and the activation energy for diffusion increases (Table III) with an increase in molecular diameter. The Arrhenius-type plots shown in Figure 14 confirm a diffusion coefficient temperature dependence of the form:

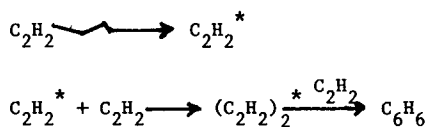
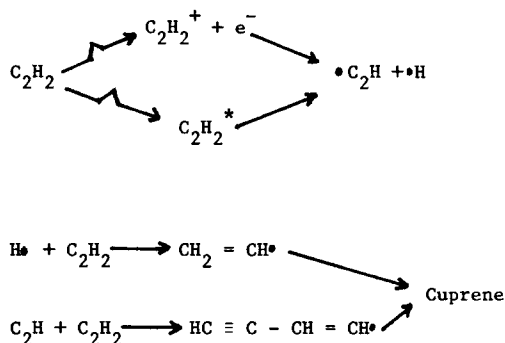
$$D = D_0 \exp(-E_D/RT)$$

The effect of temperature on the solubility coefficient of the test gases in polyethylene was calculated from the following relationship:

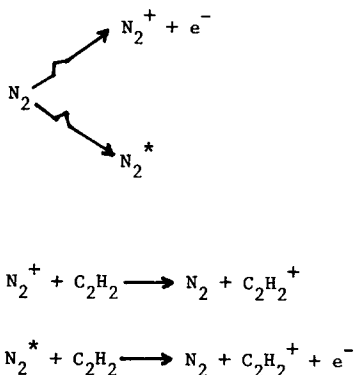
$$S = S_0 \exp(-H/RT)$$

The heat of solution is positive for helium and methane, zero for ethane, and negative for propane. An interesting observation is that the diffusivity decreases with an increase in the molecular diameter of the penetrant while the solubility increases. The effect of temperature on the solubility coefficient of test gases is shown in Figure 15.



A. Benzene Formation

 B. Cuprene Formation

 Fig. 5.  $\gamma$ -ray irradiation of acetylene.

The changes in the permeation coefficients of the test gases in irradiated polyethylene are illustrated in Figure 16. As the molecular diameter of the molecule increases, the permeation coefficient of the gas becomes more dependent on the irradiation dose. The decrease in the diffusion coefficient with an increase in irradiation dose is shown in Figure 17. A plot of the permeabilities of the test gases (at irradiation doses of 0, 20, and 50 Mrad) versus the molecular diameter of the gases is shown in Figure 18. Similar plots for the diffusivity and solubility for irradiated films are illustrated in Figures 19 and 20. As would be expected from Raoult's law, the more easily condensable gases have higher solubility coefficients, as shown in Figure 21. Figure 22 is a plot of the solubility coefficients of the gases versus their Lennard-Jones force constants. The solubility of a gas is shown to increase as the force constant of the gas increases.


 Fig. 6.  $\gamma$ -ray irradiation of acetylene-nitrogen mixture.

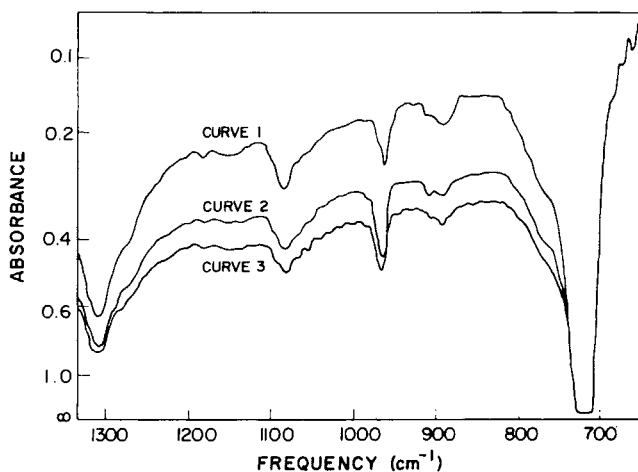


Fig. 7. Effect of irradiation atmosphere on infrared spectra of polyethylene. 1, Acetylene-nitrogen irradiated polyethylene (50 Mrad); 2, acetylene (1 atm) irradiated polyethylene (50 Mrad); 3, vacuum irradiated polyethylene (50 Mrad).

## DISCUSSION OF RESULTS

### Analysis of Irradiated Films

#### *Gel Experiments*

Polyethylene film samples were exposed to irradiation doses ranging from 0 to 50 Mrad in vacuum, acetylene, and acetylene-nitrogen atmospheres. The percent gel, a measure of the crosslink density, increased with irradiation dose for the three cases studied. Crosslinking changes the diffusion, solubility, and permeation characteristics of the film. These properties are little affected as long as only a few polymer molecules are linked together; but at the stage where

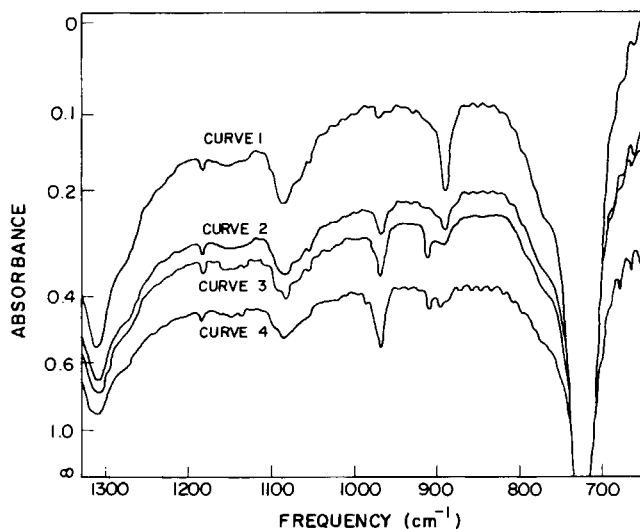


Fig. 8. Effect of irradiation dose on infrared spectra of polyethylene. 1, 0 Mrad; 2, 10 Mrad; 3, 20 Mrad; 4, 50 Mrad. All samples irradiated in a pure acetylene atmosphere.

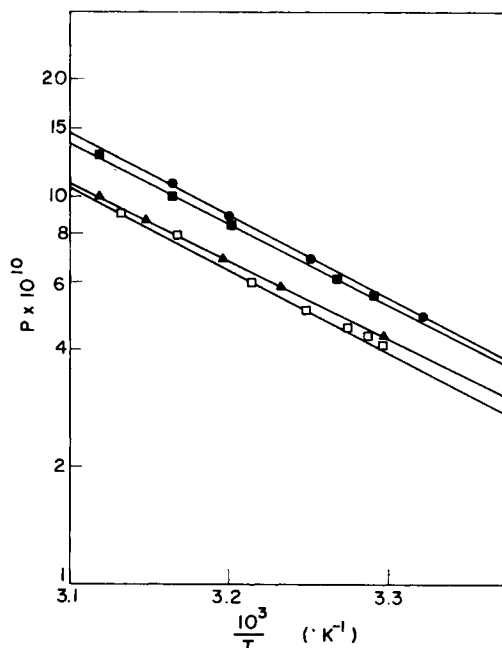


Fig. 9. Variation of methane permeability with film sample (unirradiated polyethylene). Runs 1, 2, 3, and 4. Units of permeability— $[\text{cm}^3(\text{STP})\text{-cm}/\text{four-sec}\text{-cm}^2]$ . ■, 5-mil polyethylene (sample A), 9.514  $E_p$  kcal/mole; ●, 5-mil polyethylene (sample B), 9.77  $E_p$  kcal/mole; □, 5-mil polyethylene (sample C), 9.623  $E_p$  kcal/mole; ▲, 10-mil polyethylene (sample D), 9.128  $E_p$  kcal/mole.

TABLE III  
Change of Activation Energy of Diffusion with Penetrant Nature and Irradiation Dose<sup>a</sup>

Test gas	Activation energy of diffusion, $E_D$		
	Irradiation dose, mrad		
	0	20	50
He	4.934	5.372	6.271
CH <sub>4</sub>	6.816	7.190	8.005
C <sub>2</sub> H <sub>6</sub>	8.234	8.989	9.494
C <sub>3</sub> H <sub>8</sub>	11.945	13.069	13.283

<sup>a</sup> Units of  $E_D$ , kcal/mole.

a three-dimensional network first extends through the system, there is a marked discontinuity as shown in the results. Up to this point (the gel point), the film is still completely soluble and the only effect of radiation is to increase the average molecular weight and degree of branching. After the gel point is reached, some of the material becomes insoluble in xylene, the solvent that dissolved the unirradiated film.

The  $G$  (crosslink) value for polyethylene has been calculated by Charlesby<sup>33</sup> from the equation:

$$G = 4.8 \times 10^5 / r_{\text{gel}} \overline{M}_w^6$$

where  $r_{\text{gel}}$  is the dose for incipient gelation and  $\overline{M}_w$  is the weight-average molecule of the initial polymer. The weight average of the polymer films was taken as 180 000. As shown in Table IV the acetylene atmospheres gives the highest

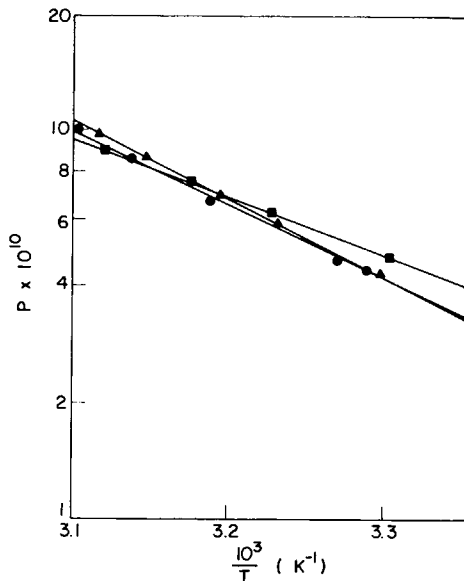


Fig. 10. Change of methane permeation constant with irradiation atmosphere, runs 5, 6, and 7. All samples irradiated for 50 Mrad. Units of permeability— $[\text{cm}^3(\text{STP})\text{-cm}/\text{torr-sec-cm}^2]$ . ■, film irradiated in vacuum; ▲, film irradiated in acetylene (1 atm); ●, film irradiated in acetylene-nitrogen mixture (12.5% acetylene).

crosslink value. The experimental  $G$  values are in good agreement with the literature value of 1.9 for air-irradiated polyethylene.<sup>37</sup> Figure 1 shows an increase in gel with an increase in the partial pressure of acetylene in an acetylene-nitrogen mixture. The magnitude of the increase levels off at about 15%

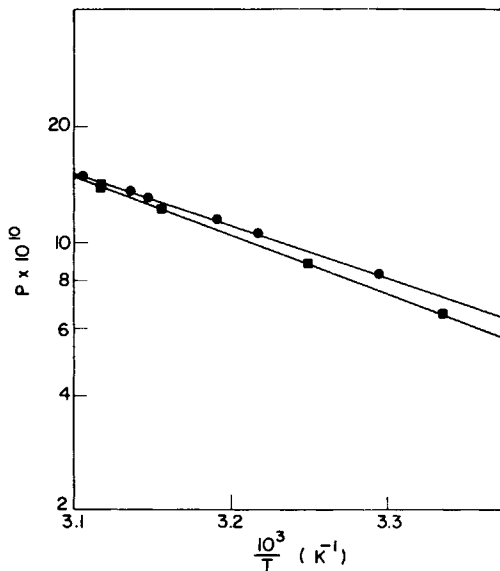


Fig. 11. Effect of temperature and irradiation dose on helium permeability of polyethylene, runs 8 and 10. Film irradiated in acetylene atmosphere. Units of permeability— $[\text{cm}^3(\text{STP})\text{-cm}/\text{torr-sec-cm}^2]$ . ●, 0 Mrad; ■, 50 Mrad.

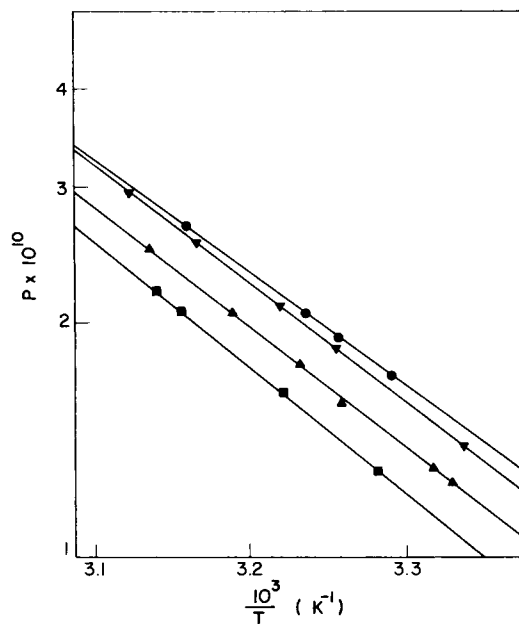


Fig. 12. Effect of temperature and irradiation dose on nitrogen permeability of polyethylene, runs 11, 12, 13, and 14. Film irradiated in acetylene atmosphere. Units of permeability—[ $\text{cm}^3(\text{STP})\text{-cm/torr-sec-cm}^2$ ]. ●, 0 Mrad; ▼, 10 Mrad; ▲, 20 Mrad; ■, 50 Mrad.

TABLE IV  
Crosslink Values of Polyethylene

Irradiation atm.	$r_{\text{gel}}$	$G$
Vacuum	1.84	1.445
12.5% $\text{C}_2\text{H}_2$ in $\text{N}_2$	1.65	1.615
$\text{C}_2\text{H}_2$	2.50	1.065

acetylene. Similar results were found by Odian and Bernstein,<sup>35</sup> who studied the effect of polyfunctional monomers on the crosslinking efficiency of polyethylene. Figures 2 and 3 show that an acetylene–nitrogen atmosphere enhances the amount of crosslinking over that of vacuum while a pure acetylene atmosphere appears to reduce the crosslinking efficiency.

Chapiro<sup>34</sup> stresses the importance of eliminating free radicals that might be trapped in the crystalline regions of the irradiated polymer before exposure to air. When the free radicals are exposed to oxygen, chain scission results. This is particularly true for the acetylene crosslinked samples. After irradiation of these samples, the films were under vacuum. Therefore when the ampoules are opened, the films quickly absorb air. The acetylene–nitrogen crosslinked samples were under one atmosphere of nitrogen in addition to the acetylene. In this case, the films would not absorb air as readily and no scatter of data was observed. When acetylene is irradiated, a polymer, cuprene, which absorbs oxygen<sup>46</sup> up to 25% by weight when exposed to air, is produced. The weight of the cuprene and absorbed oxygen trapped in the polymer network will also result in a random error in the gel percent.

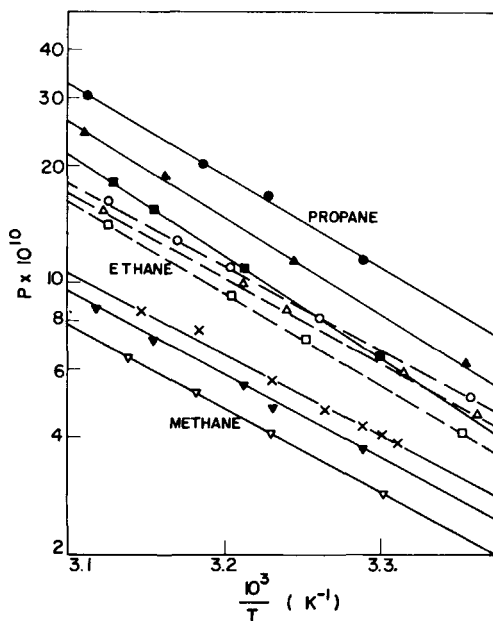


Fig. 13. Effect of temperature and irradiation dose on permeability of methane, ethane, propane through polyethylene. Methane—runs 4, 15, and 16; Ethane—runs 17, 18, and 19; Propane—runs 20, 21, and 22. Film irradiated in acetylene atmosphere. Units of permeability— $[\text{cm}^3(\text{STP})\text{-cm}/\text{torr}\text{-sec}\text{-cm}^2]$ . Methane: X, 0 Mrad;  $\blacktriangledown$ , 20 Mrad;  $\nabla$ , 50 Mrad. Ethane: O, 0 Mrad;  $\blacktriangle$ , 20 Mrad;  $\square$ , 50 Mrad. Propane:  $\bullet$ , 0 Mrad;  $\blacktriangle$ , 20 Mrad;  $\blacksquare$ , 50 Mrad.

### *$\gamma$ -Ray Irradiation Products*

By studying the irradiation chemistry of the species present during the irradiation (Figs. 4–6), it is possible to account quantitatively for the variation in crosslinking efficiency with the irradiation atmosphere. In the present study, the irradiation of polyethylene in a pure acetylene atmosphere retarded the crosslinking efficiency of polyethylene compared to vacuum irradiated film. The reason for this phenomenon is that the acetylene irradiation reaction is so fast that it proceeded independently, producing benzene and cuprene. The presence of benzene in the polymer network is believed to decrease the efficiency of the crosslinking reaction. Odian and Bernstein<sup>44</sup> postulated that the crosslinking of polyethylene in the presence of a monomer (allyl methacrylate) was a two-step process: (1) the rapid initial polymerization of the monomer and (2) the reaction of the polymerized monomer with polyethylene chains to complete the crosslinked polyethylene–poly(allyl methacrylate) network. When nitrogen was added to the acetylene, the crosslinking efficiency of polyethylene was increased over that of the vacuum irradiated samples. Under these conditions, no benzene was produced and the crosslinking reaction was more efficient than the pure acetylene case. The acetylene radicals appear to attack the polymer backbone thereby enhancing the crosslinking reaction.

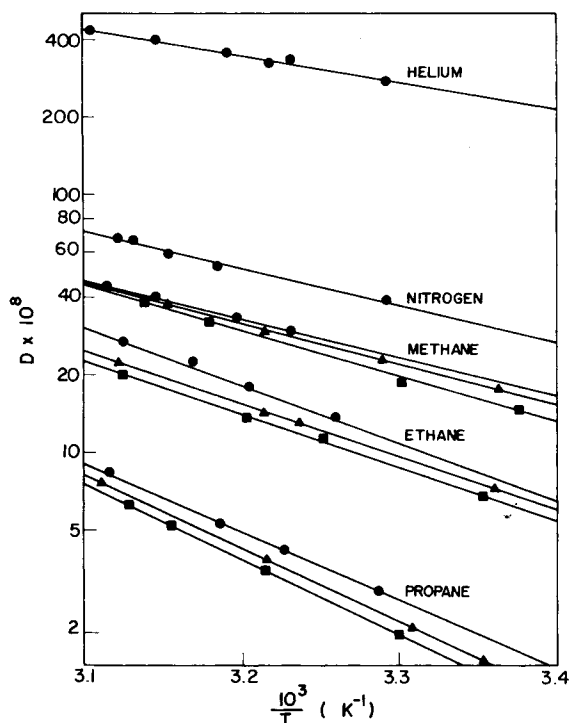


Fig. 14. Effect of temperature and irradiation dose on diffusivity of test gases in polyethylene. He = run 4; N<sub>2</sub> = run 24; CH<sub>4</sub> = runs 3, 15, and 16; C<sub>2</sub>H<sub>2</sub> = runs 17, 18, and 19; C<sub>3</sub>H<sub>8</sub> = runs 20, 21, and 22. Film irradiated in acetylene atmosphere. Units of diffusivity—cm<sup>2</sup>/sec. ●, 0 Mrad; ▲, 20 Mrad; ■, 50 Mrad.

#### Gas Chromatograph Analysis

The preceding results were confirmed from chromatographic analysis of the gas samples present in the ampoules after irradiation. The pure acetylene samples showed traces of hydrogen, low-molecular-weight hydrocarbons, and benzene. The low-molecular-weight hydrocarbons are the result of the irradiation of branched polyethylene. The chromatographic analysis of the nitrogen-acetylene irradiated gases showed the same mixture of gases as did the pure acetylene samples except that no benzene was present. This supports the earlier statement that it appears to be the benzene that retards the crosslinking efficiency of the irradiation reaction.

#### Infrared Analysis of Polyethylene

Infrared analysis of the irradiated films gave the same results for the three atmospheres studied (Fig. 7). This suggests that the final crosslinked state is the same in all three cases. Infrared data on samples of polyethylene irradiated to 10, 20, and 50 Mrad showed no major changes in the film structure compared to the unirradiated films. One peak, at a frequency of 800 cm<sup>-1</sup>, is a measure of the methyl content of the polymer chains. As the irradiation dose is increased, more of these side branches are displaced resulting in a decrease in the peak height. Another peak, at a frequency of 968 cm<sup>-1</sup>, increased with irradiation dose and is a measure of the crosslink density of the film.

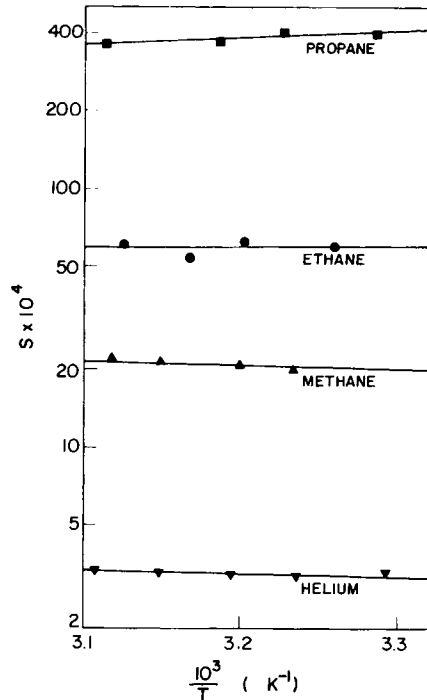


Fig. 15. Effect of temperature on solubility coefficient of test gases in polyethylene. Data calculated from  $S = P/D$ . He = run 9; CH<sub>4</sub> = run 3; C<sub>2</sub>H<sub>6</sub> = run 17; C<sub>3</sub>H<sub>8</sub> = run 20. Unirradiated polyethylene film. Units of solubility—cm<sup>3</sup> (STP)/cm<sup>3</sup>-torr. ▼, helium; ▲, methane; ●, ethane; ■, propane.

### Gas Transport Properties of $\gamma$ -Irradiated Polyethylene Film

Since diffusion and solubility require rearrangements of the molecular conformation, the behavior is closely associated with the rheological and mechanical properties of the polymer in the presence of the penetrant. Gases in polymers normally obey the ideal laws of Henry and Fick up to moderate pressures, with a diffusion coefficient that is independent of the concentration of the gas in the polymer. At higher pressures (above atmospheric), however, the solubility and diffusivity of the penetrants in highly interacting polymer-penetrant systems display a rather complicated concentration and pressure dependence.<sup>20,21</sup> The higher the upstream pressure, the higher the plasticizing activity and the greater the variation from ideality. The present experiments were carried out at low pressures ( $10^{-7}$  torr downstream and 200 torr upstream) so that the ideal laws applied, allowing the calculations of the permeation, diffusion, and solubility coefficients, respectively. Before studying the effect of irradiation on the transport properties of the film, a series of runs was completed using different film samples of the same polymer. Figure 9 shows the activation energy to be fairly constant, varying from 9.128 for a 10-mil film to  $9.635 \pm 3\%$  for a 5-mil sample. However, the permeation constants at a particular temperature (30°C) varied by as much as  $\pm 15\%$  [ $(4.7 \pm 0.7) \times 10^{10}$  cm<sup>3</sup> (STO) - cm/torr - sec - cm<sup>2</sup>]. Variations and irregularities from sample to sample and deviations obtained with the experimental method are considered to be primarily due to irregularities in the structure of the polymer. Variations of this order have also been found by



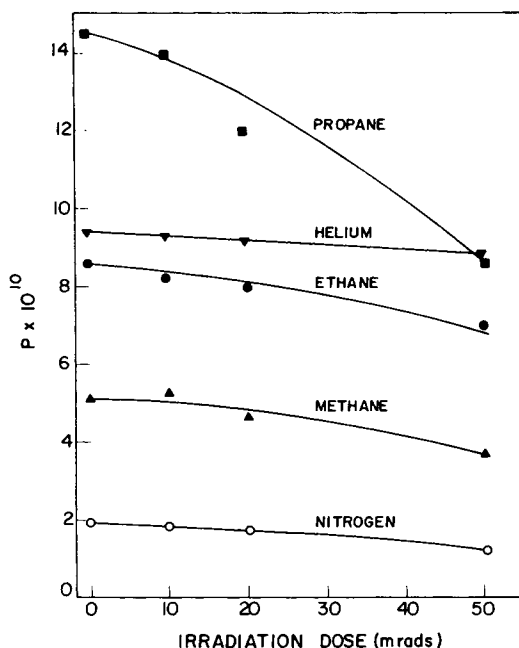


Fig. 16. Permeability coefficients of test gases in irradiated polyethylene films at 35°C. Film temp 35°C; units of permeability— $[\text{cm}^3 \text{ (STP)-cm/torr-sec-cm}^2]$ . ▼, Helium; ○, nitrogen; ▲, methane; ●, ethane; ■, propane.

Barrer and Skirrow<sup>47</sup> and Alter.<sup>48</sup> Ideally, the same film sample should be used for all of the permeation and diffusion experiments. This is impossible, however, since the organic gases plasticize the film preventing further use of the membranes. Figure 10 illustrates that the change of the permeability coefficient with irradiation atmosphere is less than the variation with film sample. Therefore, no comment can be made on how the irradiation atmosphere affects the transport properties of the polymer film. The remainder of the permeation studies were completed using pure acetylene as the irradiation atmosphere. Figures 11–13 show the temperature dependence of the permeability constant for the five gases studied. As seen in these figures, they obey the Arrhenius relationship. The permeability data agreed fairly well with that found in the literature as shown in Table V.

Significant differences in permeability did not occur until irradiation doses of 10–20 Mrad were reached. After this irradiation dose was passed, the permeability coefficients decreased and the activation energy for permeation increased as the dose was further increased. This rise in activation energy is due to a decrease in the mobility of the polymer chains as they become more highly crosslinked. The permeation coefficient of nitrogen is less than that of helium at any one temperature. This is to be expected since nitrogen has a larger molecular diameter  $d$  and therefore has a more difficult time in finding a passage way through the polymer network. The permeability of methane ( $d = 2.953 \text{ \AA}$ ), however, is higher than nitrogen ( $d = 2.709 \text{ \AA}$ ). The same results are shown for ethane and propane in Figure 9. The increase in permeability with an increase in molecular diameter is due to the plasticizing effect exerted on the polymer by the organic gases. Nitrogen and helium are permanent gases and have no

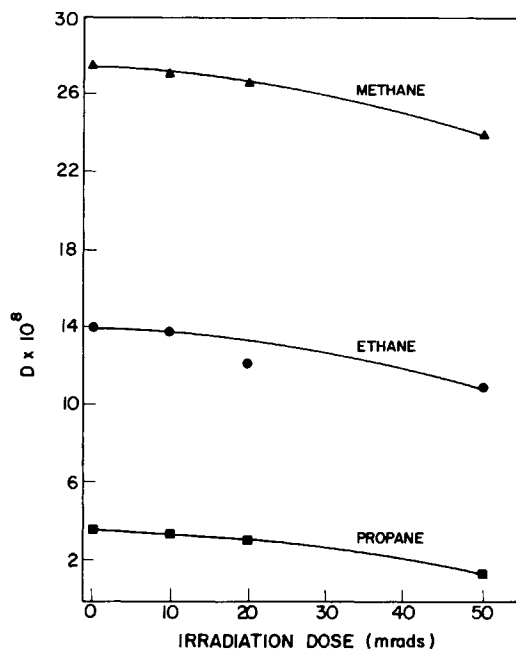


Fig. 17. Diffusion coefficients of test gases in irradiated polyethylene film at 35°C. Film temperature 35°C; units of diffusivity— $\text{cm}^2/\text{sec}$ .  $\blacktriangle$ , methane;  $\bullet$ , ethane;  $\blacksquare$ , propane.

TABLE V  
Permeability Data for Polyethylene at 25°C

Gas	Permeability coefficients $\times 10^{10}$ [ $\text{cm}^3$ (STP) - $\text{cm}/\text{torr} - \text{sec} - \text{cm}^2$ ]	
	Experimental	Literature
He	6.9	5.7 <sup>39</sup>
N <sub>2</sub>	1.4	1.0 <sup>2</sup>
CH <sub>4</sub>	3.2	3.0 <sup>2</sup>
C <sub>3</sub> H <sub>8</sub>	8.4	9.1 <sup>39</sup>

interaction with the polymer membranes. Methane, ethane, and propane interact with the membranes, and this interaction (plasticization) becomes more pronounced as the size and shape of the organic gas molecule increase. The permeability of a gas through a polymer membrane depends on the solubility and diffusion processes of the gas within the polymer. Therefore, the individual contributions of these processes toward the permeability should be considered. The time-lag method was used to find the diffusion coefficients of the test gases through the film. Figure 10 shows that the temperature dependence of the diffusion coefficient follows the Arrhenius law. An increase in the irradiation dose results in a decrease in the diffusion coefficient and an increase in the activation energy for diffusion. On the basis of Eyring's theory of hole formation, the energy of activation for diffusion corresponds with the energy required to form a hole for the infiltration of the gas molecules, to which must be added the energy needed to enable the diffusing molecules to jump into the hole. The activation energy is supplied by the kinetic energy of the gas molecules.<sup>25</sup> As the irradiation dose is increased the amorphous chain segments are gradually

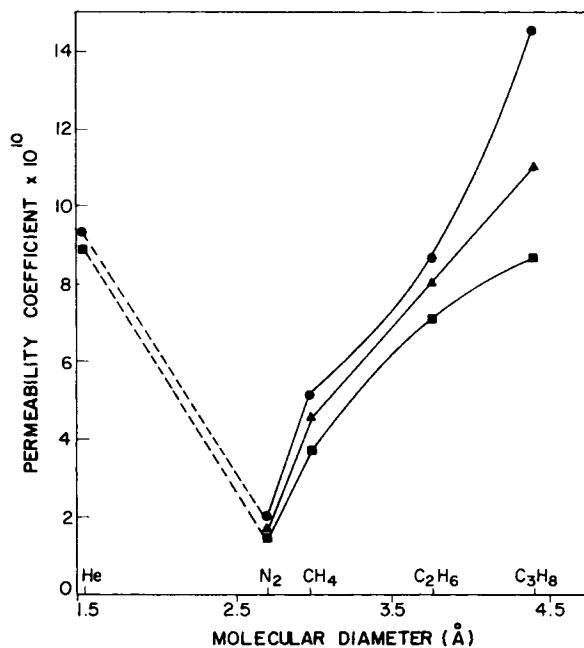


Fig. 18. Effect of molecular diameter on permeation constant of test gases in polyethylene. Film irradiated in acetylene atmosphere; film temp 35°C; units of permeability—[cm<sup>3</sup>(STP)-cm/torr-sec-cm<sup>2</sup>]. ●, 0 Mrad; ▲, 20 Mrad; ■, 50 Mrad.

restricted in their segmental mobility (kinetic energy) resulting in an increase in the activation energy.

Table VI compares the experimental diffusion data with that found in the

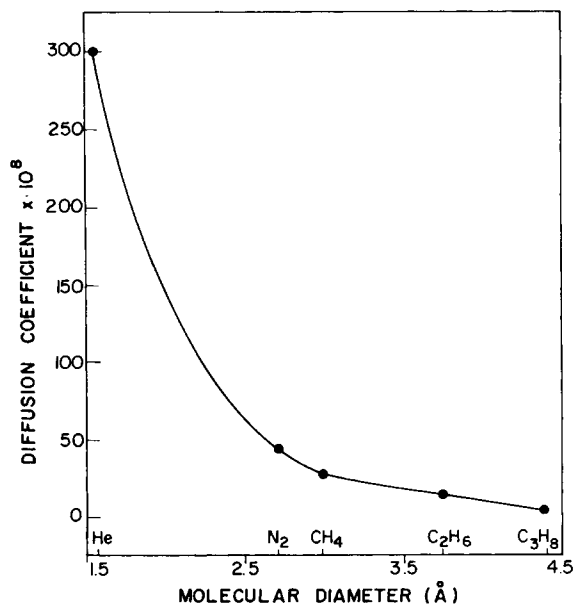


Fig. 19. Effect of molecular diameter on diffusion coefficient of test gases through polyethylene. Unirradiated polyethylene film; film temp 35°C; units of diffusivity—(cm<sup>2</sup>/sec).

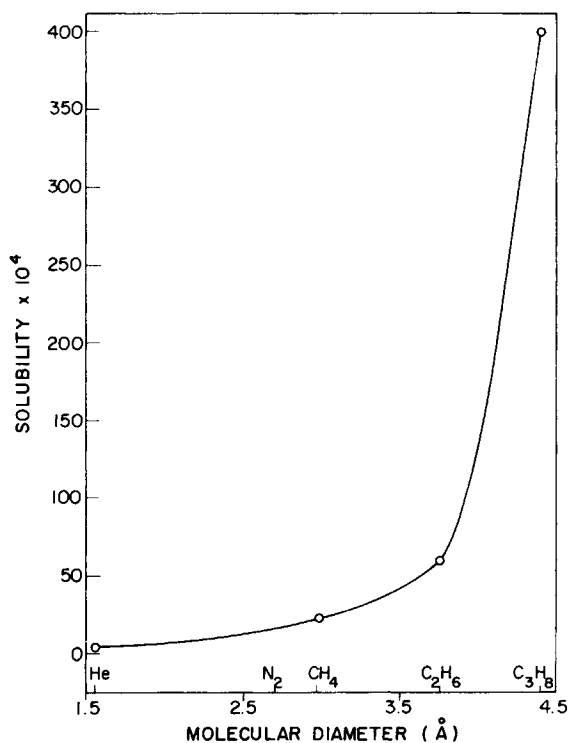


Fig. 20. Effect of molecular diameter on solubility coefficient of test gases in polyethylene. Unirradiated polyethylene film; film temp 35°C; units of solubility—[cm<sup>3</sup>(STP)/cm<sup>3</sup>-torr].

TABLE VI  
Diffusion Data for Polyethylene at 25°C

Gas	Diffusion coefficient × 10 <sup>8</sup> (cm <sup>2</sup> /sec)	
	Experimental	Literature
He	240	770 <sup>39</sup>
N <sub>2</sub>	31.5	29.0 <sup>39</sup> 50.0 <sup>2</sup>
CH <sub>4</sub>	19.6	18.0 <sup>39</sup> 20.0 <sup>2</sup>
C <sub>2</sub> H <sub>6</sub>	8.15	—
C <sub>3</sub> H <sub>8</sub>	2.0	2.6 <sup>39</sup>

literature. Table VII compares the experimental activation energies found in this article with those found by Bixler, Michaels, and Salame.<sup>39</sup>

The experimental values found in this article were consistently lower than those found in the literature. The variation is attributed to the difference in polymer films used for the experiments. Such factors as resin type and production procedure can greatly affect the size and distribution of crystallites and, therefore, the activation energies. The solubility coefficients were calculated from the relationship  $P = DS$ , and are plotted in Figure 11. Care must be taken in analyzing solubility data since any errors in the diffusion and permeability coefficients will be inherent in the solubility coefficient. As shown in Figure 15, the solubility coefficient increases as the size of the penetrant molecule increases.

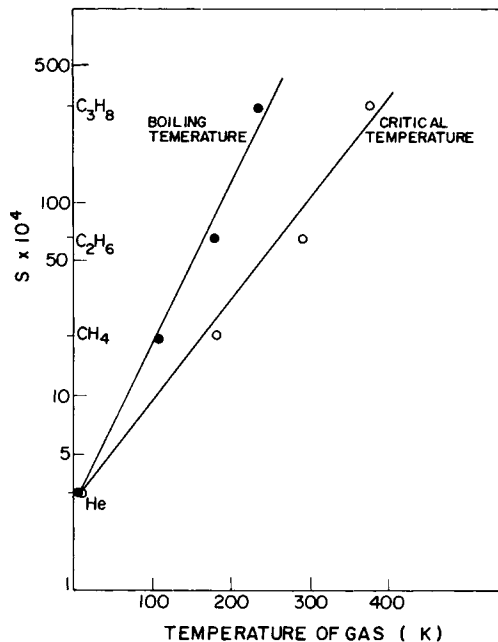


Fig. 21. Solubility coefficients of gases vs. critical temperatures and boiling temperatures. Unirradiated polyethylene film; film temp 35°C; units of solubility— $\text{cm}^3(\text{STP})/\text{cm}^3 \text{ torr}$ . ●, boiling temperature (K); ○, critical temperature (K).

TABLE VII  
Activation Energies of Diffusion and Solubility for Unirradiated Polyethylene

Gas	$E_p$ , kcal/mole		$E_D$ , kcal/mole	
	Experimental data	Literature data <sup>39</sup>	Experimental data	Literature data <sup>2</sup>
He	6.2	7.4	4.9	5.6
N <sub>2</sub>	6.7	10.6	6.8	9.7
CH <sub>4</sub>	9.6	10.9	8.2	11.3
C <sub>3</sub> H <sub>8</sub>	10.8	11.7	11.9	15.1

The solubility of most gases decreases with increasing temperature, with the exception of the highly volatile helium and nitrogen, which show a small increase as the temperature rises. The degree of solubility of a particular gas in polyethylene depends on its compatibility with the polymer, for example, on a specific interaction between the gas and the polymer molecules. Figure 16 illustrates the effect of the irradiation dose on the permeability coefficients. The permanent gases, helium and nitrogen, do not interact with the membrane and are little affected by the irradiation dose. Propane plasticizes the membrane to the greatest extent and is by far the most severely affected by an increase in irradiation dose. As seen in Table VIII, the percent change in the permeability coefficient increases as the molecular diameter of the penetrant gas molecule increases. Figure 17 shows a decrease in the diffusion coefficient with irradiation dose. If the folded chain lamellae crystal is used as the model for semicrystalline polymer, the decrease in diffusivity with irradiation dose may be explained. In this model, the crystals are visualized as folded chains or lamellae while the re-

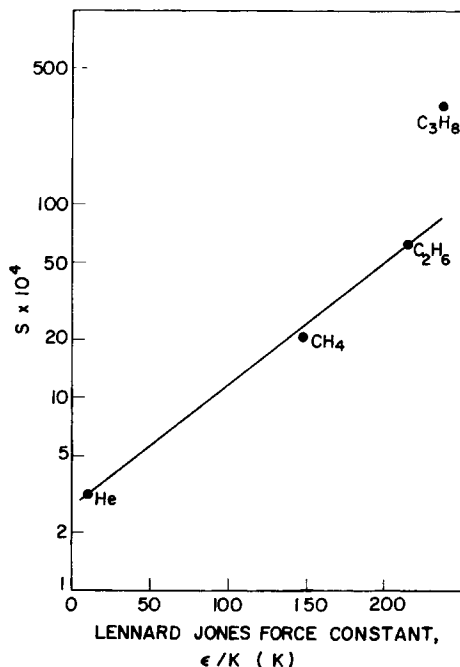


Fig. 22. Solubility coefficients of gases vs. Lennard-Jones force constant of penetrants. Unirradiated polyethylene film; film temp 35°C; units of solubility— $\text{cm}^3(\text{STP})/\text{cm}^3 \text{ torr}$ .

gions between crystallites (amorphous material) result from defects in the lamellae such as chain ends, branch points, folds, voids, and conformational defects. Geil<sup>49</sup> has shown that the folds of the lamellae are the most susceptible to attack and that crosslinking takes place between the folds of molecules in adjacent lamellae as well as in various types of defects within the lamellae. Irradiation disrupts the lattice spacings between lamellae and reduces the mobility of the chain segments resulting in a decrease in the diffusivity. The diffusivities were found to vary widely,  $\pm 20\%$ , depending on the polymer sample, film thickness, and measuring volume used. This error in the diffusivity accounts for the scatter of data in Figures 14, 15, and 17. Figures 18–20 show the effect of the molecular diameter on the transport process. The permeability decreases with the molecular diameter for the permanent gases but increases as the molecular diameter of the organic gases increases. Figure 18 also shows the increasing dependence on irradiation dose as the plasticizing ability of the gas increases. Propane, which has the highest permeability coefficient, is the most

TABLE VIII  
Effect of Nature of Penetrant on Permeability in Polyethylene

Gas	Molecular diam, Å	$P \times 10^{10}$ 35°C		% Change in permeability
		0 Mrad	50 Mrad	
He	1.55	9.4	8.8	6.4
N <sub>2</sub>	2.71	1.95	14.5	25.6
CH <sub>4</sub>	2.95	5.1	3.7	27.4
C <sub>2</sub> H <sub>6</sub>	3.75	8.7	6.25	28.2
C <sub>3</sub> H <sub>8</sub>	4.40	14.5	8.6	40.7

affected by the irradiation dose. As the chains become more and more cross-linked, the freedom of the polymer chains become greatly reduced, resulting in a decrease in the permeability. In Figure 19, it is shown that the diffusivity decreases markedly between helium and nitrogen and levels out for the low hydrocarbons. The hydrocarbons plasticize the polymer network resulting in a higher diffusion coefficient than would be expected for their size. From this, it may be concluded that the diffusion coefficient is a function of the plasticizing ability of the penetrant. Figure 20 shows a rapid increase in the solubility when going from the permanent gases to the organic gases. Solubility involves both condensation and mixing. The low solubility of permanent gases is due to their very large positive free energy of condensation at ordinary temperatures. Mixing involves the separation of polymer chains to make room for a molecule of penetrant, which has to break loose from its neighbors before it is free to take up the vacant site. The organic gases reduce the forces between the macromolecules and thereby increase the chain mobility, resulting in an increase in the solubility. A simple linear relationship has been found between the log of the solubility coefficient and the boiling point or the critical temperature of the gas, as shown in Figure 21. The same relationship applies for the solubility of gases in elastomers.<sup>25</sup> The high solubility of propane is a result of the large experimental error in the determination of the time lag. Barrer and Ferguson<sup>41</sup> had the same problem when trying to measure the diffusivities of easily condensable vapors. The time lag of propane was so large that several extrapolations had to be made, each one increasing the time lag above that which it should be. A large time lag results in a low diffusion coefficient and therefore a high solubility coefficient. These relationships have a practical value in helping one to predict the solubility of a gas in polymer where the relationship is known for the gases. If there is a linear relationship of the form

$$\log_{10} S = a + bT_c$$

then once the constants  $a$  and  $b$  are determined for a given polymer, it is possible to predict the solubility of a gas if the critical temperature is known. Apparently, the easier a gas is condensed, the higher the solubility.<sup>50</sup> Gee<sup>51</sup> has suggested the relationship:

$$-2.303 \log_{10} S = 4.5 + \mu - 10 (T_b/T)$$

where  $\mu$  is a constant and  $T_b$  is the boiling temperature of the gas. This may be adjusted by setting  $T = 50^\circ\text{C}$  and  $T_b = T_c \times 0.6$  (Guldberg-Guye Rule), and taking  $\mu = 1.5$ . This gives:

$$\log_{10} S = -2.6 + 0.008 T_c$$

so that these two relationships are substantially the same. Since Gee's relationship has some theoretical significance, the equivalence may be offered as a partial explanation of the linear relationship between  $\log_{10} S$  and  $T_c$ . Michaels and Bixler<sup>52</sup> found an even better fit to linearity between the log of the solubility and the Lennard-Jones force constant of the gas:

$$\ln S = 0.022 S/k - 5.07$$

This equation is derived by equating the chemical potential of the gas in equilibrium with the polymer to the chemical potential of the dissolved gas. This

condition is presented in Figure 22. Table II shows that the activation energy for permeation increases with both the molecular diameter and the irradiation dose. Table III shows the same to hold true for the activation energy of diffusion. The increase in the activation energies with molecular diameter is simply due to the fact that larger molecules require larger holes for passage through the polymer. The larger the hole, the more work required to form it. As the number of crosslinks are increased (an increase in irradiation dose), the polymer chains lose their segmental mobility, resulting in an increase in the activation energies for permeation and diffusion.

In summary, irradiation decreases the permeation and diffusion coefficients while the activation energies for the processes are increased. The larger the molecule, the stronger the irradiation effect. This is due to a tightening of the polymer network, which still allows a large number of the smaller molecules to pass (helium) but forms a rigid barrier against the passage of the larger molecules (propane). The permeability of helium is only decreased by 6.4% when going from 0 to 50 Mrad, whereas the large decrease in propane is due to the decreasing ability of the molecules to plasticize the film. Since helium does not plasticize the film, it is little affected by irradiation when compared to propane.

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