Permeation of Gases through Modified Polymer Films. I. Polyethylene–Styrene Graft Copolymers*

R. Y. M. HUANG and P. J. F. KANITZ, *Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada*

Synopsis

The permeabilities of nitrogen, oxygen, and carbon dioxide through polyethylene–styrene graft copolymer films were measured by means of a gas permeability apparatus based on a modification of Barrer's high vacuum technique. Polyethylene–styrene grafts were prepared by mutual γ-ray irradiation of low-density polyethylene films in styrene–methanol solution. Densities and thicknesses of the graft copolymer films were determined. It was observed that the gas permeability constants decreased with increasing grafting to minimum values at 20–30% styrene grafting and increased again above 30% grafting. These results are explained in terms of a decrease in the free volume of the amorphous regions of the polyethylene by a "filling in" effect of the grafted polystyrene chains. Above 30% grafting, disruption of the crystallites may occur resulting in increased gas permeation. Activation energies for gas permeation through polyethylene–styrene graft copolymer films were calculated and found to decrease with increasing per cent styrene grafting. For nitrogen permeation, the activation energy decreased from 11.7 kcal/mole for unirradiated polyethylene to 9.5 kcal/mole for a 50.5% graft. Corresponding values for oxygen and carbon dioxide were 10.2–8.2 kcal/mole for a 48.7% graft and 8.4–6.5 kcal/mole for a 50.5% graft.

INTRODUCTION

The permeation of gases through various types of polymer films has been widely investigated with respect to the rate of the permeation process and the general physical chemistry of the permeant–polymer interactions. However, most of these studies have dealt with homopolymer films. Relatively little is known, for example, about the permeation characteristics of graft and block copolymer films. Graft copolymerization may affect the permeation properties of the original polymer depending on the chemical nature of the grafted polymer, the per cent grafting and the distribution of graft through the backbone polymer matrix.

Stannett and co-workers[1] have studied the permeation of gases through radiation-crosslinked polymers. They reported no significant changes in the permeability of irradiated polyethylene up to a radiation dose of 10 Mrad. Stannett et al.[2] also investigated the permeation of gases through graft copolymers of polyethylene prepared by γ-ray irradiation. They

reported that the gas permeability of polyethylene–styrene graft copolymers decreased with increasing graft concentration. For higher graft concentrations, an increase in gas permeability was observed. More recently, Rogers[3,4] prepared polyethylene membranes with gradients of graft and structural composition from one surface to the other. He found that transport of gases through the graded films proceeded at different rates, depending on the direction of flow relative to the gradient of polymer composition. In the present study, the permeabilities of nitrogen, oxygen, and carbon dioxide through polyethylene–styrene graft copolymers prepared by γ-ray irradiations have been investigated. Attempts have been made to correlate the permeability data with structural changes induced by the graft copolymerization.

EXPERIMENTAL DETAILS

Apparatus

Gas Permeation Apparatus

An apparatus for measuring gas permeation through polymer films was designed and built, based on the high-vacuum technique originally introduced by Barrer.[5] Some modifications as suggested by Huldy[6] were incorporated in the design.

The equipment consisted of four main sections: (*1*) low-vacuum gas delivery system, including pressure and flow measuring devices; (*2*) film holder with temperature control and indicator; (*3*) high-vacuum measuring chamber with pressure-indicating instruments; (*4*) high-vacuum pumping system. The film holder assembly is represented in Figure 1.
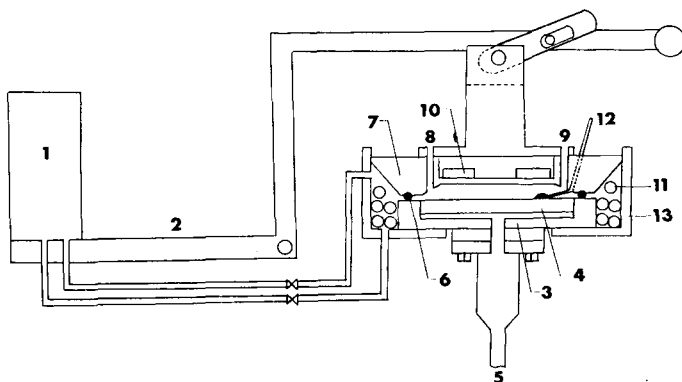

Fig. 1. Cross section of film holder and mercury reservoir: (1) mercury reservoir; (2) support arm; (3) film support plate, 316 stainless steel; (4) bronze filter plate, 40% porosity; (5) metal-to-glass connection to high-vacuum system; (6) neoprene O-ring; (7) film holder cover; (8) gas inlet; (9) gas outlet; (10) auxiliary heater, 120 W; (11) $^1/_8$-in. stainless steel heating coils; (12) Thermistor Surface Probe; (13) acrylic casing.

Low Vacuum Gas Delivery System. Gas was continuously passed over the test film at 100 mm. Hg. gas pressure. Test gas flowed from a regulated cylinder via a needle valve through a rotameter to a 316 stainless steel coil immersed in a constant temperature bath. The gas passed into the top half of the film holder and hence over the film.

Film Holder. The film holder assembly was designed to incorporate the following versatile features: (a) to provide a porous supporting surface for the test film; (b) convenient sealing of exposed areas susceptible to gas leakage; (c) simplified temperature control; (d) rapid film substitution.

The holder consisted of two parts: a 316 stainless steel bottom section with a sintered brass filter attached to the high vacuum measuring chamber and pumping system; a 316 stainless steel lid connected to the test gas supply. The film was supported by a brass filter of 40% porosity and diameter of 9 cm. It was sealed by a rubber O-ring partially set into the metal lid. When both sides of the film were evacuated, atmospheric pressure pressed the two halves of the head firmly together, securing the film into place.

The holder was enclosed in an acrylic casing. The upper half of the casing served as a guide to align the top lid of the holder onto the bottom support plate. The lower part contained a channel encircling the O-ring seal area and five $1/8$-in. diameter 316 stainless steel coils. When the supporting arm of the head was placed in the horizontal position, mercury flowed from a reservoir filling the channel and covering both O-ring seal area and the coils.

Water from a Haake constant temperature bath was continuously circulated through the coils. Mercury in the channel was used as a heat transfer agent to keep the film holder at predetermined temperatures. An auxiliary 120-W heater, situated in the upper half of the holder, was used to change to higher temperature settings rapidly. A surface thermistor on the film under test was used to measure the temperature.

On partially raising the supporting arm, mercury flowed from the channel back to the mercury reservoir. When the vacuum in the system was released and the arm raised further, the top half of the holder lifted from the film and support plate. Subsequent exposure of this area allowed for rapid film substitution.

Measuring Chamber. The vacuum in the measuring chamber was measured either intermittently by a McLeod gauge or continuously by a Varian Millitorr Ionization Gauge. The McLeod gauge was of a pneumatically controlled, self-setting compression type. Measurements in the range of 1 to 5×10^{-6} torr were made with the aid of a cathetometer. The range of the ionization gauge was 1–10^{-5} torr and provided a continuous output of 0–100 mV to a multirange recorder. Both instruments were cold-trapped to prevent oil and mercury contamination from interfering with measurements.

High-Vacuum Pumping System. The high-vacuum pumping system consisted of a coupled rotary oil pump and water cooled mercury diffusion

pump. Vacuums of 5×10^{-6} mm Hg were obtained in the measuring chamber by liquid nitrogen trapping of the mercury diffusion pump. A Pirani gauge located between the measuring chamber and pumps allowed constant observation of the pumping system.

Density Gradient Column

Density measurements were made by means of a density gradient column based on Wiley's design.[7] Isopropanol-water solutions were used to form density gradients over the range of 0.9000 to 1.0000 g/cm³ by the continuous preparation method.[8] This range covered the polyethylene–styrene graft copolymer densities encountered in this study.

Radiation Facility

The graft copolymerization reactions were carried out in a Gammacell 220 Co⁶⁰ irradiation unit. The intensity of the source during the period of use was approximately 0.7 Mrad/hr. The temperature during irradiation was maintained at 36°C by a continuous air flow.

Materials

Polyethylene Film

Low-density polyethylene film with a melt index of 2.0 g/10 min, containing no plasticizer or antiblocking agent, was supplied by the Film Division, Canadian Industries Limited, Toronto, Ontario. Vacuum-dried samples were cut into 13.5-cm circles, numbered, and weighed before use. The film thickness was 2 mil.

Reagents

Compressed nitrogen and oxygen were obtained from the Linde Division of Union Carbide Canada Limited. Compressed carbon dioxide was supplied by Matheson of Canada Limited.

Styrene (Eastman Organic Chemicals, highest purity) was washed with a 10% sodium hydroxide solution to remove the inhibitor. After washing with distilled water, the styrene was dried for 12 hr over anhydrous calcium chloride. The material was then vacuum-distilled.

Procedure

Freshly prepared styrene monomer and methanol were mixed in required proportions and poured into test tubes containing the polyethylene samples. The containers were degassed at room temperature in a vacuum oven and stored for 12 hr before use. The test tubes were placed into the Gammacell 220 Co⁶⁰ unit and subjected to a series of irradiation doses. On removal from the irradiation source, the samples were divided and treated in four different ways: (*1*) immediate removal from styrene–methanol solution and extraction with benzene for 24 hr; (*2*) contact with

the solution for an extra 20 hr and then extraction with benzene for 24 hr; (3) immediate removal and immersion in methanol for 12 hr; (4) contact with styrene–methanol solution for a further 20 hr and then immersion in methanol for 12 hr.

The samples were then dried and weighed to determine the per cent styrene grafting.

$$\text{Per cent grafting} = [(W_2 - W_1)/W_1] \times 100$$

where W_2 and W_1 are the final and initial weights of the film, respectively.

Permeability data were obtained by placing graft copolymer films into the gas permeation apparatus and subjecting them to nitrogen, oxygen and carbon dioxide atmospheres. Runs were carried out over the temperature range of 14–50°C. The pressure of the gas flow on the low vacuum side of the apparatus was maintained at approximately 100 mm Hg.

The gas permeability P has been calculated from the expression

$$P = (\Delta P/\Delta t)[(273Vl)/(760(273 + T) P_1 A)]$$

where $\Delta P/\Delta t$ is the measured pressure rise per unit of time, V and T are the volume and temperature, respectively, of the measuring chamber. P_1 is the pressure of the test gas over the film, A is the area of the film exposed to the test gas, and l is the thickness of the film.

The standard deviation of the polyethylene permeability measurements was 2%, while for the higher polyethylene–styrene grafts the standard deviation was 4%.
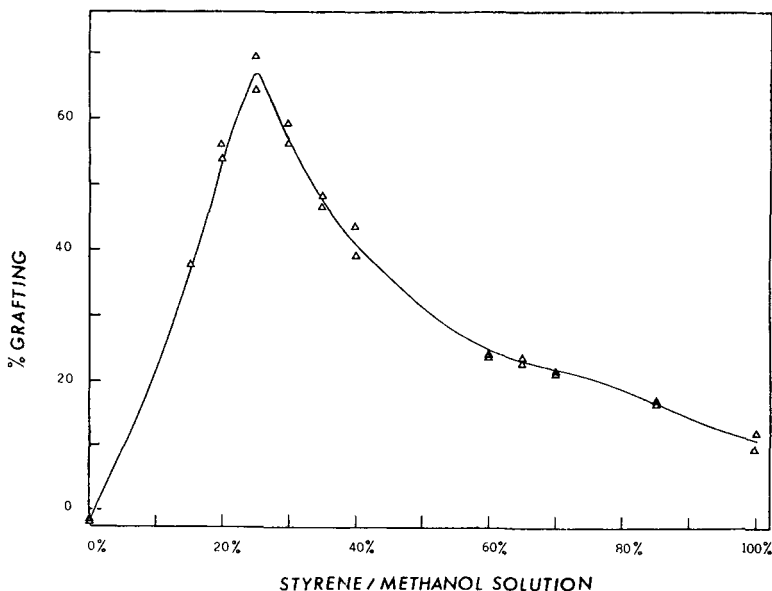

Fig. 2. Effect of styrene–methanol solution on per cent styrene grafting for polyethylene–styrene graft copolymer. Irradiation dose, 1.75 Mrad; post-irradiation sample treatment, immediately soaked in benzene for 24 hr.

All permeability data are reported in units of cc (STP)-cm/cm²-cm Hg -sec.

RESULTS

Polyethylene–Styrene Graft Copolymers

Polyethylene–styrene graft copolymers were prepared by the γ-ray irradiation of low-density polyethylene film in styrene–methanol solution. The effect of varying styrene concentration on the per cent grafting was examined using a fixed irradiation dose of 1.75 Mrad. A maximum in grafting efficiency was observed in the region of 20–30% (by volume) styrene monomer in methanol. On this basis, a 30% solution was selected for further study. The effect of varying the irradiation dose on the per cent grafting was also studied. These results are shown in Figures 2 and 3, respectively.

The effect of post-irradiation sample treatment on graft copolymers was examined by varying the procedure for extracting polystyrene homopoly-
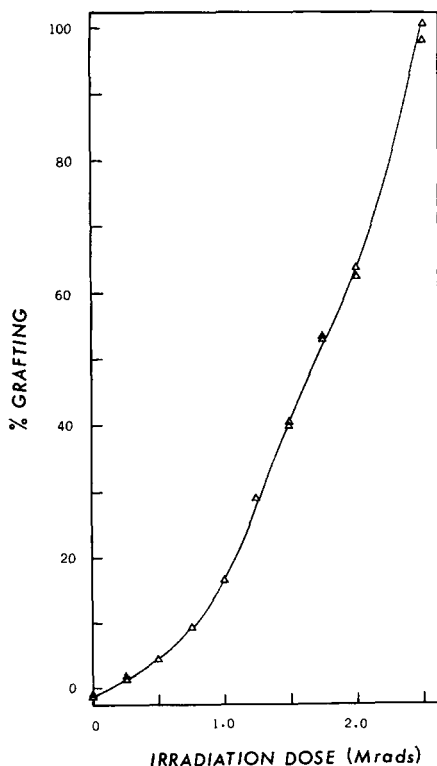

Fig. 3. Effect of irradiation dose on per cent styrene grafting for polyethylene-styrene graft copolymer. Solution composition, 30% (by volume) styrene monomer in methanol; post-irradiation sample treatment, immediately soaked in benzene for 24 hr.
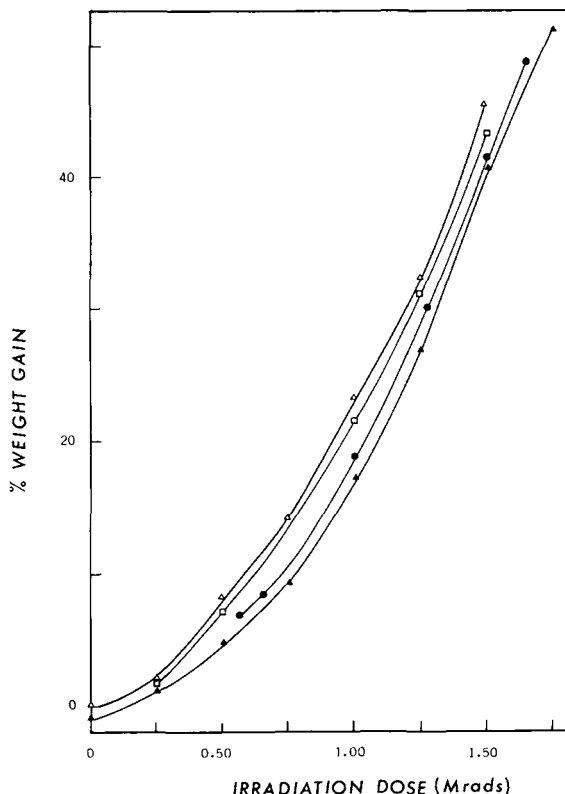
Fig. 4. Effect of post-irradiation sample treatment on the final weight gain of polyethylene–styrene graft copolymers: (▲) immediate benzene extraction for 24 hr; (●) 20 hr contract with styrene–methanol and then benzene extraction for 24 hr; (□) Immediate methanol soaking for 24 hr; (△) 20 hr contact with styrene–methanol followed by methanol soaking for 24 hr. Grafting solution composition, 30% (by volume) styrene monomer in methanol.

mer. When irradiated samples were allowed to remain in contact with styrene–methanol solution, it was found that the final weight after extraction was greater than that of similar samples removed from the solution immediately after irradiation. These results are plotted in Figure 4.

Gas Permeation through Graft Copolymers

The gas permeabilities of polyethylene–styrene graft copolymers to nitrogen, oxygen, and carbon dioxide were obtained for the film temperature range of 14–50°C. Arrhenius-type plots of the data, as shown in Figure 5, indicate a permeability constant temperature dependence of the form, $P = P_0 \exp (- E_p/RT)$. The activation energy of permeation E_p was found to decrease with increasing per cent grafting. The activation energy for nitrogen permeation decreased from 11.7 kcal/mole for unirradiated polyethylene to 9.5 kcal/mole for a 50.5% styrene graft. Similar
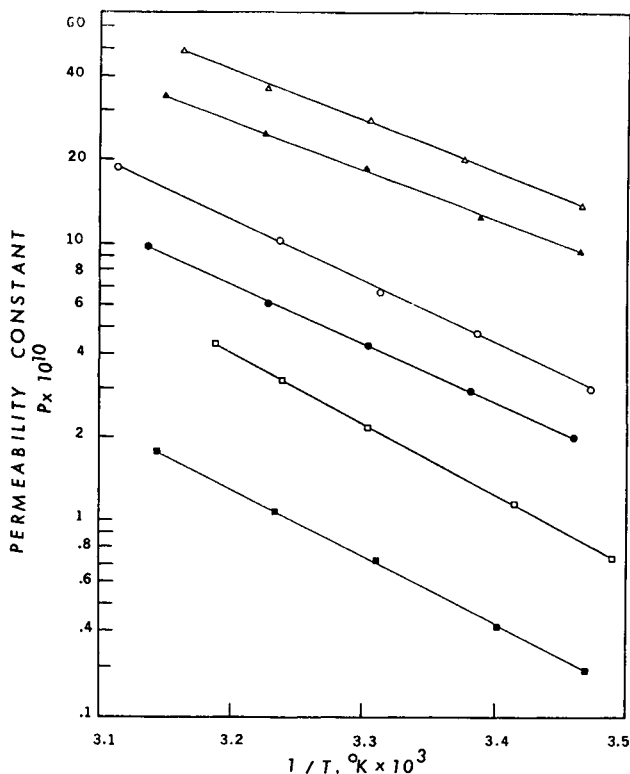
Fig. 5. Effect of temperature on the permeability constant of polyethylene–styrene graft copolymers: ($\triangle$) unirradiated polyethylene film, CO_2 gas; ($\bigcirc$) unirradiated polyethylene film, O_2 gas; ($\square$) unirradiated polyethylene film, N_2 gas; ($\blacktriangle$) polyethylene–styrene graft copolymer film, 16.7% grafting, CO_2 gas; ($\bullet$) polyethylene–styrene graft copolymer film, 16.7% grafting, O_2 gas; ($\blacksquare$) polyethylene–styrene graft copolymer film, 16.7% grafting, N_2 gas. Solution composition, 30% (by volume) styrene monomer in methanol; Post-irradiation sample treatment, soaked in benzene for 24 hr. Units of permeability P = cc (STP)-cm/cm.^{2}-cm Hg-sec.

decreases for oxygen were 10.2 kcal/mole to 8.2 kcal/mole for a 48.7% graft and 8.4 kcal/mole to 6.5 kcal/mole for a 50.5% graft for carbon dioxide permeation. This decrease is shown graphically in Figure 6.

Selected values of permeability constants were plotted against per cent grafting in Figures 7–9. By plotting the data in this manner, a significant trend in gas permeabilities with increasing per cent grafting could be observed. The permeability constants for all three gases tended to have minimum values in the area of 20–30% graft concentration. With higher grafts, the permeability began to increase again. Representative values of permeability constants for the three gases at 30°C are given in Table I.

Density of Graft Copolymers

The densities of the graft copolymers were determined by the density gradient technique. The results are plotted in Figure 10. The densities
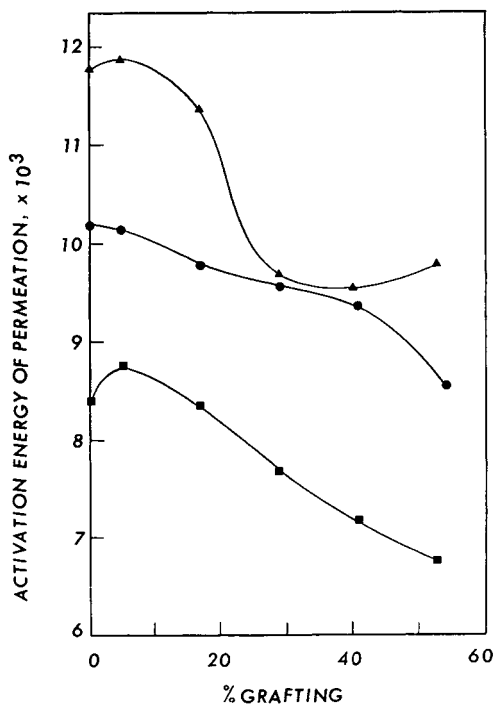
Fig. 6. Effect of per cent grafting on the activation energy (in Kcal/mole) of permeation: (▲) polyethylene–styrene graft copolymer, N_2 gas; (●) polyethylene–styrene graft copolymer, O_2 gas; (■) polyethylene–styrene graft copolymer, CO_2 gas. Grafting solution composition, 30% (by volume) styrene monomer in methanol.

of the copolymers were also used to calculate the thicknesses of the films. The variation of thickness of the film with increasing graft concentration is shown in Figure 11.

DISCUSSION

Polyethylene–Styrene Graft Copolymers

Effect of Solvent Additive

Methanol, a nonsolvent for polystyrene, has been reported to enhance the rate of grafting of styrene onto polyethylene by a form of Trommsdorff effect.[9] From Figure 2, it can be seen that under the conditions employed in this study, the maximum grafting rate occurred at approximately 25% styrene monomer in methanol. These results are similar to those previously reported by Odian et al.[9]

Effect of Irradiation Dose

Free-radical sites induced by γ-ray radiation are formed throughout the polymer film. However, styrene monomer cannot diffuse to any great
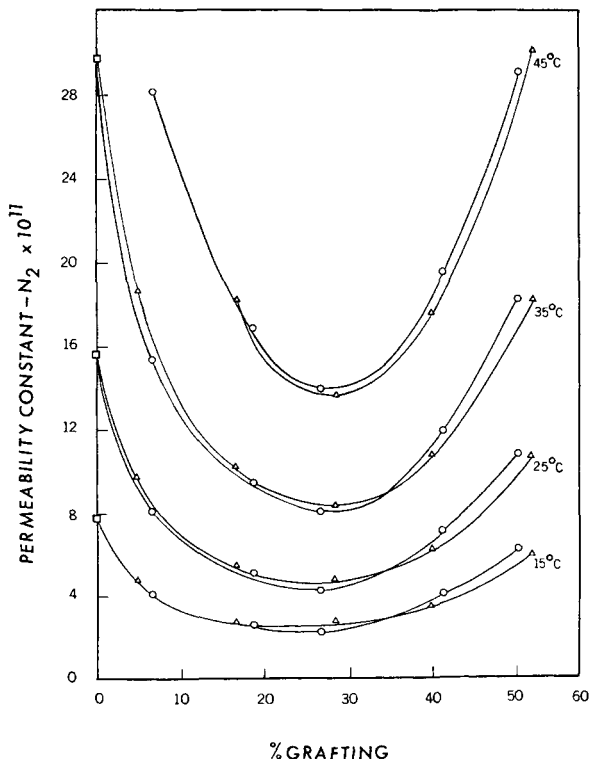
Fig. 7. Effect of styrene grafting on the isothermal nitrogen permeability constant (isotherm at 15, 25, 35, and 45°C): ($\triangle$) benzene-extracted for 24 hr; ($\square$) unirradiated polyethylene film; ($\bigcirc$) allowed to remain in contact with styrene–methanol solution for 20 hr and then benzene-soaked for 24 hr. Units of permeability P = cc (STP)-cm/cm²-cm Hg-sec.

extent into the crystalline regions of the polymer, and it is generally assumed that most of the polystyrene graft occurs in the amorphous regions.[10] Polyethylene–styrene graft copolymers with different per cent styrene grafting were prepared by varying the irradiation dose, as shown in Figure 3. Stannett[1] has found that crosslinking of polyethylene by γ-ray radiation has little effect on the gas permeability below an irradiation dose of approximately 10^7 rad. By the use of a 30% styrene monomer in methanol solution, it was possible to achieve high grafting with relatively low irradiation doses, thus avoiding the effects of any contribution from crosslinking to the permeability. Grafted membranes above 50% styrene graft were brittle and thus unsuitable for permeability measurements.

Post-Irradiation Sample Treatment

It can be seen in Figure 4 that the effect of post-irradiation sample treatment on the final weight of the graft copolymer was quite pronounced. Benzene, a solvent for polystyrene, removed most of the polystyrene homo-
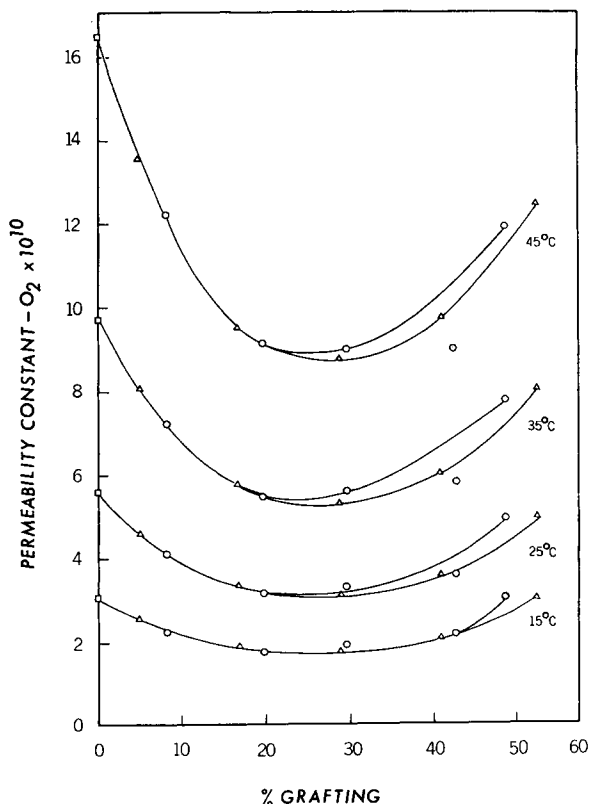
Fig. 8. Effect of styrene grafting on the isothermal oxygen permeability constant (isotherms at 15, 25, 35, and 45°C): (Δ) polyethylene–styrene graft copolymer film, benzene-extracted for 24 hr; (□) unirradiated polyethylene film; (O) polyethylene–styrene graft copolymer film allowed to remain in contact with styrene–methanol solution for 20 hr and then benzene-soaked for 24 hr. Units of permeability P = cc (STP)-cm/cm²-cm Hg-sec.

polymer entrapped in the graft copolymer. Methanol, a nonsolvent for the homopolymer, did not contribute to any weight changes, with the result that the final graft copolymer also contained polystyrene homopolymer. It was of interest to note that methanol washed films were brittle while benzene extracted films remained flexible. However, when methanol washed films were immersed briefly in benzene and dried, they also became flexible. This appeared to indicate that a molecular rearrangement or realignment of the polystyrene graft or polystyrene homopolymer molecules had taken place.

Samples subjected to post-irradiation contact with styrene–methanol solution had higher final weights. For methanol-washed samples, part of this increase could be attributed to the presence of polystyrene homopolymer which was not extracted. However, even for benzene-extracted films there was still a pronounced difference in per cent grafting. This post-
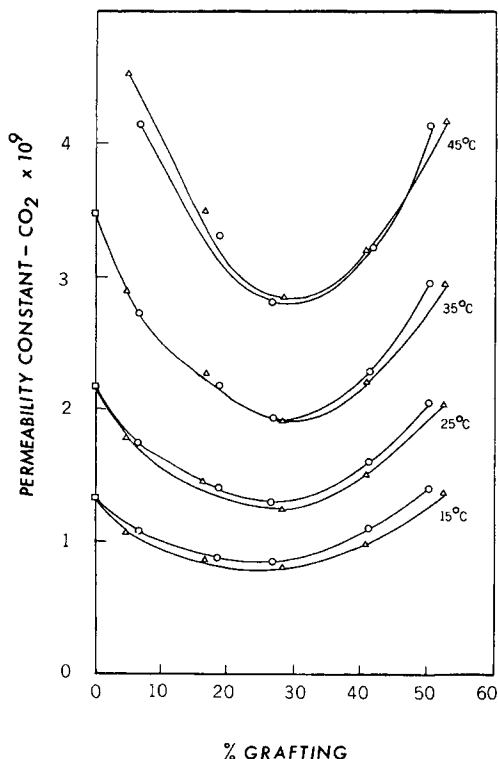
Fig. 9. Effect of styrene grafting on the isothermal carbon dioxide permeability constant (isotherms at 15, 25, 35, and 45°C): (△) polyethylene–styrene graft copolymer film, benzene-extracted for 24 hr; (□) unirradiated polyethylene film; (○) polyethylene–styrene graft copolymer film allowed to remain in contact with styrene–methanol solution for 20 hr and then benzene-soaked for 24 hr. Units of permeability P = cc (STP)-cm./cm²-cm Hg-sec.

irradiation effect is probably the result of penetration of styrene monomer into semicrystalline regions of the polymer into which diffusion occurs very slowly. Styrene could then react with trapped free radicals in these regions[11] to initiate new polystyrene grafted chains.

Gas Permeability of Polyethylene–Styrene Graft Copolymers

Activation Energy of Permeation

The temperature dependence of the permeability constant for the three gases studied was found to obey an Arrhenius-type relationship of the form, $P = P_0 \exp \{-E_p/RT\}$. The linear dependence of the logarithm of the permeability constant on the reciprocal of the absolute temperature is shown in Figure 5. It was found that the activation energy of permeation E_p decreased rapidly with increasing per cent grafting. Its value lay in between the respective values of activation energies for polyethylene and
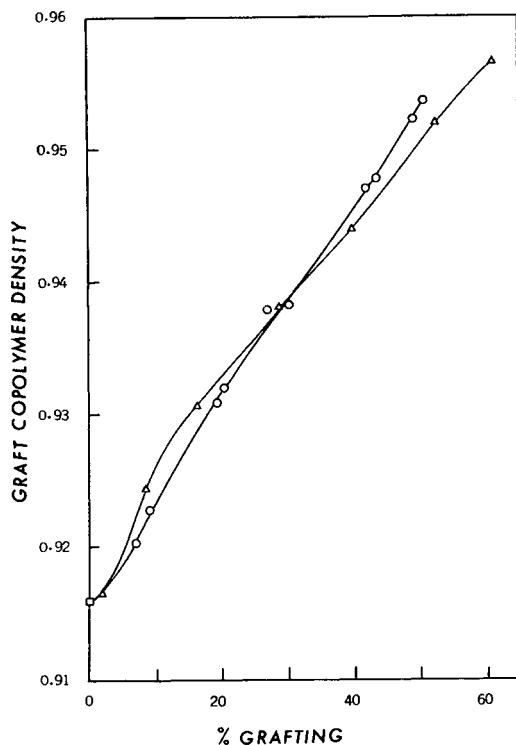
Fig. 10. Effect of post-irradiation sample treatment on the density of polyethylene–styrene graft copolymers: (□) unirradiated polyethylene film; (O) benzene-extracted for 24 hr; (△) allowed to remain in contact with styrene–methanol for 20 hr and then benzene-extracted for 24 hr. Grafting solution composition, 30% (by volume) styrene monomer in methanol.

polystyrene for all three gases, nitrogen, oxygen, and carbon dioxide. This relationship is shown in Figure 6. The permeation of a gas through a polymer depends on the solution and diffusion processes of the gas within the polymer. The activation energy of permeation is thus dependent on the heat of solution of the gas in the polymer and the activation energy for the diffusion process. Since these were not measured independently, their individual contributions to the permeation process cannot be separated.

Effect of Increasing Per Cent Styrene Grafting

The permeability of the graft copolymer to the three gases studied decreased with increasing per cent grafting until minimum values were reached in the region of 20–30% graft. After this region, the gas permeability began to increase again. These trends are similar to those reported by Stannett and co-workers,[2] except that the present work clearly indicates the presence of a minimum in the permeation constant versus grafting plot for all three gases at various temperatures. The change in the permeability constants suggests that structural changes which strongly affect the permea-
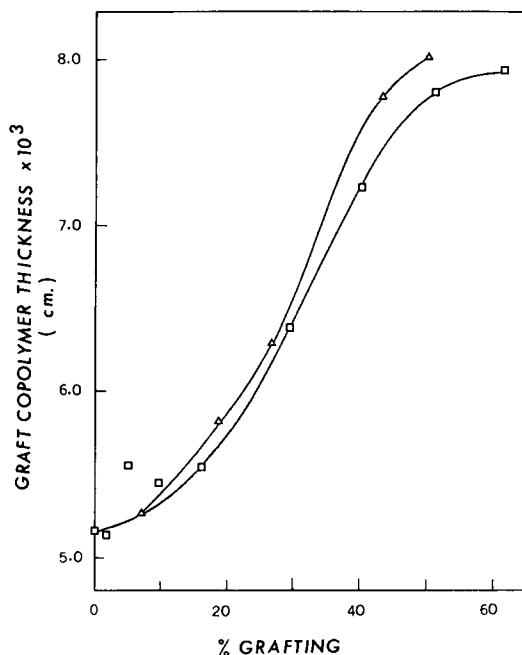
Fig. 11. Effect of post-irradiation sample treatment on the thickness of polyethylene–styrene graft copolymer films: (□) benzene-extracted for 24 hr; (△) allowed to remain in contact with styrene–methanol solution for 20 hr followed by benzene extraction for 24 hr. Solution composition, 30% (by volume) styrene monomer in methanol.

tion rates occur in the region of 20–30% grafting. Since the permeability constant is a composite of the solubility and diffusion terms, according to the equation, $P = DS$, it is not strictly correct to interpret the permeation rates solely on the basis of structural changes in the grafted polyethylene film. Due to the presence of grafted polystyrene, the solubilities of nitrogen, oxygen, and carbon dioxide in polyethylene–styrene grafts should be somewhat higher than in polyethylene depending on the amount of grafting.

The initial decrease in the permeability constant with per cent grafting can be explained in terms of a decrease in the free volume and segmental mobility of the amorphous regions. The grafted polystyrene renders the polyethylene chain segments less mobile and increases the cohesive forces opposing hole formation, resulting in a decrease in diffusion and permeation rates. The upswing in the permeation constant above 20–30% grafting indicates the appearance of other structural changes which overcome the factors contributing to the initial decrease in permeability. The increase in permeation is probably caused by changes in the amorphous–crystalline ratios. Above 20–30% grafting, the grafted polystyrene chains penetrate and disrupt some of the crystalline regions of the polyethylene and open up new regions which are available for gas permeation.

The internal structural changes which are induced by graft copolymeriza-

TABLE I
Effect of Per Cent Grafting on Permeability Constants at 30°C

Gas	Grafting, %	Permeability constant $P \times 10^{10}$, (cc (STP)-cm)/(cm²-cm Hg-sec)
Nitrogen	0.0	2.16
	27.0	0.59
	50.5	1.41
Oxygen	0.0	7.41
	20.2	4.18
	48.7	6.25
Carbon dioxide	0.0	27.34
	27.0	15.86
	50.5	24.72

tion are reflected in the values of the density and thickness of the poly-ethylene–styrene grafts. As can be seen in Figures 10 and 11, there is a rapid increase initially in density with grafting, with only a small increase in thickness. Above 20% grafting, the density does not increase as rapidly, but the change in thickness is more pronounced. These trends indicate a close relationship between structural changes in the grafted polyethylene and permeation rates. However, independent measurements of the solubility and diffusion constants will be required in order to provide a quantitative interpretation of the permeation process.

References

1. V. Stannett, M. Szwarc, R. L. Bhargava, J. A. Meyer, A. W. Meyers, and C. E. Rogers, *Tappi Monograph Ser. No. 23*, 19 (1962).

2. A. W. Meyers, C. E. Rogers, V. Stannett, and M. Szwarc, *J. Appl. Polym. Sci.*, **4**, 159 (1960).

3. C. E. Rogers, in *Transport Phenomena in Polymeric Films* (*J. Polymer Sci. C*, **10**), C. A. Kumins, Ed., Interscience, New York, 1965, p. 93.

4. S. Sternberg and C. E. Rogers, *J. Appl. Polym. Sci.*, **12**, 1017 (1968).

5. R. M. Barrer, *Diffusion in and through Solids*, *Univ.* Press, Cambridge, 1951.

6. H. J. Huldy, *J. Polym. Sci.*, **8**, 2883 (1964).

7. R. E. Wiley, *Plastics Technol.*, **8**, 31 (1962).

8. L. H. Tung and W. C. Taylor, *J. Polym. Sci.*, **21**, 144 (1956).

9. G. G. Odian, M. Sobel, A. Rossi, and R. Klein, *J. Polymer Sci.*, **55**, 663 (1961).

10. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Interscience, New York, 1962.

11. D. S. Ballantine, A. Glines, G. Adler, and D. J. Metz, *J. Polym. Sci.*, **34**, 419 (1959).