

The Permeation of Gases through Modified Polymer Films. IV. Gas Permeability and Separation Characteristics of Graft Copolymers of Polyethylene and Teflon FEP Films

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Synopsis

The effects of grafting styrene and acrylonitrile onto polyethylene and Teflon FEP films on their gas permeation and separation properties were investigated. The time-lag method was used to determine the permeability, diffusion, and solubility coefficients of nitrogen and methane gases in the grafted films. The separation factors of nitrogen-methane gas mixtures were measured by gas chromatography. Structural and morphologic changes in the modified films were examined by density, differential scanning calorimetry, and infrared measurements. Attempts were made to relate these changes to the gas permeation and separation characteristics of the films. Modification by graft copolymerization resulted in slightly improved separation factors; however, the permeability and diffusion coefficients decreased. The experimental permeability and diffusion coefficients for gas mixtures were in good agreement with those of the pure components and could be predicted by single gas permeability and diffusion coefficients.

INTRODUCTION

The present series of investigations is concerned with the transport and separation properties of polymer films modified by crosslinking and graft copolymerization. In previous papers of this series, the effects of gamma-ray irradiation on the transport properties of polyethylene¹ and Teflon FEP copolymer,² as well as a preliminary study of the effect of graft copolymerization on gas permeation through polyethylene film³ have been reported. Various modification methods such as alteration of polymer morphology, mechanical orientation, and graft copolymerizing polymer side chains onto the main backbone of the original polymer can in principle be used to improve the permeability and separation characteristics of polymer films. Of the modification procedures, the graft copolymerization method is unique in that both the diffusion and solubility properties of the original polymer can be altered.

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A large number of graft copolymers produced by a variety of methods have been developed in the past decade.^{4,5} Although many of their physical and chemical properties have been examined, relatively little work has been reported on the gas permeation and separation properties of graft copolymers. In early work, the effect of grafting styrene, acrylonitrile, and vinylpyridine onto polyethylene on gas permeation was investigated by Meyers and co-workers.⁶ Steinberg and Rogers⁷ investigated the permeation of methanol in polyethylene membranes containing linear gradients of grafted poly(vinyl acetate). Fels and Huang^{8,9} recently investigated the transport of organic liquid mixtures through polyethylene grafted with styrene.

The purpose of the present work is to investigate the effect of graft-copolymerizing styrene and acrylonitrile onto polyethylene and Teflon FEP films on the permeation, diffusion, and solubility of methane and nitrogen. The separation of a methane-nitrogen gas mixture using the graft copolymer films was also studied and the results are discussed in terms of the structural changes induced in the films by graft copolymerization.

EXPERIMENTAL DETAILS

Materials

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. The nominal film thickness was 10 mils. Teflon FEP copolymer film of 5-mil thickness was supplied by E. I. du Pont de Nemours and Company. Teflon FEP fluorocarbon film is made from a fluorinated ethylene-propylene copolymer.

Styrene and acrylonitrile monomer was freed of inhibitor by washing with sodium hydroxide solution. After rinsing with distilled water, the monomers were dried over anhydrous calcium chloride and vacuum distilled before being used.

Compressed nitrogen gas was obtained from the Linde Division of Union Carbide. Methane and helium were obtained from the Matheson Company. The gases were used as obtained without further purification.

Apparatus

The gamma-ray irradiation experiments were carried out in a Gamma-Cell 220 Co 60 irradiation unit at the University of Waterloo. The intensity of the source during the period of use was approximately 0.8 Mrads/hr. The temperature during irradiation was maintained at 35°C.

The permeability and diffusion coefficients were determined by the time-lag method while gas separation data were obtained by a chromatographic technique. The basic permeation apparatus has been described in the previous papers in this series.^{2,3} Modifications which incorporate the use of a Varian Aerograph 1520-C gas chromatograph for gas mixture analysis have also been described elsewhere.²

Density and thickness were obtained by standard procedures. A Perkin-Elmer DSC 1B differential scanning calorimeter was used for the thermal and crystallinity measurements. Infrared measurements were performed on a Perkin-Elmer Model 337 infrared spectrophotometer.

Preparation of Polyethylene and Teflon FEP Graft Copolymers

Dried polyethylene samples were weighed and placed into flat-bottom glass vessels. Freshly distilled styrene monomer and methanol were mixed in the proportion of 30% styrene and 70% methanol (by volume) and poured into the vessels. This ratio of styrene to methanol was found previously to give the maximum yield of grafted material for a given radiation dose.³ For acrylonitrile grafting, an 80% acrylonitrile, 20% benzene solution (by volume) and a saturated aqueous solution of acrylonitrile were found to give satisfactory grafting results.

The vessels were degassed and stored for 12 hr before irradiation in the Gamma-Cell 220 unit. After irradiation, the grafted films were solvent extracted in order to remove homopolymer. The samples were dried and weighed to determine the per cent grafting by the following equation:

$$\% \text{ grafting} = \left[\frac{W_2 - W_1}{W_1} \right] \times 100$$

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

Grafted Teflon FEP samples were prepared by both the mutual and preirradiation techniques. In the mutual irradiation technique, bulk monomer or monomer solution was poured into the glass vessels containing samples of known weight. The vessels were degassed and sealed prior to irradiation. After irradiation, the samples were stored at 80°C for 48 hr. The films were then washed with a solvent to remove any homopolymer, dried, and weighed to determine the amount of grafting. For preparing acrylonitrile-Teflon grafts, acrylonitrile-benzene and aqueous solutions of acrylonitrile were used, while bulk styrene and styrene-benzene solutions were used for the styrene-Teflon graft copolymerization.

A variation of this method was also used to carry out the graft copolymerization at low temperatures. Bulk styrene or acrylonitrile monomer was added to vessels containing the films. After degassing, the vessels were irradiated while immersed in a Dewar flask containing liquid nitrogen. The samples prepared by this special technique were then heated in an oven at 80°C for 72 hr.

In the preirradiation method, Teflon FEP samples were preirradiated in air or vacuum and placed into glass vessels containing styrene or acrylonitrile monomer. The vessels were evacuated, sealed, and heated at 80°C for 48 hr. After the heat treatment, grafted samples were solvent extracted, dried, and weighed.

DISCUSSION

Graft Copolymers

Graft Copolymers of Polyethylene

Samples with up to 50% grafting for polystyrene and 40% grafting for polyacrylonitrile were found suitable for permeation and characterization studies. It was found that prolonged or rigorous solvent extraction procedures often damaged or weakened the grafted films. As a result, the emphasis was placed on producing suitable films rather than trying to eliminate the last traces of removable homopolymer. Grafted films were carefully solvent extracted to avoid damage and then subjected to permeation and characterization measurements. After these measurements were completed, the films were rigorously extracted in order to determine the quantity of extractable homopolymer remaining. In most cases, the additional homopolymer removed accounted for only 1% to 4% of the total grafted weight.

The properties of the grafted polyethylene films are listed in Table I. As can be seen, the densities and thicknesses of both styrene and acrylonitrile-grafted polyethylene films increased with irradiation dose. The weight per cent crystallinity was determined by the calorimetric method¹⁰ using differential scanning calorimetry. Thermogram traces of the grafted polyethylene showed changes in both trace area and shape of the melting curve. As per cent grafting increased, the weight per cent crystallinity

TABLE I
Properties of Grafted Polyethylene Films

Sample code number ^a	Irradiation dose, Mrads	Graft, %	Thick-ness, cm	Density, g/cm ³	Crystallinity, wt-%	Solubility coefficient, cc(STP)/cc cm Hg)	
						N ₂	CH ₄
Styrene-Polyethylene Graft							
1	0	0	0.0281	0.9157	54	1.90	14.5
2	0.75	10.6	0.0294	0.9273	51	3.0	14.4
3	1.25	29.5	0.0312	0.9558	31	3.0	16.7
4	1.75	48.2	0.0351	0.9695	18	—	—
Acrylonitrile-Polyethylene Graft							
5	0.50	10.5	0.0289	0.9362	47	1.7	13.5
6	0.75	29.8	0.0304	0.9654	36	2.1	16.9
7	1.00	58.7	0.0335	0.9876	25	—	—
8	0.75	14.9	0.0292	0.9475	41	2.3	15.3
9	1.00	34.2	0.0307	0.9711	28	2.9	16.1

^a All films were grafted by the mutual irradiation method. Code numbers 1 to 4 were samples grafted in 30/70 styrene-methanol grafting solution; code numbers 5 to 7 were samples grafted in 80/20 acrylonitrile-benzene solution; code numbers 8 and 9 were samples grafted in acrylonitrile-water solution.

decreased for both styrene and acrylonitrile grafted films although this effect was more pronounced for the styrene-grafted polymer.

The grafting reaction is presumed to occur mainly in the amorphous regions of the polymer, at the folds of the lamellae or defects. The grafted side chains can grow with minimum disruptive influence on the crystalline regions, provided sufficient free volume is available. Influx of additional monomer or monomer-solvent into these regions can lead to swelling of the grafted side chains or homopolymer. The swelling process would exert large forces on the lamellae or in the defect regions, tending to force these areas apart and also lead to decreased crystallinity. Polyacrylonitrile, however, is a tightly coiled, highly compact molecule which is insoluble in its own monomer. The monomer only slightly swells polyethylene at moderate temperatures. The swelling forces on the grafted polyacrylonitrile side chains or homopolymer would be much less than those of polystyrene, resulting in less disruption of the crystalline regions at the same per cent grafting.

Graft Copolymers of Teflon FEP Copolymer Films

By varying the conditions of mutual irradiation, it is possible to prepare grafted Teflon FEP copolymer films ranging in graft concentration from surface grafts to films which are "homogeneously" grafted. The pre-irradiation technique can also be employed to prepare such films. Since Teflon FEP film is inert to most chemicals and does not swell appreciably in any common organic solvent, it is plausible to assume that the initial grafting occurs in the surface region of the film. The monomer then swells

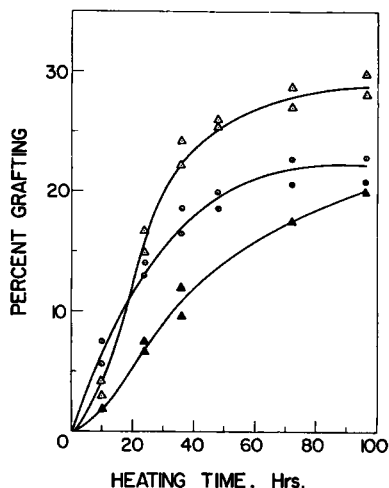


Fig. 1. Styrene and acrylonitrile grafting onto preirradiated Teflon FEP copolymer films: (O) styrene grafting onto Teflon FEP copolymer film, air-irradiated, 5 Mrads; (Δ) styrene grafting onto Teflon FEP copolymer film, vacuum-irradiated, 10 Mrads; (▲) acrylonitrile grafting onto Teflon FEP copolymer film, vacuum-irradiated, 10 Mrads. Temperature of heating period, 80°C.

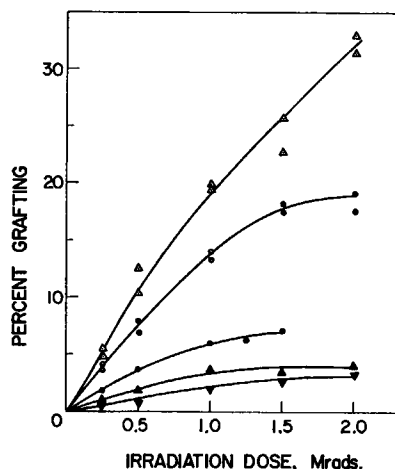


Fig. 2. Styrene and acrylonitrile grafting onto Teflon FEP copolymer films by mutual irradiation of copolymer and monomer-solvent solution: (O) styrene grafting onto Teflon FEP copolymer film, special mutual irradiation technique, styrene monomer; (●) styrene grafting onto Teflon FEP copolymer film, mutual irradiation plus heat treatment, 50% styrene monomer in benzene solution; (Δ) acrylonitrile grafting onto Teflon FEP copolymer film, special mutual irradiation technique, acrylonitrile monomer; (▲) acrylonitrile grafting onto Teflon FEP copolymer film, mutual irradiation plus heat treatment, 80% acrylonitrile monomer in benzene solution; (▼) acrylonitrile grafting onto Teflon FEP copolymer film, mutual irradiation plus heat treatment, saturated aqueous acrylonitrile solution. Heat treatment, 80°C for 50–72 hr.

the grafted region and slowly diffuses into ungrafted polymer regions. Since styrene monomer is a good swelling agent for its homopolymer and grafted side chains, it should graft throughout the copolymer matrix. On the other hand, acrylonitrile is a poor swelling agent and should take longer to graft under the same conditions.

In this work, grafted samples were subjected to heating periods at temperatures above the glass I transition (80°C) to ensure adequate diffusion of monomer. Styrene- and acrylonitrile-grafted films containing up to 20% graft were found suitable for characterization and permeation studies. The effects of varying the conditions of grafting on the per cent grafting onto Teflon FEP are shown in Figures 1 and 2.

As shown in Table III, the crystallinity of the grafted copolymers as measured by differential scanning calorimetry decreased with per cent grafting above 5%–10% graft concentration. The decrease was not as rapid for grafted polyacrylonitrile as for grafted polystyrene Teflon FEP films. The shape of the thermograms tended to flatten out to some extent, indicating a change in the size distribution of the crystallites. Grafted polyacrylonitrile side chains and homopolymer do not swell to any great extent in acrylonitrile monomer. At high graft concentration, however, the grafted polyacrylonitrile side chains can exert sufficient force to disrupt the crystalline regions of the copolymer. The decrease in crystallinity

occurs more readily at lower per cent grafting in Teflon FEP copolymer than in polyethylene due to the higher density and tightly packed structure of Teflon FEP.

Transport Properties of Grafted Polymer Films

The use of the time-lag technique for determining the diffusion coefficient in modified films is not strictly applicable if a large gradient of chemical composition or other heterogeneity exists in the polymer. In this study, every effort was made to produce homogeneously grafted copolymer films. All the grafted films except those which were prepared by surface grafting techniques were considered to be homogeneous on the macro scale. With these restrictions in mind, the time-lag method was used to obtain the diffusion coefficient and the solubility coefficient for grafted polymer films.

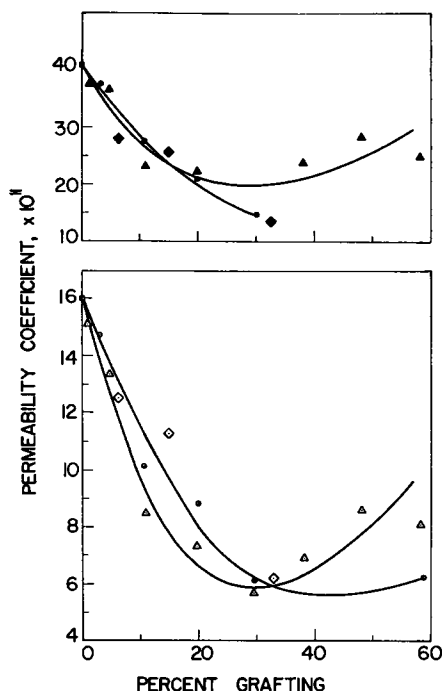


Fig. 3. Permeability coefficients of nitrogen and methane gases in graft copolymers of polyethylene at 30°C: (Δ) nitrogen permeability coefficient for polystyrene-grafted polyethylene film, mutual irradiation, 30% styrene in methanol; (\circ) nitrogen permeability coefficient for polyacrylonitrile-grafted polyethylene film, mutual irradiation, 80% acrylonitrile in benzene; (\diamond) nitrogen permeability coefficient for polyacrylonitrile-grafted polyethylene film, mutual irradiation, saturated aqueous acrylonitrile solution; (\blacktriangle) methane permeability coefficient for polystyrene-grafted polyethylene film, mutual irradiation, 30% styrene in methanol; (\bullet) methane permeability coefficient for polyacrylonitrile-grafted polyethylene film, mutual irradiation, 80% acrylonitrile in benzene; (\blacklozenge) methane permeability coefficient for polyacrylonitrile-grafted polyethylene film, mutual irradiation, saturated aqueous acrylonitrile solution. Units of permeability, cc(STP) cm/(cm Hg sec cm²).

Permeation, Diffusion, and Solubility Coefficients of Grafted Polyethylene Films

The permeation behavior of nitrogen and methane is shown in Figure 3. The permeability coefficient decreased with increasing graft concentration for both polystyrene- and polyacrylonitrile-grafted polyethylene films. Similar trends have been observed in earlier work.^{3,5} Polystyrene-grafted films showed a minimum permeability at 20–30% grafting. This has been attributed to a "filling in" effect of the amorphous regions by small amounts of grafting which reduces the available free volume for diffusion. Above 20%–30% grafting, disruption of crystallite regions occurred followed by increasing permeation. The polyacrylonitrile-grafted polyethylene films did not show this minimum in the grafting range studies, although a minimum may exist at higher graft concentration.

Figure 4 shows the diffusion coefficients for both polystyrene- and polyacrylonitrile-grafted polyethylene films. As can be seen, the diffusion coefficients decreased with increasing per cent grafting. A minimum in the

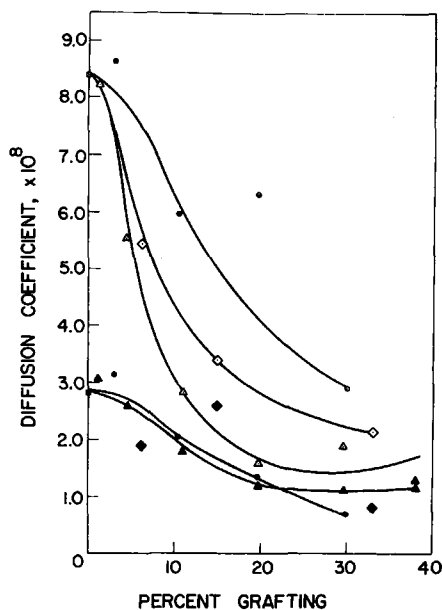


Fig. 4. Diffusion coefficients of nitrogen and methane gases in graft copolymers of polyethylene at 30°C: (Δ) nitrogen diffusion coefficient for polystyrene-grafted polyethylene film, mutual irradiation, 30% styrene in methanol; (○) nitrogen diffusion coefficient for polyacrylonitrile-grafted polyethylene film, mutual irradiation, 80% acrylonitrile in benzene; (◇) nitrogen diffusion coefficient for polyacrylonitrile-grafted polyethylene film, mutual irradiation, saturated aqueous acrylonitrile solution; (▲) methane diffusion coefficient for polystyrene-grafted polyethylene film, mutual irradiation, 30% styrene methanol; (●) methane diffusion coefficient for polyacrylonitrile-grafted polyethylene film, mutual irradiation, 80% acrylonitrile in benzene; (◆) methane diffusion coefficient for polyacrylonitrile-grafted polyethylene film, mutual irradiation, saturated aqueous acrylonitrile solution. Units of diffusion coefficient, cm^2/sec .

TABLE II
Temperature Dependence Parameters for Solution and Diffusion in Grafted Films

Sample code number ^a	Graft, %	P_0 , cc(STP) cm/(cm ² cm Hg sec)		E_p , kcal/mole		D_0 , cm ² /sec		E_D , kcal/mole		ΔH , kcal/mole	
		N ₂ × 10 ⁻⁴	CH ₄ × 10 ⁻⁴	N ₂	CH ₄	N ₂	CH ₄	N ₂	CH ₄	N ₂	CH ₄
Styrene-Grafted Polyethylene											
1	0	560	620	11.8	11.3	3.9	3.6	10.6	11.2	1.2	0.1
2	11.1	150	410	11.4	11.4	1.9	1.7	10.5	11.0	0.9	0.4
3	29.5	22	140	10.5	10.9	0.06	0.2	9.0	10.2	1.5	0.7
4	48.2	9	13	9.7	9.2	—	—	—	—	—	—
5	10.5	410	490	11.9	11.4	2.0	1.9	10.4	11.0	1.5	4.0
6	29.8	130	600	11.5	11.9	1.9	3.5	10.8	11.9	0.7	0.0
7	58.7	50	—	10.9	—	—	—	—	—	—	—
8	14.9	330	460	11.7	11.9	1.9	1.7	10.7	10.8	1.0	0.6
9	34.2	50	60	—	—	—	—	—	—	—	—
Styrene-Teflon FEP Grafts											
10	0	4.2	3.3	8.5	8.8	1.9	3.2	10.0	10.8	-1.5	-2.0
11	14.0	1.4	0.7	8.2	8.3	0.6	3.0	9.8	11.3	-1.6	-3.0
12	18.5	0.8	0.9	7.9	8.5	0.3	0.4	9.3	10.3	-1.4	-1.8
13	15.0	3.8	3.6	8.9	9.4	2.4	3.8	10.7	11.7	-1.8	-2.3
14	17.5	1.8	2.3	8.5	9.2	2.7	6.9	10.8	11.9	-2.3	-2.7
Acrylonitrile-Teflon FEP Grafts											
15	5.5	1.3	2.3	8.2	9.0	2.2	2.5	10.2	10.9	-2.0	-1.9
16	19.9	5.5	1.5	9.6	9.4	2.1	1.9	10.7	11.5	-1.1	-2.1
17	9.5	3.1	1.1	8.8	8.7	—	—	—	—	—	—
18	12.0	4.1	3.3	9.2	9.6	2.3	3.3	10.5	11.4	-1.7	-2.7

^a For details of grafting method see Tables I and III.

diffusion coefficient for polystyrene-grafted film was observed at 20%–30% grafting, similar to the trend for the permeability coefficient. No minimum was found for the polyacrylonitrile-grafted polyethylene diffusion coefficients. Since diffusion is a kinetic process, the grafted side chains interfere with the gas transport by reducing the volume available for the diffusion process. Beyond a certain grafting level, the increased presence of side chains such as polystyrene is probably sufficient to disrupt the lattice spacings and the lamellae. This creates new areas for diffusion and results in the upswing in the diffusion coefficient.

As shown in Table I, there was an increase in the solubility coefficient with increasing graft concentration for both the polystyrene- and polyacrylonitrile-grafted polyethylene. This increase can be attributed to increased sorption in the grafted side chains and/or in areas influenced by crystallite disruption. No significant differences were found in the permeation and diffusion coefficients of grafted films prepared from acrylonitrile-benzene and aqueous acrylonitrile grafting solutions.

Arrhenius plots of nitrogen and methane permeation, diffusion, and solubility coefficients gave linear relationships over the temperature ranges investigated. Activation energies, heats of solution, and preexponential factors for Arrhenius-type equations are presented in Table II. It can be seen that the activation energy of diffusion for polystyrene-grafted polyethylene films decreased with increasing graft concentration while that of polyacrylonitrile-grafted polyethylene film remained fairly constant.

Permeation, Diffusion, and Solubility Coefficients of Grafted Teflon FEP Films

The permeability, diffusion, and solubility coefficients of polystyrene- and polyacrylonitrile-grafted Teflon FEP films were measured in the same way as the grafted polyethylene films. The grafted films were solvent extracted more rigorously than grafted polyethylene samples, since it was found that the extraction treatment did not damage the films to any measurable extent. The permeability coefficients for nitrogen and methane gas in polystyrene- and polyacrylonitrile-grafted Teflon FEP films are shown in Figures 5 and 6, respectively. It can be seen that permeability decreased with increasing graft concentration. The decrease was more rapid at low graft concentrations for the grafted Teflon than for polyethylene films grafted at corresponding levels, indicating that the effect of the grafting reaction on film structure and morphology was more pronounced in Teflon. This can be attributed to the higher density of the Teflon film and the lower free volume which is available for grafting.

There was a difference between the permeabilities of styrene-grafted films prepared by the preirradiation in air and those films prepared by the special mutual irradiation and preirradiation in vacuo techniques. In general, for the same graft concentration, the permeabilities of the preirradiation films were higher than those prepared by the other two methods. The major difference between air- and vacuum-irradiated Teflon is that of oxidation. In air-irradiated film, this leads to permanent chain scission and decrease

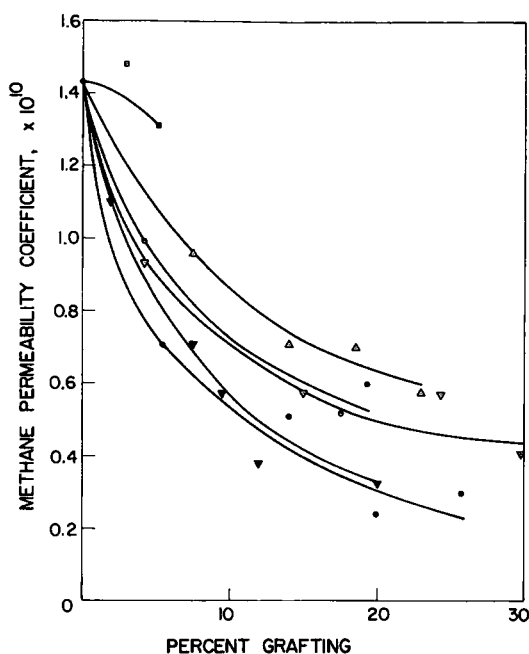


Fig. 5. Nitrogen permeability coefficient in grafted Teflon FEP copolymer films at 30°C: (Δ) polystyrene graft, preirradiation in air; (∇) polystyrene graft, preirradiation in vacuo; (\circ) polystyrene graft, special mutual irradiation plus heat treatment; (\square) polystyrene graft, mutual irradiation plus heat treatment; (\bullet) polyacrylonitrile graft, special mutual irradiation plus heat treatment; (\blacktriangledown) polyacrylonitrile graft, preirradiation in vacuo. Units of permeability coefficient, cc(STP) cm/(cm² cm Hg sec).

in molecular weight. Vacuum-irradiated samples can "heal" by branching and crosslinking reactions. The special mutual irradiation technique, in which the monomer is frozen during irradiation, is believed to give the same type of grafted copolymer as the preirradiation in vacuo technique. No decrease in permeability was observed for the grafts prepared by mutual irradiation. This is due to the fact that grafting was probably limited to the surface regions, and, as a result, had little effect on the permeation properties.

The polyacrylonitrile-grafted films also decreased in permeability with increasing graft concentration and to a greater extent than polystyrene-grafted films. As in the case of polystyrene-grafted film, there was no significant difference between the films prepared by the special mutual irradiation or preirradiation in vacuo techniques. There was a rapid decrease in the permeability coefficients at low graft concentrations. However, above these low grafting levels, the permeability coefficients were not as strongly affected by additional increases in the graft concentration. A minimum in the permeability coefficient similar to that found in polystyrene-grafted polyethylene film was not observed at the graft concentrations examined in this study. The differential scanning calorimetry results

TABLE III
Diffusion and Solubility Coefficients of Nitrogen and
Methane Gases in Grafted Teflon FEP Films

Sample code number	Grafting method ^a	Graft, %	Crystallinity, %	<i>D</i> , cm ² /sec		<i>S</i> , cc(STP)/ (cc cm Hg)	
				N ₂ ×10 ⁻⁷	CH ₄ ×10 ⁻⁴	N ₂ ×10 ⁻³	CH ₄ ×10 ⁻³
Styrene-Teflon FEP Graft							
10	—	0	40	1.11	0.50	2.7	2.9
11	A	14.0	36	0.46	0.20	3.5	3.5
12	A	18.5	32	0.50	0.14	3.2	5.0
13	B	15.0	—	0.43	0.13	3.3	4.4
14	C	17.5	36	0.42	0.17	3.1	3.1
Acrylonitrile-Teflon FEP Graft							
15	C	5.5	38	0.91	0.33	1.7	2.1
16	C	19.9	31	0.38	0.09	1.6	2.7
17	B	9.5	38	0.72	0.35	2.2	2.0
18	B	12.0	32	0.59	0.19	1.5	2.0

^a Grafting method: A, preirradiation in air; B, preirradiation in vacuo; C, mutual irradiation (−196°C) plus heat treatment; D, mutual irradiation.

indicated both a decrease in crystallinity and changes in the crystallite size distributions resembling those found in grafted polyethylene films.

As can be seen from Table III, the diffusion coefficients for both polystyrene- and polyacrylonitrile-grafted films decreased with increasing graft concentration. Initially, the grafts fill in the regions between lamellae and in defects, thereby reducing the available free volume for diffusion. Cross-linking between lamellae by grafted side chains could also lead to a reduction in the diffusion coefficient. Subsequent grafting and swelling of these grafts leads to disruption of lamellae and a lowering in the size distribution of crystallites. The increase of solubility in Teflon FEP containing a high polystyrene graft concentration can be attributed to the presence of grafted side chains and homopolymer rather than the availability of new regions for solution resulting from crystallite disruption.

The temperature dependence of the permeability, diffusion, and solubility coefficients was measured over the temperature range of 15°–50°C. A linear dependence of the logarithm of the nitrogen diffusion coefficient on the reciprocal of temperature was observed. Activation energies of diffusion and permeation, heats of solution, and preexponential factors are presented in Table II. It can be seen that there was a slight decrease in both the activation energy of diffusion and the preexponential factor D_0 with increasing polystyrene graft concentration. The activation energy of diffusion and preexponential factor for polyacrylonitrile-grafted films remained constant with increasing graft concentration. This appears to indicate that the polyacrylonitrile-grafted side chains take little part in the actual diffusion process.

Separation Factors for Graft Copolymers

The separation factor, as determined by chromatographic analysis, was calculated by means of the following equation:

$$\alpha_{\text{CH}_4/\text{N}_2} = \frac{[Y_{\text{CH}_4}/(1 - Y_{\text{CH}_4})]}{[X_{\text{CH}_4}/(1 - X_{\text{CH}_4})]}$$

where Y_{CH_4} is the mole fraction of methane on the low pressure side of the membrane and X_{CH_4} is the mole fraction of methane on the high pressure side of the membrane. The separation factor used in this study, $\alpha_{\text{CH}_4/\text{N}_2}$, denotes the permeation rate of methane relative to that of nitrogen. A separation factor of 1 would indicate equal rates of permeation and consequently gives no separation. A value greater than 1 would indicate a higher relative rate of flow of methane and thus enhanced separation of the gas mixture. There was good agreement between calculated and experimentally determined separation factors as shown in Table IV. The separation factors for polystyrene-grafted polyethylene increased slightly with

TABLE IV
Gas Separation Properties of Grafted Films

Sample code number ^a	Graft, %	Separation factor $P_{\text{CH}_4}/P_{\text{N}_2}$ calculated	Separation factor $P_{\text{CH}_4}/P_{\text{N}_2}$ measured
Styrene-Polyethylene Graft			
1	0	2.57	2.54
2	10.6	2.72	2.87
3	29.5	3.25	3.29
4	48.2	3.29	2.97
Acrylonitrile-Polyethylene Graft			
5	10.5	2.72	2.51
6	29.8	2.40	2.47
7	58.7	—	—
8	14.9	2.59	2.29
9	34.2	2.17	2.10
Styrene-Teflon FEP Graft			
10	0	2.10	2.12
11	14.0	2.29	2.36
12	18.0	2.38	2.35
13	15.0	2.47	2.49
14	17.5	2.48	2.39
Acrylonitrile-Teflon FEP Graft			
15	5.5	2.22	2.30
16	19.9	2.54	2.47
17	9.5	2.32	2.37
18	12.0	2.38	2.43

^a For description of samples 1-18, see Table I.

high polystyrene graft concentrations. From the gas solubility results, it would appear that the improved separation factor was the result of increased methane solubility in the grafted polyethylene. This increase occurred despite a significant decrease in both the methane and nitrogen diffusion coefficients. At higher graft concentrations, the slight reduction was probably due to enhanced nitrogen diffusion brought about by crystallite disruptions. For polyacrylonitrile-grafted films, no significant change in the separation factor was observed until high graft concentrations were reached. Since gas solubility in polyacrylonitrile-grafted polyethylene is

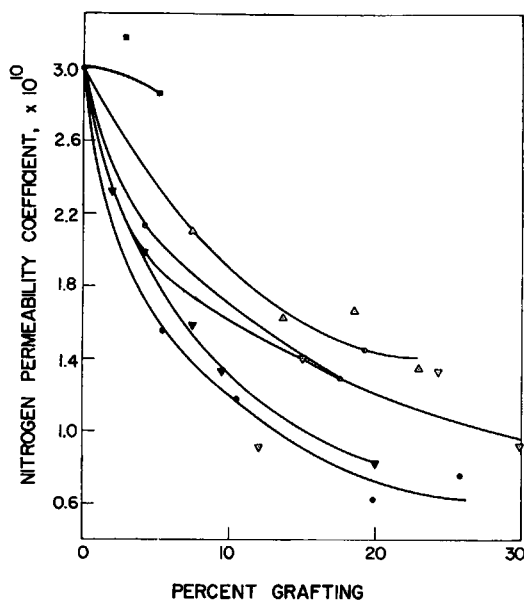


Fig. 6. Methane permeability coefficient in grafted Teflon FEP copolymer films at 30°C: (Δ) polystyrene graft, preirradiation in air; (∇) polystyrene graft, preirradiation in vacuo; (\circ) polystyrene graft, special mutual irradiation plus heat treatment; (\square) polystyrene graft, mutual irradiation plus heat treatment; (\bullet) polyacrylonitrile graft, special mutual irradiation plus heat treatment; (\blacktriangledown) polyacrylonitrile graft, preirradiation in vacuo. Units of permeability, cc(STP) cm/(cm² Hg sec).

low, the slight decrease can be attributed to the difference between the reduction in nitrogen and methane diffusion by polyacrylonitrile-grafted side chains and polyacrylonitrile homopolymer.

The nitrogen-methane separation factors for polystyrene-grafted Teflon FEP films increased with increasing graft concentration and reached a maximum at approximately 10%–20% graft concentration. For samples containing higher graft concentration, there was a decrease in the separation factor. With initial grafting, the methane diffusion coefficient is reduced more rapidly than that of nitrogen. However, increased methane solu-

bility and diffusion due to the polystyrene-grafted side chains and crystallite disruption at high degrees of grafting probably reduced the separation factor. Separation factors for polyacrylonitrile-grafted films did not show a maximum. This suggests that the minimum observed for polystyrene-grafted films was probably the result of increased methane solubility rather than the result of an increase in diffusion.

There was good agreement between calculated and measured values of the permeability and diffusion coefficients of nitrogen-methane gas mixtures in both grafted polyethylene and Teflon FEP copolymer films. The coefficients decreased with increasing graft concentration, although, after an initial rapid decrease, subsequent grafting did not influence the rate of decrease as greatly. These results are similar to those found for pure-component permeation.

CONCLUSIONS

The permeability and diffusion coefficients of all the grafted films investigated in this study decreased with increasing grafting. This was attributed to a decrease in the volume of the amorphous regions due to the presence of grafted side chains. The solubility coefficients, however, were affected only in the polystyrene-grafted polyethylene and Teflon FEP films. This increase was attributed to increased gas solubility in the grafted polystyrene side chains. The activation energies of permeation and diffusion increased in most cases, indicating decreased chain mobility due to the grafted side chains. The measured permeability and diffusion coefficients for gas mixtures showed trends similar to those exhibited by the pure components and therefore could be predicted quite accurately from the single-gas permeability and diffusion coefficients. This was taken as an indication that there was little gas-polymer interaction.

The improved separation factors show that graft copolymerization can lead to enhancement of the degree of separation of gas mixtures. This effect can probably be utilized to greater advantage by a better choice of permeant gas mixtures than the nitrogen-methane system used in this work. The penalty for the increased gas mixture separation for every modified film examined in this study, however, was the decreased rate of gas permeation. It was found that the methods employed in the preparation of the modified membrane were extremely important. Grafting technique had a strong effect on the gas permeation and separation properties of the modified films. It may be possible by selective application of the various modification techniques used in this study to obtain membranes with improved gas permeation and separation characteristics for particular gas mixtures.

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