

The Permeability of Some Graft Copolymers of Polyethylene to Gases and Vapors

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In recent years, interest in the preparation of graft copolymers by ionizing radiation has increased greatly. However, comparatively little has been published on the physical properties of such polymers although Chapiro^{1,2} and others^{3,4} have reported some of their findings. The permeability, diffusivity, and solubility of various gases and vapors have been determined for a number of graft copolymers of polyethylene and are reported here.

A. EXPERIMENTAL

1. Materials

The graft copolymers were prepared by directly irradiating polyethylene with the gamma rays from a cobalt-60 source. The polyethylene was immersed in the appropriate monomer under a vacuum. The term per cent graft refers to the weight of the grafted monomer per 100 parts by weight of the polyethylene. The permeability constants were determined by the well-known high vacuum technique, originally developed by Barrer.⁵ Details of the equipment used have been published and will not be further described.⁴ The sorption isotherms were determined with a quartz helix microbalance in a manner similar to that described by Prager and Long.⁶ The samples examined, unless otherwise stated, were prepared by Brookhaven National Laboratories. Other samples were prepared at Massachusetts Institute of Technology, the permeability constants being determined by the volumetric change method with

the use of an apparatus developed by Brubaker and Kammermeyer.^{7,8}

2. Gas Permeabilities

Fick's law can be written as:

$$\partial v/\partial t = -PA(\partial p/\partial x)$$

where P is the permeability constant (cm.³-gas-STP/cm.²/mm./sec./cm. Hg), $\partial p/\partial x$ is the partial pressure gradient across the film (cm. Hg/mm.), $\partial v/\partial t$ is the volumetric flow rate (cc. STP/sec.), and A is the area of the film (cm.²). Also, it has been found that temperature data can be correlated by an Arrhenius-type expression:

$$P = P_0 \exp\{-E_p/RT\}$$

for a given grafted film and permeating gas. P is determined by two effects,⁹ and can be written:

$$P = DS$$

where D and S refer to diffusion and solution processes, respectively. It will be shown that permeation through a polyethylene-acrylonitrile graft is primarily a diffusion process where the acrylonitrile remains inert; while in permeation through polyethylene-styrene grafts, there is also a solution effect.

The results obtained with the styrene graft copolymers at 30°C. are given in Tables I and II. It can be seen that, in general, a small decrease in the permeability is brought about at low degrees of grafting, followed by an increase at high degrees. Such behavior is probably due to a decrease in the free volume available for permeation, as grafting first occurs in the amorphous regions. (It will be shown later that, in the permeation of methyl

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TABLE I
Permeability to Gases of Styrene-Polyethylene (0.922 g./cm.³ density) Graft Copolymer at 30°C.

| Grafted styrene, % | Dose, Mrad | Time left in monomer after irradiation, hr. | Permeability constant $\times 10^9$, cc./cm. ² /mm./sec./cm. Hg | | |
|--------------------|------------|---|---|----------------|-----------------|
| | | | N ₂ | O ₂ | CO ₂ |
| 0 | — | — | 1.9 | 7.0 | 28.0 |
| 4.8 | 0.28 | 0 | 1.5 | 4.8 | 22.5 |
| 8.5 ^a | 0.20 | 1.3 | — | 7.4 | — |
| 10.5 ^a | 0.20 | 11.0 | — | 6.5 | — |
| 13.4 | 0.64 | 0 | 1.35 | — | 18.0 |
| 15.1 ^a | 0.20 | 38.0 | — | 8.1 | — |
| 20.9 | 1.19 | 0 | 0.92 | 3.45 | 14.9 |
| 27.5 ^a | 1.0 | 0.25 | — | 7.0 | — |
| 32.0 ^a | 1.0 | 17.0 | — | 5.0 | — |
| 34.4 | 2.84 | 0 | 0.97 | — | 15.8 |
| 41.3 | 4.12 | 0 | 1.05 | 4.26 | 20.2 |
| 52.0 ^a | 2.0 | 5 | — | 9.7 | — |
| 53.0 ^a | 2.0 | 6.75 | — | 9.9 | — |
| 100% polystyrene | | | 0.29 | | 8.8 |

^a Samples were prepared at MIT; data taken at 25°C. and corrected to 30°C.

bromide, there is a genuine decrease in the diffusion constant.) At very high degrees of grafting, there is undoubtedly a decrease in crystallinity which would lead to increased permeation, since permeation is through the amorphous or low percentage crystalline areas. The graft copolymers, prepared by direct irradiation followed by leaving the monomer for substantial further growth by the so-called "post effect," can be seen to have slightly larger permeabilities than those removed immediately after irradiation, although the same pattern of behavior (P versus per cent graft) is shown. Undoubtedly, the structure of such polymers is different, in particular the same per cent graft would entail fewer molecules but of higher molec-

TABLE II
Permeability to Carbon Dioxide of Styrene-Polyethylene (Linear, 0.95 g./cm.³ density) Graft Copolymers at 30°C.

| Grafted styrene, % ^a | Dose, Mrad | Time left in monomer after irradiation, hr. | $P \times 10^9$ |
|---------------------------------|------------|---|-----------------|
| | | | |
| 18 | 0.96 | 0 | 10.5 |
| 25 | 2.32 | 0 | 9.4 |
| 28 | 1.0 | 5 | 6.9 |
| 54 | 1.0 | 10 | 11.3 |
| 105 | 1.0 | 31 | 25.0 |

^a Samples prepared at MIT from Marlex 50 polyethylene (10-mil thickness); data taken at 25°C., corrected to 30°C.

ular weight. Possibly, there would be a greater tendency for breakup of the crystalline areas when trapped radicals are allowed to grow to considerable lengths before termination. At 40 to 50% grafting in the MIT-prepared films, bubbles and pockets of homopolymer (low molecular weight polystyrene) were spotted throughout the films. A detailed discussion of the structure of the polymers and of the post effect may be found in a recent paper by Hoffman.¹⁰

The linear polyethylene grafts showed a similar decrease in P with percentage grafting, followed by an increase in permeability with increasing amounts of grafted polystyrene. The small increase with the initial percentage grafting is probably due to a "relaxation" process accompanying the treatment of highly crystalline polymer in a good swelling agent such as styrene monomer. Such effects have been shown to exist with high density polyethylenes, and with the subsequent grafting, the polymer would be set in the "expanded" configuration probably brought about by the solution of small crystallites. However, this may be somewhat speculative, as the standard deviation of the data was approximately 10%.

The temperature dependence of the instantaneous grafts has been measured over the range 15–60°C., and excellent Arrhenius plots were obtained. The activation energies E_p and pre-exponential factors P_0 for the two homopolymers and for the grafts are given in Table III. It can be seen that, as grafting increases, there is a small but definite decrease in the activation energy accompanied by a decrease in the pre-exponential factor, both lying between the values of the two homopolymers. It is possible to conclude from these results that the styrene branches participate in some manner in the permeation process other than as inert fillers.

TABLE III
Temperature Dependence of the Permeability Constants for Styrene-Polyethylene Grafts

| Styrene graft, % | P_0 , cc. STP/cm. ² /mm./sec./cm. Hg | | | E_p , kcal./mole | | |
|------------------|---|----------------|----------------------|--------------------|----------------|-----------------|
| | N ₂ | O ₂ | CO ₂ | N ₂ | O ₂ | CO ₂ |
| 0 | 0.66 | 0.089 | 0.081 | 11.8 | 9.9 | 9.0 |
| 4.8 | 0.28 | 0.085 | 0.032 | 11.5 | 10.1 | 8.6 |
| 13.4 | 0.19 | — | 0.019 | 11.3 | — | 8.35 |
| 20.9 | 0.03 | 0.020 | 0.016 | 10.4 | 9.4 | 8.4 |
| 34.4 | 0.008 | — | 0.0011 | 9.6 | — | 6.7 |
| 41.3 | 0.006 | 0.0011 | 0.0004 | 9.4 | 7.5 | 6.0 |
| 100% polystyrene | 1.6×10^{-6} | — | 1.7×10^{-7} | 5.2 | — | 1.8 |

TABLE IV
Permeability at 30°C. of Acrylonitrile-Polyethylene Graft Polymers

| Acrylonitrile graft, % | Dose, Mrad | $P \times 10^9$, cc. STP/cm. ² /sec./cm. Hg | | | P_0 , cc. STP/cm. ² /sec./cm. Hg | | | E_p , kcal./mole | | |
|------------------------|------------|---|----------------|-----------------|---|----------------|-----------------|--------------------|----------------|-----------------|
| | | N ₂ | O ₂ | CO ₂ | N ₂ | O ₂ | CO ₂ | N ₂ | O ₂ | CO ₂ |
| 0 | — | 2.00 | 6.94 | 28.0 | 0.66 | 0.089 | 0.081 | 11.8 | 9.9 | 9.0 |
| 1.8 | 0.037 | 1.73 | 5.73 | 25.4 | 0.28 | 0.063 | 0.036 | 11.4 | 9.8 | 8.6 |
| 4.1 | 0.045 | 1.57 | — | 19.7 | 0.39 | — | 0.042 | 11.7 | — | 8.8 |
| 9.3 | 0.122 | 1.26 | — | 17.1 | 0.24 | — | 0.032 | 11.5 | — | 8.7 |
| 20.8 | 0.207 | 1.06 | 3.23 | 13.6 | 0.43 | 0.14 | 0.041 | 12.0 | 10.6 | 9.0 |
| 31.3 | 0.336 | 0.71 | 2.24 | 9.7 | 0.25 | 0.058 | 0.026 | 11.9 | 10.3 | 8.9 |

The results obtained with a series of acrylonitrile graft copolymers of polyethylene are given in Table IV. It can be seen that there is a continual reduction in the gas permeability figures with increasing degrees of grafting, the order of magnitude of the reduction being similar to that observed with the styrene grafts. No increase in permeability at the highest degree of grafting was observed but, since the per cent of graft is still relatively low compared to the styrene grafts, this is not unexpected. Furthermore, since polyethylene absorbs only about 1.4% of acrylonitrile compared with 11.1% of styrene at 20°C., a reduction in the crystallinity with grafting appears to be less probable. The activation energies are all similar and the reduction in permeability is expressed only by changes in the pre-exponential factors. The implication is that the changes in the pre-exponential factors. The implication is that the acrylonitrile branches act merely as impermeable fillers for the polyethylene and play no other role in the permeation process. This is entirely feasible, since the grafted polymer is probably tightly coiled in the hydrocarbon matrix and would be impermeable compared with the polyethylene. Both these conditions do not exist in the case of styrene. In this connection, it is interesting to note that the densities of the two polymers of about 21% graft (with ordinary polyethylene) were 0.95 and 0.97 with styrene and acrylonitrile, respectively.

Finally, results in Table V of the gas permeabilities of two vinylpyridine graft copolymers are given. The reductions in gas permeability brought about by grafting are greater than with the other two monomers studied although, as with acrylonitrile, no change in the activation energy, even with 60% of grafted vinylpyridine, was found. Presumably, the role of vinylpyridine is similar to that of acrylonitrile, but vinylpyridine would have considerably greater volume for the same weight of graft, causing the somewhat greater reduction in permeability.

It was thought to be of interest to follow the nitrogen permeabilities at various temperatures through the melting point of the polyethylene in the manner reported previously.¹¹ The relevant curves on the highest per cent grafts for styrene and acrylonitrile are shown in Figure 1, together with the results previously obtained on an irradiated sample of polyethylene (10 Mrad). The samples can be seen to melt at approximately the same temperature. However, whereas the polyethylene solidifies to a slightly less crystalline material after melting, manifested by somewhat higher permeabilities (not shown in Fig. 1), the styrene graft had lower permeabilities after melting and the acrylonitrile graft showed no change at all (Fig. 1). The result for styrene was confirmed by carrying out the same experiment with an intermediate graft. The doses used are not sufficient

TABLE V
Permeability at 30°C. of Polyethylene-Vinylpyridine Graft Copolymers

| Vinylpyridine graft, % | $P \times 10^9$, cc. STP/cm. ² /mm./sec./cm. Hg | | | P_0 , cc. STP/cm. ² /mm./sec./cm. Hg | | | E_p , kcal./mole | | |
|------------------------|---|----------------|-----------------|---|----------------|-----------------|--------------------|----------------|-----------------|
| | N ₂ | O ₂ | CO ₂ | N ₂ | O ₂ | CO ₂ | N ₂ | O ₂ | CO ₂ |
| 0 | 2.00 | 6.94 | 28.0 | 0.66 | 0.089 | 0.081 | 11.8 | 9.9 | 9.0 |
| 34 | 0.61 | 2.33 | 11.3 | 0.25 | 0.051 | 0.035 | 12.0 | 10.2 | 9.0 |
| 60 | 0.15 | 0.57 | 2.47 | 0.062 | 0.0074 | 0.0058 | 12.0 | 9.9 | 8.9 |

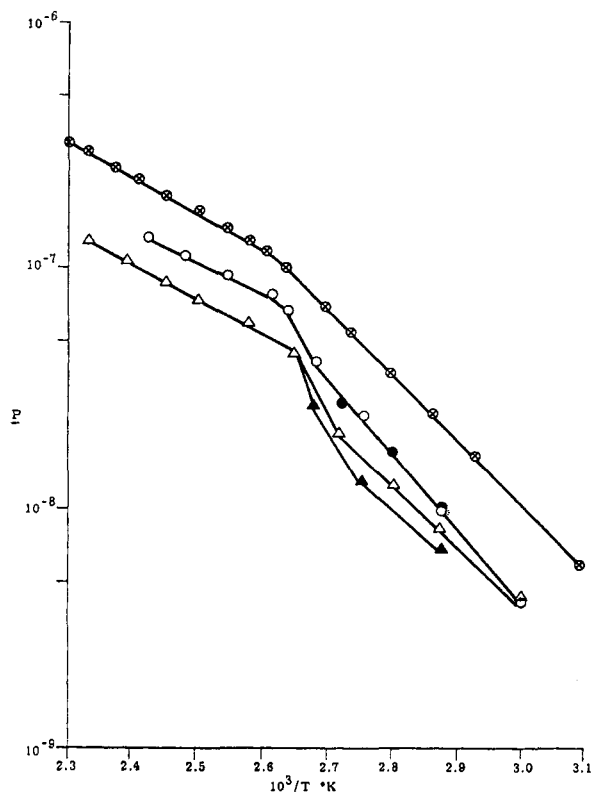


Fig. 1. Nitrogen permeability P (cc./cm.²/mm./sec./cm. Hg) of polyethylene and graft copolymer as a function of temperature: (⊗) polyethylene (10 Mrad); (○) polyethylene-31.3% acrylonitrile graft; (●) polyethylene-31.3% acrylonitrile graft after melting; (Δ) polyethylene-41.3% styrene graft; (▲) polyethylene-41.3% styrene graft after melting.

to produce enough crosslinks to cause a considerable change in the crystallinity on melting, particularly in the case of acrylonitrile (only 0.336 Mrad), and the results with this polymer confirm the inert role of the acrylonitrile graft. The close correspondence between the results obtained before and after melting were unexpected, since it was felt that the branches should interfere enormously with crystallization after melting. It is possible that the crosslinks present restricted the amount of mixing which could take place in the melt.

B. WATER VAPOR PERMEABILITY

The water vapor permeabilities at several relative humidities at 25°C. are given in Table VI. The somewhat higher results with the acrylonitrile and styrene grafts are reasonable, since both polyacrylonitrile and polystyrene have considerably greater water vapor permeabilities than polyethylene. The results obtained with the vinyl-

pyridine graft are understandable in spite of the low gas permeabilities obtained with the same polymer. The grafted polymer is highly hygroscopic, and the swelling in water accounts for both the high values obtained with water vapor permeability and for the dependence on relative humidity.

TABLE VI
Permeability of Polyethylene Graft Copolymers to Water Vapor at 25°C.

| Comonomer | Graft, % | Vapor pressure, mm. Hg | $P \times 10^8$, cc. STP/cm. ² /mm./sec./cm. Hg |
|---------------|----------|------------------------|---|
| — | 0 | 10.5 | 10.6 |
| | | 17.3 | 10.6 |
| | | 23.2 | 10.6 |
| Styrene | 20.9 | 10.0 | 19.0 |
| | | 20.0 | 19.0 |
| Acrylonitrile | 20.8 | 10.0 | 16.0 |
| | | 20.0 | 16.0 |
| Vinylpyridine | 34 | 10.0 | 850 |
| | | 15.0 | 930 |
| | | 20.0 | 1400 |

With a high-melting, noncompatible grafted polymer such as acrylonitrile, it is likely that the only change that would take place would be the melting of the polyethylene. This, indeed, is what appeared to happen. Dry, unmodified polyacrylonitrile is not very thermoplastic, even on heating at 200–300°C., and objects can be molded only with great pressure.¹⁴

C. ORGANIC VAPORS

Only two organic vapors, isobutene and methyl bromide, were investigated, since considerable information was available on the permeation of these vapors through polyethylene.¹² The measurements were carried out at 0°C., and the permeabilities at a number of pressures are shown graphically in Figures 2 and 3. With methyl bromide, there is a small reduction in the permeability constant at low vapor pressures which is maintained at the higher pressures in the case of the acrylonitrile graft (20.8% grafted). This is overcome with increasing vapor pressure with the styrene graft (20.9% grafted), until at above 350 mm. pressure, the permeability is greater with the graft than with a similar sample of ungrafted polyethylene, and, at near saturation pressure, the permeability is more than double. With 31.3% grafted acrylonitrile,

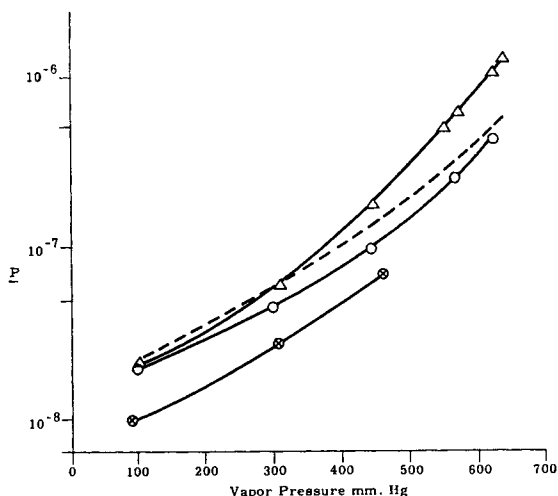


Fig. 2. Permeability constant P (cc./cm.²/mm./sec./cm. Hg) vs. vapor pressure for methyl bromide at 0°C. through (- -) polyethylene and various polyethylene graft copolymers: (Δ) 20.9% styrene; (\circ) 20.8% acrylonitrile; (\otimes) 31.3% acrylonitrile.

there is a considerable reduction which is maintained across the entire vapor pressure range. The acrylonitrile grafts give permeability-vapor pressure curves approximately parallel to those obtained with polyethylene for both methyl bromide and isobutene, again showing the inert role of the graft in the permeation process.

The isobutene curves show greater reductions than methyl bromide, which is reasonable in view of the larger size of the diffusing molecule (the molar volumes at 0°C. are 90.6 and 54.8 cc., respectively, for isobutene and methyl bromide) and the reduced swelling of all the polymers in isobutene compared with methyl bromide. For

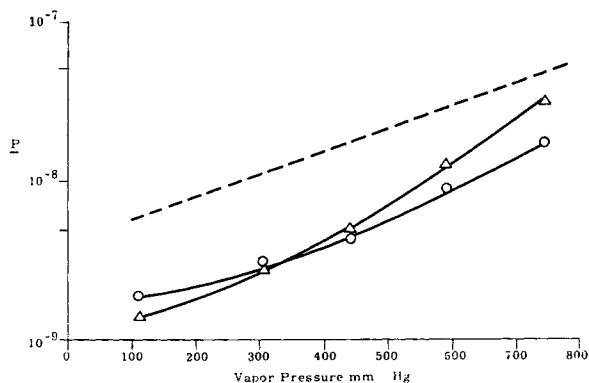


Fig. 3. Permeability constant P (cc./cm.²/mm./sec./cm. Hg) vs. vapor pressure for isobutene at 0°C. through (- -) polyethylene and various polyethylene graft copolymers: (Δ) 20.9% styrene; (\circ) 20.8% acrylonitrile.

similar reasons, the difference between the styrene and acrylonitrile grafts at high vapor pressures is much greater for methyl bromide than for isobutene.

In the case of methyl bromide, the actual sorption isotherms have been determined at 0°C. for the two similar percentage grafts of styrene and acrylonitrile and are shown in Figure 4. That

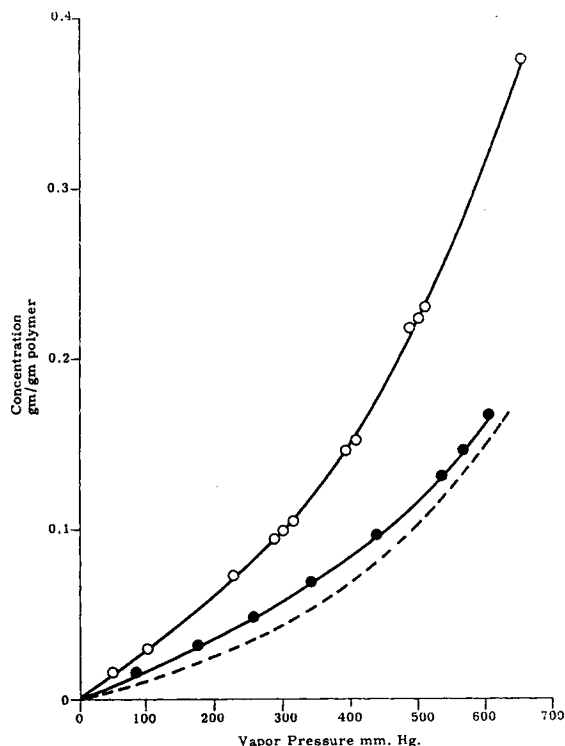


Fig. 4. Sorption isotherm at 0°C. for methyl bromide on (- -) ungrafted polyethylene; (\circ) 20.9% styrene graft; (\bullet) 20.8% acrylonitrile graft.

the swelling of the styrene grafts is greater than that of either polyethylene or the acrylonitrile graft is clearly shown. It should be pointed out that the polyethylene curves are for a similar sample of unirradiated material, and it is likely that small changes in the polyethylene are introduced by the irradiation process, even with acrylonitrile; in fact, the sorption curves indicate the possibility of a small reduction in crystallinity.

The transmission and sorption data may be combined in the manner originally used by Rouse¹³ and the transmission-concentration curves constructed. These are shown in Figure 5. Following Rouse,¹⁴ for thickness, l , one can write.

$$l d(Q)/dc = D(c)$$

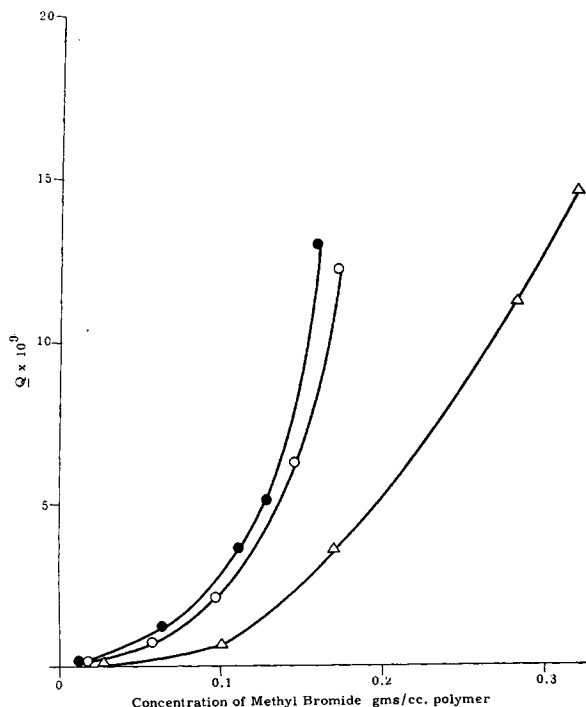


Fig. 5. Vapor transmission Q (g./sec./cm.²; calculated on 1 cm. thickness) vs. concentration of methyl bromide at 0°C. for (●) polyethylene (0.922 g./cc. density); (○) 20.8% acrylonitrile graft; (△) 20.9% styrene graft. The slopes of each curve give $D(c)$ in cm.²/sec.

where Q is the vapor transmission and $D(c)$ the differential diffusion constant at concentration c . It can be seen from Figure 5 that the diffusion constants (slope of the curve) are always less for the styrene graft than for the acrylonitrile graft, which is only slightly less than for polyethylene. These results again emphasize the role of the styrene grafts in the diffusion process compared with the inert behavior of the acrylonitrile branches and point up the great importance of the solubility component in the overall permeation process.

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Synopsis

Graft copolymers of polyethylene were prepared by gamma irradiation of polyethylene films immersed in the appropriate monomer. The majority of gas permeability measurements were made by Barrer's high vacuum technique; others were made by measuring volumetric change as a function of time. Sorption isotherms were obtained by using a quartz helix microbalance. Temperature-dependent permeability constants have been obtained for permeation of oxygen, nitrogen, and carbon dioxide through styrene, acrylonitrile, and vinylpyridine grafted to low-density polyethylene. Permeability constants at 25°C. have also been determined as a function of water vapor partial pressure for the above systems. Some values for permeation of carbon dioxide through styrene grafted to high density or linear polyethylene are also given. Organic vapors studied were methyl bromide and isobutene, permeability constants at 0°C. being determined for styrene and acrylonitrile-polyethylene graft copolymers as a function of organic vapor pressure. The data show clearly that permeation through acrylonitrile and vinylpyridine-polyethylene grafts is primarily a diffusion process, while in permeation through polyethylene-styrene grafts, there is also a crystallite solution effect. Percentage grafts varied from 0 to 100 parts monomer per 100 parts by weight polyethylene.

Résumé

On a préparé des copolymères greffés de polyéthylène en soumettant aux rayons gamma des films de polyéthylène immergés dans le monomère approprié. La plupart des mesures de perméabilité gazeuse ont été effectuées au moyen de la technique du haut vide de Barrer; d'autres ont été effectuées en mesurant le changement de volume en fonction du temps. Les isothermes d'absorption ont été obtenues en utilisant une microbalance à hélice de quartz. Les constantes de perméabilité en fonction de la température ont été obtenues pour le passage de l'oxygène, de l'azote et de l'anhydride carbonique à travers le styrène, l'acrylonitrile et la vinylpyridine greffés à du polyéthylène de faible densité. Les constantes de perméabilité à 25°C ont également été déterminées en fonction de la pression partielle en vapeur d'eau des systèmes sus-mentionnés. On donne aussi quelques valeurs pour le passage de l'anhydride carbonique à travers du styrène greffé à du polyéthylène de densité élevée ou linéaire. Les vapeurs organiques

étudiées étaient le bromure de méthyle et l'isobutène, les constantes de perméabilité à 0°C étant déterminées pour des copolymères greffés styrène-polyéthylène et acrylonitrile-polyéthylène en fonction de la pression en vapeur organique. Les résultats montrent clairement que le passage à travers les copolymères greffés d'acrylonitrile-polyéthylène et de vinylpyridine-polyéthylène est en principe un processus de diffusion tandis que pour le passage à travers des copolymères greffés styrène-polyéthylène il y a également un effet de dissolution des cristallites. Les pourcentages de produits greffés varient de 0 à 100 parties de monomère pour 100 parties en poids de polyéthylène.

Zusammenfassung

Graftcopolymere von Polyäthylen wurden durch Gammastrahlung von Polyäthylenfilmen hergestellt, die in das entsprechende Monomere eingetaucht waren. Die Mehrzahl der Gaspermeabilitätsmessungen wurden mittels der Hochvakuummethode von Barrer ausgeführt; ein Teil durch Messung der Volumsänderung als Funktion der Zeit. Sorptionsisothermen wurden mit einer Quarzspiralmikro-

wage erhalten. Für die Permeation von Sauerstoff, Stickstoff und Kohlendioxyd durch auf Polyäthylen niedriger Dichte aufgepfropftes Styrol, Acrylnitril und Vinylpyridin wurden temperaturabhängige Permeabilitätskonstanten erhalten. Für die angeführten Systeme wurden auch Permeabilitätskonstanten bei 25°C in Abhängigkeit vom Partialdruck an Wasserdampf bestimmt. Ebenso werden einige Werte für die Permeation von Kohlendioxyd durch auf Polyäthylen hoher Dichte oder lineares Polyäthylen gepfropftes Styrol angegeben. An organischen Dämpfen wurde Methylbromid und Isobuten untersucht und Permeabilitätskonstanten bei 0°C für Styrol- und Acrylnitril-Polyäthylenpfropfcopolymere in Abhängigkeit vom Dampfdruck bestimmt. Die Ergebnisse zeigen klar, dass die Permeation durch Acrylnitril- und Vinylpyridin-Polyäthylengrafts primär ein Diffusionsprozess ist, während bei der Permeation durch Polyäthylen-Styrolgrafts auch ein Kristallit-Lösungseffekt auftritt. Die prozentuelle Aufpfropfung variierte von 0 bis 100 Teile Monomeres auf 100 Gewichtsteile Polyäthylen.

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