

Gas Permeability of Highly Oriented Dibutyl Maleate-Ethylene Copolymer Films

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Synopsis

The effects of extreme uniaxial orientation on gas permeation through dibutyl maleate-ethylene copolymer films have been examined. Gases employed were helium, argon, and methane. Permeability constants were measured as functions of temperature between 25 and 55°C., in unstretched film and in films stretched to elongations of 490, 512, 540, and 608% (breaking point). Uniaxial cold drawing of dibutyl maleate-ethylene copolymer films into the stable necking region (elongation ca. 490%) causes only a small (30%) decrease in permeability and virtually no change in apparent activation energy of permeation; when the necked films are further stretched to elongations approaching the breaking point (ca. 600%), a significant decrease in permeability and increase in activation energy is observed. It is deduced that the major changes in crystalline texture and arrangement which this polymer undergoes in the necking process have only a minor effect upon total level of crystallinity, amorphous-phase properties, and diffusional impedance offered by the crystallites, suggesting that changes in crystallite orientation, perfection, and shape throughout the drawing process are compensatory. When necked polymer is further stretched, however, severe restraints are imposed upon the mobility of oriented chain segments in the amorphous regions, which are primarily responsible for the observed large changes in permeabilities and permeation activation energies.

INTRODUCTION

In order to characterize certain structural aspects of polymer films and to determine their efficiencies as separation barriers, numerous investigations have been carried out to measure the gas permeability of these films.

From earlier work performed in this laboratory^{1,2} and from the work of Stannett³ and others, it has been found that, for a wide variety of ethylene homopolymers, noncondensable gases are soluble only in the amorphous phase. Therefore a "two-phase" model of the polymer matrix, consisting of an impermeable phase (crystallites) randomly dispersed in a conducting amorphous phase, has been postulated^{1,2} and is successful in explaining the solubility data. The diffusion data^{1,2} may also be reconciled in this way and, moreover, are in agreement with the lamellar model⁴⁻⁶ of the crystalline phase in polyethylene, which is currently receiving wide acceptance.

With this background, it was decided to extend the investigation of the gas transmission properties of polyethylene to a study of the effects of uniaxial cold drawing. Permeation studies with several gases indicated that

TABLE I
Permeation Data for Stretched Linear Polyethylene (Grex)

Gas	Elongation %	Permeability constant \bar{P} at 25°C. $\times 10^8$, cc. (STP)/cm.-sec.-atm.	Apparent activation energy for permeation $E\bar{P}$, kcal./g.-mole
He	0	2.69	6.5
	17.2	2.62	6.7
	33.5	2.63	6.7
	42.6	2.58	6.7
A	0	1.05	8.3
	17.2	—	—
	33.5	1.03	8.3
	42.6	1.00	8.4

uniaxial stretching had no effect up to elongations of about 40% (Table I). Further experiments were carried out with ethylene copolymerized with a small amount of dibutyl maleate monomer. This polymer was specifically chosen because it can readily be cold-drawn to elongations of approximately 600%, at strain rate of 0.5 in./min. This obviated the necessity of stretching at very low strain rates or of providing elaborate temperature control equipment for stretching above room temperature, as would be needed to produce highly elongated films of ethylene homopolymer. It was also expected that the copolymer would be morphologically similar to linear polyethylene.

The copolymer film exhibits the phenomenon of necking, as illustrated by the stress-strain curve presented in Figure 1, and permeation measurements were made on necked films (elongation = 490%) and with unstretched copolymer.

To determine the effects of extreme orientation on gas permeation properties, elongations ranging from 512 to 608% (breaking point) were also studied, and the gas permeabilities of helium, argon, and methane, which differ significantly in molecular size and solubility, were measured over the temperature range 25–55°C.

Published data on the gas permeabilities of oriented polymer films are fairly extensive, but few attempts have been made to relate changes in gas transmission properties to morphological changes brought about by orientation. However, Reitlinger and Yarkho,⁷ and Barrie and Platt,⁸ studying natural rubber, and Lasoski and Cobbs,⁹ in their work on poly(ethylene terephthalate), found that orientation has no effect on permeability until crystallization occurs, with consequent decrease in permeability. Brandt,¹⁰ on the other hand, reports that cold drawing of low density polyethylene to 297% elongation leads to a decrease in gas permeability normal to the draw direction. Paradoxically, studies of diffusion of solvating vapors into oriented glassy, amorphous polymers (cellulose acetate) indicate that diffusivities are increased normal to the orientation direction and reduced parallel to it, relative to unoriented polymer.³ These evidently contradictory results suggest that a variety of compensatory changes in polymer

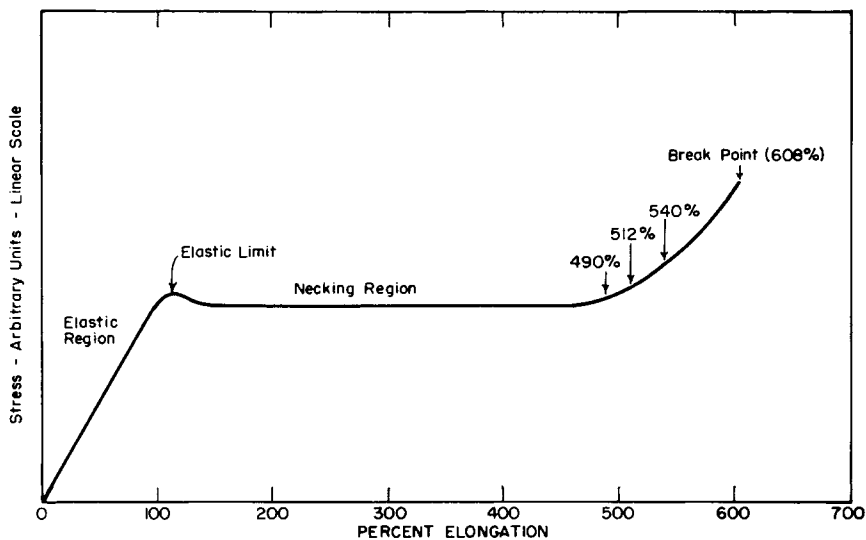


Fig. 1. Representative stress-elongation for dibutyl maleate-ethylene copolymer film.

segmental mobility and polymer-penetrant interaction must occur on orientation, those contributing to a decrease in permeability dominating in highly crystalline polymers such as polyethylene, while others contributing to increases in permeability dominating in glassy noncrystalline polymers.

To isolate the effects of orientation on the gas transmission properties of microcrystalline polymers several concurrent processes must be considered. Stretching may alter: (1) the relative proportions of amorphous and crystalline material, (2) the configuration of the crystallites, and (3) the properties of the amorphous phase.

The structure of unoriented polyethylene has been the subject of many recent investigations, and a comprehensive model of this microcrystalline polymer has been developing rapidly. Until recently, the morphology of polyethylene and other crystalline polymers has been regarded as consisting of small regions of molecular order (crystallites) embedded in an amorphous matrix. However, modification of the "fringed micelle" concept began when Keller¹² proposed that polyethylene chains fold upon themselves in crystallites from evidence obtained in the study of single crystals by x-ray diffraction and electron microscopy.

Keith and Padden,¹³ Geil,⁵ Hoffmann and Lauritzen,⁶ and Keller¹⁴ have extended this concept to polymers in bulk. The crystalline phase in polyethylene is viewed as a lamellar structure, consisting of bladlike elements stacked one upon the other. Chain folding perpendicular to the lamellar faces is indicated by diffraction patterns. The lamellae fan out radially from primary nucleation points to form spherulites which incorporate amorphous material as interlamellar links or intralamellar defects.

The effect of stress-induced orientation on the morphology of polyethylene has also received much attention, and it is apparent that the concepts which apply to the undrawn material cannot explain the results of x-ray diffraction studies of the drawn polymer.¹⁵ Spherulitic order is completely destroyed by orientation, indicating a major change in the character of the crystalline phase,¹⁶ and the average size of the lateral crystallite dimension is reduced.¹⁷ Lastly, at high elongation, crystalline regions become oriented so that *c* axes (chain directions) are parallel to the fiber axis.

In this work, a delineation of structural detail, as deduced from gas transmission measurements at various degrees of elongation, was sought, in order to aid in the development of a model of the microstructure of drawn polyethylene.

EXPERIMENTAL

A. Materials

Thin films of ethylene-dibutyl maleate copolymer were stretched on an Instron testing machine at a strain rate of 0.5 in./min. The film was necked, and allowed to relax at constant strain for 15 min. and was then removed from the Instron. The unrestrained film relaxed further for two weeks, and the final elongation was determined by measuring the distance between marks placed on the sample before stretching.

Film thickness was measured with a Pratt and Whitney super micrometer. The harmonic average of 13 measurements across the film surface was taken to be the effective film thickness.

The density of the films was measured in methanol-water density-gradient columns before and after permeation studies in the Park cells.

TABLE II
Properties of Butyl Maleate-Ethylene Copolymer

Elongation, %	Density 23°C., g./cc.	Apparent crystallinity, %	Film thickness, mils
0	0.9450	62.5	3.62
490	0.9428	61.5	1.27
(necked film)	0.9435	61.8	1.02
	(before runs)		
512	0.9436	61.8	1.02
	(after runs)		
540	0.9440	61.9	0.813
	(before runs)		
540	0.9442	61.9	0.813
	(after runs)		
608	0.9457	63.1	0.873
(break point)	(before runs)	63.1	0.873
608	0.9476	64.4	0.873
	(after runs)		

The properties of the dibutyl maleate-ethylene copolymer films are given in Table II.

B. Procedure

The permeability constant, \bar{P} , for steady permeation through a polymer membrane is defined by a form of Fick's first law:

$$J = \bar{P}\Delta p/l \quad (1)$$

if gas sorption obeys Henry's law and diffusion constants are independent of concentration, where J is the flux rate, Δp is the pressure drop across the film, and l is the film thickness in centimeters. Equation (1) is obeyed by polyethylene^{1,2} and has been assumed to apply in this investigation. Indirect evidence for the correctness of the assumption is the lack of dependence of measured values of \bar{P} on upstream pressure.

The permeability constant \bar{P} is related to the diffusion and solubility constants by eq. (2),

$$\bar{P} = Dk \quad (2)$$

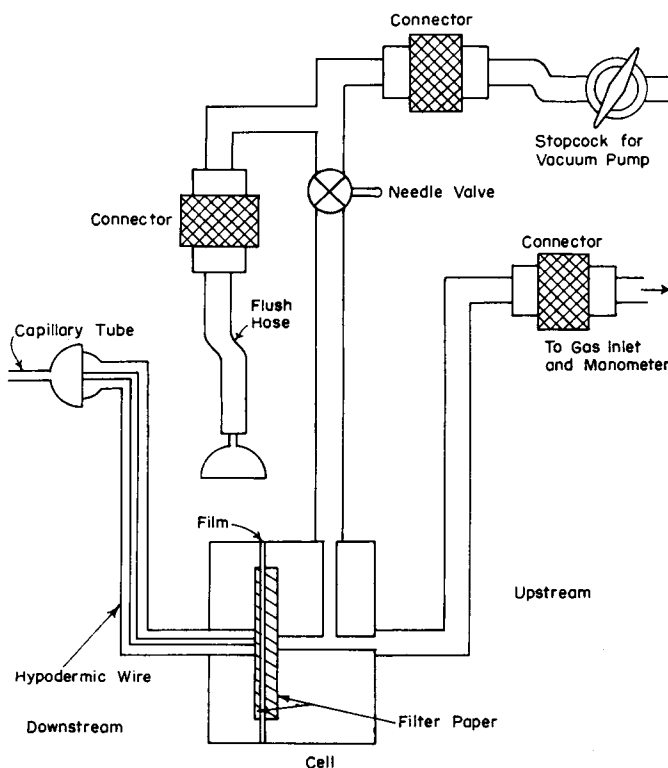


Fig. 2. Schematic diagram of the Park cell.

where D is the diffusion constant and k the solubility constant, while eq. (3) expresses the effect of temperature on the permeability constant.

$$\bar{P} = \bar{P}_0 e^{-E_{\bar{P}}/RT} \quad (3)$$

Here \bar{P}_0 is the permeability constant at infinite temperature, $E_{\bar{P}}$ is the apparent activation energy for permeation, R is the gas constant, and T is the temperature (Centigrade). In eq. (3), the apparent activation energy for permeation $E_{\bar{P}}$ is, in turn, related to the apparent activation energy for diffusion E_D and the apparent heat of solution ΔH by eq. (4).

$$E_{\bar{P}} = E_D + \Delta H \quad (4)$$

The apparatus used to obtain data in this work is known as the Park cell, designed by Dr. Robert Park of the Dow Chemical Company. The cell is sketched in Figure 2. This apparatus, based on a volumetric displacement principle, offers a convenient method for determining permeability constants.

Quarter-inch copper tubing connects the upstream side of the Park cell to the manometer and gas inlet. The downstream side of the cell consists of hypodermic tubing which is connected to a capillary tube by a ball and socket joint. The steady-state permeability is determined from the rate of advance of a drop of aqueous surfactant solution in the capillary tube. The primary source of error is in assigning values of 1 for the thin films, resulting in average precision limits of $\pm 12\%$ on values of \bar{P} .

DISCUSSION OF RESULTS

A. General Considerations

To provide an interpretive framework for this study it is assumed that the unstretched dibutyl maleate-ethylene copolymer is morphologically similar to polyethylene. Therefore, the model of Michaels, Parker, and Bixler^{1,2} may be extended to cover this case. There are several implications of this basic assumption: (1) gases are insoluble in the crystalline phase; (2) crystallites act as impermeable barriers to diffusion; (3) crystallites restrict the mobility of amorphous chain segments. The first statement may be conveniently expressed as

$$k = k^* \alpha \quad (5)$$

where α is the amorphous volume fraction and k^* is the solubility (or Henry's Law) constant in a hypothetical amorphous polyethylene. Values of α are determined from polymer density values by applying eq. (6)

$$\alpha = (\rho_c - \rho_s)/(\rho_c - \rho_a) \quad (6)$$

where ρ_a , ρ_c , and ρ_s are the amorphous density, the crystalline density, and the sample density, respectively. Previous studies have used values of $\rho_c = 0.9990$ g./cc. and $\rho_a = 0.8540$ g./cc. at 23°C.

Values of α for the unstretched copolymer film were estimated from eq. (6), with the use of the above values of ρ_a and ρ_c for polyethylene, and were compared with α 's determined by x-ray analysis.¹⁸ The results were in good agreement, lending support to the assumption that the presence of a small amount of dibutyl maleate does not significantly alter the densities of the crystalline or amorphous polymer from that of the pure homopolymer.

It would be desirable to retain the volume fraction of amorphous polymer as a correlating parameter for stretched films since there is a possibility that the density of the amorphous regions in the films investigated would be altered by orientation, this quantity can only be estimated from eq. (6) by using the value of ρ_a for unoriented polymer. The resulting values of the "apparent" amorphous volume fraction, α , which appears in Table II are useful for determining the differences in amorphous content of stretched films relative to unstretched film but may be relatively crude approximations to the absolute values of amorphous content.

According to the model of Michaels et al.^{1,2} the role of crystallinity in impeding the diffusion of small molecules in polyethylene is expressed by eq. (7).

$$D = D^*/\tau\beta \quad (7)$$

In eq. (7), D^* is the diffusion constant in completely amorphous undrawn polyethylene, τ is a geometric impedance factor expressing the increased path length for diffusion and decreased local cross-sectional area available for flow, occasioned by the presence of crystallites, and β is the chain immobilization factor, reflecting the crosslinking effect of crystallites. Equations (5) and (7) may be combined to yield an expression for \bar{P} .

$$\bar{P} = D^*k^*\alpha/\tau\beta \quad (8)$$

As the film is stretched, significant structural changes occur and the gas permeability of the film is affected markedly. However, the apparent crystallinity changes but little as shown in Table II. Brandt¹⁰ has shown that both D and k are altered by orientation of polyethylene, although the most significant change would appear to be reflected by the former quantity. In this work the changes in \bar{P} resulting from orientation will be interpreted in terms of changes in D , in view of eqs. (2) and (8). More specifically, the process of orientation may be expected to bring about changes in τ and β and the results may be interpreted accordingly. (It is recognized that orientation may alter the cohesive energy density of the amorphous phase and thus alter k^* , but it is felt that this effect is slight.)

Initially, the film stretches elastically and, if tension is released, eventually returns to its initial state. Spherulites are not disrupted, and the strain is probably concentrated as elastic deformation of the interlamellar amorphous material. Under these conditions, the change in β would be slight and τ would be unaffected.

As the stress is increased, a level is reached where permanent deformations begin to occur. At a sufficiently high strain the film necks and

elongates by a factor of about 4.9 at constant apparent stress. When the yield stress is exceeded, a catastrophic and abrupt change in crystalline structure and molecular orientation must occur at the sharp shoulder which separates necked from nearly unstretched polymer. Inferences about the nature of these structural changes can be drawn from x-ray diffraction measurements¹⁸ which indicate that, prior to necking, orientation of the (0, 0, 1) crystallite axis (or chain axis) normal to the stretch direction occurs, while after necking, the (0, 0, 1) axis is preferentially aligned parallel to the stretch direction. Evidently, the initial plastic deformation of the polymer involves relative slippage and fragmentation of lamellae, while during the necking process, virtually complete unravelling of lamellae takes place with concurrent formation of "fiber-bundle" crystallites which are highly oriented in the stretch direction. Once this highly oriented structure is formed, any further strain must be concentrated in the amorphous regions of the polymer where what little disorder that remains in the structure should be localized.

According to this picture, and to the concepts of diffusional impedance in crystalline polymers previously described, certain predictions might be made of how gas permeability should vary with uniaxial elongation. Morphologic changes in crystallite size, shape, and orientation which occur prior to and during necking should affect primarily the geometric diffusional impedance; this should be manifested as a change in gas permeability, with little to no corresponding change in activation energy. The magnitude and direction of the change in permeability will depend on the relative degrees of crystallite orientation and fragmentation: that is; orientation of lamellae in the stretch direction (or normal to the diffusion direction) will tend to increase impedance or reduce diffusion constants, while fragmentation of the lamellae will tend to reduce the impedance. Since both of these processes undoubtedly occur during stretching, their interaction may lead to only small changes in permeability over a broad range of elongation. In the fully necked state, the highly oriented fibrillar crystallites are probably very small and nearly isometric; under these conditions, the geometric impedance to diffusion may be expected to be smaller than in random, lamellar crystalline polymer of the same level of crystallinity. On the other hand, the reduction in segmental mobility of the amorphous polymer brought about a reduction in crystallite size, and molecular orientation will tend to reduce diffusion coefficients within the amorphous phase, with an accompanying increase in diffusion activation energies. The combined interplay of these factors insofar as they may affect gas permeability, however, is difficult to assess without the aid of experimental data.

B. Behavior of Linear Polyethylene at Low Elongations

Table I presents permeability data for helium and argon in quench roll-cast linear polyethylene (Phillips-type, W. R. Grace Grex of nominal density 0.960 g./cc.) when permanently stretched to elongations between 0.0 and 42.6% at room temperature. There is only a very small (and

probably not experimentally significant) change in permeability or permeation activation energy over this elongation range, and an equally insignificant density change. It is thus evident that changes in microstructure which accompany permanent elongations of this magnitude are inconsequential as regards gas diffusion.

C. Behavior of Dibutyl Sebacate-Ethylene Copolymer Film at High Elongations

The permeation characteristics and other macroscopic properties of this copolymer when cold-drawn to the fully necked state (elongation 490%), and permanently stretched to elongations up to the point of incipient rupture (elongation 608%) are presented in Tables II and III, and in Figures 3-6. Table II indicates that the polymer undergoes little change in density, and thus in apparent degree of crystallinity, over the elongation range studied; hence, it appears reasonable to assume that gas solubilities in the polymer are essentially independent of elongation. This makes it possible to relate changes in gas permeabilities directly to changes in gas diffusivities, and permeation activation energies, to diffusion activation energies.

TABLE III
Permeability Ratios at 29°C.

Elongation %	Ratio	
	$\bar{P}_{\text{He}}/\bar{P}_{\text{A}}$	$\bar{P}_{\text{He}}/P_{\text{CH}_4}$
0	2.2	1.9
490	2.6	—
512	4.3	3.7
540	5.4	4.2
608	2.2	1.4

In Figure 3, helium and argon permeabilities, and their temperature dependence, are compared for unstretched and necked film. It is found that elongation to 490% results in roughly a 20% decrease in helium permeability, a nearly 40% decrease in argon permeability, and very little change in permeability activation energy for either gas. This result is anomalous, since a change in geometric diffusional impedance on stretching should alter the permeability to each gas equally, while a change in chain immobilization would be expected to alter both absolute and relative permeabilities and also the activation energies. It is deduced from the observations that necking reduces the mean crystallite size to a point where the interstitial amorphous regions are divided into elements of dimensions comparable to those of the activation zone for diffusion of the gas molecules. Under these circumstances, many of the intercrystalline passages are virtually completely blocked to passage of helium and argon molecules, with less blockage

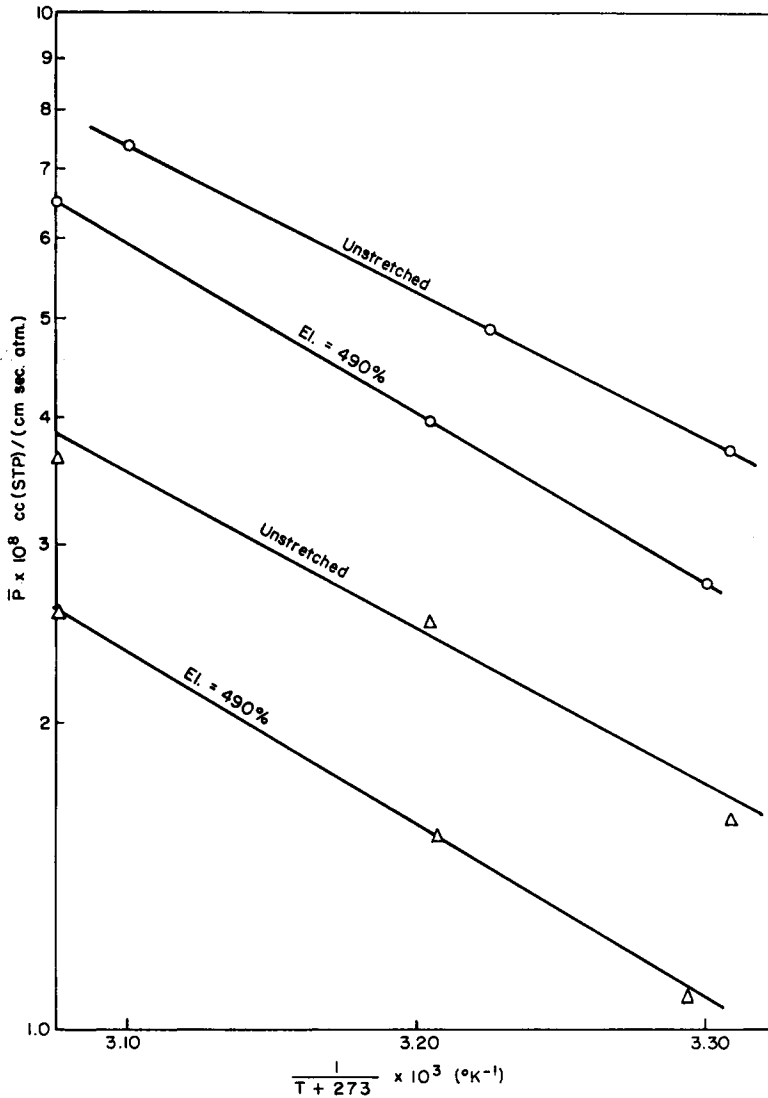


Fig. 3. Permeability constant vs. reciprocal temperature: (O) helium; (Δ) argon.

of the smaller molecule. Such a graded molecular sieve would exhibit the observed reduced permeability and enhanced selectivity with respect to molecular size, without a corresponding alteration in diffusion activation energies.

When necked polymer is further elongated, marked changes occur both in gas permeabilities and in activation energies, as shown in Figures 4-6. At 512% elongation, helium permeability (relative to unstretched polymer) drops by about 40%, argon, by about 70%, and methane, by about 70%.

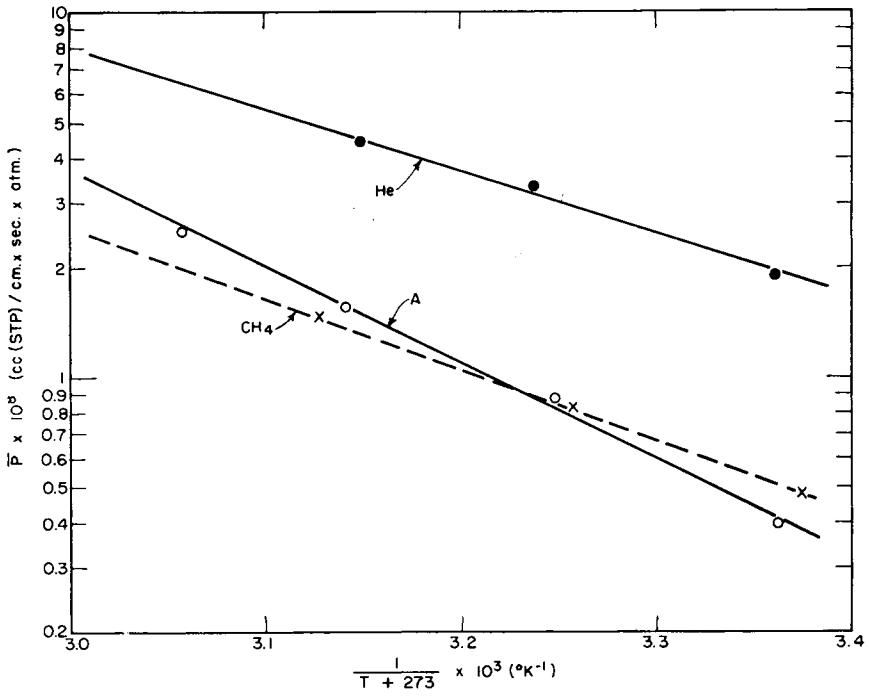


Fig. 4. Permeability constants vs. reciprocal temperature at 512% elongation: (●) He; (O) A; (X) CH₄.

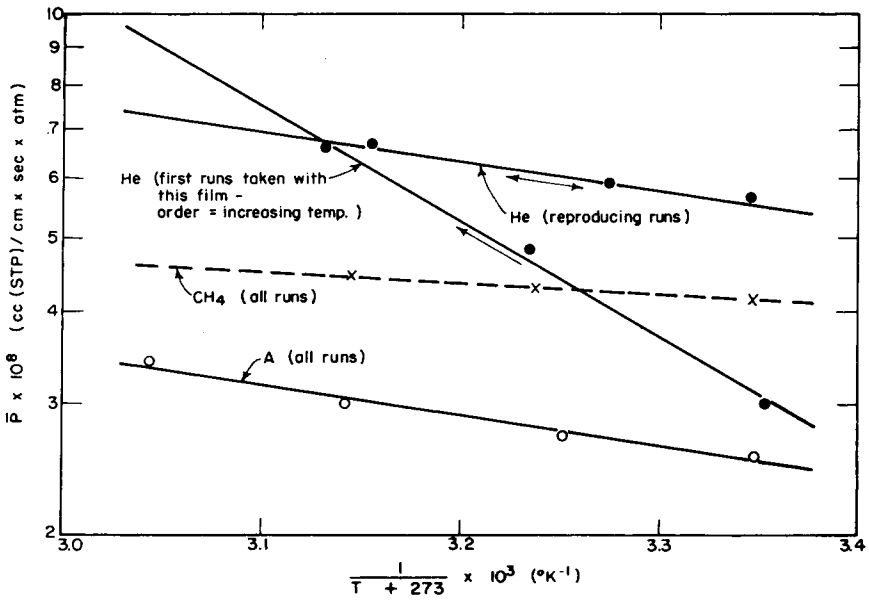


Fig. 5. Permeability constants vs. reciprocal temperature at 608% elongation: (●) He; (O) A; (X) CH₄.

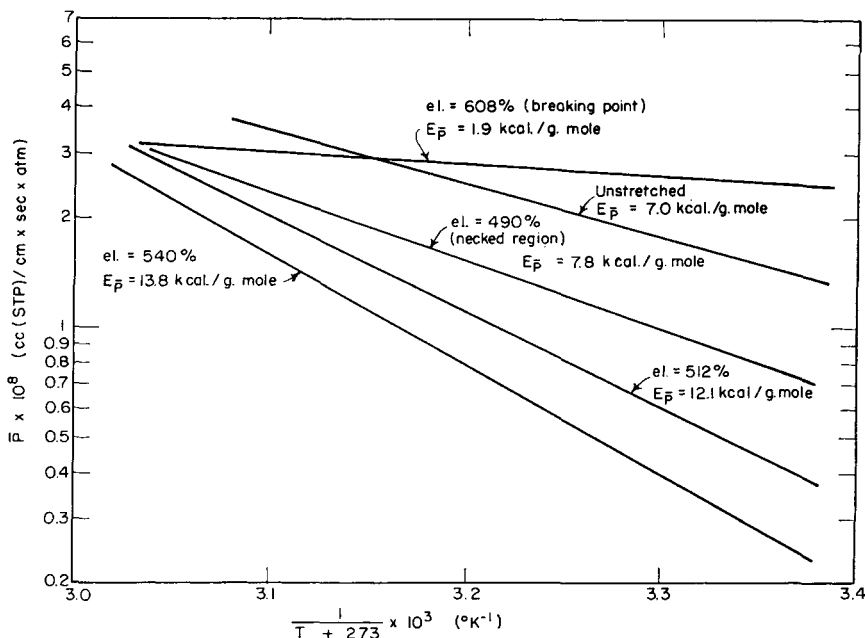


Fig. 6. Argon permeability constants vs. reciprocal temperature.

Corresponding changes in activation energies for the three gases are, respectively, +0.6 kcal., +5 kcal., and +4 kcal.

As elongation is increased to 540%, permeabilities continue to decrease and activation energies, to increase, with a consequent marked rise in the film permselectivity to helium relative to argon and methane. (The near-equality of film permeability to argon and methane, and the higher permeation energy of the former despite the larger size of the methane molecule, merely reflects the much higher solubility of methane in the polymer relative to argon and its large positive heat of solution.) At an elongation just short of the breaking point (608%) permeability measurements become unreproducible, as illustrated in Figure 5. The initial (rising temperature) series with helium yielded low permeability values which increased exceedingly rapidly with temperature, suggesting an anomalously high activation energy. However, when the sample temperature was reduced, the measured permeabilities remained high, and were only slightly temperature-dependent ($E_{\bar{p}} \cong -1.9$ kcal.). Subsequent measurements with this film, with argon and methane as penetrants, also yielded anomalously high permeabilities and low activation energies. These results are most readily explained by postulating that the thermal stresses introduced into the highly strained film during the permeation measurements caused microscopic fibrillation of the polymer, with formation of minute cracks which traversed the film thickness. Knudsen diffusion would occur in such a crack, thereby elevating the permeability, and dropping the activation

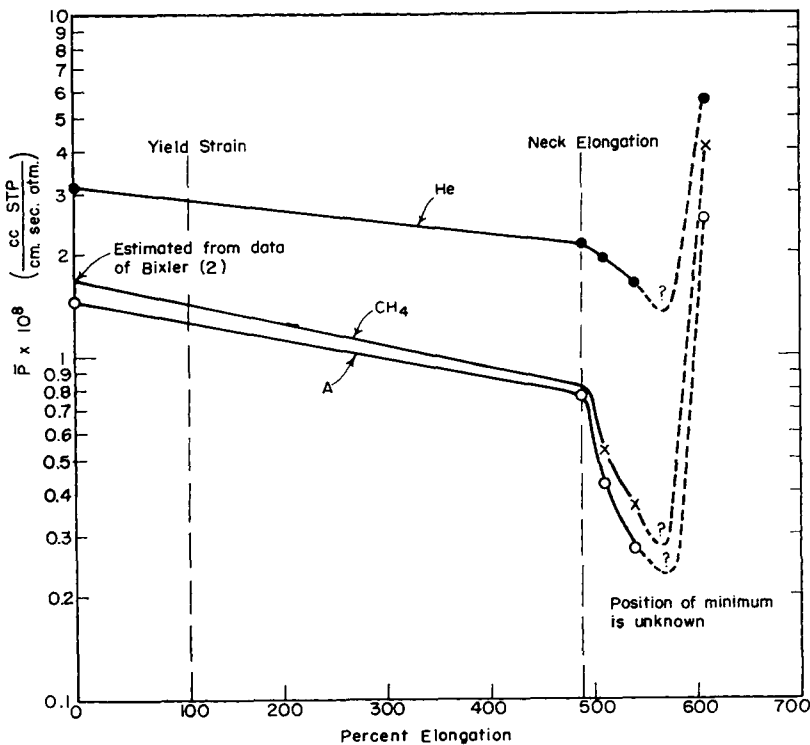


Fig. 7. \bar{P} vs. elongation at 25°C.: (●) He; (○) A; (×) CH₄.

energy. The small but detectable increase in apparent polymer density (measured by fluid displacement) before and after the permeation measurements (Table II) supports this postulate, since microcracks might be expected to propagate from microvoids generated within the polymer during stretching. Microvoids not in direct communication with the film surface would be inaccessible to the gradient column fluid, and would be responsible for a low apparent polymer density.

The salient results of this study are graphically summarized in Figures 7 and 8, as plots of \bar{P} (at 25°C.) and $E_{\bar{P}}$ as functions of elongation. The most striking—and rather unexpected—feature of these data is the extremely large change in permeability and in activation energy for permeation which occurs on stretching of drawn (necked) film. These changes take place over a very narrow strain interval, representing only about 10% elongation of necked polymer. In light of the fact that a nearly 500% elongation of the original film causes only relatively small changes in permeability, it seems hardly likely that changes in crystalline morphology are reasonable for the major alterations in gas transmission behavior which occur over the remaining 10% elongation. A more plausible explanation is likely to be found in the changes in amorphous phase structure which occur over this interval: In necked polymer, there already exists a very high de-

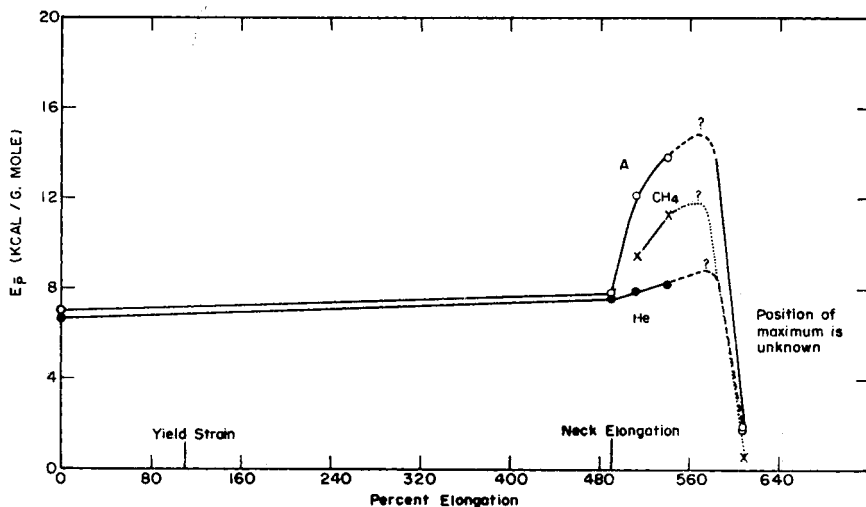


Fig. 8. E_p vs. elongation: (●) He; (○) A; (×) CH₄.

gree of unidirectional orientation of polymer chains, and considerable restraint on amorphous segment mobility imposed by the small, highly ordered fibrillar crystallites. When subjected to further strain—even of small magnitude—segmental motion in the already highly ordered amorphous regions is severely limited. (Indirect support of this picture is provided by the observed marked increase in elastic modulus when necked polymer is further elongated.) Such extreme limitation of segment motion will, according to activated diffusion theory, lead to precisely those changes in gas transmission properties which are experimentally observed: viz., greatly reduced permeability to all gases, increased permselectivity with respect to gas molecular dimensions, and increased diffusion activation energies. It would be of interest to study the infrared red and nuclear magnetic resonance spectra of highly stretched, highly crystallinity polymers, since such analyses should reveal more directly those chain conformational features which we infer from gas permeation studies.

In summary, the gas permeability reduction which occurs on necking of ethylene-butyl maleate copolymer films is relatively small and appears to be due to a rather complete reorganization of the crystalline phase and formation of a more discriminating "molecular sieve" for gas molecules. Further stretching of necked film leads to marked decreases in gas permeability and increases in activation energy for permeation, which appear to be due to strain-imposed restraints on molecular motion in noncrystalline regions of the polymer. Highly (uniaxially) stretched crystalline polymers are, therefore, likely to be superior gas barriers and to exhibit enhanced permselectivity to penetrants of differing molecular dimensions.

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Résumé

On a étudié l'effet d'une orientation maximale sur la perméabilité des gaz à travers des films de copolymère de maléate de dibutyle et d'éthylène. On a utilisé comme gaz l'hélium, l'argon et le méthane. On a déterminé l'effet de la température sur les constantes de perméabilité entre 25 et 55°C. Ces mesures ont été effectuées sur le film non-étiré et sur le film étiré à 490, 512, 540, et 608% (point de rupture). L'étrépage à froid (maximal) de copolymère d'éthylène et de maléate de dibutyle poussé jusqu'à la région d'étrépage stable c.à.d. après formation de l'étranglement (élongation de 490%) cause seulement une petite diminution (30%) de la perméabilité et ne change pas virtuellement l'énergie d'activation du phénomène; quand ces films étirés sont allongés jusqu'à un point proche du point de rupture (600%), on observe une diminution très nette de la perméabilité et une augmentation de l'énergie d'activation. On en conclut que les changements majeurs intervenant dans la structure cristalline et dans l'arrangement des chaînes qui affectent le polymère lors de la formation de l'étranglement dans le processus d'étrépage à froid, ont seulement un effet mineur sur le taux de cristallinité, sur les propriétés de la phase amorphe et sur la résistance à la diffusion offerte par les cristallites. Ceci suggère qu'il y a compensation entre les changements intervenant dans l'orientation des cristallites, leur perfection et leur forme durant le processus de filage. Lorsque le polymère étiré (jusqu'à après formation de l'étranglement) est soumis à un étrépage plus poussé, on doit admettre que l'on introduit une diminution très importante de la mobilité des chaînes dans les régions amorphes qui serait surtout responsable des changements importants intervenant dans la perméabilité et dans l'énergie d'activation du phénomène.

Zusammenfassung

Der Einfluss von extrem uniaxialer Orientierung auf die Gaspermeation durch Dibutylmaleatäthylen-Copolymerfilme wurde untersucht. Die verwendeten Gase waren Helium,

Argon und Methan. Die Permeabilitätskonstanten wurden als Funktion der Temperatur zwischen 25 und 55°C. in ungedehntem und in bis zu einer Elongation von 490, 512, 540, und 608% (Reisspunkt) gedehntem Film gemessen. Uniaxiale Kaltreckung von Dibutylmaleatäthylen-Copolymerfilmen bis zum stabilen "Einschnür"-Bereich (Elongation ca. 490%) verursacht nur eine geringe Abnahme (30%) der Permeabilität und praktisch keine Änderung der scheinbaren Aktivierungsenergie der Permeation; wenn die "eingeschnürten" Filme weiter zu Elongationen nahe des Reisspunktes (ca. 600%) gedehnt werden, so wird eine deutliche Abnahme der Permeabilität und Zunahme der Aktivierungsenergie beobachtet. Es wird geschlossen, dass die grossen Änderungen der kristallinen Textur und Anordnung, denen das Polymere im "Einschnür"-Prozess unterworfen ist, nur einen geringen Einfluss auf das gesamte Kristallinitätsniveau, Eigenschaften der amorphen Phase und Diffusionsimpedanz durch die Kristallite haben und dass die Änderungen der Kristallitorientierung, -vollkommenheit und -gestalt während des Ziehens sich gegenseitig kompensieren. Bei weiterer Reckung des eingeschnürten Polymeren wird die Beweglichkeit der orientierten Kettensegmente im amorphen Bereich stark behindert, was in erster Linie für die beobachteten grossen Änderungen der Permeabilität und der Permeationsaktivierungsenergie verantwortlich ist.

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