Sorption and Flow of Gases in Polyethylene

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INTRODUCTION

Transport and equilibrium phenomena in polymers are of interest in characterizing plastic films as barriers to gases and vapors, and, in addition, the study of these phenomena can yield valuable information on molecular motions and on polymer structure. This work was undertaken to investigate the relations between the structure of polyethylene, the fabrication history of the polymer sample, and the sorption and flow behavior of noncondensable gases.

For the steady flow of a noncondensable gas through a plane sheet of polymeric material, a permeability constant may be defined as

$$J = \bar{P}(p_1 - p_2)/L \tag{1}$$

with J being the flow rate per unit area, $\bar{P}$ the permeability constant, L the sheet thickness, and p_1 and p_2 the gas partial pressures at the inflow and outflow faces, respectively. While $\bar{P}$ is a useful index of the barrier properties of the sheet, the obeyance of this expression is not particularly informative as to mechanism, and $\bar{P}$ is often difficult to correlate directly with gas-polymer properties. The slowness of the flow process generally permits the use of an equilibrium relationship between the concentrations of sorbed gas at the interfaces and the respective partial pressures. For gases in a number of polymers, the equilibrium relation has been shown to be a linear one,[1,4] or

$$C = kp \tag{2}$$

where C is the sorbed gas per unit volume and k is the solubility constant. As a consequence, the permeability can be defined as the product of k and the diffusion constant D.[1,4] The latter quantity is defined by the expression

$$J = -D(\partial C/\partial x) \tag{3}$$

with x the distance normal to the plane of the sheet. While more difficult to obtain experimentally, values of D and k appear to be considerably more informative than those of $\bar{P}$ alone.

In this work, values of $\bar{P}$, D, and k were obtained on a series of carefully prepared polyethylene samples, where the molecular structure and sample fabrication history were well known.   Particular attention was paid to the effect of the polymer short chain branching frequency on crystallinity, and the effect of the crystallinity, in turn, on the flow mechanism.

PROCEDURE

Molded polymer sheets having uniform thicknesses ranging from 0.010 to 0.020 in. were prepared on a small laboratory press from polymers of varying branching indices.   Thin sheets of Du Pont's Mylar polyester film were used to separate the polymer from the metal press platens.   The polymer was held for 15 min. at a temperature well above the crystalline melting temperature in order to minimize "memory" effects.   Crystallization was carried out over a period of 1–5 min. at a temperature 10–20°C. below the melting point by gradually reducing the press temperature.   This procedure was found to be quite reproducible for a given polymer, both as to sample density and permeability.   Alternatively, quenched sheets could be prepared by introducing cold water into the press platens.   Still more highly quenched sheets of linear polyethylene were also employed, these having been prepared by flat-die casting continuously onto a quench drum.   Properties of the different polyethylenes used to prepare these samples are given in Table I.

TABLE I
Properties of Polyethylenes Used[a]

Polymer	Process	CH₃/ 100 C	$\bar{M}_n$	$\bar{M}_w$	Melt index
Grex olefin polymer, Lot 0126– 1X, W. R. Grace & Co., Poly- mer Chemicals Div.	Phillips	0.15[b]	40,000[c]		0.62
Super Dylan, Koppers Co.	Ziegler	0.3[b]			
Alathon-34, E. I. du Pont de Nemours & Co.	High pressure	1.0	30,000	300,000	3.3
P-76 experimental polyethyl- ene, E. I. du Pont de Ne- mours & Co.	High pressure	1.6	32,000	370,000	2
Alathon-14, E. I. du Pont de Nemours & Co.	High pressure	3.0	26,000	900,000	1.7

[a] Data for high pressure samples supplied by Research Division, Polychemicals De- partment, E. I. du Pont de Nemours & Co. and for Grex by W. R. Grace & Co.

[b] Data of Myers et al.[11]

[c] Estimated from polymer melt index.

The permeability and diffusion constants were obtained by a modifica- tion of the dynamic technique as described by Barrer,[4] known as the time- lag method.   The determination of the diffusivity by this method depends on the applicability of an unsteady-state diffusion expression, commonly

referred to as Fick's second law. D can be calculated from the time lag for diffusion as

$$D = L^2/6\theta \qquad (4)$$

where L is the sheet thickness and θ the time lag. Solubility constants could be obtained in this way as the ratio of $\bar{P}$ to D. In order to complement these results, solubility constants were obtained directly on polymer in pellet form by a method which was developed for the purpose, and which has been recently described.[10] This latter method permitted determination of k to within about 5%, an accuracy which is considerably better than that found possible by the dynamic method. In addition, the results do not depend on the assumption of any flow expression. Conventional methods of studying sorption equilibria were not applicable to the present problem because of the very small amounts of gas taken up by the polymer.

The gases used in this study were nitrogen, oxygen, carbon dioxide, and helium.
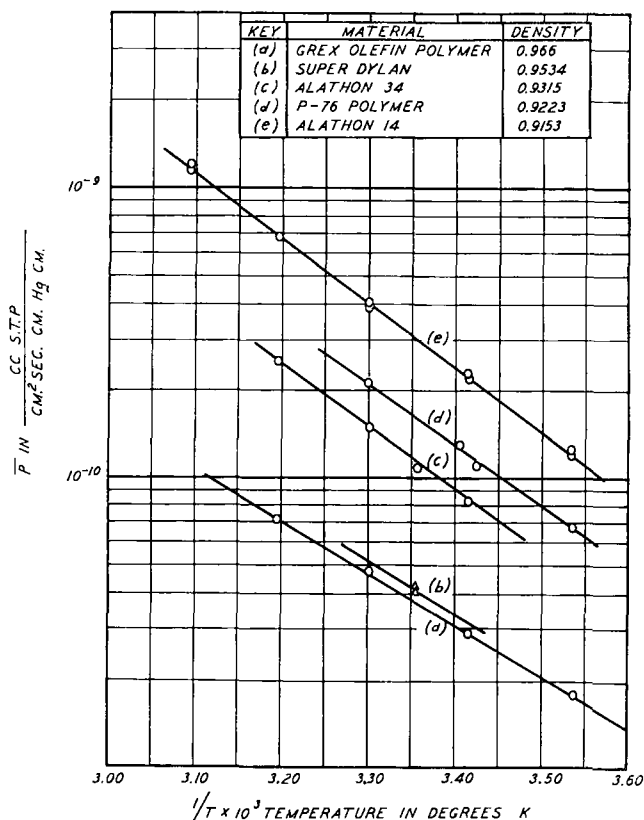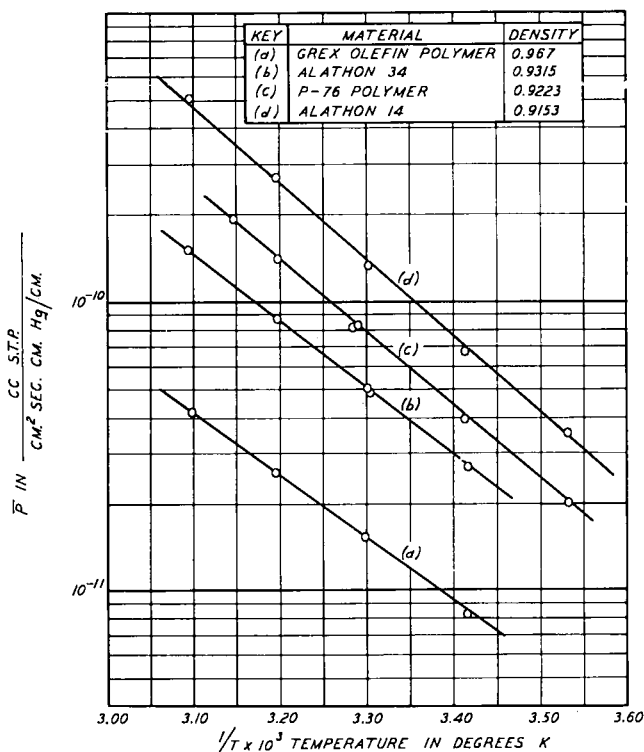

KEY	MATERIAL	DENSITY
(a)	GREX OLEFIN POLYMER	0.966
(b)	SUPER DYLAN	0.9534
(c)	ALATHON 34	0.9315
(d)	P-76 POLYMER	0.9223
(e)	ALATHON 14	0.9153

Fig. 1. O_2.

KEY	MATERIAL	DENSITY
(a)	GREX OLEFIN POLYMER	0.967
(b)	ALATHON 34	0.9315
(c)	P-76 POLYMER	0.9223
(d)	ALATHON 14	0.9153

Fig. 2. N_2.

RESULTS AND DISCUSSION

Figures 1 and 2 are Arrhenius-type plots of oxygen and nitrogen permeability constants* for a series of molded samples prepared by the slow cooling procedure. Data are given for linear polyethylene and for several polymers having progressively greater short chain branching frequencies, as shown in Table I. There is a systematic decrease in the sample density and crystallinity due to the restrictions imposed on the crystallization process by the short chain branches, with an accompanying increase in $\bar{P}$. Alternatively, Figures 3 and 4 present data for the same gases in sheets prepared from linear polyethylene, where the sample density has been progressively reduced by controlling the degree of quenching from the melt. A cross plot at 25°C. of results of this type is given as a correlation diagram in Figure 5, where the effect of the two approaches for limiting the sample crystallinity may be seen. The volume fraction of amorphous polymer (designated α) was calculated directly from the measured sample densities, reported values[4] being used for the specific volumes of crystalline and amorphous polyethylene ($v_c = 1.003$, $v_a = 1.171$ cm.^{3}/g. at 25°C.). Dotted lines have been

* Numerical data obtained in this work are on file with the National Archives Association.
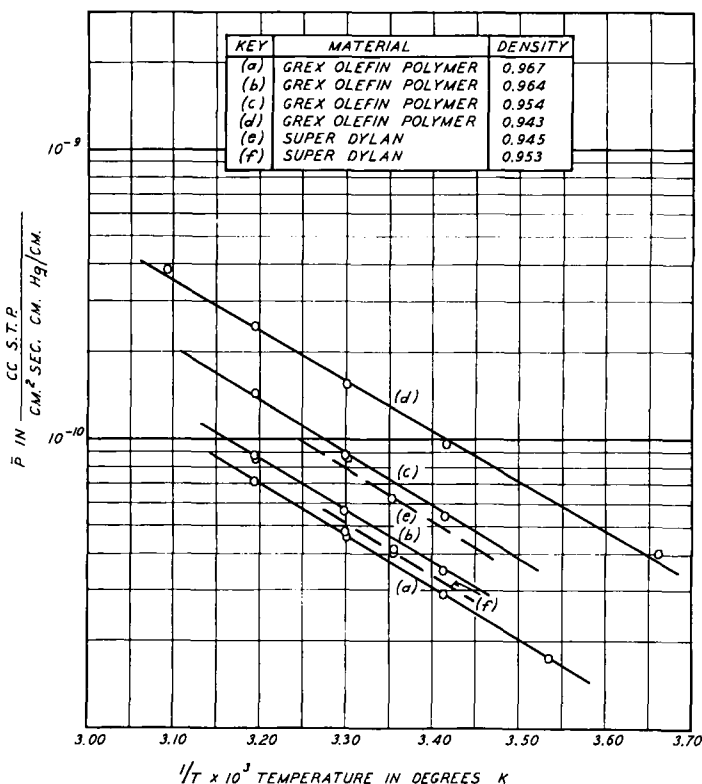
Fig. 3. O_2.

used to connect the points representing data for samples made from a given polymer at various cooling rates, and solid lines to connect points for the molded samples of different polymers. These results reveal clearly that the rates of flow cannot be related simply to the crystalline content, and that, for the gases studied, shock-cooled sheets tend to have the higher permeabilities.

Figures 1–4 show that varying the sample crystallinity in linear polyethylene has little effect on the temperature dependence of the permeability, and that in branched polyethylene the temperature dependence of $\bar{P}$ is somewhat greater than for the linear polymer. This latter effect has been noted previously[12,13] and explained as due to the increase in diffusional activation energy caused by the short chain branches. It is necessary, however, to account for an increase in activation energy of 1500–2000 cal./mole. In view of the infrequency of these branches (Table I), an alternative explanation is offered. Table II gives values of α at several temperatures for a branched polyethylene, calculated from recently reported dilatometric data on the variation of specific volume with temperature for a branched polyethylene.[7] A comparison of this result with Figure 5 indicates that the melting of the crystallites over the temperature range
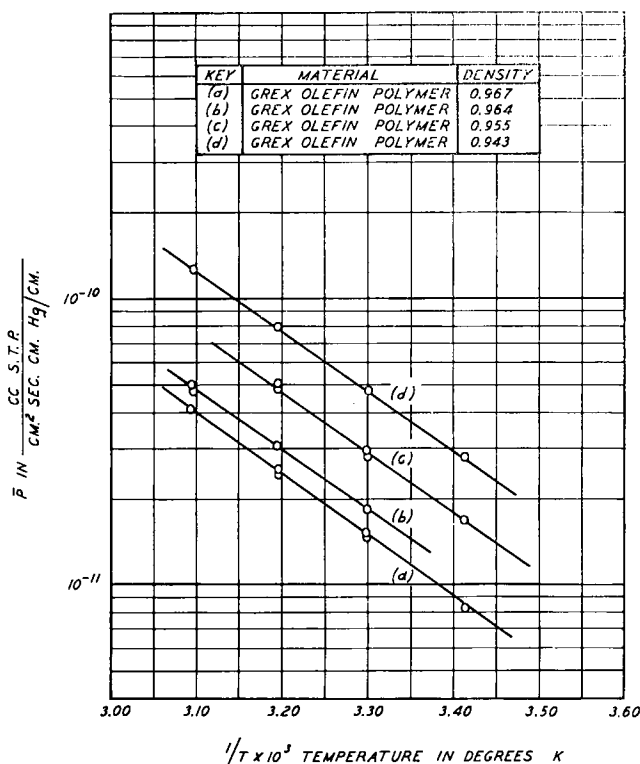
Fig. 4. N_2.

studied is indeed sufficient to explain the higher temperature dependence of the permeability in branched polyethylenes. For linear polyethylene, the dilatometric data of Tung[14] imply that the loss of crystallinity in the range 20–50°C. is negligible; in this case, the temperature variations of D and k can be used to calculate a diffusional activation energy and a gas-polymer heat of solution, respectively.

TABLE II
Variation of α with Temperature for a High Pressure Polyethylene[a]

Temperature, °C.	Volume fraction amorphous polymer, α
20	0.556
30	0.563
40	0.557
50	0.593

[a] Data of Carman.[7]

Figure 6 presents solubility constants at 25°C. obtained by the two different experimental approaches. Those obtained by the static method were for polymer in pellet form, and those obtained dynamically were cal-
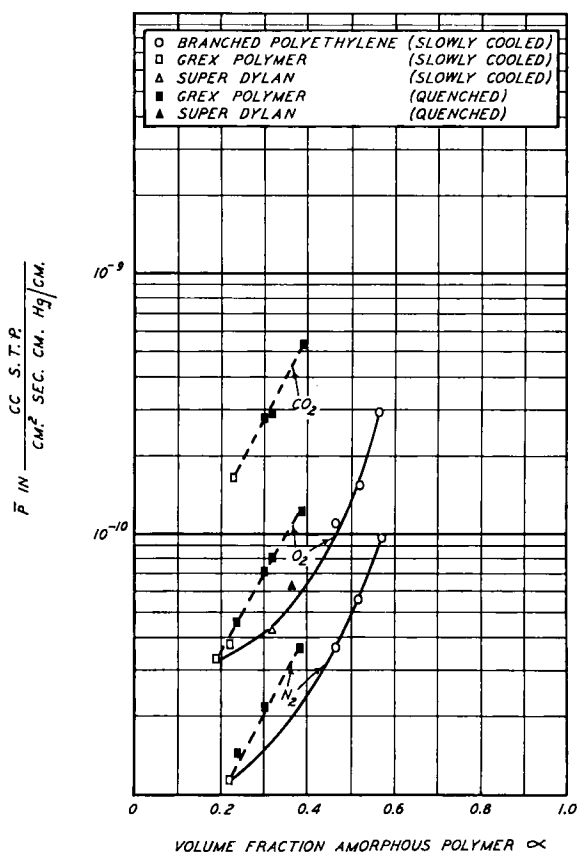
Figure 5.

culated as the ratio of values of $\bar{P}$ to D, these values being taken from plots of the type shown in Figures 1 and 7. Data are given for nitrogen and oxygen, and a similar result was obtained for carbon dioxide, which extrapolated to 0.46 cm.^{3} STP/cm.^{3} atm. at α = unity. The mean deviation of the experimental points from the linear correlation is about $\pm 8\%$, which is believed to lie well within the limits of accuracy of the time-lag solubility measurements.

A few scattered values were obtained for helium which are not reported, although the static method appears capable of determining k for this gas with reasonable accuracy. In spite of the wide variation of polyethylene types and methods of sample fabrication, the data for each gas can be expressed as

$$k = \alpha k^* \tag{5}$$

with the values of k^* not far from those reported for the solubility constants for the same gases in a series of hydrocarbon rubbers (e.g., 0.097, 0.45, and 1.00 cm.^{3} STP/cm.^{3} atm. at 25°C. for O_2, N_2, and CO_2 in polybuta-
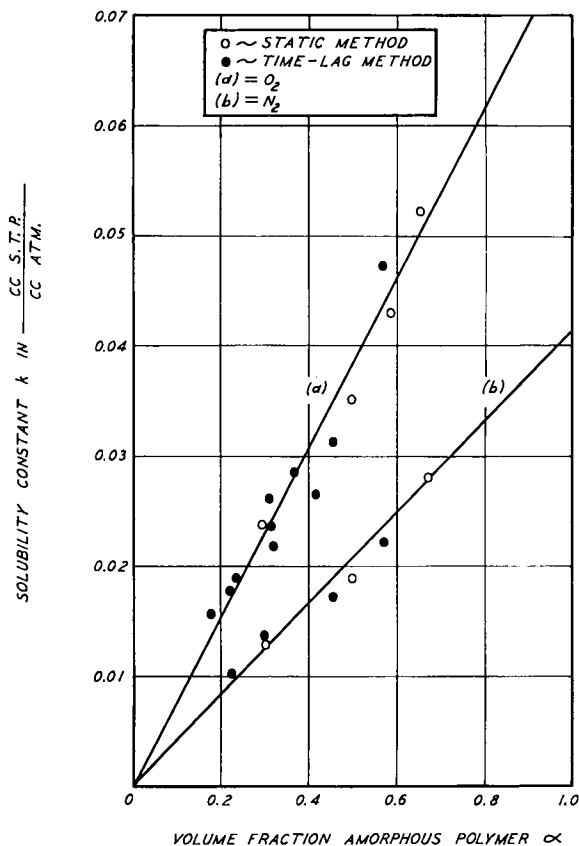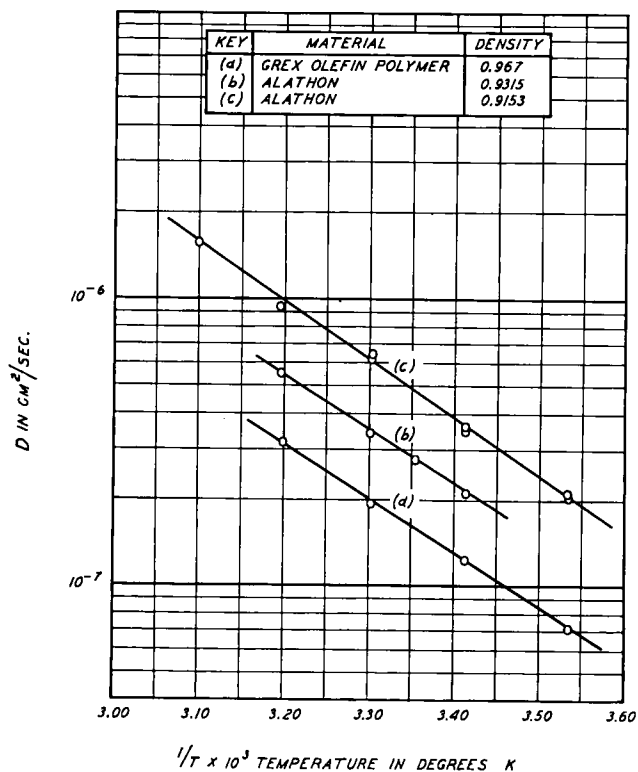
Figure 6.

diene, respectively[3]). These results clearly suggest that, for the present purpose, the concept of polyethylene as composed of distinct crystalline and amorphous phases is a useful one, and that the crystalline material acts toward the lighter gases as an impermeable dispersed phase. The size of the individual crystallites should not influence gas solubility as long as the dimensions of the intercrystalline (amorphous) regions are considerably larger than the solute molecules. Furthermore, these results lend support to the hypothesis that the amorphous phase in polyethylene is virtually uninfluenced by branching frequency or thermal history.

From the solubility constants at several temperatures for linear polyethylene as determined by the static method, heats of solution of -700 ± 300 cal./mole and $+1000 \pm 300$ cal./mole for oxygen and nitrogen, respectively, were calculated. The values determined by the time-lag method for linear polyethylene are in reasonable agreement with the above values. For carbon dioxide and linear polyethylene, the time-lag results indicate a ΔH of -1500 ± 800 cal./mole. Van Amerongen has reported -2800 cal./mole for CO_2 in natural rubber.[3]

KEY	MATERIAL	DENSITY
(a)	GREX OLEFIN POLYMER	0.967
(b)	ALATHON	0.9315
(c)	ALATHON	0.9153

Fig. 7. O_2.

Solubility-temperature data were not obtained for the branched poly-ethylenes by the static method.   However, the values of the heat of solu-tion for the branched polyethylenes calculated from the time-lag values of the activation energies for permeation and diffusion suggest that this difference is larger in the positive direction than that for linear polyethylene. This observation is in accord with the crystalline melting behavior pre-viously discussed and with the direct relationship between k and α. A heat of solution calculated from the temperature dependence of k which does not take into account the increase in α shown in Table II, provided that the calculation of ΔH is based on the temperature interval 20–50°C., will be in error by about +500 cal./mole.   It is to be noted that this error is equal to about 50% of the true value for oxygen and nitrogen, and any thermodynamic interpretation making use of ΔH and failing to account for the changes in α would be in serious difficulty.   The rather small values of the heat of solution for the permanent gases make this effect readily apparent and suggest that careful gas sorption measurements should provide a valuable tool to supplement dilatometry in the study of crystalline melting behavior.

From the above results, it is evident that the failure of the permeability

constants to correlate directly with α lies with the behavior of the diffusivities.   Figure 7 presents typical results for D obtained from the time-lag data.   In all cases, the data could be represented by an Arrhenius-type expression, although for the branched polymers the effect of crystalline melting is such that the obeyance is probably approximate and without theoretical significance.   Branched polymers showed an apparent activation energy 1000–1500 cal./mole greater than that for linear polyethylene; for the latter material, the activation energy did not vary with sample

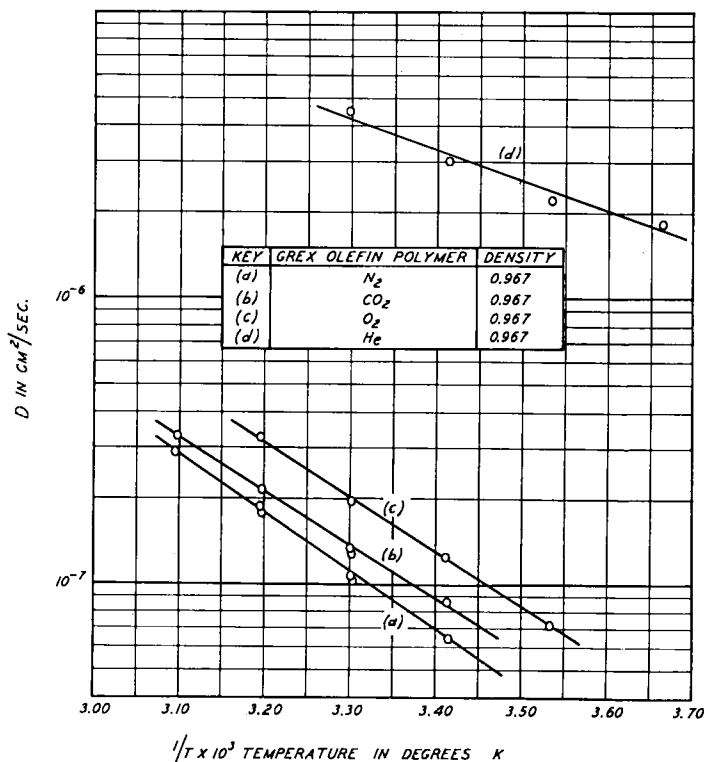| KEY	GREX OLEFIN POLYMER	DENSITY
(a)	N_2	0.967
(b)	CO_2	0.967
(c)	O_2	0.967
(d)	He	0.967

Figure 8.

crystallinity within the limits of experimental error.   Figure 8 shows the results for oxygen, nitrogen, carbon dioxide, and helium diffusing in a single sample of linear polyethylene, the CO_2 molecule apparently displaying an effective molecular size for diffusion which is intermediate between those of nitrogen and oxygen.   The high permeability of carbon dioxide relative to oxygen is due to its much higher solubility constant.   Helium diffuses very rapidly, but has an extremely low k, with a resulting permeability quite close to that of CO_2.

An explanation must now be sought for the marked dependency of the

gas diffusivities upon the crystalline content of polyethylene and upon the thermal history of the polymer.   At least two possibilities are apparent.

(1) The crystalline component of the polymer functions as an impermeable, dispersed phase, thereby constraining the gas molecules to move through irregular, constricted amorphous polymer conduits in the intercrystalline regions.   That is to say, the polymer may be considered as a "porous medium," the particles of which are the crystallites and the "pores" of which comprise the amorphous phase.   The impedance offered to diffusional transport by such a two-phase structure can be shown to depend only upon the geometry of the impermeable phase (i.e., particle shape and orientation) and its volume concentration and to be independent of the particle size (provided that the interparticle clearances are large relative to the molecules of the diffusing species or the diffusing component).

(2) The crystallites may reduce polymer chain-segment mobility in the interstitial amorphous phase, thereby raising the energy barrier for diffusional transport of gas molecules.   Clearly, this effect will manifest itself in an increased activation energy for diffusion and will be more pronounced for larger gas molecules.   Furthermore, the degree of segment immobilization will become greater as the volume fraction of crystalline phase increases and/or the average crystallite size decreases.

For the gases studied here, sufficient data are available to make possible an estimate of the magnitudes of each of these effects.

In dealing with polyethylene as a kind of porous medium one can borrow from the classical physics of flow through porous solids[15] an expression for the electrical conductivity of a porous plug whose voids are filled with conducting fluid, and write a completely analogous expression for steady-state gas-permeation in a crystalline polymer:

$$J = (\alpha'D^*/\tau)(C'_1 - C'_2)/L = (\alpha'D^*/\tau)(dC'/dx) \qquad (6)$$

where α' is the area fraction of amorphous material taken normal to the direction of flow and D^* is the diffusivity of the gas in completely amorphous polymer.   The variation in D^* with short chain branching in the samples studied is believed small and is neglected henceforth. C' refers to the point concentration of gas expressed as amount sorbed per unit volume of amorphous polymer.   The quantity τ, commonly called the "tortuosity factor," accounts for the impedance to flow offered by the irregular intercrystallite passages.   Estimation of the tortuosity factor from a knowledge of the geometry of a two-phase system is, unfortunately, not yet possible; it is significant, however, that measured tortuosity factors in porous media composed of essentially isometric particles lie in the range of 1.3–1.6, even when the volume fraction of impermeable phase is as high as 0.80.[7]   In highly consolidated, porous media and in those composed of anisometric particles, diffusional tortuosities as high as 30 are reported.   Wyllie and Gardner[16] further point out that the major contribution to tortuosity is undoubtedly the impedance to flow offered by variations in pore cross section rather than that offered by increased effective path length.

For unsteady state flow through a slab in which the local diffusional flux is given by eq. (6), it can be shown that

$$\alpha'(D^*/\tau)(\partial^2 C'/\partial x^2) = \alpha(\partial C'/\partial t) \tag{7}$$

For a randomly dispersed system showing diffusion isotropy, the area and volume fractions are the same, and $\alpha' = \alpha$. Solution of eq. (7) for the time-lag problem leads to the result that

$$D = D^*/\tau = L^2/6\theta \tag{8}$$

indicating that the time-lag result reflects the effect of tortuosity only. Since the solubility data show that $C' = k^*p$, the permeability constant can be thought of as

$$\bar{P} = \alpha D^* k^*/\tau \tag{9}$$

Examination of eqs. (8) and (9) indicates that it is natural that the static and dynamic approaches should lead to the same result for the solubility constant in a sheet of unoriented, crystalline polymer. The obeyance of the one-dimensional diffusion expression implies continuity of flow in the amorphous regions.

Evidence for the effect of the crystallites in restricting polymer chain mobility in the amorphous regions can be obtained through examination of the variation with crystallinity of the selectivity for permeation to gases having different molecular sizes. If the effect of the crystallites were solely that of an impermeable filler, the ratios of the permeability constants for any gas pair should be the same in all the polyethylene samples. The data given in Table III show that this constancy of selectivity holds for

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TABLE III

Selectivity Ratios of the Permeability
Constants for the Gas Pairs Indicated at 25°C.

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Polymer	Sample density, g./cm.^{3}	Selectivity ratios			
		O_2/N_2	He/N_2	He/O_2	He/CO_2
Grex olefin polymer	0.967	3.27			
"	0.955	3.23	8.5	2.64	0.645
"	0.953	3.34	8.35	2.51	0.522
"	0.943	3.38	7.95	2.3	0.527
Alathon 34	0.9315	3.14	7.5	2.15	
Alathon 14	0.9153	3.0			
Rubber[a]		2.9	3.88	1.34	0.238

[a] Data of van Amerongen.[2]

nitrogen and oxygen, where the molecular sizes are not very different, but that when helium is paired with either of the diatomic molecules, the selectivity to helium increases slightly with the increasing polymer crystallinity. Upon comparing these data with results for the same gases in a series of

crosslinked rubbers,[5] we can estimate that the effect of restricted chain mobility reduces D^* for nitrogen and oxygen by a factor of about 2.5, but that for helium this effect is very small.   It is expected that the magnitude of the effect will increase rapidly with the molecular size of the penetrant. In view of these observations, it becomes necessary to modify eq. (9) as follows:

$$P = \alpha D^* k^* / \tau \beta \qquad (10)$$

The quantity β may be called the chain-immobilization factor; in the same way that $(1/\tau)$ represents the fractional reduction in diffusivity arising from the geometric impedance offered by the crystallites, so $(1/\beta)$ represents the fractional reduction in diffusivity attributable to restriction of chain movement in the amorphous phase.   It should be noted that, at constant α, while τ is temperature-independent, β varies exponentially with temperature as do D^* and k^*.

Data have been recently reported on the nitrogen permeability of a lightly irradiated polyethylene at temperatures above the crystalline melting point.[11,12]   These values can be extrapolated to room temperature and combined with the values for k obtained here, which makes it possible to estimate D for a completely amorphous polyethylene as 1.0×10^{-6} cm.^{2}/-sec. at 25°C.   A corresponding value for oxygen would be 1.3×10^{-6} cm.^{2}/sec.   It is therefore necessary to account for a combined effect of tortuosity and chain-movement restriction which reduces the diffusivity by a factor of 15 in some of the samples studied in this work.

If it is assumed that the chain-segment immobilization contribution to (a) the diffusivity of helium in polyethylene and (b) that of helium, oxygen, and nitrogen in rubber is negligible, it is possible from the selectivity ratios of the Table III to estimate this contribution to the diffusivities of oxygen or nitrogen.   From eq. (10) the value of the tortuosity, τ, then follows directly.   Such calculations are summarized in Table IV for oxygen at 25°C.   Inspection reveals that β increases more or less regularly as α decreases, a trend entirely consistent with the proposed mechanistic origin of that quantity.   The tortuosity factor τ shows a similar tendency to increase with decreasing α, although a dependency upon the type of polyethylene is also apparent.   It is significant that τ is never less than about 2.0 and attains a value of nearly 6 for Super Dylan.   Inasmuch as the value of τ lies in the vicinity of 1.5 for porosities as low as 0.20 for porous beds comprised of irregular but essentially isometric particles, the conclusion that the crystallites in polyethylene are highly anisometric seems virtually inescapable.

From some rather simple theoretical considerations it is possible to arrive at an estimate of the degree of anisometry of the crystallites.   Maxwell derived an equation for the electrical conductivity of a dispersion of nonconducting spheres in a conducting medium as a function of the volume concentration of spheres, from which it can readily be shown that the ratio

TABLE IV

Estimated Tortuosity Factors for Various Polyethylenes

Polymer	Density d_{20}^{25}, g./cm.^{3}	α	O_2 permeability at 25°C., STP × cm. cm.^{2} sec. cm. Hg × 10^{11}	Effective O_2 diffusivity at 25°C., cm.^{2}/sec. × 10^7	β	τ
Grex (molded)	0.967	0.22	3.8	1.6	2.5[a]	3.3
Grex (molded)	0.965	0.24	4.6	1.9	2.4[a]	2.9
Grex (molded)	0.955	0.30	7.3	2.4	2.0	2.7
Grex (blown)	0.953	0.31	6.6	2.1	1.9	3.5
Grex (cast)	0.943	0.39	13.3	3.4	1.7	2.3
Super Dylan (molded)	0.953	0.31	4.2	1.3	1.9[a]	5.1
Super Dylan (molded)	0.945	0.37	6.6	1.8	1.8[a]	4.1
Alathon 34 (molded)	0.931	0.46	11.8	2.5	1.6	3.2
P76 (molded)	0.922	0.52	16.0	3.0	1.4[a]	3.1
Alathon 14 (molded)	0.915	0.57	31.0	5.4	1.2	2.0
Amorphous polyethylene	0.859	1.0	—	13.0[a]	1.0	1.0

[a] Estimated.

of the resistivity of the dispersion to that of the medium (the analog of τ/α) varies with the volume fraction of conducting phase (the analog of α) as follows:

$$\tau = [1.5 - (\alpha/2)] \qquad (11)$$

Fricke has further shown that if the particles are oblate or prolate spheroids, the more general relation between τ and α is

$$\tau = 1 + [(1 - \alpha)/X] \qquad (12)$$

where X is a constant for a given shape of particle, whose magnitude decreases as departure from sphericity increases. For example, X decreases from 2.0 to 1.10 as the particle shape changes from a sphere to an oblate spheroid of axial ratio 4:1. While, in theory, Maxwell's equation is applicable only to dilute suspensions, Fricke was able to demonstrate that the relation predicted suspension behavior with surprising accuracy up to dispersed-phase concentrations corresponding to close packing.

In Figure 9 the estimated tortuosities for gas diffusion in polyethylene are plotted against α, along with the theoretical lines for dispersions of spheres and of 4:1 oblate spheroids. It will be observed that (a) the experimental points lie on curves rather than straight lines, and (b) the observed tortuosities in all cases are far higher than those expected of a dis-
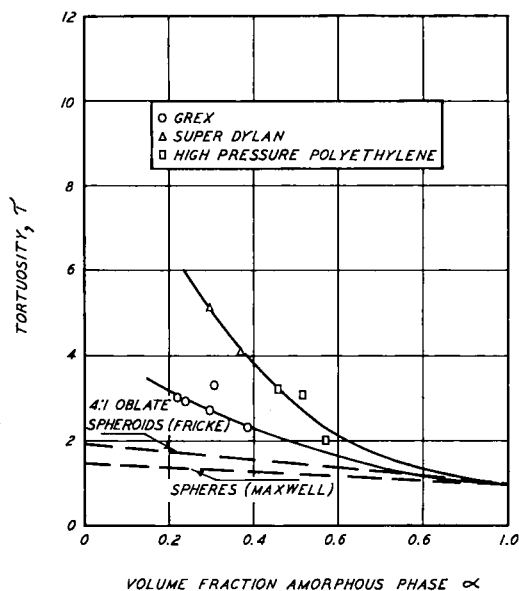
Figure 9.

persion of 4:1 oblate spheroids.   The analytical relationship between X and spheroid axial ratio is not given by Fricke; it appears, however, that X decreases rather slowly with an increase in the latter variable, so that the average axial ratio of the crystallites in polyethylene (with $\alpha \leqq 0.5$) is greater than 4:1 and probably is even far greater than 10:1.   This deduction is at variance with x-ray diffraction estimates of the shape of polyethylene crystallites, which seldom suggest axial ratios of greater than 5:1; the concept of the crystallite as a curled sheet or twisted ribbon thus appears to be supported by this work.

The observed deviations of the experimental tortuosities from linearity in α, as indicated in Figure 9, can most readily be explained in terms of variations of crystallite anisometry with α and/or polymer structure. These variations are, in turn, very closely keyed to the kinetics of nucleation and crystal growth from the polymer melt.   In a branched polyethylene, a relatively large fraction of the polymer volume is excluded from participating in the crystallization process because of side-chain hindrance; consequently, on cooling from the melt, nucleation can occur only in the more ordered regions, and, because of the rather high mobility of the chains surrounding the nuclei, crystal growth can occur rapidly with little interference by noncrystallizing molecular segments.   Such conditions favor the formation of relatively large, "equilibrium-shape" crystals which are highly anisometric.   In linear polyethylene, on the other hand, virtually all the polymer is capable of crystallizing.   On cooling from the melt, nucleation occurs randomly throughout the mass with a frequency which increases rapidly with the cooling rate.   Since a large number of nuclei are

growing in competition for the same polymer and since the polymer seg-
ment-mobility decreases quite rapidly as crystallization proceeds, crystal
growth soon becomes limited by the rate at which molecular segments can
reach the crystal. These conditions tend to favor growth of small, rela-
tively isometric crystals. The more rapid the cooling process, the greater
the nucleation rate, and the smaller and more isometric become the ulti-
mate crystallites. The observed variation in τ with rate of cooling from
the melt for Grex polymer (crystallinity also decreases with increased
quenching rate) is consistent with this picture.

The situation with Super Dylan is rather unusual in that, despite the
lower level of crystallinity in this polymer relative to Grex, it exhibits
a significantly higher tortuosity. The presence, in the former polymer,
of heterogeneous crystallization nuclei may explain this behavior. Evi-
dence supporting such theory was the observation, during the molding of
the polymer films, that crystallization of Super Dylan took place at a tem-
perature much closer to the crystalline melting point than that of Grex
polymer. Since the presence of heterogeneous nucleation sites would both
limit the number of ultimate crystals and permit growth to take place at a
higher temperature where molecular mobility is greater, the formation
of large, anisometric crystallites is to be expected. It is thus deduced
that the introduction of heterogeneous nuclei into linear polyethylene
serves to establish conditions for crystallite growth comparable to those
which exist in branched polyethylene. The fact, therefore, that the tortu-
osity data for Super Dylan and the high pressure polyethylenes lie on the
same line on Figure 9 may be more than mere coincidence.

It is clear from the foregoing analysis that the diffusional tortuosity of
polyethylene is not solely a function of the degree of polymer crystallinity,
although it is highly dependent thereon. The additional important
variable influencing tortuosity is crystallite shape, which is controlled
primarily by molecular mobility in the amorphous phase during crystal
growth. Since these two variables are not necessarily interdependent, it
follows that two polyethylenes of the same degree of crystallinity may
exhibit widely differing gas permeabilites and *vice versa*. Conditions favor-
ing a high degree of crystallinity coupled with large crystallite size (as
would be achieved with a linear polyethylene which was carefully annealed
at a temperature slightly below the crystalline melting point) can thus be
expected to result in very low gas permeabilites.

In summary, it appears that the solubility constant in any given poly-
ethylene sample depends primarily on the amount of crystallinity present,
and its magnitude reflects both the volume fraction of amorphous polymer
and the area fraction of amorphous material available for flow. The
diffusivity, however, depends on the conditions which prevail during
crystallite growth, as well as on the amount of crystallinity present.
For the lighter gases, it is primarily variations in the tortuosity effect
which cause substantial differences in the permeation rate at a given
sample density. For the gases and polymer samples studied, the crystal-

linity serves to reduce $\bar{P}$ by as much as 80-fold in some instances, this reduction being due to the combined effects of reduction of area for flow, diffusional impedance of the crystallites, and restriction of polymer chain mobility. In view of the above discussion, there is no reason to expect any kind of direct relation between the diffusivity and the crystalline content of the sample. For branched polyethylenes, the temperature dependences of D and k appear to be complicated by crystalline melting, even in the vicinity of room temperature, with appreciable variations in both τ and α with temperature occurring.

While this study has been concerned primarily with elucidating the origins of permeability variations between various polyethylenes, it is suggested that gas permeation-diffusion studies on microcrystalline polymers generally offer promise of serving as a useful tool for elaborating the fine structure of these systems.

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Synopsis

Solubilities and diffusivities of N_2, O_2, CO_2, and He in a variety of polyethylenes were measured in the temperature range 0–50°C. Polyethylene films studied covered a range of crystallinities (43–82%) and branching indices, and were prepared under a variety of

known thermal histories. Diffusivities were determined by the time-lag method; solubilities, by time-lag, and also by a newly developed and more accurate static method. Solubilities were found to obey Henry's Law; the solubility constants determined by both methods were found to agree within the limits of accuracy, confirming the applicability of the unsteady-state diffusion equation to essentially isotropic crystalline polymers. For a given gas at constant temperature, the solubility constant is directly proportional to the volume fraction of amorphous material in a polyethylene sample (as determined by density), irrespective of its origin or thermal history; the concept of the crystallites as an impermeable, dispersed phase thus appears justified. Diffusivities were found to vary widely (nearly fivefold) depending on polymer crystallinity and thermal history and were as much as tenfold lower than the values estimated for completely amorphous polyethylene. Application of principles of flow through porous media to this system leads to a conclusion that abnormally low diffusivities arise predominantly from the impedance to gas flow offered by the dispersed crystalline phase. Variations in diffusivity with branching index and thermal history correlate qualitatively with expected corresponding variations in crystallite growth kinetics and shape; the existence of highly anisometric, laminar crystallites in annealed linear polyethylene is indicated from these studies. The combined influence of crystallinity on solubility and diffusivity permits as much as a tenfold variation in gas permeability of polyethylene depending on polymerization method or fabrication process.

Résumé

Les solubilités et diffusions de N_2, O_2, CO_2 et He dans différents polyéthylènes ont été mesurées dans un intervalle de températur de 0 à 50°C. Des films de polyéthylènes étudiés convraient un intervalle de cristallinité de 43 à 82% et différents taux de ramification, et étaient préparés dans différentes conditions thermiques connues. Des diffusions ont été déterminées par le méthode du laps de temps; les solubilités de la même façon de même que par une méthode statique récente et plus précise. Les solubilités obéissent à la loi de Henry; les constantes de solubilité déterminées par les deux méthodes concordent dans les limites de la précision, confirmant la possibilité d'application d'une équation de diffusion non-stationaire à des polymères cristallins isotropiques. Pour un gaz donné à température constante la constante de solubilité est directement proportionnelle à la fraction en volume de la matière amorphe dans l'échantillon de polyéthylène (déterminée par densité) indépendamment de son mode de formation thermique; le concept de cristallites en tant que phase imperméable dispersée apparaît donc justifié. On a trouvé que les diffusions variaient largement (environ cinq fois) avec la cristallinité et les traitements thermiques antérieurs du polymère et qu'elles étaient dix fois plus faibles que les valeurs estimées pour des polyéthylènes complètement amorphes. L'application à ce système des principes de diffusion à travers des milieux poreux conduit à la conclusion que des diffusions anormalement basses sont dues surtout à la résistance que présente la phase cristalline dispersée au passage du gaz. Des variations de diffusion avec le degré de ramification et les traitements thermique antérieurs correspondent qualitativement avec les variations correspondantes prévues de la cinétique de croissance et de la forme des cristallites; l'existence de cristallites hautement anisotropiques au sein de polyéthylenes linéaires recuits est démontrée par ces études. L'influence combinée de la cristallinité sur la solubilité et la diffusion permet des variations de l'ordre de dix dans la perméabilité du polyéthylène, suivant la méthode de polymérisation ou du procédé de fabrication utilisée.

Zusammenfassung

Löslichkeit und Diffusionsvermögen von N_2, O_2, CO_2 und He in verschiedenen Polyäthylenen wurden im Temperaturbereich von 0–50°C gemessen. Die untersuchten Polyäthylenfilme hatten verschiedene Kristallinitätsgrade (43–82%) und Verzweigungs-

indizes und ihre Darstellung erfolgte unter Bedingungen, die eine verschiedenartige, thermische Vorgeschichte ergaben. Das Diffusionsvermögen wurde nach der Methode der "Verzögerungszeiten" bestimmt, die Löslichkeit nach der Verzögerungszeitmethode und auch nach einer neu entwickelten, genaueren statischen Methode. Es wurde gefunden, dass die Löslichkeiten dem Henryschen Gesetz gehorchen; die nach beiden Methoden bestimmten Löslichkeitskoeffizienten stimmten, wie gefunden wurde, innerhalb der Fehlergrenze überein, wodurch die Anwendbarkeit der Diffusionsgleichung für den nichtenstationären Zustand bei im wesentlichen isotropen, kristallinen Polymeren bestätigt wird. Für ein gegebenes Gas ist der Löslichkeitskoeffizient bei konstanter Temperatur dem Volumbruchteil an amorphem Material in einer Polyäthylenprobe (wie er sich aus der Dichte ergibt), unabhängig vom Ursprung oder der thermischen Vorgeschichte, direkt proportional; die Betrachtung der Kristallite als einer undurchlässigen, dispersen Phase scheint dadurch gerechtfertigt. Es wurde gefunden, dass das Diffusionsvermögen in Abhängigkeit von der Kristallinität des Polymeren und seiner thermischen Vorgeschichte über einen grossen Bereich variierte (nahezu um das fünffache) und bis zu zehnmal geringer als der für ein vollständig amorphes Polyäthylen geschätzte Wert war. Die Anwendung der für das Fleissen durch poröse Medien gültigen Prinzipien auf dieses System führt zu dem Schluss, dass das abnorm niedrige Diffusionsvermögen vorwiegend durch den von der dispersen, kristallinen Phase stammenden Strömungswiderstand für das Gas hervorgerufen wird. Die Abhängigkeit des Diffusionsvermögens vom Verzweigungsindex und von der thermischen Vorgeschichte steht in qualitativer Beziehung zu der erwarteten, entsprechenden Abhängigkeit der Kinetik des Kristallitwachstums und der Gestalt. Die vorliegenden Untersuchungen sprechen für das Vorhandensein von anisometrischen, plättchenförmigen Kristalliten in getempertem, linearen Polyäthylen. Der Einfluss der Kristallinität sowohl auf Löslichkeit als auch Diffusionsvermögen führt dazu, dass eine Variierung der Gasdurchlässigkeit von Polyäthylen in Abhängigkeit vom Polymerisationsverfahren oder Fabrikationsprozess bis auf das zehnfache möglich ist.