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Transport of Liquids in Structurally Modified Polyethylene

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Synopsis

Cast linear polyethylene films subjected to dry and solvent annealing display markedly different sorption and diffusion barrier properties than do untreated films. The subsequent sorption of liquid *o*- and *p*-xylene and *cis*- and *trans*-acetylene dichloride per unit volume of amorphous polymer increases as the annealing temperature and/or treating solvent concentration increases. Integral diffusivities calculated from sorption and steady-state permeation rates show a monotonic increase with sorption per unit volume of amorphous polymer. The concentration dependence, however, is less marked than observed in similar systems at low permeant activity. Apparently the above treatment reduces the effective crosslinking imposed by the crystallites on the amorphous polymer chains through disentangling and incorporating some of these chains into crystallites. Thus the polymer is capable of a greater degree of swelling when brought into contact with a compatible liquid in spite of a higher degree of crystallinity. The low concentration dependence of the diffusivities is probably due to heterogeneous distribution of excess permeant in a treated film. If the excess permeant were preferentially sorbed in regions of low polymer concentration then the above observations could be explained. Long-duration, osmotic stress-induced swelling and recrystallization have been cited to account for time-dependent permeation rates in treated and untreated films.

I. INTRODUCTION

The field of polymer permeability has gained in importance in recent years, due to the increasing use of polymeric materials as barriers, or selective barriers, to flow. While a considerable amount of research has been concentrated on the transport of gases, little has been directed towards understanding the physical factors controlling the sorption and diffusion of liquids, particularly in crystalline polymers which represent a significant portion of polymers presently in use. In earlier work on this problem, the effect of thermal and solvent treatment of polyethylene on the permeability of liquid xylene isomers was studied.[1] These results indicated that treatment of polymer films prior to permeation, by annealing at an elevated temperature in the presence of a swelling solvent, led to increased permeation rates and sorption of the xylenes in the polymer. In addition to increasing liquid permeation rates as much as tenfold, it was found that under certain conditions the selectivity of the polymer for *p*-xylene over the other isomers could be enhanced. A major objective of the present work has been to clarify the mechanism responsible for these changes in film properties, in addition to determining the structural aspects of a crystalline polymer that affect liquid sorption and diffusion generally. The earlier work with *p*- and *o*-xylene in polyethylene[1] has been continued, and the scope has been extended to a second liquid isomeric pair, *cis*- and *trans*-acetylene dichloride (1,2-dichloroethylene).

Steady-state permeation of a solvating liquid through a polymer film can be described by Fick's law:

$$J = -D(dc/dx) \tag{1}$$

J is the steady-state mass flux per unit area. D and dc/dx are the local diffusion coefficient and the concentration gradient, respectively, at any point in the film. When the permeant concentration is maintained at zero at the downstream face, integration gives

$$Jl = \int_0^{c_1} D dc \tag{2}$$

l is the liquid swollen film thickness, and c_1 the concentration of permeant in the polymer at equilibrium with the pure liquid contacting the upstream face. Defining an integral diffusivity, D, as

$$\bar{D} = (1/c_1) \int_0^{c_1} D dc \tag{3}$$

and calling Q the permeation flux per unit film thickness, equal to Jl, substitution into eq. (2) yields

$$Q = \bar{D}_{c_1} \tag{4}$$

In calculating Q from experimental data, the dry film thickness was used. Values of Q calculated in this manner will be lower than the true values, but the maximum error in this work has been estimated to be 5%.

Equation (4) shows that the liquid permeation flux consists of a diffusion and a sorption contribution. By combining equilibrium swelling data, giving c_1, with steady-state permeation measurements, giving Q, one may obtain information about both the sorption and diffusion aspects of liquid transport in polymers.

II. PROCEDURE

A 1-mil cast linear polyethylene film of 0.942 g./cm.^{3} density, supplied by the W. R. Grace Company, was used throughout the work. Solvent treatment of films was carried out in the following way. A given concentration of a swelling solvent was introduced into the polymer at room temperature by confining weighed amounts of film and liquid in a tubular vessel. The swollen polymer was annealed by immersing the above vessel in an oil thermostat controlled to ±0.2°C. for a period of 20 ± 2 hr. The film was cooled, then dried at room temperature. An identical thermal treating procedure was used in dry-annealing.

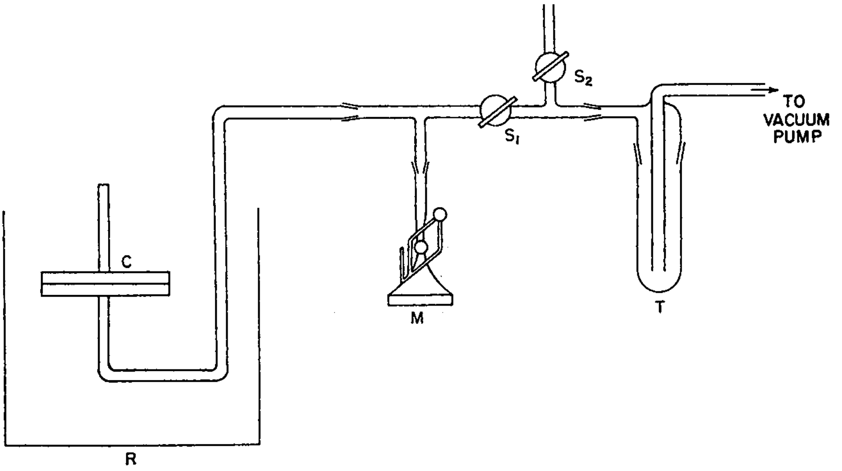

Fig. 1. Schematic diagram of apparatus for liquid permeation studies.

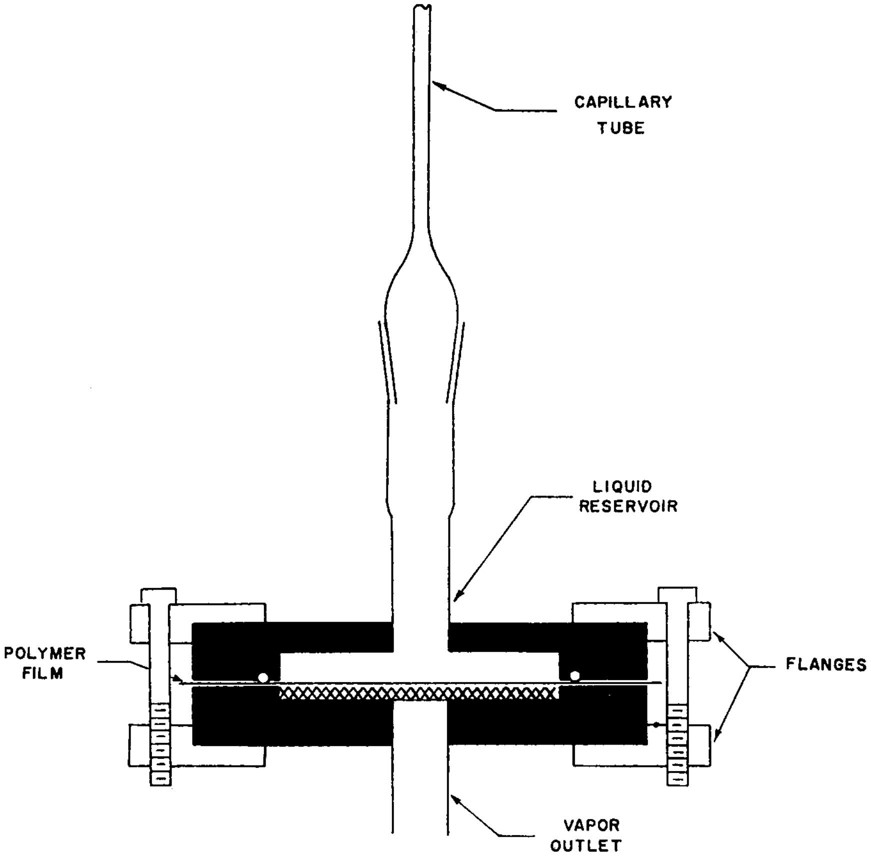

Fig. 2. Liquid permeation cell.

The apparatus used to obtain liquid permeation data is illustrated in Figure 1. The cell in which the film was mounted (detailed in Fig. 2) served as the liquid reservoir. The downstream section of the system was initially evacuated to a pressure less than 0.1 mm. Hg, following which the run was begun by slowly charging liquid to the cell. Permeation flux determinations were made by timing the rate of fall of the upstream liquid level in a uniform-bore glass capillary, replications being made by refilling the capillary. A series of such tubes, ranging from 30 to 85 mils in diameter, could be interchanged so that under given conditions of permeation the rate could be determined over a sufficiently small time period (usually 100–300 sec.). The thickness of the dry polymer film was determined to 0.01 mils by means of a Pratt and Whitney supermicrometer. The precision of the values of Q obtained by this technique was estimated to be 5.3% at the 95% confidence level. A material balance on the system, obtained by collecting the permeated liquid in the downstream trap, checked well.

To measure liquid sorption gravimetrically, a technique was developed which limited the exposure of the swollen film to the atmosphere before weighing, and hence minimized evaporation losses of liquid from the polymer. Such desorption losses can be considerable if suitable precautions are not taken. After equilibration with liquid at the desired temperature, an immersed film strip was wound directly from the liquid bath onto a spool with a sealed cylindrical container. By weighing the assembly, the liquid sorption in grams of liquid per cubic centimeter of polymer could be computed knowing the tare weight of the container, the dry film weight, and the polymer density. From replicate measurements, the precision of the technique at the 95% confidence level was estimated to be 8.6%. The integral diffusivities calculated from eq. (4) were precise to 15%.

Polymer density measurements were made in isopropanol-water density-gradient columns. The amorphous volume fraction of the polymer, α, was calculated from

$$\alpha = (\rho_c - \rho)/(\rho_c - \rho_a) \tag{5}$$

where $\rho_c = 0.9990$ g./cm.^{3} and $\rho_a = 0.8540$ g./cm.^{3}, the densities of pure crystalline and pure amorphous polyethylene, respectively, and ρ is the sample density, all at 25°C.

Gas permeability data were obtained by using Park cells, designed by Dr. Robert Park of the Dow Chemical Company, Midland, Michigan. The method consists of applying a pressure of the permeating gas at the upstream face of a supported polymer film and tracing the rate of advance of a liquid slug in a uniform-bore capillary tube fixed to the cell outlet downstream from the film.

III. RESULTS AND DISCUSSION

A. Sorption

1. Sorption of Xylene and Acetylene Dichloride Isomers at 30°C.

Sorption data for the xylene and acetylene dichloride (ADC) isomers are summarized in Table I. Important physical properties of the sorbing liquids are given in Table II. The volume of liquid sorbed per unit volume of amorphous polymer, C^*, has been calculated from the relationship

$$C^* = c/\rho_l\alpha \tag{6}$$

where c is the experimentally determined sorption in grams per cubic centimeter of total dry polymer, ρ_l the liquid density in grams per cubic centimeter, and α is the amorphous volume fraction in the dry polymer. The validity of basing sorption on amorphous content of the polymer rests on three important assumptions: (*a*) polyethylene consists of two distinct phases, crystalline and amorphous, each possessing unique properties at a given temperature; (*b*) liquid sorption occurs in the amorphous phase only, with additive liquid and amorphous-polymer volumes; (*c*) the change in the relative proportions of crystalline and amorphous material at low temperatures caused by the introduction of a swelling liquid is small. The first assumption is supported by the good agreement usually obtained among various methods used to determine the degree of crystallinity of the polymer. These methods include x-ray diffraction and infra-red spectroscopy, in which the "ordered" and "disordered" portions of the structure are distinguished; density determinations, in which values of specific volume are assigned to each phase; and thermal methods, such as calorimetry and differential thermal analysis, in which enthalpy values are assigned to each phase. Further evidence for the two-phase model and support for the assumption that liquid sorption is localized in the amorphous polymer only, comes from an analysis of solubility of permanent gases in polyethylene.[3] For all gases studied, the solubility is a linear function of the amorphous volume fraction [calculated from eq. (5)], and zero solubility at 100% crystallinity. In several studies involving solutions of liquids or solvating vapors in polyethylene, the assumptions outlined above have been applied successfully for several different purposes. Chiang and Flory,[4] investigating the melting behavior of polyethylene–liquid systems, found good agreement with melting-point depression theory when liquid concentrations were based on amorphous phase content obtained by dilatometry. Rogers, Stannett, and Szwarc[5] have used an amorphous phase basis in interpreting their vapor-sorption data in polyethylene. Finally, Barrer and Fergusson[6] found it necessary to consider vapor sorption as occurring only in the amorphous phase of polyethylene in order to obtain thermodynamic consistency in their data.

Comparison among liquids in the untreated polymer in Table I shows sorption decreasing in the order of *p*-xylene > *o*-xylene > *trans*-acetylene

TABLE I

Equilibrium Sorption of Liquids in Polyethylene (T = 30°C.)

Treatment			C^*, vol. sorbed liquid/vol. amorphous polyethylene				
Solvent	Concn., g./g.[a]	Temp., °C.	*p*-Xylene	*o*-Xylene	*trans*-ADC	*cis*-ADC	α_{25}[b]
Untreated polymer			0.297	0.253	0.208	0.183	0.396
None	0	80	0.333	0.326	0.232	0.199	0.348
None	0	97	0.370	0.355	0.226	0.191	0.305
None	0	115	0.359	0.389	0.260	0.186	0.242
p-Xylene	0.10	80	0.397	0.377	0.269	0.250	0.346
p-Xylene	0.10[c]	97	0.455	0.445	0.302	0.305	0.297
p-Xylene	0.10	115	0.490	0.563	0.346	0.311	0.226
p-Xylene	0.04	97	0.384	0.377			0.301
p-Xylene	0.20	97	0.570	0.544	0.436	0.409	0.287
p-Xylene	0.30	97	0.615	0.620	0.477	0.481	0.282
n-Decane	0.085[c]	97	0.447	0.479			0.294
Ethylene bromide	0.26[c]	97	0.488	0.481			0.281

[a] Treatment concentration expressed as grams of solvent per gram of total dry polymer.

[b] Amorphous volume fraction of dry polymer at 25°C.

[c] Represents a volume concentration of 0.10 cm.^{3} of solvent per cm.^{3} of polymer plus solvent.

dichloride > *cis*-acetylene dichloride. The trend is qualitatively consistent with the trend in the differences between the solubility parameters of liquid and polymer ($\delta_p \simeq 8.0$); a small difference in solubility parameters is indicative of a low heat (or energy) of interaction in mixing, and hence good compatibility and high solubility.

TABLE II
Physical Properties of Permeants

Permeant	ρ_1, 30°C. g./cc.	V_m 25°C., cc./g.-mole	δ, (cal./cc.)$^{1/2}$[a]	A_D, A.^{2}[b]
o-Xylene	0.872	121	9.0	31
p-Xylene	0.852	124	8.6	28
cis-ADC	1.267	76	9.1	25
trans-ADC	1.240	78	9.0	21

[a] Hildebrand solubility parameter.[2]

[b] Empirical characteristic diffusion cross-sectional area, $V'_m/l_{\max}$, where $l_{\max}$ is maximum length of extended molecule and V'_m is the molecular volume of the liquid at 25°C.

In all cases, thermal and solvent treatment cause an increase in C^*. Sorption increases with increasing treatment temperature, and the rate of increase is greater in solvent-treated film than in dry-annealed film. Sorption increases strongly with increasing treatment concentration, while the choice of specific treatment solvent appears to have little effect.

2. Limited Sorption in a Network Polymer

Before considering a morphological argument for the increases in C^* values with thermal and solvent treatment, it is worthwhile to review the thermodynamics of limited swelling of a microcrystalline polymer by a compatible solvent. A comparison can be made between a microcrystalline and a chemically crosslinked polymer. In the latter, swelling in the presence of a compatible solvent is ultimately limited by the restriction placed on network expansion by crosslinks. The polymer will expand until the osmotic pressure generated by the mixing of liquid with polymer is balanced by the elastic retractive force of the network. Similarly, when a crystalline polymer is diluted with a compatible solvent, a balancing force must be exerted, or swelling would continue without limit, resulting in ultimate dissolution of the polymer. In terms of a structural model of polyethylene, expansion of the amorphous phase is limited because the ends of amorphous chain segments are fixed in adjacent crystalline lamellae. In this way, the interlamellar segments are physically crosslinked.

In the light of these considerations, one may apply Flory's theory of equilibrium swelling to the sorption of liquids in a crystalline polymer. By equating the change in chemical potential of the liquid due to mixing to the change caused by the elastic reaction of the polymer network, and assuming isotropic swelling, one obtains[7]

$$-[\ln(1 - v_2) + v_2 + \chi_1 v_2^2] = (V_1\rho_a/M_c)[1 - (2M_c/M)][v_2^{1/3} - (2/f)v_2] \tag{7}$$

where v_2 = volume fraction of polymer in the amorphous phase solution = $1/(1 + C^*)$, ρ_a = amorphous polymer density, V_1 = liquid molar volume, χ_1 = Flory-Huggins interaction parameter = $(V_1/RT)\ (\delta_1 - \delta_2)^2$, δ_1 = solubility parameter of solvent, δ_2 = solubility parameter of amorphous polyethylene $\simeq$ 8.0 (cal./cc.)$^{1/2}$, M_c = average molecular weight of the polymer chain between crosslinks, M = primary molecular weight of the polymer, and f = functionality of crosslink.

Equation (7) can be solved for M_c, which gives a measure of the average amorphous chain segment length in the swollen polymer. Assuming $M_c << M$, and taking the crosslink functionality f as large yields

$$M_c = -V_1\rho_a v_2^{1/3}\ [\ln(1 - v_2) + v_2 + \chi_1 v_2^2]^{-1} \tag{8}$$

or in terms of the C^* defined by eq. (6)

$$M_c = V_1\rho_a \left(\frac{1}{1 + C^*}\right)^{1/3} \left[\ln\left(\frac{C^*}{C^* + 1}\right) + \left(\frac{1}{1 + C^*}\right) + \chi_1 \left(\frac{1}{1 + C^*}\right)^2\right]^{-1} \tag{9}$$

This model has been applied by Rogers, Stannett, and Szwarc[5] to vapor sorption in polyethylene. Its applicability rests on the assumption that the swelling theory is valid in the case of the relatively short chain segments that are present in a highly crystalline polymer. This limitation arises from the fact that it is necessary to assume a given distribution of root-mean-square end-to-end distances of chain segments in order to arrive at an expression for the elastic free energy, which appears in the right-hand side of eq. (7). For sufficiently long polymer chains, this distribution may be approximated by a Gaussian function. However, as the segment length decreases, the approximation becomes less accurate, and the validity of eq. (7) becomes questionable. Flory has estimated that ten chain units (methylene groups in this case) is about the lower limit for which the Gaussian distribution holds if the polymer chain is regarded as freely jointed. Restriction of bond angles, which is significant, and hindered rotation about the bond, which can be neglected for polyethylene,[7] effectively raise the lower limit for which eq. (7) is applicable. Unfortunately, there is little agreement on the magnitude of this limitation.[8] Consequently, the application of the swelling theory to obtain absolute values of the mean amorphous chain segment length is not fully justified. Nevertheless, the theory should serve to indicate relative values in treated and untreated polymers in the swollen state. Those calculated from eq. (9) are given in Table III.

The segment lengths calculated from *p*- and *o*-xylene sorption in a given polymer are for all practical purposes the same. The value of M_c equivalent to 11 methylene units for the untreated polymer agrees with that obtained by Rogers, Stannett, and Szwarc[5] from *p*-xylene vapor sorption in a polyethylene of comparable degree of crystallinity. These authors have also estimated a segment length of 16 methylene units from Richards' data on the swelling of polyethylene (about 40% crystalline) in liquid xylene.[9]

TABLE III

Calculated Average Number of Methylene Units per Amorphous Chain Segment

Treatment			From *p*-xylene sorption		From *o*-xylene sorption	
Solvent	Concn., g./g.[a]	Temp., °C.	M_c[b]	Methylene units	M_c	Methylene units
Untreated polymer			154	11	142	10
None	0	80	169	12	174	12
None	0	97	185	13	190	14
None	0	115	181	13	205	15
p-Xylene	0.10	80	197	14	199	14
p-Xylene	0.10[c]	97	224	16	234	17
p-Xylene	0.10	115	240	17	294	21
p-Xylene	0.04	97	192	14	199	14
p-Xylene	0.20	97	276	20	284	20
p-Xylene	0.30	97	303	22	334	24
n-Decane	0.085[c]	97	218	16	252	18
Ethylene bromide	0.26[c]	97	238	17	253	18

[a] Treatment concentration expressed as grams of solvent per gram of total dry polymer.

[b] Polymer molecular weight between lamellar crystallites.

[c] Represents a volume concentration of 0.10 cm.^{3} of solvent per cm.^{3} of polymer plus solvent.

The data in Table III also point up the magnitude of the increase in the amorphous chain segment length in treated films that is necessary to account for the observed increases in sorption. These results indicate that substantial changes in polymer morphology must occur during film treatment to allow segment lengths to increase to this degree in the rellswoen polymer. A model describing the causes of this structural change will be discussed below.

3. Xylene Sorption as a Function of Temperature

The sorption of *o*-xylene per unit amorphous polymer in treated and untreated films is shown as a function of temperature in Figures 3 and 4. Within experimental precision, straight lines can be drawn on a van't

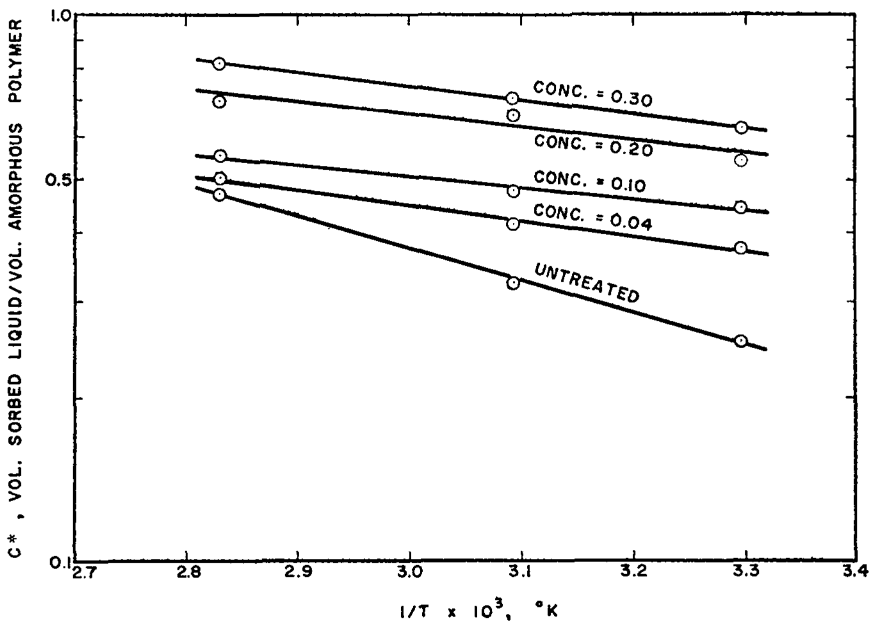

Fig. 3. *o*-Xylene sorption. Polymer treated with *p*-xylene, 97°C., at specified concentration.

Hoff plot of log C^* versus $1/T$. If there is no entropy contribution to χ_1,[7]

$$\chi_1 v_2^2 = \Delta H_s/RT \tag{10}$$

where ΔH_s is the enthalpy of mixing the sorbing liquid with the polymer.

Making use of this relationship and assuming only v_2 in eq. (8) to be a function of temperature, the following is obtained upon differentiation:

$$\left[v_2 - {}^1/_3 \frac{\rho_a V_1}{M_c} \frac{(1 - v_2)}{v_2^{2/3}}\right] d \ln (1 - v_2) = -\frac{\Delta H_s}{R} d\left(\frac{1}{T}\right) \tag{11}$$

or again, by using the definition of C^* given by eq. (6),

$$\frac{d \ln C^*}{d(1/T)} = -[f(C^*)] \frac{\Delta H_s}{R} \tag{12}$$

where

$$f(C^*) = \frac{(1 + C^*)^2}{1 - \frac{1}{3} \frac{\rho_a V_1}{M_c} C^*(1 + C^*)^{2/3}} \tag{13}$$

By using values of M_c obtained from sorption at 30°C., $f(C^*)$ was calculated at each temperature, and a mean value was used to estimate ΔH_s. $f(C^*)$ does not vary widely over the temperature range, and thus the heat

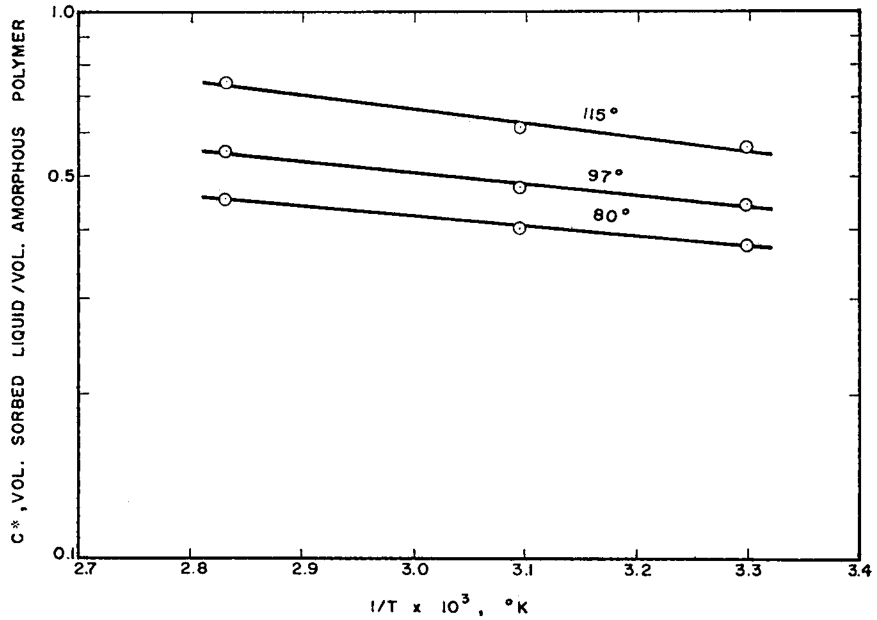

Fig. 4. *o*-Xylene sorption. Polymer treated with 10% solvent at specified temperature.

of solution should not be seriously in error from the use of a mean value. Among solvent-treated films, ΔH_s is 0.40 kcal./mole, with a maximum deviation of about 10%. A value of ΔH_s as low as this is qualitatively consistent with the high compatibility of an aromatic solvent with an aliphatic hydrocarbon polymer. This result is in fair agreement with reported data for other aromatics in polyethylene,[5] which are in the range of 0–0.3 kcal./mole.

The higher slope for the untreated polymer in Figure 3 reflects changes in polymer structure with temperature, and thus eq. (12) is inapplicable. This was determined by remeasuring sorption in a film at 30°C. after sorption at 80°C. had first been measured. An abnormally high value was obtained for untreated film from this procedure, while treated films exhibited no such hysteresis effect. Thus, the process of measuring sorption at 80°C. subjects the untreated film to solvent treatment, while treated films, having been previously exposed to a similar solvent–temperature history, underwent no additional structural changes.

4. Model of the Morphology of Heat- and Solvent-Treated Polyethylene

Prior to considering the changes in polymer structure that are brought about by thermal and solvent treatment, it is necessary to establish the nature of the morphology of the original untreated material. When polyethylene is crystallized from the melt by quenching, or rapid cooling, the initial nucleation rate is high because of a high degree of supercooling. The crystalline growth rate is rapid as long as the polymer temperature is in the range where this is permissible, but growth ceases rather abruptly due to the quench cooling. Consequently, the majority of the crystallinity develops under conditions of rapid growth. In addition, the degree of crystallinity is relatively low because of the short time period during which nucleation and growth can occur. Therefore the size of crystallites formed under these conditions, or, more correctly, the extent of regions of perfect order, is limited.

The body of evidence for a folded chain type of crystallite in bulk polymer is growing; although the resulting lamellae are probably much less perfect than in solution grown crystallites. In the first place a spectrum of lamellar step heights (corresponding to the *c* or chain axis of the crystallites) would be expected. According to Hoffman,[10] a unique lamellar step height is formed at each crystallization temperature, the step height decreasing with decreasing temperature. In a quenched polymer, the amount of crystallization that can occur at a given temperature is small before the temperature drops and lamellae characterized by a lower step height begin to form. These characteristics of the crystallization kinetics probably profoundly affect the physical properties of the uncrystallized, amorphous polymer. The continual change in step height should cause a large number of defects within lamellae, and these regions of imperfection must be considered part of the amorphous phase of the resulting polymer. The high degree of nucleation and rapid growth would be expected to establish strong competition for uncrystallized polymer among the number of growing lamellae. Thus, the probability that a given polymer chain will be incorporated into more than one lamella is very high, and the matrix should be characterized by a high degree of interlamellar linking by amorphous chain segments. In addition, there is probably considerable entanglement of polymer chains in these interlamellar links which can exert considerable interchain friction when the polymer is subjected to stress.

In contrast to quenched material, polyethylene crystallized from the melt by slow cooling will exhibit a distinctly different morphology. The degree of crystallinity of the resulting polymer is higher, since the polymer is exposed for a longer time to the temperature range in which crystallization is rapid. The crystals formed are fewer in number and greater in extent, because the polymer is not abruptly subjected to a high degree of supercooling. Since at high temperatures a greater amount of crystallinity can form at each temperature, the distribution of lamellar step heights about the mean should be narrow. The lower crystallization rates at high temperatures will alleviate the competition among growing lamellae for amorphous polymer, and the degree of interlamellar linking by amorphous chains should be low relative to quenched polymer. Entanglement of interlamellar chains is likewise considerably reduced eliminating the interchain friction referred to above. Finally, because conditions of slow cooling will lead to more nearly perfect lamellae, the amount of intralamellar amorphous polymer in the form of crystal imperfections will be less.

In the light of the considerations presented above, the structural aspects of the polymer matrix that would be expected to affect the properties of amorphous material are the degree of interlamellar linking and entanglement and the amount of intralamellar structural imperfection. The role played by the latter in the process of liquid sorption may be small, since its ability to expand to accommodate a diluent is restricted by the rigidity of the lamellae in which it is imbedded. On the other hand, it appears that interlamellar linking and entanglement would be of major importance in sorption. Referring back to the correspondence between a crystalline and a crosslinked polymer, it seems likely that quenched polyethylene, with a high degree of interlamellar linking and entanglement, is analogous to a tightly crosslinked network. The latter, of course, would limit swelling by a liquid to a greater degree than a weakly crosslinked material.

The effect of annealing a quenched polymer on interlamellar linking can be clarified by considering the melting behavior of polyethylene. It has been found experimentally that the disappearance of crystallinity begins at temperatures considerably below the final melting point.[11] Hoffman[10] and others have shown that this can be caused by the melting of small crystals, since their melting points are depressed by high surface free energy per unit volume. When the polymer is heated to a given temperature, a certain fraction of the crystallinity initially present is melted. If it is held at that temperature (annealed), recrystallization occurs under conditions of relatively slow growth. Thus, annealing not only increases the total crystallinity (as indicated by the decreased α values shown in Table I), but it effects an exchange of a portion of the initial structure, containing a high degree of interlamellar linking, for a more nearly perfect crystalline morphology, characterized by a lower degree of interlamellar linking. As the annealing temperature is increased, the degree of initial melt-out and recrystallization increases, and hence the fraction of the polymer structure exhibiting a low degree of interlamellar linking increases.

The change in polyethylene morphology induced by annealing in the swollen state, or upon solvent treating, becomes clear when it is realized that the polymer melting point is depressed by the presence of solvent. Since the activity of the swollen polymer is lowered by dilution, the melting point of crystals of any size will be reduced, and the entire melting range is shifted to lower temperatures. Consequently, at a given annealing temperature, as the solvent concentration increases, the amount of melt-out of the original crystalline structure, and its replacement by recrystallized lamellae, increases, and the degree of interlamellar linking in the structure decreases.

Qualitatively, the effects of heat and solvent treatment on interlamellar linking outlined above account for the observed increase in equilibrium sorption per unit volume of amorphous polymer with an increase in annealing temperature and/or solvent concentration. These effects can also be considered in terms of the average amorphous chain length. The osmotic pressures generated by sorption, in the range of 50–100 atm., are probably sufficient to cause some fragmentation of the internal crystalline struc-

TABLE IV
Integral Diffusivities and Permeation Rates (T = 30°C.)

Treatment			*p*-Xylene		*o*-Xylene		*trans*-ADC		*cis*-ADC	
Solvent	Concn., cm.^{3}/cm.^{3a}	Temp., °C.	$\bar{D} \times 10^7$, cm.^{2}/sec.	$Q \times 10^7$, g. cm./cm.^{2} sec.	$\bar{D} \times 10^7$, cm.^{2}/sec.	$Q \times 10^7$, g. cm./cm.^{2} sec.	$\bar{D} \times 10^7$, cm.^{2}/sec.	$Q \times 10^7$, g. cm./cm.^{2} sec.	$\bar{D} \times 10^7$, cm.^{2}/sec.	$Q \times 10^7$, g. cm./cm.^{2} sec.
Untreated polymer			1.1	0.11	0.59	0.051	4.5	0.48	1.8	1.16
None	0	80	1.3	0.13	0.59	0.058				
None	0	97	1.5	0.14	0.72	0.068	5.4	0.46	2.3	0.17
None	0	115	1.5	0.11	0.57	0.047				
p-Xylene	0.10	80	1.5	0.18	0.78	0.09	5.5	0.65	2.0	0.22
p-Xylene	0.10^b	97	1.9	0.22	0.91	0.11	5.5	0.62	2.0	0.
p-Xylene	0.10	115	1.9	0.23	0.83	0.09	6.7	0.66	2.7	0.24
p-Xylene	0.04	97	1.5	0.15	0.69	0.068				
p-Xylene	0.20	97	2.6	0.36	1.4	0.19	6.3	1.0	2.5	0.36
p-Xylene	0.30	97	2.8	0.41	1.5	0.23	7.0	1.2	2.8	0.47
n-Decane	0.085^b	97	2.0	0.22	0.89	0.11				
Ethylene bromide	0.26^b	97	2.0	0.23	1.1	0.13				

[a] Treatment concentration expressed as grams of solvent per gram of total dry polymer.

[b] Represents a volume concentration of 0.10 cm.^{3} of solvent/cm.^{3} of polymer plus solvent.

ture of the polymer, which will lengthen amorphous chain segments until the network exerts a retractive force to balance the osmotic stress. In treated films, where the degree of interlamellar linking is reduced, the osmotic force per amorphous chain is greater, and thus the disruption of crystallinity is greater, allowing the mean chain-segment length to increase. This is responsible for the changes in M_c with treatment shown in Table III. That structural changes induced in the polymer by treatment are manifested primarily when the film is reswollen, and that these changes lead to disorientation within the structure, are both supported by light-scattering data.[12]

B. Diffusion

1. Steady-State Diffusion of Xylene and Acetylene Dichloride Isomers at 30°C.

A summary of steady-state integral diffusivities at 30°C. for *p*- and *o*-xylene and *trans*- and *cis*-acetylene dichloride is given in Table IV. Comparison of diffusivities between liquids within each isomeric pair illustrates the important influence of molecular shape on diffusion in polymers. *P*-Xylene exhibits a diffusion coefficient about twice that of the *ortho* isomer. Between the acetylene dichlorides, the ratio of $\bar{D}$ for *trans* to that for *cis* is approximately 2.5. These observations are qualitatively consistent with the characteristic diffusion cross section, A_D, for these molecules presented in Table II. In developing this characteristic dimension, an effort has been made to allow for partial preferred orientation of anisometric molecules diffusing in a polymer matrix.

Thermal and solvent treatment of the polymer have a marked effect on the integral diffusivities. These effects can be characterized by the effect of treatment on C^*. It has been found that the integral diffusivities can be correlated by the following empirical relationship:

$$\bar{D} = D_{c=0} \exp \left\{\gamma C^*\right\} \tag{14}$$

Figure 5 presents a test of this relationship for the xylene isomers, and Figure 6 presents a similar test for the acetylene dichloride isomers. The fit is quite good for the xylenes and fair for the acetylene dichlorides, considering that $D(= Q/3600c)$ and C^* are dependent on sorption values de-

TABLE V
Sorption–Diffusion Correlation Parameters

	$D_{c=0} \times 10^7$, cm.^{2}/sec.	γ, cc. amorphous polymer/cc. sorbed liquid
p-Xylene	0.51	2.8
o-Xylene	0.30	2.5
trans-Acetylene dichloride	3.8	1.3
cis-Acetylene dichloride	1.7	1.1

termined separately from permeation rates. The correlating parameters for eq. (14) are presented in Table V.

It should be pointed out that eq. (14) is inconsistent with a similar relationship used by other investigators to correlate concentration dependent local diffusivities, i.e.,

$$D = D_{c=0} \exp \left\{\gamma' c'\right\} \tag{15}$$

since substitution of eq. (15) into eq. (3) and integrating yields

$$\bar{D} = \frac{D_{c=0}}{\gamma' c'} (e^{\gamma' c'} - 1) \tag{16}$$

However, on testing the data of McCall and Slichter[13,14] where local diffusivities were determined through application of eq. (15) it has been found that eq. (14) is a reasonably satisfactory approximation of eq. (16) for aromatics in linear and branched polyethylenes. Since both eqs. (14) and (15) are empirical, this inconsistency is noted only to provide a means of comparing the present data with other transport measurements reported in the literature.

A comparison between the present work with *p*-xylene can be made with the data of Rogers et al.[15] where integral diffusivities of benzene were determined in a branched polyethylene at 0°C. The data of Barrer and Fergusson[6] can also be used to calculate integral diffusivities of benzene in a branched polyethylene at 50°C. Finally, as noted above, integral diffusivities of benzene in a linear and branched polyethylene at 25°C. can be calculated from the data of McCall and Slichter.[13,14] In all of these investigations the permeant concentration in the polymer was varied by varying the permeant activity in contact with the polymer. This is in contrast with the present work, where the permeant activity was kept constant, and its concentration was varied by thermal and solvent treatment of the films.

The parameters for eq. (14) derived from these other investigators are presented in Table VI. The striking point to note is that γ from this work is appreciably lower than the value obtained in similar systems, while the extrapolated volume of $D_{c=0}$ is appreciably higher. Since *p*-xylene is a slightly better solvent for polyethylene than benzene (solubility parameter = 9.2), it would be expected that if γ were to differ it would be higher for the former if this parameter is related to a plasticizing effect on the polymer. The slightly higher temperature and lower density polymer used in this work can account for the slightly higher value of $\bar{D}_{\mathrm{sat}}$ for *p*-xylene in comparison with the value obtained for benzene in a linear polyethylene at 25°C. However, the markedly higher extrapolated value of $D_{c=0}$ for *p*-xylene cannot be accounted for by these small differences. Although the increased diffusivities caused by thermal and solvent treatment are apparently correlated by the increased permeant solubility per unit volume of amorphous polymer, these treatments must also cause structural modi-

TABLE VI

Diffusion Parameters for Aromatic Hydrocarbons in Polyethylene

Reference	Estimated polymer density, g./cc.	Permeant	Temp., °C.	$\bar{D}_{sat} \times 10^7$, cm.^{2}/sec.[a]	$D_{c=0} \times 10^7$, cm.^{2}/sec.	γ, cc. amorphous polymer/cc. sorbed liquid
Rogers et al.[15]	0.92	Benzene	0	0.6	0.021	12.2
McCall and Slichter[13,14]	0.92	Benzene	25	2.1	0.16	8.5
Barrer and Fergusson[6]	0.92	Benzene	50	—	2.4	7.1
McCall and Slichter[13,14]	0.97	Benzene	25	1.0	0.033	11.7
Present work	0.95	*p*-Xvlene	30	1.1	0.51	2.8

[a] Integral diffusivity with saturated liquid or vapor in contact with film.

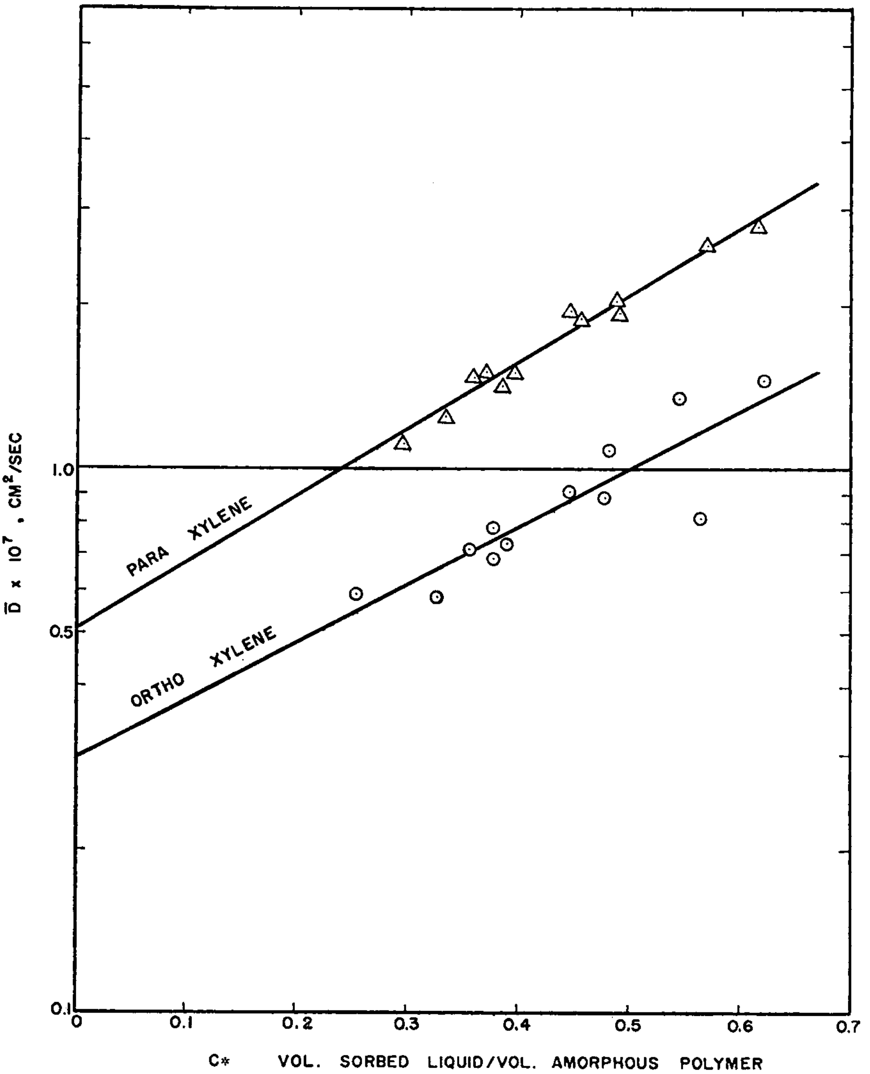

Fig. 5. Sorption–diffusion correlation for *p*- and *o*-xylene, 30°C.

fications to the polymer which do not occur or do not influence the transport process at lower permeant activities.

In attempting to develop a model to account for this behavior it has been found that Q is linear in C^*, at least for the xylene isomers studied here. For both *o*- and *p*-xylene a twofold increase in C^* results in approximately a fourfold increase in Q at 30°C. It is conceivable that the increase in C^* with thermal and solvent treatment reflects the imbibition of xylene into regions of the film where the amorphous polymer chain concentration is vanishingly small. This amounts to saying microvoids are formed in swollen treated films which contain essentially pure sorbed liquid. The

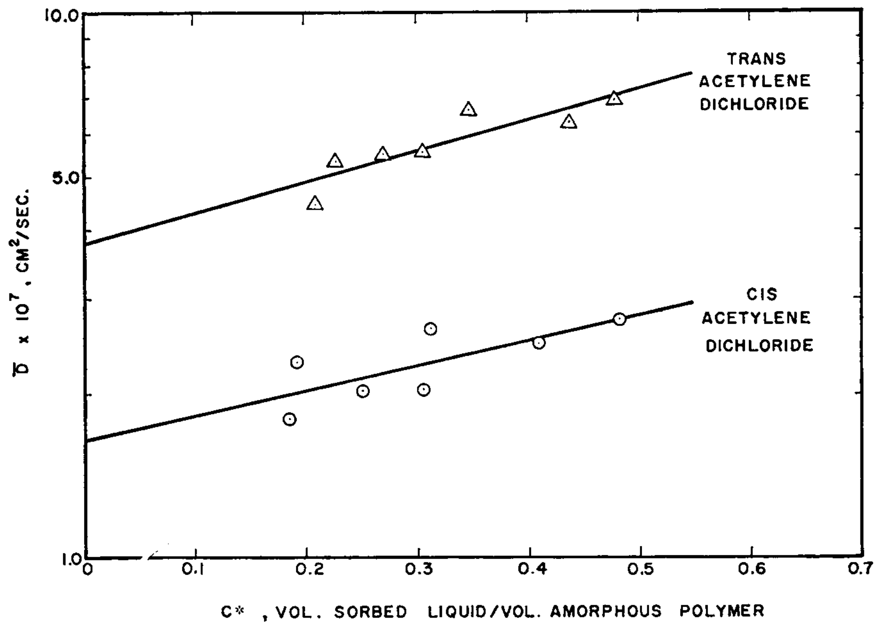

Fig. 6. Sorption–diffusion correlation for *trans*- and *cis*-acetylene dichloride, 30°C.

remaining liquid would be sorbed into amorphous regions where the polymer–liquid solution is the same as exists in the untreated film. The liquid filled microvoids would offer a minor barrier to diffusion. If the microvoids were randomly distributed the microvoid area per unit area of amorphous polymer would be equal to the microvoid volume per unit volume of amorphous polymer. Under these conditions,

$$Q_{\text{treated}} = Q_{\text{untreated}} \left(C^*_{\text{treated}}/C^*_{\text{untreated}}\right) \tag{17}$$

since a constant permeation area and the dry film thickness have been used in computing Q. If this model were correct, a twofold increase in C^* should result in a twofold rather than the observed fourfold increase in Q.

In all likelihood the increase in C^* accompanying film treatment results in a heterogeneous distribution of liquid in the amorphous matrix but not to the extent outlined above. Rather than a simple two-region type of sorption proposed above to account for the increased C^*, a gradation in the amorphous polymer concentration within the polymer–liquid solution is encountered. In some regions the polymer concentration is similar to that in the untreated film. In other regions progressively lower polymer concentrations are encountered, and finally some regions exist which for all practical purposes are microvoids. Since the local increase in C^* would be greatest in the regions of lowest polymer concentration, the major barrier to diffusion could still be offered by the regions of high polymer concentration. Accordingly, the low concentration dependence of integral diffusivities could be explained. Although it has been proposed that ther-

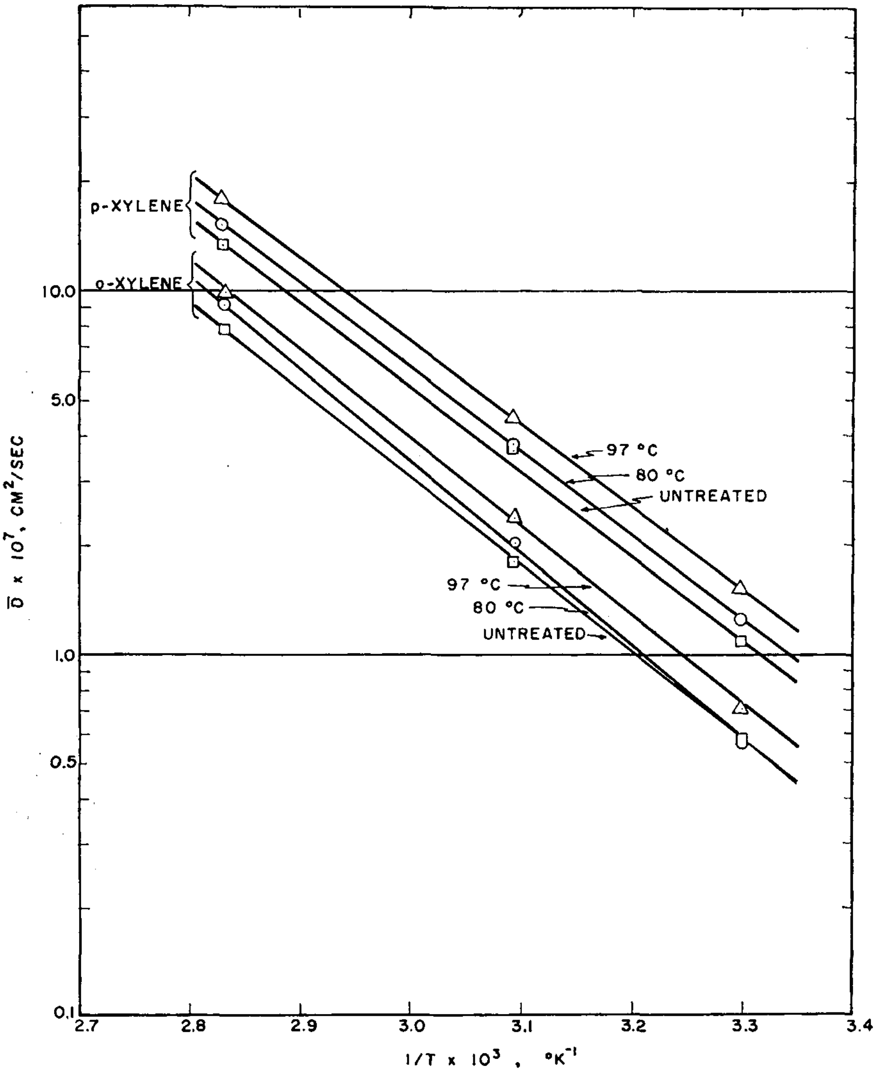

Fig. 7. Integral diffusivities for *p*- and *o*-xylene. Polymer annealed dry at specified temperature.

mal and solvent treatment result in a net decrease in the degree of interlamellar crosslinking, steric factors can prevent this decrease from being homogeneous on a scale comparable to diffusion path lengths or zone sizes.

According to this latter model, the degree to which a permeant is capable of swelling an untreated film should reflect the ability of a permeant to reduce the diffusion barrier in treated films. It will be noted in Tables I and V that there is a direct correlation between C^* values in the untreated films and the values of γ obtained from integral diffiusivities in treated films.

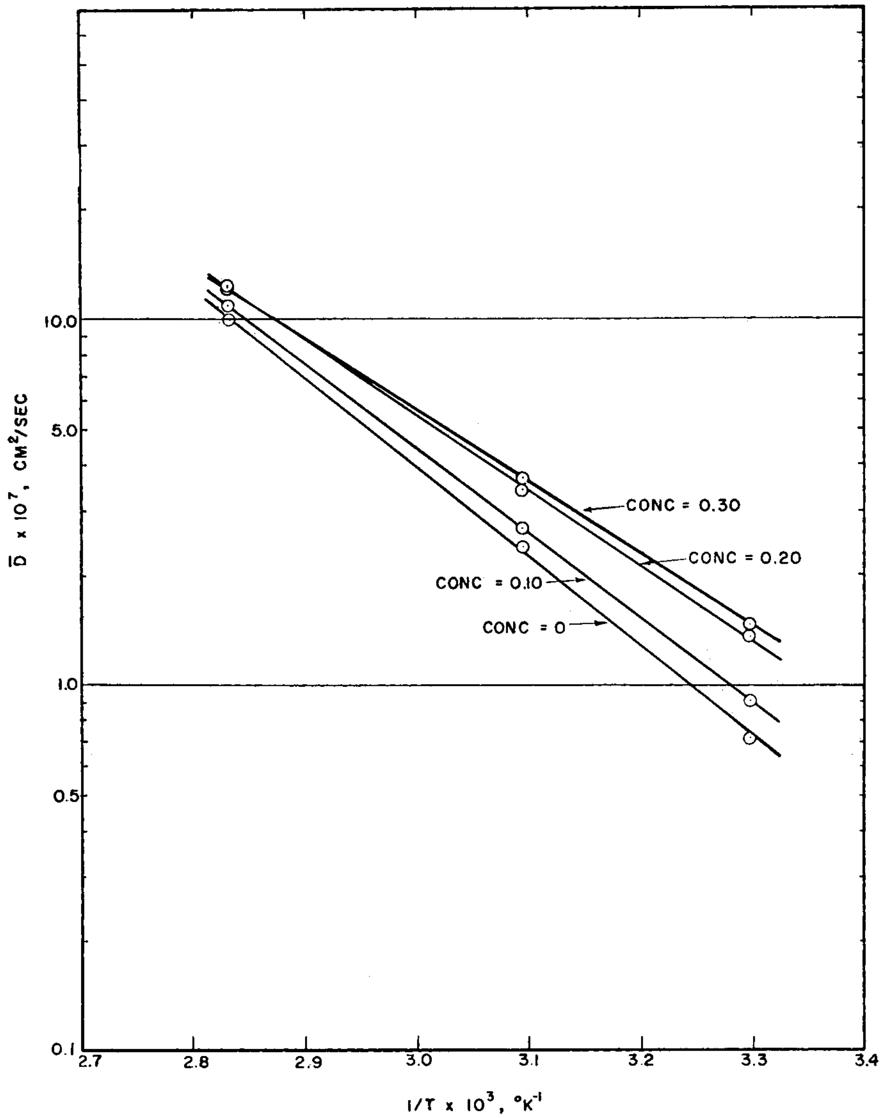

Fig. 8. Integral diffusivities for *o*-xylene. Polymer treated with *p*-xylene, 97°C., at specified concentration.

2. Xylene Diffusivity as a Function of Temperature

The integral diffusivities of the xylenes as a function of temperature are presented as Arrhenius-type plots in Figures 7–9. Activation energies have been calculated from the relationship

$$\bar{D} = \bar{D}^0 e^{-\bar{E}_D/RT} \tag{18}$$

and are summarized in Table VII.

TABLE VII
Apparent Activation Energies for Diffusion

Treatment			$\bar{E}_D$, kcal./mole	
Solvent	Concn., g./g.[a]	Temp., °C.	*o*-Xylene	*p*-Xylene
Untreated polymer			11.0	10.7
None	0	80	11.9	10.6
None	0	97	11.2	10.5
p-Xylene	0.10	80	10.7	
p-Xylene	0.10	97	10.6	
p-Xylene	0.10	115	11.4	
p-Xylene	0.20	97	9.4	
p-Xylene	0.30	97	9.0	

[a] Treatment concentration expressed as grams of solvent per gram of total dry polymer.

For untreated and annealed polymers, the mean activation energy is 10.6 kcal./mole for *p*-xylene, and 11.4 kcal./mole for *o*-xylene. While the difference between these figures is within experimental error (estimated to be about 20%), it may be significant in that it is qualitatively consistent with the difference in diffusion coefficients between the isomers (a ratio of 2:1, *para* to *ortho*).

The physical significance of these apparent activation energies for diffusion becomes more evident when they are compared with values derived from theoretical and empirical models for the diffusion process in polymers. Brandt[16] has related the activation energy to the work required to form a "hole" in the polymer matrix. Two contributions to E_D were considered by Brandt: the work required to separate polymer chain segments by overcoming intermolecular forces, which is related to internal pressure, and the work required to "bend" a chain molecule, or cause it to change position by rotation about bonds, which is related to the bond rotational hindering potential. One may calculate an activation energy from Brandt's model by specifying the necessary energy and size parameters associated with the polymer, and the molecular diameter of the diffusing fluid. Using a diameter of 8.5 A. for *o*-xylene, estimated from vapor viscosity, along with Brandt's parameters for polyethylene, the model predicts an activation energy of 19.3 kcal./mole, which is about 70% higher than the experimental value of $\bar{E}_D$.

A second estimate of the activation energy can be obtained from the correlation given by Michaels and Bixler[3] of E_D as a function of molecular diameter, and this yields a value of 19.6 kcal./mole, in agreement with the figure from Brandt's model.

The discrepancy between calculated and present experimental activation energies can be explained, at least in part, by the concentration dependence of diffusion in the xylene–polyethylene system. In Brandt's formulation, the energy parameters, such as internal pressure, are for the undiluted polymer, and would certainly differ for polymer swollen with a compatible

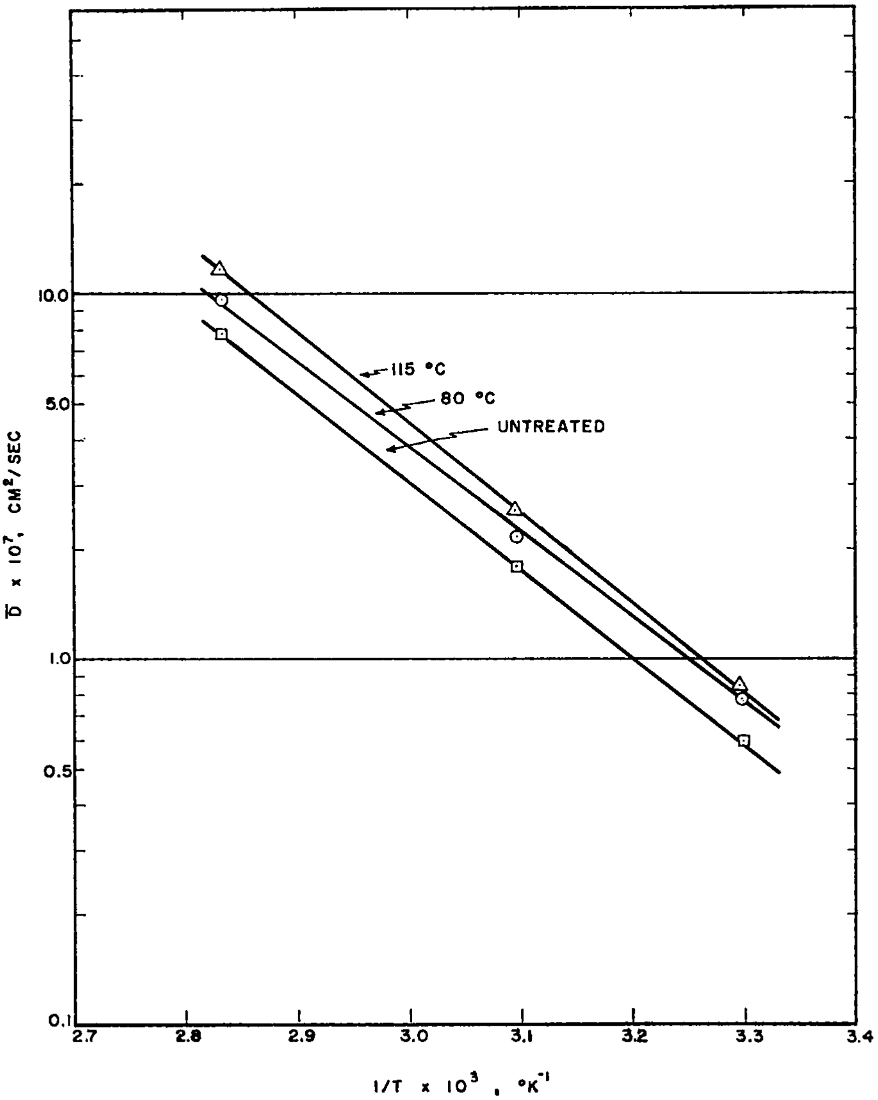

Fig. 9. Integral diffusivities for *o*-xylene. Polymer treated with 10% *p*-xylene at specified temperature.

solvent. Similarly, the correlation given by Michaels and Bixler is for the diffusion of permanent gases, and the concentrations of gas are so low that the presence of the diffusing species has a negligible effect upon polymer properties. Therefore, both estimates of the activation energy presented above represent $E_D{}^0$, the activation energy at zero concentration defined by:

$$D_{c=0} = D^0_{c=0}\, e^{-E_D{}^0/RT} \tag{19}$$

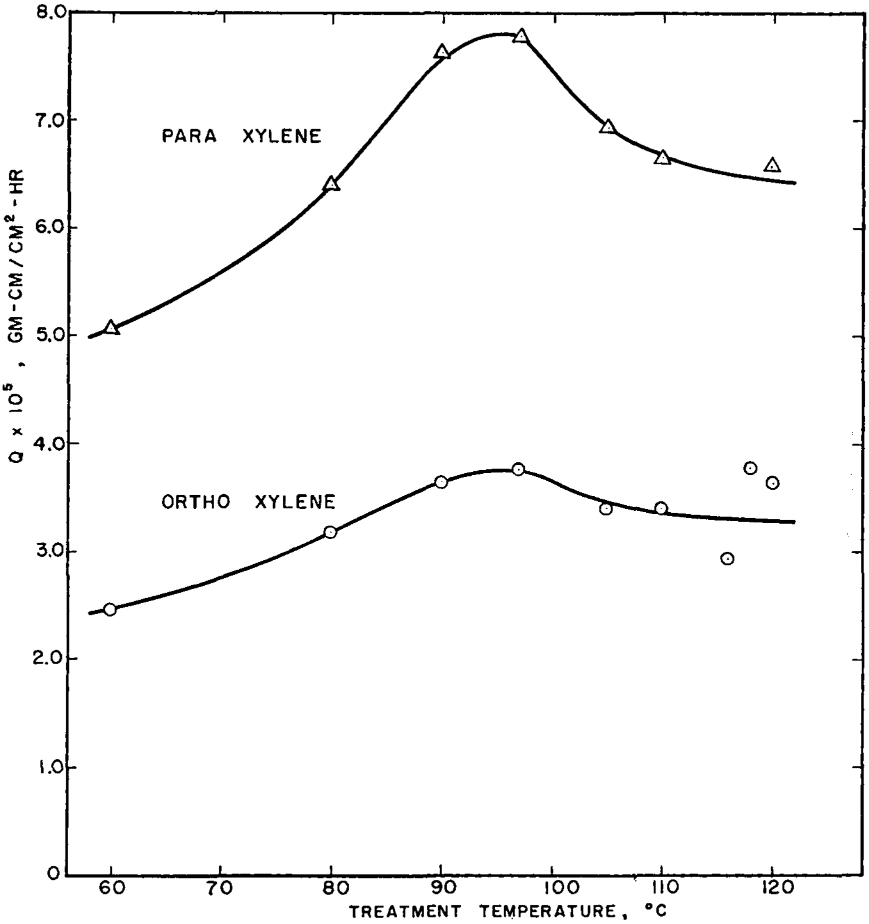

Fig. 10. Permeation flux vs. treatment temperature for *p*- and *o*-xylene, 30°C. Polymer treated with 10% *p*-xylene.

In fact these estimating procedures do give values of $E_D{}^0$ in excellent agreement with the value of 17 kcal./mole obtained for the smaller benzene molecule (d = 7.5 A.) from the data in Table VI. In the present work, however, $\bar{E}_D$ is obtained from the experimental data which is related to $E_D{}^0$ by:

$$\bar{E}_D \cong \bar{E}_D{}^0 - RT\gamma C^* \qquad (20)$$

which is obtained from a combination of eqs. (14), (18), and (19) assuming $\bar{D}^0 \cong D^0_{c=0}$. According to eq. (20), $\bar{E}_D$ should decrease with increasing C^*. Thus the decrease noted above ($\bar{E}_D - E_D{}^0 \cong 9$ kcal./mole) is consistent with the plasticizing effect brought about by increased permeant activity and concentration in untreated polyethylene films.

Although in the current work thermal treatment alone does not significantly alter the apparent $\bar{E}_D$'s there is a slight decrease in the apparent

$\bar{E}_D$'s when C^* is increased by solvent treatment as can be seen in Table VII. This decrease is less, however, than would be anticipated if the increase in C^* due to treatment resulted in a uniform decrease in the polymer concentration in the amorphous regions of the swollen films. Again, if the major barrier to diffusion is provided by regions in which the polymer concentration is not appreciably different than in the untreated film then a minor reduction in the apparent $\bar{E}_D$ would be expected.

3. *Permeability*

Having discussed the factors affecting diffusion and sorption in treated polyethylene films, it is possible to consider how these factors contribute

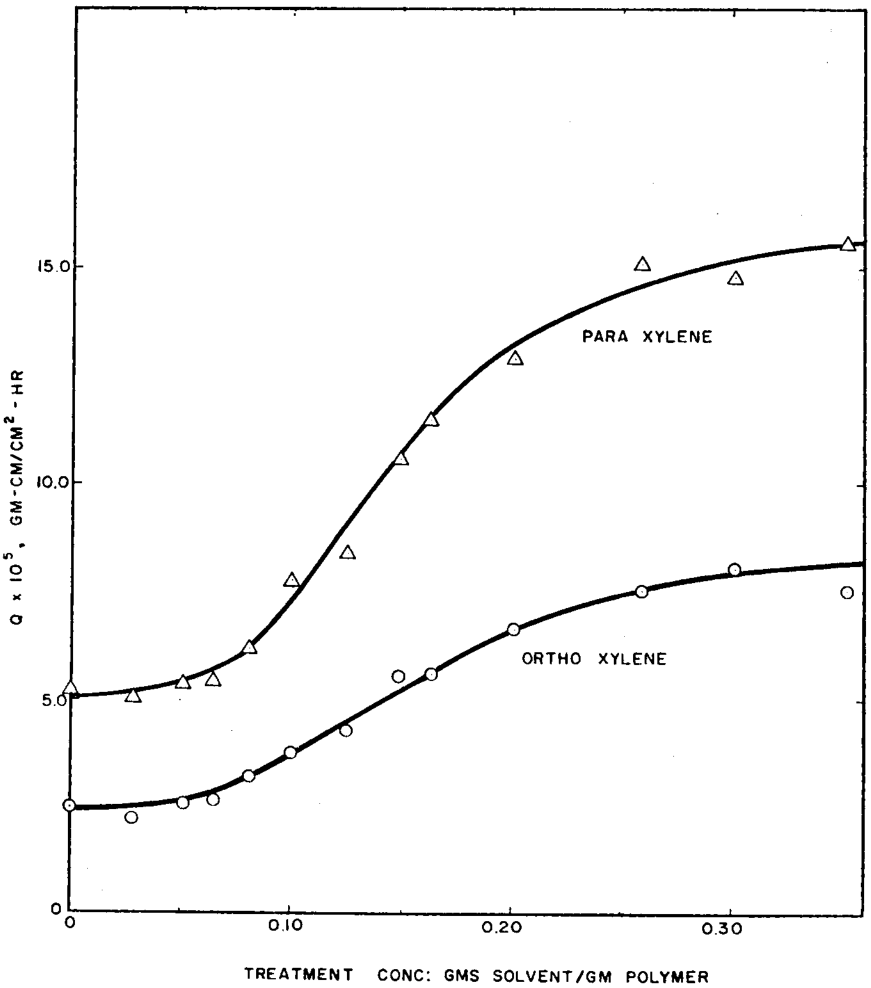

Fig. 11. Permeation flux vs. treatment concentration for *p*- and *o*-xylene at 30°C. Polymer treated with *p*-xylene at 97°C.

to the liquid permeation flux in the polymer. Combining eq. (4) with the concentration dependence of diffusivity gives

$$Q = D_{c=0}\, \rho_1 \alpha C^* \exp(\gamma C^*) \tag{21}$$

Figure 10, which gives the xylene permeation flux as a function of treatment temperature, shows that Q passes through a maximum at about 95°C. The initial rise is due to increased sorption (and, as well, diffusivity) with treatment temperature; at high temperatures, however, the decrease in α caused by treatment overtakes the sorption increase, and a reduction in Q results. In spite of the decrease in interlamellar linking through the temperature range, Q begins to fall off because less material is available for sorption and diffusion. This effect has not been observed for the acetylene dichlorides, where the increase in sorption with treatment temperature is not as marked. Rather, the permeation flux remains almost constant, since the decrease in α and the sorption increase with treatment temperature remain in balance.

Figure 11 shows that Q increases for the xylenes over the entire range of treatment concentrations. In this case, the decrease in α is small, and hence there is little reduction in the fraction of polymer available for permeation. Since both C^* and $\bar{D}$ increase markedly with treatment concentration, the increase in Q is quite high, of the order of threefold. The leveling-off of Q at high concentrations is more apparent than real. The treatment concentrations represent the amount of liquid in contact with the polymer during annealing. When this concentration exceeds the solubility limit of the solvent at the treatment temperature, no further change in the properties of the resulting polymer will be observed. The solubility of *p*-xylene, the treating solvent, at 97°C. is about 0.25–0.30 g./g., which is consistent with the point at which Q begins to level off in Figure 11. Similar behavior was observed in the permeation flux of the acetylene dichlorides as a function of treatment concentration.

4. Transient Permeation

a. Results. A series of runs was carried out to determine the behavior of the permeation flux during the approach to steady state. In order to study the effects of temperature and film history, permeation measurements were made in this fashion under a variety of conditions. The results are presented graphically in Figures 12–15.

The effects of permeation temperature on the flux-time curves for *p*-xylene are shown in Figure 12. Several facts about the transient behavior are evident. First, within the temperature range studied, the permeation flux rises to a maximum within about 1 hr., followed by a decline to the steady-state value in 2–5 hr. Second, as the permeation temperature increases from 50 to 90°C., the time over which the permeation flux is elevated above the final steady state value decreases, until, at 90°C., the maximum no longer appears. Third, as the permeation temperature increases, the time required to attain steady state decreases. Although

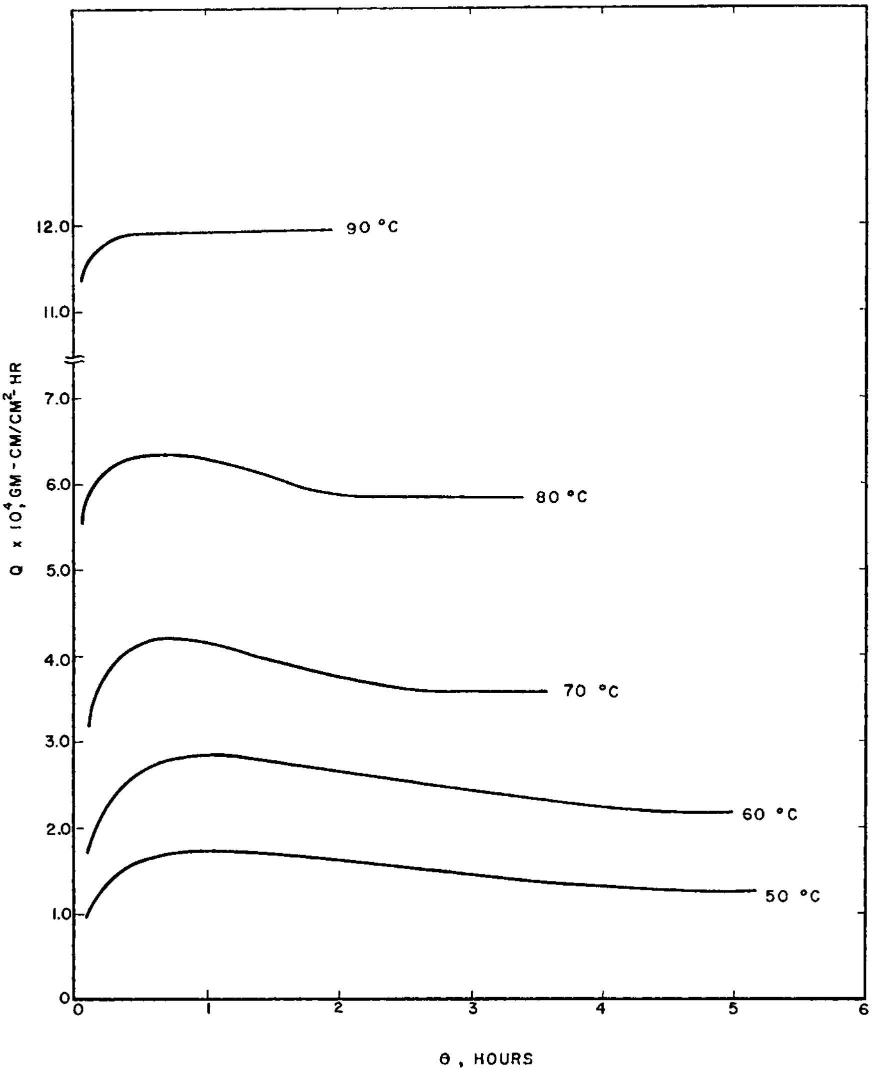

Fig. 12. Approach to steady-state permeation. *p*-Xylene permeated at specified temperature, untreated polymer.

not shown, *o*-xylene yields almost identical flux-time curves with respect to the above details.

Certain additional data are of interest, also. The density of the polymer after permeation (measured after drying and cooling) is increased over that of the initial untreated film, and the density increase is greater at higher permeation temperatures (Table VIII). The density of the polymer permeated to the maximum flux only also shows the increase. Secondly, an estimate of the time required for 95% of saturation of the film with liquid, using a diffusivity of 10^{-8} cm.^{2}/sec. (which is an order of magnitude

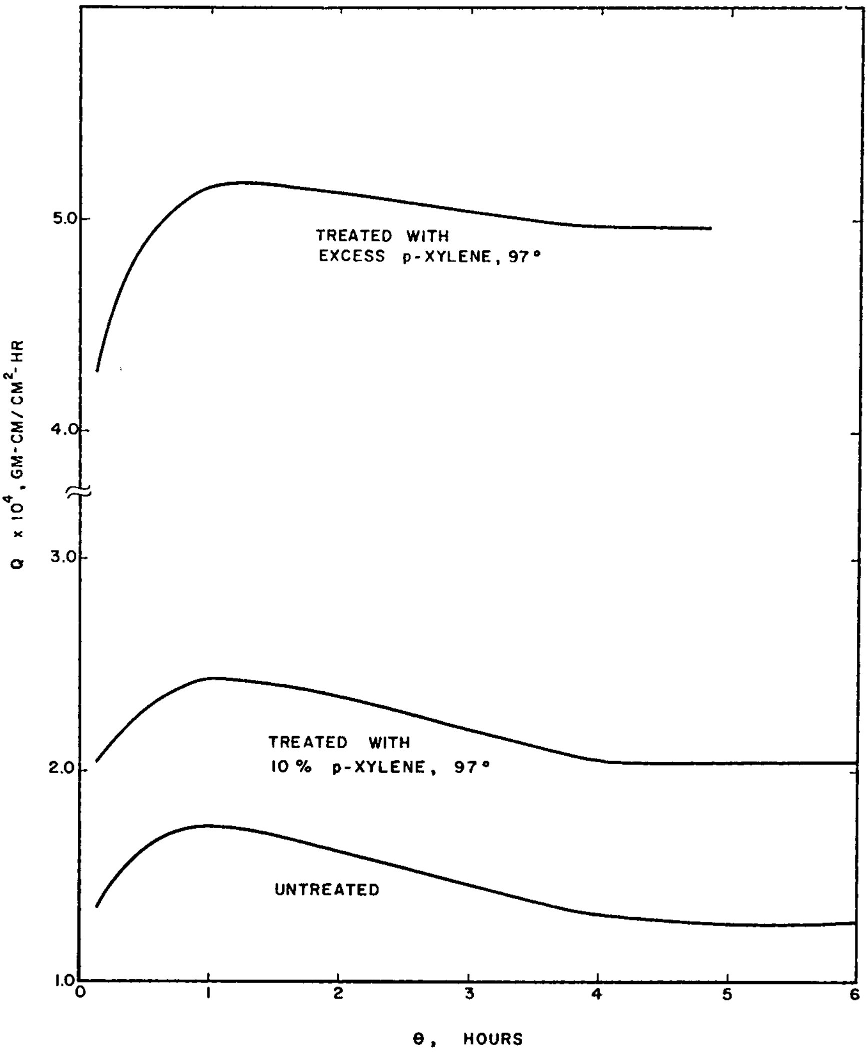

Fig. 13. Approach to steady-state permeation. *p*-Xylene, 50°C.

lower than that prevailing at steady state at 50°C.) gives a value of less than 1 min. Therefore, the changes with time observed here are not caused by diffusion transients alone.

b. Origins of Structural Changes Occurring in the Polymer During Permeation. It is likely that the causes of the transient behavior outlined above are related to slow relaxation processes occurring in the polymer as the structure adjusts in configuration to the swollen state. Undoubtedly, similar factors operate to give rise to both the non-Fickian behavior in sorption–desorption kinetics and various time-dependent effects prior to steady state that have been cited in the literature.[6,14,17,18] Indeed, typical

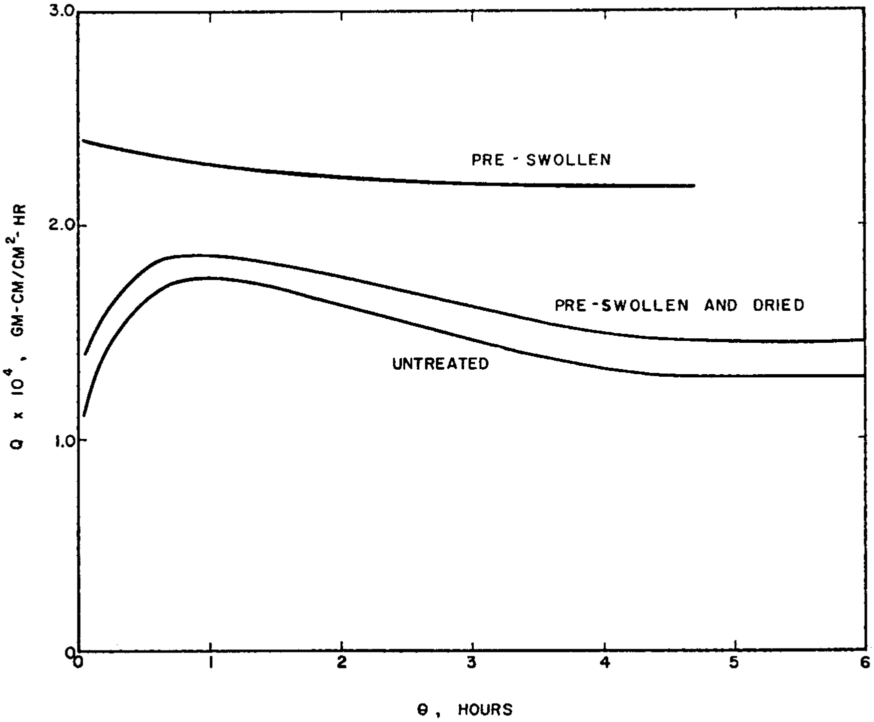

Fig. 14. Approach to steady-state permeation. *p*-Xylene, 50°C.

sigmoid-shaped sorption and nonlinear desorption versus $\theta^{1/2}$ curves have been obtained in this study for liquid *p*-xylene in polyethylene. Two studies in the literature describe a type of behavior in which the permeation flux passes through a maximum prior to the attainment of steady state, and some discussion of this work is warranted at this point. Park[18] noted this effect for methylene chloride vapor in polystyrene below the glass transition. The maxima, which were more pronounced than those obtained in the present work, were attributed to other types of flow during the tran-

TABLE VIII
Effect of Permeation on Polymer Amorphous Volume Fraction

Polymer treatment	$\alpha_{25°C.}$
Untreated, prior to permeation	0.396
Permeated to steady state at 40°C.	0.388
Permeated to steady state at 50°C.	0.381
Permeated to steady state at 80°C.	0.344
Permeated to steady state at 90°C.	0.315
Permeated to maximum rate only, 50°C.	0.377
Preswollen at 50°C. prior to permeation	0.380
Preswollen at 50°C. after permeation	0.376
Preswollen at 50°C. permeated without drying	0.376

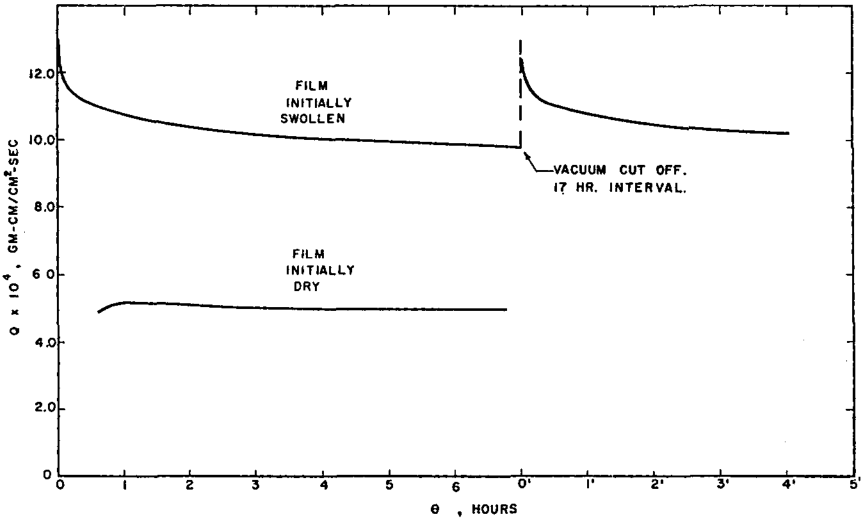

Fig. 15. Approach to steady-state permeation. *p*-Xylene permeated at 50°C., polymer treated with excess *p*-xylene at 97°C.

sient period due to an internal capillary network "frozen" into the glassy structure. This effect can be ruled out for polyethylene which is considerably above its second order transition at room temperature. Meares[17] has obtained a very sharp peak at times that were short relative to the time required to reach steady state for allyl chloride vapor in polyvinyl acetate at 40°C., about 10°C. above the glass transition. He has proposed that the stress imposed upon the underlying dry polymer when the upstream face of the film expands causes the formation of microheterogeneities, through which permeation is rapid. As the stressed polymer relaxes through the elastic reaction of the network to the applied force, the permeation rate falls. This mechanism might be applicable in the present study, except that Meares has noted that the maximum is achieved within seconds, and after the flux rate falls it gradually rises again to the steady-state value over a period of hours, or, under some conditions, even days. In the present study, permeation was carried out for 24 hr. after steady state was attained, with no change in flux. From this comparison, it appears that the effects here differ significantly from those outlined by Meares.

Since the transient behavior in this work cannot be explained completely by mechanisms proposed in the literature, it is of value, therefore, to consider the possible factors that may account for the effects described in the previous section.

1. Permeant Osmotic Pressure. As discussed earlier, the driving force for the expansion of the polymer network in sorption is osmotic pressure. These pressures can probably become high enough to cause disruption and fragmentation of the lamellar crystalline structures in the polymer. An osmotic stress, as any applied stress, is transmitted in the polymer by the slow rearrangement of amorphous chain segments into extended configurations. The extended chains exert a force on the crystalline structures to which they are connected, possibly causing fracture and further lengthening of the chain segment by unraveling from the crystal lattice. Additional amorphous chain segments form, connecting the crystalline fragments. This process should result in a disorientation of lamellar crystallites from the normal twisted ribbon structure envisioned in spherulitic untreated polymer. This disorientation has been qualitatively supported by light-scattering measurements.[12] The process continues until a sufficient number of intercrystalline links are formed such that the polymer network can exert a retractive force equal to the osmotic pressure, in this way limiting swelling. If diffusion is rapid, the rate at which this process occurs (the rate of swelling) should be controlled by the rate at which chain segments can assume extended configurations; in this respect, swelling is analogous to mechanical "creep." The permeation rate through the polymer should increase during this state because of three factors: (*1*) increasing sorption; (*2*) increasing diffusivity, due to the concentration effect on D; (*3*) the creation of more direct flow paths due to fragmentation of crystallites.

2. Osmotic-Pressure Gradient Across the Film. Since a concentration gradient exists during permeation, a gradient in osmotic pressure similarly must be established through the film. The diffusion coefficient increases with concentration, and consequently the concentration and osmotic pressure gradients must be steepest near the downstream face of the film. Thus, an expanding force is imposed on the unswollen region of the film by the swollen polymer adjacent to it, which may tend to increase the permeation rate in the unswollen region. If the tensile stresses imposed upon this region can gradually be relieved by "creep," then its permeability may slowly decrease, with consequent reduction in net flux through the film. This is analogous to the effect cited by Meares.[17]

3. Crystalline Melt-Out. In addition to the mechanical disruption of the crystalline phase brought about by osmotic pressure (and which may cause the loss of only a relatively small fraction of the total crystallinity), some melting or dissolution of lamellae will occur upon the introduction of liquid into the polymer. This may be possible at temperature as low as 30°C., and undoubtedly occurs at higher temperatures (above 70–80°C.). Crystalline melt-out will increase the permeation flux through increased sorption because of the formation of additional amorphous polymer and the removal of crosslinks. If the latter effect allows increased sorption per unit amorphous volume, the effective integral diffusivity will increase because of its concentration dependence.

4. Recrystallization. Recrystallization, or at least further crystallization, of the polymer occurs during permeation, as can be seen from the data in Table VI. It should be noted, however, that the reduction in α presented in this table need not all have resulted during the permeation process, since some crystallization could also occur when the film was cooled and dried prior to density measurement. Consequently, the density data cannot serve as a true indication of the recrystallization history during permeation. Crystallization may begin to take place as soon as a concentration of permeant is present in sufficient concentration to significantly increase amorphous chain mobility. At low permeant concentration, chain rearrangement may be restricted simply to extension due to the osmotic stress, thus hindering crystallization. The rate of crystallization should increase with time, since the permeant concentration increases with time. This should continue until the amount of crystallized material imposes restrictions on both the mobility and the number of possible configurations of remaining amorphous chain segments. Crystallization should cause a reduction in permeation flux due to the removal of permeable amorphous polymer and limitation of mobility of the remaining amorphous segments. At low temperatures, the amount of additional crystallization may be quite small, and the most important effect may be a re-ordering of the structure to yield larger (in *b* and *c* crystallographic directions) more anisometric, crystalline lamellae. This could be brought about by elimination of a fraction of the intralamellar imperfections referred to earlier. This reduction in intralamellar imperfections would reduce the permeation rate by elongating flow paths through a film. Through a combination of these effects, recrystallization probably is contributory to the decline in permeation flux from the maximum to the steady-state value.

c. Effect of Permeation Temperature and Solvation History. The considerations outlined above suggest explanations for the effect of permeation temperature on transient behavior. As the permeation temperature increases, polymer segmental mobility becomes higher. Therefore, the rate of expansion of the network increases, leading to a decrease in the time required to achieve the maximum permeation flux. This is supported by the fact that the rate of attainment of swelling equilibrium in the polymer increases with temperature. Secondly, the rate of crystallization increases with temperature, and this is manifested by a decrease in the time required to reach steady-state permeation. At 90°C., crystallization is rapid enough so that the decline in permeation flux is not observed, and the attainment of steady state is controlled only by the rate of expansion of the network.

The transient behavior of solvent-treated films is shown in Figure 13. The major differences between these and the untreated film is a reduction in the decrement between the maximum and the steady-state permeation rates. As the treatment concentration increases, going from untreated to 10% solvent to excess solvent, it has been postulated that the degree of interlamellar linking in the dry polymer decreases. Consequently, during swelling, the osmotic stress per amorphous chain segment would be higher in treated films, with an attendant reduction in the ability of the polymer to recrystallize. Furthermore solvent treatment itself results in a recrystallization of the polymer which should be more stable under conditions of permeation. If recrystallization during permeation causes the reduction in permeation rate after the maximum then a film which has been recrystallized during treatment should exhibit less tendency to recrystallize during permeation, and the trends in Figure 13 are to be expected. It is somewhat surprising that the time to attain the maximum permeation rate is not decreased due to treatment, although this may be due to the fact that the increment in permeation rates between the initial and maximum values increases with increasing solvent concentration.

For films in which preswelling was followed by permeation without drying (Figs. 14 and 15), no maximum in permeation rate was observed. Since the polymer was allowed to equilibrate with liquid for 16 hr., the structural changes outlined above would have been completed when permeation began. There is, however, a gradual decline in permeation rate with time. As can be seen in Figure 15, this phenomenon could be repeatedly observed in the same film by discontinuing pervaporation, allowing the entire film to reswell, and then again commencing pervaporation. If the flux is continuing to decrease toward the steady-state permeability of the preswollen and dried film, the gradual decrease in flux could be ascribed to the slow contraction of the downstream low-concentration region of the film due to reduction in osmotic stress. The high gradient in osmotic stress established by rapidly reducing the concentration in the downstream face to zero could be responsible for the fact that films permeated in this manner consistently ruptured after several hours of permeation. This steep gradient does not form when the dry film is permeated, since the rate of swelling is low.

An alternative explanation must be considered, however, if the flux-time curves for preswollen films are interpreted as leveling off at a steady-state flux that is higher than that attained in the preswollen and dried films. In each case, the solvation history of the downstream face was identical; each had been preswollen and dried. However, in the former, the osmotic pressure gradient had been established by desorption, and in the latter, by sorption. Conceivably, due to loss of solvent from the downstream region of the film while regions further upstream remain highly swollen, the downstream region (which normally provides the major resistance to transport) is prevented from shrinking and densifying, and thereby offers much less resistance to diffusion than "normal" polymer of equal solvent content.

5. *Gas Permeability*

Relationships between the diffusivities of permanent gases in polyethylene and certain aspects of crystalline structure have been established by Michaels, Parker, and Bixler.[3,19] It was felt that by employing concepts developed by these authors, gas diffusion data for solvent-treated films could provide information about polymer morphology that would be a valuable adjunct to the results of liquid sorption and diffusion. The permeabilities of helium and methane were determined in a series of films, (a) in the dry state (after heat or solvent treatment), and (b) reswollen with a nonvolatile paraffin oil. The latter group was studied in an attempt to

TABLE IX
Helium and Methane Permeabilities at 25°C.

Polymer	Treatment			Amorphous volume fraction	Gas permeability $\bar{P} \times 10^8$, cm.^{3} (STP) cm./cm. sec. atm.		Gas diffusivity $D \times 10^7$, cm.^{2}/sec.	
	Solvent	Concn., g./g.[a]	Temp., °C.	α	He	CH_4	He	CH_4
Dry polymer	Untreated polymer			0.396	2.91	1.27	61.3	1.58
	None	0	97	0.305	2.16	0.77	59.1	1.25
	None	0	115	0.242	1.67	0.55	57.5	1.12
	None	0	125	0.200	1.57	0.63	65.5	1.55
	p-Xylene	0.10	97	0.297	2.48	0.94	69.6	1.56
	p-Xylene	0.10	115	0.226	2.10	0.85	77.5	1.85
Oil-swollen polymer	Untreated			0.445[b]	3.25	1.74	60.9	1.93
	None	0	97	0.356[b]	2.80	1.64	65.5	2.27
	None	0	115	0.294[b]	2.53	1.45	71.7	2.43
	p-Xylene	0.10	97	0.368[b]	3.00	1.94	68.0	2.60
	p-Xylene	0.10	115	0.292[b]	2.74	1.62	78.2	2.74

[a] Treatment concentration expressed as grams of solvent per gram of total dry polymer.

[b] Corrected for the presence of oil in the amorphous phase.

obtain information about the nature of the polymer structure in the swollen state.

Diffusion coefficients were calculated from the relation

$$D = \bar{P}/k^*\alpha \qquad (22)$$

where k^* is the solubility coefficient of the gas in amorphous polyethylene. For helium, $k^* = 0.012$ cm.^{3} (STP)/cm.^{3}-atm.; for methane, $k^* = 0.203$ cm.^{3} (STP)/cm.^{3}-atm.[3] While it was assumed that k^* was the same for a given gas in both dry and oil-swollen films, the amorphous volume fraction, α, was corrected for the presence of paraffin oil in the latter, assuming solution of oil in the amorphous polymer only, and additive volumes. The experimental diffusivities are given in Table IX.

It is apparent that thermal and solvent treatment consistently increase the diffusion coefficients of helium and methane in the oil-swollen films, while this is not the case in the dry films. Also, the effect of treatment among the swollen films is greater for methane than it is for helium. These results support the concept that treatment instills the potential for structural changes in the polymer upon reswelling. By decreasing the degree of interlamellar linking, treatment allows a greater amount of disruption and fragmentation of the crystalline structure when the polymer is swollen, thus decreasing the impedance to gas flow. For the dry polymer there may be little change in the morphology presented to a diffusing gas molecule, other than an increase in the mean lamellar step height. As argued earlier, however, there may be compensating morphological effects in operation. An increase in crystallinity and lamellar anisotropy tending to decrease the diffusivity may be offset by an increase in chain mobility in the amorphous regions through reduction in the degree of entanglement. The large effect of the presence of oil on methane diffusivity may be due to its higher diffusivity in paraffin oil (98×10^{-7} cm.^{2}/sec.).[20] The helium diffusivity in amorphous polyethylene, on the other hand, is already in the range of diffusivities in low molecular weight liquids (2.2×10^{-5} cm.^{2}/sec.).[3]

IV. CONCLUSIONS

The effect of solvent and thermal treatment of linear polyethylene films, consisting of annealing in the presence or absence of a solvent, is to increase the transport rate of liquids through the polymer. The sorption of liquid per unit amorphous phase is increased by structural changes in the polymer, and an attendant increase in integral diffusivity results. The heat of solution of xylene in polyethylene, obtained from the temperature dependence of sorption, is consistent with values reported for other aromatic liquids. The temperature dependence of diffusivity gives activation energies for diffusion that decrease with polymer treatment.

A model has been proposed which relates the loss in effective crosslinking of the amorphous polymer by crystallites due to heat or solvent treatment to liquid sorption in the resulting polymer. To account for the lower concentration dependence of the effective integral diffusivities encountered in this work was compared with those found by other investigators working at lower permeant activities, it has been proposed that this reduction in crosslinking is inhomogeneous on a microscale and the major barrier to diffusion is still offered by partially swollen regions of high polymer concentration. There is evidence that fragmentation and disorientation of the polyethylene crystalline structure is brought about by the osmotic stresses imposed during swelling.

Prior to attaining steady-state permeation, the flux of the xylene and acetylene dichloride isomers passes through a maximum. The initial increase with time appears to be attributable to the effects on polymer structure of the build-up of osmotic pressure and some dissolution or fragmentation of crystallites. The decline in flux to the steady-state value may be the result of further crystallization and/or stress relaxation after the rearrangement of chain segments in the swollen state.

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Résumé

Des films de polyéthylène linéaires coulés et sèchés et recuits dans des solvants, diffèrent notablement des films non-traités par leur propriété de barière de sorption et de diffusion. La sorption ultérieure de liquide *o*- et *p*-xylène et *cis* et *trans*-acétylène dichloré par unité de volume de polymère amorphe augmente quand la température de cuisson augmente ou quand la concentration du solvant croît. Les diffusions intégrées calculées à partir de la sorption et des vitesses de pénétration à l'état stationnaire montrent une augmentation monotonique par unité de volume de polymère amorphe. La dépendance de la concentration, cependant, est moins marquée que celle observée dans des systèmes similaires ayant une activité de pénétration plus faible. Apparemment le traitement ci-dessus réduit le pontage effectif imposé par les cristallites dans les chaînes polymériques amorphes en les démèlant et en incorporant plusieurs de ces chaînes dans les cristallites. Alors le polymère est capable d'un plus grand degré de gonflement dès qu'il entre en contact avec un liquide compatible malgré un plus haut degré de cristallinité. La faible dépendance de la concentration de la diffusion est probablement due à la distribution hétérogène de l'excès de substance pénétrante dans un film traité. Si l'excès de substance perméable est préférentiellement absorbé dans des régions de basse concentration en polymère, alors les observations ci-dessus peuvent s'expliquer. Longue durée, gonflement induit par pression osmotique et recristallisation ont été cités pour expliquer la dépendance du temps des vitesses de pénétration des films traités et non-traités.

Zusammenfassung

Gegossene Filme aus linearem Polyäthylen, die der Trocken- und der Lösungsmitteltemperung unterworfen wurden, unterscheiden sich in ihrem Verhalten als Sorptions- und als diffusionsbarriere deutlich von den nicht behandelten Filmen. Die nach der Temperung erfolgende Sorption von flüssigem *o*- und *p*-Xylol und von *cis*- und *trans*-Acetylendichlorid pro Volumseinheit des amorphen Polymeren nahm mit der Temperungstemperatur und mit der bei der Behandlung verwendeten Lösungsmittelkonzentration zu. Das aus der Sorption und der stationären Permeationsgeschwindigkeit berechnete integrale Diffusionsvermögen nimmt mit der Sorption pro Volumseinheit des amorphen Polymeren monoton zu. Die Konzentrationsabhängigkeit ist jedoch weniger ausgeprägt als in ähnlichen Systemen bei niedriger Aktivität des Permeationsmittels. Die vorhin beschriebene Behandlung erniedrigt anscheinend die den amorphen Polymerketten durch die Kristallite aufgezwungene affektive Vernetzung durch Entschlingung und Einbau einiger dieser Ketten in Kristallite. Infolgedessen quillt das Polymere in Anwesenheit einer geeigneten Flüssigkeit trotz der höheren Kristallinität stärker. Die geringe Konzentrationsabhängigkeit des Diffusionsvermögens geht wahrscheinlich auf eine heterogene Verteilung des überschüssigen Permeationsmittels im behandelten Film zurück. Mit der Annahme, dass das überschüssige Permeationsmittel bevorzugt in Bereichen niedriger Polymerkonzentration sorbiert wird, lassen sich die eben angeführten Beobachtungen erklären. Als Ursache für die Zeitabhängigkeit der Permeationsgeschwindigkeit in behandelten und unbehandelten Filmen werden die lange Dauer osmotische, spannungsinduzierte Quellung und Rekristallisation genannt.

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