

The Morphological Consequences of Annealing High-Density Polyethylene in Solvents

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Synopsis

When a semicrystalline polymer imbibes solvent molecules at near-ambient temperatures it is very probable that the crystalline regions are not affected. The noncrystalline regions swell to accommodate the solvent and may also undergo structural changes which are not reversed on removing the solvent. If this happens, the sorptive capacity of the polymer is permanently changed. Pretreating a polymer membrane with liquid solvent has the same effect on sorption measurements as pretreatment with the corresponding saturated vapor only when special precautions are observed. High-density polyethylene films were used throughout the investigation, and *p*-xylene was the organic permeant. Numerous measurements of sorption and permeation rates were made, and the results are discussed in terms of a new model for the behavior of noncrystalline chains in a semicrystalline polymer. The shorter tie molecules running between the crystalline lamellae appear to be of crucial importance, and slight modification of these may have a large effect on the sorptive capacity of the sample as a whole. The possibility of solvent molecules clustering in the swollen polymer is considered in an Appendix.

INTRODUCTION

When a semicrystalline polymer such as polyethylene is exposed to solvent, either as vapor or as liquid, structural changes may occur in the polymer. The reversibility or otherwise of such changes is relevant to all polymer-solvent interactions, but most especially to the use of polymer membranes, in separation processes, for example.

The effect on the sorption-diffusion characteristics of polyethylene caused by annealing in the presence of a swelling solvent has been investigated by Michaels et al.¹ They found that annealing in liquid *p*-xylene, at temperatures close to the dissolution temperature of the polymer, modified the sorption-diffusion characteristics of the system to a much greater extent than annealing in the absence of solvent. For example, pretreatment of high-density polyethylene with liquid *p*-xylene at 100°C produced a tenfold increase in its permeability to liquid *p*-xylene at 30°C. By contrast, annealing in the absence of solvent at 97°C increased its permeability to liquid *p*-xylene at 30°C by only 25%, and annealing at 115°C caused no change in permeability.² For the liquid-pretreated sample, the increase in permeability was shown to result from increases in both the sorption and

the diffusion components of the permeation process. On the basis of these results, it was postulated that liquid pretreatment caused a significant redeployment of chains in the noncrystalline regions. Noncrystalline chains were thought to become much longer, more flexible, and far fewer in number than in untreated or dry-annealed polymer.

In subsequent papers, Baddour et al.² and Michaels et al.³ studied the effect of pretreatment with vapors at high activity on the sorption-diffusion characteristics of polyethylene and polypropylene. Broadly, their results confirmed those of Michaels et al.¹ in so far as pretreatment was found to increase the permeability of films to solvating liquids at ambient temperatures. However, it appeared that annealing in vapor was appreciably less effective in enhancing the membrane permeability than annealing in the presence of the corresponding liquid. The origin of this anomaly remained unexplained and has provided a starting point for the present work.

Before attempting any further discussion of the effects on polymer morphology of vapor and liquid annealing at elevated temperatures, experiments were carried out to permit a comparison of vapor and liquid pretreatment under the simplest possible conditions, namely, at temperatures well below the dissolution temperature of the crystalline regions. At such temperatures, it has been generally assumed⁴ that sorption of a liquid or vapor is completely reversible with respect to the sorption-diffusion characteristics of the membrane. Rogers et al.⁵ have reported such reversibility for the sorption of *n*-hexane into low-density polyethylene at 30°C. Recent work,⁶ however, has indicated that the effect of liquid sorption on polyethylene is not always reversible. The sorptive capacity of the polymer for a particular penetrant can be affected, in some instances, by the previous swelling history of the specimen.

The present work was undertaken with the aim of investigating the reversibility or otherwise of the effects caused by the sorption of solvating vapors and liquids in polyethylene at near-ambient temperatures. It was hoped that the results would also help to explain the observed differences between the effects of vapor annealing, dry annealing, and liquid annealing.

It has been assumed throughout that, at the low temperatures used for most of the experiments, there is no dissolution or modification of the purely crystalline material present in the polymer samples. Certain results in the paper support existing evidence^{7,8} that this assumption is well founded.

EXPERIMENTAL

Materials

Rigidex 50 film, thickness 75 μm , density 955 kg/m^3 , was used as received for most of the experiments, but was sometimes recrystallized to a density of 975 kg/m^3 . *p*-xylene, 99%, was supplied by I.C.I., the major contaminants being the other isomers.

Procedures

Liquid Solvent Pretreatment. The polymer film was immersed in excess solvent contained in a thermostatted water bath for seven days and dried in air to constant weight before use.

Vapor Pretreatment. The apparatus described below in connection with vapor sorption experiments was also used for pretreatment of films by vapor. Except where stated to the contrary, specimens were dried at the temperature of the pretreatment. Drying was always continued until the mass of the specimen, as indicated by the extension of the quartz spiral, had returned to its original value.

Vapor Sorption and Desorption. The apparatus⁹ used for this work was of a type used by many previous investigators. The specimen was hung on a quartz spring in a tube connected by taps to pumps and to a vapor generator. The tube was surrounded by a jacket with flowing water inside it to maintain a constant temperature. All exposed glassware was wound with heating wire to prevent condensation. The position of the quartz spring was observed with a traveling microscope. Calibration of the spring in situ showed that it had a sensitivity of about 4.33 m/g. Apparent diffusion coefficients D_a were calculated from the measured half-time for an integral desorption experiment covering the concentration range C_0 to zero.

Permeation Rates. A conventional cell, described elsewhere,⁹ was used to measure the rate of *p*-xylene permeation through the polyethylene membranes. All rates were measured with nonpermeants absent above and below the membrane.

RESULTS

The Effects of Vapor Sorption on Polymer Morphology

Variation in Sorptive Capacity with Pretreatment. Figure 1 shows the sorptive capacities of film (as received and recrystallized) at 30°C and at a *p*-xylene vapor pressure of 639 N/m² as a function of pretreatment conditions. Pretreatment is expressed in terms of the maximum concentration of *p*-xylene imbibed by the specimen prior to complete drying for determination of its sorptive capacity under the fixed conditions. The sorptive capacity of the polymer increased with the concentration of *p*-xylene imbibed in the pretreatment, provided that this concentration exceeded the uptake of *p*-xylene at 30°C and 639 N/m² for an untreated specimen. From the detailed results for the original film, it appears that the effect of pretreatment is independent of pretreatment temperature as such.

If a specimen of film is pretreated at a certain concentration, the subsequent sorption characteristics may be reversible for all lower concentrations. This proved to be the case for a specimen pretreated with liquid *p*-xylene at 50°C. A dried piece of this pretreated film was equilibrated with *p*-xylene vapor at the temperatures and vapor activities shown as initial conditions in the legend of Figure 2. After attainment of equilib-

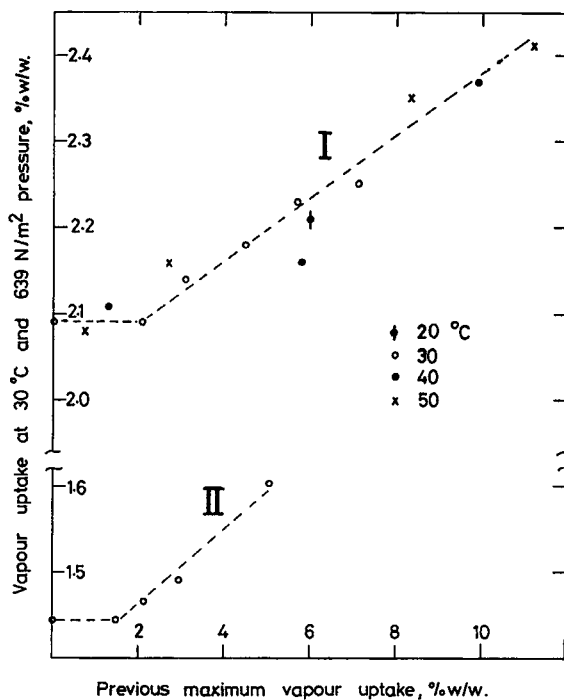


Fig. 1. Effect of vapor pretreatment at indicated temperatures on the sorptive capacity of polyethylene film as received (I) and recrystallized (II) for *p*-xylene at 30°C and 639 N/m² pressure.

rium at these initial conditions, the temperatures of vapor and specimen were adjusted, if necessary, to 30°C and the vapor pressure was changed to 706 N/m². These changes were made in such a way that the solvent uptake by the specimen did not change from its initial equilibrium value by an amount greater than the difference in solvent uptake between the initial and final equilibrium states. In each experiment equilibration to the final conditions was complete within 1 hr; and 1 hr later, the vapor pressure was reduced to zero and the rate of desorption measured in the normal way.

The effects of the various conditioning treatments on the equilibrium vapor uptake under the final conditions of temperature and pressure, and on the subsequent rates of desorption, are shown on Figure 2. Neither the final *p*-xylene uptake nor the diffusion coefficient of *p*-xylene was dependent on the extent or temperature of the intermediate swelling conditions, all of which had, of course, been preceded by the liquid pretreatment at 50°C.

Effect of Vapor Pretreatment on the Diffusion Coefficient-Concentration Relation. Figure 3 shows the apparent diffusion coefficient D_a as a function of *p*-xylene uptake at 30°C for (i) an untreated sample and (ii) a sample pretreated with *p*-xylene vapor at 50°C and at an activity of 0.98. As a general rule, the diffusion characteristics of a series of polyethylene films cannot be compared on the basis of D_a values.¹⁰ In the present context

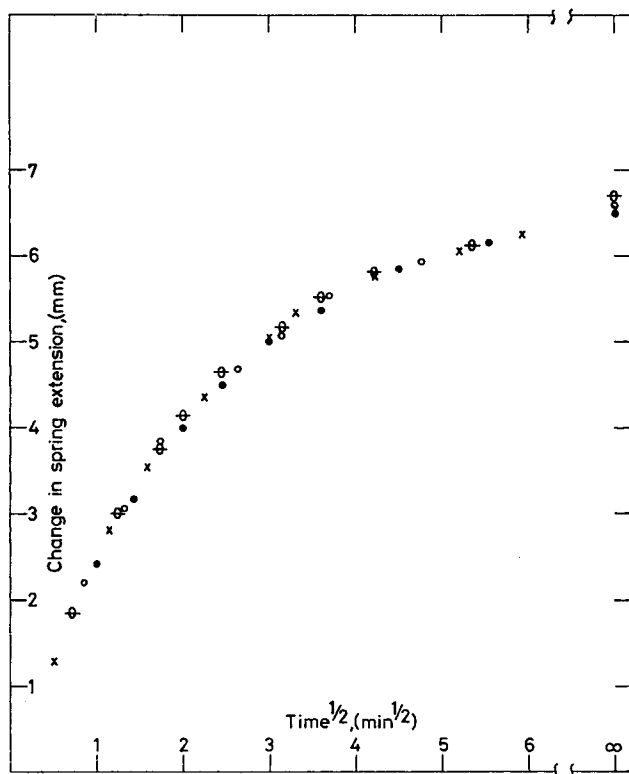


Fig. 2. Integral desorption curves for *p*-xylene in liquid-pretreated polyethylene equilibrated to 30°C and 706 N/m² pressure directly from the following initial conditions:

Code	Temp., °C	Vapor activity, p/p_0	Vapor uptake, % (w/w)
(○)	30	0.00	0.0
(×)	30	0.96	8.8
(●)	40	0.26	1.5
(⊖)	50	0.95	9.4

however, the samples to be compared are so similar with respect to density and diffusion characteristics that the relative D_a values are significant. Figure 3 shows that, despite differences in the sorptive capacity–vapor activity curves for these films at 30°C (see Fig. 5), the diffusion coefficient–concentration relationships are identical over the whole of the concentration range available to experiment.

The Effects of Liquid Sorption on Polymer Morphology

Steady-State Permeation Rates

Figure 4 shows the steady-state permeation rates of liquid *p*-xylene through untreated films and films pretreated with liquid *p*-xylene either

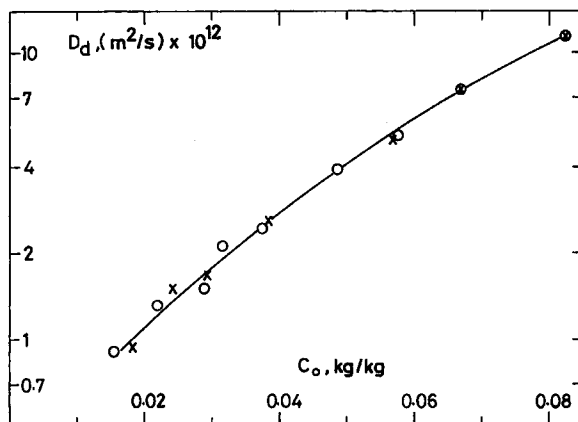


Fig. 3. Plot of D_d vs. C_0 for p -xylene at 30°C in polyethylene film before (O) and after (X) pretreatment at 50°C with p -xylene vapor at an activity of 0.98.

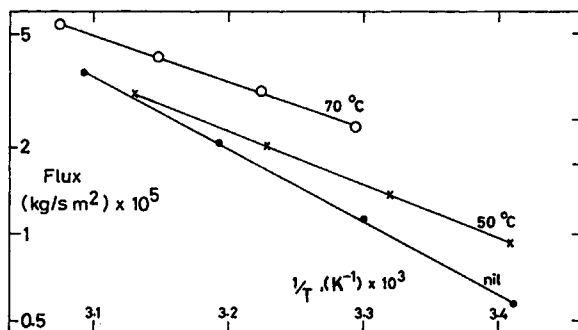


Fig. 4. Effect of pretreatment with liquid p -xylene at stated temperatures on the permeability of polyethylene film to liquid p -xylene.

at 50°C or at 70°C . Further data relevant to these experiments are shown in Table I. The permeation rates P have been taken from Figure 4. The equilibrium solubility of liquid p -xylene in the polymer, S , has been obtained by extrapolating the relevant vapor sorption isotherms to unit activity. Some of these isotherms appear on Figures 5 and 7. The apparent heat of solution of p -xylene in each type of film, $\Delta H_{S,a}$, could be estimated from the values of S at 30°C and 50°C . Likewise, the apparent activation energy for permeation, $E_{P,a}$, could be estimated from the values of P . The integral diffusion coefficients \bar{D} were calculated from P and S . The relevant defining equations are

$$P = P_0 \exp(-E_{P,a}/RT), \quad (1)$$

and

$$P = S \times \bar{D} = S_0 \times D_0 \exp -(\Delta H_{S,a} + E_{D,a})/RT \quad (2)$$

whence

$$E_{P,a} = \Delta H_{S,a} + E_{D,a}. \quad (3)$$

TABLE I
Data for Liquid *p*-Xylene Permeation at 30°C Through Liquid-
Pretreated Films of Thickness 75 μm

	Untreated	Pretreated at 50°C	Pretreated at 70°C
P , (kg/sm ²) $\times 10^5$	1.22	1.64	2.61
S , kg/m ³ dry polymer	82	99	107
\bar{D} , (m ² /s) $\times 10^{11}$	1.11	1.24	1.83
$\Delta H_{S,a}$, MJ/kmol	9.2	5.9	5.4
$E_{P,a}$, MJ/kmol	49.4	36.0	31.4
$E_{D,a}$, MJ/kmol	40.2	30.1	25.9

P is conveniently expressed in units of kg/sm² and S in kg/m³ dry polymer. To obtain \bar{D} in the usual units of m²/s, it is necessary to express P in terms of unit film thickness.

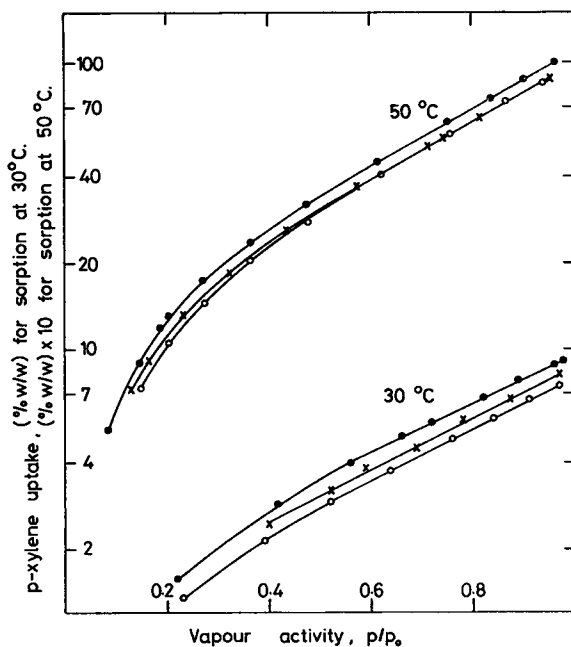


Fig. 5. *p*-Xylene vapor sorption isotherms at 30°C and 50°C for polyethylene film before (O) and after pretreatment at 50°C with *p*-xylene in the liquid (●) and vapor (×) states.

The results in Table I show that liquid pretreatment increased P , \bar{D} , and S , but decreased $E_{P,a}$, $E_{D,a}$, and $\Delta H_{S,a}$. The changes in all these quantities increased with the temperature of pretreatment, and the results are in qualitative agreement with those of Michaels et al.¹ The reasons for the increases in \bar{D} and S were examined in the following experiments.

The Sorptive Capacity of the Polymer

Figure 5 shows *p*-xylene sorption isotherms at 30°C and 50°C for films which, prior to the sorption experiments, were untreated, pretreated with *p*-xylene vapor at 50°C and at an activity of 0.98, or pretreated with liquid *p*-xylene at 50°C. At 50°C and low vapor activities, the sorptive capacity of the vapor-pretreated film was greater than that of untreated film. At higher vapor activities, the sorptive capacities of the films became indistinguishable. At 30°C, the vapor-pretreated film showed a greater sorptive capacity at all vapor pressures.

The film pretreated with liquid *p*-xylene at 50°C showed a greater sorptive capacity than the other films at all vapor pressures and temperatures. A foreseeable difference between pretreatment with liquid and saturated vapor lay in the possibility that solvent-soluble material might be removed by liquid. It seemed appropriate, therefore, to explore the possibility that the increase in sorptive capacity of the liquid-pretreated sample was largely the result of the removal of some solvent-soluble material from the film. Experiments were devised to relate the amount of solvent-soluble material to the difference in sorptive capacity, at unit vapor activity, of films pretreated with liquid or saturated vapor at the same temperature.

Extrapolation of the relevant sorption isotherms (Fig. 5) to unit activity gives some of the required data. Compared to treatment with almost saturated vapor, liquid pretreatment at 50°C increased the uptake of liquid

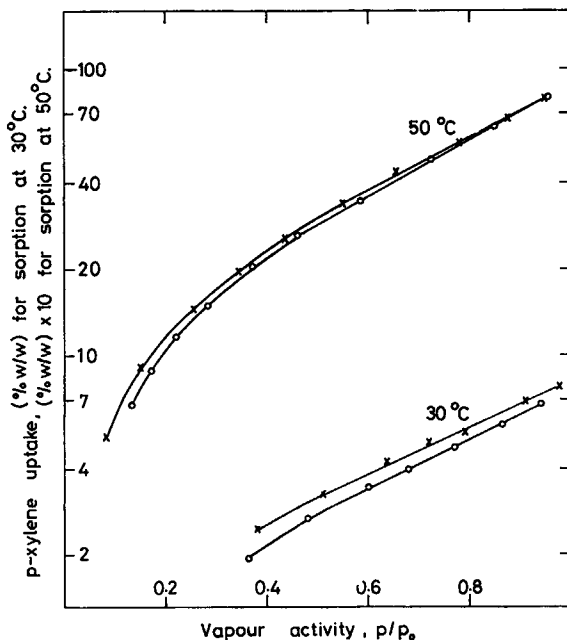


Fig. 6. *p*-Xylene vapor sorption isotherms at 30°C and 50°C for films made from partly fractionated polyethylene before (O) and after (X) pretreatment with liquid *p*-xylene at 50°C.

p-xylene by 1.1% (v/v) at 30°C, and by 1.2% at 50°C. Assuming that the soluble fraction of polymer had a density of about 850 kg/m³, the weight lost by the film during pretreatment with liquid *p*-xylene at 50°C was equivalent to 1.2% (v/v), in excellent agreement with the observed difference in sorptive capacities. The possibility that the material removed was an impurity and not low molecular weight polymer appears unlikely in view of the consistency of the data. Some additional experiments, not reported here in detail, support this view. Briefly, the weight losses from samples of the polyethylene film immersed in various solvents can be correlated very well with solubility parameters appropriate to the polymer and to each solvent.

The inference that loss of soluble material is responsible for an increased sorptive capacity is supported by the sorption isotherms for films made from partly fractionated polymer (Fig. 6). Commercial film was held in liquid *p*-xylene at 85°C for two days, dried at room temperature, and re-crystallized to a smooth film of density 955 kg/m³ by quenching into tap water in the usual way. The film thus prepared had no detectable solubility at 50°C. Sorption isotherms were determined for this film before and after pretreatment with liquid *p*-xylene at 50°C. The sorptive capacity of the liquid-pretreated sample is greater than that of the untreated sample at all vapor activities at 30°C, and at the lower vapor activities at 50°C. At high vapor activities at 50°C, the two isotherms become indistinguishable. This behavior is precisely analogous to that found (Fig. 5) for untreated and vapor-pretreated specimens containing soluble material. Liquid pretreatment of a sample containing no soluble material is therefore equivalent to pretreatment with saturated vapor of a sample which does contain soluble material.

A plausible mechanism to explain precisely why the loss of soluble material increases the sorptive capacity of the polymer would be the formation of voids of molecular size distributed uniformly throughout the noncrystalline regions. Such voids would be accessible to solvent and would have no influence on the density measured by means of the gradient column. If, however, they persisted in the dry state, they would affect the bulk density of the polymer.

Determination of the bulk density of thin polymer films by direct measurement of mass and volume is obviously prone to large errors. The method of hydrostatic weighing,¹¹ using water as the suspension medium, appeared to be the most promising, since errors arising from diffusion of water into the polymer are largely excluded by the rapidity of the determination of the mass of the film and by the low solubility of water in the polymer. Table II shows the densities of various films used in this work as determined by hydrostatic weighing and by the density gradient column. (For the hydrostatic measurements, the polymer was held under water by a brass sinker, and a little Teepol detergent was added to the water to prevent the formation of air bubbles on the surface of the polymer film.)

TABLE II
Densities and Weight Losses During *p*-Xylene Pretreatment for Several Polyethylene Films

Sample	Pretreatment		Weight loss during pretreatment, % (w/w)	Density, kg/m ³		Sorption parameters from Fig. 8	
	Medium	Temp., °C		Grad. col. (25°C)	Hydrostatic weighing (20°C)	μ	M_c
1	Nil	—	0.00	955 _s	954	0.38	240
2	Nearly sat'd vapor	50	0.00	955 _s	955	0.24	190
3	Liquid	50	1.06	956 _s	955	0.20	210
4	Liquid	70	1.85	956 _s	957	0.17	220
5	Liquid	85	3.64	958 _s	960	0.37	350

The agreement between densities determined by the two methods is very satisfactory and leads directly to the view that loss of soluble material does not result in a reduction of bulk density. It is noteworthy that the agreement between the two sets of density values supports the view^{7,8} that sorption of a swelling solvent by a semicrystalline polymer at ambient temperature does not cause dissolution of the crystalline regions. The liquids used in the density gradient column were *p*-xylene and carbon tetrachloride, both good solvents for polyethylene; and if any dissolution of the crystalline regions had occurred in the column itself, the densities recorded would have been consistently lower than those obtained by hydrostatic weighing in water, where no such dissolution could have occurred.

The effect of removing soluble material from polymer films is therefore not explicable in terms of voids.

DISCUSSION

Model for the Behavior of Noncrystalline Material

The noncrystalline regions of a semicrystalline polymer consist of whole molecules (largely of low molecular weight) and of portions of molecules partly incorporated in one or more crystalline lamellae. These portions may be chain ends, long or short loops comprising chain folds, or tie molecules running between lamellae. The number and length of the ties will depend upon the conditions of crystallization. In a quenched sample, where the chains have less time to disentangle themselves from configurations typical of the melt, one would expect a large number of ties having a wide distribution of lengths. In a slowly cooled sample, on the other hand, there should be fewer ties of more uniform length.

Consider the sorption of an organic vapor into a semicrystalline polymer at a temperature below that at which annealing in the dry state would have any significant effect. Because of the links between crystalline re-

gions, the expansion of the whole system caused by vapor sorption will be due to the localized swelling of the noncrystalline regions until the osmotic force exerted by the vapor balances the restraining force of the tie molecules. However, the osmotic swelling force may be so great that some of the shorter interlamellar tie molecules will be either pulled out of the lattice or broken during the sorption process, and it seems unlikely that such a process could be reversible on removal of the solvent. The model therefore predicts that vapor pretreatment of a semicrystalline polymer may cause a permanent increase in the average length of the interlamellar tie molecules. For a particular polymer and solvent, the extent of this increase will depend on the volume fraction of swellant imbibed. The sorptive capacity of the polymer will be increased for subsequent exposure to all vapor activities below that at which pretreatment was carried out.

From Figure 1 it is clear that vapor pretreatment did indeed have the effect of permanently enhancing the sorptive capacity of film under standard testing conditions, provided the sorption during pretreatment exceeded that of untreated film under the standard conditions. The temperature of pretreatment was apparently unimportant as such. These observations are compatible with the proposed model where the permanent change in sorptive capacity is brought about by the elimination of some relatively short interlamellar tie molecules. Unlike this permanent modification, it seems likely that other changes produced by sorption will be reversible. These changes will be associated with longer tie molecules, with chain ends, and with loose folds.

Figure 2 shows how, following a specified pretreatment with liquid, all subsequent vapor sorptions were reversible, as evidenced by the constancy of the final uptake under standard conditions and of the diffusion coefficient for desorption. Further evidence for reversibility is provided by Figure 3, where the diffusion coefficient-concentration relationships for untreated and vapor-pretreated samples are identical, despite differences in the corresponding sorption capacity-vapor activity curves (Fig. 5).

The effects of liquid pretreatment are shown by the data in Table I where the changes in the various quantities are in qualitative agreement with those reported by Michaels et al.¹ Figure 5 shows that vapor pretreatment at 30°C enhanced the sorptive capacity at all vapor activities for a sorption isotherm determined subsequently at 30°C, but for a 50°C isotherm the enhancement at high activities was not significant. Liquid pretreatment at 50°C had the effect of increasing the sorptive capacity at all vapor activities for isotherms at both 30°C and 50°C. This important difference between the effects of liquid and vapor pretreatment may be explained in terms of the morphology of the polyethylene films. It is necessary to extend the proposed model for the behavior of the noncrystalline regions of the polymer during sorption.

If a sample of semicrystalline polymer is immersed in a solvent well below the temperature of general dissolution, any soluble material will tend to diffuse out of the polymer and into the solvent. The loss of

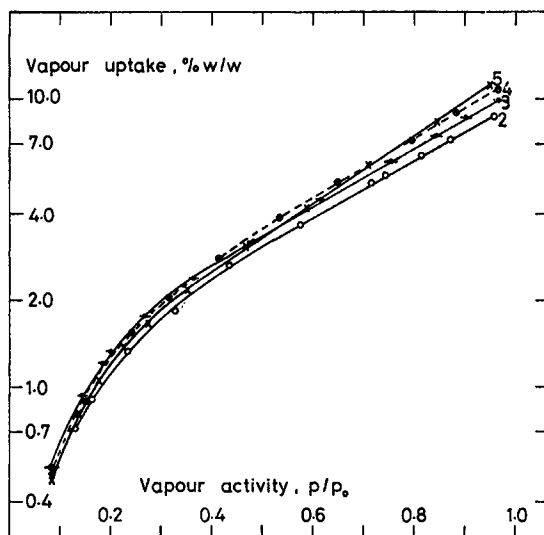


Fig. 7. *p*-Xylene vapor sorption isotherms at 50°C for pretreated polyethylene films (see Table II).

small amounts of soluble material in this way should not affect the total volume of the swollen polymer if the soluble material is replaced by an equal volume of solvent. The proposed driving force for this increased uptake of solvent is the tendency of the noncrystalline material as a whole to swell up to the limit determined largely, if not exclusively, by the average length and number of the tie molecules. On this basis, the sorptive capacity at unit vapor activity of films pretreated with liquid or saturated vapor (at the same temperature) should differ by an amount equal to the volume of the soluble material. The magnitude of the difference would depend on the temperature of pretreatment and on the amount of soluble material. For a given polymer, solvent, and pretreatment temperature, the difference should not depend on the temperature of the subsequent sorption experiments.

In addition, removal of potentially soluble material *before* casting a film of the polymer should produce a specimen affected by liquid pretreatment in the same manner as an unfractionated specimen would be affected by vapor pretreatment. These expectations were completely born out by the experimental results, which show that there is a weight loss from the films during liquid pretreatment and that this loss is very probably due to the loss of low molecular weight polymer. The results are compatible in detail with the proposed model for the behavior of the polymer film, and the most obvious possible consequence of the loss of soluble material is the creation of voids. These, however, are incompatible with the experimental evidence, and some other explanation must be sought.

Since large-scale morphologic changes are not expected at the temperatures used, the absence of voids could be due to the melting of some

crystalline material or to a reduction in the effective length of tie molecules. The former explanation appears to be excluded by the observation that liquid pretreatment increases the density of a sample. The other explanation predicts a contraction in the sample on drying, and a reduction in the effective length of tie molecules could certainly cause such a contraction, though hardly by normal crystallization. Instead of some further incorporation of chains into existing lattice structures, this could be visualized as a process by which disordered chains attained a state of improved order by lining up with one another. The minute ordered entities so formed would be like smaller versions of the micelles postulated in the fringed micelle theory or the ball-like nodules observed in an amorphous polymer.¹² These small micelles could form and disappear reversibly on removal and addition of swelling solvent.

A test of this novel model is provided by its ability to interpret the sorption isotherms of pretreated films. Figure 7 shows the *p*-xylene vapor sorption isotherms at 50°C for samples 2 to 5 listed in Table II. As the activity of the solvent vapor increases, the isotherms cross over one another. At solvent activities greater than 0.8, the uptakes increase in the order 2 to 5, whereas at the very low activities, the uptakes are tending toward the reverse order. The model predicts this behavior. At low solvent vapor activities, the micelles remain largely intact, but they are progressively loosened up and destroyed on increase in activity. In effect, the fraction of noncrystalline material is increased and, more especially, the length of the shortest ties tends to increase, thereby causing an increase in the sorptive capacity of the polymer.

The solvent swelling of semicrystalline polymers has been considered¹³ in terms of the following:

$$\chi = \mu + \frac{\bar{V}_1 d_a}{M_c} v_2^{-1/2} \quad (4)$$

where

$$\chi = \left\{ \ln \left(\frac{a_1}{v_1} \right) - v_2 \right\} / v_2^2 \quad (5)$$

where d_a = density of amorphous polymer; \bar{V}_1 = molar volume of swellant in the liquid state; a_1 = vapor activity in external vapor phase, expressed as p/p_0 ; v_1 = volume fraction of solvent in the swollen noncrystalline regions; and v_2 = volume fractions of polymer in the swollen noncrystalline regions = $1 - v_1$.

In the original paper,¹³ M_c and μ were defined as the average molecular weight of ties and the Flory-Huggins interaction parameter, respectively. It is immediately apparent, however, that the values assumed by M_c and μ are somehow related to the configuration and length of ties in the system considered here. The tie molecules, in effect, perform the same role as crosslinks in a crosslinked rubber. When solvent is imbibed, the swelling is restricted by the ties, and this is presumably why the noncrystalline

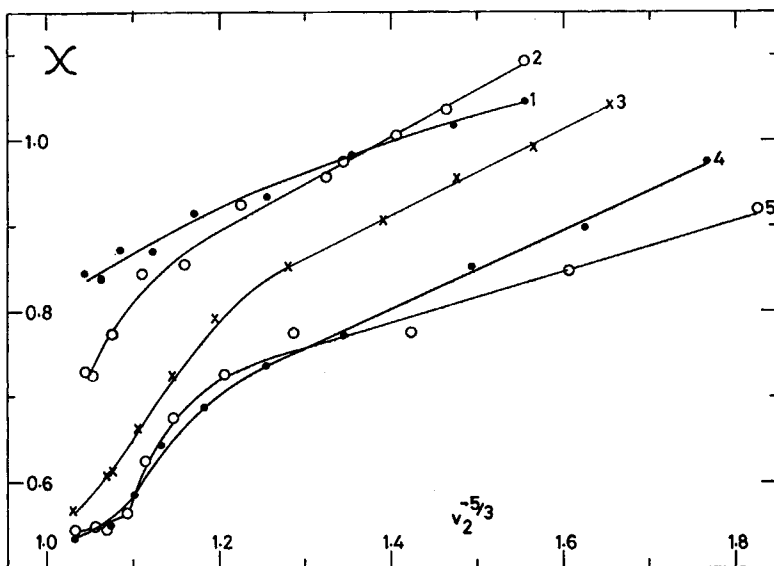


Fig. 8. Plot of (χ) vs. $v_2^{-5/3}$ at 50°C for sorption of *p*-xylene in pretreated polyethylene films.

regions in single crystals have a higher sorptive capacity¹⁰ than the non-crystalline regions in ordinary bulk-crystallized polymer.

In eq. (4), M_c will be influenced by the number of tie molecules in relation to the total amount of noncrystalline material. Factors which influence M_c may also affect the calculated value of μ . Differences in M_c for different samples of the same polymer in a given solvent are likely to reflect real differences in crosslink length only when the calculated values of μ are constant. Furthermore, constant μ values are not a sufficient argument for supposing that they are correct. Evidently the ideas associated with M_c , μ , and χ in semicrystalline polymers must be used with caution.

Figure 8 shows the sorption data at 50°C for samples 1 to 5 listed in Table II, plotted according to eq. (4). For the untreated specimen (sample 1), the curve exhibits a slight downward concavity throughout the range of values of $v_2^{-5/3}$. This may be interpreted in terms of a slight continuing increase in the average length of intercrystalline ties with increasing vapor uptake. This is to be expected on the basis of the model for the behavior of untreated films. Curves 3, 4, and 5 apply to the liquid-pretreated films, and all show marked curvature in the region of low vapor uptake. This curvature points to a continually increasing value of M_c in this region as micelles are progressively destroyed. The plot for the vapor-pretreated sample (sample 2) shows similar curvature, and micelles may therefore be formed as a result of vapor pretreatment as well as by liquid pretreatment. At very low vapor uptakes, curves 3 to 5 tend to decrease in slope, and indeed the "normal" sorption behavior of the samples in this region would

also point to more constant values of M_c here. At high vapor uptakes, the plots are linear, indicating a constant value of M_c following dissolution of all the micelles.

Tables II shows values of M_c and μ calculated for each of the pretreated samples from the slopes of the linear portions of the plots on Figure 8. For samples 2 to 5, M_c increased with the severity of pretreatment, as required by the model. The value of μ for the sample pretreated with liquid at 85°C differs from the values for the other pretreated samples by more than experimental error. Liquid pretreatment at this relatively high temperature must either reduce the number of tie molecules or reduce the actual solvent power of *p*-xylene at lower temperatures in the subsequent experiments. The latter effect is credible if the pretreatment results in some clustering of solvent molecules within the swollen polymer, and the possibility of this happening is explored in the Appendix.

The Diffusion Coefficient-Concentration Relation

Figure 9 shows the apparent diffusion coefficient D_d plotted against concentration C_0^* for *p*-xylene at 30°C in samples 1 to 5. (On this plot the penetrant concentrations C_0^* have been expressed on the basis of amorphous polymer, using the densities from Table II.) The curve for samples 1 and 2 is derived from a best fit to the data shown on Figure 3.

Pretreatment with liquid *p*-xylene had little, if any, effect on the diffusion coefficient of *p*-xylene at low concentrations in samples 3 and 4. The behavior of sample 5 is not as anomalous as it might at first appear. During pretreatment the density of this sample increased appreciably more than any of the others, and the lamellar thickening characteristic of or-

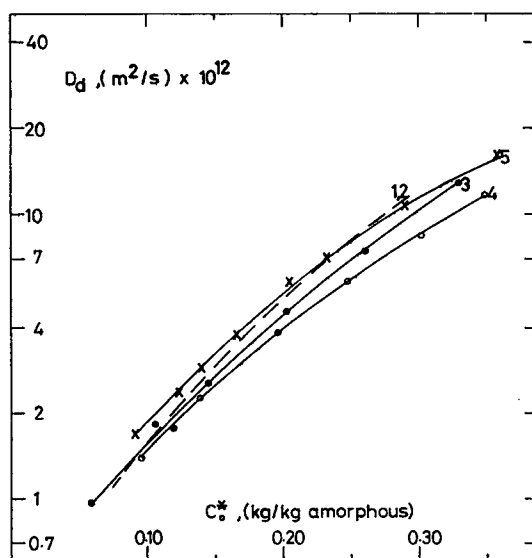


Fig. 9. Plot of D_d vs. concentration C_0 for *p*-xylene in liquid-pretreated films at 30°C.

dinary dry annealing may have occurred to a slight extent. This would certainly increase D_a at low concentrations.²

CONCLUSIONS

The sorption of solvent vapor by a semicrystalline polymer is not necessarily reversible with respect to the effect of the sorption on the structure and subsequent behavior of the polymer. The nonreversibility is believed to arise out of an increase in the average length of the tie molecules during sorption, an increase which persists after complete drying out of the specimen. The extent of the lengthening, and hence of the increased sorptive capacity of the polymer, depends primarily on the maximum solvent uptake which that specimen has experienced at any time in its history. The model proposed to explain the effects requires only a small change in the overall morphology of the polymer.

Pretreatment of polymer with solvent in liquid form may lead to effects different from those caused by pretreatment with the corresponding saturated vapor. The explanation for this lies in the ability of liquid, but not vapor, to dissolve out some low molecular weight material from the polymer. Removal of this material leads to a permanent enhancement of the sorptive capacity of the specimen concerned, and the magnitude of the enhancement corresponds very closely, on a volume basis, to the amount of material removed. The loss of this material does not lead to the formation of voids. Instead, further ordering of the noncrystalline material is believed to occur in a manner akin to, but not the same as, normal crystallization. The result is the growth of nodules or small crystallites, as in the fringed micelle model, and with all three dimensions smaller than those of lamellar crystalline entities. These small crystallites will be formed on removal of swelling solvent and destroyed reversibly when sorption occurs again. There is some evidence that similar entities are formed, though to a lesser extent, as a result of vapor pretreatment.

The essential difference between the model proposed here and that put forward by Michaels et al.¹ lies in the proportion of noncrystalline material affected irreversibly by pretreatment. In the present model the proportion is very small, whereas the earlier model postulated modification of a large fraction of both the noncrystalline and crystalline regions. The earlier model was strongly influenced by the observation that pretreatment increased both the sorption and diffusion components of the permeation process, and decreased the (apparent) activation energy for diffusion. Given real changes, at a particular concentration, in both the diffusion coefficient and the activation energy for diffusion, it would indeed be necessary to propose rather drastic morphologic changes as a consequence of pretreatment. However, the changes in \bar{D} and $E_{D,a}$ observed in the present work are not real in this sense, but are attributable to the increased sorptive capacity of the polymer following pretreatment and to the concentration dependence of the diffusion coefficient. At constant concen-

tration, the diffusion coefficient actually tends to decrease with the extent of liquid pretreatment, an effect which may be attributed to solvent clustering in these samples (see Appendix). The results highlight the fact that for systems in which the diffusion coefficient is concentration dependent, the activation energy for diffusion has real significance only if the diffusion coefficients are measured at constant concentration over a range of temperatures. Values of $E_{D,a}$ calculated from liquid permeability studies have no quantitative significance and may be grossly misleading.

It will be interesting to see if the model proposed in this paper will apply to the effects of pretreatment at higher temperatures where some of the morphologic changes will be of the type encountered in ordinary dry annealing.

In their study of the effects of vapor pretreatment on the sorption-diffusion characteristics of polyethylene, Baddour et al.² found that pretreated films showed enhanced permeability to liquids that swelled the polymer, but not to permanent gases. This observation constituted an anomaly in terms of the model proposed by Michaels et al., but is precisely the behavior predicted by the new model. If the solubility of the permeant in the polymer is low, as is the case for permanent gases at all pressures and good solvents only at low vapor activities, the effect of pretreatment on the sorptive capacity of the noncrystalline regions is negligible. Furthermore, since vapor pretreatment has little effect on the diffusion coefficient-concentration relationship, no change in the permeability with respect to a permanent gas would be expected to follow from pretreatment.

APPENDIX

The Clustering of Solvent Molecules in Swollen Polymer

Zimm and Lundberg¹⁴ derived the relationship

$$\frac{G_{11}}{\theta_1} = -v_2 \left(\frac{\partial \gamma_1}{\partial a_1} \right)_{P,T} - 1$$

where G_{11} = cluster integral; $\gamma_1 = a_1/v_1$ = volume fraction activity coefficient; θ_1 = partial molecular volume of type 1 (solvent) molecules in the mixture with type 2 (polymer) molecules; v_2 = volume fraction of polymer in swollen noncrystalline regions; and a_1 = vapor activity in external vapor phase, defined as p/p_0 . The quantity $v_1 G_{11}/\theta_1$ is the mean number of type 1 molecules in the neighborhood of a given type 1 molecule in excess of the mean concentration of type 1 molecules. It is therefore a measure of the clustering tendency of the type 1 molecules. For an ideal solution $\partial \gamma_1/\partial a_1 = 0$, and hence G_{11}/θ_1 is -1 for all concentrations. In other words, in an ideal solution a particular type 1 molecule excludes its own volume to other molecules but otherwise does not affect their distribution.

Calculation of the clustering function G_{11}/θ_1 requires evaluation of the quantity $(\partial \gamma_1/\partial a_1)_{P,T}$. This has been done graphically from the smoothed

plots of γ_1 versus a_1 for samples 1 to 5, shown on Figure 10. The smoothed clustering functions for these samples are plotted against v_1 on Figure 11. From Figure 10, the activity coefficient for the untreated sample (sample 1)

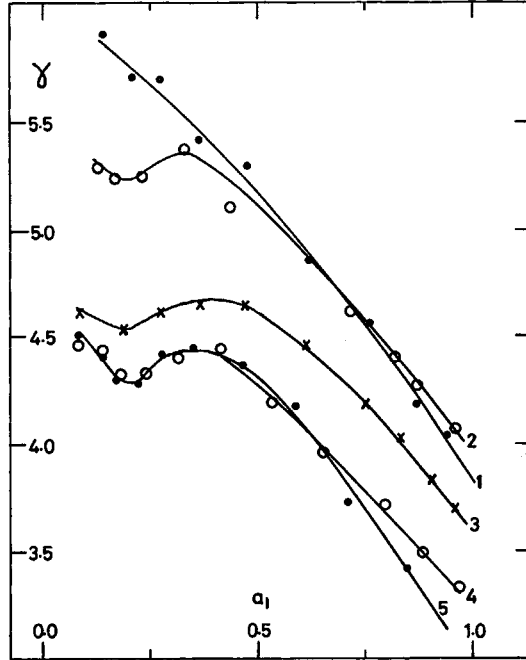


Fig. 10. Activity coefficient vs. vapor activity curves at 50°C for *p*-xylene in pretreated films.

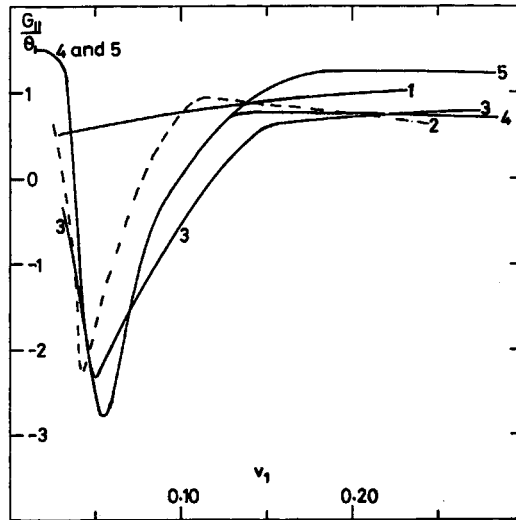


Fig. 11. Clustering function vs. vapor uptake at 50°C for *p*-xylene in untreated and pretreated films.

is seen to increase with decreasing vapor uptake, reaching 6.1 on extrapolation to zero concentration of *p*-xylene. A similar trend was observed by Zimm and Lundberg for the toluene-polystyrene and benzene-rubber systems, the former giving an activity coefficient of about 5.7 at zero concentration at 50°C. Figure 11 shows that the clustering function for the untreated sample increases slightly with solvent uptake, ranging from 0.5 to 1.0 over the accessible concentration range. This behavior is also similar to that observed by Zimm and Lundberg for nonpolar polymer-solvent systems. A positive value for G_{11}/θ_1 indicates that the solvent molecules cluster together within the polymer. Zimm and Lundberg interpreted this to mean that the first solvent molecules to enter the polymer loosen the structure and so facilitate the entry of further solvent molecules into the neighborhood.

On Figures 10 and 11, the curves for the pretreated samples are notably less simple than for the untreated sample. The region of positive slope in the activity coefficient-vapor activity curves (Fig. 10) is believed to be associated with the dissolution of crystalline micelles, an effect more clearly illustrated by the clustering functions on Figure 11. On this Figure the curves for the pretreated samples are all of similar shape, exhibiting a sharp minimum at $0.03 < v_1 < 0.06$, and a region in which G_{11}/θ_1 is almost constant. At very low solvent uptakes, $v_1 < 0.03$, G_{11}/θ_1 tends to positive values, similar in magnitude to those recorded for sorption in the untreated sample. This may be regarded as the region of "normal" sorption referred to earlier, in which the crystalline micelles remain intact and the sorptive capacity is directly related to the amount of noncrystalline material in the sample. As the uptake increases from zero, G_{11}/θ_1 decreases sharply and then increases before leveling out again at around unity. The large negative values of G_{11}/θ_1 may be associated with sorption at highly specific sites, the micelles themselves, with the result that the micelles dissolve. After their dissolution, the sorption process returns to the swelling mode of the normal type observed at all vapor concentrations in untreated specimens. The position of the minima in the clustering function tends to higher vapor uptakes with increasing severity of pretreatment. This perhaps implies that the extent of micelle formation increases in the same order.

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References

1. A. S. Michaels, R. F. Baddour, H. J. Bixler, and C. Y. Choo, *Ind. Eng. Chem., Process Des. Develop.*, **1**, 14 (1962).
2. R. F. Baddour, A. S. Michaels, H. J. Bixler, R. P. de Filippi, and J. A. Barrie, *J. Appl. Polym. Sci.*, **8**, 897 (1964).
3. A. S. Michaels, W. Vieth, A. S. Hoffman, and H. A. Alcalay, *J. Appl. Polym. Sci.*, **13**, 577 (1969).
4. V. Stannett and H. Yasuda, in *High Polymers*, Vol. XX, R. A. V. Raff and K. W. Doak, Eds., Interscience, New York, 1964.

5. C. E. Rogers, V. Stannett, and M. Szwarc, *J. Polym. Sci.*, **45**, 61 (1960).
6. R. D. Siegel and R. W. Coughlin, *J. Appl. Polym. Sci.*, **14**, 2431 (1970).
7. A. Udagawa and A. Keller, *J. Polym. Sci. A-2*, **9**, 439 (1971).
8. A. S. Michaels and R. W. Haussein, *J. Polym. Sci. C*, **10**, 61 (1965).
9. D. A. Blackadder and J. S. Keniry, to be published.
10. D. A. Blackadder and J. S. Keniry, unpublished results.
11. L. A. Wood, N. Bekkedahl, and F. L. Roth, *J. Res. Nat. Bur. Stand.*, **29**, 391 (1942).
12. G. S. Yeh and P. H. Geil, *J. Macromol. Sci. B*, **1**, 235 (1967).
13. C. E. Rogers, V. Stannett, and M. Szwarc, *J. Phys. Chem.*, **63**, 1406 (1959).
14. B. H. Zimm and J. L. Lundberg, *J. Phys. Chem.*, **60**, 425 (1956).

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