Diffusion of Toluene in Oriented Polyethylene

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ABSTRACT: The diffusion of toluene in compression-molded, quench-rolled, and cold-drawn polyethylene films is studied by the successive vapor absorption method. The diffusion coefficient is found to increase exponentially with vapor concentration in the compression-molded film. It is independent of concentration for the cold-drawn material, but increases linearly with concentration for the quench-rolled films. The linear dependence of the diffusion coefficient on concentration has not been reported previously for the diffusion of organic solvent molecules in polymers. The concentration dependence is discussed in terms of segment mobility and free volume theory.

Recently, a process of simultaneous high-speed quenching and shear was reported for the preparation of a tough and transparent polyethylene film which possesses high Young's modulus and tensile strength.[1] Information about chain orientation and morphological features was derived from studies of X-ray diffraction and melting characteristics, while the disposition of the chain segments in the amorphous region was inferred, to some extent, from mechanical properties.[2] The mechanical studies, however, measure the combined response of the amorphous and crystalline regions. It is desirable to employ a technique which probes exclusively the mobility of the amorphous segments. A method which offers such a promise is the diffusion of organic vapors in polymers. In this paper, we would like to describe the results of our study of the diffusion of toluene vapor in quench-rolled PE films. Also included in the study is a cold-drawn specimen in which the orientation of the *c* axis is in the same direction as that in the quench-rolled films. Toluene was chosen because it was found that the rate of diffusion obeyed simple Fickian equations.

Experimental Section

A high-density, linear PE, Marlex 6002 from Phillips Petroleum Co., was used in the present investigation. Four films were prepared. Film 1 is a compression-molded specimen. Films 2 and 3 are quench-rolled samples; the latter was obtained at a higher shear rate. The cold-drawn film was prepared by drawing a compression-molded specimen at room temperature to ten times its original length and subsequently annealing it at 120° for 5 hr (film 4).

The rate of diffusion of toluene vapor was measured at 30° by the successive absorption method[3] with the use of a Cahn electrobalance. The plots of the amount of absorbed vapor (M_t) against the square root of time are linear in the initial stages of absorption; the linearity extends over 70% of the amount of absorption at equilibrium (M_∞). The diffusion coefficient D was calculated in the usual manner from the initial slope of the absorption curve for each successive absorption step.[4] (Strictly speaking, the diffusion coefficient calculated from the absorption curve should be designated D_a.) The penetration of toluene molecules in the oriented films was studied in a direction perpendicular to the orientation of the *c* axis of the polymer chain.

Results and Discussion

(1) Equilibrium Absorption. The equilibrium absorption values (M_∞) of the four PE films are shown in Figure 1 at several vapor pressures. The isotherms for films 2, 3, and 4 are linear within experimental error, while that for the compression-molded film appears to show a slight but real curvature. The linear sorption isotherms indicate that the mixtures of toluene and oriented polyethylenes approach ideal solutions.

It has been demonstrated that sorption occurs only in the amorphous regions of a crystalline polymer.[5] Furthermore, the value of M_∞ for a given vapor is directly proportional to the amorphous content of the PE specimen.[6] The latter conclusion, however, has not been tested with oriented crystalline polymers. In the present study the amorphous contents of the four films are estimated from heats of fusion to be approximately 30–40%; but less than one-third of the amount of toluene was absorbed by the cold-drawn film when compared with the three other films. It appears that the constraint imposed by the crystalline regions on the amorphous segments must be very severe in the cold-drawn film, so these amorphous segments are restricted in the number of configurations they can assume and are less effective in accommodating toluene molecules. Although the amorphous segments in the quench-rolled specimen must also be oriented to some extent, they are apparently less constrained, insofar as the ability to accommodate toluene molecules is concerned. On the other hand, it is also unlikely that these segments possess the same degree of "mobility" as those in the compression-molded film, because the absorption isotherms have different shapes.

(2) Diffusion. The diffusion coefficients are plotted against the arithmetic average concentration of absorbed toluene during each absorption step. Figure 2 shows three distinct types of concentration dependence of the diffusion coefficient. (1) For the compression-molded film, the concentration dependence may be represented by the usual exponential formula,[6,7] $D = D_0 \exp(ac)$. (2) The diffusion coefficient is independent of concentration for the cold-drawn material. (3) The diffusion coefficient increases linearly with concentration for the two quench-rolled films, $D = D_0(1 + bc)$. It should be emphasized that the linear dependence of D was not an approximation of the exponential formula, because the linear relationship holds in the range where the magnitude of bc exceeded unity. To our knowledge, the linear dependence of D on C has not been reported previously for the diffusion of organic solvent molecules in polymers. It is also noted that the value of b is smaller when the quench-rolled

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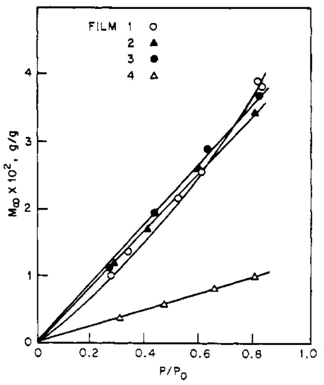

Figure 1. Equilibrium sorption of toluene by polyethylene.

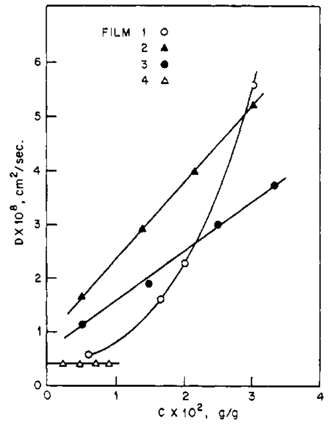

Figure 2. Diffusion of toluene in polyethylene.

TABLE I
DIFFUSION OF TOLUENE VAPOR IN PE

Material	Concentration dependence[a]		
Compression molded	$D = D_0 \exp(ac)$,	$D_0 = 3.4 \times 10^{-9}$,	$a = 93$
Quench rolled	$D = D_0(1 + bc)$,	$D_0 = 9.0 \times 10^{-9}$,	$b = 160$
Quench rolled (higher shear rate)	$D = D_0(1 + bc)$,	$D_0 = 6.9 \times 10^{-9}$,	$b = 140$
Cold drawn	$D = D_0$,	$D_0 = 4.2 \times 10^{-9}$	

[a] D_0 in cm²/sec.

film is prepared at a high shear rate. The diffusion results are summarized in Table I.

It is well known that the rate of diffusion of small molecules in crystalline polymers is sensitive to fine morphological features; for example, transport near lamella boundaries is thought to be an important factor in governing the magnitude of the diffusion rate. For this reason, the value of D is not necessarily a good measure, by itself, of the mobility of the amorphous segments. On the other hand, the concentration dependence of D appears to lend itself, at least qualitatively, to the interpretation of the mobility of the segments in the amorphous region. We compare, in this study, the diffusion of the same penetrant molecule in four PE films in which the amorphous segments differ in the degree of orientation and the constraint imposed on them by the crystallites. Ordinarily, polymer segments are quite free to mix with small organic molecules, and the presence of these organic molecules in a polymer enhances segmental mobility. Consequently, the absorption isotherms are seldom linear and a strong concentration dependence of D, *e.g.*, the exponential relationship, is usually observed. However, it is also possible to perceive an extreme case where the same segments are severely constrained so that they do not have complete freedom to mix with penetrant molecules, and the presence of a small quantity of these organic molecules fails to alter segmental mobility to a significant extent, or "plasticize" the polymer. The diffusion coefficient may then be expected to become independent of concentration. This is represented by toluene diffusion in the cold-drawn film. When the constraint is less severe than that in the extreme case, but nevertheless more than that usually encountered in a molded specimen, it is conceivable that the diffusion coefficient will be dependent on concentration but the dependence may be weaker than the exponential form. This appears to be the case with the two quench-rolled films. The lower b value found for the film prepared at a higher shear rate seems to be consistent with the notion that shear induces constraint on the amorphous segments.

In order to analyze the concentration dependence in more quantitative terms, we shall formulate our discussion in the context of the free volume theory. Let us first review the mechanism of concentration-independent diffusion, or type-A Fickian diffusion named by Frisch.[8] If the minimum void volume required to disperse the penetrant molecules in the polymer is smaller than the average free volume, the dominating mechanism for diffusion occurs by localized, activated jumps into neighboring preexisting cavities. The activation step involves perhaps the cooperative motion of a few chain segments, but clearly a large-scale redistribution of free volume is not necessary. It is also obvious that the presence of a small amount of penetrant molecules must not change the free volume distribution, so the diffusion coefficient may remain independent of concentration.

When the minimum void volume is large relative to the free volume distribution in the polymer, there are few preexisting cavities of sufficient size to accommodate the penetrant molecules, and large numbers of polymer segments must be rearranged to allow the penetrant to jump from one cavity to another. For these systems of type-B Fickian diffusion,[8] it is appropriate to consider the redistribution of free volume as outlined by Cohen and Turnbull.[9] Equation 1 describes the relationship between D and the average fractional free volume f for the above mechanism

$$D = A \exp(-B/f) \tag{1}$$

where A is a frequency factor and B is a measure of the minimum hole size for the jump process. Fujita and Kishimoto[10] further assumed that

$$f = f_0 + \beta\varphi \tag{2}$$

In eq 2, φ is the volume fraction of the penetrant and β denotes the effectiveness of the diffusant molecule for increasing the free volume of the given polymer. Combination of eq 1 and 2 yields

$$D/D_0 = \exp(B\beta\varphi/f_0(f_0 + \beta\varphi)) \tag{3}$$

where

$$D_0 = A \exp(-B/f_0) \tag{4}$$

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If $\beta\varphi$ is much smaller than f_0 (although β may be comparable to f_0[11]), then eq 3 is reduced to the familiar exponential form

$$D/D_0 \cong \exp(B\beta\varphi/f_0^2) \cong \exp(ac) \qquad (5)$$

We now examine the condition which may lead to the linear dependence of D on concentration. It is perhaps worthwhile to recall that the exponential term, $\exp(-B/f)$, in eq 1 is derived from counting the number of ways of redistributing the free volume packets within the system. As long as we utilize the concept of large-scale redistribution of free volume and allow f to change with φ, the final equation for D/D_0 will always contain an exponential term of φ or its related functions. However, if we begin with the mechanism of type-A Fickian diffusion, *i.e.*, localized, activated jumps into neighboring preexisting cavities, the jump frequency is simply proportional to the number of the preexisting cavities. If we further assume that the cavity size increases linearly with φ, with the same proportional constant applicable to all cavities, then the size distribution function (see the figure in ref 8) simply shifts linearly toward larger sizes. The number of cavities larger than a certain critical size will increase linearly with φ for small values of φ, and so will the diffusion coefficient.

In conclusion, the diffusion of organic molecules in oriented crystalline polymers affords a useful tool for understanding the state of the amorphous segments. We have also uncovered a case where the diffusion coefficient increases linearly with concentration. It is believed that this type of concentration dependence has not been reported previously.

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Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions

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ABSTRACT: The gas chromatographic technique of elution on a concentration plateau of solvent in a carrier gas, reported by Conder and Purnell, is used to determine the solubility isotherms of selected hydrocarbons in amorphous polymers. This technique, adapted for the first time to a polymeric stationary phase, permits the calculation of vapor–polymer equilibrium ratios and polymer–solvent interaction parameters over a wide range of composition, including pure polymer. The following results are reported for polystyrene in benzene at 120°, K (equilibrium ratio in pure polymer) = 4.92 and χ (interaction parameter) = 0.325; for high-density polyethylene in *n*-decane at 185°, K = 3.94 and χ = 0.12.

In a recent note,[2] Patterson, *et al.*, discuss the use of gas chromatography (gc) data to calculate the thermodynamic properties of polymer–solvent systems, and they derive equations for calculating the activity coefficient, the activity coefficient rationalized by weight fraction, and the interaction parameter. Because of the assumptions they use, their equations and procedure are valid only for systems containing an infinitesimal amount of the low molecular weight solvent. We have now found that a gc apparatus can be employed to measure the thermodynamic properties of polymer solutions with up to about 50 vol % solvent in the carrier gas.

The technique used is based on theoretical relationships that were developed by Conder and Purnell[3] and then used by them to calculate activity coefficients for such low molecular weight systems as *n*-hexane in squalane and *n*-heptane in di-*n*-nonyl phthalate at gas concentrations ranging from zero to 70 mol %.[4]

The key relationship is between the measured gc variables and the solubility of the volatile component per unit mass of polymer in the stationary phase[5]

$$q(P) = \frac{1}{V_1}\int_0^{y_0} j\,\frac{(V_R - V_M)}{1-\psi}\,dc \qquad (1)$$

where q is the solubility in moles per gram at the mean column pressure P in atmospheres, j is a correction for gas compressibility, and V_1 is the mass of the stationary polymer phase in grams. The difference between retention volumes of the solvent and air, $V_R - V_M$, is corrected for ψ, the mole fraction of solvent in the gas above the polymer, and then is integrated over the solvent concentration c in the gas up to a value determined by y_0, the mole fraction composition of the carrier gas at the outlet. Equation 1 defines a solubility isotherm and provides the basic information for calculating the vapor–polymer equilibrium ratio and the interaction parameter over a range of composition. The experimental apparatus and procedure will be described in a separate publication.[6]

One equilibrium ratio commonly used in work with polymers is the following

$$K = \frac{P_2}{P_2^0 w_2} = \frac{P\psi}{P_2^0 w_2} \qquad (2)$$

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