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during the induction period, most likely through the abstraction of the tertiary hydrogen atom of PS. The resulting PS radical, being less reactive in chain propagation, caused the retardation of the oxidation reaction.

When low-molecular-weight polystyrene was blended with PVME, the mixtures remained homogeneous throughout the oxidation reaction. The induction periods were longer and the oxidation rates slower than the values for the corresponding PS blends. Low-molecular-weight polystyrene was involved in the oxidation process both during the induction period and in the steady-state region. Cross-propagation and/or cross-termination reactions between PVME and LPS resulted in changes in the solubility, and presumably the chemical nature, of LPS.

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Registry No. PVME, 9003-09-2; PS, 9003-53-6.

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A General Free Volume Based Theory for the Diffusion of Large Molecules in Amorphous Polymers above T_g. 1. Application to Di-*n*-alkyl Phthalates in PVC

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ABSTRACT: The standard free volume theory of the diffusion of small molecules in amorphous polymers above T_g has been extended to include the fundamental motions of comparatively large molecules such as plasticizers. In addition to accounting for liberated penetrant translational entropy, a new feature consisting of an elementary displacement of the molecule that is but a fraction of its long dimension is introduced. An effective diffusion coefficient is derived for elongated molecules which is the result of averaging over probable penetrant jumps from zero up to the entire molecular length. While a necessary plasticizer efficiency parameter presently must be determined by experiment, the theory requires a minimal input database of readily accessible quantities and involves no adjustable parameters. An application of the rough theory to the di-*n*-octyl and di-*n*-decyl phthalate in PVC systems shows encouraging results.

Introduction

A general theory of the diffusion of extraordinarily large molecules in rubbery amorphous polymers is of interest, not only from the standpoint of scientific understanding but also with regard to material design and process optimization. Clearly, a broadly applicable model would be of extreme utility in consideration of the controlled trans-

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port of plasticizers, surfactants, lubricants, or biologically active molecules, as examples, through polymeric particles, films, coatings, and containers.

While, above T_g, the mobility of "large" molecules is presumably facilitated by the same long-range polymer chain segmental motions that are thought to govern the diffusion of small molecules (simple gases, organic vapors) that are usually given a spherical geometrical representation, additional attention should be paid to (a) the considerably greater redistribution of free volume required to incorporate these larger penetrants into the polymer structure as well as to permit thermal molecular translations that are of the order of the largest penetrant molecular dimensions, (b) the implications of having a penetrant molecule whose size is considerably greater than that of the surrounding polymer chain segments, and (c) the specific *shape* the penetrant molecule will assume commensurate with its minimum free energy conformation in a given polymer molecular environment.

It is intended in this paper to present but a rough diffusion model that nonetheless begins to address the above issues (a)–(c). Obvious model refinements, particularly regarding point (c), will be outlined in the Conclusions and their implementation presented in future reports. First, however, a detailed rationalization of the basic model rudiments is considered necessary and is made herein within the milieu of experimentally established facts and accepted theoretical concepts for the system at hand as well as for related polymer/plasticizer systems. Finally, we will compare rough calculated values of di-*n*-alkyl phthalate in PVC diffusion coefficients with values we have determined by experimentation using a simple gravimetric technique.

In particular, a general predictive model of this type of system can be expected to be technologically applicable to the process of the efficient dryblending of thermoplastic polymers with various plasticizers as well as to be directly related to the issue of subsequent plasticizer permanence in finished materials. Whereas the theoretical model described herein is intended for general applicability, it is initially tested against the di-*n*-octyl and di-*n*-decyl phthalate (DNOP and DNDP, respectively) in PVC systems. It is a fundamental belief that plasticizer uptake rates in individual resin particles at most practical industrial processing temperatures is largely controlled by diffusion rather than by other factors such as plasticizer liquid viscosity and capillary absorption in resin "pores",[1-3] although these variables may not in fact be insignificant in some systems especially at low temperatures. To be sure, the critical assumption of diffusion control is fortified, and the model formulation is simplified by being above the glass transition temperature.

General Diffusion Considerations

In this paper we present an initial step toward the ultimate modeling of the kinetics of a diffusion-controlled uptake of plasticizer from either zero or nonzero initial content in the polymer. The polymer will either absorb a controlled limited quantity of liquid plasticizer or will reach its full equilibrium-swollen capacity in a reservoir having excess plasticizer. The polymer is considered above the glass transition during the entire sorption process, and, of course, the accompanying progressive depression of T_g must be accounted for.

The familiar and proven concepts of fluctuating free volume that are most commonly invoked within the related contexts of long-range chain segmental mobility and the diffusion of small molecules in amorphous polymers above T_g are appropriately retained as the centerpiece of the theory. On the other hand, a simple entropic factor relating to the liberation of a translational degree of freedom for the penetrant molecule, given a local fluctuation in polymer free volume, is added, and a simple analysis of the thermal oscillation of the penetrant molecule within such an activated free volume cavity is given. The most significant modification of the conventional free volume theory is an accounting for particularly large relative sizes of the diffusing species.

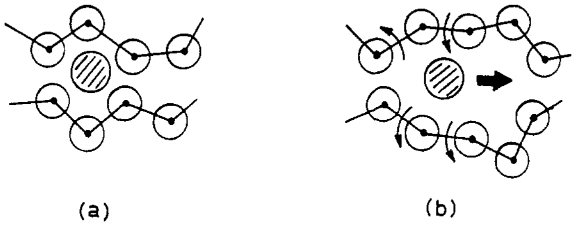

Figure 1. (a) Encapsulation of a *small* molecular penetrant by adjacent polymer chain segments. (b) Displacement of penetrant made possible by a local free volume increasing macromolecular relaxation.

Since the polymer environment is considered largely amorphous and hence spatially isotropic, it is assumed that there is no reasonable correlation between the directions of any two consecutive elementary plasticizer molecular jumps, of displacement δ, each of which occur in a time interval τ in three-dimensional space. Of course, both δ and τ must be considered as characteristic averages over assumed narrow distributions. The assumption of noncorrelation between the directions of consecutive jumps of these large molecules that will sometimes have considerable aspect ratios is further supported by the fact that above T_g the penetrant's nearest-neighbor polymer segments, being in a *fluid state*, will continuously and rapidly realign the penetrant molecule between consecutive fundamental hopping events. Then, the diffusion coefficient, D, can be given a general representation in terms of these molecular parameters by the familiar stochastic equation:[4]

$$D = \delta^2/(6\tau) \tag{1}$$

The development beyond here will concentrate on providing reasonable theoretical values for δ and τ that reflect the physical state of the polymer as well as plasticizer molecular structure.

Diffusion by the Relaxation of Polymer Free Volume and Considerations of Penetrant Molecular Motion

The diffusion of low molecular weight penetrants in simple amorphous polymers above T_g is believed to be facilitated by a temperature-dependent chain-segmental relaxation mechanism. A small molecule embedded in a polymer is visualized as being encapsulated in a *cell* defined by nearest-neighbor polymer segments, as shown in Figure 1a. An assumption that the penetrant molecules do not "pool", i.e., are mainly dispersed in single isolation throughout the volume of polymer, is made. Naturally, this assumption becomes weaker as the plasticizer content increases to considerable levels. Above T_g the polymer molecular structure is dynamic in that frequent local conformational transitions can serve to create transient adjacent pockets of sufficiently large free volume into which the penetrant molecule can jump as the result of its own thermal kinetic energy (Figure 1b).

An excellent summary of earlier models of diffusion in macromolecular systems is given by Kumins and Kwei in the volume by Crank and Park.[5] The pioneering works of Barrer,[6,7] Meares,[8] Bueche,[9] Brandt,[10] and DiBenedetto and Paul[11-13] are of special prominence.

The Cohen–Turnbull theory provides an explicit expression for the diffusion coefficient for small molecules above T_g in terms of the average available free volume per polymer chain segment and the penetrant molecular space-filling requirement.[14] In this theory, the period of unit flow is essentially the time required for the penetrant, moving at the gas kinetic velocity, to traverse a distance of approximately one penetrant molecular diameter.

Vrentas and Duda formulated a theory of polymer–solvent diffusion via slight modifications of standard free volume theory.[15-17] While this model seems to have been primarily applied to concentrated polymer solutions or solvents in molten polymers, i.e. to purely viscous polymer–solvent diffusion processes, these investigators have also reported an application to the diffusion of large molecules in amorphous polymers.[17b] In our view, an important feature of this model, which we have in fact explicitly incorporated in our theory, is the allowance for a fundamental penetrant molecular jump that only involves a portion of the molecule. Given the validity of this concept, the specific shape of the penetrant molecule becomes an important factor. Although this reasonable theory has been shown to be generally valid within its intended realm of application, a serious limitation of its usage from the standpoint of prediction seems to reside in the requirement of a rather large body of experimental data. Specifically, for both pure polymer and pure solvent and as a function of temperature, not only density and viscosity data but also at least three values of the diffusivity itself are called for. Furthermore, the Flory–Huggins polymer–solvent interaction parameter must be determined by thermodynamic means. While our theory, as reported herein and as refined in succeeding papers, is not wholly independent of experimental data, we present a modest effort to formulate a model that not only is similar to that of Vrentas and Duda but also is, however, grounded on more specific molecular fundamental concepts.

Pace and Datyner have presented a rather elaborate statistical mechanical model for the diffusion of both simple and "complex" penetrants in polymers.[18] While this theoretical formulation is impressive in both breadth and detail, its utility in the optimization of a diffusion process for a practical situation appears to be quite limited. While the approach outlined in this report does not possess the mathematical complexity or level of molecular detail as that of Pace and Datyner, it does represent, in our view, a reasonable and straightforward model using readily available or easily determined physical parameters.

Given the sudden presence of a sufficiently large adjacent hole, the penetrant molecule, of mass m, will be assumed to acquire one translational degree of freedom in the direction of the hole with a velocity v specified by its thermal kinetic energy

$$(1/2)mv^2 = (1/2)kT \tag{2}$$

where k is Boltzmann's constant. In cases of the diffusion of small molecules, a successful molecular jump is usually considered to involve a net displacement equal to the mean molecular diameter, $\bar{d}$, wherein the jump time is on the order of $\sqrt{m\bar{d}^2/(kT)}$.

For the temperature range of interest (i.e. somewhat above T_g), the time scale of the α relaxation for PVC is considerably longer than these jump times.[19] If the relaxation time of the α process is identified with the cooperative motion of consecutive chain segments to create the transient hole, then it is clear that a large number of penetrant molecule collisions can occur with the "walls" of this activated cell before its enlarged volume relaxes back to its former value. Therefore, the contribution of this vibratory delocalization to the overall probability of an ultimate *successful* (net nonzero) displacement is simply 1/2. In other words, the penetrant molecule has an equal chance of being trapped at its original position as it has to execute a maximum excursion from it.

Although the average free volume per polymer repeat unit, V_f, remains constant at a given fixed temperature, the total available free volume must become dynamically *redistributed* to create the local excess free volume required for this transient hole formation. The Cohen and Turnbull theory[14] states that the probability of finding a hole, due to free volume redistribution among the repeat units with no internal energy change, wherein the hole is of volume V^* or greater, is $\exp(-\gamma V^*/V_f)$. In this expression, γ is a dimensionless factor that accounts for possible free volume overlap, where $1/2 \leq \gamma \leq 1$. In this work, γV^* will be considered as the effective volume requirement of the penetrant molecule, which will simply be written as V^*. Within the framework of this model then, the quantity $-RV^*/V_f$, where R is the universal gas constant, can be considered to be an entropy of hole activation with V^*/V_f as a lower bound on the number of repeat units that must cooperate in providing an adequately large hole.

In a statistical mechanical sense, we can consider an ensemble of a large number, N_0, of independent microsystems, each consisting of the penetrant molecule plus an average number of surrounding polymer repeat units that is sufficiently large to define a cell. This number of repeat units, in fact, will conceivably be greater than, say, an average coordination number for them about the penetrant molecule because the local polymer chain reorganization will necessarily extend beyond the nearest-neighbor shell of repeat units. The α-relaxation process does in fact involve chain-segmental motion on a rather large scale. Again, it will be stated that the assumption of the independence of these microsystems is meaningful to the extent that the penetrant is dispersed uniformly and in reasonably dilute fashion throughout the polymer volume.

The quantity $-RV^*/V_f$ represents a local *decrease* in entropy per mole of microsystems due to thermal fluctuations. On the other hand, given the loosening of at least V^*/V_f polymer "degrees of freedom" in this way, a *positive* contribution to entropic change results from the liberation of the translational degree of freedom of the penetrant molecule. This additional entropic factor is not accounted for in the Cohen–Turnbull model of free volume fluctuation.

It was earlier stated, and also assumed in the theory of Cohen and Turnbull, that the loosened penetrant molecule would then assume a velocity equal to that of a particle of mass m at temperature T as in a one-dimensional ideal gas. Strictly speaking, however, the situation is more reminiscent of the familiar quantum-mechanical problem of a particle confined in a one-dimensional box[20] in that the penetrant molecule can be expected to rebound with great frequency from the walls of the activated cell whose dimensions in this case are in fact only slightly greater than those of the particle. One can then proceed to calculate the energy levels of such a particle in an infinite square-wall potential of width $\bar{d}$ and discover that the difference between consecutive levels, n and $n + 1$, for typical plasticizer molecules is only about $(2n + 1) \times 10^{-6}$ eV, which suggests regarding the kinetic energy distribution as being continuous rather than discrete. We note that Frisch and Rogers had also earlier invoked the particle in a box model in the analysis of the diffusive motions of small molecules in synthetic natural rubber and polyethylene.[21]

Finally, using the standard derivation, it can be seen that *for these molecules* $(1/2)mv^2 = (1/2)kT$; i.e., the use of the thermal translational velocity for one degree of freedom is, after all, justified. It can also be shown that the entropy per mole of activated cells is given by $R \ln (\bar{d}/\Lambda) + (1/2)R$, where Λ, the thermal de Broglie wavelength, is equal to $h/(2\pi mkT)^{1/2}$, where h = Planck's constant. Λ, for the system at hand, is around 5 Å, i.e. roughly one-half the size of the penetrant molecule.

If it is assumed that the molecule's translational entropy in its preactivated, totally encapsulated state is zero, neglecting vibrational motions of small amplitudes, then, after adjacent hole-formation, the local entropic gain per mole will be taken as $R \ln(\bar{d}/\Lambda) + (1/2)R$. This increase in disorder is similar to that as discussed in the communal entropy concept appearing in cell theories of the liquid state.[22]

Finally, the probability of adjacent hole formation, followed by successful particle displacement, is

$$\begin{aligned} P &= (1/2)\exp(-V^*/V_f)\exp[\ln(\bar{d}/\Lambda) + 1/2] \\ &\approx \exp(1/2 - V^*/V_f) \end{aligned} \tag{3}$$

where $\bar{d}/2\Lambda$, as mentioned for the molecules under consideration, is on the order of unity and will effectively be set equal to one. This approximation accounts for the disappearance of the prefactor 1/2 in the last expression.

For a statistical ensemble of N_0 penetrant-containing cells, at a given instant, only PN_0 cells will contain molecules that will be able to jump. In a relative sense, the jump time will be considered so short, that, in this interval, essentially $(1 - P)N_0$ cells still remain dormant. The justification for this assumption resides in the realization that the polymer relaxation time is much longer than the jump time. If the rate of depopulation of the original molecular positions is treated as being fixed, then it is clear that the *effective hopping time*, τ, that is, the time to wait for *all* molecules in the ensemble to undergo a successful displacement, is $P^{-1}\sqrt{m\delta^2/(kT)}$. This number can be considered as a *retarded hopping time*. An effective diffusion coefficient, allowing for jump retardation, can then be written as

$$D = (\delta/6)\sqrt{RT/M}\exp(1/2 - V^*/V_f) \tag{4}$$

where M is the molecular weight of the penetrant.

It should be noted that in this approximate form, eq 4 is the same as the Cohen–Turnbull result, save for the 1/2 in the exponent. Therefore, this equation should predict comparatively higher D's. In physical terms, the increase in diffusivity over that as predicted by the conventional free volume theory can be attributed to the added positive increase in penetrant translational entropy that now detracts from the usual negative entropy of hole activation due to the redistribution of free volume.

Numerous past works, described in the earlier cited literature, have discussed energies of activation (ΔE) for the diffusion of large and small, polar and nonpolar molecules through a number of polymers above and below T_g. ΔE's have been formally extracted from experimental log D vs T^{-1} plots in the spirit of the absolute rate concept initiated by Eyring.[23] Indeed this concept has been directly patched onto the Cohen–Turnbull formalism in relation to modeling the viscosity of and diffusion in liquids.[24,25] In the theoretical realm, ΔE's have been directly computed from intermolecular energetics, the most ambitious effort being that of Pace and Datyner.[18]

On the other hand, Ferry, in considering WLF form equations for above-T_g diffusion, has concluded that the purely free volume interpretation of the temperature dependence of diffusion is quite satisfactory.[26] Reinforcing this point of view are the results of several investigators who have performed dielectric relaxation studies of PVC.[27] It was concluded in these studies that the curvature of the log frequency vs T^{-1} plot for the α relaxation is consistent with an equation of the WLF form. As mentioned earlier, this primary relaxation is directly implicated in mediating diffusion. While we have adopted this free volume dominated viewpoint in our approach, we also believe that molecular energetics are important but in this case are largely manifest through other variables such as T_g and the plasticizer efficiency parameter. In fact, it will be later mentioned that the free volume theory of diffusion has been firmly established as being appropriate in rationalizing both temperature and plasticizer concentration behavior in PVC itself. In short, there is no strong motivation for directly incorporating a formal activation energy in a theoretical expression for the diffusion coefficient.

If V is the total volume per mole of polymer repeat units or per individual chain segment (steric volume + free volume) at the temperature $T > T_g$, then the molar free volume or free volume per chain segment will be written in usual fashion as

$$V_f = V[0.025 + \alpha_f(T - T_g)] \tag{5}$$

where α_f, the temperature coefficient of free volume expansion, is taken to be approximately equal to the difference between the thermal expansion coefficients of the polymer above and below T_g.[28]

Ferry points out that the temperature shift factor for amorphous polymers incorporating low molecular weight diluents is also given by a WLF equation

$$\log a_T = -C_1^g(T - T_g)/(C_2^g + T - T_g) \tag{6}$$

wherein the "constants" C_1^g and C_2^g do not vary greatly.[29] Therefore, the polymer primary relaxation times are altered mainly by shifting T_g by changing diluent concentration.

If w_1 is the weight fraction of diluent in the polymer and T_{g_2} is the glass transition for the pure polymer, then the depression in T_g can often be written as[29,30]

$$T_g = T_{g_2} - kw_1 \tag{7}$$

T_g vs w_1 curves for some polymer/plasticizer systems can exhibit curvature over a broad range of w_1.[31-34] Also, there exists a more complex theoretical equation, developed by Couchman and Karasz[35-37] for polymer blends and polymer/diluent mixtures that expresses the mixture T_g in terms of (a) the glass transition temperatures of pure polymer and pure diluent, (b) the difference in specific heat above and below the glass transition for both polymer and diluent, and (c) w_1. The applicability of this theory in the prediction of the variation of T_g for PVC, for a few plasticizer compositions, has been tested by Fried et al.[38] While it was claimed that the fit of a special restrictive form of the Couchman–Karasz equation to DOP (di-2-ethylhexyl phthalate) in PVC data[39] was satisfactory, it was seen in our experiments that eq 7 is quite appropriate for the system under study, as our T_g vs w_1 graphs appear linear.

k, the plasticizer effectiveness, is a measure of the degree of generation of additional free volume by the insertion of penetrant molecules into the polymer structure.[29] Despite the reasonable expectation that k would depend on polymer–diluent energetics as well as on the size, shape, and concentration of diluent, this parameter is presently inaccessible by means of a theoretical molecular model.

The free volume will then be represented by the following familiar equation, as was done earlier by Fujita and Kishimoto:[40a]

$$V_f = V[0.025 + \alpha_f(T - T_{g_2} + kw_1)] \qquad (8)$$

On combining eq 3 and 8, it is seen that for a given δ and V^*, and with all other factors remaining constant, the effective hopping time, τ, decreases markedly with increasing penetrant concentration, w_1.

Experimental Determination of Plasticizer Efficiency Parameter, *k*

Materials. Commercial dryblend-grade PVC resin particle samples were supplied by Exxon Chemical Co. Experimental quantities of DNOP and DNDP plasticizers were provided by L. Krauskopf and B. Brueggeman of Exxon Intermediates Technology Division.

Thermal Analysis. The glass transition temperatures of plasticized PVC samples were obtained by using a Du Pont 910 DSC module attached to a 9900 thermal analyzer. All thermograms were produced by using a programmed heating rate of 10 °C/min and a nitrogen atmosphere. Hermetically sealed sample pans were used to prevent volatilization of plasticizers at high temperatures.

Sample Preparation. Approximately 0.2 g, to the nearest 0.02 mg, of PVC resin powder was weighed into a stainless-steel amalgamator capsule (Wig L Bug, Crescent Dental Mfg. Co.). Controlled quantities of plasticizer were added to the capsule by using a syringe. The actual weight of plasticizer added was determined to the nearest 0.02 mg, by difference. The capsule was sealed and agitated on the amalgamator for 10 min. After this time, the capsule was removed and the contents were stirred by using a small spatula. The capsule was resealed and agitated for an additional 10 min.

A portion of the resulting PVC/plasticizer mixture was encapsulated in a vapor-tight DSC pan (Du Pont Instrument Co.). Prior to thermal analysis, the sample was heated 12 h at 80 °C to ensure complete absorption of the plasticizer by the PVC. We had earlier established by gravimetric studies, as well as by observing the kinetics of the swelling of PVC particles by light microscopy, that plasticizer absorption reaches the equilibrium resin capacity within 12 h at 80 °C. Under these conditions, considering that the system was tightly closed against HCl loss, PVC degradation was considered negligible since Braun and Bezdadea[40b] state that, in general, temperatures above 100 °C are necessary to produce cleavage of HCl in open PVC systems. For this reason we did not check for PVC degradation.

Results. The T_g's measured in this way are displayed as a function of weight percent for the two plasticizers in Figures 2 and 3. As the plots are quite linear, well-defined values of k can be extracted from the slopes. Experimental k values, seen in Table I, indicate that DNOP is more effective on a per weight percent basis in lowering the T_g of PVC than is DNDP.

In future work we will generate k values thusly over a broad range of dialkyl phthalate plasticizer structures in PVC for the purpose of establishing trends with alkyl chain length and branching as well as for use as a presently necessary diffusion model parameter and report the comprehensive results in a future communication. In this work, however, we are primarily interested in laying the groundwork for the diffusion model and testing it against two long chain dialkyl phthalate plasticizer molecules that do not possess the complexity posed by branched isomers.

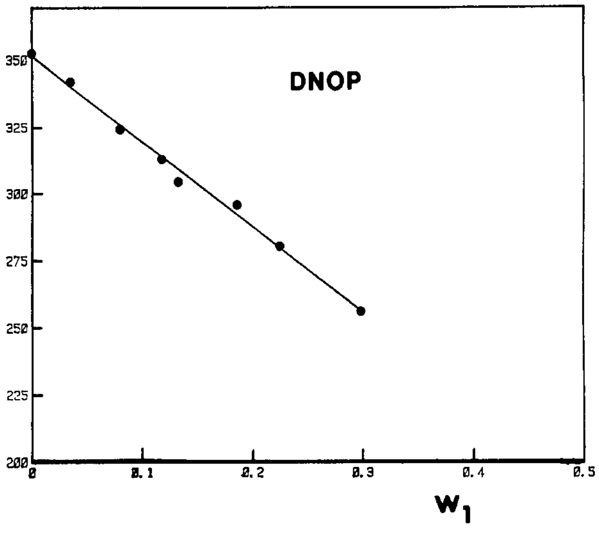

Figure 2. T_g vs w_1 for PVC containing di-*n*-octyl phthalate.

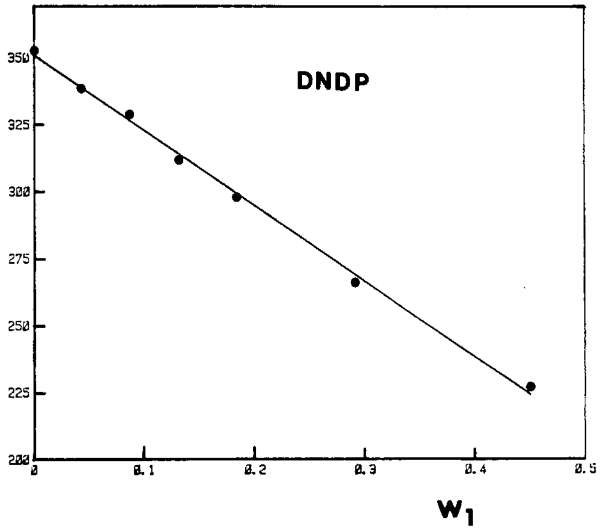

Figure 3. T_g vs w_1 for PVC containing di-*n*-decyl phthalate.

Table I

***l* and V_s for Di-*n*-octyl and Di-*n*-decyl Phthalate (DNOP and DNDP, Respectively) Molecules and *k* for PVC Containing These Plasticizers**

	l, Å	V_s, Å^3	k, K
DNOP	17.0	151	337
DNDP	19.5	169	282

Penetrant Molecular Size, Shape, and Local Polymer Environment

V^*, in a first crude approximation, will be taken as the sum of the steric (van der Waals) volumes of all the constituent atoms of the plasticizer molecule (V_s)

$$V^* = V_s = (4\pi/3)\sum_{j=1}^{M'} l_j r_j^3 \qquad (9)$$

where there are M' atomic species in the chemical formula, there being l_j atoms of type j having a hard-sphere radius of r_j. This assumed prescription for V^* is molecular shape independent. The actual shape will depend on the temperature-dependent conformations of the two alkyl chains as they pack alongside each other and within their local polymer chain environment. Also, of course, eq 9 does not discriminate between linear and branched isomers, although it will be seen that the subsequent theoretical development strongly favors model applicability to linear chains. An extension of the model to a range of molecular shapes and isomer differentiation will be reserved for a future report.

The molecular structures of most plasticizers are considerably more complex than those of gases or simple organic solvents in terms of conformation. Furthermore, their molecular sizes are appreciably greater than those of most common polymer repeat units. For these reasons, a fundamental understanding of the unit flow event and its associated jump length involves a level of complexity beyond that required for simple penetrants. Therefore, it is important to inspect the steric/conformational details of the penetrant molecule and develop a concept of how its overall shape might be most favorably incorporated into, and move through, a local array of polymer chains.

In an initial, direct, but somewhat rough approach, CPK space-filling models of the plasticizer molecules were manipulated to produce the least sterically hindered conformations while maintaining favorable C=O and C—O—C dipole orientations by inspection. The *n*-alkyl chains were made to loosely pack against each other rather than being splayed apart as the PVC polymer environment is more polar than that of pure hydrocarbons.

For DOP, the overall shape appeared to be roughly that of a thin elliptical-faced lozenge whose major and semimajor axes are about 17 and 10.5 Å, respectively, and whose thickness is about 4.5 Å. On the other hand, inspection of the DOP molecule reveals no symmetry of shape and the structure has a maximum dimension of about 15 Å. Moreover, the straight-chained molecule would have more conformational fluidity allowing it to conform more readily to the steric restrictions of its local polymer environment.

As a largely free volume based model of diffusion has been adopted in these studies, the question of accounting for energetic (in addition to entropic) changes, accompanying the redistribution of free volume necessary for hole formation, might be revisited. First, Turnbull and Cohen[41] considered the potential energy of a molecule in a cage formed by its neighbors as a function of the cage size. For large cage radii, as those required to surround a sizeable plasticizer molecule, it was reasoned that V_f could indeed be redistributed essentially without a change in internal energy. Secondly, the free volume theory has already been established as at least a good interpretive framework for plasticizer diffusion in PVC.[42]

There is the possibility, actually assumed as fact by Pace and Datyner,[18] and earlier by DiBenedetto,[13] of *local order* in the noncrystalline regions of simple polymers mainly based on X-ray diffraction and amorphous vs. crystalline density considerations. The picture is roughly that of local bundles of chains that are approximately parallel to each other. This order is viewed as persisting over distances of a few nanometers. Of course, above T_g, this local ordering must be considered as dynamic, with bundle formation followed by structural dissolution. Furthermore, the bundles might suffer constant reorientation within their lifetimes. It is well-known that commercial PVC possesses a low degree of crystallinity that increases with decreasing temperature of polymerization.[43-47] Accordingly, the syndiotacticity increases and degree of branching decreases, with a lowering of the polymerization temperature. Small- and wide-angle X-ray scattering and light scattering studies have suggested details of the crystalline structure.[48-50] Wenig[49] determined that the crystals are lamellar-shaped with a length of about 7 Å in the chain direction and dimensions of about 41 Å in the directions perpendicular to the chains. It is further believed that plasticizers will swell the amorphous regions without solvating and destroying the crystals and that the crystals act as cross-links that limit swelling.[51-55]

It might then be argued that this inherent capacity for crystallization in PVC adds weight to the previously discussed concept of short-range bundles of approximately parallel chains above T_g. We definitely do not suggest plasticizer incorporation in purely crystalline regions in contradiction of the above evidence. This picture is also somewhat reminiscent of the transient, locally parallel association of chains in polymer melts that are visualized as giving rise to the homogeneous nuclei (i.e. potential embryos) that initiate crystallization on cooling.

Accepting this hypothesis of local order, it is then natural to think of phthalate plasticizer molecules, with *unbranched* alkyl chains, as being incorporated with their average chain directions parallel to the average local polymer chain orientation for efficient packing.

Earlier studies of the diffusion of paraffins in simple polymers may offer some insight into the motion and structural incorporation of large and elongated organic molecules above T_g.[56-58] For the diffusion of *n*-paraffins in polyisobutylene, it was found that *D* will decrease with increasing number of carbon atoms but then level off to a constant after five carbon atoms. Branched and cyclic hydrocarbons, given the same number of carbon atoms, were seen to have lower diffusivities.

A computation of the volume of the hole, within polyethylene, that must be formed for diffusion to occur, based on a study of the pressure dependence of *D*, seems to be quite relevant to this analysis.[59-60] For the homologues *n*-hexane, *n*-octane, and *n*-decane, the volume of activation is practically constant and equal to that of about two chain segments. The addition of methyl side groups, however, increases this volume. While the volume of activation for benzene was found to be equal to its molar volume, those for linear paraffins are clearly less than their molar volumes. The interpretation is that *n*-paraffin molecules diffuse by motion along their chain contours while they are in general alignment with the adjacent polymer chains. The hole size required for unit flow, as well as the jump length, would seem to be independent of penetrant molecular length.

The following diffusion model formulation is strongly influenced by these experimental facts relating to penetrant molecular shape. On the other hand, while the issue of the polymer molecular environment adjacent to the penetrant molecule may well be important, we are not aware of experimentally established facts for guidance and the existence of "local order" is consequently not critical in the theory at this time.

Longitudinal Motion of Elongated Penetrant Molecules

Consider then a reasonable hypothesis wherein a high aspect ratio plasticizer molecule primarily executes its elementary diffusive jump along its long dimension. An adjacent polymer structural relaxation will provide an opportunity for the penetrant to advance along a fraction (*f*) of its long dimension as depicted in Figure 4. While this concept certainly is in harmony with an earlier proposed idea of the motion of simple molecules along virtual "tubes" formed by locally parallel chain bundles,[18] the additional specification of that motion as being limited to the direction of the penetrant molecule's long dimension is also reasonable considering that the mini-

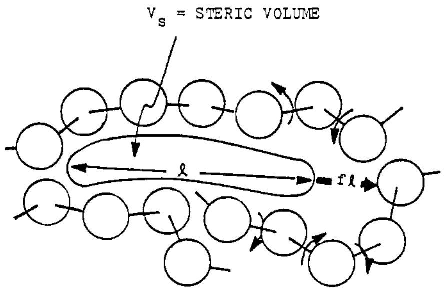

Figure 4. Encapsulation of a large elongated molecule within a cell of nearest-neighbor polymer chain segments. Also depicted is a displacement of the molecule, along its long dimension, l, equal to fl, $f < 1$, into a thermally activated pocket of free volume.

mal cross-sectional area of polymer chains in a plane perpendicular to the jump direction, which would have to be swept aside, is involved. Neither the theory no experiment can provide a value for a minimum aspect ratio above which this assumption of longitudinal motion will hold, at present. To be sure, a small relative population of penetrant molecules executing "sideways" motions must be conceded but will be ignored in its initial approximation.

Equation 4 will then be rewritten in the following way with $\delta = fl$ and $V^* = fV_s$:

$$D = (fl/6)\sqrt{RT/M}\exp(1/2 - fV_s/V_f) \qquad (10)$$

With f unspecified at this point, the following approach will be considered for its determination.

D, according to eq 10, will initially increase with increasing fractional jump length, attain a maximum value, and then rapidly decline as the probability of redistributing free volume diminishes exponentially. The following discussion will provide a simple and general thermodynamic rationale for determining the value of f corresponding to a condition of minimum free energy for an ensemble of hopping penetrant molecules wherein each molecule will be considered to undergo the same displacement magnitude.

The free energy per mole of a macroscopic ensemble of diffusing molecules can be written according to the usual thermodynamic prescription

$$\Delta u = RT(\ln a) \qquad (11)$$

where a is the thermodynamic activity of the penetrant in the polymer matrix. Let x be a spatial coordinate along which diffusion takes place. For simplicity, unidirectional diffusion will be considered, although the same net result can also be demonstrated for three-dimensional diffusion. Equation 11 can then be written as

$$\Delta u = RT\int_0^{\Delta} a^{-1}(\mathrm{d}a/\mathrm{d}x)\,\mathrm{d}x \qquad (12)$$

where Δ is the thickness of a polymer sheet having lateral dimensions $\gg \Delta$. Let $\bar{\nu}$ be the spatially averaged net velocity of diffusion, and let the driving force, F, be the gradient of the chemical potential, i.e. $RTa^{-1}\,\mathrm{d}a/\mathrm{d}x$. The diffusive mobility, U, is $\bar{\nu}/F$ which is directly related to the diffusion coefficient thru Einstein's equation:[61]

$$D = RTU = \bar{\nu}/(a^{-1}\,\mathrm{d}a/\mathrm{d}x) \qquad (13)$$

Equations 12 and 13 can be combined to yield

$$\Delta u = RT\bar{\nu}\Delta/D \qquad (14)$$

From eq 14 it is clear that the free energy is minimized by maximizing D for a given $\bar{\nu}$, Δ, and T. This result is physically reasonable considering that diffusion is essentially an entropy-driven process that strives for maximum disorder.

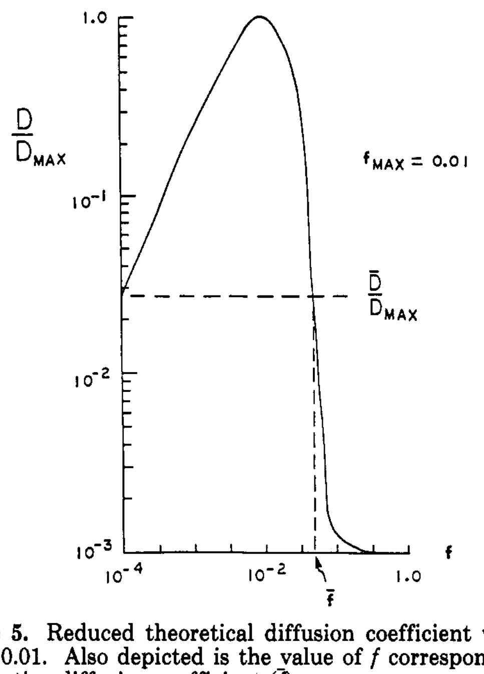

Figure 5. Reduced theoretical diffusion coefficient vs f for $f_{\max} = 0.01$. Also depicted is the value of f corresponding to the effective diffusion coefficient ($\bar{f}$).

Return, therefore, to eq 10 and find the value of f for which $\partial D/\partial f = 0$. This value, $f_{\max} = V_f/V_s < 1$, will increase linearly with increasing temperature owing to eq 8. When substituted back into eq 10, the maximum value for the diffusion coefficient becomes

$$D_{\max} = \frac{lV_f}{6V_s}(RT/eM)^{1/2} \qquad (15)$$

Physically, this value corresponds to the state of diffusion for which the amount of disorder within a macroscopic ensemble of penetrant molecules is greatest.

Of course, the reality of *microstructural heterogeneity* in real polymers would produce a dispersion of f values about $f_{\max}$ and therefore a distribution of D values. An "effective" diffusion coefficient, $\bar{D}$, would for this reason be more properly represented by D averaged over the range of jump distances, say from zero up to the entire length of the penetrant molecule:

$$\bar{D} = \int_0^1 D\,\mathrm{d}f$$

$$= eD_{\max}[f_{\max} - (1 + f_{\max})e^{-f_{\max}^{-1}} \qquad (16)$$

$$\bar{D} \approx \frac{l}{6}\left[\frac{V_f}{V_s}\right]^2 (eRT/M)^{1/2} \quad (f_{\max} \ll 1) \qquad (17)$$

The limiting eq 17 is also the expression obtained if the upper limit of integration is infinity rather than unity. It will be seen that, for the large penetrants of interest, the limiting expression is quite appropriate.

Figure 5 is a sample distribution of D with f for $f_{\max} = 0.01$, a reasonable assignment for the present examples. Notice that $\bar{f}$, the value of f corresponding to $\bar{D}$, is 0.05. In other words, on the average, the molecule advances but 5% of its long dimension in a single displacement. In the case of di-*n*-decyl phthalate, this corresponds to a displacement of around 1.0 Å, or, in other words, the molecule must make about 20 consecutive jumps in the same direction to traverse a path equal to its length. Notice also that this displacement turns out to be of the order of that for small-sized diffusants.

Table II
Atomic Population and Radii within Di-*n*-Octyl and Di-*n*-decyl Phthalate (DNOP and DNDP, Respectively) Molecules

penetrant	j	l_j	r_j, Å
DNOP	H	38	0.67
DNDP		46	
DNOP	C(tetrahedral)	16	0.77
DNDP		20	
DNOP	C(aromatic-6)	6	1.20
DNDP		6	
DNOP	C(ethylenic)	2	1.16
DNDP		2	
DNOP	O(carbonyl)	2	0.96
DNDP		2	
DNOP	O(ether)	2	1.01
DNDP		2	

Table III
Volume per Mole of Chemical Repeat Units (V) and Free Volume per Chemical Repeat Unit (V_f) for PVC at 82 and 91 °C

plasticizer	T, °C	V, cm^3/mol	V_f, Å^3/CH$_2$CHCl unit
DNOP	82	45.6	$1.89 + 2.56w_1$
DNDP			$1.89 + 2.14w_1$
DNOP	91	46.0	$1.99 + 2.57w_1$
DNDP			$1.99 + 2.16w_1$

This model is somewhat reminiscent of the concept of polymer reptation, i.e. macromolecular self-diffusion by motion along its chain contour through entanglements with adjacent polymer molecules by a curvilinear diffusion of local "defects".[62] While the above model does involve longitudinal motion similar to curvilinear motion, the smaller, e.g. plasticizer, molecule still moves as a unit rather than by the propagation of conformational fluctuations along its length. Perhaps this amended free volume theory and its refinements may form the basis of an understanding of molecular diffusion in polymers in the ill-defined size gap between small simple molecules and long-chain polymers.

Application of Theory to Di-*n*-octyl and Di-*n*-decyl Phthalates in Rubbery PVC

Table I gives a listing of l and V_s for DNOP and DNDP molecules. The quantities relevant to eq 9 used in the determination of V_s are listed in Table II. r_j values are taken as averages between van der Waals and covalent radii obtained from Ealing CPK molecular model listings that are based on representative crystallographic data.

As mentioned, the unplasticized PVC glass transition temperature for the samples in particle form was measured at $T_{g_2} = 353$ K. The modified free volume theory was tested for 82 °C, which is slightly above T_{g_2}, and for 91 °C over a range of compositions, w_1, for DNOP and DNDP. These temperatures are relevant to the PVC resin powder/plasticizer dryblending process. The PVC molar volumes based on density, as well as the resultant V_f vs w_1 relationships, at these temperatures, are given in Table III.

α_f, as earlier defined, is taken as 10^{-4} K^{-1}, based on experimental data for PVC.[63] By comparison, the "universal" value of α_f is 4.8×10^{-4} K^{-1}.[64]

Computed values of $\bar{D}$ vs w_1, for DNOP and DNDP at 82 and 91 °C, are seen in Figure 6. The trends with molecular size, plasticizer concentration, and temperature are reasonable. The plots exhibit a slight upward curvature.

While there exists a great volume of published literature dealing with the kinetics of uptake of various plasticizers in PVC resin particles as well as in solvent-cast and hot pressed PVC films, Storey, Mauritz, and Cox[65] have provided a short summary of investigations that are most closely related to their own experimental studies of the diffusion of branched and linear dialkyl phthalates in PVC films and to the limited theoretical modeling results presented herein. We believe, however, that caution is required when comparing results between different experimental methods, between theory and experiment, and between results using samples of variable preparation. In this regard, perhaps favorable comparisons of diffusion coefficient orders of magnitude and trends with variable alkyl chain lengths and branching, as well as with temperature and plasticizer concentration, are the best that can be achieved realistically.

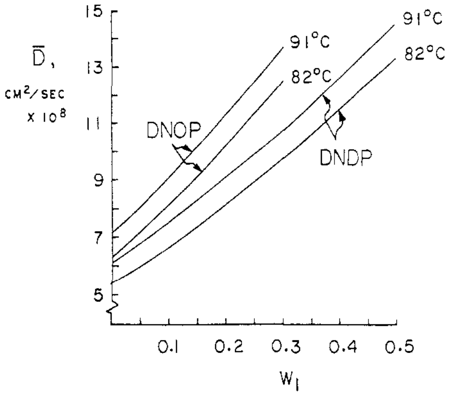

Figure 6. Theoretical effective diffusion coefficient vs weight fraction of plasticizer for di-*n*-octyl and di-*n*-decyl phthalates in PVC at 82 and 91 °C.

The works of Knappe[66] and of Grotz[67] are noteworthy but will not be recounted here as they were both limited to DOP diffusion and discussed in our earlier report.[65] We will mention, in the interest of reinforcing our view, that Grotz concluded that the rate-limiting diffusion mechanism is the movement of segments of the polymer chains.

Griffiths, Krikor, and Park[42] determined the self-diffusion coefficients of di-*n*-butyl, di-*n*-hexyl, and di-*n*-decyl phthalates in PVC films by a radiotracer method. D values were obtained from 25 to 55 °C at plasticizer concentrations in the range 28–50 wt %. D was seen to monotonically increase with increasing plasticizer concentration at fixed temperatures and, for a given concentration, increased with increasing temperature. While it is unfortunate that these measurements were not performed at temperatures above the unplasticized T_g to permit direct comparison with our results, it is noted that at the highest reported temperature (55 °C) and highest plasticizer content ($w_1 = 0.5$), D for DNDP was measured at 4.6×10^{-8} cm^2/s which falls just beneath the lower end of the theoretical $\bar{D}$ vs w_1 curve for DNDP at 82 °C. On inspection, it is obvious that increasing the temperature from 55 °C would logically displace the experimental D vs w_1 curves of Griffiths et al. toward the theoretical curves of Figure 6. We will later discuss a more meaningful way of comparing these data.

The broader experimental database of D values for commercial as well as model n-alkyl phthalate plasticizers in PVC films, which has been recently generated by Storey, Mauritz, and Cox using a mass uptake technique,[65] will be useful in the progressive development of the mathematical model of diffusion, the rudiments of which are presented in this paper. These data are directly significant in that the measurements were performed over the temperature range 60–100 °C which includes a rubbery region. In qualitative conformity with the lower temperature diffusion measurements of Griffiths, Krikor, and Park, cited above, we have noted that, with other conditions held constant, D increases with increasing temperature in the usual way and decreases with increasing n-alkyl group length. Additionally, for a given alkyl group carbon number, D decreases with increase in alkyl group branching. It would seem that a particularly important result of these experimental studies is that ln D vs number of carbons in n-alkyl phthalate chains is approximately *linear* for several temperatures above the polymer's T_g. Since the accepted general free volume model predicts that $-\ln D$ is directly proportional to the free volume requirement for penetrant hopping, the above experimental result strongly implies that diffusion occurs primarily in the direction of the long "axis" of a plasticizer molecule whose chains essentially assume extended conformations. From the standpoint of the molecular shapes of these di-n-alkyl phthalates, increasing the chain length serves only to lengthen the molecule without effectively changing its lateral dimensions. This experimentally established result lends important support to our assumption of a mode of longitudinal diffusion in the model.

On the other hand, a comparison of the curves in Figure 6 with the D values for di-n-alkyl phthalates tabulated in ref 65 indicates that the theoretical values can be greater than the experimental values at the same temperatures by about 2–3 orders of magnitude. The theoretical values are less sensitive than experimental values to temperature. For DNOP, theoretical D increases, on the average over the range of w_1, by only around 11% in going from the 82 to the 91 °C curve. In contrast, experimental D for DNOP increases by 164% in passing from 80 to 90 °C.

A number of important comments naturally arise from these observations. First, one is moved to consider adding an appropriate activation energy to the model to forcibly lower theoretical D as to be closer to the experimental value. Regarding temperature dependence, it is evident that the integration of D over f that is performed to reach eq 17, although considered a physically significant step, does nonetheless serve to lower the sensitivity of theoretical D to temperature. To be sure, it would be better to have an a priori knowledge of the "correct" f value to immediately insert into eq 10, but the elusiveness of this parameter is in fact the crux of the problem. On the other hand, one might accept eq 10 as true and then use it to calculate f for diffusants of interest *given* the experimental D's.

It is noteworthy that the experimental diffusion database established by Storey, Mauritz, and Cox[65] was obtained under transient kinetic rather than under equilibrium conditions as existed in the experiments of Griffiths, Krikor, and Park.[42] During the uptake of plasticizer in the experiments in ref 65, the T_g of PVC steadily decreased and, therefore, D's extracted from the data should be considered as concentration averaged. On the other hand, as the experimental ranges of w_1 used in the diffusion calculations were actually less than 0.1, $\bar{D}$ vs measured D value comparisons would appear somewhat better than as stated earlier. At this time experimentally determined D values for di-n-alkyl phthalates that reach high concentrations are nonexistent although Storey et al.[65] have reported results for commercial branched phthalates at higher levels of sorption.

Perhaps it is most natural to picture our theory within the context of self-diffusion in a state of dynamic equilibrium. To facilitate a more direct comparison with the results of Griffiths, Krikor, and Park, it is necessary to compare *iso-free volume* states. If the graph in Figure 3 can be applied to their DNDP in PVC systems, the actual T_g at $w_1 = 0.5$, for example, is only about −62 °C, which accounts for the corresponding diffusion coefficient of 4.6×10^{-8} cm^2/s to be large enough to fall in the range of D values displayed in Figure 6. According to eq 8 the free volume fractions within two rubbery polymers, having unequal plasticizer uptakes of w_1 and w_1' and corresponding (plasticized) glass transition temperatures of T_g and T_g', are equal at temperatures T and T' where $T - T_g = T' - T_g'$. This simple condition leads to the equation

$$T = T' + k(w_1' - w_1) \tag{18}$$

Let us determine, for example, the value of w_1 at $T = 91$ °C for DNDP ($k = 282$ K) at which the free volume fraction is the same at $T' = 55$ °C and $w_1' = 0.5$. At this value ($w_1 = 0.372$) $\bar{D} \approx 1.2 \times 10^{-7}$ cm^2/s, which is indeed within an order of magnitude of its iso-free volume value of 4.6×10^{-8} cm^2/s.

Conclusions

A modified free volume-based theory for the above-T_g diffusion of large and elongated molecules in amorphous polymers has been initiated and tested against limited experimental diffusion data for di-n-octyl and di-n-decyl phthalate plasticizers in PVC for the purpose of identifying critical aspects of future model improvement.

In addition to the usual inclusion of the probability of creating a hole of sufficient size for penetrant molecular hopping strictly due to an isoenergetic redistribution of free volume via Cohen–Turnbull theory, the increase in the translational entropy of the penetrant accompanying the enlargement of its encapsulating cell formed by adjacent polymer chain segments is accounted for. It was rationalized that a longitudinal mode of diffusion for this class of unbranched molecules is quite consistent with existing experimental evidence as well as with the obvious stereochemical difficulty of penetrant displacement in directions transverse to the molecular long dimension.

While the concept of longitudinal penetrant hopping with a unit displacement that is but a fraction of the long dimension of high aspect ratio molecules is quite reasonable, the method for determining an average f may not represent the best approach. In any case, a satisfactory alternative method is presently unavailable. On the other hand, a back-calculation of f values given eq 10 and experimental diffusion coefficients for selected penetrants will provide valuable insight into this problem and will be reserved as the subject of a future report.

Obviously, the theoretical D's can be lowered to conform to the cited experimental values by inserting a formal activation energy, in Macedo–Litovitz fashion,[24] of an appropriate magnitude. The inclusion of energetic effects via the direct computation of intermolecular energetics will in fact take place in future model refinements. In this vein, we would express the opinion that diffusion occurring in kinetic fashion, as in the plasticizer uptake experiments of Storey, Mauritz, and Cox, is by nature slower than corresponding self-diffusion at the same temperature. In the latter, simpler, time-independent situation the glass transition is fixed within a system in established equilibrium whereas in the kinetic situation the glass transition temperature is continually evolving downward as increasingly more free volume is generated in the polymer. Hence, there exists an initial macromolecular solvation energetic requirement that is nonexistent in the equilibrium state that could possibly be reflected in the lower effective diffusion coefficients observed over the course of the plasticizer uptake experiments. In this regard, perhaps, the direction of the deviation of predicted D values from those within this particular experimental database might in fact be expected.

Future theoretical refinements of this rough model will include, first, the use of a concentration-averaged D to permit more direct comparison of theoretical D's with experimental values obtained from the kinetics of penetrant uptake. Second, the model will be expanded to include large penetrant molecules of any shape. Realistically, the shape should reflect a minimum free energy molecular conformation in the polymer molecular environment. Molecular mechanics software (CHEMLAB II) will be utilized in these studies. Owing to a large molecular size, but with variable aspect ratio in the general case, penetrant jumping will be allowed for in three directions to different degrees.

Other issues, such as conformational flexibility within the penetrant molecule, penetrant molecular pooling at high concentrations, the influence of partial polymer crystallinity, and the capability of predicting the important plasticizer efficiency parameter, k, without having to resort to experimentation, to name but a few, represent more formidable problems that must, however, be ultimately resolved.

Although the theory and subsequent refinements need to be challenged by application to other large molecule systems, it appears that a better than order-of-magnitude agreement between experimental and theoretical diffusion coefficients is possible. It should also be stressed that this appears to be possible with a minimal input database involving no adjustable parameters. Clearly, more sophisticated models, based on this prototype, would be of considerable utility in material design or process optimization involving the controlled diffusion of plasticizers, surfactants, lubricants, or biologically active molecules, as examples, through polymeric particles, films, and containers.

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Registry No. DNOP, 117-84-0; DNDP, 84-77-5; PVC, 9002-86-2.

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