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Diffusion of Plasticizers in Rubbery Poly(vinyl chloride): Effects of Molecular Shape[†]

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ABSTRACT: We have used pulsed-gradient spin-echo NMR methods to study self-diffusion of 14 commercial plasticizers of molecular weights M between 194 and 531 in poly(vinyl chloride) at temperatures between 75 and 175 °C and at concentrations c from 10 to 60 wt % plasticizer. Diffusion of the neat plasticizers, dissolved in CCl_4, was also measured. In solutions trace diffusion coefficients D_0 were obtained by extrapolating the measured $D(c)$ to infinite dilution using the Fujita–Doolittle equation. The T-dependence of D in PVC generally followed the WLF expression, as did D_0 well above the glass transition. Plasticizer molecular shape affected D in PVC but not in liquid solution: while in CCl_4 D_0 was proportional to $M^{-0.70\pm0.05}$, D_0(PVC) showed no clear correlation with M. With the assumption of an intrinsic Rouse-like proportionality to M^{-1}, we found that MD_0(PVC) correlated marginally with the frontal diameter of the plasticizer molecule. The correlation was much improved when the frontal diameters were reduced by ignoring kinks and mobile side groups, i.e., when the abscissa represented the minimal local diameter required for passage given some cooperation by host segments. Similar but more complex considerations explained D in the neat plasticizers. We conclude that the motion of these highly anisometric molecules is itself anisotropic provided the host molecules offer effective lateral constraints, which need not arise from cross-links or entanglements.

I. Introduction

The study of diffusion of trace additives or contaminants in rubbery or glassy polymers has a long and important history; a wide variety of techniques is available to study diffusion in polymers.[1] As is usual in diffusion studies, much can be learned in systematic comparisons, e.g., of (a) a series of diffusants each in the same host or (b) the identical diffusant in each of a series of hosts. Studies of type a generally aim at the elucidation of those molecular attributes of the diffusants that principally influence their diffusion rate in polymer hosts. This information is best elicited at trace concentrations, since interactions among diffusants, either direct or else indirect via modification of host bulk properties, are absent only in the limit of infinite dilution. Whenever the technique in use does not permit diffusion measurements at concentrations of a fraction of 1%, measurements at several small concentrations must be performed and the results appropriately extrapolated to infinite dilution. (Such procedures are routinely applied in studies of polymer molecules diffusing in a liquid solvent.)

The most obvious variable affecting trace diffusivity D_0 is the diffusant's molecular weight M. Several studies[2,3] of D of n-paraffins in rubbery polymers (these will be taken to include entangled melts above their glass transition) have shown that

$$D_0 = k(T)\,M^a, \quad a = -1 \qquad (1)$$

where k is a function of temperature T and reflects certain attributes of both the host and the diffusant. Equation 1 applies only to molecules small enough to be unentangled with the polymer host, whether melt or network, and is useful only if the diffusants form a homologous series, leaving k constant for a single host at a given T. Under different conditions a power law may still be observed, although the exponent a will differ from the Rouse value $a = -1$. In particular, if the dilute diffusant is a polymer entangled within the host, the exponent a generally approaches the reptational[1] value -2; if the host is a low-M liquid solvent, a tends to assume a value of -0.5 to -1.0 depending on the solvent quality and the nature of the diffusant.[4] These subjects have been reviewed in detail.[5]

In addition to the diffusant concentration and the temperature, diffusion is most strongly affected by the molecular variable expressed alternately as mass or size. Considerable work has been reported on the molecular size dependence of the diffusion of smaller molecules in poly(vinyl chloride) (PVC) and other polymers both above and below the glass transition.[6-9] By comparison, the effect of the shape and flexibility of diffusant molecules has until recently attracted comparatively little attention.[10-12] Berens and Hopfenberg[11] measured the trace diffusion of a large number of light species in glassy PVC, polystyrene, and poly(methyl methacrylate), finding a decrease in D_0 of over 10 orders of magnitude as the molecular mean diameter increased by a factor of 2. Significantly, anisometric molecules were found to diffuse more rapidly than expected on the basis of their molecular volume. The authors conclude that the diffusion of these molecules in glassy hosts is itself anisotropic (more rapid along the long axis of the diffusant molecule), responding to a molecular dimension intermediate between the diameter of a sphere of equivalent volume and the minimum dimension of the extended-chain conformation.

The diffusion of plasticizers in PVC has been studied in detail for a small number of common plasticizers,[10,13-17] mainly in an effort to determine their rate of migration into liquids in contact with the plastic. In the few instances where direct comparison with our work was possible, the diffusion coefficients agreed within their combined uncertainties. The theme of molecular shape and its effects on plasticizer diffusion were recently taken up in a study[18,19] of sorption of dialkyl phthalates in PVC above and below the glass transition. The authors confirm the existence of a size effect but also clearly infer local diffusional anisotropy; they attempt to model both in terms of a free-volume theory. (These papers[18,19] also provide a valuable review of previous work in this field.)

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The severity of the effects of architectural changes on diffusion was recently illustrated in a study of linear epoxies during curing with a tetrafunctional curing agent.[20] The contribution of the decrease in D, which was attributable to short-chain branching, amounted to at least 1 order of magnitude before the gel point was reached; this decrease, however, also included a contribution from the host material, undergoing branching at the same time.

The present work was undertaken with three goals in mind: (a) to confirm the applicability of the concept of microscopic diffusional anisotropy of medium-sized molecules in rubbery hosts; (b) to provide a semiquantitative identification of the effective molecular dimension that controls diffusion, in order to permit inferences about the operative diffusion mechanisms; and (c) to examine these issues from the standpoint of Brownian motion in concentration equilibrium, using a self-diffusion technique at trace concentrations rather than the more commonly employed sorption or mutual diffusion methods. An effort is made to separate the expected effects of molecular mass (via eq 1) from those of molecular shape. We confirm the existence of pronounced molecular shape effects and outline the conditions presumed necessary for their occurrence.

The pulsed-gradient spin-echo NMR method[21] of measuring D, in use in our laboratory, does not operate reliably near or below the glass transition temperature, so that high temperatures and relatively high plasticizer concentrations are required in PVC-based solutions. In the process of searching for optimum temperatures for measuring plasticizer diffusion in PVC and producing extrapolations to infinite dilution, we confirm that these systems adhere to various aspects of orthodox free-volume theory. Alternatives to anisotropy effects as explanation for the observed variation of k (eq 1), such as molecular flexibility or electronegativity, are found to be unsatisfactory in a comparison with the data.

Oral reports of parts of this work have been given.[22] This report is based in large part on the M.S. theses (Physics, University of Akron, 1989 and 1990; unpublished) of A. Hariharan and D. Skowronski.

II. Experimental Section

A. Sample Materials and Preparation. The poly(vinyl chloride) for this work was Geon 30, supplied by B. F. Goodrich Co., and has a weight-average molecular mass near 60 000. Basic information on the plasticizers is given in Table I. They were chosen from among the many good plasticizers available for use with PVC on the basis of their complete solubility in PVC, high neat boiling point (>175 °C), low vapor pressure at high temperature, liquid state at room temperature, and convenient classifiability by molecular shape. Molecules of class 1 (Table I) consist of a central aromatic ring and two equal or nearly equal branches; class 2 molecules are linear with few side chains (DBS is terminated by rings); class 3 consists of bulky, asymmetrical molecules with at least two aromatic rings.

Plasticized PVC was prepared from intimate mixtures of granular PVC powder and plasticizer by molding 1–2-mm-thick sheets at 175 °C under pressures near 600 psi for approximately 2–5 s, longer at the lower plasticizer concentrations. Occasional evidence of possible chlorine degradation (pink tint) or failure to attain complete fusion was grounds for rejection; only colorless translucent sheets were accepted. Concentrations between 10 and 60 wt % were prepared in addition to neat plasticizer; for each plasticizer at least 3 but typically between 5 and 12 different concentrations were available for diffusion measurements. Selected samples were subjected to concentration analysis via chlorine content (Galbraith Laboratories, Knoxville, TN) and were found to have lost a small fraction of plasticizer, which increased systematically with concentration from no significant loss below 10% increasing to 4 wt % of the plasticizer supplied to samples near nominal 60%. Because these losses were the same for all plasticizers, corresponding corrections were made to the concentrations assigned to samples not analyzed. NMR samples consisted of 5-mm-diameter disks cut from the plasticized sheets and stacked some 8 mm high in the bottom of the NMR samples tubes, which were then filled with dried N_2 gas and hermetically sealed.

Table I
Properties of Plasticizers

plasticizer	class	abbrev	mol mass	neat density (25 °C), g cm^{-3}
dimethyl phthalate[a]	1	DMP	194.2	1.05
dibutyl phthalate[b]	1	DBP	278.4	0.937
bis(2-ethylhexyl) phthalate[c]	1	DOP	390.6	1.19
ditridecyl phthalate[d]	1	DTDP	530.8	0.924
diundecyl phthalate[d]	1	DUP	474.7	0.97
bis(2-ethylhexyl) adipate[c]	2	DOA	370.6	0.913
heptyl nonyl adipate[e]	2	S97	370.6	0.95
di-2-ethylhexyl sebacate[f]	2	DOS	426.7	0.954
dibenzyl sebacate[g]	2	DBS	382.5	0.97
butyl benzyl phthalate[e]	3	S160	312.4	1.091
7-(2,6,6,8-tetramethyl-4-oxa-3-oxononyl)benzyl phthalate[e]	3	S278	454.6	1.074
2-ethylhexyl diphenyl phosphate[e]	3	S141	362.4	1.12
isodecyl diphenyl phosphate[e]	3	S148	390.5	1.10
tricresyl phosphate[c]	3	TCP	368.4	1.165

[a] Eastman Chemical Co., Rochester, NY; Yellow Label stock no. 318. [b] M & T Chemical, Dover, OH. [c] B.F. Goodrich Co., Brecksville, OH. [d] Exxon Chemicals, Houston, TX. [e] Monsanto Corp., St. Louis, MO. [f] Hatco Chemical Corp., Fords, NJ. [g] Union Camp, Dover, OH.

Solutions in CCl_4 (Fisher analytical grade, <0.05% protonated impurities) were prepared at room temperature in amounts of 3–10 mL, at concentrations between 0.6 and 8 wt % plasticizer. Between two and six concentrations of each plasticizer were available for diffusion measurements; 0.25-mL aliquots were sealed by glassblowing in the 7-mm-o.d. NMR sample tubes to prevent evaporative loss of solvent.

B. Pulsed-Gradient NMR Diffusion Measurements. Data Reduction. Pulsed-gradient spin-echo (PGSE) diffusion measurements[21] were performed in the ^1H NMR at 33 MHz on resonance using radio-frequency phase-sensitive detection. Our equipment,[23] calibration and data taking practices,[24] and data reduction and analysis procedures and software[25–27] were used as described elsewhere, with various refinements and adaptations. The large-gradient PGSE method itself has been reviewed,[5] with emphasis on its application to polymer systems. Briefly, a $90°–\tau–180°$ radio-frequency pulse sequence was applied and synchronized with a two-pulse magnetic field gradient sequence; for this work $\tau = 25$ ms was chosen and the field gradient had magnitudes between 109 and 126 G/cm depending on the temperature. A small steady field gradient was also applied to narrow and stabilize the spin echo, whose height was digitally measured as a function of the duration of each field gradient pulse. Signal averaging of between 6 and 20 acquisitions/instrument setting was performed for each of at least 10 different values of gradient pulse width. The maximum gradient pulse width used corresponded to a reduction of the echo height to less than 5% of its original value (however, see below), unless the single-pass signal-to-noise ratio approached unity at a lower attenuation. Our off-line data reduction software[25,26] displayed the logarithm of the echo height as a function of a combined gradient parameter[5,21] so devised that the plot is consistent with a straight line when diffusion is characterized by a single rate. The same program then produced nonlinear least-squares fits to the data of selected theoretical expressions describing the diffusional echo attenuation.

The PGSE methods directly determine the mean-squared displacements of nuclei at resonance, and hence their host molecules, during well-defined time intervals experimentally selectable. No chemical labeling or tracer/probe species is needed. Diffusion constants are obtained from the echo height measurements assuming only the applicability of Fick's second law, although deviations from the latter, as in the case of restricted diffusion, are directly measurable as well. Our field gradient calibration methods have been described elsewhere;[23,24,28] they are conducted by reference to first principles and invoke no adjustable parameters and require no reference to known D values. As calibrated our spectrometer routinely reproduces published D values for water and other light liquids within our experimental uncertainty of some 3–5%. Measurements of D in heavier liquids and polymers, for which no convenient D values of useful precision and reproducibility are published, differ from those in light liquids solely in the use of larger calibrated field gradient values and longer pulse durations and delays generated by digital timing circuits. Significant earlier disagreements in D for polymer molecules between PGSE and more conventional methods[1] are now understood to have arisen in part from rapidly diffusing trace impurities but mainly from insufficient attention to polymer dispersity[25] during PGSE data taking and reduction.[5] These differences are now largely reconciled; the latter cause does not, in any case, apply to monodisperse plasticizers. In identical high polymers PGSE diffusion results produced by different workers on widely differing equipment agree with one another[5,29] but they tend to disagree with results of other methods using similar polymers carrying chemical labels or embedded in different host materials often at finite rather than infinitesimal concentrations.[30]

Echo attenuation plots for the neat plasticizers at 125.5 °C as well as in CCl_4 solution measured at 30.5 °C showed nearly single-component diffusion, with evidence of slight contamination by faster diffusing impurities. The fast-component amplitude was never greater than 1 or 2% of the echo and varied among plasticizers; it could be reduced by prolonged evacuation of the plasticizer near 100 °C. It was invariably sufficient, as judged by a reduced χ^2 Gauss criterion, to fit a two-component decay expression[26] to the data, attributing the intense slower component to the plasticizer motion of interest. No ^1H free induction decay or spin echo could be observed in the neat CCl_4 solvent.

In the PVC-based systems the diffusion spectrum in general displays two components, of which the slower, containing a diffusivity distribution[25] arising from polydispersity, is attributable to PVC. While PVC as well as plasticizer diffusion could be measured in this way at intermediate concentrations, at low plasticizer contents and at lower temperatures the spin–spin relaxation time T_2 for PVC was much shorter than 2τ, so that in spite of the abundance of PVC no corresponding PVC spin-echo component was observable. This interpretation was confirmed by separate relaxation measurements, which displayed two components in which the intense shorter decay had a T_2 of less than 2 ms. At the highest plasticizer concentrations the small PVC abundance compounded the effect of its faster relaxation, again making the PVC echo, and hence PVC diffusion, unobservable except at 175 °C. Because the slow PVC diffusion was only of incidental interest in this work, our data taking procedure was modified to terminate acquisition at a gradient pulse length at which the echo had been reduced to the less easily attenuatable PVC component. This procedure resulted in a reduction of effort and actually increased the precision in the extracted plasticizer diffusion rate by eliminating one adjustable parameter, leaving only two,[26] the plasticizer diffusion rate and the (nearly) unattenuatable PVC echo fraction, as illustrated in Figure 1a. By comparison with a single-component echo of equal signal strength, the need to account for the unattenuatable echo fraction increases the experimental uncertainty of D(plasticizer) from ±4% to perhaps ±5%; the larger uncertainty in the single-component fit of Figure 1b instead arises from the lower signal-to-noise ratio at lower plasticizer concentration and lower temperature.

III. Modeling: Molecular Anisotropy

Mechanical models of each of the plasticizer molecules, based on the van der Waals radii of the constituent atoms (permitted overlap was 13% or less in all cases), were constructed for the purpose of making dimensional measurements in various configurations considered likely or possible. Because of the complexity and variety of these configurations, the measurements were reduced and stylized in the following way. The diameter d of the equivalent-volume sphere were calculated from the known bulk plasticizer density ρ given the molecular weight M. With Avogadro's number referred to as N

$$d = (6M/N\pi\rho)^{1/3} \tag{2}$$

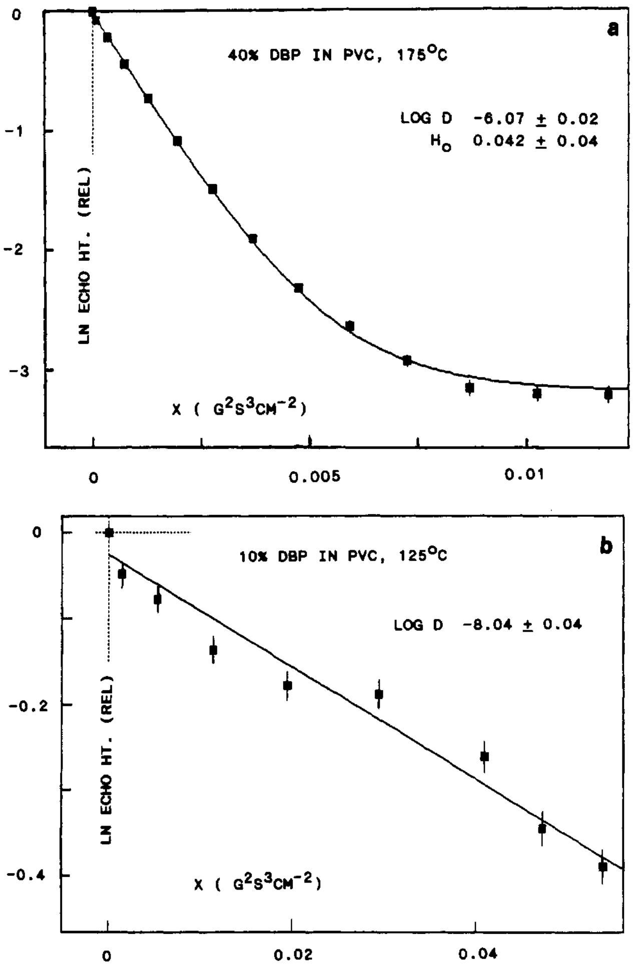

Figure 1. Diffusional echo attenuation (log echo height vs gradient parameter; see text) in DBP–PVC. At 40 wt % plasticizer and 175 °C (a), the PVC echo is visible as an asymptote; at 10 wt % and 125 °C (b), only the DBP echo is observed. D is deduced from the slope of the DBP echo attenuation.

The molecule was then described in terms of a triaxial right ellipsoid with semiaxes $r_1 \geq r_2 \geq r_3$, semiquantitatively fitted to the model. Corresponding aspect ratios may be defined as $a_2 = r_2/r_1$ and $a_3 = r_3/r_1$. With the requirement that the volume of this ellipsoid be equal to that of the equivalent sphere, it is possible to derive a frontal diameter d_{23}:

$$d_{23} = (6M/N\pi\rho a_2 a_3)^{1/3}(a_2 a_3)^{1/2} \tag{3}$$

The quantity d_{23} is intended as an estimate of the mean diameter of the molecule viewed at right angles to its longest axis. It is therefore approximately proportional to the lateral displacement of host molecules or segments required in a diffusive passage provided the molecule moves parallelly to its longest dimension.

In this approach all information about molecular anisometry resides in the ratios a_2 and a_3; these were estimated from measurements on the models. Initially, molecules were modeled in what was regarded as a neutrally relaxed conformation but with the main chain devoid of bends. Since our diffusion data suggested that d_{23} so derived might overestimate the cross section effective in retarding diffusion, the modeling was repeated with all flexible side

Table II
Plasticizer Molecular Dimensions[a]

plasticizer[b]	d, ±0.2 Å	d_{23}, ±0.3 Å	d_{23}', ±0.3 Å	d_{23}^*, ±0.2 Å
DMP	10.8	6.86	6.86	6.86
DBP	9.44	7.25	7.25	7.25
DOP	10.8	8.51	7.48	7.48
DTDP	12.1	9.05	8.05	8.05
DUP	10.6	6.92	6.92	6.92
DOA	8.03	6.67	6.44	6.44
S97	10.7	6.04	6.04	6.04
DOS	11.4	6.56	6.56	6.56
DBS	10.9	6.26	6.26	6.26
S160	9.60	7.12	7.12	6.78
S278	10.9	8.46	7.85	7.45
S141	10.2	8.20	7.86	6.87
S148	10.5	7.12	7.12	6.55
TCP	10.0	8.25	8.25	8.25

[a] See text for explanation of dimensions and methods. [b] See Table I for identification of plasticizers.

groups folded back against the main chain. Distortions of this nature are likely to be energetically unfavorable but might still need to occur to allow translational motion through a viscous or topologically restrictive medium;[31,32] for molecules capable of significant articulation, most diffusional progress in resistive media is likely to be made in streamlined configurations. The diameter derived on this basis will be referred to as d_{23}'; it represents a reduction of d_{23} for some of the plasticizers, leaving others unchanged.

A further, final effort along these lines was made in recognition of the possibility that translational motion may be most severely retarded by temporary local bottlenecks[31] in the host medium. The transverse diameter derived on this basis is called d_{23}^* and represents the mean diameter of the smallest two-dimensional opening, of adjustable shape, through which the molecule can be made to pass. (Of the three measures it is the only one that remains by definition identical within a homologous series of molecules differing only in length, e.g., the *n*-paraffins or the *n*-alkyl phthalates.) It may be relatively directly estimated by inspection of the models themselves; alternately, ellipsoidal stylization in the absence of side-group lateral extent represents a good approximation of this measure. The values used represent an average of the results of the two methods. Again, only for some of the plasticizers does d_{23}^* represent a further reduction in the effective transverse diameter. Table II lists all three lateral diameter estimates together with uncertainties in their determination.

A more liberal interpretation of d_{23}' and d_{23}^* is likely to be a better description of the molecular configurations encountered during diffusional steps than the strictly geometric construction offered above. Any improvement of the correlation of diffusion rates with these measures of transverse dimension over one based on d_{23}, rather than implying unreasonable and energetically unlikely distortions of the diffusing molecules, might instead merely suggest a mutual dynamic accommodation between diffusant and host local environment.[18,19] In this view the flexible side groups would need to be considered neither absent nor fully folded back but would simply not contribute to an effective cross section because their flexibility, in conjuction with that of nearby host segments, would enable them to evade host constraints to longitudinal motion. Of course, this interpretation preserves and, in fact, reinforces the possibility of local diffusional anisotropy based on diffusant molecular anisometry.

It is for reasons connected with this view that numerical molecular configurational modeling was not further pursued in this work. Current software provides excellent results for molecules in a (Θ) solvent of small molecules and in the presence of rigid constraints. The first case roughly corresponds to our CCl_4 solutions, in which configurational, e.g., shape-dependent, effects will be seen to be absent, obviating the need for modeling to provide an explanation; the second case has no parallel in this work. On the other hand, the case of interest here, urgently requiring realistic modeling, i.e., dynamic interactions with flexible constraints,[18] appears greatly to overtax the capabilities of molecular modeling software and available computational capacity at the present state of that art.

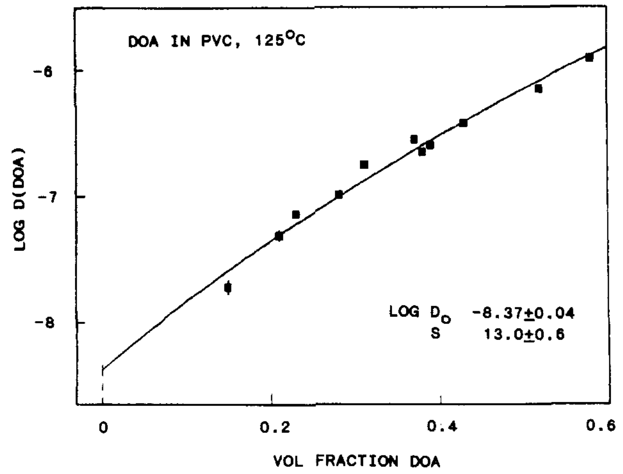

Figure 2. Concentration (volume fraction) dependence of D at 125 °C in the DOA–PVC system. The line shows a two-parameter fit of eq 4 to the data; the ordinate intercept represents log D_0.

IV. Results and Discussion

A. Concentration Dependence of *D* in PVC. The dependence of plasticizer self-diffusion at 125 °C on concentration in PVC is shown for one of the plasticizers in Figure 2, together with the two-parameter fit of the Fujita–Doolittle equation.[33] This free-volume equation may be written as

$$\log D(v_p) = \log D(0) + \frac{1}{2.303}\frac{B_d s v_p}{(1 + s f_r v_p)} \tag{4}$$

where

$$s = (f_p - f_r)/f_r^2$$

with v_p representing the volume fraction of the plasticizer and f denoting the fractional free volume of the rubbery polymer (r) or the plasticizer (p). The large-penetrant free-volume theory of Vrentas and Duda,[34] in several respects superior to eq 4, could not be used here because several of the free-volume parameters that it requires were not available for the plasticizers. The two parameters in eq 4 adjusted to fit each set of data were the trace diffusivity at the given temperature, $D_0 \equiv D(v_p{=}0)$, and the plasticizer fractional free volume f_p. In the nonlinear least-squares fit, f_r for PVC was taken from the literature;[35] at 125.5 °C, its value was 0.0422. Both fitted parameters in PVC solutions at 125 °C are listed in Table III; it will be noted that because of the relatively distant extrapolation to infinite dilution the uncertainties in log D_0(PVC) substantially exceed those in the individual diffusion measurements, which typically were of magnitude $\Delta(\log D) = 0.02$. Table III also lists the diffusivities of the neat plasticizers at 125 °C.

It should be noted that f_p(PVC, 125 °C), while differing significantly among the plasticizers, seems only vaguely

Table III
Plasticizer Diffusion Constants[a]

plasticizer[b]	log D_0(PVC, 125 °C)	f_p(PVC, 125 °C),[c] ±0.002	log D(neat, 125 °C), ±0.02	log D_0(CCl$_4$, 30 °C), ±0.02
DMP	−8.06 ± 0.1	0.063	−5.04	−5.03 ± 0.03
DBP	−8.61 ± 0.08	0.068	−5.20	−5.146 [illegible] 0.01
DOP	−8.83 ± 0.1	0.065	−5.48	−5.256 ± 0.008
DTDP	−8.88 ± 0.1	0.057	−5.78	−5.33
DUP	−7.92 ± 0.05	0.054	−5.56	−5.32
DOA	−8.37 ± 0.1	0.065	−5.23	−5.24
S97	−7.82 ± 0.05	0.056	−5.20	−5.24
DOS	−8.26 ± 0.1	0.057	−5.35	−5.29
DBS	−7.50 ± 0.05	0.051	−5.08	−5.20
S160	−8.46 ± 0.05	0.059	−5.40	−5.18
S278	−8.20 ± 0.1	0.049	−5.85	−5.28
S141	−7.68 ± 0.1	0.052	−5.29	−5.21
S148	−7.91 ± 0.08	0.055	−5.37	−5.23
TCP	−8.88 ± 0.1	0.066	−5.50	−5.22

[a] All diffusion rates D and D_0 are expressed in square centimeters per second. For definitions and procedures, see text. [b] See Table I for identification of plasticizers. [c] Plasticizer fractional free volume in PVC at 125 °C, using 0.0422 as the PVC fractional free volume f_r.

correlated with their molecular weight or any of the estimators (Table II) of molecular anisometry. This observation is in strong contrast to the case of *n*-paraffins in each of two rubbery polymers,[3] where the chain-end free volume is essentially constant and consequently f(paraffin) decreases systematically with increasing M. The free-volume theory in fact disavows any connection between D_0 and f(diffusant): the extra free volume contributed by (and located near) a diluent molecule cannot expedite the latter's own translational progress but does facilitate the movement of other nearby small molecules or host molecular segments. The geometric attribute of a molecule governing its free volume in solution may be something like a surface "roughness", which provides protected but accessible cavities for the temporary development of neighboring moieties. This property seems quite unrelated to an overall molecular anisometry and is much more difficult to quantify from molecular models irrespective of their complexity. No such attempt has been made here, and the direct interpretation of f_p is abandoned. The analysis of D_0 will occupy much of the remainder of this work.

Finally, Table III also lists the plasticizer diffusivities at infinite dilution at 30 °C in carbon tetrachloride. The extrapolations to obtain these values were minor in extent by comparison with the measured concentration range, although the latter itself was modest. Extrapolations were performed in two separate ways: as intercepts of log D plotted as function of v_p (see eq 4) and, by allusion to diffusional friction in dilute polymer solutions, as intercepts of plots of $1/D$ vs concentration c. Straight-line fits to both plots were adequate and produced extrapolations in agreement within the uncertainties. The slopes of these lines were sufficiently similar among plasticizers by comparison with their uncertainties to preclude a useful tabulation of f_p(CCl$_4$, 30 °C).

B. Temperature Dependence of D in PVC. Plasticizer diffusion in all our PVC-based systems were measured at five temperatures between 75 and 175 °C whenever practicable. At plasticizer concentrations below 20 wt % measurements at temperatures of 75 °C and occasionally 100 °C were prevented by the increasingly rapid T_2 relaxation and the consequent low echo signal-to-noise ratio. Measurements at 175 °C were performed last, but results were rejected if evidence of sample degradation was visible. Neither of these problems occurred at 125 °C, resulting in our choice of this temperature for the elucidation of anisotropy effects.

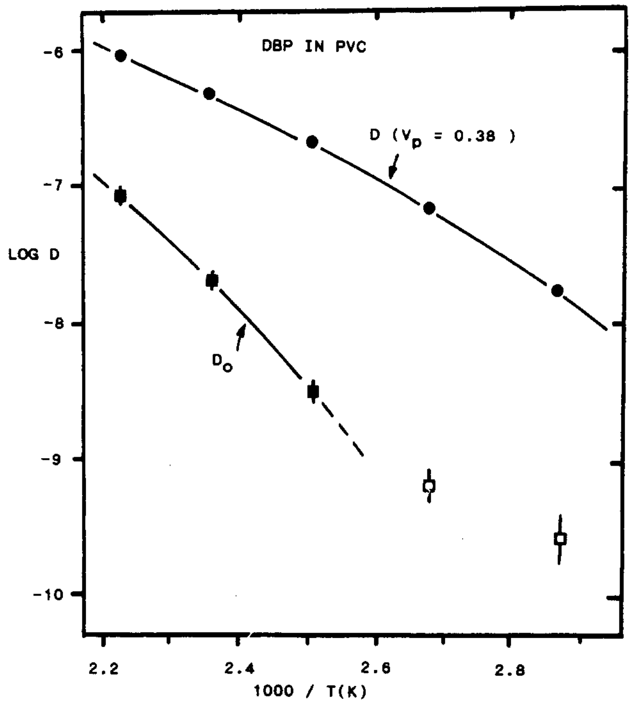

Figure 3. Temperature dependence of DBP diffusion in PVC, at 38 vol % DBP (top) and extrapolated to infinite dilution (bottom). Lines show fits of eq 5 at each concentration; parameters adjusted in each case were $D_0(T_g)$ and T_g; standard values of c_{1g} and c_{2g} were used in both cases. Open symbols denote extrapolations not included in the fit; see text.

At finite plasticizer concentrations the temperature dependence of D_p proved to be consistent with the Williams–Landel–Ferry (WLF) expression[36] in its diffusional form

$$\log D(T) = \log D(T_g) + \frac{1}{2.303} \frac{c_{1g}(T - T_g)}{c_{2g} + T - T_g} \qquad (5)$$

Equation 5 was found to correlate each set of data provided two parameters ($D(T_g)$ and either c_{1g} or c_{2g}) were free to adjust optimally. In the fits, the glass transition temperatures T_g for the solutions were postulated to be depressed below that for pure PVC ($T_g \cong 82$ °C[35]) in the manner described by standard free-volume theory.[37] With T_g of the neat plasticizers assumed to be less than 100 K, the fitted c_{1g} or c_{2g} took on values differing by less than 25% from their standard values of 40 and 52 K, respectively. As is usual in applying eq 5, the fits displayed pronounced tradeoffs between parameters; for example, an assumed increase in T_g left any fit essentially unaltered except for a compensating increase in c_{1g}. An exception to this picture was the DOA–PVC system, which was at all concentrations examined more nearly consistent with a simple Arrhenius temperature dependence than with the WLF form. The significance of this exception is not well understood.

Figure 3 (top) shows a typical temperature dependence with its WLF fit. To examine the validity of our Fujita–Doolittle extrapolations to infinite dilution, an equivalent WLF fit was attempted for the derived trace diffusivities, also illustrated in Figure 3. Keeping c_{1g} and c_{2g} the same between finite and trace concentrations, the two-parameter fit (adjusting log $D_0(T_g)$ and T_g)reproduced the known glass transition temperature of neat PVC (approximately 82 °C) provided the extrapolations for 100 and 75 °C were

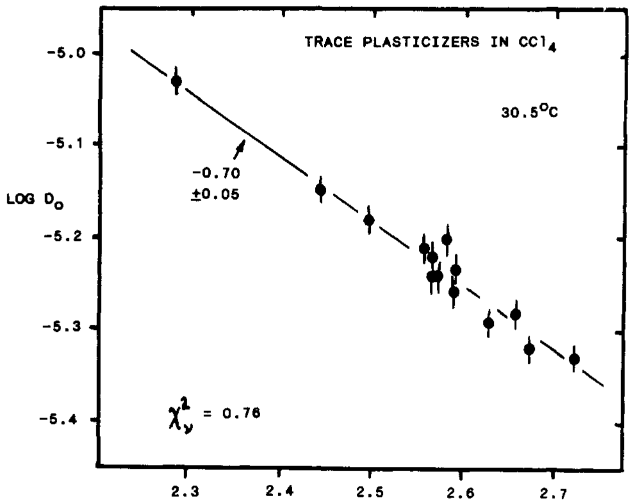

Figure 4. Molecular weight dependence of trace plasticizer diffusion in tetrachloromethane at 30.5 °C. $D_0(CCl_4)$ (see Table III) obeys a power law (line) with a slope of -0.70 ± 0.05.

omitted. This exclusion is well justified for two reasons. At the lowest temperature the Fujita–Doolittle equation may become invalid for low concentrations in PVC since these solutions are glassy; any extrapolation from entirely within the rubber regime is thus systematically in error. Moreover, the WLF expression[36] is not considered reliable until the temperature substantially exceeds T_g; in PVC solutions it should not be applied below 125 °C.

Diffusional activation energies in our systems, extracted from the data centered on 125 °C, were found to be in the range of 12–30 kcal/mol, with the higher values occurring at low plasticizer content, particularly the extrapolations to zero concentration. This trend would be expected on the basis of classical free-volume (WLF) theory, which postulates an accelerating increase in activation energy as the glass transition is isothermally approached at decreasing plasticizer content. From our data it is not clear whether any part of the observed increase is attributable[18,19] to the increasing topological constraint by host molecules in the absence of other nearby plasticizer molecules. Our observed activation energies are entirely within the range reported for dialkyl phthalates in PVC at similar temperatures and concentrations,[18] but differences among them were too small to be meaningfully correlated with molecular size or anisometry.

C. Effects of Anisometry on Plasticizer Trace Diffusion. Before we address the complex subject of plasticizer diffusion in a polymer host, it is desirable to ensure that structural or kinetic attributes of the plasticizer molecules have no significant effect on their trace diffusion rates so long as they are dissolved in a liquid consisting of small molecules. Figure 4 shows plasticizer trace diffusivities in CCl_4 plotted as a function of their molecular weight (see Tables I and III). It is seen that the data are consistent with a simple power law (eq 1). The M-exponent is found to be -0.70 ± 0.05, identical with that reported[38] for trace n-paraffins in a similar M-range dissolved in C_6F_6. In solutions of large polymer molecules in good solvents, qualitatively analogous to these cases, an M-exponent near -0.6 is theoretically expected[39] and usually observed.[4,40,41]

As indicated by the success of the χ^2-criterion of goodness of fit, no additional explanation for the differences among $D_0(CCl_4)$ is needed or, in fact, permitted on statistical grounds. Given the similarities among the densities of the neat plasticizers (Table I), a plot of log D_0 vs log d^3 (a measure of molecular volume; see Table II) would

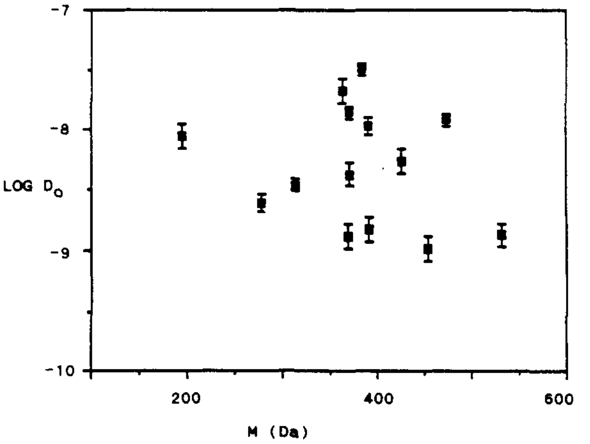

Figure 5. Molecular weight dependence of trace plasticizer diffusion in PVC at 125.5 °C; see Tables I and III. Correlation is not significant.

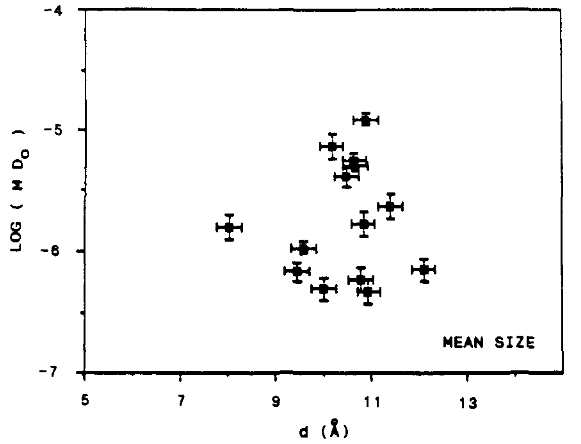

Figure 6. Molecular size dependence of D_0(PVC, 125.5 °C) corrected for an assumed Rouse-like intrinsic friction coefficient. Ordinates represent MD_0; the abscissa is d (see Tables I–III). Correlation is insignificant.

demand identical interpretation. It should be pointed out that the analogy between this case and the diffusion of macromolecules in dilute solutions is flawed in several respects. At constant M, D_0 is higher the greater the number of arms in, e.g., a star-branched molecule, although the differences are relatively small (see, for example, refs 40 and 41 and references therein). In the present case the architectural differences are less profound than those among stars of different arm number; moreover, the issues of interpenetration and draining of the solvent within the coiled polymer molecule cannot arise here.

The trace diffusion of the plasticizers in PVC behaves quite differently. Figure 5 shows the molecular weight dependence of log D_0(PVC). It seems clear that the diffusion rate (Table III) is not related to M in any simple way; the same may be said of its dependence on molecular volume. No substantial improvement in the correlation is attained by accounting for differences in M on the basis of a constant monomeric friction coefficient (see the discussion following eq 1). While MD_0 was found to be constant for the n-paraffin series dissolved in each of two rubbery entangled polymer melts, this is not the case with the present plasticizers in PVC. Figure 6 displays log MD_0 as function of molecular mean diameter d (see Table II). The negative average slope barely detectable in Figure 5 is now removed, leaving only scatter without a discernible general trend.

A significant correlation emerges when MD_0 is plotted as function of various measures of the frontal diameter of

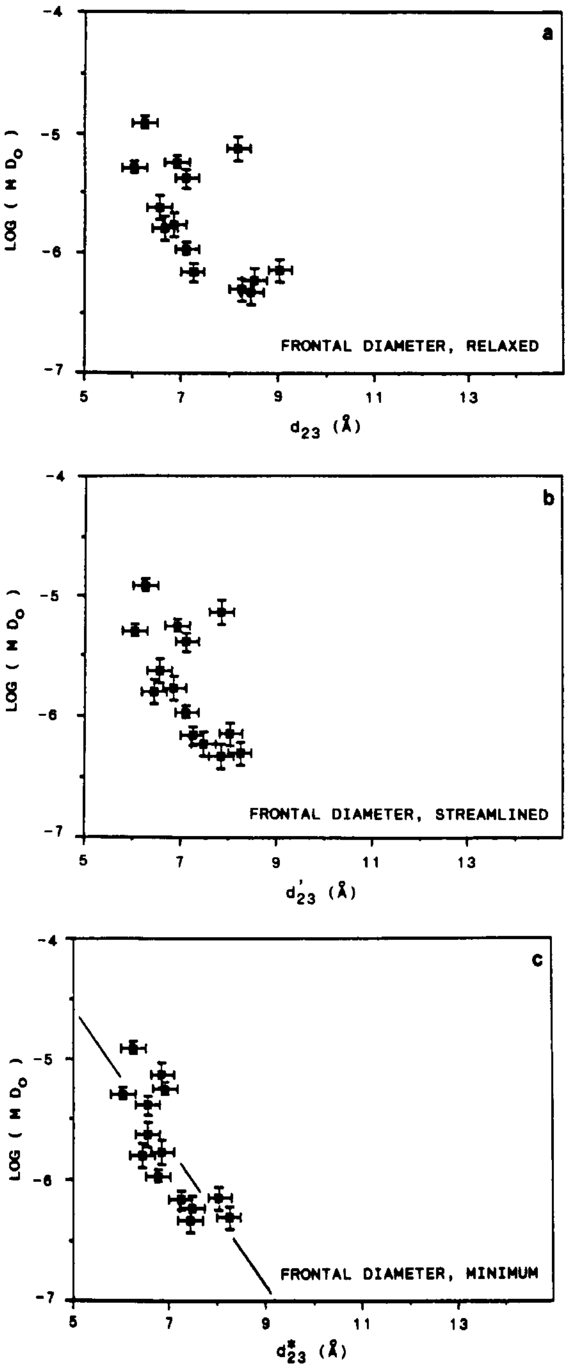

Figure 7. Dependence of MD_0(PVC, 125.5 °C) on three estimates of transverse diameter of the plasticizer molecules (see Tables I–III). Abscissa values represent d_{23} (a), d_{23}' (b), and d_{23}^* (c); ordinate values are the same in each plot. Correlation improves in the order a to b to c; line in c provides an acceptable fit to the data.

the plasticizer molecules, as displayed in Figure 7. The abscissa quantities are d_{23}, d_{23}', and d_{23}^* (see Table II) for parts a–c of Figure 7, respectively. The correlation greatly improves as increasing configurational adaptability to the host is invoked. In fact, the correlation shown in Figure 7c is satisfactory without the need for additional variables: given the limited precision of ordinate as well as abscissa values (see above), a straight-line fit to the data passes the χ^2 test. The slope of the fitted line corresponds to a decrease in D_0 by a factor of approximately 3 per extra angstrom of streamlined frontal diameter; this rate is in semiquantitative agreement with the average rate of decrease of D_0 with mean molecular diameter, which was observed[11] for somewhat smaller molecules in glassy PVC and PMMA hosts and for *n*-alkyl phthalates in rubbery PVC.[18]

The success of this correlation strongly suggests that the host chains of entangled PVC melt constitute an environment unlikely to yield over distances approaching the full dimension of a plasticizer molecule. Thus most diffusional center-of-mass displacements of isolated plasticizer molecules take place along the molecular long axes and in streamlined configurations, although the host environment is probably able to accommodate the passage of flexible plasticizer side groups through compensatory fluctuations. This conclusion is in agreement with qualitative inferences of other recent diffusion studies of the PVC–plasticizer system[18,19] but is somewhat at variance with findings in similar polymers below the glass transition:[11] there the effective molecule dimension that correlated D_0 of various smaller molecules was found to be intermediate between two measures referred to here as d and d_{23}. It is not clear whether this difference arises as a result in the earlier study of the glassy host or of the less highly articulatable smaller diffusants.

Another consequence of the success of the anisometry-based interpretation of Figure 7c is that possible additional contributions to the trace diffusivities are lost in the noise. It is, however, fair to ask whether such contributions might not be dominant and could be themselves provide equally satisfactory alternate explanations for the trace diffusivities. We attempted preliminary quantifications for two possible molecular attributes, electronegativity and backbone flexibility, and found that these did not result in successful correlations. For example, MD_0 was not monotonically related to the number of aromatic rings per molecule, nor was this product even approximately the same for all molecules having the same number of rings. Two possibilities arise: either these alternate effects are small in our systems by comparison with the anisometry effects or else they are large but differ only a little among these plasticizers. In view of the architectural variety of these molecules coupled with the large changes in D_0, the second of these possibilities seem remote. In either case, the variation in MD_0 is accounted for mainly by variations in anisometry, even if its absolute value should contain other significant contributions.

It should be pointed out that at finite concentrations the self-diffusion coefficients measured by methods such as PGSE differ in principle[30] from the binary mutual diffusion coefficients required to predict mass transport, although one may be inferred from the other by one of several model-dependent relationships based on, e.g., free-volume theory.[34] In the case of strongly interacting systems such as plasticizers + PVC the expected solution nonidealities will further complicate these relationships; thus, caution is indicated in the application of the present results to problems involving sorption, etc. However, mutual and self-diffusion rates are identical at the extremes of the concentration range, e.g., in the limit of trace plasticizer concentration.

D. Diffusion of Neat Plasticizers. The reason for the attractiveness of trace diffusivity to study the behavior of different diffusants is the removal of an irrelevant experimental variable through the provision of an identical host material. Diffusant interactions prevent this desirable state of affairs at finite concentrations and, as an extreme instance, in the neat diffusant liquid. Nevertheless, useful semiquantitative interpretations are possible in these cases. Figure 8 shows D for the plasticizers at 125.5 °C as a function of M. This temperature was high above the melting point and/or glass transition of any

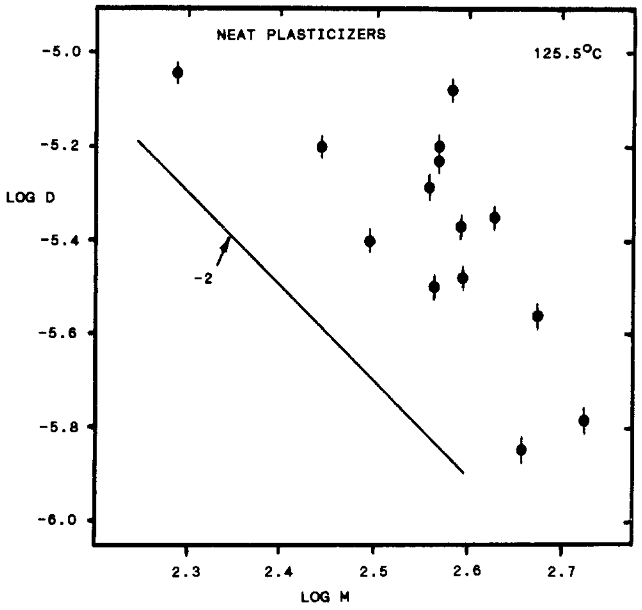

Figure 8. Molecular weight dependence of diffusion in neat plasticizer liquids at 125.5 °C. Data and behavior in other systems suggest an M^{-2} dependence, superimposed here on molecular shape effects. Correlation in a plot of log M^2D vs d_{23}* (not shown) is marginally acceptable.

specimen (all plasticizers were inviscid liquids at room temperature), so that differential proximity to a phase transition could not affect the results.

A general downward trend in $D(M)$ is clearly observable in Figure 8. By comparison, D in neat n-paraffins and polyethylene at elevated temperatures[29,38] follows a power law of the form of eq 1 with an exponent near −2. This exponent persists into the entangled regime ($M > 3000$), where it is explained by the applicable reptation theory;[1] for $M < 600$ the M^{-2} behavior is likely to be a fortuitous combination of an intrinsic Rouse proportionality of D to M^{-1} and the effect of the decreasing chain-end free volume with increasing M. The latter does not result in a simple power law,[28] but the combination often closely resembles eq 1 with $a = -2$.

Accordingly, an attempt to minimize (to very low order) the effects of differences in intermolecular friction was made by forming the product M^2D and proceeding as in the case of D_0. No fully acceptable correlation of log M^2D with measures of molecular anisometry was found. However, the least unsatisfactory attempt was visually quite pleasing; it used d_{23}* as the abscissa variable and resulted in a reduced χ^2 of 2.8 with respect to the best fit straight line. (Its slope was equal within uncertainty to that in Figure 7c.) We suspect that the remaining uncompensated host differences affecting intermolecular friction may well be entirely responsible for the marginal quality of this correlation.

A less heuristic view of diffusion in liquids regards the latter as trace diffusants dissolved in identical host materials.[38,42] To obtain molecular shape effects, D must be corrected for shape-unrelated differences in intermolecular friction generated by the diffusant and by the host. The first correction calls for multiplying D by M, as was done for D_0(PVC). The second, host, friction effect is mainly related to free volume. According to Cohen and Turnbull[43]

$$D \propto e^{-B/f}, \quad B \cong B_d \cong 1 \qquad (6)$$

In the present case the system free-volume fraction is identified as f_p, which may be approximated by the value obtained at the same temperature (125.5 °C) in PVC at infinite dilution. The host correction thus consists of a multiplication by the reciprocal of eq 6; the quantity to be correlated with measures of molecular anisometry is thus log $[DM \exp(1/f_p)]$. This attempt, however, failed because of the extreme sensitivity of eq 6 to f_p with its large relative uncertainty (Table III). Also, the assumption of a constancy among plasticizers of free-volume-unrelated host friction, implicit in this correction, may be unrealistic.

It seems clear that the systematics of D in the neat plasticizer melts resembles trace diffusion in PVC much more closely than it does trace diffusion in CCl_4. In particular, the neighboring complex, flexible and interlocking plasticizer molecules seem to provide mechanical and hydrodynamic constraints similar to those generated by polymer chain segments. Trace diffusion of larger molecules, either bulky and rigid or flexible, in a solvent consisting of small molecules has been shown[44,45] to be associated with a diffusant effective mass in excess of its molecular mass, that is, with cooperative displacements of several nearby solvent molecules. It may be speculated that extensive cooperative evasion involving many molecules, unlikely in complex hosts, may provide the hydrodynamic screening required to obscure the details of the diffusants' shape to distant points in the matrix and so greatly reduce its diffusional anisotropy.

V. Summary and Conclusion

We have measured the diffusion of plasticizers in the neat liquid as well as dissolved in PVC and in CCl_4, using the pulsed-gradient spin-echo method. Trace diffusivities were obtained by extrapolation to infinite dilution. Simple molecular modeling provided the basis for an assessment of low-order anisometry of the molecules in several configurations. The following points will summarize the main findings and conclusions of this study:

(1) Diffusion of the plasticizers in PVC adheres to the classical free-volume theory, i.e., the Fujita–Doolittle concentration dependence and (except for DOA–PVC) the WLF temperature dependence; the free-volume parameters extracted from the data have physically reasonable values. Traces diffusivities distantly extrapolated via the Fujita–Doolittle equation pass several tests of validity.

(2) Trace diffusivities of plasticizers in CCl_4 obey a molecular weight power law with an exponent of −0.70 ± 0.05 and do not depend on molecular anisometry. These findings parallel those in the study[38] of n-paraffin diffusion in C_6F_6 and resemble typical results for trace diffusion of polymer molecules in light solvents.

(3) Plasticizer trace diffusion rates in PVC depend weakly on molecular weight and much more strongly on molecular anisometry; no other significant contribution could be deduced. There is strong circumstantial evidence that plasticizers in PVC cover most of the diffusion distance in at least partially streamlined configurations, in a direction locally perpendicular to their smallest diameter, and hence parallel to their longest dimension. Passage of plasticizer side groups is probably facilitated through dynamic compliance of the host chains. At 125 °C, increasing the minimal frontal molecular diameter by 1 Å results in a decrease of trace diffusivity by a factor of 3.

(4) Plasticizer diffusion in their own neat melt depends on molecular weight more strongly than does trace diffusion in PVC but appears to correlate with molecular anisometry in roughly the same way in both cases. A quantitative extraction of molecular shape effects requires corrections for other contributions to intermolecular

friction of each plasticizer, in its role as host and as diffusant.

(5) These results suggest that concentrated complex nonpolymeric host molecules and packed polymer chain segments offer similar topological and hydrodynamic constraints to the translation of embedded midsized molecules. In both cases the interlocking among host moieties may prevent extensive cooperative displacements and would force translational diffusion to rely on local mechanisms that strongly favor the minimal host adjustments resulting from anisotropic, streamline motion. Such an effect is only distantly related to the reptative motion of polymer molecules entangled with a polymeric melt or network. In particular, plasticizer molecules are likely to progress as a unit, i.e., as one or very few jumping segments, unable to establish or propagate conformal fluctuations within a curved constraining tube as is characteristic of reptation.

(6) Our results at least qualitatively parallel and extend recent findings for plasticizers in rubbery PVC[18,19] and earlier results for smaller molecules[11] in glassy PVC, PMMA, and PS. In that study[11] diffusional anisotropy was less pronounced than the corresponding molecular anisometry, whereas the opposite is the case in the present work. The reasons for this difference are not clearly understood.

(7) The pulsed-gradient spin-echo NMR method is well suited for the extraction of information about the dependence of diffusivity on molecular architecture. In comparison to other methods in common use,[1] its advantages, particularly its lack of need for chemical labeling and for concentration gradients of the diffusing species, far outweigh its disadvantages for such studies, e.g., a somewhat smaller sensitivity in the detection of diffusants and a reduced ability to operate in a rigid host environment.

The present work is part of an ongoing effort of this laboratory to characterize the effects of molecular architecture on diffusion in polymeric hosts and in dilute solutions. Its experimental variables include number and location of branches, side chain vs main chain molecular mass, and stiffness of the component chains, as well as total molecular weight, concentration, and temperature.

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