$$b_9 = 510609(4/9) - 2906956x + 7040042x^2 - 9114193(1/3)x^3 + 6605145x^4 - 2588428x^5 + 484298x^6 - 32128x^7 + 469x^8$$

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A General Free Volume Based Theory for the Diffusion of Large Molecules in Amorphous Polymers above T_g. 2. Molecular Shape Dependence

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ABSTRACT: The free volume based theory of Mauritz and Storey for the diffusion of extraordinarily large and elongated molecules in rubbery polymers has been generalized in this work to include large molecules of any shape, regular or irregular. As in the original theory, the diffusant molecular hopping displacement is but a fraction of the molecular dimension along a given direction of motion. The accounting for an increase in entropy accompanying the liberation of one penetrant translational degree of freedom after adjacent hole creation, by random thermal fluctuation, has also been retained from our original theory. The basic improvement to the original restrictive model was affected by considering the elementary penetrant diffusive hopping vector to be the vector sum of component displacements along the instantaneous directions of the three principal axes passing through the molecular center of mass. The theory predicts that, for a fixed penetrant molecular volume, compacted structures migrate slower than corresponding extended structures, in qualitative accord with available experimental evidence. Present model shortcomings and suggestions for future improvement are outlined.

Introduction

Mauritz et al. have recently introduced a modified free volume based theory for the above-T_g diffusion of inordinately large molecules in amorphous polymers.[1] In its initial form, the theory was biased toward penetrant molecules having large aspect ratios, which would reasonably be expected to execute hopping primarily along the direction of their long dimensions. Model predictions were roughly compared with available experimental diffusion data for di-*n*-octyl and di-*n*-decyl phthalate plasticizers in PVC. This initial evaluation, although limited in scope, did suggest that a better than order-of-magnitude agreement between experimental and theoretical diffusion coefficients is possible. Assumptions critical to the development of the model were carefully rationalized in the light of suggestions offered by a considerable body of experimental studies of the diffusion of large molecules of various shapes in rubbery polymers. The reader is referred to an earlier paper for a detailed discussion and numerous cited references, which will not be repeated here in the interest of space.[1]

The general equation for the diffusion coefficient for a large and rather elongated molecule of length l, steric volume V_s, and molecular weight M, as derived in our earlier work,[1] is

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

where R is the universal gas constant, T the Kelvin temperature, and V_f the average free volume per polymer chain segment in the rubbery state at a given fixed temperature and concentration of diffusant. The simple linear equation of Fujita and Kishimoto[2] relating V_f to temperature and concentration is commonly employed but this will not be of direct concern in the following derivation. The familiar multiple of 1/6 in the exponential prefactor is due to a reasonable assumption of noncorrelated consecutive penetrant jumps in three dimensions as a consequence of the continual and rapid realignment of the penetrant molecule that is surrounded by fluid polymer chain segments. The 1/2 in the exponent, which is not present in the corresponding equation in the conventional free volume theory,[3a] accounts for the liberation of one penetrant translational degree of freedom after adjacent hole creation by random thermal fluctuation. The quantity reflective of the diffusion of particularly large molecules is f, the fraction of the long dimension

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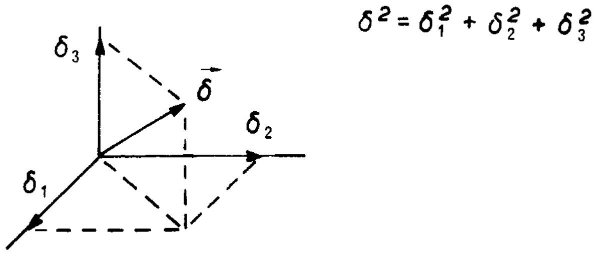

Figure 1. Penetrant molecular displacement vector $\vec{\delta}$ with orthogonal components (δ_i) along the three principal axes at a given instant.

that constitutes an average elementary hop. f, of course, is unknown and inaccessible by present theory.

Vrentas and Duda formulated a free volume based theory of polymer–solvent diffusion, which has been applied to the diffusion of large molecules in amorphous polymers.[3b] While this theory does consider a fundamental penetrant molecular jump that involves only a portion of the molecule, as in our theory, a serious limitation of its usage, from our more fundamental point of view, is the requirement of a large body of preexisting experimental data. For both pure polymer and pure solvent, and as a function of temperature, not only density and viscosity data but at least three values of the diffusivity itself as well as the appropriate Flory–Huggins polymer–solvent interaction parameter are required.

The parameter f was conveniently eliminated by defining an effective diffusion coefficient, $\bar{D}$, as an average of eq 1 over the range of f to account for penetrant local environmental heterogeneity in a general way. The resulting equation is

$$\bar{D} = \frac{l}{6}\left(\frac{V_f}{V_s}\right)^2\left(\frac{eRT}{M}\right)^{1/2} \tag{2}$$

providing $V_f/V_s \ll 1$. The latter condition is satisfied and, in fact, serves as our definition of a "large" molecule. If V_f/V_s is not extreme valued in this way, a more complex equation must be used.[1] The factor of e in the radical of eq 2 is due to the term 1/2 in the exponent of eq 1. The inclusion of this factor imparts a greater diffusivity and entropy to the system as would exist within the framework of the conventional Cohen–Turnbull theory of diffusion.

In this report, we wish to extend the versatility of our model by allowing for the possibility of penetrant molecular hopping in more than one direction at a given instantaneous location, as would be envisioned for molecules having low aspect ratios. It is well-established that, for isomeric diffusants, the compact structures will migrate slower than the extended ones.[1,4]

Shape-Dependent Diffusion of Large Penetrant Molecules

Consider the instantaneous directions of the three mutually orthogonal principal axes for an arbitrary penetrant molecule, as depicted in Figure 1. These axes, all of which intersect at the center of mass, undergo rapid and continuous orientation because of the high mobility of polymer chain segments adjacent to the penetrant molecule. As before, consider an ensemble-averaged elementary molecular displacement of magnitude δ that occurs within a characteristic time τ. At a given instant in time at a given penetrant molecular position, the vector $\vec{\delta}$ can be broken down into component displacements, δ_i, i = 1–3, for motion purely along each of the principal axes so that $\delta^2 = \delta_1^2 + \delta_2^2 + \delta_3^2$. Then we can write

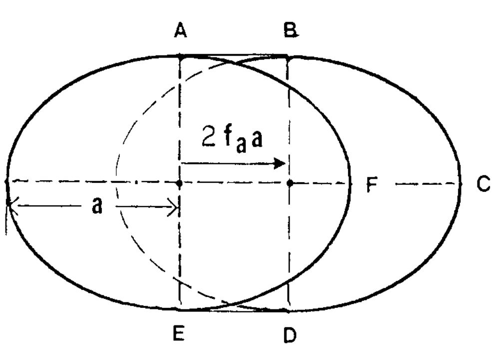

Figure 2. The minimum free volume (V^*) that must be created so that an ellipsoid of semiaxes a, b, and c can be displaced along the a axis by an amount $2f_aa$ and has a projection onto the a–b plane bounded by the piecewise closed curve ABCDEFA. V^* is also equal to the volume of the elliptical cylinder whose projection onto the a–b plane is bounded by the rectangle ABDE.

$$D = \frac{\delta^2}{6\tau} = \frac{1}{3}\left(\frac{\delta_1^{\,2}}{2\tau} + \frac{\delta_2^{\,2}}{2\tau} + \frac{\delta_3^{\,2}}{2\tau}\right) \tag{3}$$

The three terms within the parentheses are in fact the one-dimensional diffusion coefficients, D_1, D_2, and D_3, for motion purely along the principal axes, that is

$$D = (D_1 + D_2 + D_3)/3 \tag{4}$$

Thus far, we have assumed that $D_2 = D_3 = 0$. This restriction will now be lifted.

Consider the following basic equation, from part 1 of this work,[1] that is general and not dependent on the subsequent assumption of a longitudinal mode of diffusion specifically for elongated molecules:

$$D = (\delta/6)(RT/M)^{1/2}\exp((1/2) - V^*/V_f) \tag{5}$$

where V^* is the free volume required for a molecular displacement of δ. The one-dimensional counterpart of this equation is

$$D_1 = (\delta_1/2)(RT/M)^{1/2}\exp((1/2) - V^*_1/V_f) \tag{6}$$

and similarly for the other two orthogonal directions. We will begin by analyzing hypothetical diffusing particles having common shapes of high symmetry. The general problem consists of finding V^*_1 for a given δ_1 that is equal to a fraction, f_1, of the particle's dimension along this principal axis. Having accomplished this for the 2 and 3 directions, as well, the three-dimensional diffusion coefficient can be assembled by using eq 4.

Ellipsoids, ranging between being extremely prolate and extremely oblate, can represent a broad spectrum of rough molecular shapes. If a, b, and c are the lengths of the ellipsoid semiaxes, then $V_s = (4/3)\pi abc$. If $\delta_a = f_a(2a)$, then the quantity of free volume that must be created so that the ellipsoid can advance by this amount is about $V^*_a = (\pi bc)(f_a 2a) = (3/2)f_a V_s$, as depicted in Figure 2. In similar fashion, it can be shown that for such a displacement along either elliptical axis of an elliptical disk, $V^*_i = (4/\pi)f_i V_s$, where $V_s = \pi abh$, a and b being the elliptical axial semilengths and h being the thickness of the disk. For the axial displacement of a cylinder having any cross-sectional shape, $V^*_l = flV_s$, where $V_s = Al$, A being the cross-sectional area at right angles to the height direction, the height being l.

In general, one can write the requisite free volume for displacement along a principal axis of length l_i as a frac-

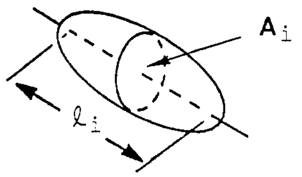

Figure 3. Maximum cross-sectional area (A_i) presented by a penetrant molecule (in this case, prolate spheroidal) in a plane that is perpendicular to the principal axis of length l_i.

tion, f_i, of a shape-dependent multiple, Q_i, of the total molecular volume as

$$V^*_i = Q_i f_i V_s \tag{7}$$

Then, eq 6 becomes

$$D_i = (1/2) f_i l_i (RT/M)^{1/2} \exp((1/2) - Q_i f_i V_s/V_f) \tag{8}$$

where $f_1 \neq f_2 \neq f_3$, in general. As before,[1] the condition $\partial D_i/\partial f_i = 0$ can be applied to eq 8 to yield the maximal quantities

$$f_{i,\max} = V_f/(Q_i V_s) \tag{9}$$

$$D_{i,\max} = \frac{1}{2}\frac{l_i V_f}{Q_i V_s}\left(\frac{RT}{eM}\right)^{1/2} \tag{10}$$

By use of eq 9 and 10, eq 8 can be written compactly in the following reduced form:

$$D_{i,\mathrm{red}} = e\mu_i \exp(-\mu_i) \tag{11}$$

where $D_{i,\mathrm{red}} = D_i/D_{i,\max}$ and $\mu_i = f_i/f_{i,\max}$.

The unknown quantities f_i, $i = 1$–3, can be eliminated as before by averaging the respective D_i over the range of jump distances from zero up to the corresponding l_i:

$$\begin{aligned} \bar{D}_i &= \int_0^1 D_i \, \mathrm{d}f_i \\ &= eD_{i,\max} \quad (f_{i,\max} \ll 1) \\ &= \frac{l_i}{2Q_i^2}\left(\frac{V_f}{V_s}\right)^2\left(\frac{eRT}{M}\right)^{1/2} \end{aligned} \tag{12}$$

The implications of these equations are better understood when they are transformed in the following way. Let A_i be the value of the *maximum cross-sectional area* presented by the penetrant molecule at right angles to the ith direction, as depicted in Figure 3. It is easily seen that the relationship $V_s/l_i = A_i/Q_i$ holds true. It should be stressed that this relationship applies to molecules of *any shape*, however irregular, and that for structures as large and complex as commercial plasticizers, the perimeter enclosing A_i is a piecewise contour of successive arcs of circles with van der Waals radii of constituent atoms. Let us now utilize this geometrical relationship to introduce A_i in eq 12 and then assemble the effective three-dimensional diffusion coefficient, $\bar{D}$, using eq 4:

$$\bar{D} = \frac{V_f^2}{6}\left(\frac{eRT}{M}\right)^{1/2}\sum_{i=1}^{3}\frac{1}{l_i A_i^2} \tag{13}$$

Equation 13, then, is the *general* form for the diffusion coefficient for a large molecule *of any shape* in a rubbery polymer.

For the theoretical condition of holding the factors T, one of the A_i, and two of the l_i constant, $\bar{D}$ gradually decreases with increasing M. It is not only reasonable to expect that the molecular mobility within such a homologous series will gradually decrease with increasing length along a given elongated dimension but, also, the experiments of Storey et al. on the diffusion of various di-n-alkyl phthalates in rubbery PVC establish this as fact for these important and applicable plasticized systems.[4] On the other hand, the inverse dependence of $\bar{D}$ on A_i^2 indicates a strong dependence of the translational mobility of penetrant molecules along the i direction on their characteristic dimensions transverse to this axis. Perhaps one might imagine that the number of fluid polymer chains that are required to be swept aside, so that the penetrant molecule can execute an elementary jump along its principal axis i, is proportional to the quantity A_i. Bear in mind when utilizing eq 13 to analyze diffusivity trends within a series of penetrant molecules that the parameters therein are interrelated. Particularly ubiquitous at this time is the dependence of the plasticizer efficiency parameter, k, on polymer–penetrant structures and interactions.

Results and Discussion

We will now illustrate the penetrant shape sensitivity of $\bar{D}$ by examining eq 13 as applied to the simple case of the hypothetical ellipsoid referred to earlier. For this particular geometry, the quantity $l_i A_i^2$ is $2\pi^2 ab^2c^2$, $2\pi^2 a^2bc^2$, and $2\pi^2 a^2b^2c$ along the principal axes of semilengths a, b, and c, respectively. Then, eq 13 becomes

$$\bar{D} = \frac{V_f^2(a+b+c)}{12\pi^2 a^2b^2c^2}\left(\frac{eRT}{M}\right)^{1/2} \tag{14}$$

For example, let a = 11 Å, b = 2.0 Å, and c = 3.5 Å and inquire as to the relative magnitudes of the contributions to $\bar{D}$ that are due to penetrant hopping along each of these axes. A simple calculation shows that the $D_i/(3\bar{D})$ are 67%, 12%, and 21% for the a, b, and c axes motions, respectively. It is interesting to note that while this "molecule" is somewhat elongated, a significant 33% of its overall diffusive hopping occurs in directions transverse to the long dimension.

Substitute $\pi^2a^2b^2c^2 = 9V_s^2/16$ in eq 14 to yield the following expression

$$\bar{D} = \frac{1}{3}\left(\frac{2V_f}{3V_s}\right)^2(a+b+c)\left(\frac{eRT}{M}\right)^{1/2} \tag{15}$$

and consider $\bar{D}$ as a function of a, b, and c under the constraint V_s = constant. Then, only two ellipsoidal dimensions are independent variables, say a and b, so that $\bar{D} = (\mathrm{const})F(a,b)$ where

$$F(a,b) = a + b + 3V_s/(4\pi ab) \tag{16}$$

The minimum of this function lies on a curve defined by a cut through the surface $F(a,b)$ by the plane defined by the condition $a = b$ at the point $a = b = c$. Therefore, within the framework of this model, and for the general class of ellipsoidal molecules, the *sphere* has the lowest diffusivity. This result is at least in qualitative harmony with the earlier cited experimental fact that for dialkyl phthalate isomers, the compacted (i.e., branched chain) structures migrate slower than do the extended (i.e., linear chain) ones.[4] The reader is also directed to ref 1, which contains a discussion of studies that unambiguously indicate that, for the same carbon number, linear hydrocarbons diffuse faster than their branched and cyclic counterparts in rubbery polymers. The minimum value for $\bar{D}$ corresponds to a sphere of radius $r_0 = [3V_s/(4\pi)]^{1/3}$ and is given by

$$\bar{D}_{\min} = \frac{V_f^2}{4\pi^2 r_0^5}\left(\frac{eRT}{M}\right)^{1/2} \tag{17}$$

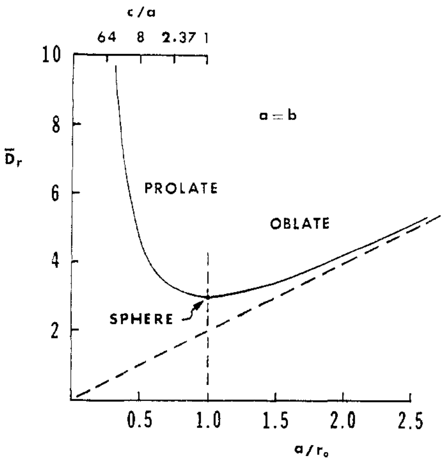

Figure 4. Theoretical reduced diffusion coefficient, $\bar{D}_r$, versus a/r_0 and aspect ratio c/a for spheroids of revolution about the c axis at constant volume $V_s = (4/3)\pi r_0^3$. The asymptotic dashed line has a slope of 2.00.

One should bear in mind that this formula applies to spheres for which $1.50V_s \gg V_f$ and not to small molecules for which the spherical approximation is commonly made.

Now consider the relative diffusivity of spheroids for which $a = b$ at constant volume as a function of their deviation from sphericity, which will be characterized by the unitless parameter a/r_0. Then, define a unitless relative diffusion coefficient in the following way:

$$\bar{D}_r = \frac{F(a,a)}{r_0} = \frac{3\bar{D}}{r_0}\left(\frac{3V_s}{2V_f}\right)^2\left(\frac{M}{eRT}\right)^{1/2} \tag{18}$$

The aspect ratio for the case of prolate spheroids ($a < r_0$) is $c/a = (a/r_0)^{-3}$. The $\bar{D}_r$ versus a/r_0 *master curve*, so defined, is shown in Figure 4. In excursion from the curve minimum, $\bar{D}_r$ increases more rapidly in proceeding toward prolate (elongated) shapes than it does in proceeding toward oblate (flattened) shapes from the $a/r_0 = 1$ point. This behavior is easily comprehended in terms of viewing the A_i's presented for these two shapes. Prolate spheroids have a major axis at right angles to which the A_i can become progressively smaller by simultaneously decreasing the magnitudes of both of the two orthogonal dimensions in the plane of A_i by the same amount as a/r_0 continually decreases. On the other hand, while an oblate figure becomes progressively thinner in but one dimension as a/r_0 increases from 1.00, it must also become broader in the remaining two dimensions in order to compensate for the constraint of constant volume.

While the master curve for such a given penetrant shape classification holds potential value in understanding diffusivity trends in this fashion, it should be recalled that the relationship between plasticizer efficiency (and therefore V_f) and molecular shape for a given constant V_s is presently unpredictable. While caution should therefore be exercised in arriving at conclusions, it is also true, however, that experimental k values do not appear to vary profoundly with molecular weight within the important family of the higher phthalate plasticizers. In addition, we note that k for the isomers dioctyl (2-ethylhexyl)phthalate[5] and di-n-octyl phthalate[1] is 323 K and 337 K, respectively.

One can derive similar equations for $\bar{D}$ for penetrants of other regular shapes of high symmetry. For example, the following equation applies to elliptical-based right cylinders of height h and elliptical semiaxes a and b:

$$\bar{D} = \frac{V_f^2}{6\pi^2(abh)^2}\left(\frac{eRT}{M}\right)^{1/2}\left[\frac{\pi^2}{8}(a+b) + h\right] \tag{19}$$

For this geometry, it can be shown in the same manner as above that for a given fixed volume V_s the minimum diffusion coefficient corresponds to a cylinder having a circular base of radius $2V_s^{1/3}/\pi$ and a height of $\pi V_s^{1/3}/4$. Note that this slowest diffusing shape is neither a flattened nor elongated but rather is a compacted cylinder.

Conclusions

First, let us review the significant concepts of the above-presented model that are either novel or are refinements over the conventional free volume theory of penetrant diffusion in rubbery polymers.

(a) A nonempirical, fundamental molecular, and generally applicable mathematical formalism, represented by eq 13, that can be applied to diffusant molecules that are uncommonly large compared to the size of a typical polymer chain segment and of any shape, whether of high symmetry or arbitrarily irregular, has been developed.

(b) The consideration and direct mathematical incorporation of a diffusant molecular hopping displacement that is but a fraction of the molecular dimension along a given direction of motion we believe to be a rather novel concept. This concept naturally arose from the visualization of the probable motions of large diffusants through a liquidlike medium, as suggested by earlier diffusion experiments involving simple model systems as discussed in detail in part 1 of this series.

(c) The term 1/2 in the exponent of eq 1, which in turn gives rise to the factor e in the radical of eq 2, is a novel addition to the free volume theory of diffusion. Physically, this modification accounts for an increase in entropy accompanying the liberation of one penetrant translational degree of freedom, after adjacent hole creation occurs by random thermal polymer density fluctuation. The physical consequence of this modification is to impart to the system entropies that are greater by $(1/2)R$ and diffusivities that are greater by a factor of $e^{1/2}$ than the corresponding entropies and diffusivities existing within the framework of the conventional Cohen–Turnbull theory of diffusion.

(d) To be sure, a significant concept of the proposed theory is the mathematical resolution of the average net penetrant hopping displacement into its orthogonal components along the three principal axes of inertia that pass through the penetrant center of mass. As a rather large nonspherical penetrant would necessarily possess hopping anisotropy, it is this particular treatment that renders the model molecular shape dependent.

This modified free volume theory predicts that for constant penetrant molecular volume, compacted structures migrate slower than corresponding extended structures. This result is at least in qualitative accord with available experimental diffusion evidence for simple systems, as discussed earlier.

In our previous report[1] we had outlined a number of planned future refinements of the primitive free volume based theory of the above-T_g diffusion of large molecules initiated therein. In this manuscript, one of those improvements, namely, the general mathematical formalism for the implicit incorporation of penetrant shapes that are either highly regular and symmetric or arbitrarily irregular, has been affected and shown to be physically reasonable against limited but relevant experimental knowledge in qualitative terms. Our ongoing efforts to impart significant model sophistication, and therefore versatility in its application, by determining "actual" complex penetrant shapes reflective of their minimum free energy conformations by utilizing powerful molecular mechanics software (CHEMLAB II) will be reported in a future paper. Special numerical algorithms will be developed and used to evaluate the A_i's, which, in essence, are created by the "shadows" of the total aggregate of van der Waals radii of penetrant constituent atoms on the planes perpendicular to the molecular principal axes. With these numbers, as well as the l_i, eq 13 will then be used directly to compute diffusion coefficients without the exercise of fitting regular symmetric shapes to a highly irregular structure.

It was earlier suggested, based perhaps on limited experimental results, that diffusion coefficient values predicted by this model in its earlier version may be somewhat high.[1] To be sure, a more exhaustive model evaluation against the experimental behavior of the coefficients of self-diffusion for a variety of large molecules at fixed concentrations in a number of polymers in the equilibrium rubbery state is required to assess the wisdom of incorporating an activation energy in the usual way. In any case, a formal activation energy can be easily inserted into the model accompanied by the usual remarks appropriate to the rationalization of this procedure.[6] It would seem that the simplest approach, at least from a mathematical standpoint, would be to assume that the energy required to create an adjacent hole, of volume $Q_i f_i V_s$, to allow for a penetrant molecular jump length of $f_i l_i$, is

$$\Delta E^*_i = Q_i f_i V_s E_v \tag{20}$$

where E_v is a "local" cohesive energy density that strictly has meaning on about the 50-Å level, considering the size of the penetrants of interest. Physically, E_v is the volume concentration of all pairwise, short-ranged, nonbonded, intersegmental interactions in the neighborhood of the hole before its appearance. Meares discussed this cohesive energy density approach some time ago.[7] The resulting mathematical modification of the theory simply involves making the following replacement in eq 13:

$$V_f \rightarrow \frac{V_f}{1 + [E_v/(RT)]V_f} \tag{21}$$

E_v might be crudely estimated as is commonly done by using solubility parameters.[8] A considerably more involved computational procedure would consist of a direct determination of polymer interchain energetics by using theoretical conformational analysis within an appropriate sample volume in which the free volume per chain segment is held at V_f. We are presently considering both approaches as well as using eq 13, as amended according to the substitution (21), in conjunction with experimental diffusion data to determine the magnitudes of E_v that are in fact required to bring theory in closer alignment with experiment.

One might adopt an alternate viewpoint that the appearance of a hole that would accommodate a penetrant molecular jump of $f_i l_i$ creates a surface of area a^*_i with an energy expense of σa^*_i. Strictly, σ should be a surface energy defined in the polymer chain environment adjacent to the penetrant, although the concept of "surface" at this level of molecular granularity is somewhat nebulous in itself. σ is assumed to be constant in the analysis of small-molecule diffusion through rubbery polymers and is taken as the macroscopic surface energy, or surface tension, of the rubbery polymer,[9] although Litt[10] has introduced a simple geometric adjustment that depends on the ratio of the hole diameter to the polymer chain segment diameter. In this case, however, a^*_i is not directly proportional to f_i and a more complex mathematical modification would result. We are presently evaluating these modifications for the direct incorporation of energetics.

Further theoretical refinements will include the formulation of a penetrant concentration averaged diffusivity to allow for a more meaningful comparison of theoretical D's with experimental values obtained from the *kinetics* of plasticizer uptake, as, for example, the values generated in our earlier studies.[4] Ultimately, polymer–penetrant interactions will be theoretically represented in a more direct fashion, rather than indirectly as is presently done through the use of the experimental plasticizer efficiency parameter, k. Other model improvements have been discussed in the earlier paper.[1]

To be sure, we must consider the model in its present form to be at the prototype stage and it should be challenged against additional relevant experimental diffusion data, which, unfortunately, does not exist in the open literature to our knowledge. We are, however, encouraged by what appears to be a correct prediction of the diffusivity of large molecules in rubbery polymers with regard to order of magnitude and trends with molecular shape.

It is envisioned that more structurally sophisticated mathematical models, based on this prototype, would be of considerable practical utility in polymer material design or process optimization involving the controlled diffusion of plasticizers (dryblending, plasticizer permanence), surfactants, lubricants, or large biologically active molecules, as examples, through polymeric particles, films, membranes, and containers. From a more fundamental theoretical perspective, our diffusion model bears, in part, a similarity to the concept of polymer reptation or curvilinear macromolecular motion through entanglements, especially in consideration of rather elongated penetrant molecules. While our model, as applied to elongated molecules, does involve a primarily longitudinal motion similar to the curvilinear motion envisioned in polymer reptation, the smaller penetrant molecule, in contrast, moves as a solid unit rather than by the propagation of successive conformational fluctuations along its "long direction." The penetrant molecule, owing to its short length relative to the contour length of a high molecular weight macromolecule, does not participate in multiple entanglement in the strict sense of that concept. It is in fact hoped that this modified free volume based theory and its refinements will form the basis of viewing and predicting diffusion in polymers in the nebulous size regime between small simple molecules and long-chain polymers that are above their critical entanglement degrees of polymerization.

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Sensitivity of Peptide Conformation to Methods and Geometrical Parameters. A Comparative ab Initio and Molecular Mechanics Study of Oligomers of α-Aminoisobutyric Acid

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ABSTRACT: The conformational behavior of α-aminoisobutyric acid has been investigated by means of ab initio and empirical methods. Empirical computations performed with fixed bond lengths and valence angles using well-known force fields show that C_5, C_7, and helical structures correspond to energy minima, but the relative stability of different conformers is strongly dependent on the parametrization. Ab initio computations performed to solve these discrepancies suggest that the three structures are essentially isoenergetic. An alternative set of net charges significantly improves the agreement between ab initio and molecular mechanics results. Complete geometry optimization using both ab initio and empirical methods does not affect the relative stabilities of C_5 and C_7 structures but significantly destabilizes the helical one. Zero point and entropy effects, although slightly destabilizing the C_7 structure, do not alter this general trend. The stabilization of helical structures with respect to C_5 and, especially, C_7 ones in polar solvents has been recovered by varying the dielectric constant governing intramolecular electrostatic interactions. Computations performed for oligomers of alanine and α-aminoisobutyric acid up to the octamer confirm the faster onset of helical structures for α-aminoisobutyric acid evidenced by experimental observations.

Introduction

The α,α-dialkylated, α-amino acid residue Aib (Aib = α-aminoisobutyric acid) extensively occurs in the transmembrane channel-forming peptide antibiotics of the alamethicin family.[1,2] As widely demonstrated by a large amount of theoretical investigation, replacement of the hydrogen atom at the C^α carbon atom in the Ala (Ala = Alanine) residue by a methyl group produces severe restriction of the conformational freedom of the resulting Aib residue.[3-6] This characteristic has stimulated many experimental studies, both in solution and in the solid state,[3,6-11] which suggest a pronounced tendency of the Aib residue to favor helical structures.

The first theoretical analyses[5,6] of the conformational space available to this residue found only small regions of the Ramachandran map energentically favorable, corresponding to helical structures of the 3_{10} ($\Phi \approx \pm 60°$, $\Psi \approx \pm 30°$) and α ($\Phi \approx \pm 55°$, $\Psi \approx \pm 45°$) types. The energy difference between the 3_{10} and α helix was small, whereas the other low-energy conformations characteristic of common protein residues were significantly less stable.[6] Subsequently, quantum mechanical calculations (using the PCILO method),[6] NMR experiments in nonpolar solvents,[7] and theoretical investigations by means of empirical functions[12,13] have, however, demonstrated that also C_5 ($\Phi \approx \Psi \approx 180°$) and C_7 ($\Phi \approx \pm 70°$, $\Psi \approx \mp 60°$) conformations are of relevant importance for this peptide. In particular, in polar media the α-helix conformation is favored with respect to the C_7 and C_5 ones, while in apolar solvents the C_5 and C_7 structures become significantly more stable.[9]

A more recent ab initio study confirms the great stability of the helical structures, although the narrow minima corresponding to the other low-energy conformations cannot be excluded, in view of the approximate procedure and large grid used in these calculations.[14]

A critical evaluation of the above results points out the influence of the methodology for characterization of the whole conformational space for a given molecule.

Both experimental and theoretical studies have further evidenced the importance of structural parameters in determining the relative stability of the different helical structures, namely, the 3_{10} and α ones. In particular a symmetric tetrahedral geometry around the C^α atom favors the α helix, whereas an asymmetric geometry shifts the energy minimum toward the 3_{10} helix.[15] Systematic theoretical studies on the conformational properties of α,α-dialkylated peptides have then demonstrated that the overall conformational behavior of this class of molecules does not depend on the symmetry around the C^α atom, but rather on the actual values of $NC^\alpha C'$ (hereafter referred to as τ) and $C^\beta C^\alpha C^{\beta'}$ (hereafter referred to as σ) valence angles.[13,16,17] In particular small values of τ favor α helical and C_5 structures, whereas small values

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