Effect of Vinyl Content on Self-Diffusion in Polybutadiene Melts

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ABSTRACT: Diffusion coefficients, *D*, have been measured at five temperatures for melts of 14 samples of polybutadiene with varying vinyl content, f_v, covering a broad range. Seven of the samples have a molecular weight, *M*, near 1300, and the other seven have *M* near 3400. The experiments show that *D* tends to decrease with increasing f_v. This trend in the experiments can be rationalized by two seemingly different approaches. One successful approach utilizes free volume theory. The other successful approach is a Monte Carlo simulation that employs different jump rates for beads representing the two types of butadiene units. The two methods may not be as different as they appear initially, because they both incorporate, directly or indirectly, the fact that the glass transition temperature moves closer to the temperature used for measurement of *D* as f_v increases.

Introduction

Various numbers of short branches are often attached to chain molecules. Within the class of polymeric hydrocarbons, these short branches can be introduced in well-controlled patterns, as in the methyl branches of hydrogenated poly(1,4-isoprene),[1] or in more random patterns, as illustrated by either the ethylene−1-alkene copolymers[2] or polybutadiene containing a mixture of 1,2- and 1,4-units.[3] The properties of the amorphous materials are often affected by the presence of the short branches.[4,5] One such property is the diffusion of the chains in the melt. The issue of diffusion is addressed here, for the case where the short branches are uniform in structure but randomly distributed along the chain.

The investigation consists of two parts. First, four seemingly distinct mechanisms by which the introduction of increasing numbers of short branches might change the self-diffusion coefficient, *D*, are considered sequentially. The qualitative trend for *D* vs the fraction of monomer units that contribute short branches, f_v, is estimated by simulation and theory for cases where each of the four mechanisms in turn dominates all other mechanisms. Then attention is turned to the behavior of an important real system, which is polybutadiene with varying content of vinyl groups.[3] The behavior of *D* vs f_v is evaluated from experiment, using the pulsed-gradient spin-echo proton NMR method.[6] Comparison of the trend of *D* vs f_v in the experiment with the trends expected when different mechanisms are dominant provides insight into the physical origin of the changes in the mean-square displacement of the center of mass of the chains in the melts of polybutadiene.

Simulation and Theory

This section considers in turn the likely qualitative consequences of four apparently distinguishable mechanisms by which an increase in f_v might affect *D*. We first consider the consequences of the change in the short-range intramolecular interactions, which causes the mean-square unperturbed dimensions of the chain to be a function of f_v. Then we turn to the intermolecular interactions (and long-range intramolecular interactions) of nonbonded pairs of monomer units, which depend on whether the interacting monomer units do, or do not, bear a short branch. Next we return to short-range intramolecular considerations, but this time with an emphasis on the rates of the conformational transitions between stable rotational isomeric states, instead of the prior emphasis on the equilibrium populations of the rotational isomeric state themselves. Finally, we look at the system from the perspective of free volume theory.

Changes in the Mean-Square Unperturbed Dimensions of the Chain. Attachment of a short branch to a chain molecule creates a trifunctional branch point. The population of rotational isomeric states is altered at the bonds in the main chain that are near this branch point, which in turn implies that the mean-square dimensions of the chain become a function of f_v.[7] The change in mean-square dimensions may in turn affect *D*, directly and indirectly.

The influence of f_v on the mean-square dimensions of a polyethylene chain has been determined previously,[8] using the rotational isomeric state model.[9,10] The mean square end-to-end distance experiences a monotonic decrease as the number of ethyl branches increases from nil to 40 per 100 carbon atoms in the main chain.[8] This decrease in dimensions arises because bonds to the trifunctional carbon atom are less likely to adopt trans placements (defined in terms of carbon atoms in the main chain) than are bonds remote from the branch point.[8]

The qualitative influence of 2-carbon (vinyl) branches on the mean-square dimensions of polybutadiene at constant molecular weight was estimated specifically for this work because this polymer is the one that is addressed in the experiments described later in the article. First, well-established matrix methods are used

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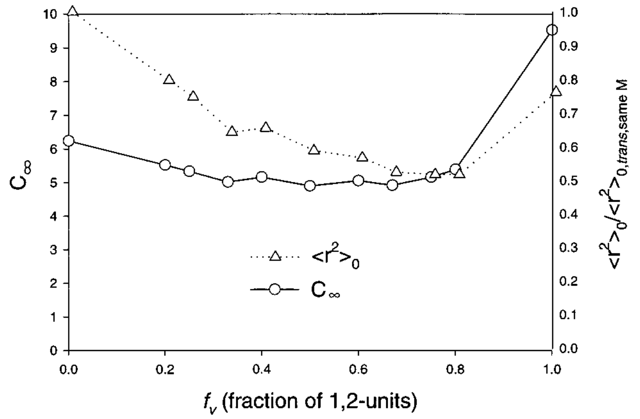

Figure 1. Estimates of the changes in C_∞ and $\langle r^2\rangle_0$ with the fraction of 1,2-units, f_v, in polybutadiene.

to calculate the characteristic ratio, C_∞.

$$C_\infty \equiv \lim_{n\to\infty} \frac{\langle r^2\rangle_0}{nl^2} \tag{1}$$

Here $\langle r^2\rangle_0$ denotes the mean-square unperturbed end-to-end distance for the chain with n bonds of mean square length l^2. Using the rotational isomeric state model of Abe and Flory,[11,12] the results at 304 and 394 K for chains consisting of a random sequence of 1,4-*trans*-butadiene and 1,4-*cis*-butadiene units can be summarized reasonably well by eqs 2 and 3, respectively.

$$C_\infty = 5.08 + 1.15 f_{tt} \quad \text{at 304 K} \tag{2}$$

$$C_\infty = 5.16 + 0.99 f_{tt} \quad \text{at 394 K} \tag{3}$$

Here f_{tt} denotes the fraction of adjacent pairs of butadiene units that is 1,4-*trans*−1,4-*trans*. The root-mean-square deviation of 22 different chains (covering the range of f_{tt} from 0 to 1) from the predictions of these two equations is about 0.5% of C_∞ at 304 K and 1.3% of C_∞ at 394 K.

For the introduction of 1,2-butadiene units, we tentatively assume as a rough first approximation that the first- and second-order interactions of the vinyl group with the atoms in the main chain can be estimated by replacement of the vinyl group with a methyl group. This approximation allows the formulation of the pertinent statistical weight matrices by modification of those required for polyethylene[13] and polypropylene.[14] When the branched butadiene units are introduced into poly(1,4-*trans*-butadiene), with the assumption that the stereochemical composition of the vinyl units is atactic (probability of a meso "diad" is $^1/_2$) and the stereochemical sequence is Bernoullian, C_∞ depends on the fraction of units that are 1,2-butadiene (denoted f_v) as depicted in Figure 1. The C_∞ decreases initially, passes through a broad minimum near $f_v = 0.7$, and then rises sharply to the estimate for atactic poly(1,2-butadiene). The decline in C_∞ from $f_v = 0$ to $f_v = 0.7$ is about 20%.

Figure 1 also shows the same data plotted in terms of the change in $\langle r^2\rangle_0$ for chains with the same molecular weight. The influence of f_v appears stronger when the data are examined in this fashion, with the minimum now appearing at $f_v = 0.8$ and the overall decrease from $f_v = 0$ to $f_v = 0.8$ being 50%. The stronger effect is seen in this representation because each 1,2-unit contributes only two bonds to the main chain, whereas each 1,4-unit contributes four bonds. Therefore, at constant molecular weight, M, the main chain contains fewer bonds as f_v increases. This effect produces a larger decrease in C_∞ (via $\langle r^2\rangle_0 \sim n$) than does the change in the populations of rotational isomeric states for bonds near the 1,2-unit. For this reason, refinement in the rotational isomeric state treatment of the 1,2-unit was not pursued.

Figure 2. Sequence of the beads representing the coarse-grained chain without branches. The smaller beads represent CH=CH (or CH=CH$_2$) units, and the larger beads represent CH$_2$−CH$_2$ (or CH−CH$_2$) units. Only the larger beads participate in the long-range interactions in the simulation.

This rotational isomeric state analysis of the polybutadienes, as well as the prior analysis of ethylene−1-butene copolymers,[8] leads to the conclusion that the mean-square dimensions of the chain will decrease upon the random incorporation of a few vinyl units in the polybutadiene or a few ethyl side chains in the polyethylene. The decrease in mean-square dimensions implies an increase in D with increasing branch content, if this effect dominates all others.

Changes in the Intermolecular (and Long-Range Intramolecular) Interactions. The average mass per bond in the main chain of polybutadiene varies from 13.5 to 27 (in atomic mass units) as the microstructure changes from poly(1,4-butadiene) to poly(1,2-butadiene). The density of interacting sites along the contour of the chain increases as the vinyl content increases, because the chain adopts a microstructure with a shorter contour length, but M is unchanged. The qualitative effect on D can be estimated by an adaptation of our simulation of coarse-grained models of polyethylene melts, which was reviewed recently.[15] Readers interested in greater detail are referred to this review. In this coarse-grained model, each CH$_2$CH$_2$ unit in polyethylene is represented by a single bead.[16] The short-range intramolecular interactions of the beads are controlled by an adaptation[17] of the classic rotational isomeric state model of Abe et al.[13] for unperturbed polyethylene chains. The intermolecular interactions of the beads are controlled by a Lennard-Jones potential energy function, mapped onto the discrete space defined by the high coordination lattice on which the simulation is performed.[18] In the present adaptation of the simulation, the intermolecular interaction is handled somewhat differently.

For the chain in which no branches are present, the beads alternate in type, as depicted in Figure 2. Beads represented by the larger circles participate in interactions with one another, using a discretized Lennard-Jones potential energy function based on $\sigma = 0.5$ nm and $\epsilon/k_B = 410$ K. These Lennard-Jones parameters describe the interaction of a pair of four-carbon fragments (n-butane) in the gas phase.[19] Beads represented by the smaller circles do not participate in any long-range interactions at all; the burden of the long-range interactions is borne exclusively by the beads represented by the larger circles. This approach amounts to the use of one Lennard-Jones center for each butadiene unit in the chain. Dynamic Monte Carlo simulations are often even more coarsely grained, using one interacting site per "segment", where the segment contains several monomer units. For representation of the polybutadiene backbone, we identify the larger beads with the CH$_2$−

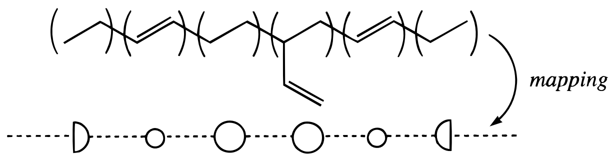

Figure 3. Sequence of beads that represent the segment of a chain passing through three butadiene units, in the sequence 1,4-butadiene−1,2-butadiene−1,4-butadiene.

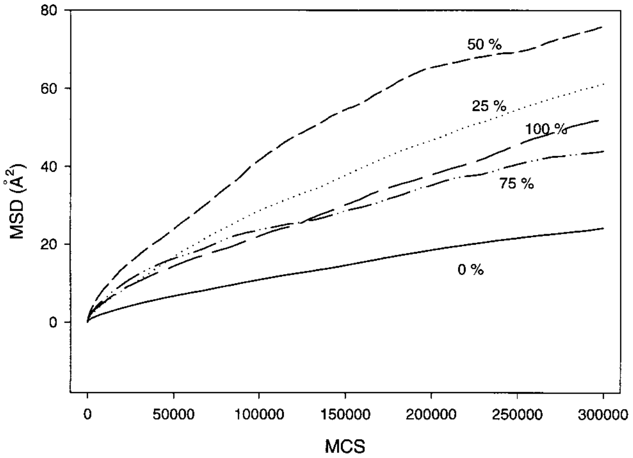

Figure 4. Mean-square displacement of the center of mass of the chains in melts where 0, 25, 50, 75, and 100% of the monomers are treated as 1,2-units.

CH_2 (or $CH_2{-}CH$) fragments and the smaller beads with the CH═CH (or $CH{=}CH_2$) fragments. Therefore, the backbone portion of a segment of three monomer units in the sequence 1,4-butadiene−1,2-butadiene−1,4-butadiene is represented in the simulation by five beads, as shown in Figure 3. The vinyl side chain is not represented explicitly, because the Lennard-Jones contributions of its monomer unit are borne entirely by the large bead in the main chain that represents the $CH{-}CH_2$ unit to which CH═CH is attached. With this representation, a poly(1,4-butadiene) chain of x monomer units is represented by $2x$ beads, alternating between large and small circles, but a poly(1,2-butadiene) chain with the same number of monomer units is represented by only x beads, all of which are large circles.

Since our focus here is exclusively on the influence of the Lennard-Jones interactions, the same rotational isomeric state model (the adaptation of the one described by Abe et al.) is used throughout, independent of the number and type of beads. The simulation employs nine independent parent chains of C100, and all of the chains in a given simulation have the same sequence of beads. The temperature is 443 K, with 1 million Monte Carlo Steps (MCS) for equilibration, followed by another million MCS steps that are used for the analysis. The interaction energies for pairs of large beads are 27.8, 1.9, −2.0, and −0.7 kJ/mol for the first, second, third, and fourth shell, respectively, of the high coordination lattice. The density is 0.75 g/cm^3. Figure 4 depicts the mean-square displacement of the centers of mass of the chains as a function of MCS in the equilibrated melts. The changes with increasing branch content are not monotonic. They imply an increase in D as the branch content rises from 0 to 25 to 50%, followed by a decrease as the branch content increases further to 75% and 100%. At low branch content, D responds primarily to the shortening of the chain of beads as the branch content increases. Only when the branch content is larger than 50% does D decrease, in response to the closer spacing of the interacting Lennard-Jones centers. This qualitative conclusion is not likely to be overturned by small changes in σ or ϵ.

We conclude that D for polybutadiene will initially increase with increasing vinyl content, if the energies of the intermolecular interactions completely dominate all other effects on the diffusion coefficient.

Differentiation of the Barrier Heights for Rotation about $CH_2{-}CH$ and $CH_2{-}CH_2$ Bonds. The intrinsic barrier height for rotational isomeric state transitions between trans and gauche states at a $CH_2{-}CH_2$ bond is larger than the intrinsic barrier height for rotational isomeric state transitions between the two skew states at a $CH{-}CH_2$ bond.[13,20] Therefore, one anticipates differences in the intrinsic mobility in the vicinity of the backbone at a 1,4-butadiene unit (with two highly mobile $CH{-}CH_2$ bonds and one less mobile $CH_2{-}CH_2$ bond) and a 1,2-butadiene unit (with two of the less mobile bonds between sp^3-hydridized carbon atoms, with their larger barrier heights between stable rotational isomeric states). A polybutadiene chain with x monomer units has a number of CH═CH bonds in the backbone that is given by $x(1 - f_v)$; i.e., the backbone contains fewer of the mobile $CH{-}CH_2$ as f_v increases. The qualitative effect of this difference in intrinsic mobility is intuitively obvious. Intuition can be tested by a Monte Carlo simulation in which the beads representing 1,4-butadiene units and 1,2-butadiene units have different intrinsic jump rates. For purposes of illustration, we use a ratio of jump rates of 0.31. This numerical value is estimated from the sums in eq 4, with each sum evaluated over all six types of rotational isomeric state transitions (trans ↔ gauche$^{\pm}$ and gauche^{+} ↔ gauche^{-} for a sp^3−sp^3 bond, cis ↔ skew$^{\pm}$ and skew^{+} ↔ skew^{-} for a sp^2−sp^3 bond).

$$\text{ratio} = \frac{\sum^{\mathrm{sp^3-sp^3}} \exp\left(-\frac{E_a}{k_B T}\right)}{\sum^{\mathrm{sp^3-sp^3}} \exp\left(-\frac{E_a}{k_B T}\right)} \tag{4}$$

The product of Boltzmann's constant and temperature is k_BT. Using the PCFF force field from Molecular Simulations, Inc., and a minimization of the conformational energy at various fixed values of the torsion angle to determine E_a, the ratio of these sums is about 0.31 at 443 K, with the larger sum for the $CH{-}CH_2$ bond.

The difference in intrinsic jump rate is incorporated by first selecting a bead at random. If the bead represents a 1,4-butadiene unit, a move of this bead is attempted. If the bead represents a 1,2-butadiene unit, a move is attempted only 31% of the time. The mean-square displacement of the center of mass in the chains in the melt is depicted in Figure 5. Although longer simulations would be required for accurate values of D, that degree of accuracy is not necessary for present purposes. We only require a qualitative assessment of the trend of D with f_v. There is a monotonic increase in D as the chain is enriched in the more mobile beads, as would be expected intuitively. Since the less mobile beads are the ones that bear the branches, D is predicted to decrease as f_v increases. Therefore, this

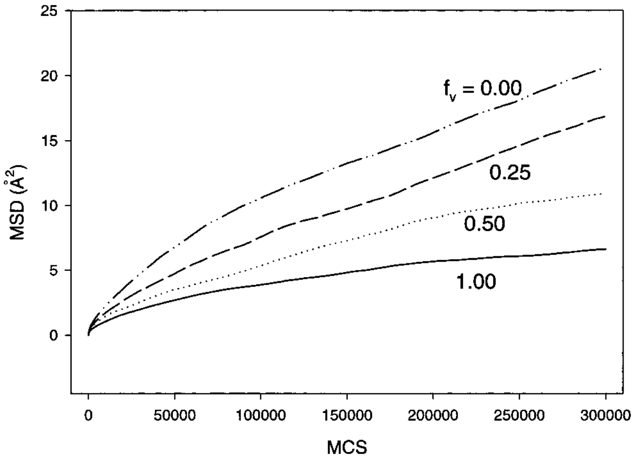

Figure 5. Mean-square displacements of the center of mass as the fraction of the more mobile beads increases from 0 to 1 (as f_v decreases from 1 to 0).

effect is different from the ones identified in the previous two sections. It suggests that D should decrease with increasing vinyl content, whereas the consideration of the mean-square dimensions suggested an increase in D as f_v increases, and a consideration of the intermolecular interactions (and long-range intramolecular interactions) leads to an initial increase in D, followed by a decrease.

Estimate Using the Concept of Free Volume. For molecular weights below the onset of well-developed entanglement effects on diffusion—as is the case here—the theoretical framework includes an absolute rate A independent of experimental variables T, M, and f_v; a small contribution from the thermal activation energy E_a; the well-known Rouse melt behavior[21] inversely proportional to M; and a term encompassing the complex host behavior, based on the fractional free volume $f(T,M,f_v)$ with its several contribution. The combined expression may be written as follows:[22]

$$D(T,M,f_v) = \frac{A}{M}\exp\left(-\frac{E_a}{RT}\right)\exp\left(-\frac{B_d}{f}\right) \tag{5}$$

The free volume overlap parameter B_d tends to assume a value near unity. The fractional free volume f incorporates the glass transition temperature T_g, the corresponding glassy free volume f_g, and the free volume expansivity $\Delta\alpha$. At finite M it further invokes a chain-end free volume V_E and requires knowledge of the density ρ. The following form was elaborated by Bueche:[23,24]

$$f(T,M,f_v) = f_g + \Delta\alpha(T - T_{g\infty}) + \frac{2V_E\rho}{M} \tag{6}$$

The literature[25,26] suggests numerical values for polybutadienes of $f_g = 0.038$ and $\Delta\alpha = 0.00048$ °C^{-1}; these values will be used here. The last term in eq 6 is required when measurements of T_g are available only for high-molecular-weight specimens ($M \to \infty$) rather than for the low-M samples examined and simulated in this study. The glass transition temperature for higher-M polybutadienes was reported[27,28] to display a dramatic rise from $T_{g\infty} = -108$ °C for the neat 1,4-structure ($f_v = 0$) to an average near -18 °C for neat 1,2 specimens ($f_v = 1$). In the absence of significant volume change upon mixing, a linear f_v dependence of $T_{g\infty}$ is an immediate consequence of volume additivity. We thus write

$$T_{g\infty}(f_v) = T_{g\infty}(0) + f_v\frac{dT_{g\infty}}{df_v} \tag{7}$$

The chain-end free volume V_E will have dependences on both T and f_v, and we propose the linear form

$$V_E(T,f_v) = \left[V_E(25\ °\mathrm{C},0) + f_v\frac{dV_E}{df_v}\right][1 + \Delta\alpha(T - 25\ °\mathrm{C})] \tag{8}$$

The f_v dependences of $T_{g\infty}$ and V_E should arise from a common cause and thus be related, both contributing to a similar decrease of f with increasing f_v. On this basis we may expect V_E to take the usual value of 10−20 cm^3 per mole of chain ends at $f_v = 0$, with dV_E/df_v negative, estimated to reduce V_E at $f_v = 1$ to about half its value at $f_v = 0$. It will, however, be necessary to extract their numerical values from a comparison with observation.

The density will, in general, depend on all three variables. In the absence of detailed data, we adapt our earlier successful model for densities in the n-alkane and polyethylene melts and blends[22,29] and propose the form

$$\rho(T,M,f_v) = \left[\frac{1}{\rho(T,\infty,f_v)} + \frac{2V_E(T,f_v)}{M}\right]^{-1} \tag{9}$$

where

$$\rho(T,\infty,f_v) = \frac{\rho(25\ °\mathrm{C},\infty,0)}{1 + \alpha(T - 25\ °\mathrm{C})}\left(1 + f_v\frac{d\rho}{df_v}\right) \tag{10}$$

Literature values[25,26] for polybutadiene density, relatively sparsely available at various T and especially f_v, are best reproduced by setting $\alpha = 7.5 \times 10^{-4}$ °C^{-1}, ρ (25 °C,∞,0) = 1.01 g/mol, and $d\rho/df_v = -0.05$ g/(mol °C).

Finally, in keeping with earlier experience in interpreting diffusion in n-alkane melts,[22] eq 5 invokes an intrinsic thermal activation energy E_a for diffusional jumps. To be sure, the T dependence resulting from this term is expected to be modest and dominated by the host free volume effects described by eqs 6−10, but ignoring E_a might lead to a distortion of the other parameters in a later comparison with data. We propose

$$E_a(f_v) = E_a(0) + f_v\frac{dE_a}{df_v} \tag{11}$$

with $E_a(0)$ on the order of 1−2 kcal/mol. Its f_v dependence dE_a/df_v is difficult to predict with confidence even as to sign; we initially estimate zero. It will be necessary to determine both of these values, as well, by comparing with experimental data.

Numerical evaluations of eq 5 with substitutions eqs 6−11 based on literature and estimated parameters clearly reveal several significant trends. First, D increases with increasing T as expected. The apparent diffusional activation energy is, indeed, mainly the result of the free volume term and thus dwarfs its energetic ingredient based on E_a. Moreover, the apparent activation energy increases across the range of f_v, nearly doubling for low M = 1300 g/mol. Second, at all values of T and M, the f_v dependence of log D is negative and concave downward. This trend is most pronounced at low M and high f_v and is mainly the result of the rapid increase of T_g with increasing vinyl content. While physically reasonable changes in the estimated parameters do affect the results $D(T,M,f_v)$ in minor ways, none of these is able to invalidate or reverse the trends observed.

Experimental Measurements of Self-Diffusion

We used the pulsed-gradient spin-echo (PGSE) method, based on nuclear magnetic resonance, to make direct measurements of molecular self-diffusion in two sets of seven nearly monodisperse polybutadiene specimens each. The two series had molecular weights near 1300 and 3400 g/mol, respectively, and each covered nearly the full range of random 1,2-content. These specimens had been comprehensively characterized as described previously;[3] Table 1 summarizes their molecular attributes. Our measurements were conducted at temperatures of 30.5, 45.5, 60.5, 90.5, and 120.5 °C, each maintained within ±0.3 °C.

Our implementation of the PGSE experiment has been described in detail elsewhere[30−33] and was used essentially as reported in recent studies of n-alkane and polyethylene systems.[22,29] In brief, we elicited the proton spin echo at 33 MHz using the stimulated echo and, using signal averaging, measured its attentuation at each of up to 20 settings of the duration δ of the two applied magnetic field gradient pulses of magnitude G separated by a constant delay Δ. G was calibrated at each temperature; its value was 652 ± 12 G/cm at 60.5 °C. The timing of the gradient pulses was coordinated with that of the three-pulse radio-frequency sequence and in the present case was set to give an effective diffusion time $(\Delta - \langle\delta\rangle/3) = 100$ ms. For interpretive convenience a steady field gradient of $G_0 = 0.4$ G/cm was also applied throughout the experiments.

The interpretation of the experiment calls for an analysis of the spin-echo amplitude $A(X)$ as a function of the combined gradient parameter $X = \delta^2 G^2(\Delta - \delta/3)$; small additional terms proportional to GG_0 are also included in X. In the general case of several molecular species i whose fractional echo contributions and diffusion rates are a_i and D_i, respectively, the relationship for unrestricted, Fickian diffusion is[6]

$$\frac{A(X)}{A(0)} = \sum_i a_i \exp(-\gamma^2 D_i X) \tag{12}$$

where γ represents the gyromagnetic ratio of the nuclear species at resonance (here protons). Figure 6 shows two sample echo attentuation plots, ln $[A(X)/A(0)]$ vs X. A small upward curvature signals the presence of a diffusivity distribution, simulated in eq 12 by mapping it onto the known molecular-weight dispersity;[34] the single fitted parameter is $D(M_{\mathrm{ref}})$, with M_{ref} chosen to be M_n. In Figure 6b, an additional rapid diffusion rate arises from a trace of solvent remaining from the final steps of the synthesis; its amount is greatly exaggerated in the data because the solvent's spin−spin relaxation time, and hence its relative echo contribution at large Δ, greatly exceeds that of the polymer. The results for $D(M_n)$, extracted in this case from the three-parameter fit,[35] are essentially unaffected by solvents at trace concentrations.

Table 1. Molecular Weight, Polydispersity, and Vinyl Content of the Samples, Reported Previously by Han et al.[3]

sample[a]	M_n (GPC)	M_w/M_n (GPC)	M_n (MS[b])	M_w/M_n (MS)
PB_7L	1050	1.07	1372	1.05
PB_16L	1350	1.07	1468	1.04
PB_28L	1200	1.07	1379	1.05
PB_41L	1150	1.08	1338	1.05
PB_52L	1200	1.07	1404	1.04
PB_84L	1000	1.16	1597	1.09
PB_93L	1100	1.07	1452	1.03
PB_7H	3400	1.05	3714	1.02
PB_26H	3000	1.06	3399	1.02
PB_32H	3000	1.06	3438	1.02
PB_43H	3400	1.05	3882	1.02
PB_50H	3000	1.07	3586	1.02
PB_61H	3000	1.07	3562	1.04
PB_78H	3400	1.04	4127	1.02

[a] The number in the sample code is $100f_v$. [b] MS = MALDI mass spectroscopy.

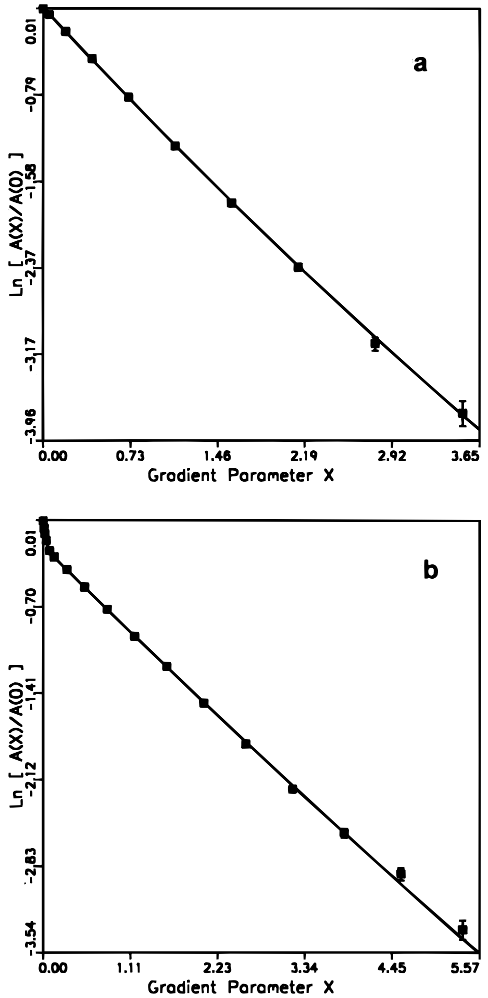

Figure 6. Diffusional echo attentuation measured (symbols) in (a) sample PB_16L at 60.5 °C and (b) sample PG_78H at 120.5 °C. In both cases the fitted expression, eq 12, was based on the known M-dispersity; in (b) an additional rapidly diffusing component is due to a trace of solvent (see text).

The results for D as functions of f_v at each T for the two series are shown in Figure 7 (symbols). The lines represent the theory of eqs 5−11, fitted simultaneously to all 60 data points by optimizing the five parameters not precisely known. One cosmetic alternation was applied because the molecular weights within each sample series were not exactly the same. To permit smooth isotherms to be drawn at constant M, the experimental D values in these Figures (but not in the

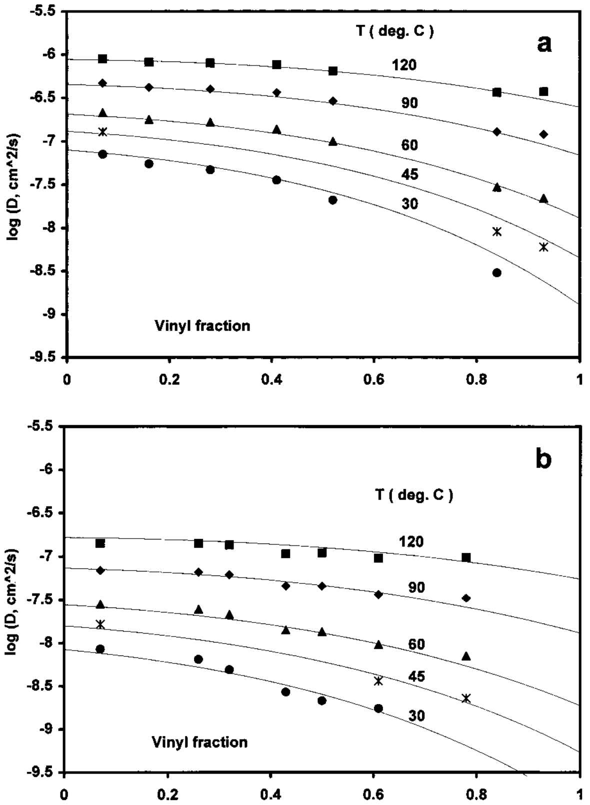

Figure 7. Diffusion coefficient measured (symbols) as a function of 1,2-content in the two series of polybutadiene melts of mean molecular weight (a) 1300 g/mol and (b) 3400 g/mol, at five temperatures from top to bottom: 120.5, 90.5, 60.5, 45.5, and 30.5 °C. Lines represent theory of eqs 5−11 with five parameters fitted to all data points. Data are plotted with adjustments for slightly unequal M (see text).

fits) have been multiplied by $M/\langle M\rangle$ to implement a first-order correction for the principal M dependence of D, arising from the Rouse term of eq 5. The $\langle M\rangle$ selected for the two series were 1300 and 3400 g/mol, respectively, and the theory is plotted was evaluated at these $M = \langle M\rangle$ with the parameters optimized in the nonlinear weighted least-squares fits[36] to the original data.

The optimized parameters assumed the following values:

$$A = 3.32 \pm 0.02 \quad \mathrm{cm}^2\ \mathrm{mol/(s\ g)} \tag{13}$$

$$V_E(f_v{=}0) = 20.6 \pm 0.4 \quad \mathrm{cm}^3/(\text{mol of chain ends}) \tag{14}$$

$$dV_E/df_v = -13.6 \pm 0.3 \quad \mathrm{cm}^3/(\text{mol of chain ends}) \tag{15}$$

$$E_a(f_v{=}0) = 1.66 \pm 0.05 \quad \mathrm{kcal/mol} \tag{16}$$

$$dE_a/df_v = -1.5 \pm 0.3 \quad \mathrm{kcal/mol} \tag{17}$$

Several observations are in order. The fit is satisfying and semiquantitatively acceptable; reduced chi-square is on the order of 5. This means, however, that minor systematic deviations remain, as is evident particularly at low M, low T, and high f_v. Thus, while all the trends exhibited by the data are quite well represented by the model, some of the assumptions it contains may be suspect. This problem affects principally the terms which contributed least to the theory. For example, the optimized value for dE_a/df_v, eq 17 unreasonably suggests that the neat 1,2-structure requires essentially no thermal activation to perform a jump.

Analysis of the Validity of the Potential Mechanisms

Comparison of the trends for D vs f_v in the experiments with the trends from the four predictions permits immediate elimination of two of the possibilities. If the trends for D were dominated by changes in the mean-square dimensions or in the intermolecular interactions captured by a Lennard-Jones potential energy function, D should experience an initial increase with f_v, but the opposite behavior is observed. Therefore, D must respond to some other f_v-dependent attribute of the system.

The qualitative trend is predicted correctly by two seemingly different approaches. One approach is a dynamic Monte Carlo simulation that incorporates different jump rates for the beads representing 1,2- and 1,4-butadiene units. This simulation is motivated by the well-known existence of a smaller size of E_a for rotational isomeric state transitions between skew states at a $CH-CH_2$ bond than for rotational isomeric state transitions between the trans and gauche states at a CH_2-CH_2 bond. The other successful approach is a theoretical analysis of the temperature and molecular weight dependence of D using a free volume theory employed previously for the analysis of diffusion coefficients in other systems.

The success of the two seemingly different approaches may provide an important insight. They both incorporate, explicitly or by inference, the manner in which the glass transition temperature depends on f_v. The glass transition temperature enters the theoretical treatment explicitly in eq 6, where $T - T_{g\infty}$ influences the fractional free volume. Although T_g does not appear explicitly in the successful simulation, its influence may be incorporated indirectly. That incorporation occurs via the assumption that the paramount influence of f_v on D arises from differences in the intrinsic mobility of 1,2- and 1,4-butadiene units, at the level of the rate of rotational isomeric state transitions at individual bonds in the main chain.

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