moment for free rotation of the C_δ–O bond as 1.2 D. This value is in good agreement with the experimental one for PMLG.

In the case of PBLG, the dipole moment of the benzyl group (0.4 D)[16] is smaller than that of the O–$C_\zeta H_3$ group. Therefore the higher frequency process of PBLG seems to be predominantly caused by C_δ–O bond rotation. If we take the dipole moment of the benzyl group into account, the effective moment for the C_δ–O bond rotation is calculated as 1.0 D and agrees completely with the experimental one. The fact that the value τ_h of PBLG is larger than that of PMLG indicates an increase in the moment of inertia of the motional unit.

Adachi et al.[17] pointed out from a dielectric study on dichloromethane solutions of PBLG with concentrations of 20–100 wt % that dipoles of the side chains cannot reorient freely in all directions. The present results indicate that such restriction is confined only in the motions of C–C bonds close to the backbone chain in dilute solution.

It is clear from a comparison between the dipole moments of PpClBLG and PBLG that the high-frequency process for PpClBLG is caused not only by the C_δ–O bond rotation but also by the O–C_ζ bond rotation. If the O–C_ζ bond rotation is assumed to be free and the dipole moment of *p*-chlorotoluene (1.9 D)[16] is taken as that of the *p*-chlorobenzyl group, the effective moments for the C_δ–O and O–C_ζ bond rotations are calculated as 0.3 and 1.7 D, respectively. When each rotation occurs independently, the total moment is obtained simply as 1.7 D $[=(0.3^2 + 1.7^2)^{1/2}$ D] and agrees well with the experimental value. It may be concluded that contribution of the O–C_ζ bond rotation to the higher frequency process is predominant and the O–C_ζ bond rotation occurs at nearly the same rate as the C_δ–O bond rotation.

Relaxations observed in this work clarify the elementary processes in side-chain motions of poly(α-amino acids). Motions of the C–C bonds neighboring to the backbone chain are fairly restricted but rotations of the C–O bonds in the end of the side chain are nearly free. We believe that the TDR method is one of the most effective techniques for studying physical, chemical, and biological functions due to elementary processes of molecular motions.

References and Notes

(1) Fraser, R. D. B.; Harrap, B. S.; Ledger, R.; MacRae, T. P.; Stewart, F. H. C.; Suzuki, E. *Biopolymers* **1967**, *5*, 797.
(2) Hiltner, A.; Anderson, J. M.; Bolkowski, E. *Macromolecules* **1972**, *5*, 446.
(3) Wada, A. *Adv. Biophys.* **1976**, *9*, 1.
(4) Tsutsumi, A.; Hikichi, K.; Takahashi, T.; Yamashita, Y.; Matsushima, N.; Kanke, M.; Kaneko, M. *J. Macromol. Sci., Phys.* **1973**, *B8*, 413.
(5) Sasaki, N.; Yamashita, Y.; Tsutsumi, A.; Hikichi, K. *Polym. J.* **1978**, *10*, 207.
(6) (a) Yagihara, S.; Hikichi, K. *Polym. J.* **1981**, *13*, 579. (b) *Ibid.* **1982**, *14*, 233.
(7) Hikichi, K. In *Contemp. Top. Polym. Sci.* **1984**, *4*, 715.
(8) Nakamura, H.; Mashimo, S.; Wada, A. *Macromolecules* **1981**, *14*, 1698.
(9) Cole, R. H.; Mashimo, S.; Winsor, P., IV. *J. Phys. Chem.* **1980**, *84*, 786.
(10) Mashimo, S.; Yagihara, S.; Chiba, A. *Macromolecules* **1984**, *17*, 630.
(11) Nakamura, H.; Mashimo, S.; Wada, A. *Jpn. J. Appl. Phys.* **1982**, *21*, 1022.
(12) Bradbury, E. M.; Carpenter, B. E.; Goldman, H. *Biopolymers* **1968**, *6*, 837.
(13) Debye, P. In "Polar Molecules"; Reinhold: New York, 1929; Chapter V.
(14) Fröhlich, H. In "Theory of Dielectrics"; Oxford University Press: London, 1949; Chapter II.
(15) (a) Mashimo, S.; Yagihara, S.; Iwasa, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1761. (b) Tanaka, A.; Ishida, Y. *Ibid.* **1974**, *12*, 335.
(16) Hill, N. E.; Vaughan, W. E.; Price, A. H.; Davies, M. In "Dielectric Properties and Molecular Behaviour"; Reinhold: London, 1969; Chapter 4.
(17) Adachi, K.; Hirose, Y.; Ishida, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 737.

Self-Diffusion Coefficient in Melts of Linear Polymers: Chain Length and Temperature Dependence for Hydrogenated Polybutadiene

Craig R. Bartels and Buckley Crist*

Materials Research Center, Northwestern University, Evanston, Illinois 60201

William W. Graessley

Exxon Research and Engineering Company, Corporate Research Laboratories, Annandale, New Jersey 08801.

Received April 23, 1984

ABSTRACT: Self-diffusion coefficients in the molten state were determined for several samples of linear hydrogenated polybutadiene (HPB), a polymer which closely resembles polyethylene in structure and melt properties. Films with alternating layers of protonated and partially deuterated chains with the same chemical structure were used. Values of D were obtained from the growth of coherent neutron scattering intensity as the layers interdiffused. The temperature dependence of D was independent of molecular weight but slightly weaker than that for the melt viscosity. The magnitude of the difference was shown to be consistent with predictions based on recent theories of entangled-chain dynamics. The chain length dependence accurately obeyed the inverse square law predicted by reptation, $D = k_D M^{-2}$. The value of k_D, extrapolated to 176 °C, agrees fairly well with Klein's diffusion-couple results at that temperature for both HPB and linear polyethylene. It also agrees well with a theoretical prediction of k_D based on viscoelastic measurements.

Introduction

Recent theories[1-5] on polymer chain dynamics in concentrated solutions and melts lead to a series of predictions about the effect of chain length on dynamic properties. According to the reptation model of de Gennes,[1] the translational diffusion coefficient of long, linear polymer chains in the melt is inversely proportional to the square of molecular weight:

$$D = k_D M^{-2} \qquad (1)$$

Klein and Briscoe[6] first verified the inverse square dependence by classical diffusion-couple experiments,

0024-9297/84/2217-2702$01.50/0

measuring D for a series of linear polyethylene fractions in a matrix of much longer polyethylene chains. Klein also showed that D is insensitive of the molecular weight of the matrix polymer,[7] another prediction of reptation theory.[2] That method has been extended recently to linear and three-arm star versions of hydrogenated polybutadiene,[8] a polymer which closely resembles polyethylene in structure. The M^{-2} dependence has been confirmed independently by NMR measurements of D in melts of linear polyethylene and polystyrene[9,10] and by the forced Rayleigh scattering measurements in polystyrene solutions of moderate concentration.[11]

In this paper, we expand upon a previous report[12] of measuring D in polymer melts with a technique based on small-angle neutron scattering (SANS). In that work we showed that SANS technique can be used to evaluate even rather small diffusion coefficients ($D < 10^{-10}$ cm^2/s) in a matter of hours; this was accomplished by making the diffusion length small, on the order of a few microns. Results are presented here for the molecular weight dependence and temperature dependence of D measured with hydrogenated polybutadiene (HPB) and partially deuterated versions of the same polymer (DPB). These fully saturated, crystallizable polymers, made by reacting polybutadiene with either H_2 or D_2, are models for polyethylene, but with the important additional features that the HPB/DPB pairs are precisely matched in chemical structure and have very narrow molecular weight distributions. Systems of matched pairs are especially well-suited for SANS studies as demonstrated in our previous experiments with HPB and DPB.[13] The equations required to determine D from the development of coherent scattering by a film composed initially of alternating protonated and deuterated layers are presented below.

Development of Equations

Consider a matched pair of monodisperse polymers, identical in all respects except for isotopic substitution. One is fully protonated (HPB), and the other has some portion of its protons replaced by deuterons (DPB). If the polymers mix ideally, the coherent SANS intensity per unit scattering volume for a homogeneous mixture containing ϕ_H and ϕ_D volume fractions ($\phi = \phi_D$, $1 - \phi = \phi_H$) is given by[14]

$$I_c(q) = K\phi(1 - \phi)P(q)N \tag{2}$$

where $q = 4\pi\lambda^{-1} \sin (\theta/2)$ is the magnitude of the scattering vector (λ is the neutron wavelength; θ is the scattering angle), N is the degree of polymerization of the chains, and $P(q)$ is the single-chain scattering function ($P(0) = 1$). The coefficient K is independent of θ, q, and N; its absolute value, which can be calculated from the degree of isotopic substitution and appropriate calibrations,[15] is of no direct concern for the purposes here. Equation 2 still applies locally when ϕ varies with position in the scattering volume as long as this change in composition is small over distances on the order of q^{-1}. For that case, the product $\phi(1 - \phi)$ can be replaced in eq 2 by its spatial average:

$$\langle \phi(1 - \phi) \rangle = \frac{1}{V}\int_0^V \phi(1 - \phi)\, dV \tag{3}$$

Consider now a film composed of alternating layers of the two polymers with a layer thickness L that is large compared to R_g, the radius of gyration of the chains. From eq 2 and 3, $I_c(q)$ is zero for normal incidence of the neutron beam if the interfaces between layers are perfectly sharp: $\phi(1 - \phi)$ is zero everywhere. (Diffraction peaks from the layered structure would appear at unobservably small angles, $q \sim 10^{-5}$ Å^{-1} for $L = 1 - 10$ μm, even if the film were reoriented to satisfy the diffraction condition.)

Contrast develops as the layers homogenize; $\langle \phi(1 - \phi) \rangle$ increases from zero and eventually approaches the equilibrium value, which, for alternating layers of equal thickness, is $\langle \phi(1 - \phi) \rangle_\infty = 1/4$ (a uniform mixture with $\phi = 1/2$ everywhere). Thus, if $P(q)$ is independent of mixing, the SANS intensity is a factorable function of diffusion time and scattering angle:

$$I_c(q,t) = \frac{K}{4}F(t)P(q)N \tag{4}$$

where

$$F(t) = \frac{\langle \phi(1 - \phi) \rangle_t}{\langle \phi(1 - \phi) \rangle_\infty} \tag{5}$$

An expression for $F(t)$ can be obtained by solving the diffusion equation

$$\frac{\partial \phi}{\partial t} = D\frac{\partial^2 \phi}{\partial x^2} \tag{6}$$

with a square wave as the initial profile for the volume fraction of labeled chains:

$$\phi(x,0) = 0 \qquad ((j - 1)L < x < jL) \tag{7a}$$

$$\phi(x,0) = 1 \qquad (jL < x < (j + 1)L) \tag{7b}$$

where x is the distance measured from an interface and $j = 0, \pm2, \pm4, ...$ When the dynamics are unaffected by isotopic substitution, D is the self-diffusion coefficient. The solution is

$$\phi(x,t) = \frac{1}{2} + \frac{2}{\pi} \sum_{\substack{\text{odd}\\ n}} \frac{1}{n} \sin \left(\frac{n\pi x}{L}\right) \exp(-n^2\pi^2Dt/L^2) \tag{8}$$

and the required average

$$\langle \phi(1 - \phi) \rangle_t = \frac{1}{2L}\int_0^{2L} \phi(x,t)[1 - \phi(x,t)]\, dx \tag{9}$$

gives finally

$$F(t) = 1 - \frac{8}{\pi^2} \sum_{\substack{\text{odd}\\ n}} \frac{1}{n^2} \exp(-n^2\xi) \tag{10}$$

where ξ is the dimensionless time:

$$\xi = 2\pi^2Dt/L^2 \tag{11}$$

The coherent intensity from the interdiffused macromolecules (see eq 4 and 5) can be used to obtain $F(t)$ according to

$$F(t) = I_c(q,t)/I_c(q,\infty) \tag{12}$$

The value of D is then derived from eq 10 and 11 with known values of initial layer thickness L and diffusion time t.

The leading term ($n = 1$) dominates the sum in eq 10. It contributes a fraction $8/\pi^2 = 0.81$ of the total at $\xi = 0$, rising to 0.94 at $\xi = 0.1$ and 0.98 at $\xi = 0.2$. The expression obtained by omitting the higher terms entirely

$$D = \frac{L^2}{2\pi^2 t} \ln \left[\frac{8}{\pi^2(1 - F)}\right] \tag{13}$$

gives D with an error of less than 3% for $F(t) > 0.4$.

It should be emphasized that the simple and useful form of eq 4 is achieved only with perfectly matched pairs of nearly monodisperse deuterated and protonated polymers. If the two polymers are not matched in molecular size and

Table I
Characterization of Hydrogenated Polybutadienes

sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_m, °C
HPB-46	48 000	1.03	108.1
HPB-70	73 000	1.03	108.7
HPB-101	105 000	1.03	108.6
HPB-153	159 000	1.02	107.8
HPB-206	214 000	1.03	106.8

dynamics, the simple consequences of Fick's second law, embodied in eq 6–11, will not be realized. Furthermore, even ideal mixing of mismatched polymers leads to an angular dependence that varies with concentration,[14] obviating eq 2. Matched polydisperse polymers could perhaps be used, though the time evolution of the intensity would be complicated because of the range of D's present. The apparent $P(q)$ would then depend on time, being dominated by the most rapidly diffusing molecules at short times. It is thus important that the *shape* of the coherent SANS pattern be independent of concentration, allowing intensity changes to be interpreted directly as changes in $F(t)$. There is no stipulation that $P(q)$ be of any particular form, e.g., a Debye function, but it should be independent of ϕ. Finally, the uniformity of layers must be considered. Some distribution of L values must always occur, the effect being to change the observed form of $F(t)$ even for perfectly matched pairs. The test in this case is whether the same values of D are obtained from eq 10–13 for different times of diffusion.

Experimental Procedures

Polybutadiene precursors with very narrow distributions of molecular weight ($\bar{M}_w/\bar{M}_n < 1.1$) were prepared by anionic polymerization. They were reacted with either H_2 (to form HPB) or D_2 (to form DPB) at 70 °C and 500 psi in cyclohexane solution over a catalyst of Pd supported on $CaCO_3$. Previous work in these laboratories[15,16] has shown that this process is quantitative and without side reactions (chain scission, cross-linking, etc.) that alter the molecular structure. Exchange as well as addition occurs during this reaction; deuterium substitution in the DPB is approximately 40% in all samples.[15]

Matched pairs of HPB and DPB (made from the same precursor polybutadiene) with molecular weights ranging from 48 000 to 214 000 were used. The values in Table I are obtained by low-angle laser light scattering measurements in cyclohexane solutions of the polybutadienes; a correction factor of 56/54 was applied to account for the effect of hydrogenation. Sample designations indicate the polybutadiene molecular weight in 1000's, e.g., HPB-46 was derived from a polybutadiene precursor with a light scattering molecular weight of 46 300. The dispersity index $\bar{M}_w/\bar{M}_n$ was obtained for the polybutadienes by GPC. Additional molecular weight characterization on these and similar samples is reported elsewhere.[15]

The polymers contain 18 ethyl branches per 1000 backbone carbon atoms, a result of 8% 1,2 additions during the butadiene polymerization. They are structurally equivalent to copolymers of ethylene and ~4% 1-butene. The final melting temperatures measured by DSC for quenched HPB are reported in Table I; T_m for the corresponding DPB is 1.5–2.0 °C lower. This relatively small depression of T_m is probably due to the fact that DPB is only partially deuterated ($\Delta T_m = -6$ °C for fully deuterated polyethylene[17]). The segregation or clustering effects, very prevalent in mixtures of polyethylene and its fully deuterated analogue, are absent in quenched samples of matched HPB/DPB mixtures.[13,15]

Sample Preparation. Films with alternating layers of HPB and DPB for the diffusion studies were prepared with layer thicknesses ($3 < L < 15$ μm) chosen to keep homogenization times in the order of a few hours. Separate solutions of HPB and DPB were prepared in cyclohexane (concentration ~10^{-3}–10^{-2} g/mL) at 75 °C. A fixed aliquot of one solution was pipetted into a 40 mm × 40 mm frame backed with poly(tetrafluoroethylene), after which the solvent was evaporated rapidly, leaving a layer of the desired thickness. An aliquot of the second solution was then added to form the next layer. This process was repeated until ~25 bilayers of alternating HPB and DPB had been deposited. The layered film was then stripped from the casting frame and dried at 60 °C in a vacuum oven. The average layer thickness $\langle L \rangle$ was measured by dividing the laminate thickness by the number of layers. Experiments were done to establish that the variation in layer thickness was less than ±10% from the mean. Several films were stacked together to provide a sample of thickness 0.7 mm for the SANS studies.

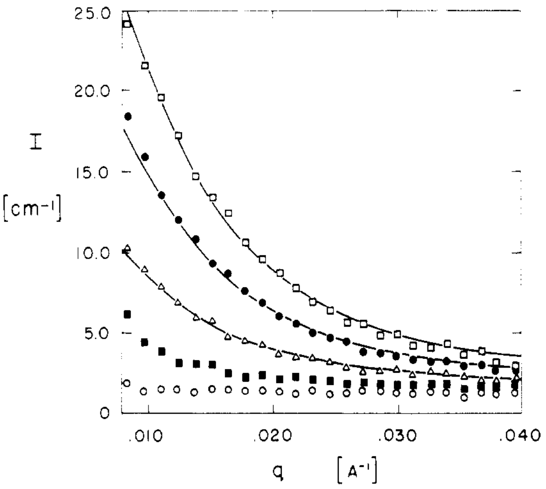

Figure 1. Diffusion times of 0 (■), 5 (△), and 20 (●) min at 125 °C. Also shown are scattering results for the compositionally homogeneous mixture, $t = \infty$ (□), and for the pure HPB blank (○).

SANS Measurements. The 30-m SANS facility at Oak Ridge National Laboratory was used for these experiments. The layered films were oriented with the incident beam perpendicular to the film surface. Sample dimensions were typically 20 mm × 20 mm × 0.7 mm. With a neutron wavelength λ of 4.75 Å and a sample–detector distance of 11 m, scattered intensity was recorded in the range $0.008 < q < 0.045$ Å^{-1}. The patterns were isotropic, permitting azimuthal averaging to enhance the counting statistics. All SANS measurements were made at room temperature.

Initial SANS patterns were recorded for the layered films. Each film was then wrapped in aluminum foil and immersed in an oil bath at a temperature above the melting point (T = 125, 145, and 165 °C). After the desired time the film was quenched in ice water to arrest the diffusion, and the SANS pattern was again recorded. In most cases the film was reheated to permit another cycle of diffusion. In a typical experiment the patterns were recorded for diffusion times of 0, 5, and 30 min. The pattern for the fully homogenized state (corresponding to $t = \infty$) was obtained with a mixture ($\phi = 0.5$) made by solution blending HPB and DPB, precipitating in methanol, compression molding at 150 °C, and quenching from the melt.

Results

A representative set of total scattering curves for a layered film (M = 73 500) is shown in Figure 1. Also shown are the SANS patterns for a solution-blended sample, corresponding to $t = \infty$, and for the pure HPB. The scattering intensity for the latter is small and essentially independent of scattering angle, the major contribution being incoherent scattering from the protons. We have found that $I(q)$ for pure DPB is similar in magnitude for the same q range;[15] it is assumed that this "background scattering" is constant for all stages of diffusion and is adequately represented by the pure HPB pattern. Our analysis is furthermore restricted to the range of smallest q ($0.008 < q < 0.023$ Å^{-1}) so that any errors from an imperfect definition of background are minimized by a large ratio of coherent signal to background. With this reasonable assumption that the observed intensity is the sum of the coherent pattern of interest and a time-dependent background, $I(q,t) = I_c(q,t) + I_{HPB}(q)$, eq 12 then becomes

$$F(t) = \frac{I(q,t) - I_{HPB}(q)}{I(q,\infty) - I_{HPB}(q)} \qquad (14)$$

As mentioned previously, the validity of eq 12 or 14 rests on the assumption that $P(q)$ is independent of the extent of diffusion. This is verified by the scattering curves in Figure 1, in which the solid lines are calculated for a Gaussian chain with $R_g = 140$ Å. The same scattering function $P(q)$ obviously fits the coherent intensity for diffusion times of 5 min, 20 min, and infinity (solution-blended sample). We have discussed elsewhere[13,15] the interesting fact that this $P(q)$ implies Gaussian conformations for semicrystalline HPB, at least over the large distances observed here.

The as-prepared layered film ($t = 0$) shows some enhanced scattering relative to pure HPB. We take this to indicate a small degree of initial mixing at the interfaces, an effect which is considered in more detail below.

Values of $F(t)$, typically in the range 0.3–0.6, were obtained from eq 14. In each case the results for approximately 20 values of q between 0.008 and 0.023 Å^{-1} were averaged. No drift with q was found: $F(t)$ was constant within 3% over the range, again supporting the form of the coherent signal expected from eq 4. The value of ξ was deduced from the experimental $F(t)$ with eq 10, and the diffusion coefficient was obtained from eq 11 after applying two rather small and partially offsetting corrections to the diffusion time.

One of these corrections allows for the mixing that took place at the interfaces during film preparation. Diffusion in the melt begins from some already finite value of $\langle \phi(1 - \phi) \rangle$, corresponding, at least approximately, to an extra time t_0 of diffusion at the test temperature. The other correction allows for the time t_1 to heat the film to the test temperature. Experiments with a thermocouple imbedded in the sample gave $t_1 \sim 30$ s and showed that quenching to the crystallization temperature, $T_c \sim 85$ °C, is essentially instantaneous. These corrections were made with the equation

$$D = \frac{t}{t + t_0 - nt_1} D' \qquad (15)$$

where n is the number of heating cycles experienced by the film and D' is the diffusion coefficient evaluated from $F(t)$ (eq 10) without time corrections:

$$D' = \xi L^2 / 2\pi^2 t \qquad (16)$$

The effective initial value of $F(t = 0) = F(t_0)$ was estimated from the observed intensity profile for the unheated film, $I(q,0)$, from the final profile, $I(q,\infty)$, and from the initial profile that the same film would have had with no interfacial mixing, I_{HPB}, giving

$$F(t_0) = \frac{I(q,0) - I_{HPB}}{I(q,\infty) - I_{HPB}} \qquad (17)$$

The required value of t_0 was then obtained from eq 10 and 11 using D'. The corrected D was then calculated from eq 15 with $t_1 = 30$ s and the appropriate value of n. An example showing the effect of these corrections is given in Table II. It is obvious that appreciable differences between D' and D are seen only with the smallest heating times, though even here they are always less than 20%.

The results for D are given in Table III. Duplicate measurements on HPB-101 and HPB-153 show that the results are reproducible and independent of layer thickness. For a given film the values obtained at longer diffusion times tend to be slightly smaller. We assume this to be the result of a small nonuniformity in the layer thickness.

Table II
Correction of Observed Diffusion Coefficients (HPB-153, T = 145 °C)

t, s	D', cm^2/s	D, cm^2/s
330	1.60×10^{-11}	1.39×10^{-11}
1170	1.36×10^{-11}	1.38×10^{-11}
2340	1.31×10^{-11}	1.31×10^{-11}

Table III
Diffusion Coefficients for Linear Hydrogenated Polybutadiene

sample	T, °C	$\langle L \rangle$, μm	t, s	t_0, s	$F(t)$	$10^{11}D$, cm^2/s
HBP-46	125	13.7	300	13	0.422	11.6
			1500	13	0.813	9.64
HBP-70	125	11.2	300	45	0.348	4.71
			1200	45	0.680	4.97
HPB-101	125	6.8	300	28	0.383	2.22
			1800	28	0.794	1.82
	125	8.5	300	29	0.302	2.10
	145	8.5	1800		0.823	2.78
	165	11.0	300	39	0.346	4.52
			1800	39	0.721	4.84
HPB-153	125	6.0	300	67	0.308	0.97
			1800	67	0.648	0.84
	125	9.8	600	160	0.262	0.90
			2700	160	0.490	0.80
	145	7.8	330	70	0.295	1.39
			1170	70	0.520	1.38
			2340	70	0.699	1.31
	165	9.0	300	69	0.258	1.91
			1800	69	0.651	1.90
HPB-206	125	4.2	360	50	0.347	0.54
			1860	50	0.726	0.45

Discussion

Temperature Dependence. The temperature dependences of self-diffusion coefficient D and viscosity at zero shear rate η_0 are closely related properties in liquids. Theory suggests in particular that the product $(D/T)\eta_0$ should be rather insensitive to temperature.[3,18] The temperature dependence of viscosity for linear high molecular weight HPB melts (130–190 °C) is well described by the Arrhenius form[19]

$$\eta_0(T) = A \exp(E_v/RT) \qquad (18)$$

where the flow activation energy, $E_v = 30$ kJ/mol (7.2 kcal/mol), is independent of M. Arrhenius plots of D/T are shown in Figure 2 for two HPB samples. The temperature coefficient is independent of M, but $E_{D/T} \equiv -R \, \mathrm{d} \ln (D/T)/\mathrm{d}T^{-1}$ is 23 kJ/mol, a value which is significantly smaller than E_v. (The diffusional activation energy, $E_D \equiv -R \, \mathrm{d} \ln D/\mathrm{d}T^{-1} = 26$ kJ/mol, is larger but still less than E_v.) It turns out that a difference between E_v and $E_{D/T}$ can be explained by the recent theories of entangled-chain dynamics (Appendix A). The difference predicted for either linear polyethylene or HPB

$$\Delta E = E_v - E_{D/T} = 8 \text{ kJ/mol} \qquad (19)$$

agrees well with the observed $\Delta E = 30 - 23 = 7$ kJ/mol.

Klein has reported $E_D = 24$ kJ/mol for linear polyethylene,[20] which translates to $E_{D/T} = 21$ kJ/mol; for linear polyethylene, $E_v = 27$ kJ/mol,[21] giving $\Delta E = 6$ kJ/mol, again in reasonable accord with eq 19.

Molecular Weight Dependence. Values of D measured at 125 °C are plotted as a function of HPB molecular weight in Figure 3. A least-squares fit of the data gives

$$D = 0.25M^{-2} \qquad (20)$$

with an uncertainty of ±0.08 in the exponent. Thus, the

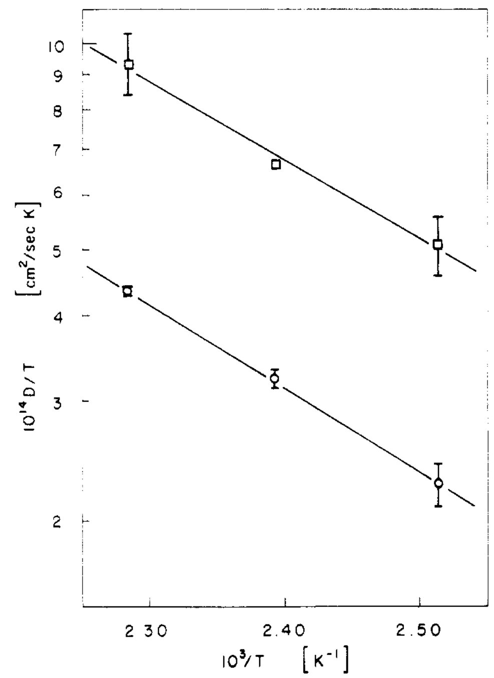

Figure 2. Arrhenius plots of D/T for HPB-101 (□) and HPB-153 (○).

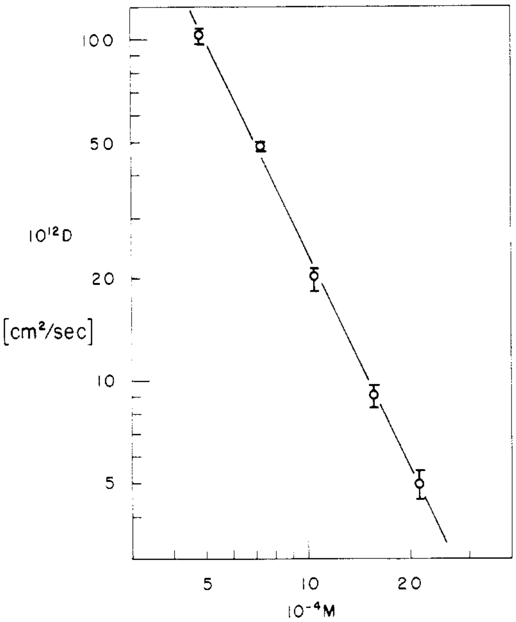

Figure 3. Diffusion coefficient vs. molecular weight for linear HPB samples at 125 °C. The solid line is the least-squares fit.

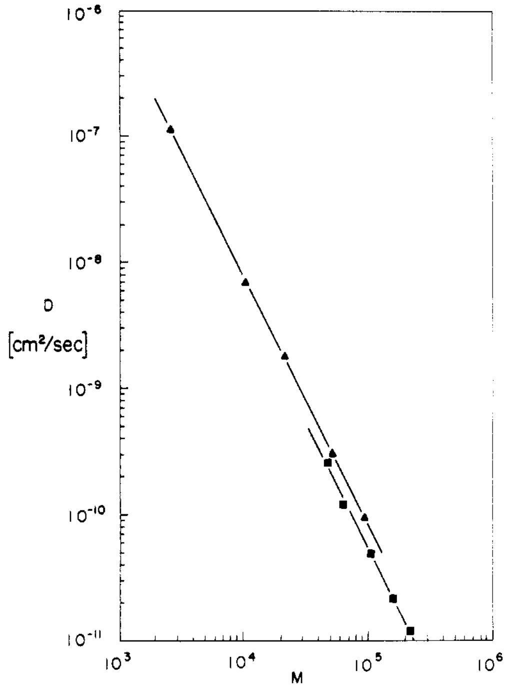

Figure 4. Diffusion coefficients of linear HPB at 176 °C. Symbols indicate results from ref 8 (▲) and this work (■).

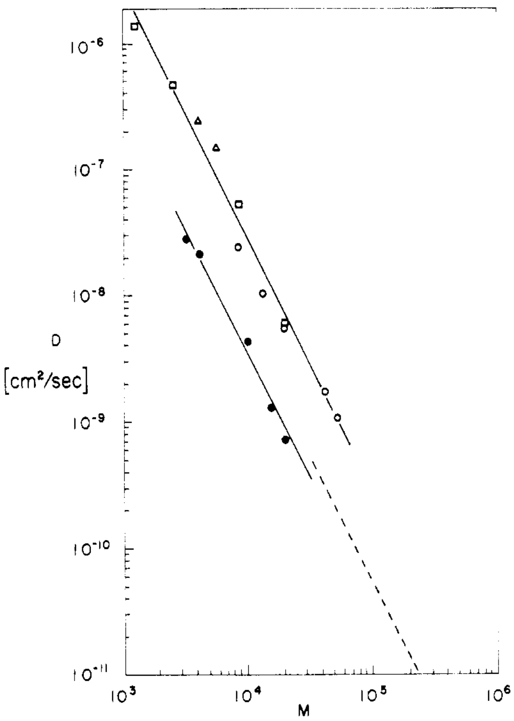

Figure 5. Diffusion coefficients of linear polyethylene at 176 °C. The dashed line represents the self-diffusion data for HPB in Figure 4 ($k_D = 0.58$). Symbols indicate results from ref 6 (●), ref 22 (△), ref 10 (○), and ref 9 (□).

chain length dependence is in excellent agreement with expectations for entangled linear chains (eq 1) and with other studies of HPB and linear PE.[6-10,22]

The present data were compared with other results on HPB and linear polyethylene at a common reference temperature of 176 °C. Adjustments from temperatures of measurement were made with the values of E_D reported in each investigation. Data for HPB are shown in Figure 4 and for linear polyethylene in Figure 5. All molecular weights have been converted to those for the protonated species.

Although prepared from precursor polybutadienes that were made under slightly different conditions, the HPB's used in the two studies represented in Figure 4 should be essentially identical in chemical microstructure. The conditions of diffusion differ slightly, however. The results of our study are self-diffusion coefficients, with HPB and DPB chains moving through an HPB/DPB matrix. In the Klein–Fletcher–Fetters study,[8] DPB chains move through a matrix of high molecular weight, linear polyethylene. This may account, at least in part, for the slight difference in magnitude of the diffusion coefficients: $k_D = 0.58$ and 0.82, respectively, at 176 °C. Nevertheless, the agreement is fairly good, considering the difference in the methods used.

The data of Klein and Briscoe[6] for diffusion of linear PE chains in a high molecular weight PE matrix are compared in Figure 5 with self-diffusion results for linear PE from three field gradient NMR studies.[9,10,22] The NMR results, although reasonably consistent among themselves, are clearly displaced from the diffusion-couple results of Klein and Briscoe. For the Klein–Briscoe studies, k_D = 0.32; for the NMR studies, k_D = 2.9, giving an average discrepancy of roughly a factor of 9.[9]

All the studies on PE (as opposed to HPB) must contend with a substantial molecular weight heterogeneity. The directness of the diffusion-couple experiment allowed Klein and Briscoe to take the distribution into account, at least approximately. The moderately good agreement in k_D between linear PE (0.32), nearly monodisperse HPB (0.82) obtained by the same method, and the present HPB results (0.58) suggests that any errors involved in dispersity corrections are not too serious. It is less clear how to handle polydispersity in the NMR experiment. That problem has been recognized and analysis has been started.[9] Moreover, what one measures there is the diffusion of nuclear spins, and it is possible that other mechanisms could compete with center of gravity motions of the chains carrying the nuclei. On the other hand, it would be surprising if such effects only increased the apparent magnitude of D without also influencing the M^{-2} chain length dependence. Perhaps some additional factor is operative in the NMR experiments, rescaling the apparent magnitude of D at all chain lengths. It would certainly be useful to find the reason for this discrepancy, since the NMR technique is otherwise a very attractive one for measurements of D greater than 10^{-10} cm^2/s.

The Doi–Edwards theory[3] provides the possibility of estimating the absolute value of D from viscoelastic measurements:[4]

$$k_D = DM^2 = \frac{G_N^\circ}{135}\frac{M_e^2 M_c}{\eta_0(M_c)}\frac{\langle r^2\rangle}{M} \tag{21}$$

where G_N° is the plateau modulus of the polymer, $M_e = \rho RT/G_N^\circ$ is the entanglement molecular weight, M_c is the characteristic molecular weight for viscosity ($\eta_0 \propto M^{3.4}$ for $M > M_c$), and $\langle r^2\rangle$ is the unperturbed mean-square end-to-end distance of the chains. Graessley[4] has used eq 21 to obtain k_D = 0.34 for PE at 176 °C; this value agrees rather well with the Klein–Briscoe data and with the results for HPB as well. NMR experiments give a value which is about 5 times larger than this estimate.

A similar situation can be seen to exist for polystyrene. Diffusion coefficients have been measured by NMR for narrow-distribution polystyrene in two studies.[9,10] Agreement between investigators is excellent, $D \propto M^{-2}$ is obtained, and the result at 230 °C is k_D = 1.0 cm^2/s. With values appropriate for polystyrene at 230 °C[18,23] ($G_N^\circ = 2.0 \times 10^6$ dyn/cm^2, M_e = 18 000, M_c = 35 000, $\langle r^2\rangle/M = 0.46 \times 10^{-16}$ cm^2, and $\eta_0(M_c) \approx 36$ P, the latter extrapolated to 230 °C from lower temperatures), eq 21 gives k_D = 0.22, resulting in a similar discrepancy with NMR results as found for polyethylene.

Scope of the Method. The layered film method has the advantage that rather small diffusion coefficients can be measured in conveniently short diffusion times ($D = 5 \times 10^{-12}$ cm^2/s for M = 214 000, obtained with less than 1 h of diffusion). Assuming that if one can prepare uniformly segregated structures with diffusion distance on the order of 1 μm, the technique should be applicable for D as small as 10^{-15} cm^2/s. As noted earlier, however, simplicity of analysis requires labeled and unlabeled chains of closely matched structures and uniformity of layer thickness.

The method is limited at low chain lengths by practical handling requirements. We have been unable to work below $M \sim 40\,000$ in the HPB/DPB system because the films are brittle at room temperature. Supporting the melted films would also pose a problem at lower molecular weights. We are, therefore, prevented from examining the curious behavior that short chains appear to conform to the M^{-2} law even when M is smaller than M_e.

To test the ability of the SANS method to measure very small D's we recently investigated a system of matched HPB/DPB three-arm star chains. The presence of the third arm is expected to hinder reptation and thus slow the diffusion considerably.[8,24] Our preliminary results for a three-arm star with total molecular weight M = 75 000 give $D \sim 1 \times 10^{-13}$ cm^2/s at 165 °C (L = 8 μm; t = 14 h). This is approximately 600 times smaller than D for a linear chain with the same total molecular weight. The viscosity of the star melt is larger,[25] but by only a factor of about 5. A more complete study of star-branched HPB is currently under way.

Acknowledgment. This research was supported by the Northwestern University Materials Research Center (NSF/MRL Program Grant DMR-82-16972), by a fellowship from IBM Corp. (C.R.B.), and by a grant from Exxon Chemical Co. We are indebted to Professor J. E. Hilliard for stimulating discussions during the early phases of this work.

Appendix. Temperature Coefficients of Diffusion and Viscosity

The temperature dependences of diffusion coefficient and viscosity reflect primarily the temperature coefficient of the molecular friction coefficient ζ:[18] $D \propto \zeta^{-1}$ and $\eta_0 \propto \zeta$. Differences in d ln D/dT and –d ln η_0/dT come from other temperature-dependent terms and are difficult to observe unless, as happens to be the case of polyethylene melts, the magnitude of d ln ζ/dT itself is rather small. The following analysis provides an estimate of this difference for entangled, linear-chain liquids.

According to the Doi–Edwards theory[3] the diffusion coefficient for entangled linear chains is given by

$$D = \frac{kT}{\zeta}\frac{1}{3N} \tag{A1}$$

where k is the Boltzmann constant, T is the temperature, and N is a parameter of the model, the number of steps in the primitive path of the chain. The same theory relates N to the plateau modulus G_N° of the polymer:

$$N = \frac{5}{4}\frac{G_N^\circ}{\nu kT} \tag{A2}$$

where ν is the number density of chains in the melt, a quantity which varies with temperature like the melt density ρ. The temperature dependence of G_N° can be estimated from a generalized correlation,[26] giving

$$G_N^\circ(T) \propto T\rho^a\langle r^2\rangle^{2a-3} \tag{A3}$$

where $a \sim 2.3$ for ethylenic polymers.[5] Combination of eq A1–A3 leads to

$$\frac{\mathrm{d}\ln(D/T)}{\mathrm{d}T} = -\frac{\mathrm{d}\ln\zeta}{\mathrm{d}T} - (1-a)\alpha + (3-2a)\kappa \tag{A4}$$

where α is the thermal expansion coefficient

$$\alpha = -\mathrm{d}\ln\rho/\mathrm{d}T \tag{A5}$$

and κ is the temperature coefficient of chain dimensions:

$$\kappa = \mathrm{d} \ln \langle r^2 \rangle / \mathrm{d}T \tag{A6}$$

Aside from numerical factors, the viscosity for entangled linear chain liquids can be written as[27]

$$\eta_0 = \zeta \langle r^2 \rangle \nu N^b \tag{A7}$$

where $b \sim 2.4$. Equations A2, A3, and A7 combine to give

$$\frac{\mathrm{d} \ln \eta_0}{\mathrm{d}T} = \frac{\mathrm{d} \ln \zeta}{\mathrm{d}T} - (1 + ab - b)\alpha + (1 + 2ab - 3b)\kappa \tag{A8}$$

When temperature dependence is expressed as an activation energy, $E_{D/T} \equiv -R \ \mathrm{d} \ln (D/T)/\mathrm{d}T^{-1}$ and $E_\zeta \equiv +R \ \mathrm{d} \ln \zeta/\mathrm{d}T^{-1}$, eq A4 becomes (for $a = 2.3$ and $b = 2.4$)

$$E_{D/T} = E_\zeta + RT_{\mathrm{av}}^2(1.3\alpha - 1.6\kappa) \tag{A9}$$

and eq A8, with $E_{\mathrm{v}} \equiv +R \ \mathrm{d} \ln \eta_0/\mathrm{d}T^{-1}$, becomes

$$E_{\mathrm{v}} = E_\zeta + RT_{\mathrm{av}}^2(4.12\alpha - 4.84\kappa) \tag{A10}$$

where T_{av} is some midrange (average) value of the experimental temperatures. For polyethylene melts[28,29]

$$\alpha = 0.68 \times 10^{-3} \ \mathrm{K}^{-1} \tag{A11}$$

$$\kappa = -1.15 \times 10^{-3} \ \mathrm{K}^{-1} \tag{A12}$$

which gives, for $T_{\mathrm{av}} = 418$ K (145 °C)

$$E_{\mathrm{v}} - E_{D/T} = +8.2 \ \mathrm{kJ/mol} \tag{A13}$$

and, with $E_{D/T} = 22.8$ kJ/mol

$$E_\zeta = 18.0 \ \mathrm{kJ/mol} \tag{A14}$$

References and Notes

(1) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(2) Klein, J. *Macromolecules* **1978**, *11*, 852.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802.
(4) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.
(5) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(6) Klein, J.; Briscoe, B. J. *Proc. R. Soc. London, Ser. A* **1979**, *365*, 53.
(7) Klein, J. *Philos. Mag. A* **1981**, *43*, 771.
(8) Klein, J.; Fletcher, D.; Fetters, L. J. *Nature (London)* **1983**, *304*, 526.
(9) Bachus, R.; Kimmich, R. *Polymer* **1983**, *24*, 964.
(10) Fleischer, G. *Polym. Bull.* **1983**, *9*, 152.
(11) Leger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732.
(12) Bartels, C.; Graessley, W. W.; Crist, B. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 495.
(13) Crist, B.; Graessley, W. W.; Wignall, G. D. *Polymer* **1982**, *23*, 1561.
(14) Boué, F.; Nierlich, M.; Leibler, L. *Polymer* **1982**, *23*, 29.
(15) Tanzer, J. D.; Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2708.
(16) Rachapady, H.; Smith, G. G.; Raju, V. R.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1211.
(17) Stamm, M.; Fischer, E. W.; Dettenmaier, M.; Convert, P. *Discuss. Faraday Soc.* **1979**, *68*, 263.
(18) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(19) Raju, V. R.; Rachapady, H.; Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1223.
(20) Klein, J.; Fletcher, D.; Fetters, L. J. *Faraday Symp. Chem. Soc.* **1983**, *No. 18*, 159.
(21) Mendelson, R. A.; Bowles, W. A.; Finger, F. L. *J. Polym. Sci., Part A-2* **1970**, *8*, 105.
(22) McCall, D. W.; Douglass, D. C.; Anderson, E. W. *J. Chem. Phys.* **1959**, *30*, 771.
(23) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959.
(24) de Gennes, P.-G. *J. Phys. (Paris)* **1975**, *36*, 1199.
(25) Graessley, W. W.; Raju, V. R. *J. Polym. Sci., Polym. Symp.* **1984**, *No. 71*, 77.
(26) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.
(27) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(28) Richardson, M. J.; Flory, P. J.; Jackson, J. B. *Polymer* **1963**, *4*, 221.
(29) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969.

Dimensions of Polymer Chains in the Semicrystalline Solid State

Joseph D. Tanzer, Craig R. Bartels, and Buckley Crist*

Materials Research Center, Northwestern University, Evanston, Illinois 60201

William W. Graessley

Exxon Research and Engineering Company, Corporate Research Laboratories, Annandale, New Jersey 08801.

Received May 23, 1984

ABSTRACT: Chain dimensions in the semicrystalline solid state have been investigated by small-angle neutron scattering (SANS) for a series of well-characterized hydrogenated polybutadienes. Labeled and unlabeled samples with matched chemical structures and narrow molecular weight distributions were used. The coherent SANS patterns for matched mixtures were found to fit the predicted shapes for monodisperse random coils. The data yielded values of radius of gyration R_g which also obeyed the random coil model: $R_g \propto M^{1/2}$ for the linear chains and $(R_g^2)_B/(R_g^2)_L = 0.80$ for a three-arm star, in good agreement with the theoretical value of $^7/_9 = 0.78$. Chain dimensions in the semicrystalline solid state were slightly larger (~13%) than those for linear polyethylene at the Θ condition.

Introduction

Small-angle neutron scattering (SANS) is now widely applied to obtain information on the conformation of chains in bulk polymers. In particular, the SANS technique has been used to investigate chain dimensions in the semicrystalline solid state for polyethylene,[1-3] isotactic polypropylene,[4] isotactic polystyrene,[5] and hydrogenated polybutadiene.[6] In this paper more extensive data are reported for hydrogenated polybutadiene, a model material that is equivalent in composition to an ethylene–1-butene copolymer (~4 mol % 1-butene or ~18 ethyl branches/1000 skeletal carbon atoms) with a uniform chemical microstructure and narrow molecular weight distribution. The polymers were prepared by anionic polymerization of butadiene, followed by saturation of the double bonds, either with H_2 to give hydrogenated polybutadiene (HPB)

0024-9297/84/2217-2708$01.50/0