Viscosity and Self-Diffusion Coefficient of Hydrogenated Polybutadiene

Dale S. Pearson,[†] Lewis J. Fetters, and William W. Graessley[*,‡]

Exxon Research and Engineering Company, Annandale, New Jersey 08801

Gary Ver Strate

Exxon Chemical Company, Linden, New Jersey 07036

Ernst von Meerwall

Department of Physics, University of Akron, Akron, Ohio 44325

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ABSTRACT: The self-diffusion coefficient, D, and zero-shear rate viscosity, η, were measured in the melt state for a series of nearly monodisperse model polyethylenes ranging in molecular weight from 10^3 to 10^6. The samples were prepared by hydrogenating anionically polymerized polybutadienes and contain ~2 ethyl branches/100 CH_2 units. The results were compared with molecular theory, both as the product ηD, whose value is independent of the monomeric friction factor, and as individual values of η and D after correcting to a constant friction factor. At low molecular weights ηD and the corrected η and D separately agree very well with predictions based on the Rouse model. At higher molecular weights, where chain entanglement becomes important, the data clearly show that relaxation mechanisms beyond those considered in the Doi–Edwards tube model make significant contributions to both self-diffusion and viscosity. Comparisons with data for polystyrene and hydrogenated polyisoprene suggest that these departures are universal.

Introduction

Some years ago we reported an extensive study of both the zero-shear viscosity η and self-diffusion coefficient D of linear polyethylene (PE) in the melt state.[1] We determined η and D from the melting point of each sample up to approximately 225 °C for 15 samples beginning with the normal alkane $C_{16}H_{34}$ ($M = 226$) and ending with a high molecular weight polymer ($M_w = 120\,000$). One reason for conducting that research was to test molecular theories of polymer melt dynamics. The broad range of molecular weights covered allowed examination of models appropriate for both low molecular weight (unentangled) and high molecular weight (entangled) polymers. For the former we considered the Rouse model which predicts that the viscosity and diffusion coefficient are given by[1]

$$D_{\text{Rouse}} = kTM_0/\zeta M \tag{1}$$

and

$$\eta_{\text{Rouse}} = \rho\zeta N_{\text{Av}}\langle R_G^2\rangle/6m_0 \tag{2}$$

and for the latter we investigated the reptation model which predicts[1]

$$D_{\text{rep}} = \frac{4}{15}D_{\text{Rouse}}\frac{M_e}{M} \tag{3}$$

and

$$\eta_{\text{rep}} = \frac{15}{4}\eta_{\text{Rouse}}\left(\frac{M}{M_e}\right)^2 \tag{4}$$

In these equations m_0 is the monomer molecular weight, ζ is the monomeric friction factor, M is the polymer molecular weight, ρ is the density, N_{Av} is Avogadro's number, and $\langle R_G^2\rangle$ is the mean-square radius of gyration. The molecular weight between entanglements, M_e, comes from the Ferry formula[2]

$$M_e \equiv \rho RT/G_N \tag{5}$$

where G_N is the plateau modulus.

A question that always arises in comparing experimental data with theory is how to handle the monomeric friction factor, ζ.[3] At present ζ cannot be obtained by independent experimental measurements, nor can it be calculated theoretically. However, in the above theories and others to be described below, the viscosity is proportional to the friction factor and the diffusion coefficient is inversely proportional to it, so the quantity ηD is independent of ζ and can therefore provide a quantitative test of theory. For linear molecules at least, the value of ηD is expected to be almost constant for short molecules, below the entanglement threshold, and then to increase with molecular weight beyond. This is what we found in our earlier polyethylene study.[1]

However, the method used for measuring the diffusion coefficient was pulsed field gradient (PFG) NMR[4] which is very sensitive to the short molecules in the sample.[1] The viscosity measurements, on the other hand, are sensitive to the long molecules in the sample. Because the molecular weight distribution of the samples was not accurately known and also because the effect of distribution on η and D are in general unknown, comparison of ηD with molecular theories was less certain than desired.

In the present study we minimized the polydispersity problem by using polymers prepared by anionically polymerizing butadiene.[5] These materials were then hydrogenated, yielding model copolymers of ethylene and butene-1 with about 2 ethyl branches/100 carbon atoms from the 8% 1,2 enchainment of the butadiene. Hence, the abbreviation PEB-2 is used. Polymers prepared in the way have a very narrow molecular weight distribution ($M_w/M_n \le 1.1$), and the need to correct for polydispersity is much reduced. These new data also extend the molecular weight range of the previous study by approximately a factor of 4.

[†] Department of Chemical and Nuclear Engineering and Materials Department, University of California, Santa Barbara, CA 93106. Deceased October 29, 1993.

[‡] Present address: Department of Chemical Engineering, Princeton University, Princeton, NJ 08540.

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Table 1. Molecular Characteristics of Hydrogenated Polybutadiene (PEB-2)

sample no.	ref	polybutadiene $M_w \times 10^{-3}$ (SEC)	expected PEB-2 $M_w \times 10^{-3}$	PEB-2 $M_w \times 10^{-3}$ (SEC)	PEB-2 $M_w \times 10^{-3}$ (LS)	mean of columns 4–6 $M_w \times 10^{-3}$ (av)	M_w/M_n (SEC)
1	[a]	0.93	0.96	0.96	1.22	1.05	1.07
2	[a]	2.12	2.20	2.35	2.97	2.51	1.08
3	[a]	3.73	3.89	3.79	4.37	4.02	1.04
4	[a]	4.43	4.59	4.85	4.69	4.71	1.07
5	[a]	6.95	7.21	7.48	6.42	7.04	1.05
6	[a]	10.5	10.9	10.8	10.1	10.6	1.05
7	[a]	20.0	20.7	22.9	23.7	22.4	1.02
8	[a]	48.0	49.8	47.6	45.8	47.7	1.06
9	[a]	58.0	60.1			60.1	
10	[a]	70.9	73.5	75.7	71.5	73.6	1.04
11	6	46.3	48	44.0	46.2	46.1	
12	6	70.3	73	69.7	70.2	80.0	
13	6	101.3	105	104	101	103	
14	6	153.3	159	158	153	157	
15	6	206.3	214	210	206	210	
16	11	427.3	443			443	
17	12			1.76		1.76	1.06
18	12			3.27		3.27	1.04
19	12			12.0		12.0	1.05
20	12			45.2		45.2	1.03
21	12			146		146	1.03
22	12			304		304	1.03
23	[a]	130	135	115	135	128	
24	[a]	458	475			475	
25	[a]	571	592	500	490	527	
26	[a]	925	959			959	

[a] This work.

Although the PFG technique for measuring diffusion coefficients is conceptually simple, there have been concerns that it does not measure the true diffusion coefficient.[6] This issue is addressed by comparing our results with self-diffusion coefficients obtained by other methods.

The same samples were used in rheological tests for measuring the viscosity, and the combined results were used to reexamine the behavior of ηD. The viscosity was also compared with the properties of linear polyethylene. Although the chemical structures of hydrogenated polybutadiene and linear polyethylene are slightly different, we find their viscosities at the same molecular weight to be essentially the same. This result provides further evidence that narrow molecular weight distribution hydrogenated polybutadiene samples are useful model materials for studying the liquid-state properties of polyethylene.[7]

Finally, our previous results on the temperature dependence of PE[1] provide the information needed to adjust the PEB-2 data to a constant friction factor. Using these corrected data, we show that additional molecular relaxation processes beyond those in the original reptation model have a large effect on D and η, especially near and even somewhat beyond the crossover from entangled to unentangled behavior.[8] Our findings are reasonably consistent with studies on other polymers and suggest that the chain-length dependence of the self-diffusion coefficient and viscosity is universal.

Experimental Procedures

Polymer Synthesis. All but 2 of the 14 polybutadiene precursor polymers used in this study (samples 1–10 and 23–26) were prepared by anionic polymerization techniques that have been described previously in the literature.[5] Samples 1 and 8 were obtained from M. Ambler at Goodyear Tire and Rubber Co. and were made there using techniques similar to our own. All samples were hydrogenated in a pressurized reactor containing palladium on calcium carbonate as the catalyst, a method that we and others have used previously.[9,10]

Molecular Characterization. The polybutadiene precursors were characterized with a Waters 150C size-exclusion chromatograph (SEC) using tetrahydrofuran at 25 °C as the elution solvent. Number- and weight-average molecular weights, M_n and M_w, were determined using calibration data and methods described in a previous study.[5] The hydrogenated polybutadiene samples were characterized in a similar way in another Waters 150C chromatograph, operating at 135 °C with trichlorobenzene as the elution solvent. That instrument was equipped with both a differential refractometer and a small-angle light scattering cell (Chromatix KMX-6), and the data from the two detectors were combined to provide M_n and M_w. Calibration data were obtained from normal alkanes and polyethylene samples as reported in ref 1.

The characterization results are summarized in Table 1. They confirm that hydrogenation does not change the molecular weight or molecular weight distribution. The polydispersity index M_w/M_n was between 1.02 and 1.08 in all cases. Also included in Table 1 are the molecular weights of additional PEB-2 samples prepared and characterized in similar ways by other groups.[6,11,12] Columns 1 and 2 label the samples and identify their sources. Column 3 is the molecular weight of the polybutadiene precursor, and column 4 contains the expected molecular weight of the hydrogenated polymer, obtained by multiplying the precursor molecular weight by 56/54 to account for the expected increase with saturation. Columns 5 and 6 contain M_w obtained for PEB-2 samples using the SEC calibration and the light scattering detector, respectively. Column 7 is the average of columns 4–6 and is the value of M_w used to correlate the diffusion and viscosity data described below. Column 8 is M_w/M_n from SEC measurements on the PEB-2 samples.

Diffusion Measurements. Values of D for samples 1–10 in Table 1[13] were determined by PFG-NMR methods. Because the equipment and experimental technique have been described in earlier publications,[14,15] only a brief review is given here. A pulse gradient of duration δ and magnitude G is applied during a conventional 90–180° radio-frequency pulse sequence.[4] Under these conditions, the spin echo is attenuated by spin–spin relaxation as well as molecular diffusion. The gradient G was typically on the order of 250 Gs/cm, and the time between pulses Δ was 25–500 ms. The ratio of the echo height with and without the field gradient pulses is given by[4]

$$R = \exp[-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D] \qquad (6)$$

where $\gamma = 2.68 \times 10^4$ rad/Gs/s is the gyromagnetic ratio of protons.[4] The value of D is obtained from the slope of a plot of ln R vs $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$.

Table 2. Diffusion Coefficient and Viscosity of Hydrogenated Polybutadiene at 175 °C[a]

sample	ref	$M_w \times 10^{-3}$	diff coeff (cm^2/s)	viscosity (P)	$\zeta(\infty,175)/\zeta(M,175)$[d]
1	*b*	1.05	2×10^{-6}	6.4×10^{-2}	1.96
2	*b*	2.51	4×10^{-7}	2.53×10^{-1}	1.43
3	*b*	4.02	1.4×10^{-7}	7.05×10^{-1}	1.22
4	*b*	4.71	7.6×10^{-8}	1.34×10^{0}	1.19
5	*b*	7.04	2.6×10^{-8}	4.68×10^{0}	1.12
6	*b*	10.6	9.6×10^{-9}	1.83×10^{1}	1.08
7	*b*	22.4	1.7×10^{-9}	2.3×10^{2}	1.04
8	*b*	47.7	4.1×10^{-10}	3.8×10^{3}	1.02
9	*b*	60.1	2.0×10^{-10}	1.02×10^{4}	1.01
10	*b*	73.6	1.1×10^{-10}	1.46×10^{4}	1.01
11	6	46.1	2.5×10^{-10}	2.71×10^{3}	1.02
12	6	80.0	1.2×10^{-10}	(2.07×10^{4})[c]	1.01
13	6	103	4.8×10^{-11}	5.36×10^{4}	1.01
14	6	157	2.2×10^{-11}	1.73×10^{5}	1.01
15	6	210	1.2×10^{-11}	5.98×10^{5}	1.00
16	11	443	3.0×10^{-12}	7.25×10^{6}	1.00
17	12	1.76	6.7×10^{-7}		1.54
18	12	3.27	2.2×10^{-7}		1.27
19	12	12.0	4.2×10^{-9}	(3.1×10^{1})[c]	1.07
20	12	45.2	2.2×10^{-10}	(2.9×10^{3})[c]	1.02
21	12	146	2.8×10^{-11}	(1.6×10^{5})[c]	1.01
22	12	304	6.3×10^{-12}	(2.0×10^{6})[c]	1.00
23	*b*	128		1.52×10^{5}	1.01
24	*b*	475		7.1×10^{6}	1.00
25	*b*	527		1.6×10^{7}	1.00
26	*b*	959		8.4×10^{7}	1.00

[a] Diffusion coefficients and viscosities from refs 6, 11, and 12 were corrected to 175 °C using information in Appendix B. [b] This work. [c] Viscosities in parentheses were interpolated. [d] Dividing the diffusion coefficient and multiplying the viscosity by this ratio converts them to the constant friction factor results shown in Figures 4–6.

Except for the first three samples, it was found that the diffusion coefficient depended on the diffusion time Δ. Although such behavior is possible if Δ is on the order of $\langle R_G^2 \rangle/\tau$ where τ is the longest molecular relaxation time, it was unexpected for the molecular weights and values of Δ we used (see Appendix A). Furthermore, the change of D with Δ was larger than one would predict from a reasonable molecular argument. The problem was resolved when it was shown that such behavior was caused by residual field gradients that remain after the pulses in our experiment.[16]

This effect was eliminated by continuing the experiments to larger values of Δ until the measured value of D was independent of the diffusion time. In some cases this required using very large values of Δ (≈500 ms) and the stimulated echo (three-pulse) sequence[17] to avoid excessive damping of the signal from spin–spin relaxation. Only the constant values of D obtained in this way are reported in Table 2.

Viscosity Measurements. The viscosities of samples 1–6 were measured in calibrated glass capillary viscometers (Cannon Instrument Co.). The kinematic viscosities so obtained were converted to absolute viscosities by multiplying by the density, which we assumed to be equal to that of PE at ther same temperature and molecular weight.[1] The viscosities of samples 7–10 and 23–26[13] were determined with a rheometer (Rheometrics Model System 4). The dynamic viscosity, $\eta^*(\omega)$, was measured as a function of frequency using parallel disk fixtures. The constant value attained at low frequency is the value of η shown in Table 2.

Results

Figure 1 shows the molecular weight dependence of the self-diffusion coefficients measured by PFG-NMR at 175 °C. The molecular weights range from about 1000 to 75 000.

Three other groups[6,11,12] have reported self-diffusion measurements on hydrogenated polybutadiene. Their materials were prepared in the same way as ours: anionic polymerization of butadiene followed by saturation of the polymer with hydrogen or deuterium in the presence of palladium on calcium carbonate. The molecular characteristics and the values of D and η interpolated to 175 °C are shown in Tables 1 and 2, respectively.

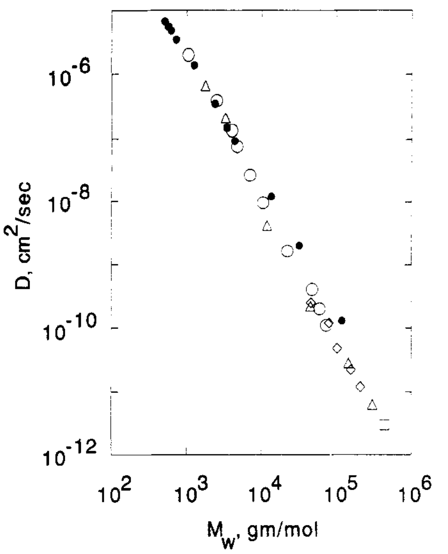

Figure 1. Self-diffusion coefficients of hydrogenated polybutadiene (PEB-2) as a function of molecular weight at 175 °C: (○) by PFG-NMR (this work); (△) by scanning infrared microscopy;[12] (◇) by neutron scattering from protonated and deuterated layers;[6] (□) by forward recoil spectrometry.[11] The results marked by ● are from our previous study on polyethylene. The three highest molecular weight polyethylene samples are the ones most effected by polydispersity and hence are not expected to correlate with the weight-average molecular weight (see ref 1).

Bartels, Crist, and Graessley[6] made composites consisting of alternating layers of hydrogenated polybutadiene and partially deuterated polybutadiene. Five matched pairs of samples with molecular weights from about 50 000 to 200 000 were used. By monitoring the rate of increase of coherent neutron scattering from the layers as they interdiffuse, they were able to obtain the self-diffusion coefficient. In this way, values of D an order of magnitude smaller than ours ($D \cong 10^{-11}$ cm^2/s) were determined. The viscosities of four of these samples were also measured.

Crist, Green, Jones, and Kramer[11] evaluated D for an additional matched pair by forward recoil spectrometry.[18] Their sample had a molecular weight of 443 000 and further extended the range of diffusion coefficients to 3×10^{-12} cm^2/s.

von Seggern, Klotz, and Cantow[12] also measured the diffusion coefficient of matched hydrogenated and partially deuterated polybutadienes using a scanning infrared microscope to follow the concentration profile at the interface between diffusion couples. Their molecular weight ranged from about 1000 to 300 000 and diffusion coefficients from $\sim 6 \times 10^{-6}$ to $\sim 6 \times 10^{-12}$ cm^2/s.

All these diffusion data are included with our own in Figure 1. The excellent agreement among these four distinct methods for measuring D is reassuring. It also clearly demonstrates that the self-diffusion coefficients of high molecular weight polymers determined by PFG-NMR agree with those obtained by other techniques.

The polyethylene diffusion data from our previous study[1] are also shown in Figure 1. When data are compared at constant M_w, the more polydisperse high molecular weight polyethylene samples have larger diffusion coefficients. This natural consequence of polydispersity is explained in the appendix of ref 1.

Bartels et al.[6] found that, for high molecular weight samples studied by the neutron scattering method, the product DM^2 attains a constant value of 0.58 cm^2/s at 175 °C in close agreement with results on linear polyethylene.[19,20] However, as the molecular weight decreases, the value of DM^2 rises above this asymptotic value and then

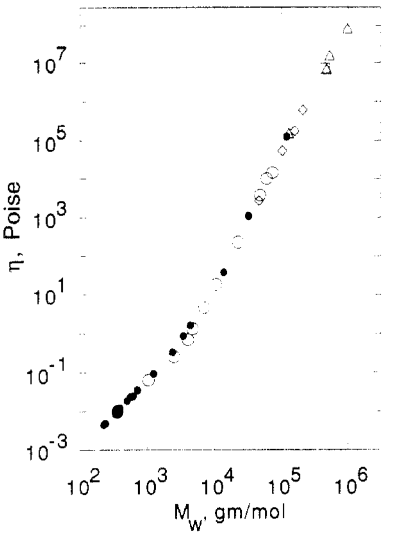

Figure 2. Viscosities of hydrogenated polybutadiene (PEB-2) as a function of molecular weight at 175 °C: (○) samples used for PFG-NMR measurements (this study); (◇) samples used for neutron scattering measurements;[6] (□) sample used for forward recoil spectrometry study;[11] (△) additional samples not used in diffusion studies. The results marked by ● are from our previous study on polyethylene.

eventually falls below it. Further discussion of diffusion measurements in this lower molecular weight region will be deferred until we apply our method for correcting these data to a constant monomeric friction factor.

Klein, Fletcher, and Fetters[21] have measured the tracer diffusion coefficient of hydrogenated polybutadiene diffusing in a high molecular weight linear polyethylene matrix. Although not a true self-diffusion coefficient, and therefore not shown in Figure 1, the results are consistent with what has been shown before for polystyrene:[22] tracer diffusion and self-diffusion coefficients are very similar at high molecular weights.

The molecular weight dependence of viscosity at 175 °C is shown in Figure 2. Polyethylene viscosity data from our previous study[1] are also shown. Unlike the diffusion coefficients, the viscosities for PE and PEB-2 at the same M_w are essentially identical at 175 °C over the entire range of molecular weight.

Discussion

Figure 3a shows the product of the viscosity and diffusion coefficient, ηD, as a function of molecular weight for all of the polymer samples we studied. Also included are the data of Bartels et al.[6] Crist et al.,[11] and von Seggern et al.[12] Viscosities for a few of these latter materials (samples 12 and 19–22) were not measured, so values were estimated by interpolating the data in Figure 2 to the required molecular weights.

As explained in the Introduction, the value of ηD can be unambiguously compared with molecular theory because, in contrast to η or D separately, this product is independent of the unknown monomeric friction factor. The Rouse model is presumed appropriate for describing viscous and diffusive behavior for low molecular weight polymers. Hence, from eqs 1 and 2,

$$(\eta D)_{\mathrm{Rouse}} = \rho RT\langle R_G^{\,2}\rangle/6M \qquad (7)$$

The melt density ρ at 175 °C is 0.806 g cm^{-3}. The quantity $\langle R_G^2\rangle/M$ has been determined for PEB-2 melts over a range of temperatures by Horton et al.[23] and Boothroyd et al.[24] and is essentially constant for the molecular weights employed in this study. Using their average value of 1.97 × 10^{-17} cm^2 mol/g, we calculate $(\eta D)_{\mathrm{Rouse}} = 9.38 \times 10^{-8}$ dyn at 175 °C.

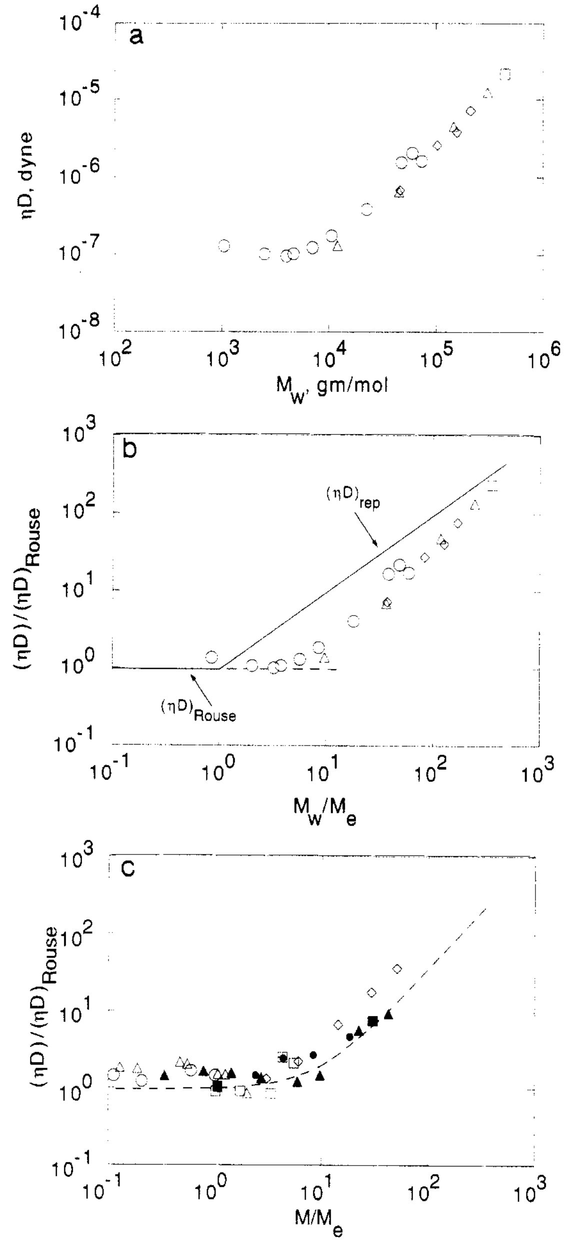

Figure 3. Product of ηD as a function of molecular weight for PEB-2 samples: (○) samples from this study; (◇) samples from ref 6; (△) samples from ref 12; (□) sample from ref 11. (b) Product of ηD made dimensionless by $(\eta D)_{\mathrm{Rouse}}$ as a function of M/M_e for PEB-2 samples: (○) samples from this study; (◇) samples from ref 6; (△) samples from ref 12; (□) sample from ref 11. The horizontal line indicates the prediction of the Rouse model, and the slanted line indicates the prediction of the original reptation model. (c) Product of ηD made dimensionless by $(\eta D)_{\mathrm{Rouse}}$ as a function of M/M_e for polystyrene melts and solutions: (⊞) sample from ref 26; (△) samples from ref 27; (○) samples from ref 28; (□) samples from ref 29; (◇) samples from ref 30; (●) samples from ref 33 (40%); (▲) samples from ref 34 (13%); (■) samples from ref 34 (18%). The dashed line represents the behavior of the PEB-2 data from Figure 3b (see eqs 20 and 21).

The reptation model is intended to apply for high molecular weight entangled polymers, and from eqs 1–4,

$$(\eta D)_{\mathrm{rep}} = \rho RT\langle R_G^{\,2}\rangle/6M_e \qquad (8a)$$

or

$$(\eta D)_{\mathrm{rep}} = (\eta D)_{\mathrm{Rouse}}(M/M_e) \qquad (8b)$$

Thus, $(\eta D)_{\mathrm{rep}}$ is equal to $(\eta D)_{\mathrm{Rouse}}$ at $M = M_e$ and then increases linearly with M beyond M_e. After dividing all experimental ηD values by $(\eta D)_{\mathrm{Rouse}}$ from eq 7, the data of Figure 3a are shown again in Figure 3b as a function of M/M_e. A value of $M_e = 1240$, obtained from eq 5 with G_N

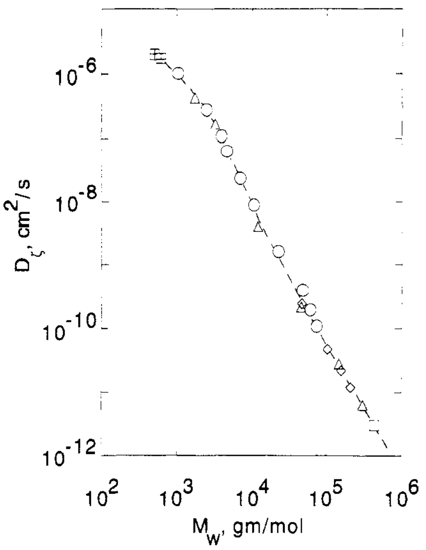

Figure 4. Diffusion coefficients corrected to constant friction factor D_ζ as a function of molecular weight: (○) samples from this study; (◇) samples from ref 6; (△) samples from ref 12; (□) sample from ref 11; (⊞) monodisperse C_{36} and C_{44} normal alkanes. The dashed line is a fit to eq 13 using parameters in eqs 14 and 15.

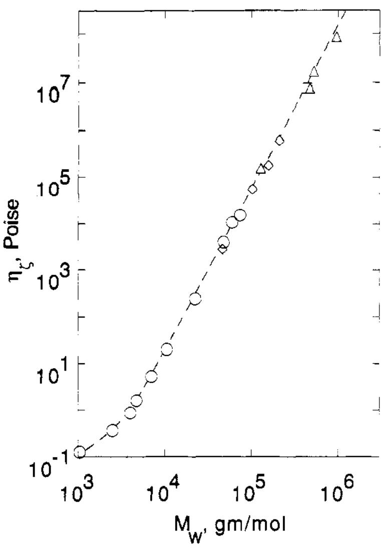

Figure 5. Viscosities corrected to constant friction factor η_ζ as a function of molecular weight: (○,△) samples from this study; (◇) samples from ref 6; (□) sample from ref 11. The dashed line is a fit to eq 18 using parameters in eq 19.

$= 2.3 \times 10^7$ for the plateau modulus for PEB-2,[25] was used. The horizontal line representing the Rouse model is in good agreement with the low molecular weight data. Another line representing the reptation model (eq 8b), having a log–log slope of 1 and intersecting the Rouse model line at $M/M_e = 1$, is also shown. Note for later discussion that all of the experimental results for ηD lie below this line but are approaching it from below as molecular weight increases.

Data for nearly monodisperse samples of hydrogenated polyisoprene (PEP) are also consistent with the PEB-2 results (see Appendix C). The molecular weight range is more limited for PEP, but the data for the two polymers superpose almost perfectly.

Similar results on ηD for polystyrene are shown in Figure 3c. Self-diffusion coefficients for polystyrene melts are available from various sources.[26–30] Values of the viscosities at the same molecular weight were interpolated from the data of Allen and Fox[31] and then corrected to the temperature of the diffusion measurement using information given by them. Viscosities corresponding to the highest molecular weight samples in ref 30 were obtained from data given by Plazek and O'Rourke.[32] Self-diffusion coefficients and viscosities on concentrated polystyrene solutions were determined by Nemoto et al.[33,34] All values of ηD obtained from these sources were normalized by $(\eta D)_{\mathrm{Rouse}}$ from eq 7.[35] The trend of values for PEB-2 (Figure 3b) is shown as a dashed line in Figure 3c. It is clear that the results for both polymers are rather similar, suggesting that the departures of the ηD predictions from the tube model are universal.

The original reptation model is based on a single process of relaxation: each polymer molecule, constrained by uncrossability of neighboring molecules, moves and changes its configuration by diffusing along the one-dimensional tube that is defined by its own average contour. Two other mechanisms, constraint release and tube length fluctuations, can also contribute and thereby increase the rate of diffusion and decrease the viscosity relative to the pure reptation prediction. Both have been extensively described elsewhere,[36–47] so we provide only a brief summary. Constraint release allows a molecule to move and relax because the surrounding molecules are in fact mobile and diffuse away. Tube length fluctuations permit additional rapid relaxation to occur by disentanglement near the chain ends. Both mechanisms are expected to be important near the crossover from unentangled to entangled behavior.

To proceed further and evaluate these additional effects on diffusion and viscosity, it is necessary first to correct the data to a constant friction factor. The procedure and data needed for this were given in our previous study of the temperature dependence of the viscosity of linear polyethylene.[1] The same method was applied to the PEB-2 data, details of which can be found in Appendix B. The diffusion and viscosity data shown in Figures 1 and 2 are replotted in Figures 4 and 5 after making these corrections (see Table 2).

The product ηD agrees closely with the Rouse model prediction at low molecular weights, and, according to the model, the corrected diffusion coefficient in this region (eq 1) is expected to behave as

$$D_{\mathrm{Rouse}} = D_0/M \tag{9}$$

where D_0 is a molecular weight independent factor, kTm_0/ζ. At the highest molecular weights, the diffusion coefficient is proportional to M^{-2} and according to the reptation model:[1]

$$D_{\mathrm{rep}} = D_1/M^2 \tag{10}$$

where the constant D_1 is also a molecular weight independent factor and from eqs 1–3 is equal to $4D_0M_e/15$.

For entangled polymers near M_e (say, $M \leq 10M_e$), it has been shown in experiments on polystyrene[22] and hydrogenated polybutadiene[12] that the process of constraint release contributes to self-diffusion with the following molecular weight dependence

$$D_{\mathrm{cr}} = \alpha D_{\mathrm{rep}}(M_e/M)^2 \tag{11}$$

where α is a parameter related to the ratio of the reptation time, τ_{rep}, to the constraint release time, τ_{cr}, for a tube segment. Data in refs 12 and 22 show that α is in the range of 10–20. Fluctuations in the primitive path length would not be expected to have a large effect on the center of mass motion. Hence, our analysis of D does not consider the effect of fluctuations.[48]

The processes of reptation and constraint release are assumed to be uncorrelated and to act in parallel, so their contributions should be added to obtain an expression for the diffusion coefficient of entangled polymers:

$$D_{\text{ent}} = D_{\text{rep}} + D_{\text{cr}} = D_{\text{rep}}[1 + \alpha(M_{\text{e}}/M)^2] \qquad (12)$$

In contrast to this, unrestricted Rouse-like motion and reptation are competing mechanisms that occur at one another's expense. The overall diffusion coefficient in the crossover from unentangled to entangled behavior can therefore be estimated by adding diffusive resistances, which are proportional to the reciprocals of their respective diffusion coefficients:

$$1/D = 1/D_{\text{Rouse}} + 1/D_{\text{ent}} \qquad (13a)$$

or

$$D = D_{\text{Rouse}}D_{\text{ent}}/(D_{\text{Rouse}} + D_{\text{ent}}) \qquad (13b)$$

The corrected diffusion data for PEB-2, together with the assumption of a constant percentage uncertainty in D, were used with eq 13 in a nonlinear least-squares regression algorithm to determine the three parameters, D_0, D_1, and α. The results are (175 °C):

$$D_{\text{Rouse}} = D_0/M = (1.00 \pm 0.084) \times 10^{-3}/M \text{ cm}^2/\text{s} \qquad (14)$$

$$D_{\text{rep}} = D_1/M^2 = (0.59 \pm 0.03)/M^2 \text{ cm}^2/\text{s} \qquad (15a)$$

and

$$\alpha = 39.1 \pm 7.7 \qquad (15b)$$

This information, when substituted in eq 13, produces the dashed line in Figure 4.

The value of D_0, when combined with the viscosity data described below, agrees with the Rouse model. The value of $D_1 = 0.59$ is almost the same as the 0.58 found by Bartels et al.[6] using the data from samples 11–15 and the value 0.54 found by von Seggern et al. for samples 17–22. These values, however, are somewhat larger than the reptation model prediction of $D_1 = 4D_0M_{\text{e}}/15$ which is equal to 0.34.

The value of the constraint release parameter α is bigger than the value of $\alpha = 11$ found by Green and Kramer[22] for polystyrene and the value $\alpha = 9.7$ found by von Seggern et al.[12] This may result from the fact that the quality of the fit is not affected greatly by the magnitude of α. The correlation coefficient from our fit is 0.9993 and only decreases to 0.9988 for $\alpha = 20$ or 0.9974 for $\alpha = 10$.

The viscosity data corrected to a constant friction factor are shown in Figure 5. Because the ηD products agree so well with the Rouse theory at low molecular weights, we expect the viscosity in this region to be given by

$$\eta_{\text{Rouse}} = \frac{\rho RT}{6}\frac{\langle R_{\text{G}}^2\rangle}{M}\frac{1}{D_{\text{Rouse}}} \equiv KM \qquad (16)$$

At high molecular weights the following empirical power law has been found to describe the data well[3]

$$\eta_{\text{ent}} = KM(M/M_{\text{c}})^b \qquad (17)$$

The exponent b is normally around of 2.4 and $M_{\text{c}} \cong 2\text{–}3M_{\text{e}}$. From the reasoning used to develop eq 13, the resistances from these two mechanisms should be roughly additive, and the result of that has been shown to describe successfully both regimes and the crossover:[5]

$$\eta = \eta_{\text{Rouse}} + \eta_{\text{ent}} = KM[1 + (M/M_{\text{c}})^b] \qquad (18)$$

When the data of Figure 5, and the assumption of constant percent uncertainty in η, are used to determine the three parameters in eq 18, the results are (175 °C):

$$\eta_{\text{Rouse}} = KM = (9.59 \pm 1.6) \times 10^{-5}M \text{ P} \qquad (19)$$

and

$$b = 2.42 \pm 0.03$$
$$M_{\text{c}} = 3180 \pm 320 \cong 2.5M_{\text{e}}$$

Equations 14 and 19 can be used to test if the product of D_{Rouse} and η_{Rouse} from fitting the experimental data is consistent with the value calculated from eq 7. The agreement is good: $(\eta D)_{\text{Rouse,exp}}/(\eta D)_{\text{Rouse,calc}} = 1.02$.

Thus relationships, like eqs 13 and 19, can accurately describe diffusion and viscosity data in the unentangled and entangled regions and also in the crossover between the two. The behavior in Figure 3b suggests that a similar relationship should be valid for their product. We find that the following expression describes the results rather well:

$$\eta D = (\eta D)_{\text{Rouse}} + (\eta D)_{\text{ent}} = (\eta D)_{\text{Rouse}}[1 + (M/M_{\text{c}''})^d] \qquad (20)$$

where $M_{\text{c}''}$ locates the transition and d is an exponent on the order of 1.4 as suggested by eqs 13 and 19. When the ηD data in Figure 3b are used in a nonlinear regression algorithm, the following parameters are found:

$$M_{\text{c}''} = (9.5 \pm 1.1)M_{\text{e}} \qquad (21a)$$

and

$$d = 1.5 \pm 0.1 \qquad (21b)$$

The usefulness of this result extends beyond its ability merely to describe experimental data. It also provides a method to estimate the diffusion coefficient by making a usually simpler measurement of the viscosity. From Figure 3c, this same formula should be applicable to other polymers, too. Information on $\langle R_{\text{G}}^2\rangle/M$ for calculating the quantity $(\eta D)_{\text{Rouse}}$ with eq 7 and on M_{e} is needed, but it is readily available in the literature for many common polymer species.[2] Although we have suggested that eqs 20 and 21 are of general value, it must be cautioned that they apply only to linear monodisperse polymers, and corrections for polydispersity must be developed separately. Also, theory suggests that the exponent d should eventually decrease to a value of 1, so our correlation may not apply for values of M/M_{e} beyond 350 which is the limit of our study.

Doi was the first to suggest that fluctuations in the primitive path length could have a large effect on the viscosity. This conjecture was confirmed both by approximate analytical models[49,50] and by computer simulations.[51–53] At low molecular weights fluctuations decrease the viscosity below the reptation limit and then eventually become unimportant at high molecular weights ($M \geq 500M_{\text{e}}$). Although this mechanism does not produce a true power law in the η–M relationship, it is known that the calculated behavior is remarkably similar to eq 18.[49,52,53] Recently, O'Connor and Ball[53] used their computer simulations of fluctuating chains together with a constraint release model proposed by des Cloizeaux.[43] This model replaces the Doi–Edwards[47] stress rule with another that describes in a simple and direct way the combined effect of reptation and release of entanglement constraints by the reptation of the surrounding molecules. According to des Cloizeaux[43] and Tsenoglou,[40] the stress is proportional to the square of the fraction of material that has not yet relaxed by reptation. They and others[54] have shown that this gives a remarkably good fit to linear viscoelastic data on polydisperse blends. The viscosity of entangled chains,

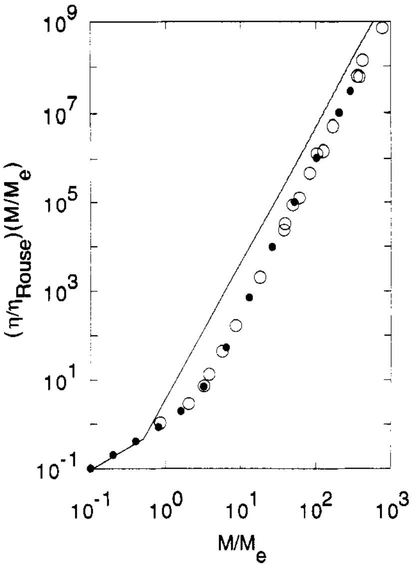

Figure 6. Ratio of $(\eta M)/(\eta_{Rouse})M_e)$ as a function of M/M_e (○) experimental data on PEB-2 using η_{Rouse} from eq 19; (●) theoretical results from O'Connor and Ball.[53] The solid lines represent the predictions of the Rouse model $((\eta M)/(\eta_{Rouse}M_e) = M/M_e)$ and the original reptation model $((\eta M)/(\eta_{Rouse}M_e) = (15/4)(M/M_e)^3)$.

including reptation, fluctuations, and constraint release, was calculated in this way by Ball and O'Connor.[53] They combined their results with the viscosity of unentangled chains as suggested by eq 18,

$$\begin{aligned}\eta &= \eta_{Rouse} + \eta_{ent}\\ &= \eta_{Rouse}[1 + f(M/M_e)]\end{aligned} \tag{22}$$

where $\eta_{Rouse} = KM$ and the function $f(M/M_e) = \eta_{ent}/\eta_{Rouse}$ is tabulated in ref 53. Values calculated from this equation together with the experimental viscosity data on PEB-2 are shown in Figure 6. The agreement is remarkable considering that no adjustable parameters other than η_{Rouse} and M_e are used.

Conclusions

The hydrogenated polybutadiene used in this study, PEB-2, has a chemical structure closely resembling that of linear polyethylene. Although there might be small differences in monomeric friction coefficients and the values of M_e for the two polymers, we have shown that their viscosity and self-diffusion coefficient are approximately the same. These results suggest that PEB-2 is an excellent model material for studying the behavior of polyethylene in the liquid state.

Diffusion coefficients determined by PFG-NMR were compared to values obtained with three other techniques. The good agreement attested to the reliability of this method. PFG-NMR also has the ability to provide information on molecular motion at much shorter time scales—similar to the spin-echo neutron experiment.[55] How this might be accomplished is discussed in Appendix A.

The value of the product ηD, which is free from any uncertainties about the value of the monomeric friction factor, undergoes a sharp change from Rouse-like behavior to behavior indicative of entangled polymers. The transition occurs at a molecular weight approximately $\sim 9\ M_e$. Beyond this point, the value of ηD is always below the prediction of the original reptation model but approaches it as M/M_e increases. This suggests that other processes are contributing to diffusive motion and viscoelastic relaxation. After correcting the individual values of η and D to a constant friction factor, we tested two possible mechanisms—constraint release and tube length fluctuations. The data consistently agreed with the predictions of these models.

Comparisons with data for other polymers indicate a universal pattern of behavior that emphasizes the general importance of other disentanglement processes besides pure reptation.

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Appendix A. Frequency-Dependent Diffusion Coefficients and Their Measurement by PFG-NMR

The frequency-dependent diffusion coefficient, $\hat{D}(\omega)$, is obtained from the Fourier transform of the velocity autocorrelation function:[56]

$$\hat{D}(\omega) = \frac{1}{3}\int_0^\infty dt\, \exp(i\omega t)\langle v(0)\, v(t)\rangle \tag{A1}$$

Explicit results for $\hat{D}(\omega)$ can be calculated with eq A1 and information on $\langle v(0)\, v(t)\rangle$ or, as will be shown below, the mean-square displacement function, $\langle \Delta R^2(t)\rangle$. The values of $\langle \Delta R^2(t)\rangle$ for both the Rouse model and the reptation model are known.[47] We show the details of the calculation for the latter model because it represents the slow motion of highly entangled polymers and therefore is more suited for measurement with current NMR equipment.

The mean-square displacement of a point s along a reptating chain of length L $(0 \leq s \leq L)$ is given by[47]

$$\langle \Delta R^2(t;s)\rangle = \frac{2}{Z}D_c|t| + \sum_{p=1}^{\infty}\frac{4La}{\rho^2\pi^2}\cos^2\frac{p\pi s}{L}\left(1 - \exp\left(\frac{-p^2|t|}{\tau_{rep}}\right)\right) \tag{A2}$$

where a is the distance between entanglements, $Z = L/a = 5M/4M_e$ is the number of entanglements per chain, and D_c is the curvilinear diffusion coefficient of the chain moving along the tubelike region in which it is confined.[47]

The velocity autocorrelation function of this point is given by

$$\begin{aligned}\langle v(0;s)\, v(t;s)\rangle &= \frac{1}{2}\frac{d^2\langle \Delta R^2(t;s)\rangle}{dt^2}\\ &= \frac{2}{Z}D_c\delta(t) + \sum_{p=1}^{\infty}\frac{2La}{\pi^2\tau_{rep}}\cos^2\frac{p\pi s}{L}\left(2\delta(t) - \frac{p^2}{\tau_{rep}}[2H(t) - 1]^2\right)\exp\left(\frac{-p^2|t|}{\tau_{rep}}\right)\end{aligned} \tag{A3}$$

where $\delta(t)$ is the Dirac delta function and $H(t)$ is the Heaviside function. Substituting eq A3 into eq A1 yields the following expression for the diffusion coefficient of point s:

$$\hat{D}(\omega;s) = D + \sum_{p=1}^{\infty}\frac{4La}{3\pi^2\tau_d}\cos^2\frac{p\pi s}{L}\left[\frac{\omega^2\tau_d^{\ 2}}{p^4 + \omega^2\tau_d^{\ 2}}\right] \tag{A4}$$

where $D = D_c/3Z$. If all material points along the chain are chemically identical, the PFG-NMR method will measure the following average of eq A4:

$$\hat{D}(\omega) = \frac{1}{L}\int_0^L \mathrm{d}s\, \hat{D}(\omega;s) = Df(\nu) \tag{A5}$$

where $\nu = \pi(2\omega\tau_{\mathrm{rep}})^{1/2}$ and

$$f(\nu) = \frac{1}{2} + \frac{\nu}{4}\frac{\sinh \nu + \sin \nu}{\cosh \nu - \cos \nu} \tag{A6}$$

If the sample is polydisperse, a further averaging over a distribution of L values can be done, a procedure that would be necessary before making comparisons with experimental data.

The PFG-NMR technique measures an apparent diffusion coefficient, $D_{\mathrm{app}}(\Delta,\delta)$, which is related to $\hat{D}(\omega)$ through information on the magnetic gradient pulse width (δ) and spacing (Δ).[57] D_{app} is given by the equation

$$D_{\mathrm{app}}(\Delta,\delta) = \frac{\int_{-\infty}^{\infty}\mathrm{d}\omega\, \hat{D}(\omega)\, S(\omega;\Delta,\delta)}{\int_{-\infty}^{\infty}\mathrm{d}\omega\, S(\omega;\Delta,\delta)} \tag{A7}$$

where $S(\omega;\Delta,\delta)$, the power spectrum of the magnetic field gradient pulses, is defined in ref 57. For a typical 90–180° pulse sequence, S has the following form:[57]

$$S(\omega;\Delta,\delta) = \left[\frac{4G}{\omega^2}\sin\left(\frac{\omega\Delta}{2}\right)\sin\left(\frac{\omega\delta}{2}\right)\right]^2 \tag{A8}$$

which when inserted into eq A7 gives an expression for D_{app}:

$$\frac{D_{\mathrm{app}}(R,r)}{D} = \frac{r}{\pi(1 - r/3)}\int_{-\infty}^{\infty}\mathrm{d}x\, \frac{f(2\pi(x/rR)^{1/2})\sin^2 x\,\sin^2(x/r)}{x^4} \tag{A9}$$

Here $x = \omega\delta/2$, $r = \delta/\Delta$, $R = \Delta/\tau_{\mathrm{rep}}$, and D is the self-diffusion coefficient obtained from the zero-frequency limit of eq A5. By making use of the low- and high-frequency limits of eq A6, it can be shown that, for $R = \Delta/\tau_{\mathrm{rep}} \gg 1$, $D_{\mathrm{app}} = D$ and, for $R \ll 1$, $D_{\mathrm{app}} \propto (\tau_{\mathrm{rep}}/\Delta)^{1/2}$. This latter result is similar to the high-frequency behavior of $\hat{D}(\omega)$ which is proportional to $(\omega\tau_{\mathrm{rep}})^{1/2}$ when $\omega\tau_{\mathrm{rep}} \gg 1$. Experimental results reported in this paper were all obtained in the $R \gg 1$ limit. However, by working in the opposite limit, $R \ll 1$, it is possible to observe short time-scale motion similar to that seen in neutron spin-echo experiments.

Appendix B. Correction of Viscosity and Diffusion Data to a Constant Friction Factor

In our previous study of polyethylene,[1] we fitted the temperature dependence of the monomeric friction factor to the Vogel equation

$$\zeta(M,T) = \zeta_\infty \exp\left[\frac{B}{\Delta\alpha(T - T_0)}\right] \tag{B1}$$

where ζ_∞ is the high-temperature limit of ζ and B is a constant. It was determined that $\zeta_\infty = 3.7 \times 10^{11}$ dyn s/cm and $B = 0.60$. The quantities $\Delta\alpha$ and T_0 are the difference in the thermal expansion coefficient of the liquid and occupied volumes and the critical temperature at which ζ diverges. We found that these parameters depend on molecular weight in the following way:[1]

$$\Delta\alpha = \alpha_l - \alpha_0 = \alpha^\infty(1 + \beta/M) \tag{B2}$$

$$T_0 = T_0^\infty/(1 + \gamma/M) \tag{B3}$$

with $\alpha^\infty = 5.1 \times 10^{-4}$/°C, $T_0^\infty = 160$ K, $\beta = 160$ g/mol, and $\gamma = 80$ g/mol.

Table 3. Self-Diffusion Coefficients and Viscosities of Hydrogenated Polyisoprene (PEP) at 100 °C

sample	$M_w \times 10^{-3}$	D (cm^2/s)	η (P)	$\eta D/(\eta D)_{\mathrm{Rouse}}$[a]	M/M_e[b]
HI-9	0.93	$4.3_5 \times 10^{-7}$	0.14_9	1.06	0.40
HI-1	1.00	2.7×10^{-7}	0.23_6	1.05	0.44
HI-10	2.7_0	3.8×10^{-8}	1.4_9	0.93	1.17
HI-7	5.2	8.9×10^{-9}	8.1	1.18	2.26
Gu-2	$10._0$	$1.9_5 \times 10^{-9}$	$52._0$	1.67	4.35

[a] $(\eta D)_{\mathrm{Rouse}} = 6.09 \times 10^{-8}$ dyn calculated with eq 7 using $\rho = 0.813$ g/cm^3 and $\langle R_G{}^2\rangle/M = 1.45 \times 10^{-17}$ cm^2 mol/g for PEP at 100 °C. [b] $M_e = 2300$ calculated with eq 5 using $G_N = 1.09 \times 10^7$ dyn/cm^2 for PEP at 100 °C.

Therefore, the ratio of friction factors for an infinite molecular weight chain to that of a chain of molecular weight M is given by

$$\frac{\zeta(\infty,175)}{\zeta(M,175)} = \frac{59.3}{\exp\left[\frac{1176M(M + 80)}{(M + 160)(288M + 35840)}\right]} \tag{B4}$$

The constant friction factor results shown in Figures 4 and 5 were obtained by multiplying the viscosities and dividing the diffusion coefficients by eq B4. Values of this ratio are also listed in Table 2.

Appendix C. Self-Diffusion Coefficient and Viscosity for Hydrogenated Polyisoprene (PEP) at 100 °C

The methods described here were also applied to nearly monodisperse samples of hydrogenated 1,4-polyisoprene (PEP = poly(ethylenepropylene)). The polyisoprene precursors (~92% 1,4 enchainment) were prepared by anionic polymerization and catalytically saturated with H_2, resulting in five PEP samples with $M_w/M_n < 1.07$ and molecular weights (from light scattering and SEC-LALLS) ranging from 980 to 10 000. Diffusion coefficients were determined by the PFG-NMR method, and viscosities were determined from capillary flow times or dynamic oscillatory viscometry. The results are shown in Table 3. Also given are the values of $\eta D/(\eta D)_{\mathrm{Rouse}}$ and M/M_e where $M_e = 2300$ and $(\eta D)_{\mathrm{Rouse}} = 6.09 \times 10^{-8}$ dyn were calculated from eqs 5 and 7, respectively, with data for PEP at 100 °C: $\rho = 0.813$ g/cm^3, $\langle R_G{}^2\rangle/M = 1.45 \times 10^{-17}$ cm^2 mol/g, and $G_N = 1.09 \times 10^7$ dyn/cm^2.

The PEB data cover a much narrower range of molecular weights than the PEB-2 data, mainly the unentangled region and the onset of crossover, but the results for the two species are very similar. Thus, the product ηD for the lowest molecular weights is in almost quantitative agreement with $(\eta D)_{\mathrm{Rouse}}$, calculated with eq 7, and the entanglement crossover for ηD begins in the vicinity of $M = 9M_e$. Unfortunately, the PEP data on the temperature dependence of η and D (unpublished) are too limited to permit correction to constant monomeric friction for separate comparisons with the model predictions.

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