is the connectivity of the more conductive phase. Increasing the connectedness of this phase will increase the effective diffusion coefficient; conversely, decreasing its connectedness will decrease the effective diffusion coefficient. No obvious effect of interfacial volume fraction on the effective diffusion coefficient was found, although the solubilities of the samples with the larger interfacial volume fractions were observed to be less than that predicted by the additivity rule. (2) The highly simplified models presented by Sax and Ottino for predicting the diffusion properties of materials having small-scale order and large-scale disorder work very well for the case of ordered two-phase block copolymers. It should be noted that the models neglect the effect of orientation of the ordered grains, the effect of interfacial material, and the phase continuity across grain boundaries which is often observed for block copolymers. In addition, the models assume that the transport behavior in the polybutadiene and polystyrene microdomains is the same as that in the pure components, which may not be the case. Although the models could be improved to account for these effects, they seem to do quite well as they are.

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Registry No. CO_2, 124-38-9; (styrene)(butadiene) (block copolymer), 106107-54-4; polystyrene, 9003-53-6.

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Viscosity and Self-Diffusion Coefficient of Linear Polyethylene

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ABSTRACT: The viscosity and self-diffusion coefficient were measured for polyethylene samples in the molecular weight range $200 < M < 120000$. The viscosity η was determined by capillary flow or in a parallel-plate rheometer; the diffusion coefficient was obtained from the attenuation of NMR spin echoes in a pulsed-field gradient. The molecular weight dependence of the viscosity at 175 °C can be described by two power-law regions, $\eta \propto M^{1.8}$ below $M = 5000$ and $\eta \propto M^{3.6}$ above 5000. The diffusion coefficient on the other hand can be characterized by a single power law $D \propto M^{-2}$ over the entire range studied. Comparisons with molecular theory were made by examining the product ηD. At low molecular weights ηD agrees well with predictions of the Rouse model. At high molecular weights ηD increases with molecular weight, approaching the prediction of the reptation model from below. The temperature dependence of the viscosity follows the Vogel–Fulcher equation, $\eta \sim e^{B'/(T-T_0)}$, with parameters that are consistent with the free volume theory of the liquid state. When the data at low molecular weights are compared at a constant free volume state, the viscosity and diffusion coefficient are proportional to M and M^{-1} as required by the Rouse model.

Introduction

Data on the viscosity, η, and the self-diffusion coefficient, D, of polymer melts have often been used to test molecular theories of transport properties.[2,3] Qualitative comparisons that are concerned only with establishing the molecular weight dependence of these functions are easily made. Quantitative comparisons are frequently hampered because both η and D depend on the monomeric friction factor, ζ, a parameter that is difficult to determine. The current theories of liquids are not sufficiently developed to calculate it directly and experimental methods to estimate ζ are often inaccurate. This is especially so for low molecular weight polymers and for crystallizable polymers like polyethylene that are tested far from their glass transition temperature.[2]

There have been very few studies in which both η and D were measured on the same polymer samples.[4,5] A systematic program to do so could be very worthwhile because the product ηD is predicted to be independent of ζ, thereby providing rather direct and simple tests of theory. In this study we report new data on the viscosity and self-diffusion coefficient for a number of polyethylene samples. The experiments include a sufficiently wide range of molecular weights to test models of transport for both unentangled and entangled liquids.

Our findings are also valuable in a more practical sense since they provide a simple method to estimate the diffusion coefficient from a knowledge of chain length and viscosity alone.

Molecular Characterization

It is well-known that the melt rheological behavior of polymers is very sensitive to molecular weight, molecular weight distribution, and long-chain branching.[6] To avoid complications from the latter

Table I
Molecular Characteristics of Polyethylene Samples

sample	material	M_n (Osm)	M_n (NMR)[c]	M_n (GPC)	M_w/M_n (GPC)	M_w	$[\eta]$, mL/g	T_m,[j] °C
1	PW 500 (15109)	505[a]	540	550[d]	1.09	590[f]	2.8[h]	80
2	PW 655 (15210)	620[a]	630	740[d]	1.10	695[f]	4.1[h]	90
3	PW 1000 (14854)	1040[a]	1185	1220[d]	1.08	1 280[f]	7.0[h]	113
4	PW 2000 (15445)	1980[a]	2135	2385[d,k]	1.12	2 390[f]	12.1[h]	127
5	PW 3000 (KQ140)	2725[a]	2900	3530[d]	1.14	3 310[f]	15.8[h]	127
6	PW 4000 (KZ45B)		3600	4640[d,l]	1.14	4 100[f]	18.7[h]	
7	NBS 1482	11400[b]	12400		1.19[e]	13 600[g]	40.2[i]	
8	NBS 1483	28900[b]			1.11[e]	32 100[g]	79.4[i]	
9	NBS 1484	100500[b]			1.19[e]	119 600[g]	197.9[i]	

[a] Vapor pressure osmometry at 110 °C in *o*-dichlorobenzene.[12] [b] Membrane osmometry at 130 °C in α-chloronaphthalene.[13] [c] End-group analysis by NMR at 110 °C in trichlorobenzene/dioxane [80/20]. [d] Gel permeation chromatography at 135 °C in trichlorobenzene. [e] M_w by light scattering; M_n by osmometry. [f] M_n by NMR times M_w/M_n by GPC. [g] Light scattering at 135 °C in α-chloronaphthalene.[14] [h] Limiting viscosity number at 135 °C in trichlorobenzene. [i] Limiting viscosity number at 130 °C in trichlorobenzene.[9] [j] Temperature at peak of DSC endotherm. [k] About 1% of the mass is in a low molecular weight tail in this sample. [l] A value of M_w = 4400 was obtained for this sample by light scattering in trichlorobenzene.

two variables, the samples chosen for this study were linear and nearly monodisperse. The techniques used to characterize them depended on the molecular weight of the samples.

***n*-Alkanes.** Six normal alkanes (C_{16}, C_{17}, C_{24}, C_{28}, C_{36}, and C_{44}) were obtained from MCB Chemical, Aldrich Chemical, and Humphrey Chemical Co. The manufacturers stated purity was 98–99% and chromatographic analyses indicated only a single component was present. Hence we used the calculated value for the molecular weight ($M = 14n + 2$). In one case (C_{44}) the molecular weight was checked by an end-group analysis using NMR (see below) and found to be within 2% of the expected value.

Low Molecular Weight Polyethylene. Six polyethylene samples with molecular weights from approximately 500 to 4000 were obtained from J. Nichols of the Specialty Polymer Division of Petrolite Corp. The number-average molecular weights ($\bar{M}_n$) of these samples were determined by the manufacturer using vapor phase osmometry (VPO) at 110 °C in *o*-dichlorobenzene. The values so obtained are listed in Table I.

The number-average molecular weight was also determined by detecting the terminal carbon atoms using ^{13}C NMR. Samples were prepared as 40% (w/v) solutions in a 4/1 mixture of trichlorobenzene and *p*-dioxane-d_8 and observed at 110 °C. The recorded spectra consisted of 350–650 scans on a Varian XL-200 spectrometer. The necessary conditions for quantitative measurements were established by determining the nuclear Overhauser enhancement (NOE) and relaxation time, T_1,[7] using the lowest molecular weight polymer (PW500). The NMR molecular weights for all of the samples are given in Table I. There appear to be no systematic differences in $\bar{M}_n$ determined by the two methods. The largest difference between the VPO and NMR measurements is 13.5% and the average difference was 7.3%.

In order to verify the linear nature of these polymers longer accumulations (4000–15 000 scans) of ^{13}C NMR data were used to measure the branch content (tertiary carbon atoms). We found that the total branching was no greater than 0.8 branches per 1000 methylene carbons. The branch types that have been identified are approximately equal amounts of a methyl branch and a long branch containing six or more carbons. Because the longest polymer in this series contains less than 400 carbons we concluded that amount of branching is negligible.

Molecular weight distributions were determined with a Waters 150C gel permeation chromatograph equipped with four columns (Shodex 802–805).[8] The samples were dissolved in trichlorobenzene and injected at 135 °C. A calibration curve in the range of interest was established by using *n*-alkanes (C_{10}, C_{22}, C_{36}, and C_{44}) and the NBS standards (see below). Values of the weight-average molecular weight, $\bar{M}_w$, and the ratio $\bar{M}_w/\bar{M}_n$ determined by this method are given in Table I. These measurements confirmed the expected narrow molecular weight distribution of these samples ($\bar{M}_w/\bar{M}_n \cong 1.15$). It was generally found that $\bar{M}_n$ from GPC agreed well with the other two methods. The largest discrepancy was for the highest molecular weight sample $\bar{M}_n$(GPC)/$\bar{M}_n$(NMR) = 1.13.

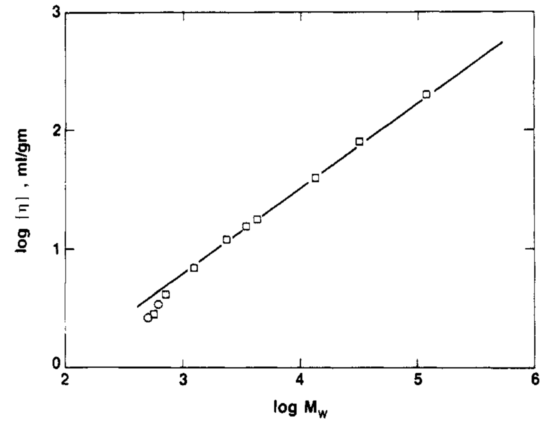

Figure 1. Intrinsic viscosity of polyethylene samples measured in trichlorobenzene at 135 °C. The two circles are for the *n*-alkanes C_{36} and C_{44}. The remaining data points marked by squares are for samples 1–9 listed in Table I. The solid line represents the relationship $[\eta] = 0.0392\ M^{0.725}$ determined in ref 9.

The viscosity of polymer melts is a function of the weight-average molecular weight.[2] Values of $\bar{M}_w$ were obtained directly from the GPC results and by multiplying the $\bar{M}_n$ from VPO and NMR by the $\bar{M}_w/\bar{M}_n$ ratio from GPC. Both results are reported in Table I, but because the choice does not affect our latter conclusions an average of the two has been used.

As a further check on molecular weights we determined the intrinsic viscosity, $[\eta]$, at 135 °C in trichlorobenzene. The results are plotted in Figure 1. At high molecular weights the values of $[\eta]$ conform well with the Mark–Houwink relation established for this polymer.[9] At low molecular weights ($M < 1000$) $[\eta]$ smoothly falls below this correlation. This behavior is consistent with that found by others for low molecular weight polyethylene.[10]

The melting points (T_m) of the polymers were determined with a Perkin-Elmer DSC-2 at a rate of 20 °C/min. The temperature at the peak of the melting endotherm is listed in Table I.[11] When either the Broadhurst[15] or Flory–Vrij[16] equations are used to relate T_m to molecular weight, the values so obtained are within 5% of the $\bar{M}_w$ of our samples.

High Molecular Weight Polyethylene. Three high molecular weight samples of polyethylene were obtained from the National Bureau of Standards. These polymers were prepared from linear polyethylene by a fractionation technique.[17] The values of $\bar{M}_n$ and $\bar{M}_w$ as determined by the NBS are reported in Table I and indicate that the samples have a narrow molecular weight dis-

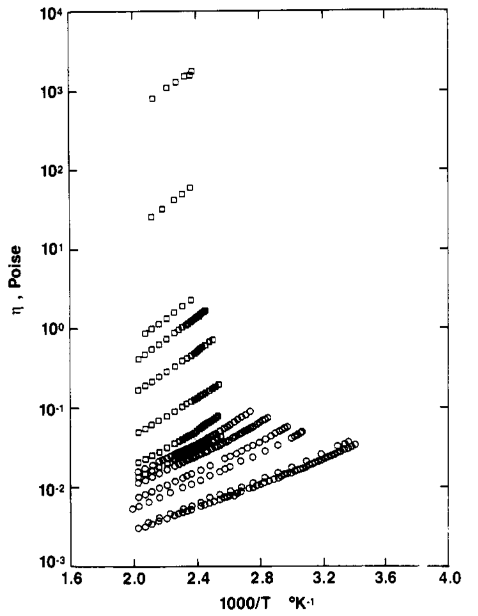

Figure 2. Viscosity, η, as a function of reciprocal absolute temperature. From the bottom, samples indicated by circles are the normal alkanes C_{16}, C_{17}, C_{24}, C_{28}, C_{36}, and C_{44}. The remaining samples indicated by squares are samples 1–8 in Table I.

tribution similar to the low molecular weight samples.

As a check on the accuracy of the NMR method for determining number-average molecular weights we analyzed NBS 1482 and found a value within 8% of the reported one (see Table I).

Results

Viscosity. The kinematic viscosities (ν) of all samples except the two highest molecular weights were measured in calibrated Cannon–Ubbelohde glass viscometers that were thermostated in a silicone oil bath. The viscometers were equipped with fiber optic timers (Wescan Instruments, Inc.) to detect the meniscus as it passed the timing marks above and below the measuring bulb. When the flow times were kept above 150 s, kinetic energy corrections were negligible.[18]

The kinematic viscosities were converted to absolute viscosities by multiplying by the density, $\eta = \nu\rho$, using values calculated from parameters given by Orwoll and Flory.[19] Doolittle,[20] who studied some of the same alkanes (C_{17}, C_{36}, C_{44}), reported values of η and ρ that agree within 1% with those determined here.

The viscosities of NBS 1483 and 1484 were measured with a Rheometrics System 4 rheometer using parallel-disk geometry. The absolute value of dynamic viscosity, $|\eta^*(\omega)|$, was measured as a function of frequency and the constant value attained at low frequency was used for η.

Each sample was studied from a few degrees above its melting point to approximately 225 °C. The results of these measurements are shown in Figure 2, where the logarithm of the viscosity is given as a function of the reciprocal of the temperature. The lines are slightly curved, indicating that the temperature dependence, as in most polymers, does not obey the Arrhenius equation.[21]

An apparent activation energy was determined for each sample from the slope at 150 °C. The values so obtained for the low molecular weight polymers are plotted in Figure 3. As noted by others[22] the activation energy increases with chain length. At the highest molecular weight shown ($\bar{M}_w \cong 4400$) the activation energy is 6.6 kcal, which is similar to the average value found for NBS 1482-4 (6.7 kcal) and the values reported by others[23,24] for high molecular weight linear polyethylene (6.1–6.9 kcal).

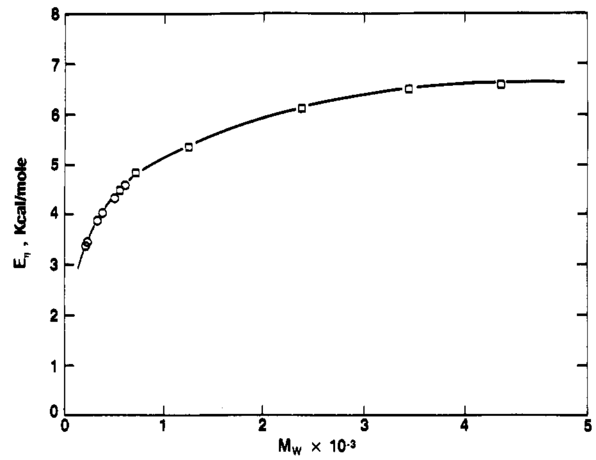

Figure 3. Apparent activation energy for viscous flow, E_η, determined at 150 °C as a function of molecular weight. Circles are n-alkanes and squares are samples 1–6 in Table II.

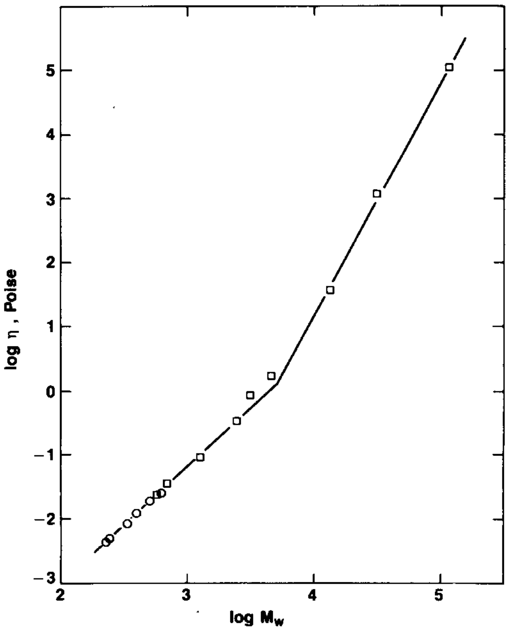

Figure 4. Viscosity as a function of molecular weight at 175 °C. Circles represent n-alkanes and squares are samples 1–9 in Table I.

Figure 4 shows the viscosity as a function of molecular weight at 175 °C. At low molecular weight ($M < 5000$), the viscosity is well described by the power law

$$\eta = 2.1 \times 10^{-7}\bar{M}_w^{1.8} \text{ P} \qquad (1a)$$

Because the flow activation energy is a function of molecular weight the exponent on M_w changes somewhat with temperature, but the effect is not large over the range of temperatures that are usually studied (1.87 at 150 °C and 1.75 at 190 °C).

At high molecular weight ($M > 5000$) the M dependence is much stronger. At 175 °C

$$\eta = 3.76 \times 10^{-14}\bar{M}_w^{3.64} \text{ P} \qquad (1b)$$

This equation and our data are within 10% of the results reported by Raju et al.[24] when their values are corrected to 175 °C.

These correlations of data for low and high molecular weight polyethylene intersect at a molecular weight M_c of approximately 5200, a value that is somewhat larger than reported by others[25–27] ($M_c \cong$ 3800–4000). The determination of M_c and the slope of the viscosity molecular weight

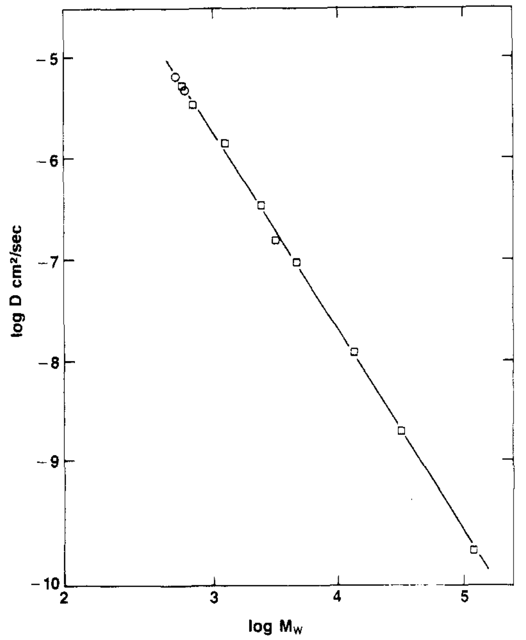

Figure 5. Self-diffusion coefficient as a function of molecular weight at 175 °C. Two circles are C_{36} and C_{44}. Squares are samples 1–9 in Table I.

relationship are discussed in more detail below.

Self-Diffusion Coefficient. The diffusion coefficient D of all samples was determined by the pulsed-gradient spin-echo NMR method. The equipment and experimental techniques have been described in earlier publications.[28,29] A magnetic gradient pulse of duration δ and magnitude G is applied during a conventional 90°–180° radio-frequency pulse sequence,[30] and the spin echo is attenuated by molecular diffusion. Typically G was on the order of 250 G/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[30]

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

where γ is the gyromagnetic ratio of the protons. The value of D is obtained from the slope of a plot of log R vs. $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$.

For the highest molecular weight samples (NBS 1483 and NBS 1484), it was found that the diffusion coefficient obtained by this method depended on the diffusion time (Δ). It was necessary to use quite large values of Δ ($\sim$500 ms) before D became constant. For these long times we employed the stimulated echo (three-pulse) sequence[31] to avoid excessive damping of the echo due to spin–spin relaxation. Similar time-dependent behavior has been found by others,[32,33] which we will discuss at greater length in a separate publication.[34] The results reported below were obtained from the large Δ region where D is independent of time.

Figure 5 shows the self-diffusion coefficient as a function of molecular weight at 175 °C. All of the data from M = 600 to 120 000 follow a power law

$$D = 1.65/\bar{M}_w^{1.98} \quad \text{cm}^2/\text{s} \qquad (3)$$

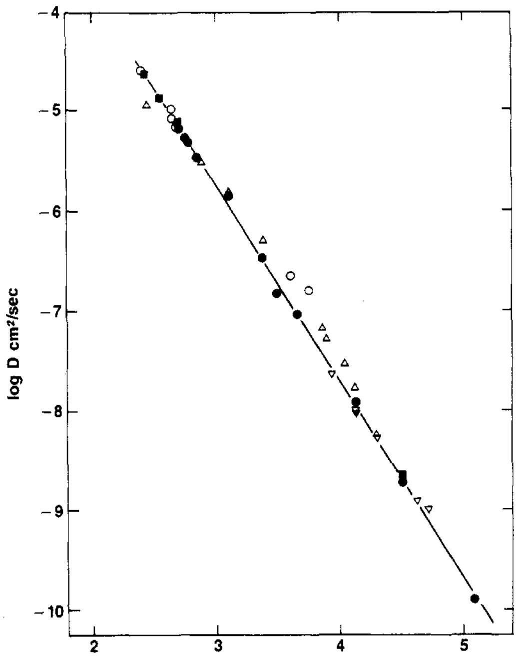

Figure 6. Self-diffusion coefficient as function of molecular weight at 175 °C. Filled circles are from this study (Figure 5); open circles, ref 35; filled squares, ref 33; open Δ, ref 36 and 37; inverted triangle, ref 32.

In Figure 6 we compare our results with other data on the self-diffusion coefficient of polyethylene.[32,33,35-38] These results were also obtained by field-gradient NMR. In most cases it was necessary to make small corrections to this data so that the comparison could be made at 175 °C. We did so by using either the known temperature dependence of D[39] or with information on the temperature dependence of η and its relationship to the temperature dependence of D.[40] The agreement between this study and other work as illustrated in Figure 6 is quite satisfactory.

Our self-diffusion coefficients are almost a factor of 5 larger than the tracer diffusion coefficients of deuteriated polyethylene diffusing into a high molecular weight protonated polyethylene matrix.[41] The latter results were obtained by Klein from the time dependence of the concentration profile of deuteriated molecules at the interface between two polyethylene samples, one of which contained 2 wt % deuteriated polyethylene. Tracer coefficients for low molecular weight polymers diffusing into a high molecular weight polymer are often smaller because the slower moving matrix retards the shorter molecules.[42] However, a ratio of 5 is more than would be expected in this molecular weight range.[42]

It is likely that some of the discrepancy between the two methods is due to the fact that the NMR experiments are sensitive to a different moment of the molecular weight distribution. The effect of molecular weight distribution on NMR measurements is discussed in more detail in the Appendix. It is shown there that the magnitude of D at a given value of $\bar{M}_w$ might be 2 or more times larger for NMR experiments than for the Klein method.

We are not inclined to believe that our larger values are a fault of the NMR technique.[40,43] Recently we have obtained diffusion results for narrow molecular weight distribution samples by NMR[44,45] and compared them to those determined by forced Rayleigh scattering[46] and neutron scattering.[40] We found that they were essentially the same.

Further experiments may be required to resolve the discrepancy. Because of the extensive molecular weight characterization we have done on the samples, they may be of value to other research workers. The samples are available from us in small quantities.

Discussion

The Product of η and D. The most useful results for describing the behavior of unentangled and entangled polymers melts are obtained from the Rouse[47] and reptation[48,49] models. Both of these models predict that the viscosity is the product of two quantities

$$\eta = F\zeta \tag{4}$$

where F is a function of the large-scale molecular structure of the polymers and ζ is the local friction factor per chain unit.[2] In a similar manner the self-diffusion coefficient is the product[3]

$$D = (kT/\zeta)G \tag{5}$$

where again G is a function of the molecular structure.

In the Rouse model each of the N units of the chain are free to hop independently of the other chains. The hopping rate is inversely proportional to the friction factor, ζ. On the order of N^2 hops are required for the polymer to diffuse a distance equal to its size, and after moving this far, a stress produced by a previous strain will have relaxed to zero. With this model the functions F and G have been determined. They are given by[47,50]

$$F_{\text{Rouse}} = \frac{1}{6}\rho N_A \frac{\langle S^2 \rangle}{M} N \tag{6a}$$

and

$$G_{\text{Rouse}} = 1/N \tag{6b}$$

where ρ is the density, N_A is Avogadros' number, and $\langle S^2 \rangle / M$ is the mean-square radius of gyration divided by the molecular weight.

In the reptation model the entanglement constraints prevent the chain units from hopping independently. Instead they are assumed to translate at a velocity inversely proportional to ζ along a tubelike region that roughly parallels the local chain axis. The extra motion required to move a radius of gyration increases the viscosity and lowers the diffusion coefficient. The functions F and G in this case are given by[49,51]

$$F_{\text{reptation}} = \frac{5}{8}\rho N_A \frac{\langle S^2 \rangle}{M}\left(\frac{M}{M_e}\right)^2 N \tag{7a}$$

and

$$G_{\text{reptation}} = \frac{4}{15}\frac{1}{N}\left(\frac{M_e}{M}\right) \tag{7b}$$

M_e is the molecular weight between entanglements defined by $M_e \equiv \rho RT/G_N$ and G_N is the elastic shear modulus in the plateau region.[52]

At low molecular weights the functions F and G predict that

$$F_{\text{Rouse}} \propto M \tag{8}$$

and

$$G_{\text{Rouse}} \propto 1/M \tag{9}$$

although in this region both ρ and $\langle S^2 \rangle / M$ are changing with molecular weight so that F_{Rouse} increases slightly faster than indicated. However, this effect accounts for only a small part of our finding that the viscosity is proportional to $M^{1.8}$. If the Rouse model is correct the extra molecular weight dependence must be contained in the friction factor. The product of viscosity and diffusion on the other hand does not depend on ζ and according to eq 4 and 5 should be nearly constant at low molecular weights.

A test of this idea is shown in Figure 7 where we have plotted the kinematic viscosity, $\nu = \eta/\rho$, times the diffusion coefficient as a function of the molecular weight. The graph shows quite clearly that for M less than 5000 the product νD is constant and then begins to increase like $M^{1.6}$ beyond $M \cong 5000$.

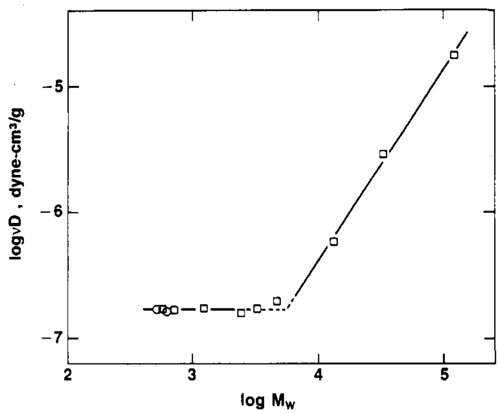

Figure 7. Product of kinematic viscosity and self-diffusion coefficient as a function of molecular weight at 175 °C. Two circles are C_{36} and C_{44}. Squares are samples 1–9 in Table I.

Table II
Viscosity, Diffusion Coefficient, Density, and Chain Dimensions of Polyethylene at 175 °C

sample	η, P	$10^6 D$, cm^2/s	ρ, g/mL	$\langle S^2 \rangle / M$, Å^2/Da
C_{16}	4.48×10^{-3}		0.663	0.088
C_{17}	4.84×10^{-3}		0.669	0.091
C_{24}	8.59×10^{-3}		0.698	0.108
C_{28}	1.20×10^{-2}		0.708	0.115
C_{36}	1.85×10^{-2}	6.6	0.721	0.126
C_{44}	2.48×10^{-2}	4.8	0.729	0.135
1	2.32×10^{-2}	5.4	0.724	0.133
2	3.5×10^{-2}	3.5	0.730	0.140
3	9.2×10^{-2}	1.4	0.748	0.157
4	3.38×10^{-1}	0.35	0.756	0.170
5	8.73×10^{-1}	0.15	0.759	0.173
6	1.63	0.093	0.761	0.176
7	3.77×10^{1}	1.2×10^{-2}	0.766	0.176
8	1.1×10^{3}	2.0×10^{-3}	0.766	0.176
9	1.25×10^{5}	1.3×10^{-4}	0.766	0.176

A more quantitative comparison with theory can be made by dividing ηD by $\rho RT\langle S^2 \rangle / 6M$.

$$\frac{\eta D}{[\rho RT\langle S^2 \rangle / 6M]} = \frac{\eta D}{kT(FG)_{\text{Rouse}}} \tag{10}$$

According to eq 6 and 7, this quantity should be equal to 1 in the unentangled regime (i.e., for $M < M_e$) and equal to M/M_e for entangled polymers (i.e., for $M > M_e$).

Table II lists the experimental values of η and D and calculated values of ρ and $\langle S^2 \rangle / M$ that are needed for the comparison. The last quantity was obtained with the rotational isomeric state method.[53] An M_e value of approximately 900 has been obtained for polyethylene by Carella, Graessley, and Fetters.[54]

Figure 8 shows $\eta D / [\rho RT\langle S^2 \rangle / 6M]$ as a function of molecular weight. For $M < M_e$ the value is near 2, which is in reasonably good agreement with the Rouse model considering that the comparison is made without adjustable parameters.

For $M > M_e$ the value of $\eta D / [\rho RT\langle S^2 \rangle / 6M]$ decreases slightly but stays near the Rouse model until it increases sharply near $M = 5000$. The combination of eq 6 and 7 indicates that for $M \geqslant M_e$

$$(\eta D)_{\text{reptation}} = (\eta D)_{\text{Rouse}}(M/M_e) \tag{11}$$

The dashed line in Figure 8 was drawn in accordance with this equation. The experimental data beyond M_e are always less than the reptation model but approach it from below as the molecular weight increases. At $M = 120\,000$ the value of ηD is approximately 1.6 times smaller than predicted by eq 11. This behavior is consistent with

Table III
Vogel-Fulcher Parameters and Viscosity at Constant Friction Factor

						$\zeta = 2.3 \times 10^9$	
sample	$\bar{M}_w$[a]	T_0, °C	B', °C	$B'(\alpha_l - \alpha_0)$	$10^{11}\zeta_\infty$, dyn·s/cm	T, °C	η, P
C_{16}	227	-154	681	0.59	5.8	31	0.027
C_{17}	241	-155	718	0.61	5.1	35	0.030
C_{24}	339	-154	868	0.63	3.4	52	0.051
C_{28}	395	-131	779	0.54	3.9	60	0.062
C_{36}	507	-124	818	0.53	3.5	71	0.083
C_{44}	619	-98	722	0.45	4.1	81	0.11
PW 500	570	-150	1003	0.64	2.5	72	0.097
PW 655	720	-120	965	0.60	2.3	100	0.10
PW 1000	1250	-124	1053	0.60	2.3	106	0.26
PW 2000	2390	-145	1400	0.76	1.8	142	0.54
PW 3000	3420	-105	1115	0.60	4.8	184	0.68
PW 4000	4370	-112	1225	0.65	5.1	210	0.89

[a] Average of M_w (GPC) and M_w from M_n (NMR) and M_w/M_n (GPC).

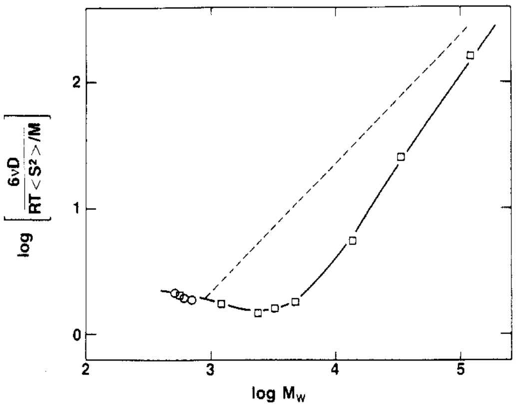

Figure 8. Product of viscosity and self-diffusion coefficient divided by $RT\langle S^2\rangle/6M$ at 175 °C. Symbols are same as Figure 7.

current molecular models[55-57] that propose that path-length fluctuations[55] and tube renewal[57] decrease η and increase D such that their product remains below the reptation limit. A more thorough comparison of experimental and theoretical values of ηD at high molecular weights will be given elsewhere[45] (see also discussion in Appendix).

Temperature Dependence of η. The temperature dependence of the viscosity of polyethylene is often assumed to follow an Arrhenius law,[23,24] i.e.

$$\eta \sim e^{E_\eta/RT} \tag{12}$$

However, when data are examined from samples covering a wide range of molecular weights and temperatures such as those used in the Doolittle[20] study and the present investigation, it is clear that this is not the case (see Figure 2).

The most highly temperature-dependent quantity in the viscosity and the diffusion coefficient is the friction factor, ζ. From the molecular weight dependence of the product of η and D we can assume that at low molecular weights ($M < 5000$) the behavior is well described by the Rouse model. Therefore by confining our analysis to these samples we can determine the temperature dependence of ζ by analyzing

$$\zeta = \eta/F_{\text{Rouse}} \tag{13}$$

A nonlinear regression technique was used to fit ζ to the Vogel–Fulcher equation.[2,21,58,59]

$$\zeta = \zeta_\infty e^{B'/(T-T_0)} \tag{14}$$

The results of this analysis are given in Table III. Figure 9 is a typical graph that shows the linear relationship between log ζ and $1/(T - T_0)$.

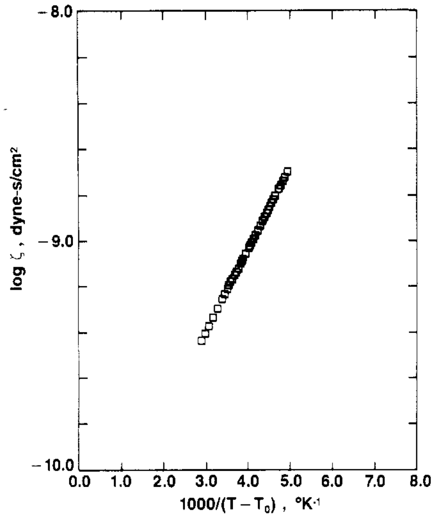

Figure 9. Friction factor from eq 13 as a function of $1/(T - T_0)$ for C_{36}. $T_0 = -124$ °C.

The changes in B' and T_0 as the molecular weight increases are somewhat scattered but larger values of B' are compensated for by smaller values of T_0 so that the quantity $B'/(T - T_0)$ increases smoothly with molecular weight at any temperature. Also as the molecular weight increases there is an upward trend in T_0 until at high molecular weights it approaches a limit of $T_0^\infty \cong 170$–180 K. Our data are consistent with the finding[2] that

$$T_0 = T_0^\infty(1 - \gamma/M) \tag{15}$$

if a γ value of 55 is used.

According to the free volume theory of the liquid state,[2,21] the quantity $B'/(T - T_0)$ should be proportional to the reciprocal of the fractional free volume, $f = (v - v_0)/v_0$, where v is the volume of the liquid and v_0 is some suitably defined hard-core or occupied volume. With the assumption that both the liquid and the occupied volume expand linearly with temperature, it follows that

$$f = (\alpha_l - \alpha_0)(T - T_0) \tag{16}$$

where α_l and α_0 are the thermal expansion coefficients of the liquid and the occupied volume and T_0 is the temperature where the two volumes become equal.

With this interpretation, the product of B' and $(\alpha_l - \alpha_0)$ should be a constant, say B. Values of α_l for polyethylene can be obtained from the work of Orwoll and Flory.[19] The constant α_0 can be estimated from the temperature dependence of the hard-core volume in Flory's equation of state[19] or from the thermal expansion coefficient of polyethylene crystals.[60] Both methods give $\alpha_0 \cong 2 \times 10^{-4}$/°C. In Table III we list the product of B' and $\alpha_l - \alpha_0$ for all the

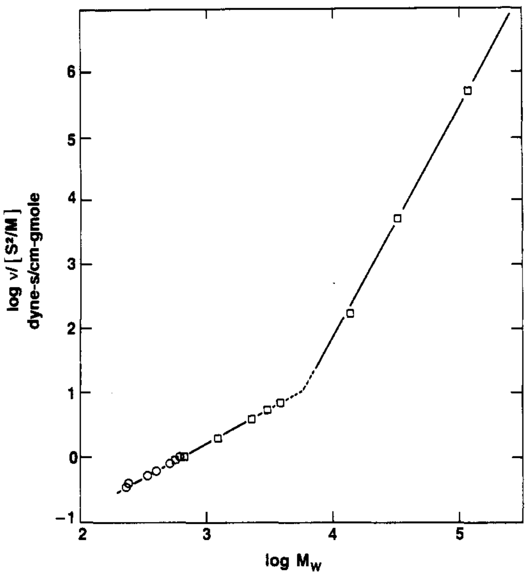

Figure 10. Kinematic viscosity divided by $\langle S^2\rangle/M$ corrected to constant friction factor, $\zeta = 2.3 \times 10^{-9}$ dyn·s/cm. Circles are n-alkanes and squares are samples 1–9, Table I.

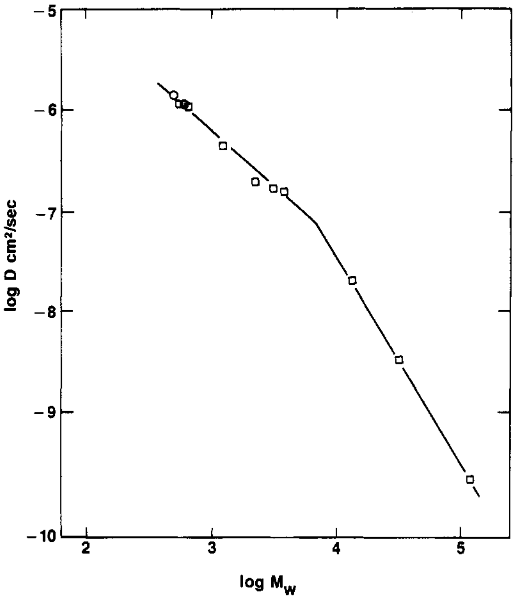

Figure 11. Self-diffusion coefficient corrected to the temperature at which the friction factor for viscosity equals 2.3×10^{-9} dyn·s/cm. Temperatures are listed in Table III. Symbols are same as Figure 5.

polymers studied. It is essentially constant with an average value of $B = 0.6$, in good agreement with values found by others.[21]

We also show in Table III the high-temperature limit of the friction factor, ζ_∞, obtained from eq 14. Its magnitude is essentially independent of molecular weight and the average value of 3.7×10^{-11} dyn·s/cm is close to the value found for the polymers analyzed by Berry and Fox ($\zeta_\infty = 2.5 \times 10^{-11}$).[2]

Because ζ_∞ does not depend on molecular weight, comparing viscosity at constant friction factor is equivalent to a comparison at constant free volume. In the last two columns of Table III we tabulate the temperature and the viscosity when the friction factor is equal to 2.3×10^{-9} dyn·s/cm. These values of η divided by $\rho\langle S^2\rangle$ are shown in Figure 10 as a function of the molecular weight. The data now are proportional to M^1 below $M = 5600$, consistent with the Rouse model.

Usually we determined the diffusion coefficient at two temperatures (150 and 175 °C). Because we cannot evaluate the Vogel parameters from this limited amount of data, our conclusions about its temperature dependence will be less precise. However, for the low molecular samples the temperature dependence of D/T according to eq 6 should be the same as the temperature dependence of $\eta/\rho\langle S^2\rangle$. Using this information, we estimated the diffusion coefficient at the temperatures corresponding to constant ζ (see Table III). The values so obtained are plotted in Figure 11 with the result that $D \sim M^{-1}$ for $M \leq 5600$ in agreement with eq 6 and 7. Unlike the viscosity it is only after free volume corrections are made that the onset of entangled behavior can be seen in the diffusion data.

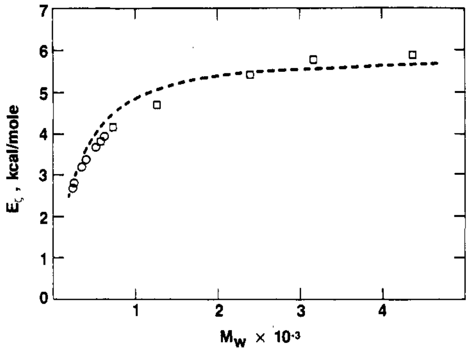

Figure 12. Apparent activation energy, E_ζ, determined at 150 °C for the local friction factor (eq 13). The dashed line represents E_ζ calculated from eq 18b using eq 15 and 19 ($T_0^\infty = 170$ K, $\gamma = 55$, $\alpha^\infty = 5.1 \times 10^{-4}$/K, $\beta = 160$).

The free volume theory can also be used to explain the molecular weight dependence of the apparent flow activation energy shown in Figure 3. By combining eq 14 and 16, we have

$$\zeta = \zeta_\infty e^{B/\alpha(T-T_0)} \tag{17}$$

which has an apparent activation energy

$$E_\zeta = R\frac{\mathrm{d}\ln\zeta}{\mathrm{d}(1/T)} \tag{18a}$$

$$= \frac{BRT^2}{\alpha(T-T_0)^2} \tag{18b}$$

In deriving eq 18b we have assumed that the thermal expansion coefficient $\alpha = \alpha_1 - \alpha_0$ is independent of temperature.

The two molecular weight dependent quantities in eq 18 are T_0 and α. Values of the thermal expansion coefficient for polyethylene[19] are well described by[2]

$$\alpha = \alpha^\infty(1 + \beta/M) \tag{19}$$

where $\alpha^\infty \cong 5.1 \times 10^{-4}/°\mathrm{C}$ and $\beta = 160$.

By substituting eq 15 and 19 into eq 18b we can calculate E_ζ as a function of molecular weight. The values so obtained are shown by the dashed line in Figure 12. Figure 12 also shows the E_ζ that was experimentally determined from the temperature dependence of ζ (eq 13) at 150 °C. The agreement is quite good.

Remarks

We have emphasized the value of determining the product ηD when testing molecular theories. This procedure eliminates the local friction factor so that comparisons with the Rouse theory require no unknown parameters and comparisons with the Doi–Edwards reptation theory require only the molecular weight between entanglements, M_e, a parameter that can be easily determined from independent measurements. Although this study was con-

Table IV
Effect of Polydispersity on the Calculated Diffusion Coefficient

$\bar{M}_w/\bar{M}_n$	β	$\bar{K}/K$
1.05	20	1.16
1.20	5	1.8
1.50	2	4.5

cerned with the molecular weight dependence of ηD for polymer melts, it would be useful to determine the concentration dependence of ηD and compare that with theories of polymer solutions.

Acknowledgment. We thank J. Nichols of Petrolite Corp. for his assistance in obtaining the low molecular weight polyethylene samples used in this study. We also acknowledge many useful discussions with Bill Graessley and the help of Alan Tonelli, who calculated the radius of gyration as a function of molecular weight and temperature. After this work was completed we received a preprint from G. Fleischer that also discusses the effects of polydispersity and free volume on the self-diffusion coefficient of polyethylene.

Appendix

The effect of polydispersity on diffusion coefficients measured by NMR has been discussed by one of us[61,62] and by Callaghan and Pinder.[63] The papers of Bernard and Noolandi[64] and Lodge et al.[65] also contain material and earlier references that are relevant to the problem.

The attenuation of spin echoes given by eq 2 only applies to monodisperse materials. When polydisperse samples are studied, both the diffusion coefficient and the nuclear relaxation times of each length molecule in the mixture will be different. Experimental conditions can usually be chosen so that the effects of molecular weight dependent relaxation times are not important.[61] The discussion to follow assumes that this is the case.

When eq 2 is rewritten to account for molecular weight dependent diffusion coefficients, we obtain

$$R = \int_0^\infty W(M) \exp[-QD(M)]\, \mathrm{d}M \tag{A-1}$$

$$Q = \gamma^2 G^2 \delta^2 (\Delta - \delta/3) \tag{A-2}$$

where $W(M)$ is the mass fraction of polymers with mass M. Let the diffusion coefficient for monodisperse polymers obey a power law

$$D = K/M^\alpha \tag{A-3}$$

In general it should be possible to use echo attenuation data covering a wide range of Q with a nonlinear regression method to obtain the constants K and α.

In the work reported here we used a more limited procedure that extracted D from the initial slope of ln R vs. Q. The value of D so obtained was correlated with the weight-average molecular weight, $\bar{M}_w$. We intend to show that the constant $\bar{K}$ in the correlation we used (eq 3)

$$D = \bar{K}/\bar{M}_w^{\ \alpha} \tag{A-4}$$

will depend on the molecular weight distribution of the sample. By expansion of the exponential in eq A-1, it can be seen that the absolute value of the initial slope in a plot of ln R vs. Q is given by

$$\int_0^\infty W(M)D(M)\, \mathrm{d}M \tag{A-5}$$

The Schulz–Zimm distribution function should be suitable to use in eq A-5 for the narrow molecular distribution samples in this study. Accordingly[66]

$$W(M) = \frac{\beta^{\beta+1}}{\Gamma(\beta+1)\bar{M}_n}\left(\frac{M}{\bar{M}_n}\right)^\beta \exp[-\beta M/\bar{M}_n] \tag{A-6}$$

where $\beta = [(\bar{M}_w/\bar{M}_n) - 1]^{-1}$ and $\Gamma(x)$ is the gamma function.[67]

High molecular weight polymers in the entangled regime have a value of $\alpha \simeq 2$. Our calculations are limited to this case although it is easy to generalize them to other values of α. Using eq A-5 and A-6, we find

$$D(\bar{M}_w) = \frac{\bar{K}}{\bar{M}_w^{\ 2}} = \frac{(\beta+1)^2}{\beta(\beta-1)} \frac{K}{\bar{M}_w^{\ 2}} \tag{A-7}$$

As suggested by eq A-7 the value of $\bar{K}$ is larger than the K for monodisperse polymers and strongly dependent on molecular weight distribution. Table IV gives the magnitude of the effect. Note that the diffusion coefficient at fixed $\bar{M}_w$ rises sharply with increased polydispersity. Changing $\bar{M}_w/\bar{M}_n$ from 1.05 to only 1.2 raises $D_{\mathrm{NMR}}(\bar{M}_w)$ by 55%.

This sensitivity to molecular weight distribution may account for some of the difference between Klein's study and this one. Klein has shown that the diffusion coefficient obtained by his tracer method is independent of molecular weight distribution if $\alpha = 2$ and the comparison is done at constant $\bar{M}_w$.[43]

Molecular weight distribution effects could also cause the product $\eta D(\bar{M}_w)$ to be larger and therefore closer to the Doi–Edwards theory than realistically is the case. If corrections for polydispersity were made, they would moderately decrease the experimental values of ηD in Figure 8.

We are now investigating some very narrow molecular distribution polyethylene-like samples prepared by hydrogenating polybutadiene.[45] Use of these samples should eliminate the need for polydispersity corrections.

Registry No. Polyethylene, 9002-88-4.

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Equilibrium Partitioning of Flexible Macromolecules between Bulk Solution and Cylindrical Pores

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ABSTRACT: A Monte Carlo technique was used to investigate the effects of segment length and chain length on the partitioning of freely jointed chains between bulk solution and cylindrical pores. The results demonstrate that the partition coefficient, or equilibrium pore-to-bulk concentration ratio, of a chain with finite segment length can be substantially higher than that of a chain with an infinite number of infinitesimally short segments but with the same radius of gyration. These differences are prominent even for chains having more than 400 segments and become increasingly important as the radius of gyration of the macromolecule approaches and exceeds the pore radius. The effects of attractive interactions between chain segments and the pore wall, in the form of a square-well potential, were also investigated with the Monte Carlo technique. The introduction of small, attractive interaction energies produced dramatic increases in the partition coefficients of finite chains.

Introduction

The behavior of flexible macromolecules in finely porous materials plays an important role in separtion processes such as ultrafiltration and size-exclusion chromatography. The equilibrium distribution of macromolecules between bulk solution and the porous medium must be known in order to understand these processes. This equilibrium is usually expressed in terms of the partition coefficient or equilibrium pore-to-bulk concentration ratio.

In one of the earliest theoretical studies of the partitioning of flexible macromolecules, Casassa[1] derived expressions for the partition coefficient of a random-flight chain in pores of various shapes. Using an analogy to heat conduction, he found the partition coefficient, K, for a chain with radius of gyration $\langle s^2 \rangle_0^{1/2}$ in a cylindrical pore of radius R to be

$$K = 4 \sum_{i=1}^{\infty} (1/\alpha_i^2) \exp(-\alpha_i^2 \lambda_G^2) \tag{1}$$

where $\lambda_G = \langle s^2 \rangle_0^{1/2}/R$ and the α_i are the roots of $J_0(\alpha) = 0$, J_0 representing the Bessel function of the first kind and of order zero. While the analysis is valid for a chain with an arbitrary distribution of segment lengths, the results were obtained for the limiting case of an infinite number of chain segments with vanishingly small mean length. (The boundary condition used in the derivation is physically reasonable only in this limit.) Casassa's concise and elegant result indicates the importance of the molecule-

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