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Linear Viscoelasticity and Translational Diffusion of Linear Flexible Polymers

Y.-H. Lin

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

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ABSTRACT: An extensive quantitative agreement between the K_d values ($K_d = DM^2$, where D is the diffusion constant and M the molecular weight) obtained directly from the diffusion measurements and calculated from the viscoelastic data in terms of the developed general theory has been obtained. The agreement confirms that the theoretical bases in the Doi–Edwards theory are valid. Several results indicate that a chain entanglement effect exists in the molecular weight (MW) region as low as M_e to M_c. The traditional idea of describing the viscoelastic behavior in terms of the Rouse theory in this low-MW region should be abandoned. It is shown that the entanglement effect as described by the developed general linear viscoelastic theory explains the difference of a factor of 3 between the K_d value obtained from the diffusion measurements and that calculated from the viscosity value at M_c in terms of the Rouse theory. It is suggested that the difference between the two K_d values in the case of polyethylene, which is more than can be corrected for by the factor of 3, is related to its abnormally high M_c/M_e ratio.

As a polymer chain reptates out of its original tube following a step deformation, the stress caused by the deformation is relaxed, and the reptation process has a definite effect on the translational diffusion of the center of mass of a polymer chain.

The reptation chain model[1–5] has stimulated many studies in both viscoelasticity and molecular diffusion of nearly monodisperse polymers. The Doi–Edwards theory[2–5] gives the molecular weight (MW) dependence of the zero shear viscosity and diffusion constant as

$$\eta_0 = \rho R T \pi^2 K M^3 / 15 M_e^{\,2} \tag{1}$$

$$D_G = K_d M^{-2} \tag{2}$$

where K is the friction factor ($= \zeta b^2 N_0^{\,2} / k T \pi^2 M^2$, where ζ, b, and M/N_0 are the friction constant, length, and mass associated with each Kuhn segment) and K_d is related to K as[2,3,6,7]

$$K_d = K_\infty M_e / 3\pi^2 K \tag{3}$$

where K_∞ is the ratio of the mean-square end-to-end distance of the polymer molecule to the molecular weight ($R_e^{\,2}/M$) and M_e is the entanglement MW ($=4\rho RT/5G_N$). Equation 1 deviates somewhat from the experimental observation of the 3.4 power law in the MW region above M_c, where most experimental measurements have been made. Either by getting around eq 1 or by using a further developed theory, two approaches to check the consistency between the viscoelasticity data and diffusion data have been proposed:

(a) Theoretically both the Rouse theory[8,9] and the Doi–Edwards theory share the same K value.[6,7,10–12] Graessley[11] proposed using the viscosity value at M_c (the critical molecular weight, at which the zero shear viscosity transits from $\propto M$ to $\propto M^{3.4}$) to calculate the K value in terms of the Rouse theory[8,9]

$$K = 36 \eta_0(M_c) / \rho R T \pi^2 M_c \tag{4}$$

and then the K_d value (eq 3) for comparison with that obtained from the diffusion measurements. The relation linking K_d and $\eta_0(M_c)$ is

$$K_d = (\rho R T)^2 K_\infty M_c / 135 G_N \eta_0(M_c) \tag{5}$$

(b) The diffusion constant is for describing the motion of the center of mass and thus to good accuracy should not be affected by intramolecular motions. On the basis of such a position, Lin[7,13] compared the *pure* reptation time, $\tau_c°$, calculated from the diffusion data and that obtained by correcting the terminal relaxation time (obtained from the detailed shape analyses of the viscoelastic spectra in terms of the developed general theory) for the effect of chain contour length fluctuation, an intramolecular motion.

Through approach a Graessley[11] using $G_N = 2 \times 10^7$ dyn/cm^2, $\rho = 0.767$ g/mL, $K_\infty = 1 \times 10^{-16}$, and $\eta(M_c) = 0.32$ P at $M_c = 3800$ calculated $K_d = 0.34$ (cm^2 g)/(s mol^2) for linear polyethylene at 176 °C. This value is in good agreement with $K_d = 0.26$ (cm^2 g)/(s mol^2) obtained by Klein.[14] However, later diffusion measurements of linear polyethylene by NMR[15–17] and hydrogenated polybutadiene by neutron scattering[18] gives K_d values to be 1.68–2.9 and 0.58 (cm^2 g)/(s mol^2), respectively (corrected to 176 °C). The $\eta_0(M_c)$ value used by Graessley appears too small compared to more recent values. Based on viscosity data obtained by Pearson et al.,[17] $\eta(M_c{=}3800)$ should be at least 0.72 P (corresponding to $\eta_0 = 0.96$ P at $M_c = 5000$, corrected to 176 °C; and the value should be higher if correction for the difference of free volume is made). Lodge[19] obtained $\eta(M_c) = 1.15$ P at $M_c = 5200$ (correspondingly, $\eta(M_c) = 0.84$ P at $M_c = 3800$). On the basis of these more recent viscosity data and by use of $G_N = 2.7 \times 10^7$ dyn/cm^2, $\rho = 0.767$ g/mL, and $K_\infty = 1.1 \times 10^{-16}$,[20,21] the K_d value calculated according to eq 5 should be $\sim$0.13. This value is about 4.5–22 times smaller than the K_d values obtained from the more recent diffusion motion measurements.

In the case of polystyrene, more consistent viscosity and diffusion data are available. Diffusion data at 237 °C obtained by Bueche[22] via radiolabeling can be corrected to 174 °C by using the temperature dependence results of viscosity at high MWs.[23] This gives $K_d = (9 \pm 2.8) \times 10^{-3}$. Kramer et al.[24,25] using forward recoil spectrometry and a marker displacement method obtained at 174 °C $K_d = 8 \times 10^{-3}$ and 7×10^{-3}, respectively, in good agreement with the result of Bueche. Antonietti et al.[26] using forced Ray-

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leigh scattering of polystyrene with a low-concentration dye label obtained $K_d = 8 \times 10^{-3}$ (corrected to 174 °C) in close agreement with the above values.

Based on the results of Plazek and O'Rouke[23] and corrected for the T_g difference at different MWs in the low-MW region,[27] $\eta_0(M_c)$ at 174 °C should be in the close neighborhood at 2810 P at $M_c = 33\,000$. Lodge[19] obtained $\eta(M_c) = 2760$ P at $M_c = 33\,000$ (corresponding to his value $\eta(M_c) = 2930$ at $M_c = 35\,000$). Using the obtained $\eta(M_c)$ value, $K_\infty = 0.43 \times 10^{-16}$,[20,28,29] $G_N = 2.1 \times 10^6$ dyn/cm^2,[6,30] and $\rho = 0.96$ g/mL, K_d is calculated to be 0.0023, which is about a factor of 3 smaller than the K_d values determined from the diffusion motion measurements. Recently Lodge[19] pointed out this difference factor and suggested that, in addition to the reptation process, other modes of motions contribute to the diffusion mobility. If it were so, since the diffusion motion should be independent of the intramolecular motions, the possible remaining choice could be one of the constraint release models.[31-34]

The detailed shapes of the linear viscoelastic spectra have been extensively analyzed in terms of the developed general theory, which takes the chain contour length fluctuation effect into account.[6,35,36] Equivalently to approach b, one can calculate the K_d value through eq 3 from the friction factor, K, obtained from the line-shape analyses of the viscoelastic spectra.[6] It has been tested with experimental results that the K value is independent of MW to MW as low as $1.24M_e$.[35] At 185 ± 1 and 154 ± 1 °C, the K values have been determined to be 4.8×10^{-13} with $M_e = 13\,000$ and 1.85×10^{-11} with $M_e = 13\,800$, respectively.[6] Using the temperature dependence of viscosity,[23] K_d is calculated to be 1.39×10^{-2} and 1.30×10^{-2} at 174 °C from the above two sets of data. The K values were obtained by using samples whose MWs are relatively high ($>14M_e$).[6] It has been discussed[35,36] that, because of the broader molecular weight distribution (MWD) in this relatively high MW region, the K values obtained from the line-shape analyses are about 30% smaller than what they should be. Corrected for this effect, $K_d = 9.4 \times 10^{-3}$ (the average of the two).

$K = 5 \times 10^{-9}$ (see Figure 17 of ref 35, the K value in the MW region below 100 000, where the effect of MWD appears to be negligible) with $M_e = 13\,500$ has been obtained from the line-shape analyses of the linear viscoelastic spectra at 127.5 ± 0.5 °C. Corrected for the temperature dependence,[23] K_d is calculated to be 8.8×10^{-3} at 174 °C from this set of data.

In the high-MW region (>100 000), the contributions of the two fast relaxation processes, $\mu_A(t)$, the Rouse motion of an entanglement strand, and $\mu_X(t)$, the chain slippage through entanglement links, to the zero shear viscosity are negligible.[6,35,36] When these two processes are neglected, the zero shear viscosity as a function of MW can be derived from the general theory and has the following analytical form[6,36]

$$\eta_0 = \frac{\rho R T \pi^2}{15} K \frac{M^3}{{M_e}^2}\left[(1 - (M_e/M)^{0.5})^3 + \frac{1}{3}(M_e/M)^{1.5} \right]$$
$$= \frac{\pi^2}{12} K G_N \frac{M^3}{M_e}\left[(1 - (M_e/M)^{0.5})^3 + \frac{1}{3}(M_e/M)^{1.5} \right] \quad (6)$$

When the viscosity data of Plazek and O'Rourke[23] at $M_w = 189 \times 10^3$ and 600×10^3 is used, the K values are determined to be 2.5×10^{-12} and 2.8×10^{-12}, respectively, at 174 °C from eq 6 with $M_e = 13\,500$. In turn, $K_d = 7.8 \times 10^{-3}$ and 7.1×10^{-3} are calculated from eq 3.

The K_d values obtained from the diffusion measurements and from analysis of the viscoelastic results in terms of the general theory as described above are listed in Table I. One can notice the consistent agreement within experimental errors between the K_d values obtained from these two types of studies.

Table I

	$K_d \times 10^3$, (cm^2 g)/(s mol^2) (174 °C)
Diffusion Measurements	
(1) Bueche (1968), radiolabeling	9 ± 2.8[a]
(2) Kramer et al. (1984), forward recoil spectrometry	8
(3) Kramer et al. (1985), marker displacement	7
(4) Antonietti et al. (1984), forced Rayleigh scattering	8[a]
	ave. 8 ± 10%
Viscoelastic Measurements	
(1) Plazek and O'Rourke (1971)	
$\eta_0 = 8.7 \times 10^5$ at $M_w = 189 \times 10^3$ at 174 °C	7.8
$\eta_0 = 4.7 \times 10^7$ at $M_w = 600 \times 10^3$ at 174 °C	7.1
analyzed in terms of eq 6 with $M_e = 13\,500$	
(2) Lin (1984), shape analyses of the viscoelastic spectra	
$K = 4.8 \times 10^{-13}$ with $M_e = 13\,000$ at 185 ± 1 °C	9.5[a]
$K = 1.85 \times 10^{-11}$ with $M_e = 13\,800$ at 154 ± 1 °C	9[a]
30% correction due to a MWD effect (see refs 35 and 36)	
(3) Lin (1986), shape analyses of the viscoelastic spectra	
$K = 5 \times 10^{-9}$ with $M_e = 13\,500$ at 127.5 ± 0.5 °C	8.8[a]
(4) Plazek and O'Rouke (1971), Lodge (1990)	
$\eta_0(M_c) = 2808$ at $M_c = 33\,000$	
$\eta_0(M_c) = 2703$ at $M_c = 33\,000$	7.1
analyzed in terms of Graessley's method but corrected for chain entanglement effect existing in the MW region of M_e to M_c as shown in Figure 1; also, including a 10% correction for the difference between the conventional and theoretical T_g correction	
	ave. 8.2 ± 13%

[a] Corrected to 174 °C by using the temperature dependence of viscosity data in ref 23.

This agreement is consistent with the conclusion that the constraint release process is nil in a monodisperse system as drawn from the quantitative line-shape analyses of the linear viscoelastic spectra in terms of the proposed general theory[6,7,12,35,36] and also drawn from the studies of the binary blend systems (consisting of two nearly monodisperse polymers).[37,38]

Clearly, there is a discrepancy between the conclusions reached at through approaches a and b. In this paper, we explain what causes the difference.

The justification for using eq 5 is based on the idea that in the MW region between M_e and M_c the Rouse theory is applicable and there is no entanglement. This idea has been traditionally accepted because, after correction to a state of iso-free-volume at different MWs, the MW dependence of the zero shear viscosity in the region between M_e and M_c follows that of the Rouse theory ($\propto M$).[9] However, several observations as listed below have been made, which suggest that this concept be abandoned.

(1) It has been shown[36] that the line shape of the linear viscoelastic spectrum of a nearly monodisperse polystyrene sample just above M_e ($1.24M_e$) is not described by the Rouse theory but is well described by the general theory, which contains the effect of entanglement. Just below M_e, the line shape is well described by the Rouse theory. The transition point at M_e appears quite sharp.

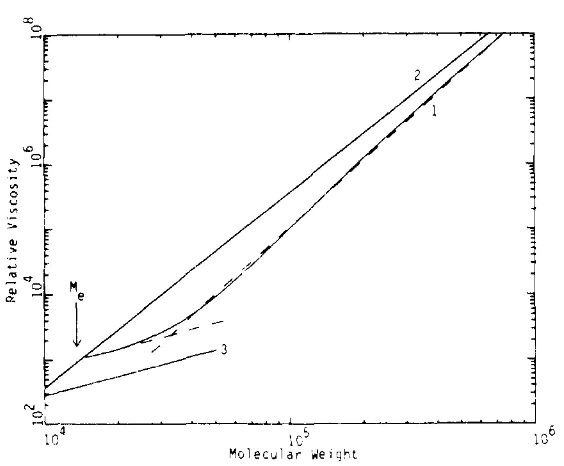

Figure 1. Reproduced from Figure 2 of ref 36. Comparison of the theoretical curve (curve 1) of the general linear viscoelastic theory with $K'/K = 5.5$ and the power law relations $\eta_0 \propto M^{3.4}$ above M_c and $\eta_0 \propto M$ below M_c (the dashed lines). Also shown are the curves of the Doi–Edwards theory (curve 2) and the Rouse theory (curve 3). The curves are calculated with $M_e = 13\,500$ for polystyrene (M_e determined from the plateau modulus is the only parameter used in the calculation). M_c occurring at 33 000 is predicted on curve 1. The theoretical curve calculated with $K'/K = 5.5$ includes the contributions from $K'/K = 3.3$ (see eq 5 of ref 39) and the glassy relaxation (see ref 36 for details). The theoretical curves calculated with $K'/K = 5.5$ and $K'/K = 3.3$ over the whole MW range are virtually identical above M_c and differ ~20% at M_e.

(2) The MW dependence of the polymer glass transition temperature shows a clear transition point at M_e. It has been shown that this transition point is related to the onset of the topological constraint effect due to entanglement at M_e[27,36] (2 is related to 1).

(3) The general theory explains very well the MW dependence of the zero shear viscosity including (a) the 3.4 power law in the MW region above M_c, where most experimental measurements have been made, (b) the transition point, M_c, and (c) the linear dependence on M in the MW region between M_e and M_c.[6,36,39] The solid line 1 in Figure 1 is calculated from the general theory with $K'/K = 5.5$ (K' being the K value in the glass–rubber transition region, i.e., the $\mu_A(t)$ process region. From the shape analyses of the linear viscoelastic spectra, it has been found that K'/K decreases from a plateau value (3.3 at MW > $10M_e$) to 1 as the decreasing MW approaches M_e (see eq 5 of ref 39 and the figure caption of Figure 1), remaining constant over the whole MW range, and corresponds to the theoretical values at the iso-free-volume state. See ref 35 and 36 for details. It is clear that the calculated zero shear viscosity between M_e and M_c, while apparently proportional to M as would be expected from the Rouse theory, is larger than the Rouse value by a factor of about 2.8. This is due to the effect of chain entanglement existing at MW as low as M_e to M_c.

In the case of polystyrene, the K_d value calculated from eq 5 is smaller than that obtained from the diffusion measurements by a factor of about 3, as mentioned above. On the basis of the result described in point 3, the experimental viscosity value $\eta_0(M_c)$ used in eq 5 to calculate K_d is in fact about 2.8 times larger than the Rouse value, which, though nonexistent between M_e and M_c, should have been used. Corrected for this factor, the two K_d values become in good agreement. In other words, approach a, after this correction is made, becomes consistent with approach b in comparison of the viscoelasticity and diffusion data of polystyrene. This agreement supports specifically that the developed general theory bridges the gap between the Rouse theory and the Doi–Edwards theory. This conclusion was previously reached in the study of a series of concentrated polystyrene solutions[12] consisting of a nearly monodisperse high-MW polystyrene component ($M \gg M_e$) and another nearly monodisperse polystyrene component with MW just below M_e. The contribution to the total viscoelastic spectrum from the high-MW component was analyzed in terms of the general theory and that from the low-MW component in terms of the Rouse theory. Within experimental error, the friction factor in the general theory part is found to be identical with that in the Rouse theory part.

Note that a figure similar to Figure 1 showing the factor of difference of ~2.8 was first published in 1984,[6] when the general theory was proposed. It was suggested then that the entanglement constraint effect exists in the $M_e < M < M_c$ region.

On the basis of the MW dependence of T_g values[27] and the temperature dependence of viscosity data[23] of polystyrene, it is found that between M_e and M_c the conventional iso-free-volume correction is not exactly identical with that based on comparison of theoretical viscosity values [namely, comparison of calculated values using $K'/K = 5.5$ or $K'/K = 3.3$[35,36] over the entire MW range and using the MW dependence of K'/K (eq 5 of ref 39)]. Listed is the comparison of the correction factors.

MW	conventional (corrected to 174 °C)	theoretical $K'/K = 5.5$	$K'/K = 3.3$
15 000	2	1.8	1.5
33 000	1.6	1.4	1.2

The conventional way of correction does not take anisotropy of the friction factor (i.e., $K'/K > 1$) into account. It has been shown from the detailed shape analyses of the measured viscoelastic spectra that K is independent of MW to as low as $1.24M_e$. K being independent of MW has a buffering effect on the degree to which the MW dependence of free volume or T_g affects the viscosity value in the MW region of M_e to M_c, especially at M_c. This is most likely the reason why the conventional correction is slightly larger than the theoretical correction. The difference of the correction factors is not great. It can be easily buried within the experimental errors of the measured viscosity and T_g values. When approach a is used to calculate K_d, as described above, the $\eta_0(M_c)$ value used in the calculation is based on the conventional correction. Thus, the correction factor for K_d should be slightly larger than 2.8 and is around 3.1. This brings approaches a and b into closer agreement. This corrected K_d value is also listed in Table I.

In the case of polyethylene, the two K_d values differ by a factor more than can be corrected for by the factor of 3.1. As explained below, this can be associated with the unusually large M_c/M_e ratio of polyethylene.

Most polymers (e.g., polystyrene, poly(α-methylstyrene), poly(vinyl acetate), polyisobutylene, polyisoprene) have $M_c/M_e \sim 2.4$, while some polymers, typically those with high values of the plateau modulus have significantly larger M_c/M_e ratios ($M_c/M_e \approx 5.2$–6.8 for polyethylene and $M_c/M_e \approx 4.3$ for polybutadiene).[39-41] We may consider $M_c/M_e \sim 2.4$ as a "normal case". The developed general theory should explain very well the viscoelastic data including those in the region of M_e to M_c of the polymers in this category, as has been demonstrated in the case of polystyrene.[35,36] It was suggested[39] that the higher M_c/M_e values of the polymers in the "abnormal" category should

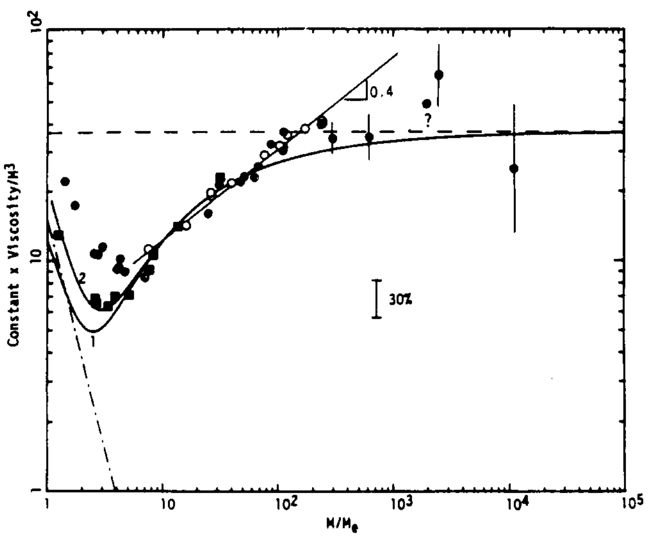

Figure 2. Reproduced from Figure 2 of ref 39. Comparison of the zero shear viscosity data (η_0/M^3 vs M/M_e) of nearly monodisperse polybutadiene (● from Table XI of ref 41; ○ from ref 42) and polystyrene (■ from ref 36) samples with the general theory (curve 2). The experimental values are without the iso-free-volume correction and so is curve 2 (see ref 39 for details). The M_e values used for normalizing MW (for the horizontal coordinate) in plotting the experimental data are 1480 and 13 500 for polybutadiene and polystyrene, respectively. Also shown are the line of slope 0.4, and the values calculated by using the same value of the friction factor, K, from the Rouse theory (- · -) and the Doi–Edwards theory (- -). At M_e, the zero shear viscosity value of curve 2 is higher than the Rouse value by ~30%. Curve 1 is calculated from the general theory without including the $\mu_A(t)$ and $\mu_X(t)$ processes (eq 29 of ref 6).

be caused by (perturbation) effects additional to those considered in the general theory.

Figure 2 (reproduced from Figure 2 of ref 39) shows the comparison of the viscosity data of polystyrene[36] and polybutadiene[41,42] with the general theory in a normalized way: η_0/M^3 vs M/M_e. Unlike the solid line shown in Figure 1, curve 2 (calculated from the general theory with the MW dependence of K'/K as shown in Figure 1 of ref 39, i.e., eq 5 of ref 39) and experimental values shown in Figure 2 are all without the iso-free-volume correction. As explained in ref 39, it is preferable to compare these theoretical and experimental results all without the correction. Doing so or not does not affect the main point we are going to make here: While the experimental data points of polystyrene are in good agreement with the theoretical values (curve 2) over the whole MW range; the data points of polybutadiene in the region of M_e to M_c (M_c is about at the minimum point of η_0/M^3) are 40–70% higher than the polystyrene points and curve 2. It is apparent from Figure 2 that the high viscosity values of polybutadiene in the region of M_e to M_c are associated with its unusually high M_c/M_e ratio. Having a very high M_c/M_e ratio, polyethylene should have a similar effect. Then, one would expect that the $\eta_0(M_c)$ value used in eq 5 for calculating the K_d value of polyethylene be larger than the Rouse value by a factor significantly larger than 3. This would lead to the large difference between the K_d value for polyethylene obtained from the diffusion measurements and that calculated from the viscosity at M_c in terms of the Rouse theory (approach a).

In summary, an extensive quantitative agreement between the K_d values obtained directly from the diffusion measurements using different techniques and calculated from the viscoelastic data of reliable sources in terms of the developed general theory has been obtained. The agreement confirms that the theoretical bases in the Doi–Edwards theory are valid. The deviation of $\eta_0 \propto M^3$ as given by the pure reptation model from the experimental results ($\eta_0 \propto M^{3.4}$) in the MW region above M_c where most experimental measurements have been made is mainly due to the chain contour length fluctuation effect as incorporated into the general theory. This is in accord with the earlier conclusion that the viscoelastic relaxation is not affected by the so-called constraint release process in a monodisperse system as drawn from the detailed shape analyses of the linear viscoelastic spectra in terms of the general theory[6,7,12,35,36] and also drawn from the studies of the binary blend systems.[37,38] The developed stress relaxation function contains the structural factors for the relaxation strengths and times of four relaxation modes and the friction factor K (K' in the $\mu_A(t)$ region). The combined theoretical form of the structural factors allows for quantitative shape analyses of the viscoelastic spectra.[6,35] The theory explains the MW dependence of the zero shear viscosity and the steady-state compliance and their respective transition points, M_c and M_c'.[6,36] Here it is shown that the developed general theory is quantitatively valid as well in considering the friction factor (i.e., comparing the K_d values).

As pointed out in earlier reports,[6,27,35,36,39] chain entanglement already affects the viscoelastic behavior in the region of M_e to M_c. The two K_d values obtained for comparison in approach a for polystyrene are in good agreement after correcting for a factor of about 3.1 due to the chain entanglement effect as described by the general theory. It is suggested that whatever effect that causes the unusually high M_c/M_e ratio of polyethylene should be responsible for the large difference between its two K_d values obtained in approach a. It has been shown that some uncertainty of the diffusion constant of polyethylene measured using pulse field gradient NMR can be due to the molecular weight distribution of the sample,[17] but the error cannot account for the large difference between the two K_d values obtained in approach a for polyethylene.

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Registry No. Polyethylene, 9002-88-4; polystyrene, 9003-53-6; poly(α-methylstyrene), 25014-31-7; poly(vinyl acetate), 9003-20-7; polyisobutylene, 9003-27-4; polyisoprene, 9003-31-0; polybutadiene, 9003-17-2.