Macromolecules 1984, *17*, 431-437

Influence of Multiple Length Scales on the Behavior of Polymer Self-Diffusion in the Semidilute Regime

P. T. Callaghan* and D. N. Pinder

Department of Chemistry, Biochemistry, and Biophysics, Massey University, Palmerston North, New Zealand. *Received June 23, 1983*

ABSTRACT: The pulsed field gradient NMR method has been used to obtain self-diffusion coefficients of polystyrene in carbon tetrachloride and perdeuteriobenzene over a wide range of concentration and molar mass. These observations have been used to examine critically the various available theoretical models pertaining to the dynamical behavior of semidilute solutions of random coil polymers. We find that the theoretical predictions are unable to completely account for experimental behavior in the semidilute regime. In particular the simple de Gennes scaling law $D_s \sim M^{-2}c^{-1.75}$ is not confirmed, which indicates that there is no unique length scale in semidilute solutions. Neither is the adaptive model developed by Schaefer et al. from the mean field theory supported by our measurements, for no extensive "marginal" region is found in which $D_s \sim M^{-2}c^{-2.5}$. The crossover model of Weill and des Cloizeaux has been applied to reptational motion in semidilute solutions. Despite inconsistencies in this adaptation, the predictions of the crossover model are more in accord with observation for the concentration dependence of D_s, although the $D_s \sim M^{-2}$ dependence implied both in this model and the marginal solvent model is observed only at concentrations sufficiently high that the system displays asymptotic Θ-like behavior. Thus the assumptions inherent in all these approximate reptation-based models are open to question, and further theoretical investigation is appropriate.

Introduction

The semidilute concentration regime in random coil polymer solutions spans the domain in which each chain suffers topological constraints (entanglements) due to neighboring coils but the free segments between entanglements are sufficiently long that their conformation resembles that of an isolated polymer chain. Such behavior is held to exist between the lower and upper semidilute concentration limits c^* and c^{**}, respectively. c^* marks the boundary between coil overlap and separation such that the mean interentanglement distance, ξ, comprises a complete chain. c^{**} corresponds to the high-concentration extreme, where the number of monomer subunits in ξ is so small that the usual assumptions about chain statistics no longer apply. In this sense c^{**} may be regarded as the flexibility limit.

The precise definition of c^*, c^{**}, and ξ will depend on the model employed. This is particularly obvious in the case of c^* where it is necessary to define the size of the fundamental statistical segment. For c^* a geometrical description requires

$$c^* = M/R^3 \tag{1}$$

where M is the polymer molar mass and R the polymer coil dimension, which may be chosen variously as the radius of gyration or the root mean square end to end length. Notice c^{**} is expected to be molar mass independent while $c^* \sim M^{-0.80}$. It is convenient therefore to adopt the empirical view that c^* and c^{**} mark the limits of the concentration regime over which "model" semidilute behavior is observed. Such a yardstick has been commonly employed in the examination of one of the most useful experimental parameters, the polymer self-diffusion coefficient, D_s. The danger inherent in such an approach is obvious since it allows the choice of a regime of data to fit the model at hand. Given these difficulties it is reasonable to adopt the view that the most successful semidilute model is that which describes the data over the widest possible concentration range and which is consistent with a reasonable definition of the boundaries c^* and c^{**}. There is also another check in that c^* and c^{**} should vary with molar mass in the predicted manner. It is the nature of the model behavior and its consistency with data which is the subject of close scrutiny in this paper.

Central to the concept of semidilute solutions is the length scale ξ, which may be defined either in terms of a monomer-monomer pair correlation function or as a screening length in the monomer-monomer interaction.[1,2] Furthermore ξ may enter the theory of semidilute solutions in either a static or dynamic guise. An example of a static length is the mean distance between entanglements relating ξ to c by the geometrical relation

$$c = gm/\xi^3 \tag{2}$$

where m is the statistical subunit mass and g is the number of subunits within ξ. The hydrodynamic length contained in the friction coefficient of the interentanglement segment is an obvious example of a dynamical use. Fundamental to a simple scaling model for semidilute solutions is the view that ξ exists as a single length scale differing only in constant numerical coefficients between the various length definitions. Such a view was first proposed by de Gennes in 1976.[3,4] We now review this model and two subsequent modifications. Then we apply the various predictions to our self-diffusion data for polystyrene random coils in two solvents, carbon tetrachloride and perdeuteriobenzene.

de Gennes Model. Here the assumption of a unique length scale is incorporated in a depiction of the semidilute random coil polymer solution as a melt of blobs as shown in Figure 1. This amalgam has been a powerful aid in the understanding of entangled polymer dynamics. de Gennes proposed that in good solvents the blob represents the segment of the polymer chain between adjacent topological constraints (such as interchain entanglements) and within the blob one defines an isolated solvated random coil comprised of g monomer subunits obeying excluded volume statistics. On a scale larger than the blob root mean square dimension ξ, a close-packed melt is defined in which a random coil comprised of l blob subunits obeys Gaussian statistics. Thus if we write the total chain root mean square end to end separation as R then

$$R \simeq \xi l^{1/2} \quad \text{(Gaussian behavior)} \tag{3a}$$

$$\xi \simeq a g^{\nu} \quad \text{(excluded-volume behavior)} \tag{3b}$$

where ν is the Flory index and is taken to be close to 0.6, and a is the individual monomer or statistical subunit dimension for which the subunit molar mass is m. The total number, N, of statistical segments in the polymer

0024-9297/84/2217-0431$01.50/0

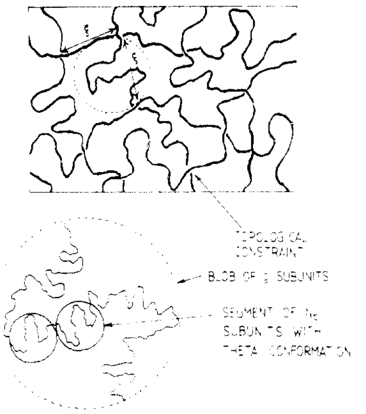

Figure 1. Schematic diagram of length scales in semidilute solution. Note that ξ may be defined variously as ξ_t, the distance between entanglements (tube radius), ξ_G, the blob radius of gyration, ξ_ρ, the monomer–monomer correlation length, and ξ_D, the blob hydrodynamic radius or hydrodynamic screening length.

chain may then be expressed as gl or Mm^{-1}, where M is the polymer molar mass.

The diffusion of the polymer chain in the tube defined by the topological constraints is known as reptation. The blob-reptation theory of de Gennes yields a molar mass and concentration scaling law self-diffusion in the semidilute regime, namely

$$D_s \simeq [l^{-2}kT]/[(18\pi\eta)\xi_D] \tag{4a}$$

$$\sim M^{-2}\xi_D^{-1}\xi_G^{2/\nu} \tag{4b}$$

where ξ_D and ξ_G are dynamic and static lengths, respectively. Assuming the uniqueness of the length scale ξ and relations 2 and 3b

$$D_s \sim M^{-2}c^{(2-\nu)/(1-3\nu)} \tag{5a}$$

and for $\nu = 0.6$

$$D_s \sim M^{-2}c^{-1.75} \tag{5b}$$

Brochard and de Gennes[5] have extended the model to random coil polymers dissolved in Θ solvents. In the semidilute regime the corresponding scaling law for self-diffusion is

$$D_s \sim M^{-2}c^{-3} \tag{6}$$

Mean Field Theory Approach (Marginal Solvent Model). Shaefer, Joanny, and Pincus[6] have also developed a theory for the dynamical behavior of polymer solutions based on the reptation ideas of de Gennes and incorporating the mean field theory for the excluded-volume interaction. Essentially these authors use the mean field theory to calculate the range, ξ_ρ, of the static monomer pair correlation function. They then adopt the de Gennes approach of assuming relationships between the various correlation lengths and, using the concept of reptation, they generate relationships for the variation of dynamical parameters with molar mass and concentration. The most important consequence of this model is the prediction that the de Gennes scaling laws for good and Θ solvent behavior are merely asymptotic limits of a more general relationship which applies in *any* solvent. The regime intermediate between these asymptotes is termed, in solvent description, marginal. Schaefer et al. maintain that polymers at semidilute concentrations in many solvents commonly considered to be "good" in fact display such marginal solvent behavior.

Schaefer et al. have used the reptational concept of de Gennes to obtain the dependence of self-diffusion on M and c throughout the whole range of polymer concentration. Their predicted marginal solvent behavior is quite new and is stated to be characterized by

$$D_s \sim M^{-2}c^{-2.5} \tag{7}$$

although the concentration range over which this expression is expected to obtain is not precisely specified. It is important to note that those authors obtain scaling-like expressions despite the fact that the system is not governed by a single length scale. In particular their model contains two different static lengths, the tube radius, ξ_t, defined according to eq 2 and the static pair correlation length, ξ_ρ, defined by mean field theory. Furthermore the derivation of the M^{-2} relationship (as with the de Gennes theory) depends on the identification of the hydrodynamic screening length for the polymer interentanglement segment, with the range of the static pair correlation function. This identification is a delicate point in the analysis and will be further discussed in the Conclusion. The M^{-2} relationship is one of the major aspects investigated in this work.

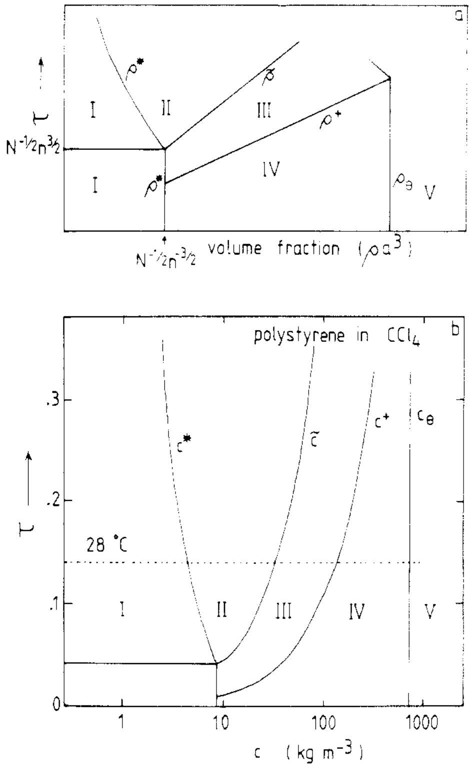

Figure 2. Reduced-temperature–density diagram of Schaefer et al. after Daoud and Jannink. (a) Schematic division of regions; I, dilute (Θ and good solvent); II, semidilute good solvent; III, semidilute marginal; IV, semidilute Θ; V, concentrated. (b) For polystyrene and CCl_4 by using a log scale for concentration. We use $N_\tau = 200$ and $\Theta = -12$ °C, obtained from analysis of molar mass dependence of infinite dilution self-diffusion coefficients.

The predictions of the model of polymer solution dynamics based on the mean field theory approach can be summarized in a reduced-temperature–density diagram (see Figure 2) after the manner of Daoud and Jannink.[7] Notice that in accord with these authors we preserve the use of the monomer density ρ to represent the polymer concentration. The reduced-temperature–density diagram has been divided into five separate regions as suggested by Schaefer et al. and following those authors, can be characterized in terms of parameters a, n, and τ, which apply for a given polymer–solvent system. a is the fundamental subunit size as defined earlier. τ is the system reduced-temperature difference from the Θ point. n is given by the relationship $N_\tau = n^3\tau^{-2}$, where N_τ represents the number of monomers below which excluded volume effects are masked for a given reduced temperature τ. Clearly, at the Θ temperature $N_\tau = N$, the total number of chain monomer units. The concentration regions are as follows:

(I) Dilute $\rho < \rho^*$

(II) Good solvent, semidilute $\rho^* < \rho < \tilde{\rho} = \tau n^{-3} a^{-3}$, where $\xi_\rho \sim a(\rho a^3)^{-3/4} n^{-1/4} \tau^{-1/4}$

(III) Marginal solvent, semidilute $\tilde{\rho} < \rho < \rho^+ = a^{-3}\tau$, where $\xi_\rho \sim a(\rho a^3)^{-1/2} n^{1/2} \tau^{-1/2}$

(IV) Θ semidilute $\rho^+ < \rho < \rho_\Theta = a^{-3} n^{-1/2}$, where $\xi_\rho \sim a(\rho a^3)^{-1} n^{1/2}$

(V) Concentrated $\rho_\Theta < \rho$, where $\xi_\rho \leq b$, the size of the smallest "flexible" subunit

The expressions for the length scales in the various regimes enable us to predict the behavior of dynamical parameters. In particular one can predict the variation of D_s with c (see Schaefer[8]).

$$D_s \sim M^{-2} \rho^{-1.75} \quad \text{(region II)} \tag{8a}$$

$$\sim M^{-2} \rho^{-2.50} \quad \text{(region III)} \tag{8b}$$

$$\sim M^{-2} \rho^{-3.0} \quad \text{(region IV)} \tag{8c}$$

However it should be noted at this stage that there is no firm foundation for the sharp division between regions III and IV as indicated in Figure 2. Throughout these regions the model predicts

$$\xi_\rho = a n^{1/2} (\tau \rho a^3 + \rho^2 a^6)^{-1/2} \tag{9}$$

and the bold division into two regions may not be supported by experimental observations. Indeed there may be no observable extended region of concentration over which $D_s \sim M^{-2} c^{-2.5}$.

In summary, the diagram represented in Figure 2 implies that an investigation of the variation with concentration of a dynamical parameter such as D_s for a fixed molar mass polymer at a fixed temperature corresponds to a horizontal traverse and therefore the system might be expected to display dilute, semidilute good solvent, marginal solvent, Θ solvent, and concentrated behavior successively as the polymer concentration is increased. However the theory does not readily enable us to define in a quantitative manner the crossover from one regime to another and, as indicated above, the extent of marginal solvent behavior is not clearly specified.

In changing the molar mass, the effect on Figure 2 is to alter the intersection point of the ρ^* and $\tilde{\rho}$ lines, but the slope of the $\tilde{\rho}$ and ρ^+ lines remains fixed. The extent of the semidilute good solvent region (II) can thus be increased by changing the molar mass, but the concentration at which crossover from II to III to IV occurs remains molar mass independent. These molar mass dependences are examined in this work.

Crossover Model. Farnoux et al.[9] have pointed out that the distance between monomers i and j along an *isolated* chain scales according to two different laws for small and large values of $|i - j|$. For small $|i - j|$ the probability of monomer–monomer collision is small and the intermonomer separation therefore obeys the Gaussian behavior of the random walk. For large $|i - j|$ however the arguments that lead to excluded-volume behavior apply and the intermonomer distance has the features of the self-avoiding walk. More recently Weill and des Cloizeaux[10] proposed a simple model in which an abrupt crossover in chain statistics occurs for $|i - j| = N_\tau$, where N_τ is independent of the molar mass.

The same viewpoint may be applied to the free segment, ξ, in semidilute solutions, but it is immediately obvious that a careful distinction must be made between static and dynamic dimensions in the Weill and des Cloizeaux picture. This is shown in the different dependences on intermonomer separation of the mean square radius of gyration ξ_G and the Kirkwood–Riseman approximation for the hydrodynamic radius, ξ_D.

$$\xi_G^2 = (1/2N^2) \sum_{ij} \langle r_{ij}^2 \rangle \tag{10a}$$

$$\xi_D^{-1} = (1/2N^2) \sum_{ij} \langle r_{ij}^{-1} \rangle \tag{10b}$$

Both Pouyet et al.[11] and ourselves[12,13] have applied this model to semidilute solutions in order to predict respectively sedimentation and self-diffusion coefficients. As such these applications represent ad hoc modifications to the de Gennes scaling law approach. Consequently the theoretical basis is somewhat suspect for although this so-called crossover model allows multiple length scales throughout the semidilute regime this breakdown of scaling is presumed to disable concentration scaling while apparently allowing molar mass scaling to persist unscathed. The existence of any simple scaling law where multiple length scales occur may well be forbidden. However the model does predict that the de Gennes good and Θ solvent scaling laws are asymptotes of a more general relationship, and to this extent at least, the predictions of the crossover model are similar to those of the marginal solvent model. The crossover model does have an added advantage. It can be used to predict continuous curves for the variation of D_s with polymer concentration, which can be compared with observation.

In essence the crossover modification to semidilute theory consists in employing variable exponents in expressions for the static and dynamic blob sizes such that $\xi_G \sim g^{\nu_G(g)}$ and $\xi_D \sim g^{\nu_D(g)}$, where $\nu_G(g)$ and $\nu_D(g)$ are precisely defined in the model. Using these relationships and the concept of reptation the theory predicts exponent relationships for the dynamic parameters of semidilute polymer solutions. In particular we obtain

$$D_s \sim M^{-2} c^{(2-\nu_D(g))/(1-3\nu_G(g))} \tag{11}$$

where the relationship between c and g derives from the geometrical rule (eq 2) in which ξ is taken to be the static dimension ξ_G. A fundamental parameter in the crossover model is the concentration c_τ at which the number of monomers in the blob is precisely N_τ. At concentrations in excess of c_τ the asymptotic indices $\nu_G = \nu_D = {}^1/_2$ apply exactly and simple scaling $D_s \sim c^{-3.0}$ applies. Below this concentration ν_G and ν_D vary at different rates toward the asymptote ${}^3/_5$ and concentration scaling is no longer manifest.

The asymptotic regions where $D_s \sim c^{-1.75}$ and $D_s \sim c^{-3.0}$ may be identified with the predominance of excluded-volume and Gaussian chain statistics, respectively. To the extent that the respective asymptotic exponents agree, these two concentration regions correspond with the good and Θ solvent extremes of the mean field predictions of Schaefer et al.

In Figure 3 we show the concentration dependence of D_s, predicted by the crossover model. It is a crucial aspect of this model that molar mass scaling ($D_s \sim M^{-2}$) will apply *throughout* the semidilute regime only if c_τ is molar mass independent. In other words the existence of universal molar mass scaling requires that the locus of c_τ values for varying molar masses be parallel to the ordinate.

Experimental Section

With any technique to measure polymer self-diffusion it is important to use a displacement observation time larger than the entanglement renewal or reptation time T_r. For PFGNMR the observation time is a few tens of milliseconds and this limits this

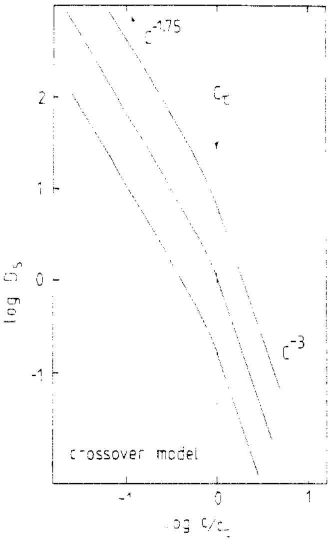

Figure 3. Theoretical crossover master curves for the concentration dependence of self-diffusion by using the models of ref 10, 11, and 12. We define a concentration c_τ above which Gaussian statistics apply at all scales in the polymer. At low concentration the curves meet another asymptotic region where excluded-volume statistics prevail on a scale smaller than ξ.

Table I
Polystyrene Used in This Work

source	M_w	M_w/M_n
Pressure Chemicals	110 000	<1.06
Pressure Chemicals	233 000	<1.06
Polysciences	293 000	<1.06
Pressure Chemicals	350 000	<1.10
Polysciences	598 000	<1.10
Polysciences	929 000	<1.10

technique to $M < 2 \times 10^6$ if self-diffusion alone is to be observed.[14] We now present semidilute data for 110 000, 233 000, 293 000, 350 000,[15] 598 800, and 929 000 molar mass polystyrene in carbon tetrachloride and deuteriobenzene. In all experiments the polymer center of mass displacement over the experimental time scale was ≳1000 Å and thus much larger than any internal segmental motion relative to the polymer center of mass. All data were obtained at 28.0 °C.

Monodisperse polystyrene was obtained from the Pressure Chemical Co. and Polysciences Inc., who quote M_w/M_n ratios as given in Table I. Our pulsed field gradient system has been described in detail elsewhere.[17] Proton spin echoes at 60 MHz are accumulated and Fourier transformed on a JEOL FX60 spectrometer utilizing a special home-built pulsed field gradient probe and current pulse generator. The polystyrene proton data presented here all obeyed the Stejskal–Tanner relationship[18] for the attenuation of an echo signal under the influence of a pair of magnetic field gradient pulses of magnitude G, duration δ, and separation Δ

$$A(G)/A(0) = \exp(-D_s\gamma^2G^2\delta^2(\Delta - (1/3)\delta)) \qquad (12)$$

γ is the nuclear gyromagnetic ratio, and D_s is the polymer self-diffusion coefficient which, in all experiments reported here, is found to be independent of the effective observation time ($\Delta - (1/3)\delta$) over the tens of milliseconds available as the echo envelope decays due to spin–spin relaxation. This time independence of D_s clearly indicates that the self-diffusion coefficient is well-defined in the PFGNMR experiment and there is not an increasing admixture of self- and cooperative diffusion.[14]

Our system has been calibrated to 1% by using water and accurately reproduces literature values for benzene and glycerol in the fast and slow diffusion regimes, respectively. Our system produces the same diffusion coefficient for monodeuteriobenzene, obtained alternatively by deuteron and proton PFGNMR.[19] We obtain the same self-diffusion coefficient for 2% 110 000 polystyrene in deuteriobenzene as interpolated from Hervet et al.[20] using the forced Rayleigh scattering method. We agree with the self-diffusion coefficients obtained for dextran in water by Laurent et al., who used fluorescent labeling methods.[21] Finally we obtain the same diffusion coefficient at semidilute concentration for 390 000 polystyrene in CCl_4 as that found by using an entirely different PFGNMR apparatus at the University of British Columbia.[22]

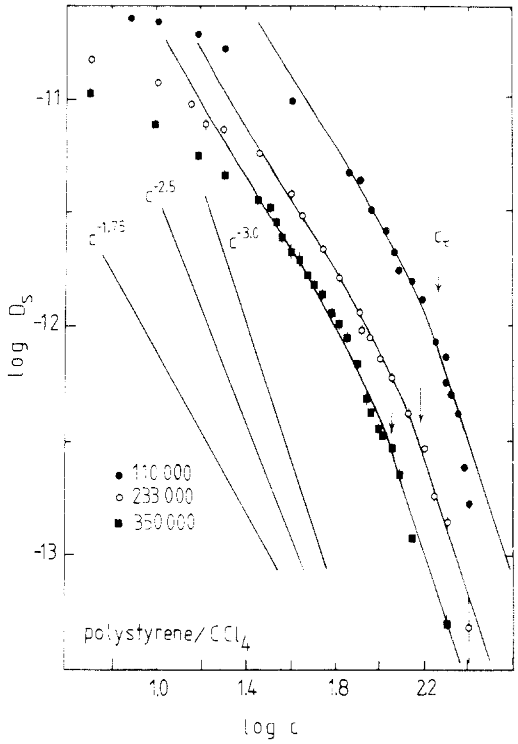

Figure 4. Self-diffusion of polystyrene in carbon tetrachloride at 28.0 °C for 110 000, 233 000, and 350 000 daltons molar masses. The data do not exhibit simple scaling behavior over a wide concentration regime although asymptotic exponents of −1.75 and −3.0 are consistent with lower and higher concentrations, respectively. No wide $D_s \sim c^{-2.5}$ region is apparent. The curves fitted to the data are those of the crossover model, and these yield a good representation of the data over a wide concentration span provided that c_τ is allowed to vary with molar mass.

Results and Discussion

Variation of D_s with c. Figures 4 and 5 display the log D_s vs. log c observations for 110 000, 233 000, and 350 000 molar mass polystyrene at 28 °C in carbon tetrachloride and in deuteriobenzene, respectively. Also included are the theoretical predictions for the variation of D_s with c. It is immediately apparent that the data do not confirm the simple de Gennes scaling law model for self-diffusion. It could be argued that the data pertaining to the lower molar masses exhibit simple scaling regions with indices greater than de Gennes predicted value of 1.75. However, the data for the 350 000 molar mass polystyrene clearly indicate that such a simple scaling law is not obtained throughout the semidilute regime.

The alternative theories predict that the log D_s vs. log c curves should display asymptotic regions of the same slope namely −1.75 at low concentration and −3 at large concentration. The details of the connection between asymptotes are defined in the crossover model. No such detail is available in the marginal solvent model except that Schaefer et al. imply that an extended region should be discernable in which an index of −2.5 is obtained. This prediction is not confirmed by the observations reported here, rather the experimental curves smoothly vary in slope from ∼−1.75 to ∼−3 with no discernible plateau region.

We have previously pointed out that such a plateau region is not necessarily implied by the algebra of the marginal solvent model, and its absence in our data should

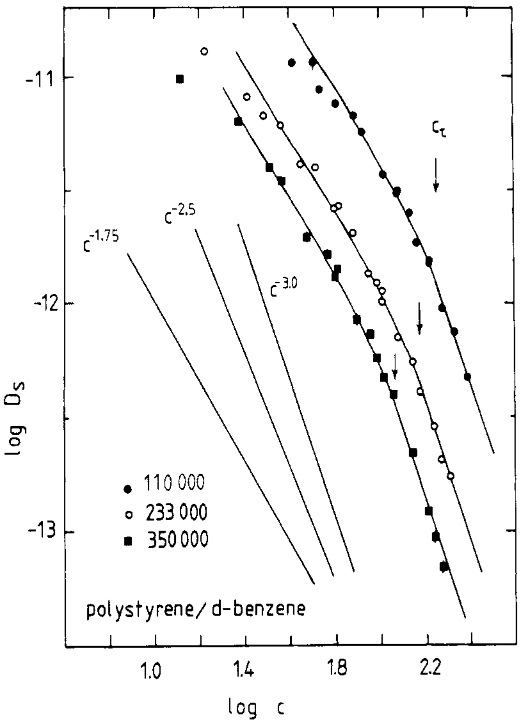

Figure 5. As for Figure 4 but for polystyrene in perdeuteriobenzene at 28.0 °C.

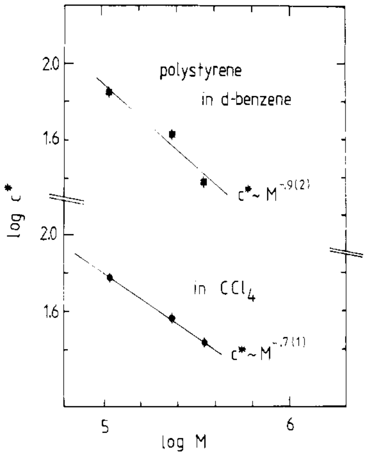

Figure 6. The dependence of c^* on M for polystyrene in CCl$_4$ and deuteriobenzene. c^* values have been obtained from Figures 4 and 5 by observing where smooth curves drawn through the data deviate from the theoretical predictions of semidilute behavior.

not be taken to invalidate the model.

The detailed curves generated by the crossover model have been fitted to our data. These curves give a good representation of the concentration dependence over a wide concentration region. The empirical boundaries of this region are thus subject to check. Few measurements are available at very large concentrations due to the very slow diffusion so the measurements cannot be used to check that c^{**} is molar mass independent as required by theory. However one is able to estimate c^* and check the molar mass dependence since all models assert that $c^* \sim M^{-0.80}$. Figure 6 shows the log c^* vs. log M data obtained from Figures 4 and 5 and the empirical exponents of −0.7(1) and −0.9(2), respectively, lend support to our identification of the semidilute regime.

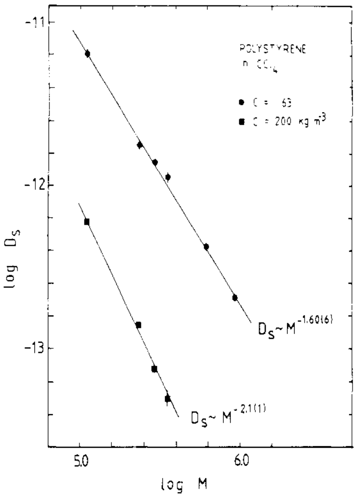

Figure 7. The dependence of self-diffusion on molar mass for polystyrene in carbon tetrachloride at two concentrations in the semidilute regime. For c = 63 kg m^{-3} the data falls in the asymptotic excluded-volume region for all molar masses and we find $D_s \sim M^{-\beta}$, where β = 1.60(6), significantly less than 2. In contrast the data at 200 kg m^{-3} has $c > c_\tau$ for all molar masses, and the de Gennes reptational scaling law is observed in this Gaussian regime where β = 2.1(1). Because of experimental limitations self-diffusion coefficients could not be obtained for the two highest molar masses at c = 200 kg m^{-3}.

While the agreement between the data and the crossover model is good, this agreement is deceptive for it has been obtained by displacing the theoretical curve not only along the ordinate but also along the abcissa from one molar mass to another. Thus the data imply that the crossover concentration, c_τ, is molar mass dependent. Such a dependence is not predicted by either the crossover or the marginal solvent theory. The implication of such a dependence, as foreshadowed in the introduction, is that the $D_s \sim M^{-2}$ relationship cannot be obtained throughout the semidilute regime.

Variation of D_s with M. All three theoretical models for the dynamical behavior of semidilute random coil polymer solutions predict the relationship $D_s \sim M^{-2}$. Indeed it has been suggested that this is the touchstone for reptational motion. The relationship has been adequately verified for polymers in the melt by boundary spreading measurements in labeled systems; however, the verification in the semidilute regime has not been universally accepted. Callaghan and Pinder[23] have investigated various polystyrenes dissolved in carbon tetrachloride and presented their data as a normalized graph of log $D_s c^{1.75}$ vs. log M. They reported a scaling index of −1.4. Although the validity of using $c^{1.75}$ as a normalization parameter is open to irrefutable criticism due to the failure of data to conform to the simple de Gennes concentration scaling law, it is interesting to note that Amis and Han have recently used the same normalization procedure when presenting their data on polystyrene dissolved in tetrahydrofuran,[24] and over the same molar mass range as used by Callaghan and Pinder their data yield the same molar mass, D_s relationship, namely $D_s \sim M^{-1.4}$.

If c_τ were independent of molar mass, it would be possible to have $D_s \sim M^{-2}$ throughout the whole semidilute regime. Given the observed molar mass dependence of c_τ any scaling of D_s with M must occur with different exponents for concentrations in the two asymptotic regimes. We must then pose the question as to which asymptotic region, if any, the reptational exponent −2 will apply. To address this question we have carefully examined the dependence of D_s on M for polystyrene dissolved in both carbon tetrachloride and deuteriobenzene at various concentrations in the semidilute regime.

Figure 7 presents the data for polystyrene dissolved in carbon tetrachloride at two concentrations. For 200 kg m^{-3} all data have been collected at $c < c_\tau$ while for 200 kg m^{-3}

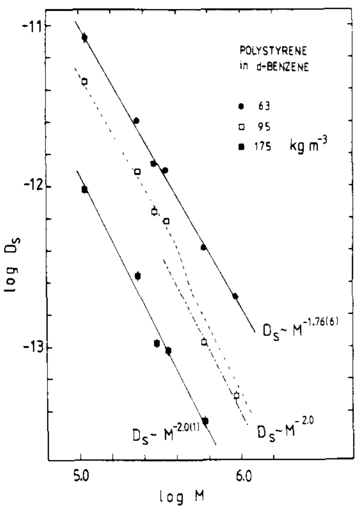

Figure 8. The dependence of self-diffusion on molar mass for polystyrene in deuteriobenzene. As for carbon tetrachloride, $c = 63$ kg m^{-3} corresponds to excluded-volume blob statistics, and we find $\beta = 1.76(6)$. For $c = 175$ kg m^{-3}, $c > c_\tau$ and $\beta = 2.0(1)$. The data for $c = 95$ kg m^{-3} fall in both asymptotic regimes and reveal the details of crossover. For the four lowest molar masses the data is consistent with $D_s \sim M^{-1.75}$ while for the two highest it agrees with $D_s \sim M^{-2.0}$. The dashed line is generated from the crossover theory allowing for the observed molar mass dependence of c_τ.

all data have been collected at $c > c_\tau$ in the so-called Θ-like or Gaussian region. It is clear that only those data pertaining to the Θ-like region are consistent with the predicted $D_s \sim M^{-2}$ relationship. Those data collected at the lower concentration conform to the relationship $D_s \sim M^{-1.60(6)}$.

Figure 8 presents similar data for polystyrene dissolved in deuteriobenzene. These data were sought specifically because it has been previously reported[25] that polystyrene dissolved in deuteriobenzene does conform to the $D_s \sim M^{-2}$ relationship. Three concentrations were used for this more detailed investigation; for 63 kg m^{-3} all data were collected at $c < c_\tau$, for 175 kg m^{-3} all data were collected at $c > c_\tau$, and for 95 kg m^{-3} the lower molar mass data were collected at $c < c_\tau$ and the higher molar mass data were collected at $c > c_\tau$. We note immediately that those data collected in the Θ-like region display $D_s \sim M^{2.0(1)}$ in accordance with theory and in agreement with the carbon tetrachloride data. In contrast those data collected at $c < c_\tau$ display $D_s \sim M^{-1.76(6)}$ for which the index deviates significantly from −2. This deviation corresponds with the behavior observed by using carbon tetrachloride, but the precise value of the exponent is clearly and surprisingly solvent dependent. The data obtained at the intermediate concentration show particularly interesting behavior. If the data were less precise, a single straight line could be drawn having a slope of −2.1(1) thereby seemingly verifying the molar mass scaling relationship. However the data presented here show systematic deviations from linearity, indicating that a piecewise linear analysis could be more appropriate, the double-dog-leg discontinuity being centered on the molar mass whose c_τ value is 95 kg m^{-3}. The crossover model is capable of generating a theoretical curve if the empirical molar mass dependence of c_τ is incorporated. This theoretical relationship is also shown in Figure 8, and some discrepancies in detail are apparent. The qualitative predictions are however thoroughly vindicated.

Sedimentation. The three theoretical models for dynamic behavior of semidilute random coil polymer solutions can also be applied to sedimentation. The de Gennes model predicts a sedimentation scaling law $s \sim M^0c^{-0.5}$.

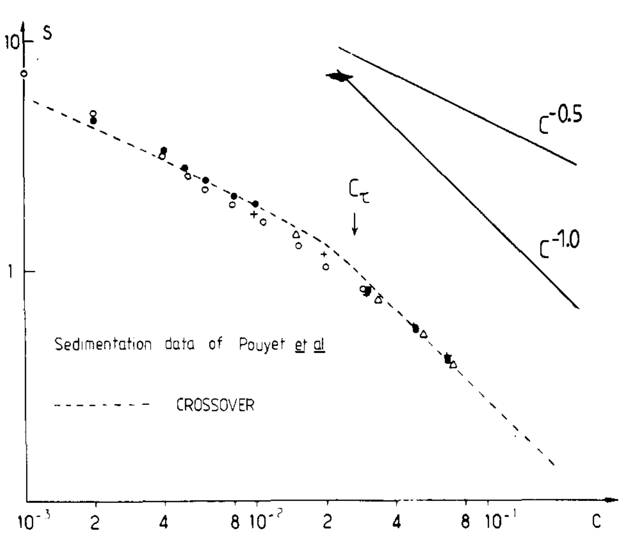

Figure 9. The sedimentation data of ref 11: (+) $M_w = 6.2 \times 10^5$ in bromobenzene; (■) $M_w = 3.2 \times 10^5$; (△) $M_w = 9.6 \times 10^5$ in bromobenzene; (○) $M_w = 1 \times 10^7$ in bromobenzene; (●) $M_w = 3.8 \times 10^6$ in benzene. Pouyet et al. discount solvent effects since the intrinsic viscosities of the two solvents are so similar. Notice the three models for dynamical behavior for semidilute solutions predict s to be molar mass independent, and this prediction is only verified at large concentrations in the Θ-like or Gaussian regime. Also note the slope of the low-concentration asymptote is molar mass or solvent dependent. In these aspects these sedimentation data resemble the self-diffusion data presented in this work.

The marginal solvent model predicts a low concentration asymptotic index of −0.5, a marginal concentration index, also −0.5, and a high concentration asymptotic index of −1.0. The crossover model predicts a continuous curve for the variation of log s with log c with low and high concentration asymptotic indices again being −0.5 and −1.0, respectively. Figure 9 presents the data of Pouyet et al.[11] together with the predictions of the three theoretical models. Clearly the de Gennes model fails to account for the concentration dependence of the data. The crossover and the mean field models account for the data rather well except that the magnitude of the low concentration exponent would appear to be greater than 0.5 and molar mass dependent. The Θ-like region data are not in conflict with the theoretical index of −1.0. Despite the paucity of data we note once again that it is the Θ-like region of concentration which best displays the predicted molar mass dependence ($s \sim M^0$).

Conclusion

The introduction of the de Gennes scaling law approach to semidilute random coil polymer solutions was a major advance in the study of the dynamical behavior of such solutions. However, close study of the accumulated data reveals significant deviations from this simple model, and at least two other derivative theories have been proposed in an attempt to better reconcile theory with experiment.

The crossover model applied by Pouyet et al. and Callaghan and Pinder has been developed from the work of Farnoux, Weill, and des Cloizeaux and is essentially an ad hoc modification to the de Gennes theory. Despite these difficulties the crossover model provides a good description of the variation with concentration of the self-diffusion coefficient of random coil polymers in the semidilute regime.

The marginal solvent model developed by Schaefer et al. uses the mean field theory for the monomer–monomer excluded-volume interaction to calculate ξ_ρ. Then, assuming simple relationships between the various correlation lengths, Schaefer et al. adopt the de Gennes reptation concept to obtain expressions for the variation of D_s with concentration. The weakness in this model lies in the identification of relationships between the correlation lengths. This particular aspect has recently been addressed by Muthukumar and Edwards,[26] who conclude that such identifications are not supported by theory for semidilute solutions of real (nonphantom) chains. Given these theoretical *caveats* the marginal solvent model does predict the appropriate asymptotic variation of dynamical parameters with concentration in the semidilute regime. Nonetheless the predicted discernable $D_s \sim c^{-2.5}$ behavior has not been observed here and would seem to have been too bold a distillation from the algebra. Both the marginal solvent and crossover modification to the de Gennes reptation theory predict M^{-2} scaling for D_s throughout the semidilute regime. However this relationship has been observed to prevail only in the high concentration asymptotic region labeled respectively Θ-like and Gaussian in the two models. Consequently the observed molar mass variation of D_s is not encompassed by any of the models proposed.

This inability of the models to predict the observed variation of self-diffusion with molar mass is a serious problem yet to be resolved. It would seem that the most likely reason for this is, as indicated by Muthukumar and Edwards, the lack of theoretical justification for assuming simple relationships between the various correlation lengths defined in semidilute solutions. Indeed Muthukumar and Edwards allow that a more complicated dependence may exist when they state that "the question of whether the entanglement constraints change the ratio of (dynamic to static) screening lengths only merely by a constant or by a functional dependence on concentration remains open".

Registry No. Polystyrene (homopolymer), 9003-53-6.

References and Notes

(1) Edwards, S. F.; Freed K. F. *J. Chem. Phys.* **1976**, *61*, 1189.
(2) Edwards, S. F. *J. Phys. A* **1975**, *8*, 1670.
(3) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(4) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(5) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(6) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(7) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1976**, *37*, 973.
(8) Schaefer, D. W. *Polymer Prepr. Am. Chem. Soc., Div. Polym. Chem.* **1982**, *23*, 53.
(9) Farnoux, B.; Boué, F.; Cotton, J. P.; Daoud, M.; Jannink, G.; Nierlich, M.; de Gennes, P.-G. *J. Phys. (Paris)* **1978**, *39*, 77.
(10) Weill, G.; de Cloizeaux, J. *J. Phys. (Paris)* **1979**, *40*, 99.
(11) Pouyet, G.; Francois, J.; Dayantis, J.; Weill, G. *Macromolecules*, **1980**, *13*, 176.
(12) Callaghan, P. T.; Pinder, D. N. *Macromolecules*, **1981**, *14*, 1334.
(13) Callaghan, P. T.; Pinder, D. N. *Polym. Bull.* **1981**, *5*, 305.
(14) For $M > 2 \times 10^6$ PFGNMR can detect an admixed cooperative diffusion coefficient. Any influence from cooperative modes will be shown as a dependence of D_s on $(\Delta - (1/3)\delta)$.
(15) The manufacturers, Pressure Chemical Co., quote M_w = 390 000 daltons for this polymer. However it is apparent that D_0,[12] k_f,[12] and k_D[16] are more consistent with that expected by interpolation between neighboring molar masses if the true molar mass were 350 000 daltons.
(16) King, T. A.; Knox, A.; McAdam, J. D. G. *Polymer* **1973**, *14*, 293.
(17) Callaghan, P. T.; Trotter, C. M.; Jolley, K. W. *J. Magn. Reson.* **1980**, *37*, 247.
(18) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.
(19) Callaghan, P. T.; Le Gros, M.; Pinder, D. N. *J. Chem. Phys.* **1983**, *79*, 6372.
(20) Hervet, H.; Leger, L.; Rondelez, F. *Phys. Rev. Lett.* **1979**, *42*, 1681.
(21) Laurent, T. C.; Sundelöf, L. O.; Wik, K. V.; Wärmegåard, B. *Eur. J. Biochem.* **1976**, *68*, 95.
(22) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1983**, *16*, 968.
(23) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085.
(24) Amis, E. J.; Han, C. C. *Polymer* **1982**, *23*, 1403.
(25) Lêger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732.
(26) Muthumukar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.

Computer Simulation of the Effect of Primitive Path Length Fluctuations in the Reptation Model

R. J. Needs

Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom.
Received May 16, 1983

ABSTRACT: A dynamics of the primitive path of a reptating polymer is proposed. The dynamics are equivalent to a Metropolis algorithm. This dynamics allows fluctuations in the number of primitive path segments N about a mean of $\bar{N}$ obeying a distribution where the probability P of a primitive path of N segments is given by $P(N) \propto \exp(-3(N - \bar{N})^2/2\bar{N})$. The diffusion constant of the center of mass and the zero shear rate viscosity η_0 are calculated by computer simulation for $\bar{N}$ in the range 5–60. Although the viscosity is lowered by the inclusion of these fluctuations, the simulation data do not provide an explanation of the experimental $\eta_0 \propto \bar{N}^{3.4}$.

Introduction

The reptation model of de Gennes[1] has been successful in describing many of the viscoelastic properties of polymer melts. The most intriguing discrepancy is in the molecular weight dependence of the zero shear rate viscosity η_0. Experiments indicate[2] that η_0 is proportional to the molecular weight to a power about 3.4, while the reptation theory gives $\eta_0 \propto M^3$. Doi has argued[3] that these results can be reconciled by considering fluctuations in the length of the primitive path of the polymer, sometimes called breathing motions; see Figure 1.

In the reptation theory[1,4-8] the stress remaining at time t after a small strain at time 0 is proportional to the fraction $F(t)$ of original primitive path still occupied. This is related to the zero shear viscosity by

$$\eta_0 = G_N{}^\circ \int_0^\infty F(t)\,dt \qquad (1)$$

where $G_N{}^\circ$ is the plateau modulus. Also the recoverable compliance $J_e{}^\circ$ is given by

$$J_e{}^\circ = G_N{}^\circ/\eta_0{}^2 \int_0^\infty tF(t)\,dt \qquad (2)$$

0024-9297/84/2217-0437$01.50/0 © 1984 American Chemical Society