on two parameters: one for parallel diffusion

$$D_{\parallel} = 1 + (d-1)c \qquad \text{(A2)}$$

which is exact for all c, and another for transverse diffusion

$$D_{\perp} = 1 + \frac{2(d-1)}{(d+1)}c + O(c^2) \qquad \text{(A3)}$$

as $c \rightarrow 0$. These equations agree with earlier results.[8,10]

The c^2 correction depends on the solution for diffusion past two cylinders, which is not known for arbitrary orientation distributions. For parallel cylinders, however, Peterson and Hermans[8] give the c^2 contribution to $D_{\perp}$ (cf. Howells'[7] calculation of the flow permeability in a distribution of parallel cylinders). Putting $b = (1 - d)/(1 + d)$, this gives

$$D_{\perp} = 1 - 2bc + 2(b^2 - 8bA(b))c^2 + O(c^3) \qquad \text{(A4)}$$

as $c \rightarrow 0$, where

$$A(b) = \frac{1}{2}\int_0^{\infty} \sinh 2\xi \left[-1 + 4\sum_{n=1}^{\infty} \frac{n \sinh^2 \xi}{e^{2n\xi} - b^2 e^{-2n\xi}} \right] d\xi \qquad \text{(A5)}$$

For impermeable cylinders, when $b = 1$, numerical integration of $A(b)$ to four significant figures gives

$$D_{\perp} = 1 - 2c + 1.255c^2 + O(c^3) \qquad \text{(A6)}$$

as $c \rightarrow 0$. Numerical values for other cases are given by Peterson and Hermans.[8]

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Polymer Self-Diffusion in Ternary Solutions and the Monomer and Segmental Self-Diffusion Coefficients

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ABSTRACT: The monomer self-diffusion coefficient of polystyrene in Θ and non-Θ solutions is determined as a function of concentration. Also the concentration dependence of the segmental self-diffusion coefficient (which includes hydrodynamic screening effects) is measured for polystyrenes in non-Θ solutions. These two quantities are shown to be distinct. The self-diffusion coefficients of polystyrenes in semidilute non-Θ solutions have been corrected by using both the monomer and the segmental self-diffusion coefficients, and these corrected data have been compared with the scaling laws and with the theory of Hess. This theory, which applies to non-Θ solutions with concentrations less than the crossover concentration, is shown to be in agreement with the data for concentrations close to the overlap concentration, for larger concentrations the data decreases faster than theory would allow.

Introduction

The dynamical behavior of polymer chains at concentrations close to and above the coil overlap concentration, c^*, has excited considerable interest. Theories have been developed to describe the behavior, and various experimental procedures have been applied to measure the dynamical parameters. The self-diffusion coefficient, D_s, has proved to be a particularly useful dynamical property for investigating the motion of a single chain among others in semidilute solutions.

Major theoretical developments were engendered by the scaling and reptation models proposed by de Gennes[1,2] based on the concept of the "effective tube" originally introduced by Edwards.[3] Theories based on these models assume that in semidilute solutions the impediment to motion of a single chain is caused by chain entanglements; no account is taken of any increase in monomer friction coefficient as the polymer concentration increases. These theories predict the simple scaling laws

$$D_s \sim M^{-2}c^{-1.75} \qquad \text{for non-}\Theta\text{ solutions}$$

$$D_s \sim M^{-2}c^{-3} \qquad \text{for }\Theta\text{ solutions}$$

where M is the polymer molar mass and c the polymer concentration.

The scaling theory for non-Θ solutions has been extended to include the concept of the concentration crossover. This modification accounts for the behavior of real non-Θ solu-

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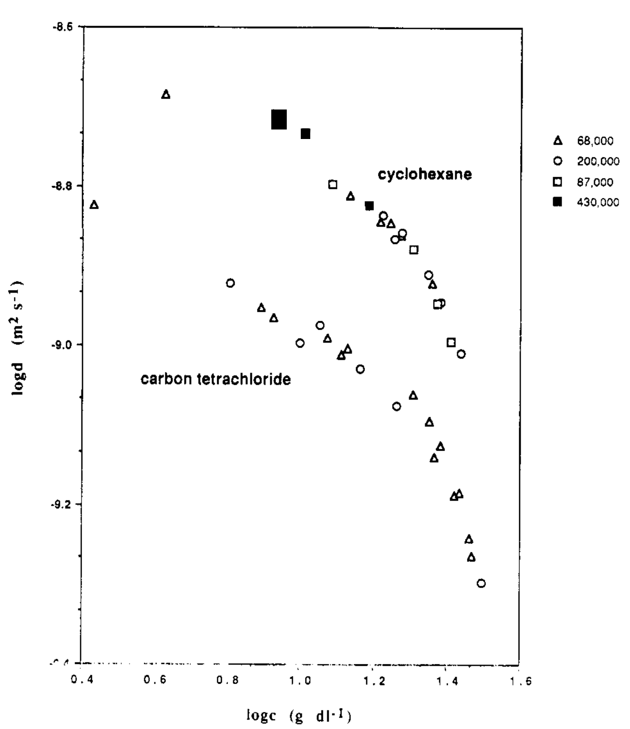

Figure 1. Variation of the self-diffusion coefficient of styrene, d_{st}, in ternary solutions with deuterated polystyrenes and either Θ (cyclohexane) or non-Θ (carbon tetrachloride) solvents. The deuterated polystyrenes used as the matrix are specified. The uncertainties are indicated by the size of the symbols.

tions, which exhibit classical non-Θ behavior at low polymer concentrations but Θ-like behavior at concentrations greater than a critical value, c_Θ. Hence the modified scaling law for non-Θ solutions reads

$$D_s \sim M^{-2}c^{-1.75} \qquad c < c_\Theta$$

$$D_s \sim M^{-2}c^{-3} \qquad c > c_\Theta$$

These scaling theories do not include any indication of the range of polymer concentration over which the scaling is expected to occur. They are more an ingenious synthesis of sweeping approximations and fine physical intuition than a physical theory based on first principles.

Another major theoretical development for non-Θ solutions is due to Hess.[4,5] Starting from first principles Hess has developed a microscopic model of entangled and nonentangled polymer solutions and showed that the self-diffusion coefficient of a chain in a non-Θ solution can be expressed as

$$D_s \sim D_{seg} f(\Psi)$$

where $f(\Psi)$ is an overlap function representing the impediment to motion due to coil overlap and D_{seg} is the net effective segmental diffusion coefficient. This can be written as $kT/N\zeta^0$, where N is the degree of polymerization and ζ^0 the average segmental friction coefficient per segment. The overlap function $f(\Psi)$ is expected to be a function of M and c and ζ^0 is expected to be a function of c only. Hess has shown that in the high concentration limit (the semidilute non-Θ regime in this theory) D_{seg} varies as $Mc^{-0.5}$ and $f(\Psi)$ varies as $Mc^{-1.25}$; thus the simple semidilute non-Θ scaling law can be obtained as the high concentration limit of the Hess theory. Shiwa[6] has used renormalization group methods to calculate D_{seg} and $f(\Psi)$ as functions of M and c. The results are presented as normalized plots of log D_s/D_{so} against log X for dilute and semidilute non-Θ solutions (where X, the overlap parameter, is proportional to c/c^*). Shiwa has shown that the asymptotic slope is not reached before X is of the order 10. The Hess theory is limited to non-Θ conditions only so these analyses fail to predict the concentration crossover from non-Θ to Θ-like behavior at high semidilute polymer concentrations. Thus the Hess theory describes the dynamical behavior of non-Θ solutions at concentrations less than c_Θ.

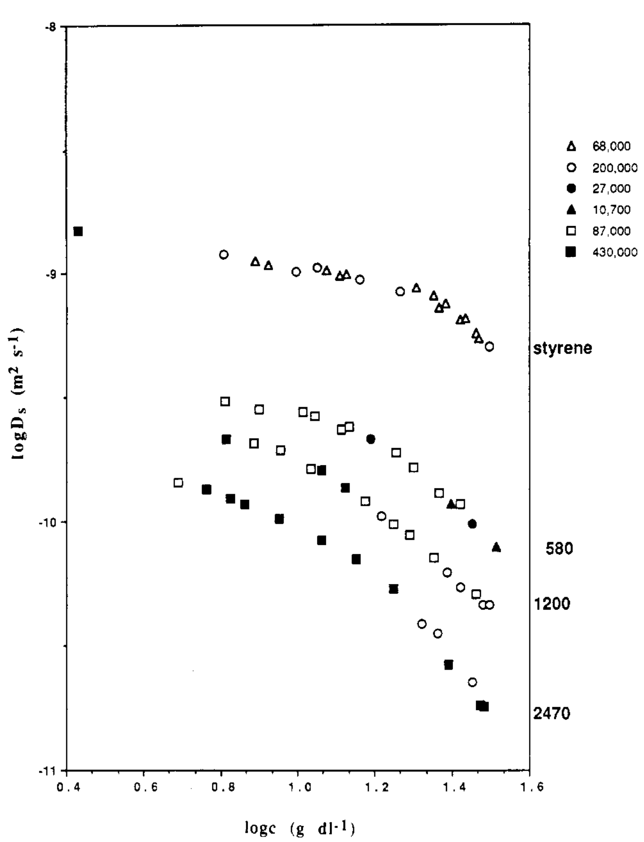

Figure 2. Variation with concentration of the self-diffusion coefficient of low molar mass polystyrenes in ternary solution with deuterated polystyrenes and carbon tetrachloride. The deuterated polystyrene used as the matrix is specified. The uncertainties are indicated by the size of the symbols.

The polymer self-diffusion coefficient has been measured by various experimental techniques and a considerable body of experimental data has been accumulated for both non-Θ[7-9] and Θ[10] solutions. This experimental data has been interpreted as confirming the scaling laws, certainly the molar mass variation follows a power law with an exponent close to −2 in both Θ and non-Θ solutions, and the concentration power law for Θ solutions has been verified. However the data pertaining to non-Θ solutions do not completely confirm the scaling law. Callaghan and Pinder showed that their data from carbon tetrachloride and deuterated benzene solutions are consistent with the modified scaling law only if c_Θ is assumed to be molar mass dependent, which the model does not allow.

The notion of separating the expression for D_s into two parts, one containing the entanglement contribution and the other the monomer friction contribution, has been applied to data collected from non-Θ polymer solutions in an ad hoc fashion. The assumption was made that the concentration dependence of the monomer self-diffusion coefficient would be taken into account if the scaling law expression for D_s were multiplied by the self-diffusion coefficient of the polymer monomer. The "corrected" data should then obey the scaling laws. Marmonier et al.,[11] von Meerwall et al.,[12] and Kim et al.[13] have all estimated the concentration dependence of the monomer diffusion coefficient by measuring the self-diffusion coefficient of a small molecule in semidilute (ternary) solutions and then assuming that the concentration dependence of the self-diffusion coefficient of this small molecule is the same as that of the monomer, since the monomer and the small molecule are of similar size. Kim et al. and von Meerwall et al. find that the variation of the self-diffusion coefficient of the small molecule with polymer concentration can be well represented by free volume theory even at low polymer concentrations. Kim et al. have shown that the thus "corrected" polymer self-diffusion coefficients confirm the modified non-Θ scaling law, including the molar mass independence of c_Θ, thereby adding credence to this procedure. However, von Meerwall et al. have shown that the "corrected" data conform to $c^{-1.75}$ scaling for both entangled and nonentangled solutions (where such scaling is not expected). One objection to this procedure is that the appropriate quantity to be used for the correction should be the effective segmental diffusion coefficient and not the monomer diffusion coefficient. These quantities differ because the former includes hydrodynamic interactions that the latter does not. Also there are no good reasons for applying the "correction" to the data collected from non-Θ solutions and not applying it to those data collected from Θ solutions (except for the obvious reason that these data do not require "correction"). This could be explained if it could be demonstrated that the monomer self-diffusion coefficient in Θ solution was effectively independent of polymer concentration. This is unlikely.

Results and Discussion

The study presented here uses pfgnmr[14] to measure directly the monomer self-diffusion coefficient of polystyrene in Θ and in non-Θ solutions by determining the self-diffusion coefficient of styrene in ternary solution with deuterated polystyrene and an appropriate solvent. There is therefore no need to assume that the monomer self-diffusion coefficient is identical with that of a different small molecular species added to the solution. The segmental diffusion coefficient is also estimated for non-Θ solutions by studying the diffusion of low molar mass polystyrenes in ternary solution with deuterated polystyrene and carbon tetrachloride. These estimates of the monomer and segmental diffusion coefficients, d_{st} and d_{sa}, respectively, are used to compare the scaling and Hess models of polymer self-diffusion with experiment.

The non-Θ solvent chosen for this study was carbon tetrachloride (because it has no proton NMR signal); these non-Θ solvent data were collected at 30 °C. The Θ solvent used was deuterated cyclohexane; these data were collected at 40 °C. Deuterated polystyrenes were used to suppress the NMR signal from the polystyrene; however, the polystyrene deuteration was incomplete (~98%) and a small NMR signal was detected from the hydrogen atoms in the polystyrene. This signal was insignificant except at the largest polystyrene concentrations studied. The properties of the materials used in this work are shown in Table I.

Ideally the styrene should be present in only trace amounts; however, experimental sensitivity demands that the styrene concentration shall not be less than 0.02 g/mL. The concentration of the trace used here is less than half that used in the study reported by von Meerwall et al.; neither Leger et al. nor Kim et al. indicate the concentration of the trace used in their studies.

Table I

Solvents Used in This Work

	source	quality
carbon tetrachloride	BDH	spectroscopy
deuterated cyclohexane	Aldrich	99.5 atom %

Polystyrenes Used in This Work

source	M_w	M_w/M_n	deuteration
Polymer Laboratories	580	<1.15	zero
Polymer Laboratories	1 200	<1.08	zero
Polymer Laboratories	2 470	<1.06	zero
Pressure Chemicals	110 000	<1.06	zero
Pressure Chemicals	233 000	<1.06	zero
Pressure Chemicals	350 000	<1.10	zero
Polymer Laboratories	10 670	<1.07	98+ atom %
Polymer Laboratories	27 000	<1.06	98+ atom %
Polymer Laboratories	68 000	<1.07	98+ atom %
Polymer Laboratories	87 000	<1.05	98+ atom %
Polymer Laboratories	205 000	<1.14	98+ atom %
Polymer Laboratories	430 000	<1.12	98+ atom %

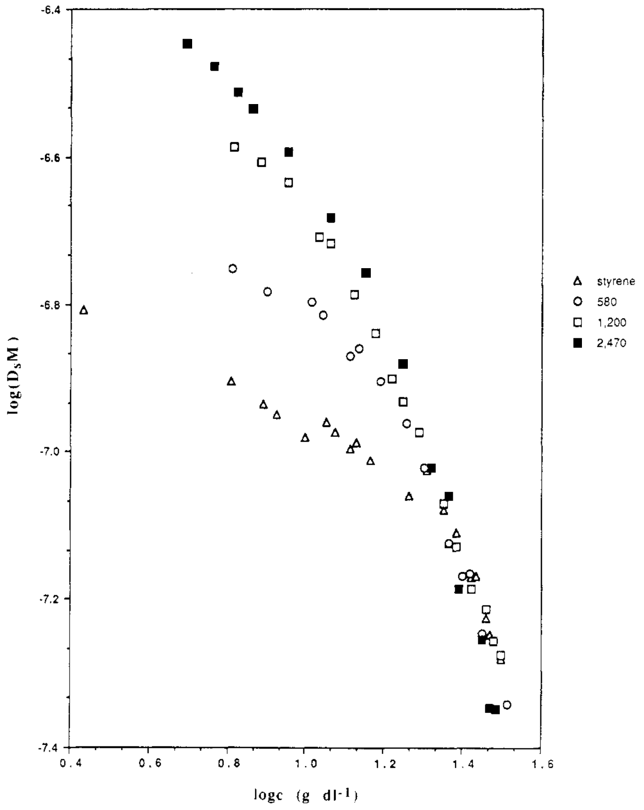

Figure 3. Variation with concentration of the self-diffusion coefficient multiplied by the molar mass of low molar mass polystyrenes in ternary solution with deuterated polystyrenes and carbon tetrachloride. Styrene data are also included for comparison purposes. The uncertainties are indicated by the size of the symbols.

The data for the self-diffusion coefficient of styrene, d_{st}, are presented in Figure 1. As expected d_{st} is independent of the molar mass of the deuterated polystyrene also present in solution. Also d_{st} decreases with polystyrene concentration, increasingly so for polymer concentrations in excess of 20%, where the free volume theory would be applicable. Moreover the concentration dependence of d_{st} in Θ solutions is of the same form as that in non-Θ solutions, so if d_{st} correction is appropriate for non-Θ solutions, then it is also appropriate for Θ solutions.

An estimate of the segmental self-diffusion coefficient, d_{sa}, was obtained from the study of ternary solutions of trace amounts of low molar mass polystyrenes

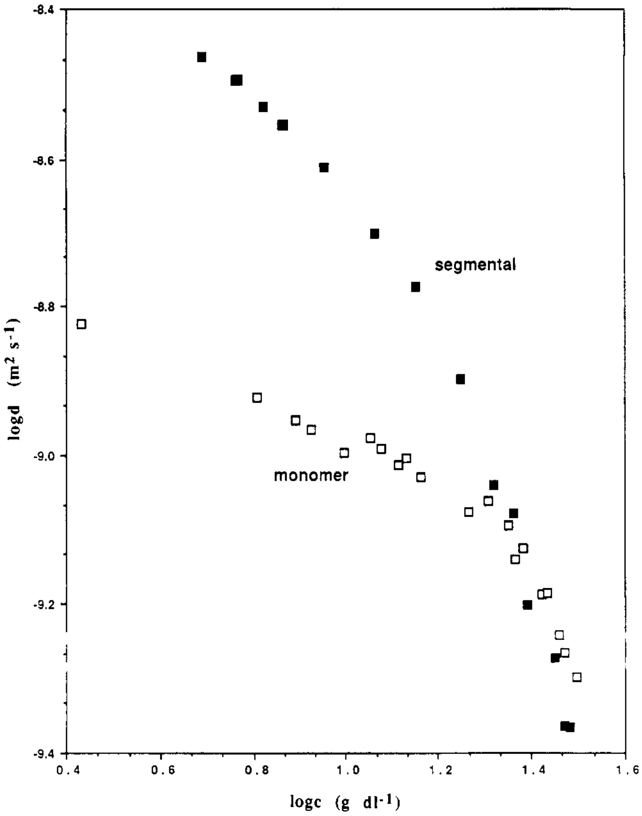

Figure 4. Comparison between the concentration dependence of the monomer self-diffusion coefficient and the segmental self diffusion coefficient. The uncertainties are indicated by the size of the symbols.

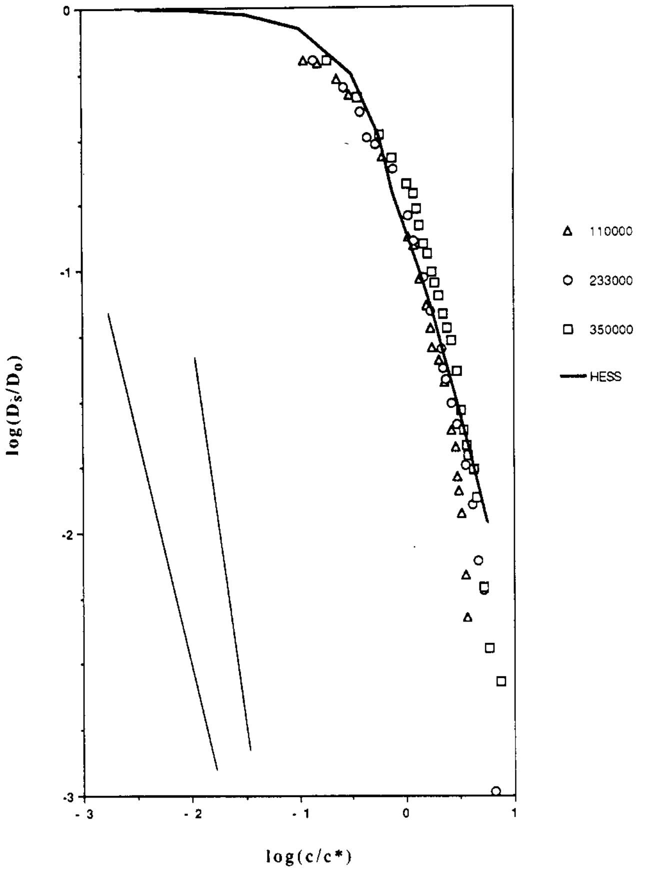

Figure 5. Variation with concentration of the self-diffusion coefficient of polystyrenes dissolved in carbon tetrachloride plotted to normalized logarithmic scales. The predictions of the Hess theory are also shown, where the unknown proportionality constant between X and c/c^* has been adjusted. Lines of slopes −1.75 and −3 are also shown. The uncertainties are indicated by the size of the symbols.

in semidilute solutions of deuterated polystyrenes of large molar mass.

The self-diffusion coefficients of three low molar mass polystyrenes (480, 1200, and 2470) in ternary non-Θ solutions with deuterated polystyrene and carbon tetrachloride were determined by pfgnmr; the data are presented in Figure 2. The self-diffusion coefficients of the low molar mass polystyrene are independent of the molar mass of the polymer also present in the solution. The assumption that D_s varies as M^{-1} for these nonentangled polystyrenes is investigated in Figure 3, where the data are presented as D_sM plotted against c to logarithmic scales. It is clear that $D_s \sim M^{-1}$ over a wide concentration range for polymers with a degree of polymerization greater than 10. Thereby supporting the contention that

$$D_s \sim kT(N\zeta^0)^{-1} = d_{sa}/N = d_{sa}(M/m)^{-1}$$

where m is the monomer molar mass. This relationship was used to obtain an estimate of the segmental diffusion coefficient. The data for 2470 polystyrene were used for this calculation.

The data for styrene are also included in Figure 3; these data do not obey the inverse mass scaling law except at the largest concentrations investigated.

Figure 4 compares the non-Θ solution monomer self-diffusion coefficient with the segmental self-diffusion coefficient, where each is plotted against concentration to logarithmic scales. These two quantities are clearly distinct; the segmental self-diffusion coefficient varies more strongly with polymer concentration in the dilute and semidilute regimes but approaches the monomer self-diffusion coefficient at the largest concentrations investigated.

The data from ref 9 are replotted in Figure 5 normalized to D_0 and c^*, which would seem to be the natural way to normalize the data. Although the data are broadly consistent with the scaling laws, it is not entirely so and these data do not fall on a universal curve. The scaling laws are only approximations carrying no information regarding the expected range of the scaling regions so whether or not the agreement displayed in Figure 5 should be considered satisfactory is uncertain.

These data can be "corrected" by using either d_{st} or d_{sa} after the manner of ref 11–13. Such "corrected" plots are shown in Figures 6 and 7. It is noteworthy that the "corrected" data better approximate universal curves, thereby rendering c_Θ less molar mass dependent, so lending support to the contention that such correction is appropriate. The "corrected" data are in better agreement with the scaling laws irrespective of whether d_{st} or d_{sa} is used as the correcting agent. However the agreement is better when d_{sa} is used. Lines of slopes −1.75 and −3 are drawn on Figures 5–7 for comparison purposes only.

These data can be used to examine the theory of Hess. The entanglement function, $f(\Psi)$, was evaluated as a function of X by using the procedure described by Shiwa.[6] The data for the Hess theory were supplied by Professor Shiwa; however, these data are also available from Figure 2 of ref 6. Figure 5 includes the prediction of the Hess theory where the unknown proportionality constant between X and c/c^* has been adjusted. This theory applies only to semidilute non-Θ solutions with concentrations less than c_Θ (as was mentioned above). The data are in quantitative agreement with this theory for small concentrations; however, when the concentration is greater than 3 times the overlap concentration, the data

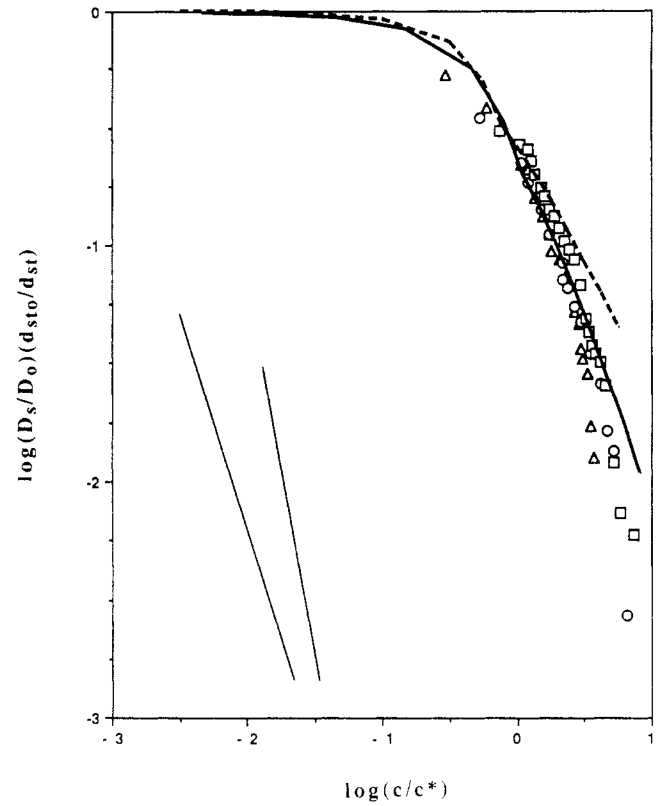

Figure 6. Same data as Figure 5 "corrected" by using the monomer self-diffusion coefficient. The predictions of the Hess theory (continuous line) and the entanglement function $f(\Psi)$ (broken line) are shown. The unknown proportionality constants between X and c/c^* have been adjusted separately. Lines of slopes −1.75 and −3 are included. The uncertainties are indicated by the size of the symbols.

decrease more rapidly with concentration than the Hess theory would allow; this could be due to the data manifesting crossover effects that this theory does not address. We can examine the Hess theory in greater detail since the normalized diffusion coefficients "corrected" by using d_{sa} should properly be identified with the overlap function $f(\Psi)$. Figures 6 and 7 also include $f(\Psi)$. The entanglement function is in quantitative agreement with those data normalized by using the segmental self-diffusion coefficient d_{sa} only for concentrations less than 3 times the overlap concentration; at larger concentrations the data decrease more rapidly than $f(\Psi)$. If these discrepancies between the Hess theory and experiment are due to the data manifesting crossover effects, then these effects occur before the Hess theory attains the asymptotic scaling values (at X is approximately 10). This implies either that the Hess theory in its present form is of limited utility or that there is no scaling region in the concentration range $c^* < c < c_\Theta$. Another disturbing aspect is that Figure 7 indicates good agreement between the Hess theory and the data corrected by using d_{sa}; such agreement is quite unexpected.

Conclusion

The monomer self-diffusion coefficient has been determined in both Θ and non-Θ solutions; these quantities are shown to exhibit similar polymer concentration dependencies. The monomer self-diffusion coefficient has been demonstrated to be distinct from the segmental self-diffusion coefficient. It has also been confirmed that the "correction" of polymer self-diffusion coefficients by the use of the monomer self-diffusion coefficient renders the data more consistent with the scaling laws, appropriately normalized quantities fall on universal curves, and the crossover concentration is independent of molar mass. The "corrected" self-diffusion coefficients of random coil polymers in semidilute non-Θ solutions have also been compared with the theory of Hess and agreement between theory and experiment demonstrated. The segmental self-diffusion coefficient was determined, and the thus "corrected" polymer data were compared with the scaling laws and with the Hess theory and more properly with the Hess entanglement function. There was a measure of agreement between the data and the entanglement function for concentrations less than about three times the overlap concentration; however, at larger concentrations the data decreased more rapidly than theory would allow. This could be caused by the onset of crossover effects, if so then it would appear that crossover effects occur before the Hess theory attains its asymptotic scaling region. Surprisingly there was enhanced agreement between the data corrected by using d_{sa} and the Hess expression for D_s.

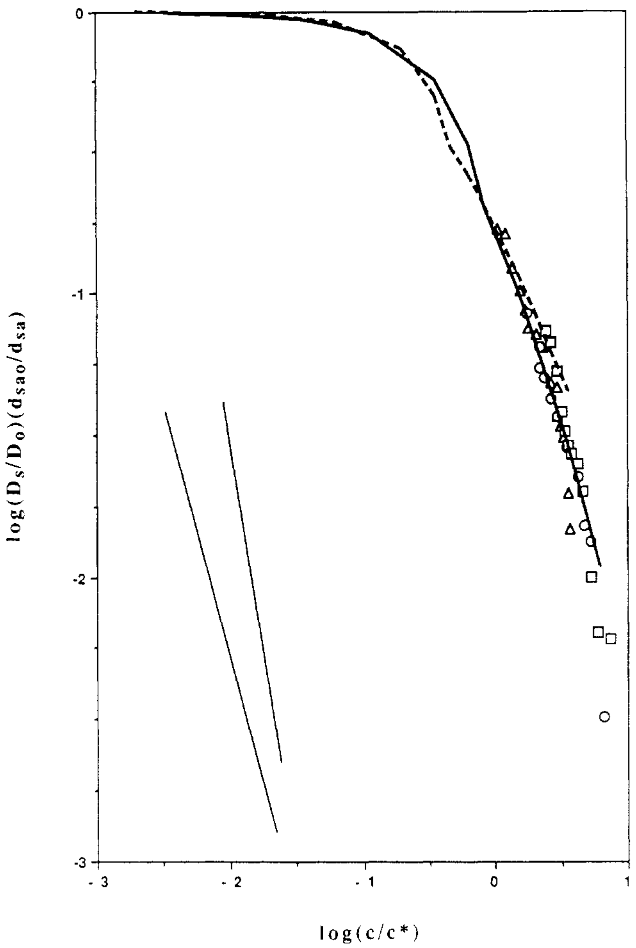

Figure 7. Same data as Figure 5 "corrected" by using the segmental self-diffusion coefficient. The predictions of the Hess theory (continuous line) and the entanglement function (broken line) are shown. The unknown proportionality constants between X and c/c^* have been adjusted separately. Lines of slopes −1.75 and −3 are included. The uncertainties are indicated by the size of the symbols.

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Registry No. Polystyrene, 9003-53-6; styrene, 100-42-5.

Conformation of Star Polymers without Excluded Volume

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ABSTRACT: Nonideal behavior in the vicinity of the point where chains are attached together can significantly affect the dimensions of branched polymers. Several features of the branch point are considered, and their effect on the radius of gyration of star-shaped molecules is calculated. Two classes of behavior are found according to whether the description treats only specific geometrical properties of the monomers close to the junction or perceives the branch point more generally, as a region of reduced accessibility to more distant parts of the molecule. A new model is introduced within the latter category in which a repulsive potential surrounds the branch point and acts on all the monomers. For the special case of a hard-sphere potential an exact solution is found, from which a general relationship, $\langle S^2\rangle^{1/2} - \langle S^2\rangle_0^{1/2} \approx c$, is derived, linking the mean squared radius of gyration, $\langle S^2\rangle$, to its value in the unperturbed state, $\langle S^2\rangle_0$, and to a length, c, characteristic of the range of the potential. It is shown how the effect of the repulsive potential can be distinguished experimentally from local, geometrical properties of the branch point, and from the available data it is concluded that this repulsive nature of the branch-point region is the more important factor in determining the size of star-branched polymers.

Introduction

The simplest descriptions of polymer chain conformation are based on the random walk or Gaussian model. The central assumption of such theories is that in a statistical ensemble of chains of equal length, the distance r_{ij} between monomers i and j is governed by a Gaussian distribution whose variance is proportional to the number of monomers between i and j along the backbone of the chain, that is, $\langle r_{ij}^2\rangle = K|i - j|$. The effects of local interactions between a monomer and its first few closest neighbors are factored into the stiffness constant, K, but interactions between monomers well-separated along the chain are ignored. Chains that comply with the above considerations are referred to as "unperturbed" chains, and it follows directly from the Gaussian assumption that the mean squared radius of gyration, $\langle S^2\rangle$, is proportional to N, the total number of monomers in the chain.[1] All the statistical properties of unperturbed chains may be expressed in terms of the single parameter $\langle S^2\rangle$.

The random walk model is known from experiment to apply to flexible linear polymers in the molten state and is also a good approximation in polymer solutions at the Θ temperature, where the combination of solution entropy and interaction energy conspires to eliminate the effects of long-range binary interactions. More generally, however, the statistical properties of polymers in solution *are* influenced by two-body interactions, and the random walk model must be adjusted by the inclusion of a second parameter, the "excluded volume".[2]

An extension of the random walk concept to branched chains was provided by Zimm and Stockmayer,[3] who assumed that the Gaussian distribution for r_{ij} applies whether i and j are on the same branch or not. In other words, two subchains joined at a point to one or more others behave statistically, as if they were one continuous linear chain. However, in spite of the success of the random walk model with linear chains, its application to branched molecules is much less tenable. Two factors are important. First, the effect of intramolecular excluded volume is more significant in a branched molecule because the number of segment–segment contacts increases as the intramolecular segment density becomes larger. Second, the Gaussian assumption fails to recognize the singular nature of the branch point. When several branches are attached together, spatial crowding prevents lateral motion and forces the chains to radiate away from each other. This imposes rigid correlations upon the initial trajectories of the arms, and a local increase in stiffness is likely. Furthermore, the region around the branch point is less accessible to monomers from further out on the molecule because it is not easy to force a path through the anchored branches, so random walking near to the branch point is inhibited.

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