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Cooperative Diffusion in Semidilute Polystyrene Solutions at Good and Θ Solvent Conditions

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ABSTRACT: The concentration dependence of the cooperative diffusion coefficient (D) in semidilute solutions of sharp fractions (both low and high molecular weights) of polystyrene has been studied in a good solvent (toluene) and in a Θ solvent (cyclohexane) by means of the classical gradient diffusion technique. At good solvent conditions and high molecular weights D varies as $c^{0.70}$ at the onset of the semidilute regime, while at Θ conditions $D \sim c^{0.95}$. These exponents are both somewhat smaller than those expected on the basis of the de Gennes model in the asymptotic limit of infinite molecular weight, i.e., 0.75 and 1.00, respectively. However, the exponents obtained for the low molecular weight samples at the onset of the semidilute regime are significantly smaller than the above values. Tentative explanations of this behavior are presented.

Introduction

Macromolecular dynamics in semidilute solutions has been the subject of several experimental and theoretical investigations in recent years. Experimental studies of diffusion and sedimentation velocity were found to be powerful in surveying dynamical properties in entangled polymer solutions. Questions concerning the diffusion and sedimentation behavior in semidilute solutions have been reviewed quite recently.[1]

From a theoretical point of view, the introduction of a new approach, based on an analogy[2-4] between problems in magnetic phase transitions and in polymer solutions from which scaling laws emerged, has been of crucial importance in interpreting and predicting features in semidilute solutions both at good and Θ solvent conditions. The present status of scaling laws describing dynamical phenomena in semidilute solutions has been summarized and reviewed.[5,6]

The basic picture of an entangled non-Θ polymer solution[7] is that the polymer chains overlap strongly and a transient network with a characteristic mesh size ξ, the screening length, is formed. This screening length decreases with increasing concentration but is regarded as independent of the molecular weight of the dissolved polymer.

In the semidilute regime a cooperative diffusion coefficient, D, associated with long-wavelength fluctuations of the polymer concentration can be defined. Scaling laws describing the concentration dependence of the cooperative diffusion coefficient of solutions of flexible polymers at both good[8] and Θ[9] solvent conditions have been elaborated.

The coefficient D can be probed by quasi-elastic light scattering (QELS) measurements or by classical gradient diffusion (CGD) experiments, i.e., by establishing an artificial concentration gradient and observing the relaxation of this gradient with time. Measurements have demonstrated[10,11] that the techniques of QELS and CGD give, at corresponding conditions, within experimental error, consistent values of the diffusion coefficients.

Recently, the concentration dependence of the cooperative diffusion coefficient of good solutions of polystyrene was studied[12-14] by means of laser light scattering spectroscopy in the hetrodyne mode. These investigations confirmed the essential features of the scaling law hypothesis. However, the experimental work was restricted to study the diffusion behavior of very high molecular weight samples.

The principal objective of the present paper is to examine the concentration dependence of the cooperative diffusion coefficient at both good and Θ solvent conditions for low and high molecular weight samples of polystyrene. The observed features will be discussed and analyzed within the framework of the scaling law concept.

This investigation presents results from CGD measurements in the semidilute concentration regime for polystyrene ($M = 8.6 \times 10^5$ and $M = 2.88 \times 10^6$) in toluene at 25 °C (good solvent conditions) and for polystyrene ($M = 3.9 \times 10^5$ and $M = 8.6 \times 10^5$) in cyclohexane at 35 °C (Θ solvent conditions).

Experimental Section

Materials and Preparation of Solutions. Two sharp fractions of polystyrene with nominal molecular weights of $M = 3.9 \times 10^5$ ($\bar{M}_w/\bar{M}_n \leq 1.10$) and $M = 8.6 \times 10^5$ ($\bar{M}_w/\bar{M}_n \leq 1.15$) (manufacturer's data for lot nos. 3b and 6a, respectively), were supplied by Pressure Chemical Co. In addition, a TSK standard polystyrene sample ($M = 2.88 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.09$, manufacturer's data for lot no. T10) obtained from the Toyo Soda Manufacturing Co. Ltd., Japan, was utilized. All samples were used as received.

The solvents cyclohexane and toluene of p.a. grade (Merck A.G.) were used without further purification.

All solutions were prepared by weighing. After addition of solvent, the polymer was allowed to swell before the solution was homogenized by gentle stirring for several days.

Diffusion. Diffusion measurements were carried out in an apparatus designed and built at this Institute.[15] The apparatus is provided with an air thermostat regulated within ±0.01 °C at the temperatures studied. A shearing-type cell[16,17] for free diffusion was utilized; the functioning of this type of shear cell has been described previously.[10] The spreading of the initial boundary was followed with a schlieren optical system[18] and registered photographically. Only a slight asymmetry could be observed in the schlieren pattern.

At low concentrations, the boundary was formed between solution and solvent and at higher concentrations between two solutions of different solute concentration. The initial concentration step, $\Delta c = c_{\text{bottom}} - c_{\text{top}}$, was between 10 and 20 kg m^{-3}; the determined diffusion coefficient is assumed to be equal to the differential diffusion coefficient at $\bar{c} = {}^1/_2(c_{\text{top}} + c_{\text{bottom}})$. In all the experiments the initial boundary was sharp; the starting time correction could be taken as zero within the experimental accuracy.

The evaluation of the diffusion coefficients were performed in accordance with the principles discussed elsewhere.[10]

Results and Discussion

In the semidilute regime a cooperative diffusion coefficient, D, associated with network deformations can be defined by[8]

$$D \sim kT/6\pi\eta_0\xi \qquad (1)$$

where k is Boltzmann's constant, T the absolute temper-

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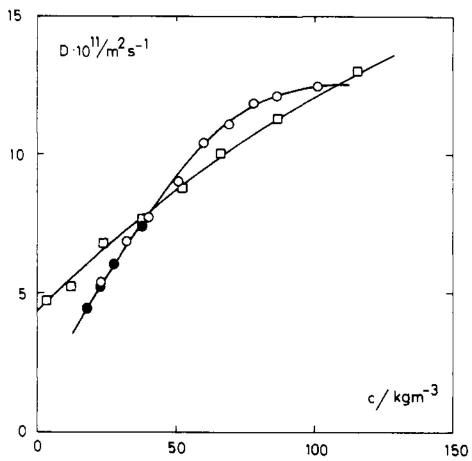

Figure 1. Concentration dependence at 25 °C of the cooperative diffusion coefficient for the system polystyrene/toluene: (□) $M = 1.10 \times 10^5$ (data from ref 10); (○) $M = 8.60 \times 10^5$; (●) $M = 2.88 \times 10^6$.

ature, and η_0 the solvent viscosity. Scaling arguments have been used to show that the concentration dependence of the screening length ξ can be expressed by the relations[4,19,20]

$$\begin{aligned} \xi &\sim c^{-0.75} \quad \text{(good solvent conditions)} \\ \xi &\sim c^{-1.0} \quad (\Theta \text{ solvent conditions}) \end{aligned} \tag{2}$$

which lead to the following power laws for D:

$$\begin{aligned} D &\sim c^{0.75} \quad \text{(good solvent conditions)} \\ D &\sim c^{1.0} \quad (\Theta \text{ solvent conditions}) \end{aligned} \tag{3}$$

The theoretically predicted exponents describing the concentration dependence of the quantity ξ have been verified from small-angle neutron scattering experiments.[4,21]

Although, the scaling laws are only strictly applicable in limit of infinite molecular weight, we will express the concentration dependence of the cooperative diffusion by using exponents and simple power law dependencies in order to obtain a quantitative perception of the features.

In Figure 1 the concentration dependence of the cooperative diffusion coefficient is illustrated for the thermodynamically good system polystyrene/toluene. For the two highest molecular weights D increases considerably with concentration and the behavior can be represented by a single curve. For the lowest fraction[10] ($M = 1.1 \times 10^5$) the increased in D is less pronounced.

Figure 2 constitutes a log–log representation of the cooperative diffusion coefficient vs. concentration for the same polymer–solvent system. At concentrations higher than about 12 kg m^{-3} the resulting curve for the low molecular weight fraction exhibits a noticeable departure from its initially modest concentration dependence, probably reflecting the transition from dilute to semidilute solution behavior. The transition region is centered roughly at $c = 1/[\eta]$, ($[\eta]$ is the limiting viscosity number), which, according to Simha et al.,[22] corresponds to a concentration where the polymer coils show incipient overlap. This concentration is indicated by a vertical dashed line. The corresponding concentrations c^*, where the high molecular weight samples show an analogous transition, are at far lower concentrations.

The data for the low molecular weight sample ($M = 1.1 \times 10^5$) may in the region where semidilute solution behavior prevails be represented by c^γ, with $\gamma = 0.49 \pm 0.02$. For the other two samples ($M = 8.6 \times 10^5$ and $M = 2.88 \times 10^6$) D in the semidilute regime is proportional to c^γ, with $\gamma = 0.70 \pm 0.01$.

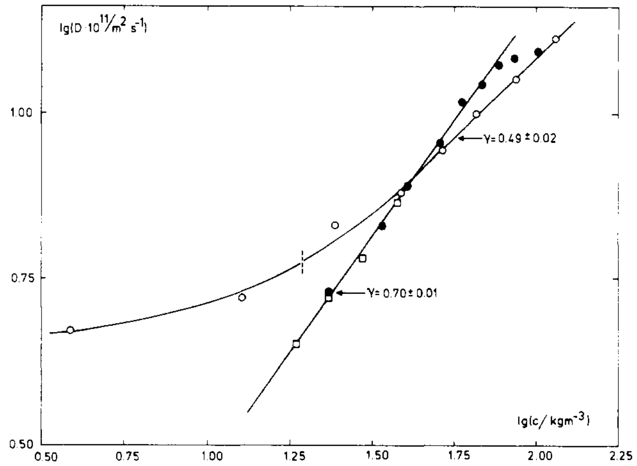

Figure 2. Log–log representation of the cooperative diffusion coefficient vs. concentration for the system polystyrene/toluene at 25 °C (the dashed vertical line indicates $c^* = 1/[\eta]$): (○) $M = 1.10 \times 10^5$ (data from ref 10); (●) $M = 8.6 \times 10^5$; (□) $M = 2.88 \times 10^6$.

The value 0.49 is consistent with those that may represent D for polystyrene in the same molecular weight range, in good solvents and from concentrations ranging from c^* up to 250 kg m^{-3}.[24] The experimental value of 0.70 for the high molecular weight samples is somewhat smaller than the theoretically predicted value of 0.75 (cf. eq 3) for infinite molecular weight but agrees very well with those observed for similar polymer–solvent systems in the same molecular weight range and the same concentration range. By utilizing quasi-elastic light scattering spectroscopy, Adam and Delsanti[14] found a value of $\gamma = 0.67 \pm 0.02$ for polystyrene ($M > 1 \times 10^6$) in benzene, and Munch et al.[13] reported values of 0.68 ± 0.01 for the system polystyrene ($M = 7 \times 10^5$)/benzene.

This observed apparent molecular weight dependence is likely associated with a different behavior at the onset of the semidilute regime which occurs at different concentrations for different molecular weights. However, this apparent molecular weight dependence virtually disappears for sufficiently high molecular weights. A similar deviation has been observed for the concentration dependence of the sedimentation coefficient at the onset of the semidilute region for high and low molecular weights.[25] This supports the above observation for the diffusion coefficient since the sedimentation and diffusion coefficients are related to each other through the expression $D \sim s\ \partial\pi/\partial c$ (where π is the osmotic pressure).

These effects observed in diffusion and sedimentation experiments as well as the residual discrepancy between the exponents of the high molecular weight samples and the theoretical value are probably associated with an effect analogous to the des Cloizeaux–Weill correction[26] for flexible chains in dilute solutions. According to this hypothesis, the discrepancy between the exponents defining the molecular weight dependence of static and dynamical properties is attributed to a larger influence of the spatial crossover on hydrodynamic properties. This effect could explain the difference[27] in molecular weight dependence between the radius of gyration (R_G) (a static property) and the hydrodynamic radius ($R_H = kT/6\pi\eta_0 D_0$) of a polymer in a dilute solution.

In a recent investigation[28] it was shown that R_H cannot be represented by a simple power law, viz., $R_H \sim M^{\nu_H}$, whereas the radius of gyration satisfies the relation $R_G \sim M^\nu$. However, a power law fit to experimental data would

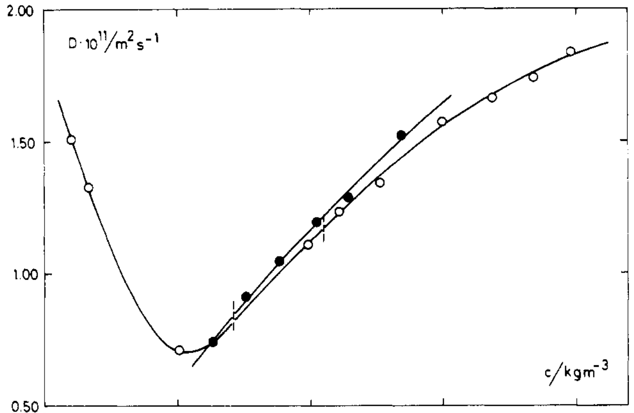

Figure 3. Concentration dependence at 35 °C for D for the Θ system polystyrene/cyclohexane (the dashed lines indicate the concentration $c^{\dagger}$ (cf. main text): (○) $M = 3.9 \times 10^5$; (●) $M = 8.6 \times 10^5$.

yield $\nu_H < \nu$ and the numerical value of ν_H should depend on the range of molecular weights used in the experiment. The theory of des Cloizeaux and Weill predicts that in the asymptotic limit of infinite molecular weight $\nu_H = \nu$. des Cloizeaux and Weill[26] also claimed that the hydrodynamic properties of the screening length, which is the characteristic length in a semidilute solution, should be sensitive to the same crossover effects as an isolated chain.

A semidilute solution can be visualized as a sequence of blobs of size ξ and each occupying a volume proportional to ξ.[3] The word "blob" denotes the chain portion between successive entanglement points.[7] Each blob acts as an individual unit with both hydrodynamic and excluded-volume interactions.

In analogy with the above picture for dilute solutions we may distinguish between a static (ξ_s) and a dynamic (ξ_H) screening length, where ξ_s varies with concentration as $c^{-\beta_s}$ and ξ_H varies as $c^{-\beta_H}$. The conjecture is that the dynamical exponent β_H exhibits an anomalous molecular weight dependence, whereas the static exponent β_s approaches its asymptotic value already at low molecular weights. Furthermore, we expect that $\beta_s > \beta_H$ (in order to obtain an overall consistent picture for the concentration dependence of D, s, and π) and that in the asymptotic limit of infinite molecular weight $\beta_s = \beta_H$. The above tentative arguments may explain the discrepancy between the theoretical and the experimental values of γ since the power law for the concentration dependence of D (cf. eq 3) has implicitly been derived in the asymptotic limit. It has previously been argued that one may distinguish between a static and dynamic screening length.[14,29,30]

Before the results for Θ solvent conditions are presented and discussed some general aspects will be given. In a Θ solvent, the polymer coil tends to shrink and to form many knots on itself, while in a good solvent the chain expands and makes but few knots on itself.[9] The effects of self-knotting may have repercussions on the network structure formed in semidilute solutions and, ultimately, on the diffusion features. Thus, the dynamical behavior at Θ solvent conditions is expected to be more complex than at good solvent conditions. Furthermore, it is important in this context to remember that D is governed by both hydrodynamic and thermodynamic properties[10] (vide supra).

Figure 3 shows plots of D vs. concentration for the Θ system polystyrene/cyclohexane. The data for the low molecular weight sample ($M = 3.9 \times 10^5$) clearly indicate that the diffusion behavior at the Θ temperature is rather complex. The value of D first decreases with increasing concentration and passes through a minimum; upon further increase in concentration D increases. At still higher concentrations the resulting curve tends to become concave downward. Similar observations for Θ systems have been reported from both CGD[10,23] and QELS[31] measurements.

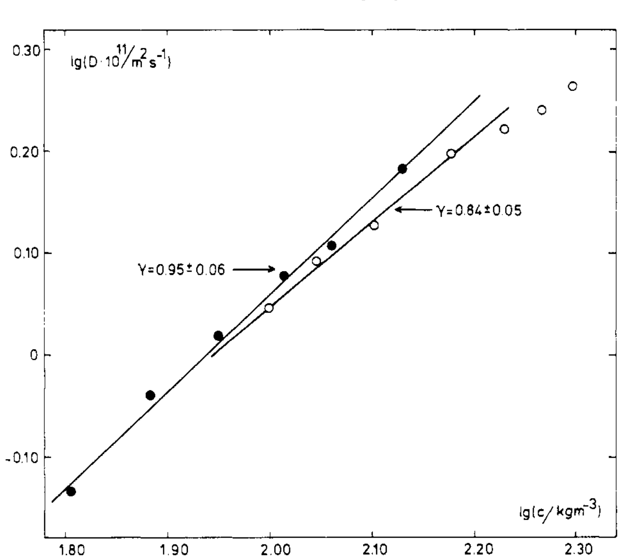

Figure 4. Log-log plots of the cooperative diffusion coefficient as a function of concentration for the Θ system polystyrene/cyclohexane at 35 °C: (○) $M = 3.9 \times 10^5$; (●) $M = 8.6 \times 10^5$.

For the high molecular weight sample the minimum of the diffusion curve is expected at a lower concentration than for the low molecular weight sample. The minimum of the diffusion curve is correlated to the maximum of the phase equilibrium curve and is ultimately due to an interplay between hydrodynamic and thermodynamic properties.[10]

The relevant concentration at Θ conditions for the transition to semidilute solution behavior seems to be located roughly at

$$c^{\dagger} = M/N_A\langle s^2\rangle^{3/2} \tag{4}$$

where M is the molar mass (kg/mol), $\langle s^2\rangle$ the mean-square radius of gyration, and N_A Avogadro's constant. The concentration $c^{\dagger}$ (indicated by vertical dashed lines in Figure 3) corresponds to a situation where a uniform polymer segment density over the available volume prevails.[32,32]

Figure 4 shows log-log plots of D vs. c for the system polystyrene/cyclohexane in the semidilute regime. At concentrations above $c^{\dagger}$ D increases with concentration as c^{γ}, with $\gamma = 0.84 \pm 0.05$ and $\gamma = 0.95 \pm 0.06$ for the low and the high molecular weights, respectively. At high concentrations the experimental points for the low molecular weight seem to deviate from the linear representation, which probably is associated with the onset of the concentrated-solution regime.

The value 0.95 is in good agreement with the prediction for infinite molecular weight (cf. eq 3). It is, within experimental error, not possible to indicate any significant difference between the experimental and the theoretical values. If these is a real discrepancy, its existence and origin must be established by further experiments.

The value 0.84 for the low molecular weight sample, on the other hand, deviates significantly from the theoretically predicted values. This discrepancy can probably be explained by the following arguments. The scaling law relations emerge from asymptotic dimensional analysis for infinitely long flexible chains, i.e., infinite molecular weight. In this limit the Θ temperature is equivalent with the upper critical solution temperature (UCST). However, for finite molecular weights the difference between the Θ temperature and the UCST increases with decreasing molecular weight. Furthermore, the minimum of the diffusion curve (see Figure 3) will be displaced toward higher concentration with decreasing molecular weight which should reduce the range for "effective" semidilute solution behavior. Furthermore, in this range for "effective" semidilute solution behavior (centered around $c^{\dagger}$) it is not unlikely that the concentration dependence of the sedimentation coefficient is stronger than predicted (i.e., $s \sim c^{-\beta}$ with $\beta > 1$) due to enhanced monomer–monomer friction. The concentration dependence of the osmotic pressure, on the other hand, can virtually be described by c^{α} with $\alpha \approx 3$ (the theoretical value for infinite molecular weight); this can be anticipated from ref 34 and 35. In this context it is interesting to note that sedimentation measurements on semidilute solutions of polystyrene (wide range of molecular weights) in various Θ solvents yielded exponents[1,34] (evaluated close to c^*) which were in very good agreement with the theoretically predicted value.

Conclusions

In this paper the concentration dependence of the cooperative diffusion coefficient has been studied at both good and Θ solvent conditions. The results have been interpreted in terms of scaling law concepts and some significant features have emerged from this analysis.

First, at good solvent conditions the concentration dependence of the diffusion coefficient at the onset of semidilute solution behavior could not be described by a single power law for all molecular weights. This anomalous behavior is probably associated with an effect analogous to the des Cloizeaux–Weill correction for dilute solutions.

Second, at Θ solvent conditions the aberrant exponent observed for the low molecular weight sample is suspected to be related to thermodynamic factors.

Third, even for high molecular weights there is a residual discrepancy between the experimentally determined and the theorectically predicted values of the exponent. For a rigorous analysis of this discrepancy the influence of reference frames should be considered.[36] The theoretical models are deduced for the solvent-fixed frame, whereas experiments are performed in the cell-fixed frame (which in most cases can be approximated with the volume-fixed frame). The solvent-fixed and volume-fixed reference frames are correlated through the factor $1 - v_2c$ (v_2 is the partial specific volume of solute).

The overall conclusion from the present study is that diffusion experiments should be performed with sufficiently high molecular weight samples in order to obtain dynamic scaling exponents in the semidilute regime that are consistent with the theoretically predicted values.

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