Pulsed field gradient n.m.r. measurements and theoretical interpretation of the self-diffusion of polystyrene in solution

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The self-diffusion coefficients of polystyrene dissolved in C_6D_6 were measured by means of pulsed field gradient n.m.r.. The dependence on the molecular weight was of the power of -2 in accordance with the reptation model. The concentration dependence was theoretically calculated within the blob concept which shows that in the crossover region the self-diffusion coefficient is determined only by the blob dimensions and the monomeric friction coefficient is constant. The calculated concentration dependence agrees well with that observed by the authors.

(**Keywords: self-diffusion; polystyrene solutions; pulsed field gradient n.m.r.; reptation; blob model**)

INTRODUCTION

The investigation of the self-diffusion of macromolecules is a sensitive test of the reptation model proposed by de Gennes[1]. For the self-diffusion coefficient D of a polymer chain in the semidilute concentration region, a scaling treatment using the mean field critical index $v = 0.6$ gives

$$D \sim c^{-1.75} \cdot N^{-2} \qquad (1)$$

Here c is the concentration of the chain molecules and N is the degree of polymerization.

There is a lot of data concerned with the self-diffusion of macromolecules in the melt, but very little exists for macromolecules in solution. The self-diffusion of polystyrene dissolved in benzene was investigated by Leger et al.[2] using the forced Rayleigh scattering technique. They confirmed relation (1) in the semidilute region. With the n.m.r. pulsed field gradient technique Callaghan and Pinder[3,4] found for polystyrene in carbon tetrachloride that $D \sim c^{-1.84}$ whereas the dependence of the self-diffusion coefficient on N was only of the power of -1.4. An observed fast process was interpreted as cooperative diffusion. Wesson et al.[5] investigated the self-diffusion of polystyrene in THF in a broader concentration and molecular weight range by the forced Rayleigh scattering technique. Their results agree well with those obtained by us which can be satisfactorily described with the more elaborate theoretical approach given in the present paper. The interpretation of recently reported measurements of self-diffusion in semidilute solutions by the quasielastic light scattering technique[6,7] does not seem well established[8].

An analysis of the experimental data shows that the reptation concept is well confirmed, but most of the experiments are performed in the crossover region between excluded-volume and ideal behaviour in the semidilute region and a scaling approach is not sufficient for the explanation of these experiments.

In the present investigation we examined the self-diffusion of polystyrene in benzene in a broader concentration and molecular weight range by means of the n.m.r. pulsed field gradient technique. Here we will present a version of the blob model (in the reptation concept of de Gennes[1]) for single chain dynamics in polymer solutions where the coils overlap. This goes beyond the usual scaling treatment and is suitable for the analysis of our diffusion data. It takes into account excluded-volume effects, hydrodynamic interaction and non-uniform coil expansion. It is possible to conclude that in a broad concentration range the self-diffusion coefficient is determined by the blob dimensions only and the friction mechanism is concentration independent. The observed concentration dependence of the self-diffusion coefficient is described satisfactorily by the theory presented.

PULSED FIELD GRADIENT N.M.R.

The mean square displacements of the spins of molecules in a given time interval can be measured using pulsed field gradient n.m.r. During the spin echo experiment the spins are labelled by their Larmor frequencies in the spatially varying magnetic field of the field gradients. If the spins have changed their positions during the time between the two field gradient pulses this results in an attenuation of the echo in addition to nuclear magnetic relaxation.

For spins undergoing random motion with a Gaussian

probability distribution the attenuation of the spin echo depends on the magnitude g and the duration δ of the field gradient pulses in the form of

$$\psi(\Delta,\delta g)=\exp\left(-\gamma^2\delta^2 g^2\frac{\langle z^2\rangle}{2}\right) \quad (2)$$

where γ is the gyromagnetic ratio.

If the mean square displacement $\langle z^2\rangle$ of the spins in the diffusion time Δ obeys the Einstein equation

$$\langle z^2\rangle=2D\Delta \quad (3)$$

we obtain the well-known relation[9]

$$\psi(\Delta,\delta g)=\exp(-\gamma^2\delta^2 g^2 D\Delta) \quad (4)$$

Here we assume that $\delta\ll\Delta$.

If the spin diffusion is governed by two mechanisms, e.g. by simultaneous gel-like fluctuations and self-diffusion of the coils by reptation characterized by the cooperative diffusion coefficient D_c and the self-diffusion coefficient D, respectively, the displacement z of the spin after the time interval Δ is the sum of the contributions of the two mechanisms z_s+z_c. We assume that the two processes are non-correlated. For the self-diffusion process the random walk is valid whereas for cooperative diffusion we use the model of a particle undergoing diffusion in a harmonic potential with frictional damping as treated by Stejskal[9] and applied by Callaghan and Pinder[3]. On the assumption that the probability distributions are symmetric the echo may be given by the relation

$$\psi(\Delta,\delta g)=\exp(-\gamma^2\delta^2 g^2 D\Delta)\cdot\exp\left(-\gamma^2\delta^2 g^2 D_c\frac{1-e^{-\beta\Delta}}{\beta}\right) \quad (5)$$

β is a parameter characterizing the restoring force acting on a segment in cooperative diffusion. In this case the echo attenuation is exponential, being characterized by an 'apparent' diffusion coefficient

$$D_{app}=D+D_c\frac{1-e^{-\beta\Delta}}{\beta\Delta} \quad (6)$$

D_{app} depends on the diffusion time Δ, so that a separate evaluation of D and D_c is possible by variation of the time over which diffusion takes place.

If the displacement of the spin during the diffusion time is smaller than the radius of the coil, equation (3) does not hold any longer and must be replaced (see ref. 10).

$$\langle z^2\rangle\sim\Delta^{1/2} \quad (7)$$

In this case we measure the self-diffusion of segments inside the coil. The measured self-diffusion coefficient then also becomes time dependent in the form of

$$D\sim\Delta^{-1/2} \quad (8)$$

The minimum spin displacements which can be detected by the echo attenuation are given by

$$\gamma^2\delta^2 g^2\frac{\langle z^2\rangle_{min}}{2}\gtrsim 1 \quad (9)$$

With our measuring parameters ($\delta_{max}\approx 4$ ms, $g_{max}\approx 5$ T m^{-1}) we obtain a value of $\langle z^2\rangle_{min}^{1/2}\approx 0.25$ μm for these displacements. Consequently, it is only possible to detect gel-like fluctuations with amplitudes of the spin displacements greater than about 2500 Å.

If there are two sorts of molecules, e.g. polymer and solvent molecules, diffusing independently of each other the echo attenuation is the sum of two exponentials

$$\psi(\Delta,\delta g)=A_1\exp(-\gamma^2\delta^2 g^2 D_1\Delta)+A_2\exp(-\gamma^2\delta^2 g^2 D_2\Delta) \quad (10)$$

where the relative intensities A_i depend on the mass fractions of the two components and on their nuclear relaxation times.

THEORY

We consider the self-diffusion coefficient of a chain molecule in a solution above the overlap concentration c^x. Following the picture, suggested by de Gennes[1], that the excluded-volume effect and hydrodynamic interaction only act within a concentration dependent correlation length l_b (the blob length) and that they are screened out above this length scale, we apply the so-called 'blob concept' as the simplest realization of this picture to our problem.

The self-diffusion coefficient is given by

$$D=\langle R^2\rangle/6T_d \quad (11)$$

where

$$\langle R^2\rangle=l_b^2 N_b \quad (12)$$

is the mean square end-to-end distance of a random flight chain consisting of N_b blobs with a mean square blob length l_b^2 and g statistical segments in each blob, i.e. $N_b=N_{st}/g$. The disengagement time T_d is determined by the curvilinear diffusion coefficient D_1 and the contour length of the 'blob-molecule' $N_b l_b$

$$T_d=(N_b l_b)^2/2D_1; \qquad D_1=3D_b/N_b \quad (13)$$

D_b is the diffusion coefficient of an isolated blob. Equations (11)–(13) give the well-known result

$$D=D_b g^2/N_{st}^2 \quad (14)$$

The number of segments per blob is determined by

$$n_{st}=g\bigg/\left(\left(\frac{4\pi}{3.8}\right)(\alpha_R^2(z_g)l_{st}^2 g)^{3/2}\right) \quad (15a)$$

or

$$\alpha_R^3(z_g)z_g=\left(\frac{3.8}{4\pi}\right)(z/N_{st}^{1/2})\bigg/n_{st}l_{st}^3 \quad (15b)$$

following de Gennes'[1] proposal that the mean segment density of a blob is equal to the mean number density n_{st} of statistical segments. $z_g=(z/N_{st}^{1/2})g^{1/2}$ is the excluded-volume parameter of a blob, $\alpha_R(z_g)$ is the corresponding expansion factor and l_{st} is the statistical segment length. $z/N_{st}^{1/2}$ is characteristic of a given polymer–solvent system. For PS in benzene we derived $z/N_{st}^{1/2}\approx 8.5\times 10^{-2}$ (from ref. 11).

For D_b we use the Kirkwood formula in the limit of strong hydrodynamic interaction

$$D_b = (kT/\eta_0 6\pi g^2) \sum_{i \neq j} \langle 1/R_{ij} \rangle \qquad (16)$$

Introducing reduced segment–segment distances $x_{ij} = R_{ij}/(l_{st}|j-i|^{1/2})$ and reduced subchain lengths $t = |j-i|/g$ and replacing summation by integration, equation (16) may be transformed to

$$D_b = \frac{kT}{\eta_0 l_{st}} \frac{2}{6\pi g^{1/2}} \int_0^1 dt \frac{1-t}{t^{1/2}\langle x(t)\rangle}$$

$$= \frac{kT}{\eta_0 l_{st}} \frac{4.6^{1/2}}{9\pi^{3/2} g^{1/2}} \alpha_H^{-1}(z_g) \qquad (17)$$

where we have assumed that $\langle 1/R_{ij} \rangle$ depends on the subchain length only. In the second line of equation (17) the expansion factor of the hydrodynamic radius is introduced with regard to the result of the uniform expansion approximation (UEA) for D_b. From equations (14) and (17) we finally get the self-diffusion coefficient

$$D_{th} = \frac{kT}{\eta_0 l_{st}} N_{st}^{-2} \frac{4.6^{1/2}}{9\pi^{3/2}} g^{3/2} \alpha_H^{-1}(z_g)$$

$$= \frac{kT}{\eta_0 l_{st}} N_{st}^{-2} \cdot D_{r,th} \qquad (18)$$

Equations (15), (17) and (18) show that the reduced self-diffusion coefficient $D_{r,th}$ is only a function of the reduced segment density $n_r = n_{st} l_{st}^3$.

The calculation of $D_{r,th}$ demands the knowledge of $\alpha^2_R(z_g)$ for a solution of equation (15) and we have to take the average in equation (17). For both tasks the distribution functions for segment–segment distances which are obtained by a hierarchy approach[12], already applied to the investigations of the effects of the nonuniform coil expansion on the intrinsic viscosity[13] and scattering properties[14] were used. The solution of equation (15) was carried out numerically by inverse interpolation of an $\alpha^3_R(z_g) \cdot z_g$ versus z_g. The integration in equation (17) was performed numerically with a Gauss-type formula.

EXPERIMENTAL

The self-diffusion coefficients of the polymer molecules were measured by means of the pulsed field gradient n.m.r. technique. The method of the stimulated echo was used[15] with the pulse program shown in *Figure 1*. We used the home-built spectrometer FEGRIS 80 with a measuring frequency of 60 MHz. At low concentrations when the signal-to-noise ratio was small the signals were accumulated using the waveform analyser system 5500 (EMG Budapest). The magnitude of the field gradients was about 5 Tm^{-1} and was calibrated using known samples. The width of the field gradient pulsed δ was up to 4 ms and the diffusion time Δ was typically between 20 and 100 ms. The self-diffusion coefficients were evaluated from the slope of the echo attentuation plot $\ln\psi$ vs. δ^2.

For the lowest (and sometimes the highest) polymer concentrations we observed a small fast decay at the beginning of the echo attenuation plot which was caused by residual protons in the deuterated benzene and/or low molecular traces in the polymer. This fast decay was omitted in the evaluation of D. The measurements of the
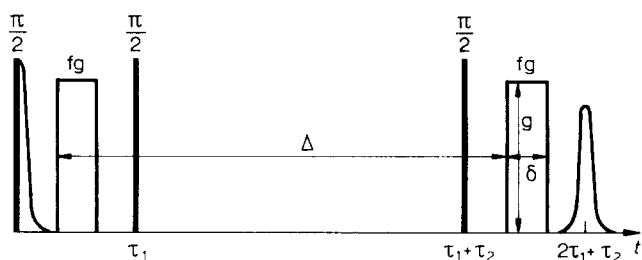

Figure 1 Pulse program for pulsed field gradient n.m.r. with the stimulated echo. $\frac{\pi}{2}$: rf-pulses, fg: field gradient pulses of magnitude g, duration δ and separation Δ

lowest self-diffusion coefficients must be done very carefully since the large field gradients may influence the radio frequency pulses and also mechanical vibrations and shocks may cause additional displacements both leading to an overestimation of D.

Each of the data points is the average of several measurements. The relative errors are $\pm 20\%$ for the highest and the lowest concentrations and decrease to $\pm 5\%$ for the middle region of the concentration range. All measurements were performed at room temperature (25°C).

Monodisperse polystyrenes with molecular weights from 1.2×10^4 up to 1.8×10^6 were standards purchased from Knauer GmbH Berlin (West). Perdeuterated benzene (C_6D_6) was supplied by Isocommerz GmbH Leipzig and IBJ Swierk (Poland). The samples were prepared by weighing in 7.5 mm o.d. glass tubes. Concentrations are given as the volume fraction of polymer in the solution.

We have related the measured self-diffusion coefficients to the geometric mean of the molecular weights $\bar{M}_n$ and $\bar{M}_w$ (as carried out by Leger *et al.*[2]) though recent publications have pointed out the difficulties arising from the molecular weight distribution[16] especially in pulsed field gradient n.m.r.[17]. The self-diffusion coefficient was always evaluated from the echo attenuation plot up to $\ln\psi \approx -1$, so all values are comparable. Also all standards had about the same $\bar{M}_w/\bar{M}_n = 1.06$ except for the highest molecular weight standard which has a slightly higher $\bar{M}_w/\bar{M}_n$.

RESULTS AND DISCUSSION

The observed echo attenuation plots were exponential in all cases. Over the whole range of observation times Δ a dependence of the measured self-diffusion coefficient on the diffusion time was not observed and the spin displacements within the diffusion time were much greater than the radii of gyration, so that the measured self-diffusion coefficients are clearly those of the centre of mass of the polymer molecules. The measured self-diffusion coefficients increased slightly with decreasing diffusion time only at the highest concentrations (when the self-diffusion coefficients were very small, i.e. when we had to apply very large field gradient pulses). We still could not decide whether this is an artifact of the measuring device or a real effect due to gel-like fluctuations or segmental diffusion inside the coils. This effect is under further investigation. As shown earlier, an observed short fast decay in the echo attenuation plot cannot be interpreted as cooperative diffusion (carried out by Callaghan and Pinder[3]). Cooperative diffusion should manifest itself in a time dependence

of the experimentally determined self-diffusion coefficient which increases with decreasing diffusion time.

The concentration dependence of the measured self-diffusion coefficients is shown in *Figure 2* in a double logarithmic plot. We have shifted together all the curves by a factor N_{exp}^2 into one master curve according to the expected dependence on the molecular weight given in equations (1) and (14). The data points at the concentration $\phi_2 = 0.002$ are diffusion coefficients D_0 measured by Adam and Delsanti[18] with quasielastic light scattering (the correction for this finite concentration which is very small was taken into account). Since these diffusion coefficients are equal to the self-diffusion coefficients for infinite dilution, the self-diffusion coefficients must reach these values at very high dilutions. This is in good agreement. The dependence $D \sim N^{-2}$ is valid for all concentrations above the dilute region. This can be seen in *Figure 3* where the inverse shift factors N_{exp}^{-2} *versus* the polymerization index N are displayed. In the range from the overlap concentration up to $\phi_2 = 0.08$ the master curve nearly obeys the relation

$$D = 1.6 \times 10^{-7} \, \text{m}^2 \, \text{s}^{-1} \, \phi_2^{-1.75} N^{-2} \qquad (19)$$

In this concentration range our data are consistent with those of Leger *et al.*[2], Callaghan and Pinder[3,4] and Wesson *et al.*[5]. Above this concentration our data deviate from those of Leger *et al.*[2] and of Callaghan and Pinder[3,4] who measured higher values of D, but in the whole concentration range the agreement of our data with those of Wesson *et al.*[5] measured recently is very good.

The concentration dependences of the theoretical values for the self-diffusion coefficient $D_{th} = D_{r,th} \cdot K$ and for the blob length l_b (= tube diameter) are also shown in *Figure 2*. K is a shift factor which facilitates the comparison of the concentration dependence of experimental and theoretical values; (this will be discussed below). The agreement between theory and experiment is fairly satisfactory up to a concentration c^{xxx} (indicated by arrow 3). This shows that in this concentration region the concentration dependence of the self-diffusion coefficient is completely determined by the concentration dependence of the blob dimensions l_b and no concentration dependence of the monomeric friction coefficient occurs. The experimental values available are mainly in the crossover region from excluded-volume to ideal behaviour of the blobs between $z_g \simeq 1$ and $z_g \simeq 0.1$ (indicated by arrows
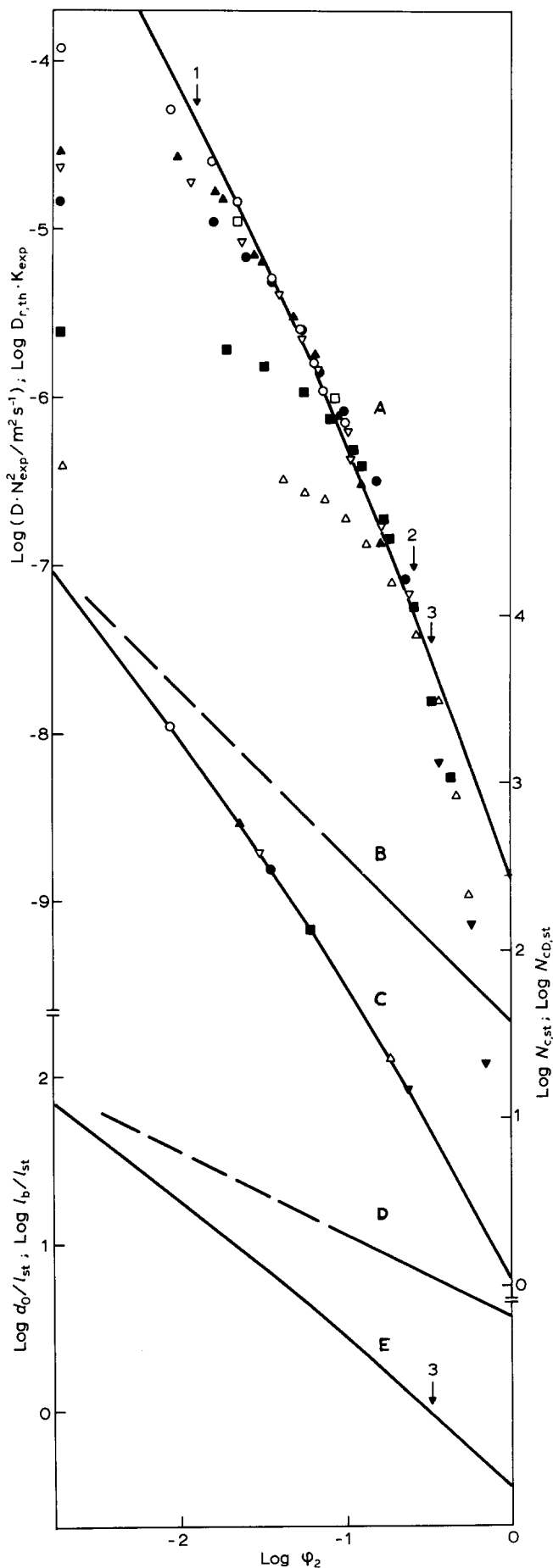

Figure 2 Log–log plot of the measured self-diffusion coefficients $D \cdot N_{exp}^2$, the calculated self-diffusion coefficients $D_{r,th} \cdot K_{exp}$ (curve A), the critical segment number of mechanical properties $N_{c,st}$ (curve B), the experimental critical segment number $N_{cD,st}$ (curve C) for self-diffusion together with the curve $10 \cdot N_{st}^x$ (where N_{st}^x is the calculated critical segment number), the reduced blob length l_b/l_{st} (curve D) and the tube diameter by entanglement effects d_0/l_{st} (curve E) *versus* the volume fraction ϕ_2 of polystyrene dissolved in benzene. l_{st} is the statistical segment length of polystyrene (20 Å). The factors N_{exp}^2 shift the measured values of the self-diffusion coefficients for each molecular weight into one master curve, the factor K_{exp} shifts the theoretically calculated curve $D_{r,th}$ onto the experimental master curve. Arrow 1 indicates c^x, (the beginning of the crossover region from excluded-volume to ideal behaviour), arrow 2 indicates c^{xx}, the beginning of ideal blobs and arrow 3 indicates c^{xxx}, the onset of entanglement effects (the blob length is equal to the statistical segment length). The molecular weights are: (○): $1.8 \, 10^6$; (□): $8.0 \, 10^5$; (▲): $4.7 \, 10^5$; (△): $3.15 \, 10^5$; (●): $2.5 \, 10^5$; (■): $1.1 \, 10^5$; (▽): $1.9 \, 10^4$; (▲): $1.2 \, 10^4$
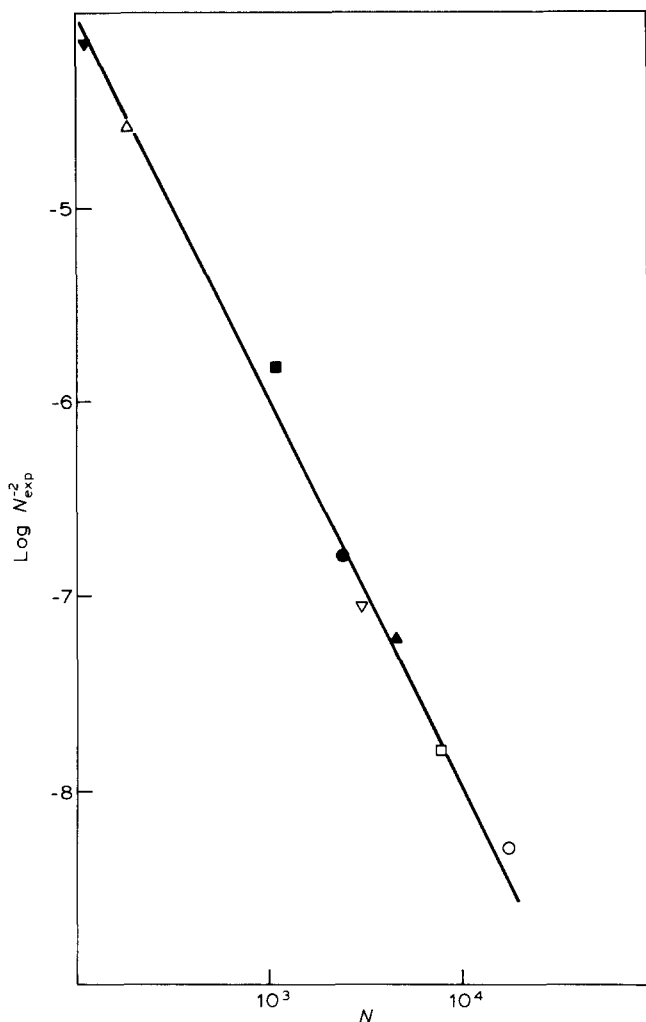
Figure 3 Log–log plot of the inverse shift factors N_{exp}^{-2} versus polymerization index N. The straight line is drawn as $N_{exp}^{-2} = N^{-2}$

1 and 2) (see also *Figure 4*). Consequently, we observe a downward curvature from the asymptotic power law $D_r \sim n_r^{(2-v)(1-3v)} \sim n_r^{-1.841}$ for $v = 0.588$ [19] in the case of large z_g to $D_r \sim n_r^{-3}$ for $v = 0.5$ in the case of screened excluded-volume effects (ideal blobs) for $c \gtrsim c^{xx}$.

The result that the onset of the reptation behaviour at a critical segment number $N_{cD,st}$ is closely related to the overlap concentration or the critical segment number N_{st}^x is in complete agreement with the conclusion that between the overlap concentration c^x (which depends on the segment number N_{st}) and c^{xxx} the self-diffusion coefficient is determined by the blob dimensions alone. The critical segment numbers $N_{cD,st}$ at which the experimental values deviate from the master curve together with the curve $N_{cD,st} = 10N_{st}^x$ are plotted in *Figure 2*. The curve agrees very well with values for $N_{cD,st}$ calculated from the hydrodynamic radii for polystyrene in benzene determined by Adam and Delsanti[18] from the diffusion coefficients D_0. A more extensive discussion of the relation between $N_{cD,st}$ and N_{st}^x will be given below. From the relationship between $N_{cD,st}$ and N_{st}^x it follows that up to c^{xxx} the self-diffusion coefficient is *not* influenced by entanglement effects. This conclusion is further supported by a comparison of the critical segment number for the onset of reptation behaviour for mechanical properties $N_{c,st}$ with $N_{cD,st}$. $N_{c,st}$ follows the scaling relation

$N_{c,st} \sim 209 \, n_r^{-1}$ which is equivalent to $\langle R^2(N_{c,st}) \rangle^{1/2} = 1.7 \, d_0$, i.e., $N_{c,st}$ is determined by the entanglement tube radius and is much greater than $N_{cD,st}$.

This can also be proved by a comparison of the blob length l_b with the values of $d_0/l_{st} = 8.51 \, n_r^{-1/2}$ characterizing the tube radius d_0 determined by entanglement effects. l_b is much smaller than d_0 calculated with an entanglement model with random flight chains[20] (the dashed part of the curve in *Figure 2* is a simple extrapolation to the excluded-volume region). The values of d_0 presented here are in complete agreement with the scaling relations, describing the plateau modulus data of a large number of polymers[21]. The concentration c^{xxx} corresponds to $l_b = l_{st}$. The mean distances between the chains at c^{xxx} are comparable with the statistical segment length l_{st}. A diffusion completely within the tubes filled by the solvent is then impossible for $c \gtrsim c^{xxx}$. New friction mechanisms and an increasing importance of entanglement effects have to be expected.

Our interpretation of the experimental data agrees with the conclusions of Wesson *et al.*[5] that the presence of entanglements is not necessary for establishing reptation as the dominant kind of motion. But we cannot agree with some further conclusions drawn in ref. 5 applying results of the Doi–Edwards theory[22]. This theory is based on random flight chains and therefore valid only for $c > c^{xx}$. Any application for $c < c^{xx}$ where excluded volume effects play an increasing role (especially for the exponents) is in contradiction to the basic assumptions of this approach. It should be noted that the very strong concentration dependence of the monomeric friction coefficient in ref. 5
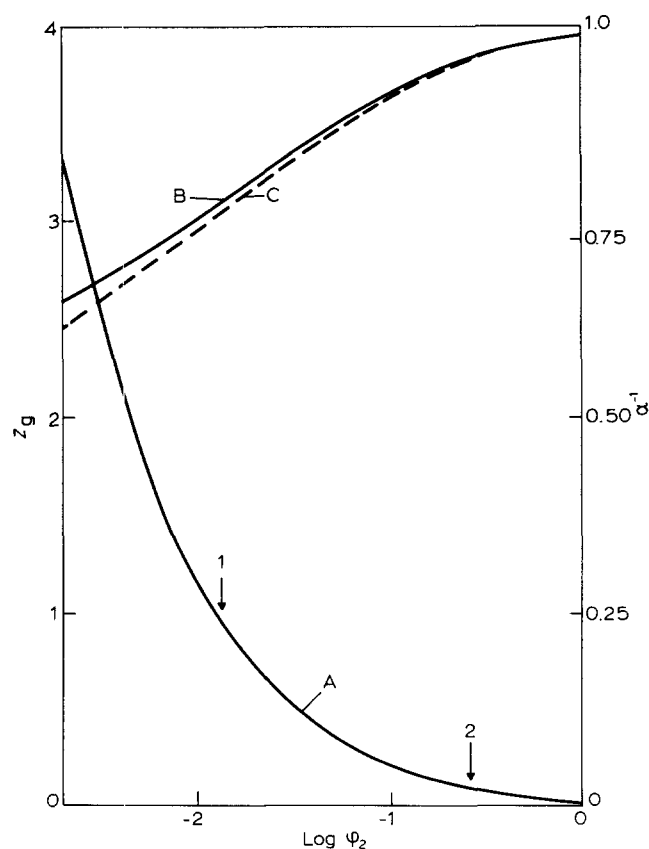

Figure 4 Excluded-volume parameter of a blob x_g (curve A) and inverse expansion factors of the hydrodynamic radius α_H^{-1} (curve B) and of the end-to-end distance α_R^{-1} of a blob *versus* log ϕ_2. (See *Figure 2* for explanation of the arrows)

is an artifact due to an unjustified application of relations valid for $c > c^{xx}$ only. Omission of the hydrodynamic interaction gives $D \sim g$, and the use of $g \sim c^{-1}$, a relation which is valid in the case where the blob dimensions are controlled by entanglement effects, results in ref. 5 in $D \sim c^{-1}$ (equation (13)). We expect that a relation similar to equation (13) in ref. 5 with a concentration dependent monomeric friction coefficient describes the self-diffusion for $c > c^{xxx}$, but such a relation must not be applied for $c < c^{xx}$.

In *Figure 4* α_H^{-1} and α_R^{-1} together with the excluded-volume characteristic z_g are plotted *versus* concentration. As already known from investigations of the intrinsic viscosity of dilute polymer solutions α_H^{-1} and α_H^{-1} differ for $z \gtrsim 1$ due to the nonuniform coil expansion and show also different asymptotic power laws. But the influence of this difference on the self-diffusion coefficient is negligible for $c^x \leqslant c \leqslant c^{xx}$. The concentration dependence of D is determined almost completely by $g^{3/2}$, the replacement $\alpha_H^{-1} \rightarrow \alpha_R^{-1}$ is not visible in the double logarithmic plot of *Figure 2*. The influence of the nonuniform expansion on the diffusion coefficient is investigated in ref. 23 on the basis of a simple phenomenological blob model. Our results for α_H^{-1} are similar but the validity of the non-monotonic behaviour in ref. 23 must be doubted. It seems to be caused by the artificial sharp transition from ideal to excluded-volume behaviour of the blobs in the model used.

In the preceding discussion we have focussed our attention to the concentration dependence of D alone. Using for η_0 the viscosity of the pure solvent we get a theoretical value of $K = (kT/\eta_0 l_{st})(N/N_{st})^2 = 2.0 \times 10^{-7}$ m^2 s^{-1} and an experimental value of $K_{exp} = 2.2 \times 10^{-6}$ mol^2 s^{-1}, i.e., the calculated values of $D_{r,th}$ are too small (by a factor of about 10) and we have to look for an explanation of this difference. Equation (18) shows that D_{th} is determined mainly by the number of segments in the blob, which is estimated very roughly by equation (15). Further, we have to take into account that any correlation between the motion of the blobs will decrease the solvent–polymer friction and lead to apparently higher values of g. It may be of interest to note that the introduction of a factor $f^3 = 0.6$ in the denominator of equation (15) (which implies that only a part of the blob extension is effective) will further improve the agreement between theory and experiment in the region of $\phi_2 \approx 0.1$ and reduce the difference to a factor of 2. In addition we then get $N_{cD,st} \simeq 3 N_{st}^x$ (instead of $N_{cD,st} \simeq 10 N_{st}^x$) or $\langle R^2 \rangle_{cD}^{1/2} \simeq 1.7 l_b$, a relation which is identical with the relation between the critical molecular weight for mechanical properties and the tube dimensions d_0, discussed above.

We may finally conclude from our interpretation of the measured self-diffusion data that between c^x and c^{xxx} the self-diffusion coefficient may be very well understood within the reptation concept of de Gennes[1]. In this concentration range the self-diffusion coefficient is determined by the blob dimensions only and the blob

dimensions are controlled by excluded-volume effects; the monomeric friction coefficient does not depend on concentration. The latter result is supported by n.m.r. relaxation investigations which show that the correlation times of segmental motion of polystyrene in solution do not significantly vary up to a concentration of about 30%[24], but at a concentration of about 40% polymer–polymer interaction becomes visible[25]. The remaining quantitative differences between theory and experiment must be related to the assumption of an uncorrelated motion of isolated blobs and to the simple scaling approach for the determination of the blob dimensions. Our results show that obviously entanglement effects are not equally efficient for different dynamic properties. We may further conclude that l_b and d_0 must not be set equal as is frequently done in qualitative investigations (see for example ref. 26).

ACKNOWLEDGEMENTS

REFERENCES

1 de Gennes, P. G. in 'Scaling Concepts in Polymer Physics', Cornell Univ. Press, Ithaca, 1979
2 Leger, L., Hervet, H. and Rondeles, F. *Macromolecules* 1981, **14**, 1732
3 Callaghan, P. T. and Pinder, D. N. *Macromolecules* 1980, **13**, 1085
4 Callaghan, P. T. and Pinder, D. N. *Macromolecules* 1981, **14**, 1334
5 Wesson, J. A., Noh, I., Kitano, T. and Yu, H. *Macromolecules* 1984, **17**, 782
6 Amis, E. J., Janmey, P. A., Ferry, J. D. and Yu, H. *Polym. Bull.* 1981, **6**, 13
7 Amis, E. J. and Han, C. J. *Polymer* 1982, **23**, 1403
8 Brown, W., Johnsen, R. M. and Stilbs, P. *Polym. Bull.* 1983, **9**, 305
9 Stejskal, E. O. *J. Chem. Phys.* 1965, **43**, 3597
10 de Gennes, P. G. *J. Chem. Phys.* 1980, **72**, 4756
11 Miyaki, J. and Fujita, H. *Macromolecules* 1981, **14**, 742
12 Straube, E. and Oeltze, K. *Acta Polym.* 1979, **30**, 623
13 Berger, H. R. and Straube, E. *Acta Polym.* 1982, **33**, 291
14 Berger, H. R. and Straube, E. submitted to *Polymer*
15 Tanner, J. E. *J. Chem. Phys.* 1970, **52**, 2523
16 Noolandi, J. and Bernard, D. A. *Macromolecules* 1983, **16**, 548
17 von Meerwall, E. D. *J. Magn. Reson.* 1982, **50**, 409
18 Adam, M. and Delsanti, M. *J. Phys. (Paris)* 1976, **37**, 1045
19 Le Guillou, J. C. and Zinn-Justin, J. *Phys. Rev. Lett.* 1977, **39**, 95
20 Heinrich, G. and Straube, E. *Acta Polym.* 1983, **34**, 589
21 Graessley, W. W. and Edwards, S. F. *Polymer* 1981, **22**, 1329
22 Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans. 2* 1978, **74**, 1789, 1802, 1818
23 Daoud, M. and Jannink, G. *J. Phys. Lett.* 1980, **41**, L-217
24 Heatley, F. and Begum, A. *Polymer* 1976, **17**, 399
25 Geschke, D., Kurze, W. and Brückner, H. *Faserforsch. Textiltech. Z. Polym.* 1978, **29**, 148
26 Brochard, F. *J. Phys. (Paris)* 1983, **44**, 39