On the generalized concentration and molecular mass dependencies of macromolecular self-diffusion in polymer solutions

V. D. Skirda*, V. I. Sundukov, A. I. Maklakov, O. E. Zgadzai, I. R. Gafurov and G. I. Vasiljev
Department of Physics, Kazan State University, Kazan, USSR

(*Received 23 July 1987; revised 15 January 1988; accepted 15 January 1988*)

Self-diffusion experimental data obtained with the n.m.r. pulsed gradient spin–echo method in polyethylene oxide (PEO), polystyrene (PS), dextran, gelatine, cellulose triacetate (CT), poly(dimethyl siloxane) (PDMS) solutions and melts in a wide range of solvents, with molecular mass (M) and concentration (ϕ), were analysed to show the existence of common dependencies for $D_s(M)$ and $D_s(\phi)$. The general law for $D_s(\phi)$ is expressed as $f(\phi/\hat{\phi})=D_s(\phi)/L(\phi)D_s(0)$ and is correct for the solvent quality ranging from θ to 'good'. The existence of the generalized $f(\phi/\hat{\phi})$ was examined for the 17 different polymer–solvent systems. With the use of the generalized function, where $D_s(0)=\lim\limits_{\phi\to 0} D_s/\hat{\phi}$, $D_s(0)\sim M^{-\beta}$, $\hat{\phi}\sim M^{-\frac{2-\beta}{3}}$, nearly 100 $D_s(\phi)$ dependencies were described. The renormalization function $L(\phi)$ accounts for the local dynamic properties of the concentration dependence.

(Keywords: self-diffusion; generalized function; critical molecular mass; solvent quality)

INTRODUCTION

One of the factors which led to the growth of experimental research in macromolecular self-diffusion in polymer systems was the development of scaling concepts and reptation theory[1,2] of the mechanisms of motion of polymer chains. Such problems as the concentration and molecular mass dependencies of the self-diffusion coefficient, D_s, of the polymer chains remain unsolved in spite of the large quantity of the experimental data collected. For instance, the concentration dependence of D_s is usually discussed only in terms of prediction on the basis of asymptotical scaling laws. In addition, experimental data are usually obtained for a single polymer system over a limited range of concentration and are very often contradictory. Typically, the dependence of D_s on molecular mass (M) shows an absence of any anomalies in the region of the so-called critical entanglement molecular weight (M_c) in most studies[3-5], and the coupling with concentration dependence of D_s is not clarified.

The purpose of the present article is an attempt to find the most common laws for the dependence of $D_s(\phi)$ and $D_s(M)$ on the basis of the analysis of experimental data obtained in different polymer solutions over a wide range of volume concentration (ϕ) and molecular mass, and in a large number of solvents. The main assumption made is that the $D_s(\phi)$ dependence can be described by the universal function $f(\phi/\hat{\phi})$ of the parameter $\phi/\hat{\phi}$, where $\hat{\phi}$ is a critical concentration, depending on polymer molecular mass[6,7]. The pulsed gradient spin-echo method[8-12] was used to measure macromolecular self-diffusion of PS (Pressure Chemical standard) with $M_n=2\times10^3$–7×10^6 ($M_w/M_n\leqslant1.1$), in benzene (303–353 K), chloroform and cyclohexane (313–333 K), CCl_4 (303–333 K) and dibutylphthalate (313–373 K) solutions; PEO (Fluka-Buchs), with $M_n=2\times10^3$–4×10^4 ($M_w/M_n\lesssim1.1$) and $M_n=3\times10^6$ ($M_w/M_n\sim3$) from Union Carbide in dioxane, acetonitrile, benzene (333–363 K) and dibutylphthalate (373 K) solutions; PDMS fractions with $M_n=1.5\times10^4$–7.3×10^5 ($M_w/M_n\leqslant1.5$) in methylethylketone and toluene (313 K) solutions; dextran (Pharmacia) samples with $M_n=6\times10^3$–2×10^5 ($M_w/M_n\leqslant2$) in dimethylsulphoxide, formamide and water (303–363 K); a gelatine (Russelot) sample with $M_n=9\times10^4$ ($M_w/M_n\sim2.2$) in water (313–333 K) and also CT fractions with $M_n=4.8\times10^4$–1.2×10^5 ($M_w/M_n\sim2.5$) in benzyl alcohol (393–433 K). The maximum concentration varied in the range 3×10^{-3}–1 in PEO and PDMS solutions, 3×10^{-3}–8×10^{-1} in PS solutions, and 3×10^{-3}–4×10^{-1} in solutions of dextran, gelatine and CT.

The range of accessible values of ϕ_s depends on the sensitivity of the n.m.r. apparatus, n.m.r. relaxation properties of macromolecules in solution and also on the low limit (10^{-14}–$10^{-15}\,m^2\,s^{-1}$) of the measurable self-diffusion coefficient.

The polymers studied possess different physicochemical properties, for example, PEO is a crystallizable polymer, PEO and PDMS have their glass transition temperatures much lower, and PS, dextran, gelatine and CT have much higher glass transition temperatures than that measured. The last three polymers are natural products, and dextran is a branched polymer having, on average, one branch every 25–30 units.

The investigations were conducted with the n.m.r. apparatus operating at the ^1H resonance frequency of

---

* To whom correspondence should be addressed

0032-3861/88/071294–07$03.00

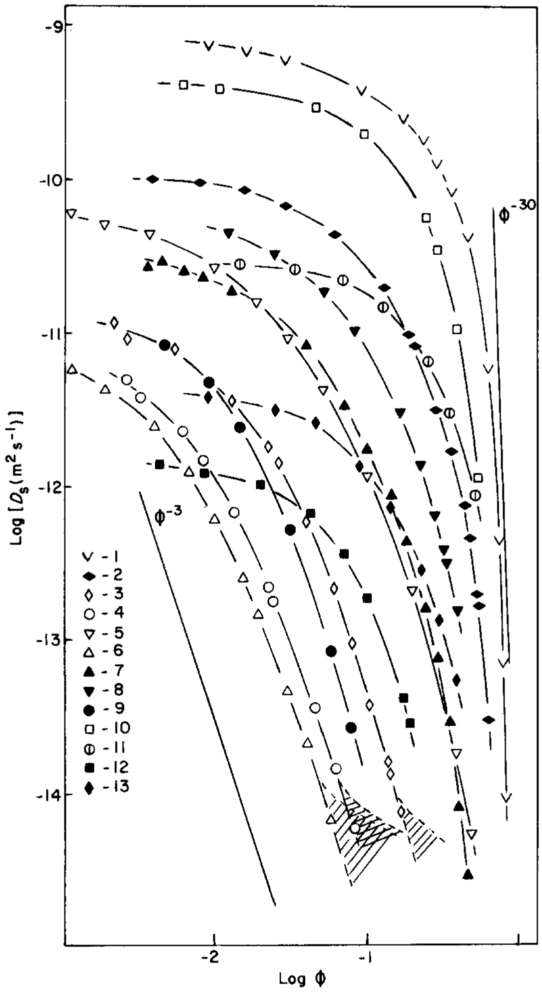

Figure 1 Log D_S *versus* log ϕ dependencies of polystyrene macromolecular self-diffusion in solutions with chloroform (1–4), benzene (5, 6), CCl_4 (7, 8), cyclohexane (9, 10) and dibutylphthalate (11, 13) where $M_n=2\times10^3$ (1, 10, 11), 5×10^4 (2, 13), 7×10^4 (8), 2×10^5 (12), 2.5×10^5 (5), 2×10^6 (3, 9) and 7×10^6 (4, 6). Temperatures = 303 (5–8) and 313 K (1–4, 9–13)

60 MHz and a maximum pulsed gradient value of 50 T1 m^{-1} (refs. 7 and 9), the steady gradient being $<10^{-2}$ T1 m^{-1}. The form of the diffusion decay of the spin-echo amplitude, $A(g^2)$, of the polymer protons in all systems deviated from simple exponential behaviour, and can be described by the following:

$$A(g^2)=\sum_i p_i \exp(-\gamma^2 g^2 \delta^2 t_d D_{si}) \qquad (1)$$

where p_i is the fraction of protons in the self-diffusion component with the average D_{si} coefficient, γ is the proton gyromagnetic ratio, g and δ are the amplitude and duration of the gradient pulses, respectively, and t_d is the diffusion time.

The average self-diffusion coefficient $D_s=\sum_i p_i D_{si}$, which is obtained from the initial slope of the diffusion decay $A(g^2)$, has been used to characterize the translational mobility of the macromolecules. This coefficient corresponds to the number-average molecular weight of the polymer sample[7,13]. The δ value varied from 3×10^{-5} to 2×10^{-3} s, depending on the properties of the system. The maximum diffusion time (10^{-2}–5 s) was reached for PEO and PDMS solutions, while in the others t_d changed from 10^{-2} to 5×10^{-1} s. In most studies of the time dependence of $A(g^2)$,D_s has been shown to be independent of t_d. Analysis of the shape of $A(g^2)$, however, revealed a dependence on t_d[7,10–12]. Only in a few cases was a time dependence of the initial slope observed.

RESULTS AND DISCUSSION

The typical experimental curves for a number of the systems studied are shown in *Figures 1–3*. The hatched regions in *Figures 1–3* show the $D_s(\phi)$ regions, where dependence of D_s on t_d has been observed. This type of behaviour took place only for sufficiently concentrated solutions of high molecular weight polymers, especially flexible PEO and PDMS, and can be attributed to the failure of the inequality $\langle r^2\rangle \gg R_F^2$ for such systems, where $\langle r^2\rangle$ is the average displacement of protons and R_F is the Flory radius of the polymer coil. The D_s dependence on t_d is of special interest[5] and preliminary results have been published[14]. In the present paper we discuss only the diffusion of the macromolecular centre of mass, i.e. when $D_s \neq f(t_d)$ and $\langle r^2\rangle \gg R_F^2$.

Concentration dependence

From the examination of *Figures 1–3*, it is seen that the log D_s vs. (log ϕ) plots reveal gradual growth of the slope with ϕ. If we approximate the final parts of the plots with the use of the $D_s(\phi)\sim\phi^{-\alpha}$ dependence, then the maximum slope α reached is ~ 10 for PEO and PDMS solutions; in

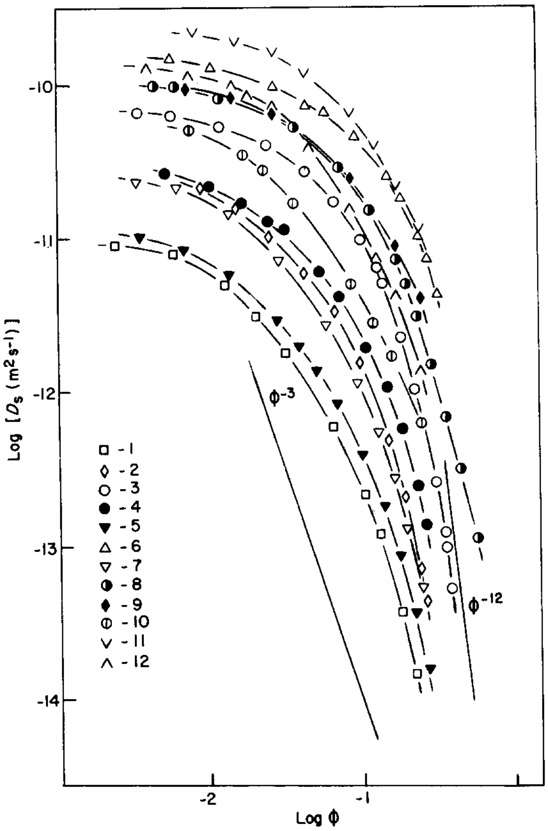

Figure 2 Concentration dependence of dextran (1–7), gelatine (8) and cellulose triacetate (9–12) macromolecular self-diffusion in dimethylsulphoxide (1–3), formamide (4, 5), water (6–8) and benzyl alcohol (9–12) solutions with $M_n=5.2\times10^3$ (3, 6), 2.7×10^4 (4), 4.4×10^4 (2), 4.8×10^4 (9, 11), 9×10^4 (8), 1.2×10^5 (10, 12) and 1.9×10^5 (1, 7). Temperature = 303 (1–7), 333 (8), 393 (9, 10) and 433 K (11, 12)

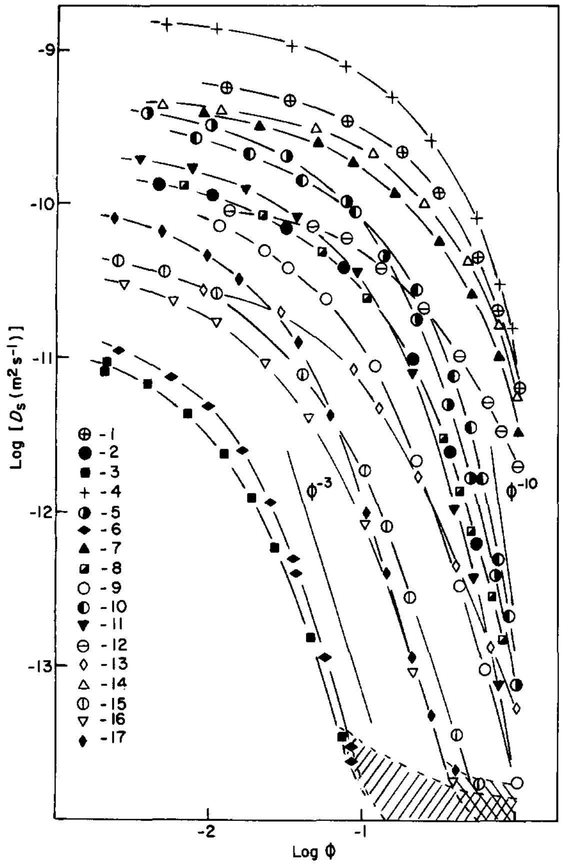

Figure 3 Log D_S *versus* log ϕ dependencies of macromolecular self-diffusion of polyethyleneoxide (1–13) and poly(dimethylsiloxane) (14–17) in chloroform (1–3), acetonitrile (4–6), dioxane (7–9), benzene (10, 11), dibutylphthalate, (12, 13), toluene (14–16) and methylethylketone (17) solutions with $M_n = 2\times10^3$ (1, 4), 3×10^3 (7), 6×10^3 (12), 1.5×10^4 (14), 2×10^4 (2, 5, 8, 10), 4×10^4 (9, 11, 13), 5.3×10^5 (15), 7.3×10^5 (16, 17) and 3×10^6 (3, 6). Temperature = 313 (14–17), 333 (1–11) and 373 K (12, 13)

dextran solutions $\alpha\sim12$ and for PS solutions is as high as ~30. Such high α values cannot follow from theoretical consideration, according to which the highest value of α equals 3 for θ-conditions[1,2]. It follows, from our early papers[6,7], and also other studies[15–17], that in analysing experimental results, it is necessary to account for local friction dependence on ϕ. The direct theoretical analysis of such a correction is rather difficult, which is why a semiempirical procedure is always used:

$$D_s'(\phi) = D_s(\phi)/L(\phi) \tag{2}$$

which is based on the dimensionless normalization function obtained from independent measurements. The question of which properties to use for $L(\phi)$ is somewhat complex, the only demand is that it must be independent of M.

Successful attempts to analyse $D_s'(\phi)$ dependencies instead of the initial experimental data have been made in references 15–17. It was assumed for $L(\phi)$ that

$$L(\phi) = \frac{D_{s1}(\phi)}{D_{s1}(0)} \tag{3}$$

where $D_{s1}(\phi)$ and $D_{s1}(0)$ are the solvent self-diffusion coefficients in solution and pure solvent, respectively. Such a procedure has been shown to be justifiable only for a limited concentration interval, and moreover, there exists a problem of the difference in the temperature dependence of polymer *versus* solvent self-diffusion. Evidently, more reliable results can be obtained when using in equation (2) the correlation time for local motion of a polymer chain[6,7] according to the expression:

$$L(\phi) = \frac{\tau_c(0)}{\tau_c(\phi)} \tag{4}$$

where $\tau_c(0) = \lim\limits_{\phi\to0} \tau_c(\phi)$.

The $\tau_c(\phi)$ dependence is obtained from independent measurements of the nuclear magnetic relaxation times, T_1 and T_2, of the polymer chain protons. In most cases a simple relation $T_1, T_2 \sim \tau_c^{-1}$ have been found to be correct for all of the systems studied. Experimental plots of $L(\phi)$ for all the polymer systems studied are given in *Figure 4*. It is possible to find a close connection between $L(\phi)$ and $D_s(\phi)$ dependencies when comparing similar plots of *Figure 4* and *Figures 1–3*.

With the use of *Figure 4*, we have normalized initial $D_s(\phi)$ data according to equation (2) to obtain $D_s'(\phi)$ plots. They had a similar form, this fact became the basis as in

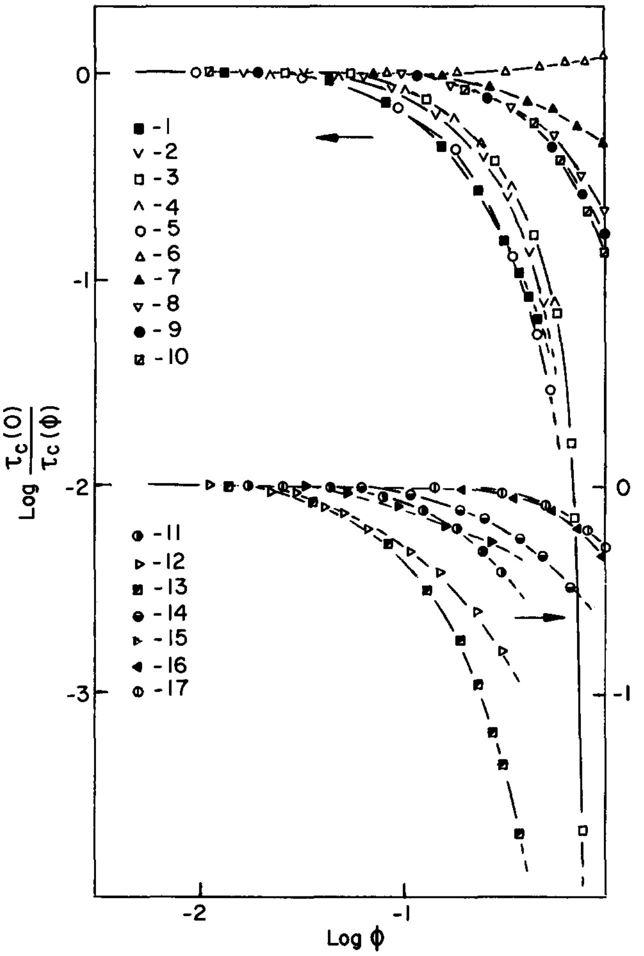

Figure 4 Concentration dependence of $\tau_c(0)/\tau_c(\phi)$ for polystyrene (1–5), polyethyleneoxide (6–10), dextran (11–13), gelatine (14), cellulose triacetate (15) and poly(dimethylsiloxane) (16, 17) macromolecules in solution with dibutylphthalate (1, 6), cyclohexane (2), chloroform (3, 8), benzene (4, 9), CCl_4 (5), acetonitrile (10), water (11, 14), formamide (12), dimethylsulphoxide (13), benzyl alcohol (15), methylethylketone (16) and toluene (17). Temperature = 303 (4, 5, 11–13), 313 (1–3, 16, 17), 333 (7–12, 14), 373 (6) and 433 K (15)

other studies[6,7], for an attempt to describe the $D_s'(\phi)$ dependence by a general function assuming the relation

$$\frac{D_s'(\phi)}{D_s(0)} = \mathrm{f}\left(\frac{\phi}{\hat{\phi}}\right) \tag{5}$$

to be correct and $D_s(0) = \lim\limits_{\phi \to 0} D_s(\phi)$.

Let us first suppose the expected form of $\mathrm{f}(\phi/\hat{\phi})$ and the behaviour of the critical concentration $\hat{\phi}(M)$. The form of $\mathrm{f}(\phi/\hat{\phi})$ must obviously agree with the molecular mass dependencies in dilute solutions and melts. With most experimental data[3-5,7,11] and the reptation model of motion[1,2] in melts at sufficiently high M, it is expected that

$$D_s(M) \sim M^{-2} \tag{6}$$

In concentrated solutions ($\phi \sim 1$) the same $D_s(M)$ dependence serves, as in melts. The $D_s(0)$ *versus* M behaviour is determined by the size of R_F in the polymer chain:

$$D_s(0) \sim R_F^{-1} \tag{7}$$

The R_F value depends on solvent quality, so that $R_F \sim M^{0.5}$ in θ-solvents and $R_F \sim M^{0.6}$ in good solvents. Consequently, it may be written as

$$D_s(0) \sim M^{-\beta} \tag{8}$$

where β changes from 0.5 to 0.6, depending on solvent quality. The most difficult thing to estimate is the $\hat{\phi}(M)$ dependence and to account for the effect of solvent quality on $\hat{\phi}(M)$. It is reasonable to start with θ-solutions, because excluded volume effects can be ignored. The chain radius R_F is in that case an essential parameter in defining the $\hat{\phi}(M)$ dependence. Thus, in the case of θ-solvents it is simple to relate the $\hat{\phi}(M)$ dependence with M dependence of the critical concentration of the coil overlapping $\phi^* \sim M/R_F^3$ (ref. 1). Taking into account the $R_F(M)$ dependence, we obtain for the θ-solvent $\hat{\phi}(M) \sim M^{-0.5}$. Then, using equations (6) and (8) with $\beta = 0.5$ and assuming asymptotic behaviour of $\mathrm{f}(\phi/\hat{\phi})$ of the form $(\phi/\hat{\phi})^{-\alpha}$, it is easy to find in the range of high concentration

$$\mathrm{f}\left(\frac{\phi}{\hat{\phi}}\right) \sim \left(\frac{\phi}{\hat{\phi}}\right)^{-3} \tag{9}$$

The form of $\mathrm{f}(\phi/\hat{\phi})$ in the region $\phi \to 0$ follows from equation (5). Actually, when $\phi \to 0$, then $D_s(\phi) \equiv D_s(0)$ and

$$\mathrm{f}\left(\frac{\phi}{\hat{\phi}}\right) = \left(\frac{\phi}{\hat{\phi}}\right)^{0} \tag{10}$$

It has been pointed out in good solvents, that the $\hat{\phi}(M)$ dependence is complicated, because it is difficult to assume the influence of solvent quality on $\hat{\phi}(M)$ beforehand. Now it is, however, possible to find the $\hat{\phi}(M)$ behaviour, proceeding from the independence of the form of $\mathrm{f}(\phi/\hat{\phi})$ on solvent quality. Considering equations (6), (8) and (9) it is easy to show that the following common relation is expected:

$$\hat{\phi}(M) \sim M^{-\gamma} \tag{11}$$

where

$$\gamma = \frac{2-\beta}{3}$$

The typical experimental results are presented in *Figure 5* in the form of plots of $\log[D_s'(\phi)/D_s(0)]$ + constant *versus* $\log(\phi/\hat{\phi})$ + constant for all the polymer–solvent systems studied. For convenience, the curves are shifted arbitrarily along coordinate axes. When obtaining the plots in *Figure 5*, we used relations (8) and (11) with the β values given in the captions of *Figure 5*, the only

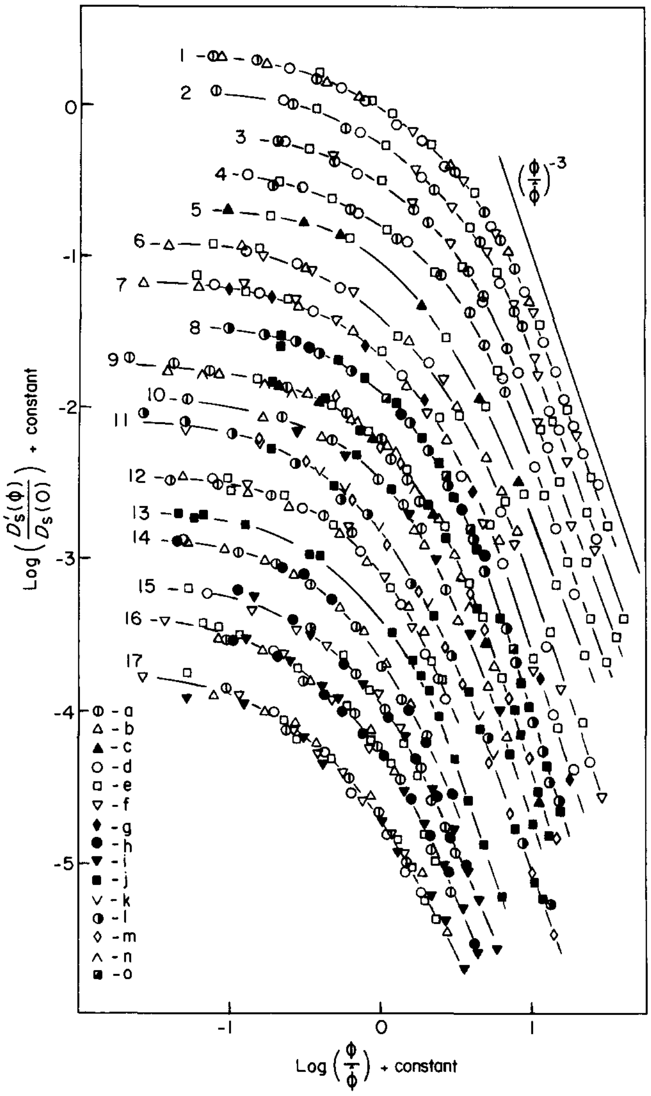

Figure 5 $\mathrm{Log}[D_s'(\phi)/D_s(0)]$ dependence on $\log(\phi/\hat{\phi})$ in: polyethylene-oxide (1–5) with $M_n = 2\times10^3$ (a), 3×10^3 (b), 6×10^3 (c), 2×10^4 (d), 4×10^4 (e) and 3×10^6 (f); poly(dimethylsiloxane) (6, 7) with $M_n = 1.5\times10^4$ (b), 1.9×10^5 (e), 5.3×10^5 (d) and 7.3×10^5 (f); polystyrene (8–12) with $M_n = 2\times10^3$ (a), 1.9×10^4 (n), 3.7×10^4 (k), 5×10^4 (b), 7×10^4 (h), 1.1×10^5 (e), 1.5×10^5 (i), 2.5×10^5 (l) 5×10^5 (o), 5.4×10^5 (c), 2×10^6 (j) and 7×10^6 (m); gelatine (13) with $M_n = 9\times10^4$ (j); cellulose triacetate (14) with $M_n = 4.8\times10^4$ (b), 6.9×10^4 (a) and 1.4×10^5 (h) and dextran (15–17) with $M_n = 5.2\times10^3$ (f), 1×10^4 (d), 2.7×10^4 (e), 4.4×10^4 (a), 7.6×10^4 (b), 1.1×10^5 (h) and 1.9×10^5 (i) in dioxane (1), acetonitrile (2), chloroform (3, 9), benzene (4, 11), dibutylphthalate (5, 12), methylethylketone (6), toluene (7), CCl_4 (8), cyclohexane (10), water (13, 15), formamide (16) and dimethylsulphoxide (17). Temperature = 303 (8, 11, 15–17), 313 (6, 7, 9–11), 333 (1–4, 13), 373 (5), and 433 K (14). The plots are obtained with the use of equations (8) and (11), where $\beta \pm 0.01 = 0.5$ (4, 6, 8, 10, 14–17), 0.51 (1), 0.54 (3), 0.55 (11), 0.56 (12), 0.57 (2, 5), 0.58 (9) and 0.6 (7)

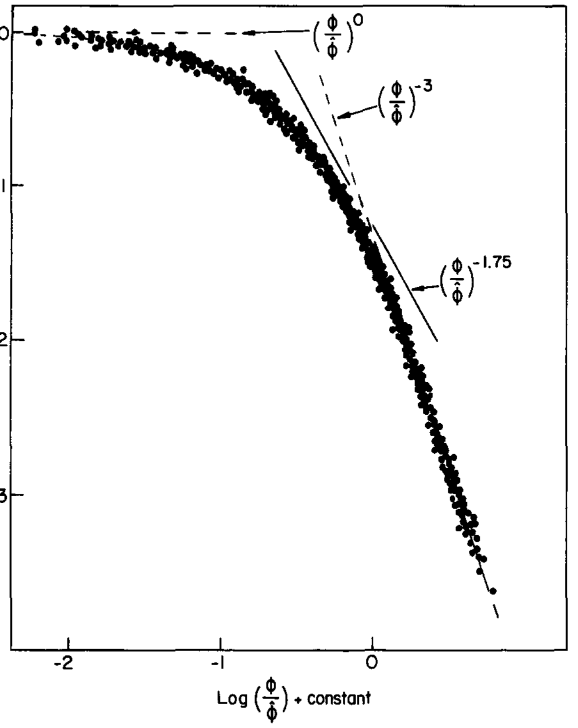

Figure 6 Generalized concentration dependence $D'_s(\phi)/D_s(0) = f(\phi/\hat{\phi})$

exception was the system of gelatine–water, for which a single molecular mass was studied.

The value of the parameter β was chosen primarily in order to superimpose the plots $D'_s(\phi)$ in the above-mentioned coordinates better. The common way of obtaining β is to plot experimental $D_s(0)$ *versus* M. The necessity of extrapolation of $D_s(\phi)$ to $\phi \rightarrow 0$, however, reduces the precision of such a procedure, especially for high M values.

Figure 5 demonstrates that for every polymer–solvent system studied the $D'_s(\phi)$ dependencies can be superimposed and consequently described by a unified relation. The form of these curves is similar, as illustrated in *Figure 6* where all the plots from *Figure 5* have been superimposed to give a common curve when shifted along the $\log(\phi/\hat{\phi})$ axis (the $\hat{\phi}$ absolute value is not defined). This common curve reflects the form of the generalized function $f(\phi/\hat{\phi})$, the existence of which was assumed for equation (5). This assumption is confirmed experimentally in *Figure 6* for the 17 different polymer–solvent systems investigated, including nearly 100 initial concentration plots of $D_s(\phi)$ with various molecular masses and temperatures. The asymptotes predicted in equations (9) and (10) are clearly observed. Examination of β values used in the superposition procedure of the $D'_s(\phi)$ curves in *Figure 5* (see caption of *Figure 5*) makes it possible to affirm that the assumptions made and the form of $f(\phi/\hat{\phi})$ are invariant to solvent quality, at any rate in the range from θ to 'good'. When obtaining $D_s(\phi)$ dependencies, a wide interval of molecular masses was covered (10^3–10^7), with polydispersity M_w/M_n varying from 1.06 to 3. The measurements were conducted below and above the glass transition temperature of the pure polymer, and also the dextran molecules were rather branched. It is worth noting that the difference in solvent viscosity (e.g. chloroform and dibutylphthalate) attained several orders of magnitude. Thus, all the facts show a high degree of agreement for the suggested procedure and the parameters of the systems. From the experimental results obtained, it follows that equation (11) reflects correctly the $\hat{\phi}(M)$ dependence in θ and good solvents. The existence of the function $f(\phi/\hat{\phi})$, different from that proposed in reference 18, must obviously be a consequence of the most common laws in translational mobility of the polymer molecules in solution. At the same time, peculiar features of solutions, that depend on the polymer–solvent interaction and temperature, are accounted for with the use of relations (2) and (4).

The practical importance of the results is the possibility of using the $f(\phi/\hat{\phi})$ dependence (*Figure 6*) to predict the value of $D'_s(\phi)$, and with equation (2) the value of $D_s(\phi)$, when direct measurements are impossible. To make it possible, it is necessary to find the form of $L(\phi)$ beforehand. The departure of the $D'_s(\phi)$ dependence from equation (5) may indicate the existence of specific interactions in the systems studied, that are not taken into account in equations (2) and (4). This situation was, for example, found in the systems PS–cyclohexane (PS–CH), gelatine–water and CT–benzyl alcohol at temperatures lower than 308, 300 and 383 K, respectively. In the system PS–CH[7,19] the deviations observed are caused by the phase separation of the system, while in the two other systems gelation occurs[7]. Similar results were obtained for the case of polyethylene solutions in *p*-xylene (353–373 K) and polymethacrylic acid–water solutions (303–343 K). The failure of equation (5) in these systems was also shown to be a consequence of phase separation and gelation. When gelation occurs, a loose but rather stable network is formed between macromolecules, reducing translational mobility of the macromolecule as a whole. The local mobility, however, for the main part of the polymer chain is not changed significantly, so the correlation times $\tau_c(\phi)$ in equation (4) are not sensitive to the process of gel formation. Another problem is that phase separation and gelation processes, occurring with decreasing solvent quality, depend on the polymer molecular mass. The normalization function $L(\phi)$ in our consideration (equation (2)) is, however, supposed to be independent of M.

Comparing the results obtained with the well known main principles[1,4,5,20], the existing theory is mostly operating with two critical concentrations: (1) the above-mentioned coil overlapping concentration ϕ^*, and (2) a molar mass (M) independent ϕ^{**} concentration, above which in good solvents excluded volume effects can be ignored. The detailed analysis shows that in good solvents a generalized function must not exist because of the difference in M dependence of ϕ^* and ϕ^{**}. This theoretical limitation contradicts experimental results, that show the possibility to superimpose the results for good and θ-solutions in one common dependence with only one critical concentration $\hat{\phi}$, independent of the solvent quality. The $\hat{\phi}(M)$ dependence, unlike $\phi^*(M)$ is determined only by $R_F(M)$ behaviour in θ-solvents. In general, the relation between $\hat{\phi}$ and R_F is more complex and up to now cannot be analysed theoretically. The concentration $\hat{\phi}$ may be interpreted as a certain dynamical critical concentration, defining the concentration dependence of polymer dynamical properties by the concentration ϕ.

Consequently, one of the reasons for the discrepancy of the existing theory with the experimental results is that, when describing dynamical properties of the polymer solutions, the basic parameters, such as critical concentrations, are assumed to depend completely on static (R_F) polymer properties. It appears then speculative to find regimes by experiment[4,5,16,21], where $D_s(\phi) \sim \phi^{-1.75}$. Such a dependence is predicted[1,20] in good solvents in the concentration interval $\phi^* < \phi < \phi^{**}$, and follows from the simple relation between ϕ^* and R_F. It is important to account for the concentration dependence of local dynamical properties of the polymer chain, the moment that is not treated in existing theories.

Molecular mass dependence

According to the above results, the concentration dependence of D_s can be described by the generalized function $f(\phi/\hat{\phi})$. Its form is connected with the molecular mass dependence of D_s in solutions, as well as in the melts. Let us write equation (2) in the form:

$$D_s(\phi, M) = D_s(0, M) \cdot L(\phi) f(\phi/\hat{\phi}(M)) \qquad (12)$$

Proceeding from the dependence of $D_s(0)$ on M from equation (8) and $\hat{\phi}(M)$ from equation (11) and an empirical form (*Figure 6*) of the function $f(\phi/\hat{\phi})$, it is easy to calculate the expected dependence $D_s(M)$ for any choice of ϕ. This is most easily fulfilled, if we use $(\phi/\hat{\phi})^{-\alpha}$ instead of $f(\phi/\hat{\phi})$, where $\alpha = 3$ in the range of high $(\phi/\hat{\phi})$ (equation (9)) and decreases to zero (equation (10)) monotonically with $(\phi/\hat{\phi})$. The exponent α is a characteristic of the tangents to the universal curve $f(\phi/\hat{\phi})$. If we consider in equation (12) the terms including the M dependence only, and take into account equation (8) and (11), then we arrive at:

$$D_s(\phi, M) \sim M^{-\frac{3\beta + \alpha(2-\beta)}{3}} \qquad (13)$$

Because of the $\hat{\phi}$ dependence on M, it is then possible at any $\phi \neq 0$ to find a polymer with a molecular weight, such that $\phi/\hat{\phi}$ falls in the region where $\alpha = 3$. Then, proceeding from equation (13), in the vicinity of the chosen values of M the law:

$$D_s(M) \sim M^{-2}$$

must be fulfilled. The argument $\phi/\hat{\phi}$ of the function $f(\phi/\hat{\phi})$ decreases with M. When M reaches the point where $\alpha < 3$, then in accordance with equation (13) $D_s(M)$ will also decrease, and so on up to the point when $\alpha = 0$ and $D_s(M) \sim M^{-\beta}$.

It follows from the universality of $f(\phi/\hat{\phi})$, that from equation (12) $D_s(M)$ must have the same form for any $\phi \neq 0$ (*Figure 3*). There remains only some inadequacy for the dilute solutions, where $D_s(M)$ is also dependent on the solvent quality.

We turn now to the analysis of the critical molecular mass M_{cD} which is similar to the well-known M_c from viscosity measurements, and is defined as a point where the tangents with slopes -1 and -2 intersect. Obviously, M_{cD} corresponds to some constant value from the argument of $f(\phi/\hat{\phi})$, close to the region where $f(\phi/\hat{\phi}) \sim (\phi/\hat{\phi})^{-3}$, i.e. $\phi/\hat{\phi}(M = M_{cD}) = \text{constant}$. Then, taking into account equation (11), the M_{cD} dependence on concentration can be expressed as:

$$M_{cD} \sim \phi^{-\frac{3}{2-\beta}} \qquad (14)$$

from where it follows, in particular, the low dependence of $M_{cD}(\phi)$ on solvent quality is $M_{cD} \sim \phi^{-2}$ for θ-solvents and $M_{cD} \sim \phi^{-2.13}$ for good solvents. *Figure 7* shows experimental dependencies of $D_s(M)$, obtained for all of the systems studied in the concentration interval $3 \times 10^{-3} \leqslant \phi \leqslant 1$. The value $M_{cD}(\phi)$ can be calculated from equation (14) with the corresponding values of β. The curves $D_s(M)$ were shifted along the ordinate axis until they superimposed best with the expected $D_s(M)$ dependence (solid line). It can be seen from *Figure 7* that experimental dependencies of $D_s(M)$ are in accordance with those calculated from $f(\phi/\hat{\phi})$. This fact justifies relation (14) suggested for the $M_{cD}(\phi)$. Considering other studies[22,23], it is necessary to note the absence in *Figure 7* of the region with the $D_s(M)$ dependence stronger than $D_s \sim M^{-2}$.

Despite the fact that the $D_s \sim M^{-2}$ dependence is clearly observed, it is not enough evidence in support of a reptational mechanism of motion of polymer chains in solution, because we cannot find any distinct differences in the $D_s(M)$ or the $D_s(\phi)$ behaviour between linear and branched (dextran) polymers. This conclusion is similar to that drawn by von Meerwall[5]. In the region of small values of M_n/M_{cD} ($\leqslant 0.1$) with melts, departures can be observed from the plot in *Figure 7* as a consequence of the failure of Gaussian statistics in oligomeric chains and the influence of chain ends[5].

Let us discuss the values of M_{cD} obtained from the analysis of the $D_s(M)$ dependencies at $\phi = 1$. The

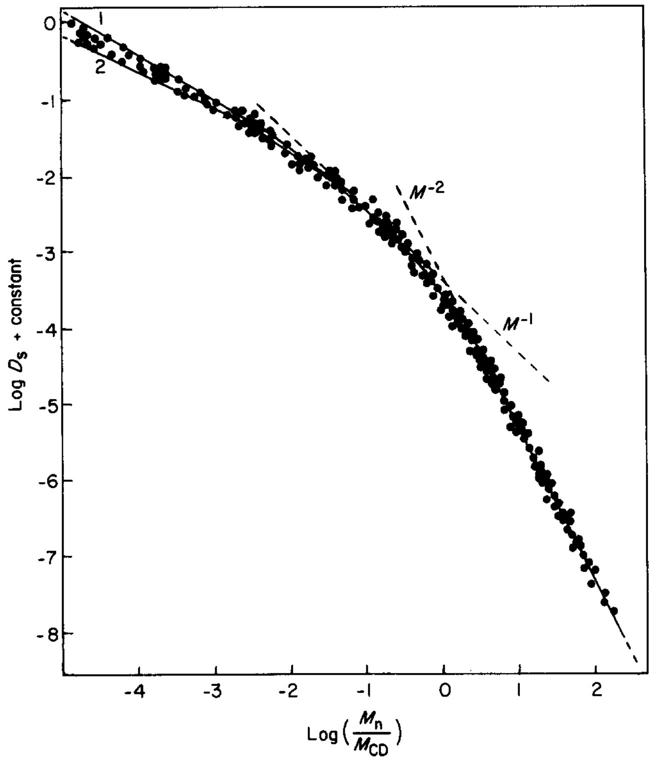

Figure 7 Generalized molecular mass dependence of the macromolecular self-diffusion, obtained with $D_s(M)$ dependencies in solutions of polyethyleneoxide and poly(dimethylsiloxane) with $\phi = 3 \times 10^{-3}$, 10^{-2}, 3×10^{-2}, 10^{-1}, 3×10^{-1}, 1, and dextran, cellulose triacetate and polystyrene solutions with $\phi = 3 \times 10^{-3}$, 10^{-2}, 3×10^{-2}, 10^{-1}, 3×10^{-1}. $M_{cD}(\phi)$ follows from equation (14) and temperatures and β values are given in the legend to *Figure 5*. The solid curves 1 and 2 were calculated according to equations (12) and (8 and 14) with $\beta = 0.6$ and 0.5, respectively, based on the form of $f(\phi/\hat{\phi})$ from *Figure 6* measurements were carried out with PEO and PDMS, and the values obtained are 2×10^3 (ref. 11) and 3×10^3, respectively. With the lack of the same data for PS and DN, we attempted to calculate M_{cD} using equation (14) with the previously estimated values of $M_{cD}(\phi)$ in solution. Doing so, we obtained for the melts of PS at $\phi = 1$, a value of $M_{cD} \sim 2 \times 10^3$ and $M_{cD} \sim 3 \times 10^3$ for DN. If we compare the M_{cD} values obtained for M_{cD} with the usual critical molecular mass M_c from viscosity measurements, it follows that M_{cD} is considerably lower than M_c[11]. Thus, for PEO, PDMS and PS, $M_c = 6 \times 10^3$, 3×10^4 and 2×10^4, respectively[24]. Such low values of M_{cD} compared with M_c seem unexpected. The difference between M_{cD} and M_c makes it possible, however, to explain most of the experimental data, where no anomalies were found in the $D_s(M)$ dependence $D_s \sim M^{-2}$ in the vicinity of $M \sim M_c$ (refs. 3–5). According to our results, the departure from the law $D_s \sim M^{-2}$ must be considered at molecular masses sufficiently lower than M_c. The difference between M_{cD} and M_c was discussed in references 7 and 11 from the point of view of the dynamical network destruction at $M < M_c$ because of mechanical stress in viscosity measurements.

It is possible, however, to find another explanation for the observed $M_{cD} < M_c$[25]. It has already been mentioned that the critical concentration $\hat{\phi}$ must be regarded as a somewhat dynamical concentration, so M_{cD} must be also considered as a dynamical molecular mass due to its close connection with $\hat{\phi}$. M_{cD} can depend, in particular, on the relation between disentanglement time and the characteristic time it takes for the macromolecule to move any typical distance, probably nearly equal to the coil diameter. In diffusion measurements this time strongly depends on D_s, which is determined in turn by the polymer M, while in viscosity measurements a similar time is set by a rotational motion. In other words, in the study of viscosity and self-diffusion, the formation of the entanglement network is in different dynamical conditions of the experiment. It is obvious that when analysing the $D_s(M)$ dependence in melts in the region of small M, it is also necessary to account for the change of the polymer free volume[5,25].

CONCLUSION

A large set of experimental data was analysed to confirm the existence of the interconnected generalized relations for $D_s(\phi)$ and $D_s(M)$ dependencies. No evidence was found for constraint release mechanisms in $D_s(M)$ dependencies. The generalized function $f(\phi/\hat{\phi})$ is observed in solutions with solvent quality changing from θ to good. The empirical concentration $\hat{\phi}$ has been found not to coincide with the usual concentration of coil overlapping ϕ^*. The critical molecular mass M_{cD} obeys the relation $M_{cD} \sim \phi^{-2}$, and in the case of polymer melts is always much lower than M_c values from viscosity measurements.

REFERENCES

1 De Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979
2 Doi, M. and Edwards, S. F. *J. Chem. Soc. Faraday Trans. 11* 1978, **74**, 1789
3 Fleischer, G. *Polym. Bull.* 1983, **9**, 152
4 Tirrell, M. *Rubber Chem. Technol.* 1984, **57**, 523
5 Von Meerwall, E. *Rubber Chem. Technol.* 1985, **58**, 527
6 Sundukov, V. I., Skirda, V. D. and Maklakov, A. I. *Polym. Bull.* 1985, **14**, 153
7 Maklakov, A. I., Skirda, V. D. and Fatkullin, N. F. 'Selfdiffusion in Polymer Solutions and Melts', Kazan University Press, Kazan, 1987
8 Tanner, J. E. *J. Chem. Phys.* 1970, **52**, 2523
9 Skirda, V. D., Sevreugin, V. A. and Sundukov, V. I. *Pribori i Technika Experimenta* 1984, **N6**, 122
10 Skirda, V. D., Sevreugin, V. A. and Maklakov, A. I. *Dokl. Akad. Nauk SSSR* 1983, **269**, 638
11 Sevreugin, V. A., Skirda, V. D. and Maklakov, A. I. *Polymer* 1986, **27**, 290
12 Maklakov, A. I., Sevreugin, V. A., Skirda, V. D. and Fatkullin, N. F. *Vysokomol. Soedin.* 1984, **A26**, 2502
13 Skirda, V. D., Ibragimov, C. I., Pimenov, G. G., Masimov, E. A. and Gadgiev, S. A. *Dokl. Akad. Nauk, Az. SSR* 1985, **N10**, 30
14 Sundukov, V. I., Skirda, V. D., Maklakov, A. I. and Doroginitzki, M. M. *Vysokomol. Soedin.* 1986, **B28**, 382
15 Budtov, V. P. *Eur. Polym. J.* 1981, **17**, 191
16 Von Meerwall, E. D., Amis, E. and Ferry, D. *Macromolecules* 1985, **18**, 260
17 Nemoto, N., Landry, M., Noh, I., Kitano, T., Wesson, J. and Yu, H. *Macromolecules* 1985, **18**, 308
18 Phillies, G. D. J. *Macromolecules* 1986, **19**, 2367
19 Maklakov, A. I., Skirda, V. D. and Serebrennikova, T. A. *Dokl. Akad. Nauk SSSR* 1986, **288**, 922
20 De Gennes, P. G. *Macromolecules* 1976, **9**, 587
21 Callaghan, P. T. and Pinder, D. N. *Macromolecules* 1980, **13**, 1085
22 Fleischer, G. *Polym. Bull.* 1984, **11**, 75
23 Fleischer, G. *Colloid Polym. Sci.* 1987, **265**, 89
24 Vinogradov, G. V. and Malkin, P. Y. 'Rheologiya Polimerov', Khimia, Moscow, 1977
25 Zgadzai, O. E., Skirda, V. D., Maklakov, A. I. and Chalykh, A. E. *Dokl. Akad. Nauk SSSR* 1987, **297**, 1407