Self-diffusion in block copolymer solutions

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Self-diffusion of poly(sulphone–ethylene oxide) copolymer macromolecules in different solvents has been investigated by pulsed field gradient nuclear magnetic resonance. The experimental response indicates a wide distribution of self-diffusion coefficients $P(D)$ for all samples studied. The distribution function $P(D)$ is shown to be represented by a logarithmic normal function and parameters characterizing its width have been obtained. The width of $P(D)$ is large at room temperature, indicating that the systems tend to gelation. The concentration dependence of the average self-diffusion coefficient $\bar{D}$ is described by the relation $\bar{D} = \varphi_2^{-\alpha}$ ($\alpha = 3.4$–3.8) in the range of polymer concentrations $\varphi_2 = 0.2$–0.6. The effect of solvent thermodynamic quality on $\bar{D}$ is considered. Anomalous concentration dependences of D observed in a number of solutions are discussed.

(Keywords: block copolymer solution; self-diffusion; non-exponential magnetization decay; long-lived clusters)

INTRODUCTION

Current knowledge of macromolecule self-diffusion in solutions is based mainly on studies of homopolymers in good solvents[1,2]. Solutions of block copolymer attract much interest but to date there have been no practical studies of macromolecule self-diffusion in these systems. Here we report an investigation of macromolecule self-diffusion in poly(sulphone–ethylene oxide) (PSEO) solutions.

EXPERIMENTAL

Three samples of unfractionated PSEO (with $M_n = 42 \times 10^3$, 46×10^3 and 44×10^3) were investigated; the molecular masses of the ethylene oxide block were 6×10^3 (PSEO-6), 3×10^3 (PSEO-3) and 1×10^3 (PSEO-1), respectively, while that of the sulphone block in all cases was 4.7×10^3. The structural formula of PSEO is given in ref. 3. Samples of poly(sulphone) (PSN) and poly(ethylene oxide) (PEO) with the same $M_n \approx 40 \times 10^3$ were also studied. The polydispersity of samples was $M_w/M_n \sim 2$, excluding PEO, for which $M_w/M_n \sim 1.2$. The solvents used were chemically pure chloroform, benzene and nitromethane; the best one was chloroform and the poorest one was nitromethane. All solutions for the experiments were prepared gravimetrically, and the polymers and solvents were weighed directly in 7 mm thin-walled glass tubes.

The self-diffusion coefficients were measured by pulsed field gradient nuclear magnetic resonance (n.m.r.) with a home-built spectrometer operating at 60 MHz on hydrogen nuclei. The method of stimulated echo[4] was used. Diffusion spin–echo decays were measured as a function of the pulsed magnetic gradient, g. The largest value of g was equal to $50\,\mathrm{T\,m^{-1}}$. The technique of obtaining such pulse gradients has been described in detail previously[5,6]. The constant magnetic field gradient did not exceed $10^{-3}\,\mathrm{T\,m^{-1}}$. Gradient pulses of duration δ from 10^{-5} to 10^{-3} s were separated by a delay Δ. The diffusion time $t_d = \Delta - \delta/3$ varied in the range 0.1–0.6 s. The radiofrequency pulse spacing was usually 2.5×10^{-3} s. It is easily shown that the coil dimensions of the studied polymers in solution are essentially smaller than the diffusion distance $(2t_dD)^{0.5}$, so that bounded segmental motions about the centres of mass of the polymer chains cannot dominate the measured diffusion coefficient[7]. All the measurements were conducted at 303 K.

RESULTS AND DISCUSSION

The typical diffusion magnetization decays $A(g^2)$ for macromolecules of PSEO-6 are shown in *Figure 1*. The part of the signal caused by solvent molecules was easily separated owing to the significant difference between the self-diffusion coefficients (SDC) of the macromolecules and that of the solvent molecules. The decays $A(g^2)$ are essentially non-exponential, the shape of the curves depending on polymer and solvent type. When the copolymer solvent is the poorest one, i.e. nitromethane (curve A), the deviation from exponential behaviour is most appreciable and it is less when the solvent is better, i.e. chloroform (curve B). Non-exponential decays $A(g^2)$ are observed in PSN (curve C) and PEO (curve D) solutions as well, but the degree of non-exponentiality is considerably smaller than in copolymer solution. In the general case, the diffusion decays can be described by:

$$A(g^2) = \int_0^\infty P(D) \exp(-\gamma^2 \delta^2 g^2 D t_d)\, \mathrm{d}D \qquad (1)$$

where γ is the proton gyromagnetic ratio and $P(D)$ is the SDC's distribution function ($\int_0^\infty P(D)\,\mathrm{d}D = 1$).

Let us consider the problem of analysing the non-exponential diffusion decays (1). At the present time, accurate methods of obtaining the type of $P(D)$ from experimental curves $A(g^2)$ have not been developed. Usually, the diffusion decays (1) are represented as a sum of exponents, under the assumption that $P(D)$ is a discrete

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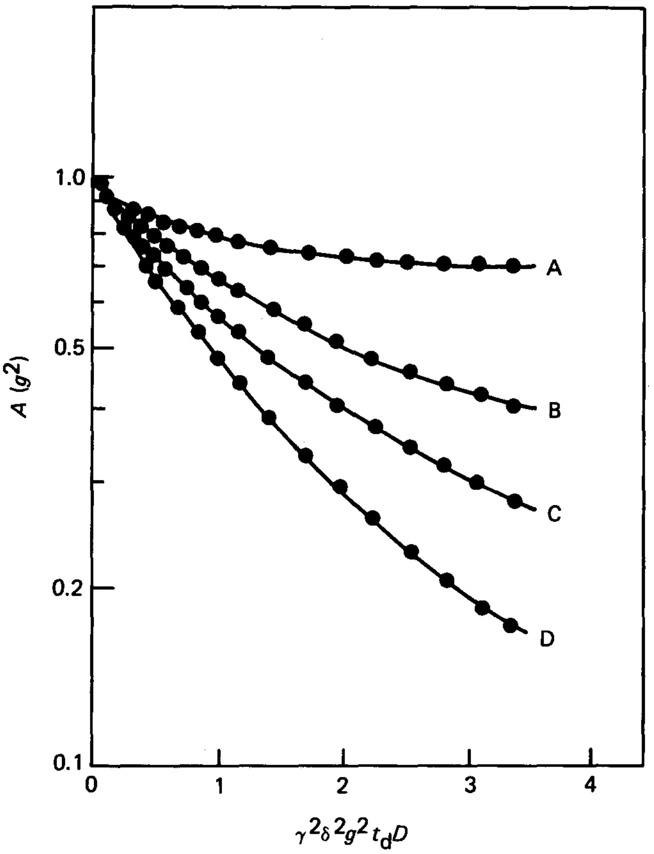

Figure 1 Typical diffusion magnetization decays in studied systems: curve A, PSEO-6 in nitromethane; curve B, PSEO-6 in chloroform; curve C, PSN in chloroform; curve D, PEO in chloroform. Polymer volume concentration φ_2 equals 0.35 volume fractions

spectrum. Expansion of the experimental curves $A(g^2)$ into exponential components was undertaken by us with a computer using standard methods[8]. However, we failed to obtain an unambiguous spectrum $P(D)$ using different methods of expansion. This is caused mainly by experimental errors in measuring of amplitudes $A(g^2)$ and by the relatively small (1–2 orders) dynamic range of the diffusion decay. Thus we attempted to find characteristics of the SDC spectrum that would be independent of the way in which $A(g^2)$ was expanded into exponents. Such a characteristic could be the average SDC $\bar{D}$ for all macromolecules:

$$\bar{D}=\int_0^\infty DP(D)\,\mathrm{d}D \tag{2}$$

and also the average SDC for some arbitrarily chosen part of the macromolecules (if the corresponding part of the signal is not less than ~20% of the whole signal).

Let us define the average SDC for that half ($\bar{D}_{0.5}$) and quarter ($\bar{D}_{0.25}$) of the macromolecules with the lowest mobility, namely:

$$\bar{D}_{0.5}=\left(\int_0^{D^*} DP(D)\,\mathrm{d}D\right)\Big/\left(\int_0^{D^*} P(D)\,\mathrm{d}D\right) \tag{2a}$$

$$\bar{D}_{0.25}=\left(\int_0^{D^{**}} DP(D)\,\mathrm{d}D\right)\Big/\left(\int_0^{D^{**}} P(D)\,\mathrm{d}D\right) \tag{2b}$$

where D^* and D^{**} are chosen from the conditions:

$$\int_0^{D^*} P(D)\,\mathrm{d}D=0.5 \tag{3a}$$

$$\int_0^{D^{**}} P(D)\,\mathrm{d}D=0.25 \tag{3b}$$

One can use the values $\bar{D}_{0.5}$ and $\bar{D}_{0.25}$ to estimate the width of $P(D)$. With this aim we introduce the parameters $n_{0.5}$ and $n_{0.25}$:

$$n_{0.5}=\ln(\bar{D}/\bar{D}_{0.5}) \tag{4a}$$

$$n_{0.25}=\ln(\bar{D}/\bar{D}_{0.25}) \tag{4b}$$

Evidently, when $P(D)$ is wider, the values of $n_{0.5}$ and $n_{0.25}$ are higher. For exponential decays (i.e. there is not any distribution of SDCs), $n_{0.5}=n_{0.25}=0$. The attractive feature of these parameters, to us, is that the quantities entering them have clear physical meaning and can be obtained from experimental diffusion decays with satisfactory accuracy by expanding the latter into exponents. As we have already mentioned above, the way of expanding $A(g^2)$ is not essential for obtaining average values $\bar{D}$, $\bar{D}_{0.5}$ and $\bar{D}_{0.25}$. Moreover, simple calculations enable one to establish the relations between $n_{0.5}$ and $n_{0.25}$ for different types of function $P(D)$ (here some analogy can be found with the method of moments in n.m.r. lineshape theory). For the most acceptable (in polymer systems[9]) log-normal function $P(D)$:

$$P\left(\ln\left(\frac{D}{D_0}\right)\right)=\frac{1}{\sigma(2\pi)^{1/2}}\exp\left(-\frac{\ln^2(D/D_0)}{2\sigma^2}\right) \tag{5}$$

the following relations hold:

$$n_{0.5}=\ln\left(\frac{0.5}{0.5-\phi(\sigma)}\right) \tag{6}$$

$$n_{0.25}=\ln\left(\frac{0.25}{0.5-\phi(0.67+\sigma)}\right) \tag{7}$$

where σ is the distribution width, D_0 is the most probable value and $\phi(\sigma)$ is a probability integral[10]:

$$\phi(\sigma)=\frac{1}{(2\pi)^{1/2}}\int_0^\sigma \exp\left(-\frac{y^2}{2}\right)\mathrm{d}y$$

When $0\leqslant\sigma\leqslant 3$, which is typical for our experiment, relations (6) and (7) take the form:

$$n_{0.5}\approx 1.15\sigma^{1.5} \tag{8}$$

$$n_{0.25}\approx 1.4(n_{0.5})^{0.9} \tag{9}$$

The experimental values $\bar{D}$, $\bar{D}_{0.5}$ and $\bar{D}_{0.25}$ were obtained on the assumption of a discrete spectrum of SDCs expanding $A(g^2)$ into exponential components[8] and calculating the quantities:

$$\bar{D}=\sum P_i D_i \tag{10}$$

$$\bar{D}_{0.5(0.25)}=\frac{\sum_{i=1}^{k-1} P_i D_i+\beta P_k D_k}{\sum_{i=1}^{k-1} P_i+\beta P_k} \tag{11}$$

where k and β should be chosen from the conditions:

$$\sum_{i=1}^{k} P_i+\beta P_k=0.5(0.25) \quad \text{and} \quad 0\leqslant\beta\leqslant 1$$

P_i is that part of the signal characterized by SDC D_i (the higher values of D_i correspond to higher values of i). The expressions (10) and (11) are analogues of (2) and (2a,b) when diffusion decay is described by a sum of exponents with a discrete SDC spectrum.

For samples studied, the following relation was established to be valid:

$$n_{0.25}=1.4(n_{0.5})^{0.9}\pm 0.15 \tag{12}$$

Comparison of (12) and (9) shows that, in our solutions, a log-normal type of SDC distribution represents an adequate approximation. Accordingly the values of σ are obtained from (6) or (8).

In *Figure 2* the experimental dependence of σ on polymer concentration φ_2 is presented. It is clearly seen that as φ_2 rises the SDC spectrum becomes wider. It is widest for PSEO-6 solutions in nitromethane (curve A), which is the worst solvent, and the values of σ are lower at the same φ_2 when the solvent is better (curves B and C). The smallest values of σ and its weak dependence on φ_2 are observed for PEO solutions in chloroform.

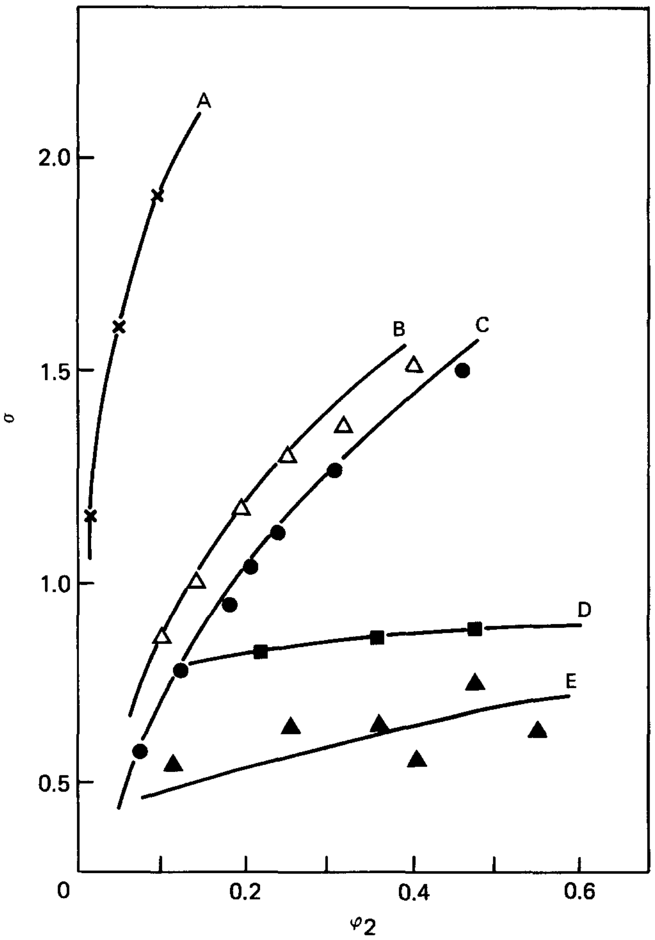

Figure 2 The dependence of parameter σ on polymer volume concentration φ_2 in studied systems: curve A, PSEO-6 in nitromethane; curve B, PSEO-6 in benzene; curve C, PSEO-6 in chloroform; curve D, polydisperse sample (see text); curve E, PEO in chloroform

Now consider the possible reasons for the existence of a spectrum of SDCs in copolymer solutions. There are two reasons considered in the literature: first, polymer polydispersity[9]; and, secondly, the presence in polymer solutions of a net fluctuation of entanglements due to which dynamic clusters of several macromolecules seem to exist for some time (10^{-2}–10^{1} s)[11,12]. In order to estimate the effect of sample polydispersity, we prepared a mixture of narrow PEO fractions with M_n and final M_w/M_n coinciding with those of the investigated PSEO. The mixture was further dissolved in chloroform. The behaviour of σ for this sample is presented by curve D in *Figure 2*. Comparison of curves A–C with curve D gives no evidence to suggest that sample polydispersity is the main reason for observing high values of σ in our experiment. The other possible reason for $A(g^2)$ non-exponentiality was discussed by others[11,12], where polystyrene solutions in CCl_4 covering a wide concentration range and PEO melts were explored. The non-exponentiality of $A(g^2)$ in these systems corresponds to the largest values of $\sigma \sim 1$ and thus should not be used to give a reasonable explanation of our results.

Investigations undertaken by one of us[13] showed that essentially a wide spectrum of macromolecule SDCs (σ is estimated as ~ 2) is found in gelatin solutions under conditions approaching gelation. This fact was supposed to be connected with the existence of long-lived macromolecular clusters with a wide size distribution[14,15]. Besides, the SDC spectrum in the mentioned solutions was shown to become narrower with decrease in polymer concentration or increase in temperature (that is, on getting away from the conditions of gelation). Therefore, we suggest that the non-exponentiality of $A(g^2)$ in PSEO solutions when $\sigma > 1$ is not only due to sample polydispersity and the existence of dynamic clusters, but mainly to the existence of long-lived clusters with a wide size distribution, which usually arise in systems when approaching the conditions of gelation. It may be supposed that the investigated PSEO solutions with high σ display a tendency to gelation. In view of this consideration the solution of PSEO-6 in nitromethane (the poorest of the solvents used) tends to gelation at low enough concentration $\varphi_2 < 0.15$ (see curve A, *Figure 2*), while PSEO-6 solutions in benzene and chloroform possibly show such a tendency at higher φ_2. These conclusions are confirmed by an observation of sample viscosity.

In *Figure 3* the concentration dependences of average SDC $\bar{D}$ are shown. The curves A–E corresponding to PSN, PEO and PSEO-6 solutions look similar and in the range of $\varphi_2 = 0.2$–0.6 can be fitted by a relation

$$\bar{D} \sim \varphi_2^{-\alpha}$$

where $\alpha = 3.4$–3.8 independently of polymer and solvent type. The lowest SDCs are observed for PSEO-6 macromolecules when the solvent is poorest, in agreement with the results of ref. 16. As the solvent becomes better, $\bar{D}$ increases. The average SDCs of hard

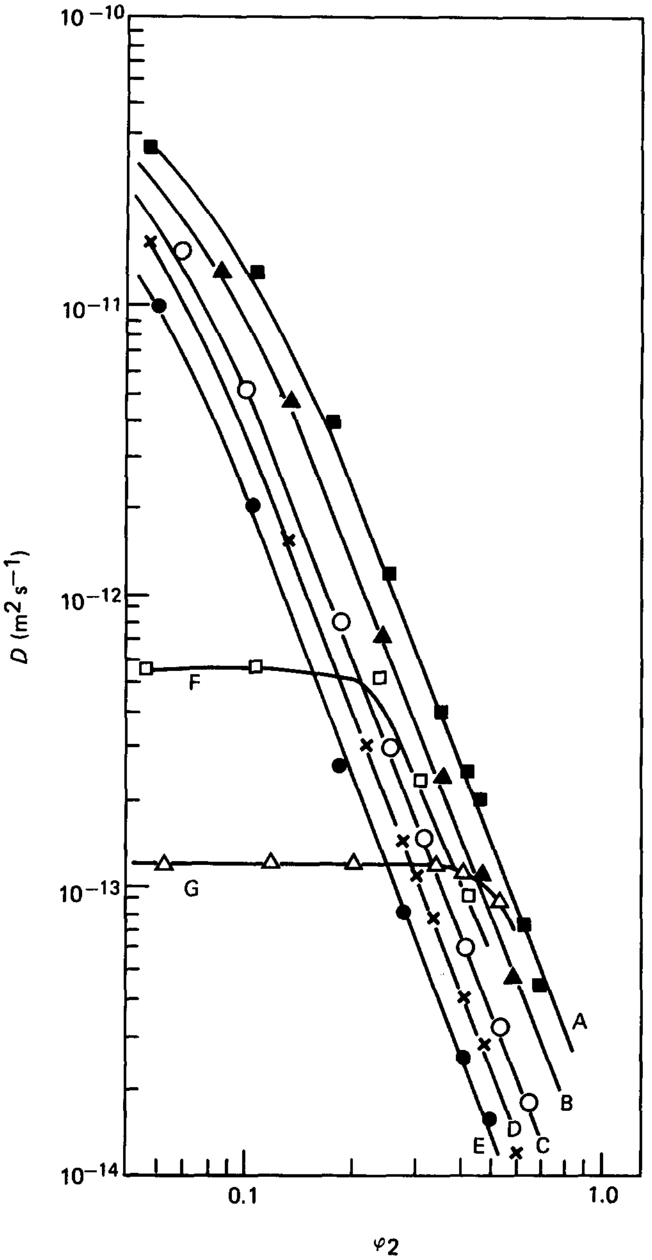

Figure 3 The dependence of macromolecule SDC on polymer volume concentration φ_2 for studied systems: curve A, PSEO-6 in chloroform; curve B, PEO in chloroform; curve C, PSEO-6 in benzene; curve D, PSN in chloroform; curve E, PSEO-6 in nitromethane; curve F, PSEO-3 in benzene; curve G, PSEO-1 in benzene

PSN chains are lower than that of flexible PEO chains at the same φ_2. But the values of $\bar{D}$ of copolymer molecules (i.e. of PSEO-6 with alternating PSN and PEO blocks) are somewhat higher than that of both homopolymers (compare curves A, B and D in *Figure 3*).

Anomalous concentration dependences of $\bar{D}$ are found for PSEO-3 and PSEO-1 in benzene solutions (curves F and G). It is clearly seen that a wide enough range of concentrations exist in these curves when $\bar{D}$ remains practically constant. Such a behaviour of $\bar{D}(\varphi_2)$ can be understood on the assumption that the indicated solutions are separated ones, containing precipitated and diluted phases. Then, in fact, within the temperature–composition equilibrium curve (TCEC) (i.e. for phase-separated solutions), the change of sample concentration φ_2 up to the intercept with the TCEC should not lead to a change of concentration in each phase. So the values of $\bar{D}$ within this range should be independent of φ_2 and correspond to the concentration of the precipitated phase. When the latter becomes smaller than φ_2 (i.e. for single-phase solutions), then the usual dependence of $\bar{D}(\varphi_2)$ should appear, as is observed for curve F. The latter considerations are consistent with visual observations showing that samples with $\bar{D}$ independent of φ_2 are macroscopically separated ones and contain precipitated phase and those with $\bar{D}$ depending on φ_2 are single-phase ones. To conclude, it may be noted that SDC measurements allow one to obtain information concerning system phase diagrams.

REFERENCES

1 De Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
2 Callaghan, P. T. and Pinder, D. N. *Macromolecules* 1980, **13**, 1085
3 Grinberg, F. A., Maklakov, A. I., Rogovina, L. Z. and Storogyk, I. P. *Vysokomol. Soedin.* 1984, **B26**, 777
4 Tanner, J. E. *J. Chem. Phys.* 1970, **52**, 2523
5 Scirda, V. D. and Sevreugin, V. A. *Pribori Technika Experimenta* 1982, **N5**, 112
6 Scirda, V. D., Sevreugin, V. A. and Sundukov, V. I. *Pribori Technika Experimenta* 1984, **N6**, 122
7 von Meerwall, E. *Macromolecules* 1985, **18**, 260
8 Clark, A. H. and Lillford, P. J. *J. Magn. Reson.* 1980, **41**, 42
9 von Meerwall, E. *J. Magn. Reson.* 1982, **50**, 409
10 Korn, G. A. and Korn, T. M. 'Mathematical Handbook', 2nd Enlarg. Rev. Edn., McGraw-Hill, New York, San Francisco, Toronto, London, Sydney, 1968
11 Maklakov, A. I., Sevreugin, V. A., Scirda, V. D. and Fatkullin, N. F. *Vysokomol. Soedin.* 1984, **A26**, 2502
12 Scirda, V. D., Sevreugin, V. A. and Maklakov, A. I. *Dokl. Akad. Nauk SSSR* 1983, **269**, 638
13 Masimov, E. A., Scirda, V. D., Pimenov, G. G. and Ibragimov, C. I. *Dokl. Akad. Nauk SSSR* 1983, **278**, 919
14 De Gennes, P. J. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979
15 Stauffer, D. J. *J. Chem. Soc., Faraday Trans. II* 1976, **72**, 1354
16 Maklakov, A. I. and Dvoyashkin, N. S. *Vysokomol. Soedin.* 1983, **B25**, 424