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 $(2t_d D)^{0.5}$, 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