Macromolecule self-diffusion in poly(ethylene glycol) melts

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Macromolecule self-diffusion in poly(ethylene glycol)s with $M_n=3\times10^2$ to 4×10^4 and $M_w/M_n\approx1.1$ was investigated by pulsed field gradient nuclear magnetic resonance. Samples with $M_n<3\times10^3$ were characterized by a single self-diffusion coefficient, D. In the fraction with high M_n, a spectrum of values of D was found, its width depending on the diffusion time. The existence of the spectrum of D is explained by the existence of macromolecule dynamic clusters with a finite lifetime in melts. The dependence of the average self-diffusion coefficients on molecular weights is described by a curve with two linear regions, the change in slope occurring where the entanglement network first appears.

(Keywords: self-diffusion; melts; entanglements; macromolecular cluster)

INTRODUCTION

It follows from existing theories[1,2] that, for the dependence of macromolecule self-diffusion coefficients, D, on molecular mass, the following relations should hold: $D\sim M^{-1}$ (ref. 1) when $M<M_c$; $D\sim M^{-2}$ (ref. 2) or $D\sim M^{-2.5}$ (ref. 1) when $M>M_c$; where M_c is a critical molecular mass which is characterized by the appearance of the entanglement net. The results of recent experimental investigations[3,4] of self-diffusion in polyethylene (PE) and polystyrene (PS) melts indicate, however, the absence of any special features near M_c, which differs from the nature of the molecular mass dependence on viscosity[5].

The purpose of the present work was to study macromolecule self-diffusion in poly(ethylene glycol) (PEG) melts with different molecular masses by pulsed field gradient nuclear magnetic resonance (n.m.r.).

EXPERIMENTAL

The experiments were carried out with fractions of poly(ethylene glycol). The weight averages of the molecular weights were from 3×10^2 to 4×10^4. The polydispersity of the samples was $M_w/M_n\leqslant1.1$. The samples were purchased from Fluka-Buchs, West Berlin.

The self-diffusion coefficients were measured by pulsed field gradient n.m.r. with a home-built spectrometer operating at 60 MHz on hydrogen nuclei. The method of stimulated echo[6] 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 T m^{-1}. The technique of obtaining subh pulse gradients has been described in detail previously[7,8]. The constant magnetic field gradient did not exceed 10^{-3} T m^{-1}. The diffusion time, $t_d=\Delta-\delta/3$, where δ is the duration of gradient pulses and Δ is the time interval between them. The δ values were of the order 10^{-5} to 10^{-3} s while t_d varied in the range of 10^{-2} to 2 s.

The high values of g allow one to use both short δ and short intervals between the first two r.f. pulses in the stimulated echo sequence. It gave us the opportunity to exclude the effect of spin–spin relaxation non-exponentiality. The cylindrical samples were evacuated with a high-vacuum pump at 373 K for 2 h. Then they were sealed in 7 mm glass thin-walled tubes. The g direction was perpendicular to sample axis.

We did not observe the disturbing effect of the pulse gradient on the data since the highest value of the magnetic field existing in the sample due to the pulse gradient is equal to $g/2\approx0.15$ T, which is much less than the main field $H_0=1.5$ T.

All the measurements were conducted at 373 K with the use of digital storage.

RESULTS AND DISCUSSION

Figure 1 shows experimental spin–echo diffusion attenuation $A(g^2)$. The curves are exponential for PEG when $M_n<3\times10^3$, i.e. they can be described by the following relation:

$$A(g^2)=A_0\exp(-Y^2g^2\delta^2t_dD) \tag{1}$$

where Y is the gyromagnetic ratio. For the samples with $M_n\geqslant3\times10^3$, the diffusion decay shapes are non-exponential and can be described by the following expression:

$$A(g^2)=A_0\sum_i^n P_i\exp(-Y^2g^2\delta^2t_dD_i) \tag{2}$$

where P_i is that part of the protons with self-diffusion coefficients D_i and $n>2$. Thus, to describe $A(g^2)$ it is necessary to introduce a set of coefficients D_i. Besides, for samples with $M_n\geqslant3\times10^3$, the shape of diffusion decays appeared to depend on diffusion time t_d (*Figure 2*), the shape of $A(g^2)$ approaching an exponential function with increase of t_d.

A change of the diffusion time t_d in the stimulated echo pulse sequence simultaneously causes a change in the

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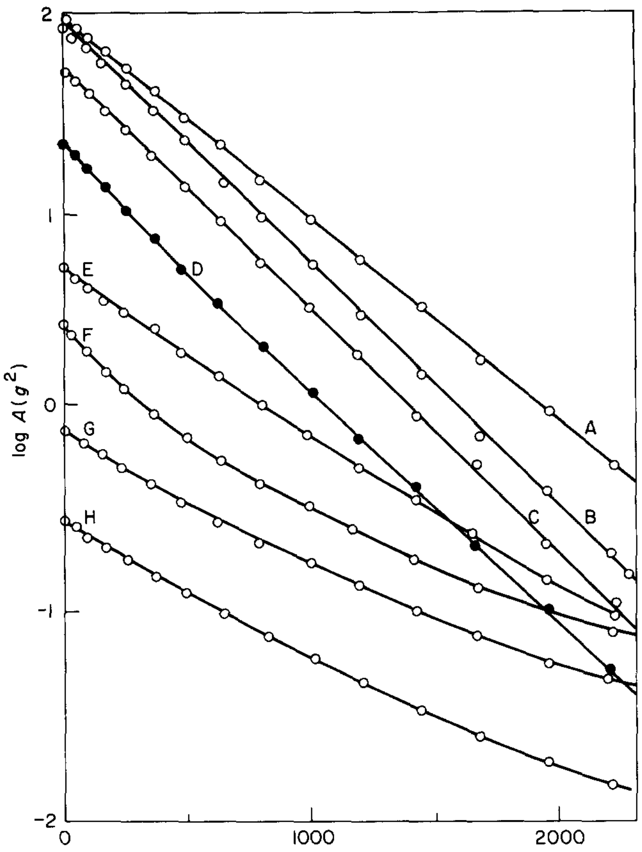

Figure 1 Spin-echo diffusion attenuation in PEG melts: curve A, $M_n = 0.6 \times 10^3$; B, 10^3; C, 2×10^3; D, 3×10^3; E, 6×10^3; F, 1.5×10^4; G, 2×10^4; H, 4×10^4. The measurements were carried out at diffusion times $t_d = 10^{-2}$ s (A–D), 2×10^{-2} s (E), 1×10^{-1} s (F, G) and 2×10^{-1} s (H)

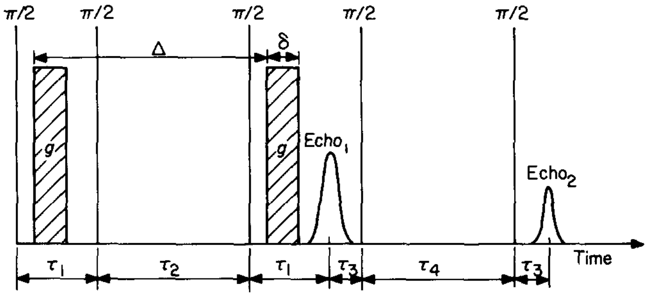

Figure 2 Pulse sequence for the determination of the influence of spin–lattice relaxation on spin attenuation shape

interval between the second and third pulses, and hence a change of the time interval T_r during which the spin–lattice relaxation is taking place. Therefore, when estimating the influence of the value of t_d on the shape of $A(g^2)$, it is necessary to take into account spin–lattice relaxation non-exponentiality.

With this aim we used the pulse sequence shown in *Figure 2* and then observed the echo amplitude decay. In the sequence mentioned, the time interval $T_r = \tau_2 + \tau_4$ while the diffusion time $t_d \approx \tau_1 + \tau_2$. Thus the values of T_r and t_d can be changed independently of each other by changing either τ_2 or τ_4. Then the echo amplitude attenuation $A(g^2)$ was observed (a) at a fixed T_r and changing t_d and (b) at a fixed t_d and changing T_r.

In the former case the shape of $A(g^2)$ depends on the value of t_d as it does in the usual stimulated echo sequence. A dependence of $A(g^2)$ on T_r was not found. These data allowed one to correlate the observed dependence of $A(g^2)$ on t_d with the specific features of translational mobility of macromolecules.

An average value of self-diffusion coefficient

$$\bar{D} = \sum_i^n P_i D_i$$

independent of experimental parameters was used as one of the characteristics of translational mobility of PEG macromolecules with $M_n \geqslant 3 \times 10^3$. As can be seen from equation (2), this average value is derived from initial slope of diffusion decays[9]. $\bar{D}$ is expressed by the equation:

$$\bar{D} = \left. \frac{\partial \ln A(g^2)}{\partial(-Y^2 \delta^2 g^2 t_d)} \right|_{g \to 0} \tag{3}$$

The analysis of the curves $A(g^2)$ made with the aid of a computer showed the diffusion decays to be satisfactorily described by expression (2) with $n \sim 10$–12.

The maximum (D_a) and minimum (D_b) values of self-diffusion coefficients obtained as a result of the expansion can be used as the parameters characterizing the width of the spectrum of D_i. The expansion of $A(g^2)$ was done in such a way that proton fractions P_a and P_b corresponding to the coefficients D_a and D_b were $\sim 10\%$. Why does the spectrum of D_i appear when $M_n > 10^3$? Earlier[9,10] we supposed that the presence of set D_i is connected with the existence of clusters with different sizes in the melts of narrow polymer fractions, these clusters being formed due to the heterogeneity of entanglement nets. These clusters should be dynamic, which is why every macromolecule can move from cluster to cluster.

According to the theory of self-diffusion in multiphase systems[11], it is possible to show that the shape of attenuation $A(g^2)$ depends on the relation between the value of t_d and the lifetime τ of a macromolecule in the cluster when the exchange between 'phases' takes place. Thus, when $\tau \gg t_d$ the curve $A(g^2)$ is non-exponential, when $\tau \ll t_d$ it is exponential and in the both cases it is independent of t_d. When $\tau \sim t_d$ the shape of $A(g^2)$ depends on t_d.

The value of the average self-diffusion coefficient defined from the initial slope of $A(g^2)$ remains constant

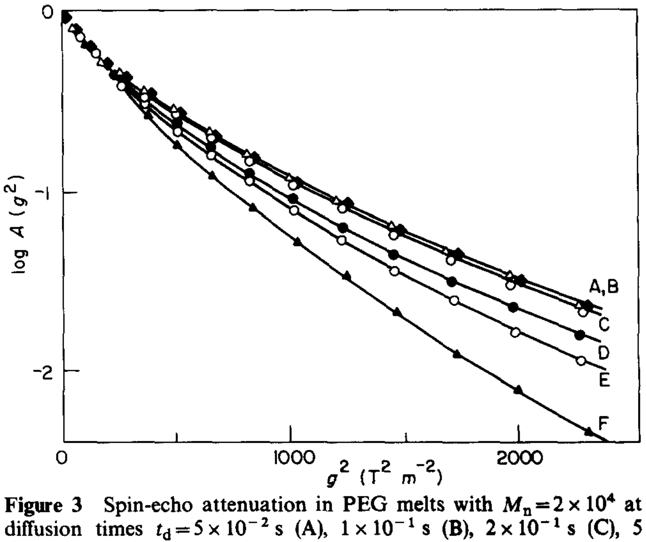

Figure 3 Spin-echo attenuation in PEG melts with $M_n = 2 \times 10^4$ at diffusion times $t_d = 5 \times 10^{-2}$ s (A), 1×10^{-1} s (B), 2×10^{-1} s (C), 5×10^{-1} s (D), 1 s (E) and 2 s (F). Temperature of measurements is 373 K

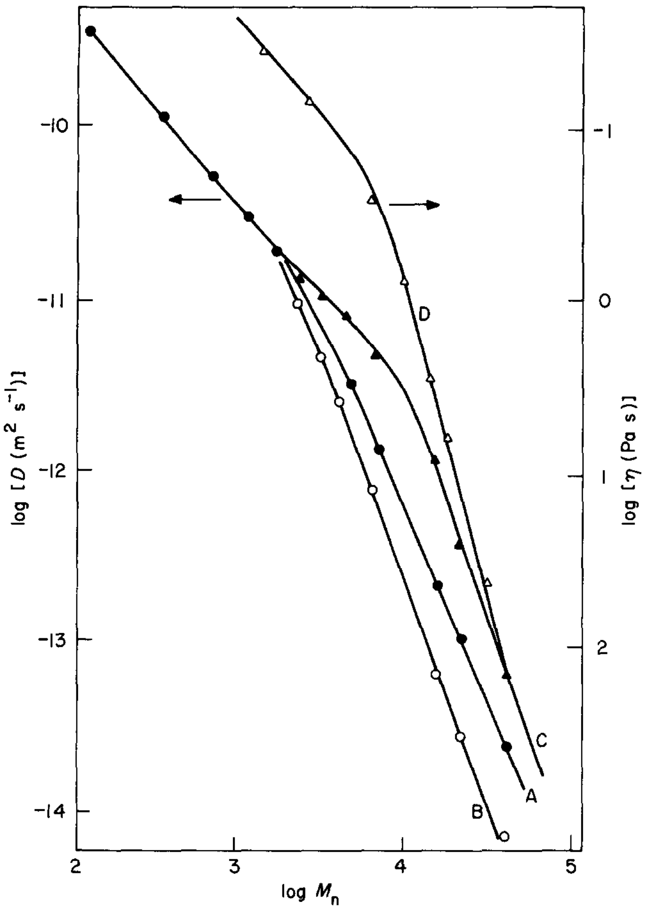

Figure 4 Molecular weight dependences of self-diffusion coefficients $\bar{D}$, D_a, D_b (curves A, B, C, respectively) and viscosity η (ref. 13) (curve D)

irrespective of the relation between τ and t_d (ref. 11). The behaviour of the dependence of $A(g^2)$ on t_d is in accordance with the conclusions mentioned above (*Figure 3*). The minimum value of t_d when the dependence of $A(g^2)$ on t_d appears can be considered as the lowest bound of the cluster lifetime.

Thus for PEG with $M_n = 2 \times 10^4$ at $T = 373$ K, $\tau \gtrsim 0.5$ s (*Figure 2*). Existence of the set of self-diffusion coefficients may be explained by the existence of different amounts of immobile imperfections in different macromolecules, which is possible in the generalized reptation model[12].

Let us consider molecular mass dependences of the average self-diffusion coefficients (*Figure 4*). As may be seen from *Figure 4* the dependence of D on M_n can be described by the relation:

$$\bar{D} \sim M_n^{-\beta} \qquad (4)$$

where $\beta \approx 1$ for $M_n \leqslant 10^3$ and $\beta \approx 2$ for $M_n > 3 \times 10^3$. Here the dependence of initial Newtonian viscosity η on M_n is also given[13] (curve D), which is described by the relation:

$$\eta \sim M_n^{\gamma} \qquad (5)$$

with $\gamma \approx 1.3$ when $M_n < 3 \times 10^3$ and with $\gamma \approx 3.5$ when $M_n > 6 \times 10^3$. The change of γ due to the increase of molecular mass is believed[5] to be connected with the appearance of an entanglement net between the macromolecules in polymer melts.

The observed dependences $D(M_n)$ and $\eta(M_n)$ do not contradict this concept. The dependences of D on M_n obtained by us indicate that macromolecule self-diffusion without the entanglement net ($\beta \approx 1$) differs from macromolecule self-diffusion with such a net ($\beta \approx 2$).

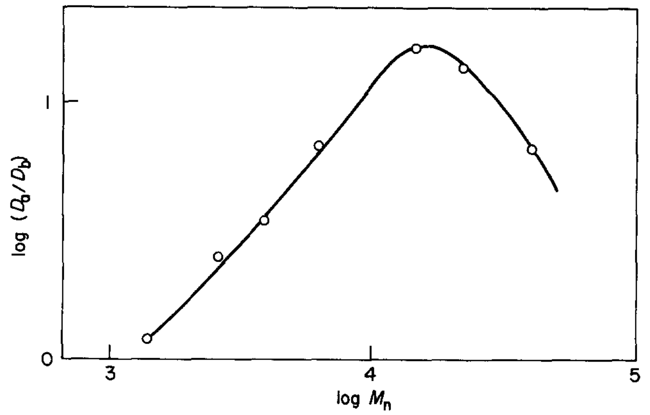

Figure 5 The dependence of $\log(D_a/D_b)$ on $\log M_n$

The critical molecular mass M_{cD} is defined as the crossing point of tangents to the low-molecular and high-molecular regions of molecular mass dependence of D and is $\sim 2 \times 10^3$. It is less than the corresponding value $M_{c\eta} \approx 7 \times 10^3$ (ref. 13) defined from the dependence $\eta(M_n)$.

It is seen from *Figure 4* that molecular mass dependences of D_a and D_b look like $\bar{D}(M_n)$, coincide with the latter when M_n are low and can be described by relation (4). The critical molecular masses M_{cD}^a and M_{cD}^b defined from the curves $D_a(M_n)$ and $D_b(M_n)$ are $\sim 1 \times 10^4$ and $\sim 3 \times 10^3$ respectively. The existence of the dependence $D_a \sim M^{-1}$ at $M_n < 10^4$ enables us to state that there exist molecules that are free from the entanglement net for these values.

For $M_n \geqslant 3 \times 10^3$ the relation $D_b \sim M^{-2}$ holds. Hence we may suppose that there is no entanglement net in polymers with $M_n < M_{cD}^b$. In polymers with $M_{cD}^b < M_n < M_{cD}^a$ part of the macromolecules are entangled while the rest are free. In polymers with $M_n > 10^4$, all the macromolecules are entangled. However, the entanglement net is not homogeneous, which accounts for the existence of the set of self-diffusion coefficients.

One of the simplest experimental parameters which can show the width of the spectrum of D_i is $\log(D_a/D_b)$. The dependence of this quantity on molecular mass is represented in *Figure 5*. It may be seen that the widest spectrum of D_i is observed for PEG with $M_n = 1.5 \times 10^4$.

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