Segmental Diffusion in Polymer Melts and Solutions of Poly(ethylene oxide) Measured with Field Gradient NMR in High-Field Gradients

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To answer the question about the reptation mechanism of diffusing chain segments in polymer melts or solutions, an investigation of the dynamics of these segments within space scales in the range between the tube diameter d_0 and the Flory radius R_F is necessary. Among others, e.g., neutron reflectometry[1] and nuclear reaction analysis,[2] two methods are of special relevance for this purpose: quasi-elastic neutron scattering (neutron spin echo) and pulsed field gradient NMR. In principle, both methods provide the self-correlation function of the hydrogen atoms in the polymer chains.[3,4] Neutron scattering probe space scales in the 0.1–10-nm region: with convenient polymers the space scale could be extended to regions larger than the tube diameter d_0 such that the spatial restrictions of the tube could be detected.[5] The space scale monitored by PFG-NMR commonly lies in the micron region. Presently much effort is devoted to increase the field gradient strength for decreasing the space scale detected with this method. The "scattering vector" in PFG-NMR is given by $\gamma\delta g$. γ is the gyromagnetic ratio, δ is the duration, and g is the magnitude of the field gradient pulses. The directions in the current work are as follows: (i) One simply increases the field gradient strength in the PFG-NMR and tries to circumvent the difficulties connected with the mechanical, electrical, and thermal requirements with a better construction of the field gradient assembly. For many years the Kazan group has applied field gradients of as large as 50 T/m and has not equaled the areas of the two pulses by hand because of the high stability of the current in the gradient coil.[6] In Leipzig at present field gradients of 25 T/m are applied and very sensitive equalization of the field gradient pulses by hand is possible.[7] (ii) Callaghan proposed a special pulse sequence MASSEY to overcome the difficulties of mismatch of the pulses and of possible mechanical shocks when using large field gradient pulses.[8] First experimental results are very promising.[9] (iii) A third direction is to work in the field gradient existing in the stray field of commercial cryomagnets used in NMR. This idea was first published by Kimmich and co-workers.[10] With this technique displacements of as small as 200 Å may be recorded, and the lower limit of D accessible now lies at about 10^{-16} m^2 s^{-1}.

We have followed the first and, particularly, the third idea. The maximum field gradient in the stray field of our cryomagnet of 8.5 T was measured as about 80 T/m. Our electronic equipment, designed and optimized for ^{2}H NMR, works at resonance frequencies near 60 MHz; therefore, we have positioned our probe head at a field strength of about 1.4 T where the field gradient is (only) 23.9 T/m. The following stimulated echo sequence was used:

$$\pi/2-\tau_1-\pi/2-\tau_2-\pi/2-\tau_1-\text{echo}$$

In the time windows of length τ_1 the field gradient yields the same situation as in the conventional pulsed field gradient NMR but without the problem of equalizing the field gradient pulses. The integrals $\int g\,dt$ between the first and second $\pi/2$ radio-frequency pulses and between the third $\pi/2$ radio-frequency pulse and the echo maximum are a priori equal. In a typical experiment the time interval τ_1 is varied; therefore, also transverse nuclear magnetic relaxation operates in the experiment. The echo height is

$$A = \exp\left(-\frac{2\tau_1}{T_2} - \gamma^2\tau_1^{\,2}\tau_2 g^2 D\right) = A_0\Psi \qquad (1)$$

with

$$A_0 = \exp\left(-\frac{2\tau_1}{T_2}\right)$$

However, this method also has a substantial disadvantage: due to the inhomogeneous B_0-field only a small slice of thickness Δz in the sample is at resonance. It is determined by the relation $\Delta\omega t_{\pi/2} \leq 1$ where $\Delta\omega = \gamma g \Delta z$ is the variation of ω_0 along the distance Δz and where $t_{\pi/2}$ is the length of the $\pi/2$ radio-frequency pulse. Our high-power transmitter allows very short pulses of duration $t_{\pi/2} = 0.4$ μs for protons, and with $g = 23.9$ T/m, we have $\Delta z \leq 0.2$ mm. However, signal accumulation is easily possible in these experiments, and therefore sufficient signal intensity can be obtained if the proton density in the sample is not too small. Another drawback may be the very small spin-echo width $\Delta\omega \approx 2/t_{\pi/2}$, but with a fast (40 MHz) transient recorder data evaluation under such conditions is possible.

From the echo attenuation plot (eq 1), the two quantities T_2 and D may be determined. In polymer samples it is advantageous to measure T_2 separately (e.g., from the decay of the Hahn spin echo in a homogeneous B_0-field) and to fit the data only to D.

For small τ_1 the slope of the echo attenuation plot (eq 1) is determined by the transverse nuclear magnetic relaxation and for long τ_1 by diffusion. If the sample is polydisperse, which is almost always the case in polymers, in the initial part of A the relaxation and fast diffusion of the lower molecular weight components in the sample are mixed in a complicated manner and an unambiguous fit of A to T_2 and D is no longer possible.

In the (conventional) pulsed field gradient NMR the time interval τ_1 is constant, and echo attenuation due to transverse nuclear magnetic relaxation is absent in a particular experiment. The time between the two field gradient pulses is equal to the diffusion time Δ (with $\delta \ll \Delta$). In the above-described experiments the diffusion time is $\tau_1 + \tau_2$, but it can be taken as τ_2 since always $\tau_1 \ll \tau_2$.

In our investigations we have considered the following two problems of polymer diffusion in melts and solutions of poly(ethylene oxide): (i) Are there deviations from normal Fickian diffusion in the melt for space scales larger than the Flory radius, i.e., for the diffusion of the center of mass of the polymer coils, as reported by Sevreugin et al.,[11] who concluded from the observed diffusion time dependence of the echo attenuations that cluster formation

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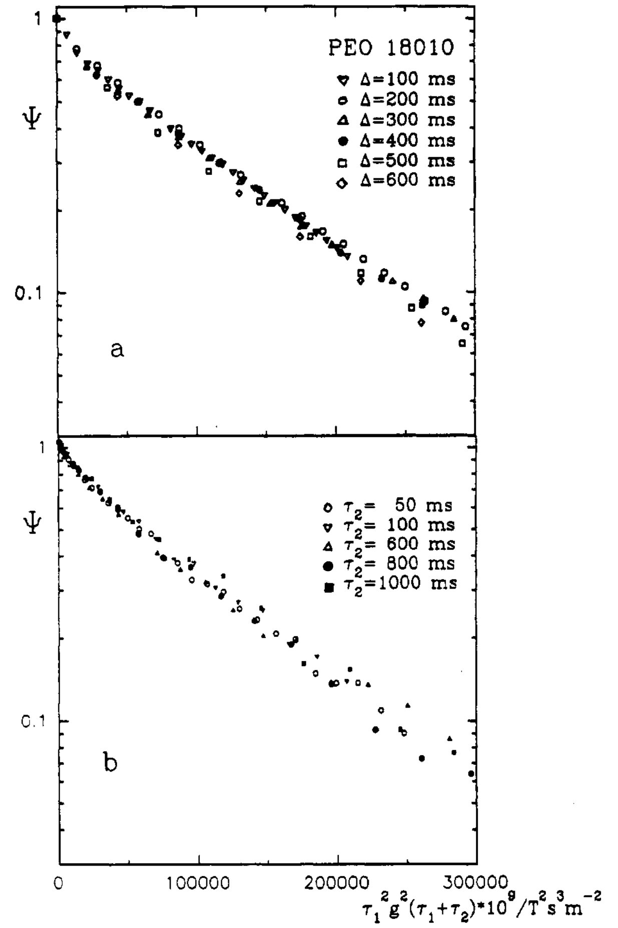

Figure 1. Echo attenuation Ψ for the PEO sample with M_w = 18 010 at T = 100 °C. (a) Measured with the FEGRIS spectrometer (PFG-NMR), $\tau_1 = \delta$, $\tau_1 + \tau_2 = \Delta$. (b) Measured in the stray field of the cryomagnet. $\Psi = A \exp(2\tau_1/48\text{ms})$; $\tau_1 \ll \tau_2$ always holds. The diffusion coefficient determined from the initial slope is 2.1×10^{-13} m^2 s^{-1} and from the linear part of the curve 9.3×10^{-14} m^2 s^{-1}.

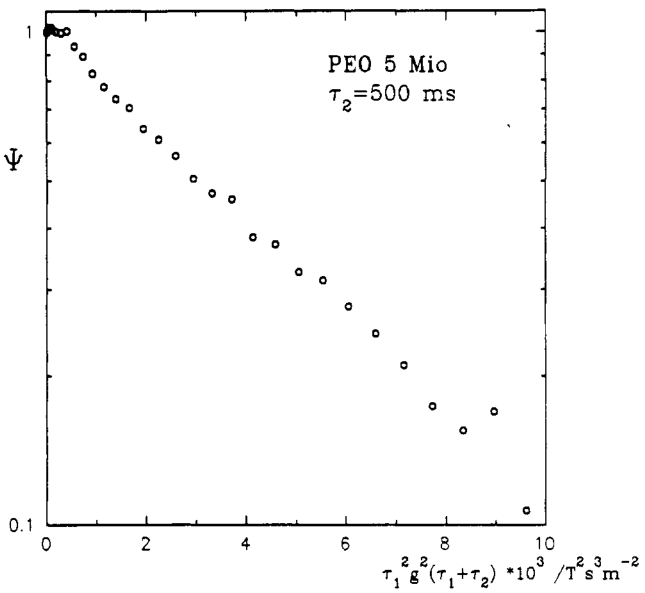

Figure 2. Echo attenuation $\Psi = A \exp(2\tau_1/7.5\text{ms})$ for the PEO 5×10^6 sample dissolved in C_6D_6 with c = 50% (w/w) and measured at T = 61 °C and a diffusion time τ_2 = 500 ms in the stray field of the cryomagnet. $\tau_1 \ll \tau_2$ always holds.

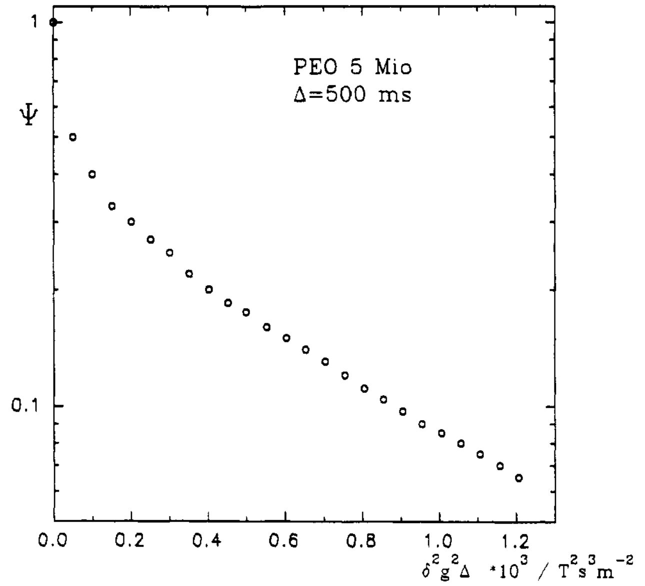

Figure 3. Echo attenuation Ψ for the PEO 5×10^6 sample dissolved in D_2O with c = 5% (w/w) and measured at T = 25 °C and a diffusion time Δ = 500 ms with the FEGRIS spectrometer.

with lifetimes between milliseconds and seconds exist? (ii) Is it possible to observe segmental diffusion within coils for distances smaller than the Flory radius where $\langle z^2 \rangle \sim t^{1/2}$ or $D_{app} \sim t^{-1/2}$,[12] respectively, should hold? Deviations from Fickian diffusion in this space scale have been reported by Sundukov et al.[13] for a very high molecular weight PEO. In this paper first results of our investigations are presented.

In parts a and b of Figure 1 the echo attenuation plots for PEO of M_w = 18 010 and M_w/M_n = 1.71 (purchased by Serva, Heidelberg) at a temperature of 100 °C are shown. The results of Figure 1b are obtained with the Mainz spectrometer (using the stray field of the cryomagnet) and those of Figure 1a by means of the specially built field gradient spectrometer FEGRIS in Leipzig with the stimulated echo pulse sequence.[7] The data in Figure 1b are corrected for T_2 relaxation with T_2 = 48 ms measured separately. Quite analagous results are obtained for PEO 6000 and 100 000. No dependence of D on the diffusion time τ_2 is observed. Therefore, cluster formation as reported by the Kazan group[11] must be excluded at least in the investigated time range from 50 ms to 1 s. The polydispersity is clearly reflected in the fast-decaying initial part of Ψ, but the curvature of the echo attenuation plot is smaller than expected from the reptation picture. This is a well-known effect[14] which should be investigated in more detail.

The diffusion of segments for $\langle z^2 \rangle^{0.5} < R_F$ was investigated with a very high molecular weight sample of PEO with a nominal M of 5×10^6. The polydispersity was unknown but certainly similar to the PEO's used above. From the R_F–M relation of ref 15 the Flory radius was calculated to be about 1400 Å. To reach the appropriate time scale for our experiments, a "plastification" of the polymer was necessary, i.e., the addition of solvent (95% D_2O and 50% C_6D_6, respectively). Two typical echo attenuation plots are shown in Figures 2 and 3. The effect of polydispersity is differently reflected in the two experiments: in the PFG-NMR a superposition of exponentials is seen, indicating a distribution of self-diffusion coefficients. In the stray field experiment the echo attenuation A was corrected with a single T_2 = 7.5 ms. This is obviously oversimplified; in this strongly entangled sample we have a dependence of T_2 on the chain length and hence a distribution of T_2 values due to the distribution of the chain lengths. The slowly relaxing but fast-diffusing short chains in the sample lead to the initial deviation of the curve corrected only with one T_2 representative for the long chains. In Figure 4 the (apparent) self-diffusion

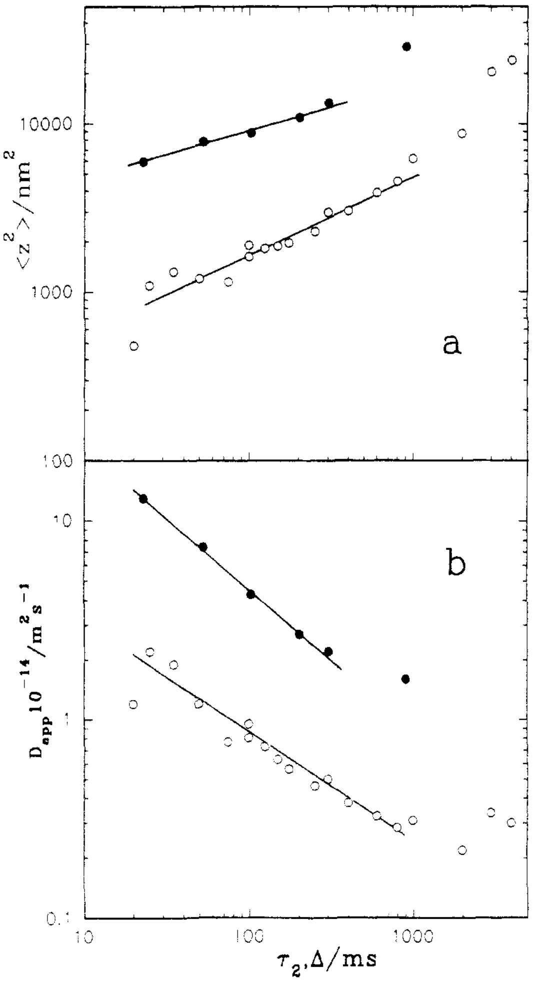

Figure 4. Mean-square displacements $\langle z^2\rangle$ (a) and the apparent self-diffusion coefficient $D_{app} = \langle z^2\rangle/2\tau_2$ (b) vs the diffusion time $\tau_2 = \Delta$ for the PEO 5 × 10^6 sample. (○) c = 50% in C_6D_6, T = 61 °C. (●) c = 5% in D_2O, T = 25 °C. The straight lines are guides for the eye.

coefficient and mean-square displacement $\langle z^2\rangle$ versus the diffusion time τ_2 is shown. We observe $D \sim \Delta^{-0.6...-0.7}$ up to a distinct time which should be equal to the reptation time T_r. At this time the crossover to free diffusion is seen. The exponents are slightly more negative than demanded by theory, but at the present state of the art the agreement is satisfactory. If we look at the mean-square displacements $\langle z^2\rangle$, the crossover from hindered diffusion of the segments within the tube to free diffusion of the coil as a whole is to be expected at $\langle z^2\rangle^{0.5} \approx R_F$, and also this is in good agreement with the experiment.

Further investigations with monodisperse samples of different molecular weights and at various concentrations are in progress.

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