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Notes

Polymer Association in a “Nonassociating” Polymer System. The Polystyrene/Toluene System

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Background

The concept of self-association of polymers in solution has mainly been discussed in systems where chemical modification of the polymer introduced strong polymer−polymer interactions. However, recently the interest of self-associating polymers has increased due to several experimental findings indicating that the phenomenon exists even in polymers that, based on the chemical structure, are not expected to show such behavior.

Computer simulations have shown that the introduction of heterogeneities in a polymer solution, or gel, will strongly alter the diffusion behavior of a probe diffusing inside the matrix, even though the heterogeneities are present only in small amounts. In particular, it was shown by Slater et al.[1] that the presence of small amounts of heterogeneities was enough to change the diffusion mechanism from reptation-like behavior (where the diffusion coefficient scales with the molar mass as $D \propto M^{-\nu}$, with $\nu = 2$) to an alternative kind of diffusion mechanism. In that case, an increase in the scaling dependence on M was observed, and scaling exponents as large as 2.8 were reported.

In a recent paper by Heckmeier et al.,[2] it was found that for polystyrene (PS) in toluene (which is a good solvent for PS at 25 °C) there existed heterogeneities in the polymer network with correlation lengths of several hundred nanometers. The heterogenities were interpreted to be an effect of associations of polymer chains. Moreover, these associations were long-lived, typically on the order of seconds. It was further noted that the fraction of the heterogeneities increased with increasing concentration of polymer and/or decreasing temperature. The conclusions were based on the interpretation of static and dynamic light scattering data in which the authors observed two correlation times. From the dynamic light scattering data it was deduced that the dynamics of both the fast and the slow mode could be described as diffusive processes.

In light of their findings, we have performed PFG-SE NMR experiments on the same system, i.e., monodisperse polystyrene in toluene at concentrations well above the overlap concentration.

The PFG-SE NMR Experiment

In the limit of short gradient pulses (usually termed the SGP limit), the echo decay in a PFG-SE NMR experiment, performed in a polydisperse polymer solution, can be described according to eq 1.[3,4]

$$E(q) = \int P(D) \exp(-4\pi^2 q^2 D\Delta)\, \mathrm{d}D \qquad (1)$$

In eq 1, $P(D)$ is the normalized distribution of diffusion coefficients and Δ is the allowed diffusion time. $q = (1/2\pi)\gamma\delta g$, where γ is the proton magnetogyric constant, δ the length of the field gradient pulse, and g is the strength of the pulse. In this context, q is the NMR equivalence to the q-vector in a scattering experiment. One main difference between light scattering and the PFG-SE experiment is that PFG-SE NMR measures self (tracer)-diffusion.

In the case of unrestricted Brownian motion in a monodisperse solution (for such a case, $P(D)$ is a δ-function), the resulting echo decay (E) is a straight line when $\log(E)$ is plotted vs $4\pi^2 q^2\Delta$. The slope then gives the molecular diffusion coefficient. If the echo decay is not linear, one can either assume a functional form for the distribution of diffusion coefficients, which leads to the use eq 1 or use of alternative evaluation processes, such as the CONTIN approach.[5,6] CONTIN numerically extracts a distribution function from a sum of exponentially decaying functions.

Experimental Details

The present investigation relies on the use of strong field gradients, and since the echo decay is monitored down to very large attenuation, strong demands have to be placed on the PFG-SE NMR hardware. In particular, the field gradient needs to be constant over the sample volume in order to ensure that any deviations from the normal diffusion behavior (a straight line when $\log(E)$ is plotted vs $4\pi^2 q^2\Delta$) arises from the diffusion behavior of the polymers. By using small sample volumes, a constant field gradient over the sample volume was achieved. The result of measuring the echo decay for a sample of glycerol is shown in Figure 1. It can be seen that the echo decay is linear down to very large echo attenuation.

A 200 MHz Bruker DMX spectrometer, equipped with a gradient probe, capable of providing 9 T/m at 40 A, was used. The signal-to-noise ratio was such that the echo could be followed down to 10^{-4}. Because of the low signal-to-noise ratios at large echo attenuation, extensive signal-to-noise averaging was necessary. On account of this, a typical experiment took about 12 h. The polystyrene was from a calibration kit supplied by Pressure Chemicals, and the samples used in this study had a molar mass of 90 kDa with $M_w/M_n = 1.04$. Deuterated toluene was supplied by Dr. Glaser, AG Basel, Switzerland.

Results and Discussion

In Figure 2, the echo decay for 12% polystyrene (PS) in deuterated toluene is shown. The echo decay is a

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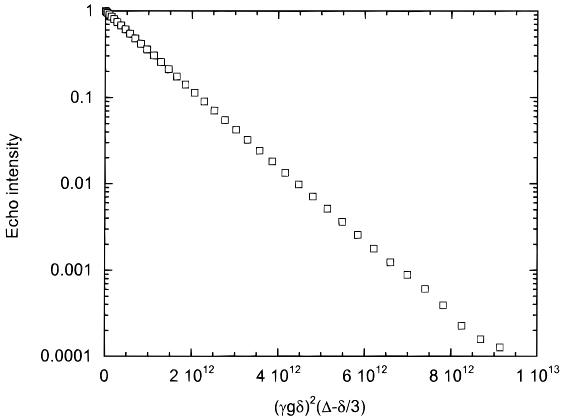

Figure 1. Echo decay for glycerol. Note that the echo decay is linear down to very large echo attenuation. Δ was in this case 100 ms, $\delta_{\max} = 4.5$ ms, and $g_{\max} = 8$ T/m.

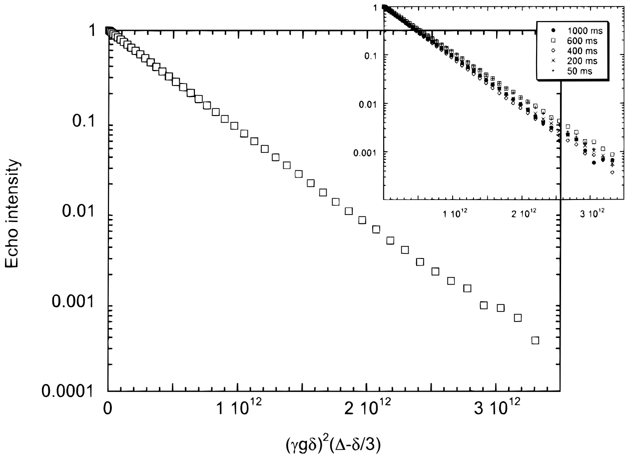

Figure 2. Echo decay for 12% PS in deuterated toluene. $\Delta = 100$ ms, $\delta_{\max} = 3$ ms, and $g_{\max} = 7.2$ T/m. The inset is the echo attenuation when changing the effective diffusion time, Δ.

straight line down to very large attenuations, which means that the polymer is relatively monodisperse and that no detectable polymer association occurs on the time scale of the experiment ($\Delta = 100$ ms). To investigate the time dependence further, the effective diffusion time was varied between 20 and 1000 ms, and no significant change in diffusion behavior was observed (as seen in the inset in Figure 2).

The small deviations from the straight line in Figure 2 are caused by polydispersity.

In Figure 3, the polymer concentration is increased to 23%. At large echo attenuation, there is a contribution arising from a second diffusing component that can be seen as a different slope in the echo decay at higher q values.

The diffusion coefficient for the second slower component is significantly smaller than the faster component. However, the fraction of the slow diffusing component is small. In Figure 4, the distribution of diffusion coefficients, $P(D)$, as obtained from CONTIN, is presented.

Also given is the result from the fit of two log-normal distributions to the CONTIN data, from which a fraction of 0.1% can be extracted for the slowly diffusing component. This is to be compared with the result of Heckmeir et al.,[2] where it was found that the volume fraction occupied by heterogeneities was approximately 0.1%. However, they pointed out that the result was at most a qualified guess, since the light scattering data are complicated by the fact that the intensity of the scattered light depends on the contrast factor, which in this case was not known. Despite this fact, there appears to be a very good agreement between light scattering and PFG NMR data.

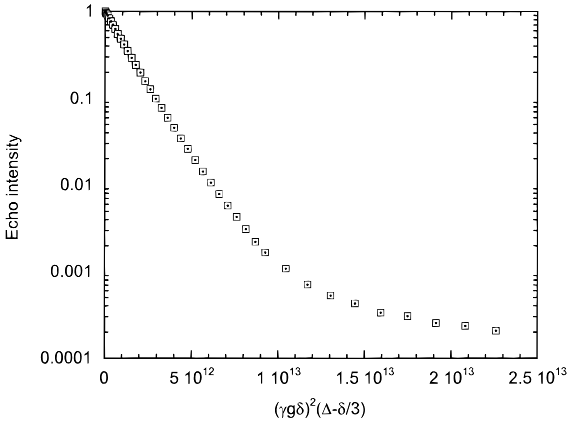

Figure 3. Echo decay for 23% PS in deuterated toluene. $\Delta = 200$ where $\delta_{\max} = 8$ ms and $g_{\max} = 5$ T/m. □ are the experimental data points, and ● shows the echo decay calculated by CONTIN. Note the different slope at high q values. When the echo attenuation is 1×10^{-4}, the signal disappears in the noise.

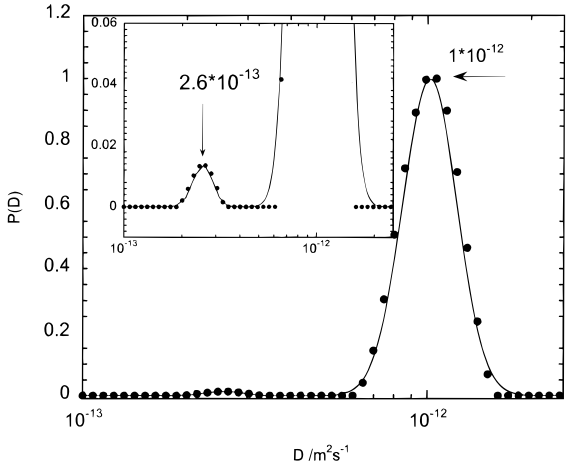

Figure 4. Distribution of diffusion coefficients according to CONTIN (●). The full line is a fit of two log-normal distribution functions to the data. The mole fraction of the slow diffusing species is 0.1%. Please note that the distribution function has not been normalized.

Conclusions

PFG-SE NMR data in toluene solutions of monodisperse polystyrene showed that a second (slower) diffusing component was present in small amounts. The mole fraction of the slower component was small (approximately 0.1%). Thus, the data presented here give further support to the experimental results presented by Heckmeier et al.[2] They showed by means of light scattering that the dynamics of the slow component (in a 25% of PS solution with $M_w = 78\,000$) could be well described by a diffusive process with $D = 2 \times 10^{-14}$ m^2 s^{-1}. This is to be compared with the value found in this work: $D = 2.6 \times 10^{-13}$ m^2 s^{-1} (in a 23% PS solution with $M_w = 90\,000$).

In the current context, we note that there are experimental difficulties and limitations to be expected from both light scattering measurements and PFG-SE NMR.

In the case of light scattering one problem is to extract the amount of scattering material from the relative intensities of the scattered light. (This is dependent not only on volume fraction but also on differences in refractive index.) In the case of PFG-SE NMR used here, the main experimental difficulty was to measure the echo intensity down to sufficiently large echo attenuation. This is essential since the amount of polymers that displayed a slow diffusion coefficient was very small.

Heterogeneous matrixes in polymer solutions have been investigated theoretically[7,8] and by computer simulations,[1,8−10] and it was noted that the introduction of heteogeneities severely changed the apparent diffusion behavior for a probe diffusing in the matrix. In particular, an increase in the scaling behavior ($D = KM^{-\nu}$) have been noted as the matrix went from being homogeneous to heterogeneous. These results have been used to explain some experimental indications of strong scaling dependencies in semidilute polymer solutions and gels.[11]

At the present stage we are not able to provide a detailed explanation concerning the reason for self-association phenomena observed in these systems. However, we note that previous work has shown that even though a polymer matrix is chemically cross-linked, a rms displacement of approximately 100 nm is obtained. Appel et al.[12] argue that one way to account for this observation is to consider cooperative fluctuations of the whole gel, since the rms displacement is too large to be an effect from chain fluctuations within the static network. Although this short length has not been observed in this work, it is our opinion that the slow component arises from the displacement of a microphase separated gel phase.

In a recent paper by Fleischer,[13] the author performed similar types of PFG-SE NMR experiments as in this work. It was found that no association effects could be seen from the echo decay in the PFG-SE NMR experiments. However, judging from the data presented in that work, we believe that the reason for this is that the signal was not attenuated enough in order for these effects to become apparent. Fleischer also draws the conclusion that if associations really occur, the concentration of clusters must be significantly smaller than 1%, which is also what we find in this work, i.e., 0.1%. As pointed out here, the signal needs to be attenuated down to less than 10^{-3} of the original signal intensity in order to see the aggregation effects.

We argue that the PFG-SE NMR method will be very important in the ongoing search for a deeper understanding of the dynamics and structure in semidilute polymer solutions and gels. In particular, we stress the potential of investigating the diffusion behavior of the slow component, using very high gradient strength (high q values). This makes possible the investigation of both structure and dynamics on short length scales (smaller than 100 nm) At these high q values it might be possible to deduce whether the slow component is originating from a gel-type structure that spans the entire sample or from “micellar-type” associations of polymers.

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