Spin Diffusion in Semidilute Random Coil Polymers Studied by Pulsed Gradient Spin-Echo NMR

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ABSTRACT: Pulsed gradient spin-echo NMR investigations of polymer mean-squared segmental displacements in semidilute solutions of high molar mass polystyrene in deuteriotoluene have revealed evidence for spin diffusion, an effect which is apparent in the difference between spin-echo and stimulated-echo experiments. The time dependence of magnetization quasi-particle displacements is found and is consistent with for intrachain diffusion, in contrast to the dominance of interchain effects in melts.

Introduction

Pulsed gradient spin-echo NMR[1] provides an effective means for investigating the role that entanglements play in determining the chain dynamics of dense, entangled polymers. This method gives information concerning mean-squared displacements of polymer segments and thus enables one to probe the diffusion of the chain segments at distance scales smaller than the polymer dimensions. The reptation theory[2,3] predicts anomalous segment diffusion, with a family of different regimes characterized by time dependences of the mean-squared segmental displacements involving distinctive t^1, $t^{1/2}$, $t^{1/4}$, and $t^{1/2}$ behaviors. In a recent article[4] we have shown that the Doi−Edwards formulation of the tube-reptation model provides a good first-order description of PGSE NMR data obtained from a wide range of high molecular mass polystyrenes in semidilute toluene solutions.

For very high molar mass polymers whose reptational motion is sufficiently slow, effective segmental diffusion coefficients may be on the order of or less than 10^{-15} $m^2\ s^{-1}$. For such rates, spin diffusion effects may play a role in determining the effective rms displacements of magnetization quasi-particles, a phenomenon first predicted by Fatkullin.[5] The influence of spin diffusion in entangled polymer melts has been seen both in our own work on semidilute solutions and in a study of self-diffusion in polymer melts by Fischer, Kimmich, and Fatkullin.[6] In the present article we present a more detailed study of the spin diffusion effect in polystyrene semidilute solutions and show that this process is largely confined to intrachain transport, a result we attribute to the greater preponderance of intrachain segmental contacts in semidilute solutions.

Theory

Spin diffusion is caused by the flip-flop terms, $(I_+^jI_-^k + I_-^jI_+^k)$, in the dipolar Hamiltonian[7] and can be observed when the nuclear magnetization component along the polarizing magnetic field, B_0, is not uniform in space. The evolution toward an equilibrium uniform magnetization by means of successive flip-flop between neighboring spins[8] is responsible for eliminating spin temperature gradients.[9] The random migration of magnetization via mutual spin flops acts to transport field gradient labeled magnetization in much the same manner as the physical displacements of the polymer segments. A detailed theory for this spin diffusion in polymeric systems has been given by Fatkullin.[5]

Since the process of spin diffusion affects only the component of magnetization lying along the direction of B_0, to observe the phenomenon, the detected magnetization must be phase-locked for a certain time along a common axis. In consequence, spin diffusion is only apparent in pulsed gradient spin-echo experiments when a stimulated echo is employed.[10] For the stimulated echo, the phase information from the first gradient pulse is embedded in the z-components of the magnetization during the “z-storage” period, during which the dipolar interaction causes energy-conserving mutual spin flops which carry this encoded phase information akin to diffusion of a quasi-particle, and indistinguishable from the effects of physical displacement of the nucleus bearing the original spin state. By contrast, in spin-echo experiments where spin magnetization is allowed to freely precess in the transverse plane, the dipolar interaction causes a loss of magnetization coherence into higher order terms of the spin ensemble density matrix, terms which are permanently lost to observable magnetization and which contribute to the effective T_2 relaxation.

The spin diffusion coefficient, D_{SD}, is given by

$$D_{SD} = cb^2W \tag{1}$$

b being the distance between the spins undergoing mutual flip-flop, c being a numeric factor on the order of unity, and W being the root-mean-square spin−spin interaction strength between neighboring spins which, in the classic dipolar case, is on the order of T_2^{-1}.[10] In rigid solids, where dipolar interactions are strong, $W \sim 10^4\ s^{-1}$ and D_{SD} is in the range $10^{-16}-10^{-17}\ m^2\ s^{-1}$. The use of pulsed gradient spin-echo NMR to detect directly the spin magnetization transport due to spin diffusion is relatively recent. Such transport will in general consist of a superposition of spin-diffusion and translational diffusion of spin-bearing particles.

In general, in ordered solids, where translational motion is suppressed, spin diffusion is dominant, and the observable magnetization migration is via spin diffusion alone. Cory and Zhang[11] used a PGSE pulse sequence, modified to match the special conditions required for solid-state NMR, to measure the spin diffusion coefficient in two directions, [001] and [111],

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of single crystal of CaF_2 and the diffusion coefficients found were on the order of 10^{-15} m^2 s^{-1}. In the limiting case of small molecular liquids, the translational diffusion dominates the spin diffusion, and the diffusion coefficient which is measured in any experiment based on magnetization transfer is the translational diffusion coefficient alone.

For entangled flexible polymer chains, the dipolar interaction between adjacent spins is expected to be weak because of motional averaging. For example, a typical polystyrene in solution, taking T_2 as 35 ms and distance between neighboring spins as 2 Å, one obtains $D \approx 1 \times 10^{-18}$ m^2 s^{-1}, an exceptionally low value, and some 2 or 3 orders of magnitude below that detectable by PGSE NMR. However the flip-flop processes can lead to much higher values of the spin diffusion coefficient provided remote spins approach within a distance of a few angstroms, for sufficient time for these processes to be effective.[12] The polymer segment then continues its Brownian with a new proton magnetization, and so the quasi-particle migrates. As a consequence of the large effective hopping distabnce b, the spin diffusion is substantially enhanced by the segmental Brownian motion. Note however that the quasi-particle still rides on the polymer chain, and so the net migration will be a sum of underlying chain displacements and spin diffusion.

The matter of how the enhanced spin diffusion compares in magnitude with physical segmental displacement is complicated in the case of polymers because of the fractal nature of the anomalous diffusion. Consider the regime in which the segmental mean-squared displacements scale with time as $t^{1/2}$ or $t^{1/4}$. Provided that the mean-squared displacments of the quasi-particles transported by spin diffusion scale as t^1, this latter transport will tend to dominate at the longest times. Such is the case in the polymer melt experiments of Fischer et al.[6] where spin diffusion was evidenced in the difference between diffusion coefficients measured using protonated chains and deuterated chains for which the quaiparticle migration is largely suppressed. In our own data, obtained in semidilute solution, we observed spin diffusion at short observation times, and spin diffusion was evidenced in the difference between diffusion coefficients returned by stimulated and spin-echo experiments. This method makes observation of the effect difficult at long times because of the T_2 limitations to the spin-echo signal. But regardless of that fact, because the spin diffusion mean-squared displacements appear to scale with an anomalously weak time exponent in semidilute solutions, the transition from $t^{1/2}$ to t^1, behavior for the segmental motion, will cause the latter to dominate at the longest times.

Experimental Section

Polymer samples used in this work were obtained from Polymer Laboratories, Church Stretton, Shropshire, UK. These polymers were dissolved in >99% perdeuteriotoluene (Aldrich, Milwaukee, WI), and were allowed to equilibrate for at least 2 months before transfer to 3.0 mm o.d. NMR tubes, following which they were sealed and allowed to equilibrate for several weeks. The PGSE NMR pulses sequences used are shown in Figure 1. All NMR experiments were performed using a Bruker AMX300 spectrometer at 300 MHz proton frequency at a controlled temperature of 27 °C. Gradient amplitudes of up to $g = 25$ T m^{-1} were employed using ramped gradient pulses along with a weak background gradient to stabilize the echo. Complete details of the pulsed gradient spin-echo experiments are given in earlier articles.[13,14] T_2 and T_1 relaxation constraints made it possible to carry out spin-echo diffusion measurements with Δ values up to of 45 ms and for stimulated-echo experiments up to 3 s. In both types of experiments when the extremes of time were being investigated, signal averaging was considerably extended, for example, by taking many hours to acquire 16 q values each with 128 acquisitions. For any distribution of displacements, Z, one may write the echo attenuation E in terms of the ensemble average $\langle \exp(i2\pi qZ)\rangle$ where q is the wavevector $(2\pi)^{-1}\delta g$, δ being the gradient pulse duration. For the present purpose we have chosen to use only small values of q such that $E(q)$ is in the range $1.0 \leq E(q) \leq 0.7$ for which, to first order, $\ln(E) \approx -2\pi^2 q^2 \langle Z^2\rangle$. Semilogarithmic plots of echo attenuation E vs squared wavevector q are used to obtain the mean-squared displacements in accordance with the low q limit and give values with a precision of around 1%. In all the data shown here, the diffusive observation time t is taken as the reduced time $\Delta_r = \Delta - \delta/3$, where Δ is the time separation of the gradient pulses.

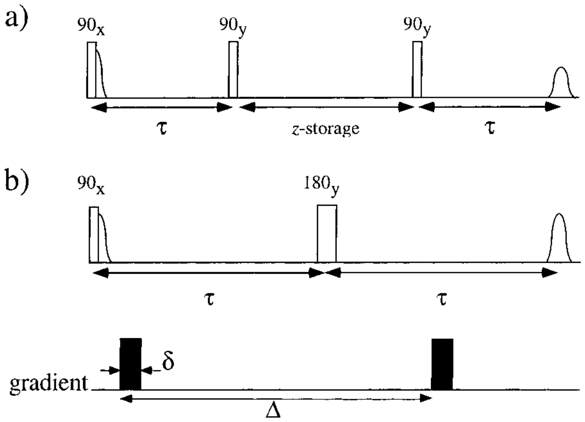

Figure 1. (a) Stimulated-echo experiment. Between the second and third pulse the magnetization is locked along the z direction, permitting spin flip-flops. (b) Spin echo in which the spin diffusion process is eliminated.

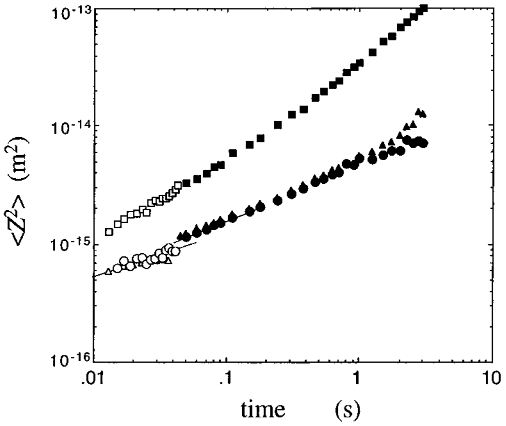

Figure 2. $\log(\langle Z^2\rangle)$ vs $\log(t)$ for 3.04×10^6 Da (squares), 15.4×10^6 Da (triangles), and 20.0×10^6 Da (circles) polystyrene at 5% (w/v) in perdeuteriotoluene. Spin-echo data are shown as open symbols, and the stimulated-echo data are shown as filled symbols.

Results

Figure 2 shows a complete set of $\langle Z^2\rangle$ vs t data for three molecular weights of polystyrene: (3.0×10^6, 15.4×10^6, and 20.0×10^6 Da) at 5.0% w/v in toluene, in which the spin-echo data are shown as open symbols while the stimulated-echo data are shown as filled symbols. The good agreement between data sets acquired using different echo schemes for the 3.0×10^6 Da sample in Figure 2 indicates that spin diffusion does

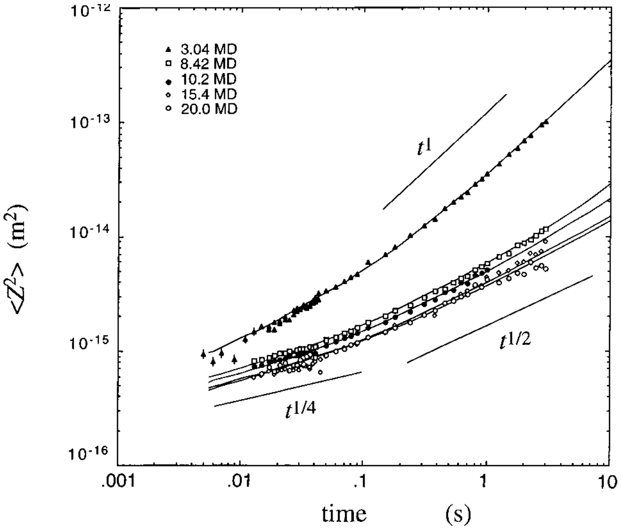

Figure 3. log($\langle Z^2\rangle$) vs log(t) for five different molar masses in perdeuteriotoluene (see legend for molar mass labels) where, in the case of the 8.42 × 10^6, 10.2 × 10^6, 15.4 × 10^6, and 20.0 × 10^6 Da polymers, the small spin diffusion correction has been made to the stimulated-echo experiment data set. Where no errors bars are shown, these are smaller than the symbol size. Asymptotic scaling exponents are shown in the straight line tangents. The data are fitted to eq 3 using only two parameters: τ_d and a.

not play a role in this data set. However, for the 15.4 × 10^6 and 20.0 × 10^6 Da samples, it can be seen that in the vicinity of the spin echo/stimulated crossover (around 40 ms) the values of $\langle Z^2\rangle$, from the spin-echo experiment, are noticeably smaller in the case of these larger molar mass polymers and that the weak spin diffusion process is now visible as a discrepancy between the two data sets. The spin diffusion process was apparent also in the 10.2 × 10^6, 8.42 × 10^6, and 6.5 × 10^6 Da 5.0% and 3.04 × 10^6 Da 10.5% samples.

A series of stimulated-echo experiments have been performed for the 15.4 × 10^6 Da 5.0% w/v sample at a fixed value of $\Delta = 45$ ms in which the time between the second pair of 90° rf pulses (the z-storage time) is varied, thus gradually transforming the stimulated echo into a spin echo, as apparent in Figure 1b. The resulting plot of total mean-squared displacement vs z-storage time indicates that the additional mean-squared displacement resulting from z-storage, attributed here to the effect of spin diffusion, is not linear in time, as one might expect in a three-dimensional Gaussian random walk. By taking the difference in displacements measured using the spin- and stimulated-echo experiments, we can examine the time exponent.[4] These additional spin-diffusion mean-squared displacements seem to vary as $t^{1/2}$. The mechanism that we have suggested for spin diffusion, in the case of semidilute solutions, is one in which the quasi-particles are largely confined to the path of the single polymer in which they originate. Escape to neighboring chains must therefore be possible only for longer times than those used for the spin-echo/stimulated-echo comparison.

We suggest that a possible reason for this semiconfinement of spin diffusion to a single chain is that in semidilute solutions, unlike the case of the melt, the probability of intersegment contacts within a chain is significantly higher that that probability of contact between two different chains despite the occasional interchain contacts associated with entanglements. Thus, confinement should persist beyond a tube step. We therefore relate the apparent mean-squared displacement (in the case of the stimulated echo) to the actual segmental displacement $\langle Z^2\rangle$ via the relation

$$\langle Z^2_{\mathrm{app}}\rangle = \langle Z^2\rangle + \frac{1}{3}(2D_{\mathrm{SD}}t)^{1/2}a \tag{2}$$

where a is, as always, the tube diameter, and $\langle Z^2\rangle = {}^1/_3\langle(R_{\mathrm{n}}(t) - R_{\mathrm{n}}(0))^2\rangle$. From these data we obtain[4] $D_{\mathrm{SD}} \approx 3.5 \times 10^{-15}$ m^2 s^{-1}, quite close to that found by Fischer et al.[6] for polymer melts. The stimulated-echo data can then be corrected to yield the complete $\langle Z^2\rangle$ vs t curve across the entire time regime, as shown in Figure 3 for the high molecular weight samples. The theoretical line is from Doi–Edwards theory in which a and D_{G} (the self-diffusion coefficient in the t^1 regime) are the sole fitting parameters. This data along with the fit is the same as that published in our earlier article.[4] That article contained a misprint in the equation used to represent the crossovers between the different regimes. The correct expression used both in that work and in the present case is

$$\phi(t) = \frac{2D_{\mathrm{c}}}{Z}t + \left(\frac{2}{\pi}\right)^{1/2} a\left\{\left(\frac{2Nb^2}{\mathrm{a}\pi}\sum_{p=1}^{\infty}\frac{1}{p^2}\frac{1}{2}(1 - \exp(-tp^2/\tau_{\mathrm{d}}))\right)^2 + \frac{4Nb^2}{3\pi^2}\sum_{p=1}^{\infty}\frac{1}{p^2}\frac{1}{2}(1 - \exp(-tp^2/\tau_{\mathrm{R}}))\right\}^{1/2} \tag{3}$$

To test the hypothesis that quasi-particle migration is largely confined to a single chain, we have carried out an experiment in which interchain flip-flops are suppressed while intrachain interactions are permitted. This we do by confining our observation to “NMR visible” protonated chains surrounded predominantly by deuterated neighbors. A mixture of 2.9% w/v protonated 3.04 × 10^6 Da polymer chain and 12.9% w/v perdeuterated polystyrene $M_{\mathrm{W}} = 3.13 \times 10^6$ (Polymer Laboratories, Shropshire, UK) was dissolved in deuterated toluene at a net concentration of 15.8.% w/v. This particular concentration was chosen to give a self-diffusion coefficient close to that found for a 10.5% solution of the protonated 3.04 × 10^6 Da polymer, for which significant spin diffusion effects were evident. Figure 4 shows the $\langle Z^2\rangle$ vs t data for this sample, along with the Doi–Edwards reptation curve. One can see that even though these interchain flip-flops are supressed, the spin diffusion process can still be observed. The size of the spin diffusion contribution, as measured by D_{SD}, is 0.6 × 10^{-15} m^2 s^{-1}, by comparison with a value of 1 × 10^{-15} m^2 s^{-1} obtained in the fully protonated sample. These values are sufficiently close to indicate the dominant role played by intrachain flip-flops.

As part of this work we investigated the concentration dependence of $\langle Z^2\rangle$ vs t, in the fully protonated polymers, for the fixed molar mass of 3 × 10^6 Da. These exhibit spin diffusion most noticeably in the 10.5% sample. In Figure 5 we show the effect of the correction where we assume a constant D_{SD} of 4 × 10^{-15} m^2 s^{-1} and allow in eq 2 for the tube diameter as fitted using the Doi–Edwards relationship for $\langle Z^2\rangle$ vs t. In the 5.0% sample the segmental translational diffusion dominates, making the spin diffusion effect a much smaller proportion of the total quasi-particle motion and therefore more

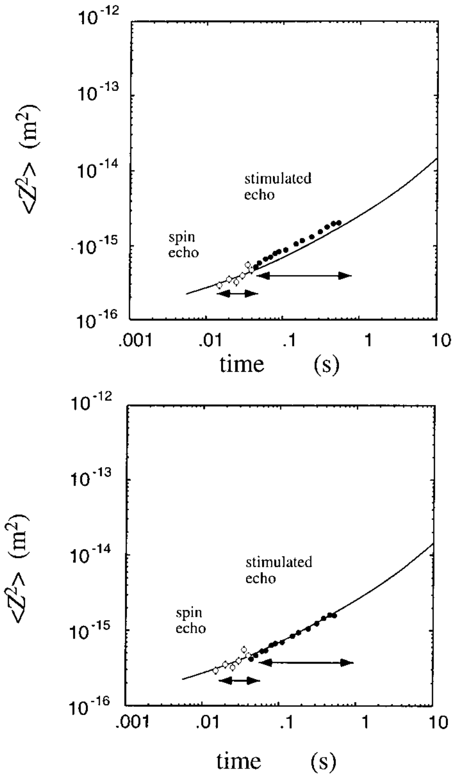

Figure 4. log($\langle Z^2 \rangle$) vs log(t) for 2.92% (w/v) 3.04 × 10^6 Da protonated polystyrene immersed in a 12.85% (w/v) solution of perdeuterated 3.13 × 10^6 Da polystyrene. The solvent is again perdeuteriotoluene. Spin-echo data are shown as open symbols, and the stimulated-echo data are shown as filled symbols. Where no errors bars are shown, these are smaller than the symbol size. (a) Before spin diffusion correction and (b) after the spin diffusion correction. The solid line corresponds to the Doi−Edwards reptation curve.

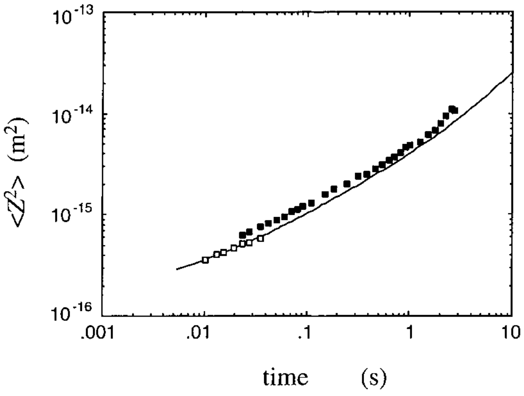

Figure 5. log($\langle Z^2 \rangle$) vs log(t) for 10.5% (w/v) 3.04 × 10^6 Da protonated polystyrene in perdeuteriotoluene. Spin-echo data are shown as open symbols, and the stimulated-echo data are shown as filled symbols; the discrepancy illustrates the effect of spin diffusion. Errors bars are smaller than the symbol size. The solid line corresponds to the Doi−Edwards reptation curve.

difficult to observe. In the case of the 16.6% and 23.6% solutions, the segmental displacements are smaller, but the spin diffusion contribution to the magnetization quasi-particle motion is also less visible for two quite subtle reasons. First, as the tube diameter decreases with increasing concentration, the laboratory frame projection of the intrachain quasi-particle diffusion decreases in accordance with eq 2. Second, because the spin diffusion contribution scales as $t^{1/2}$, once the polymer segmental motion enters the $t^{1/4}$ regime (i.e., for $t < \tau_R$), the relative effect of the spin diffusion contribution again declines. However, even allowing for these effects, the spin diffusion coefficient appears to be much lower than 1×10^{-15} m^2 s^{-1} for these higher concentration systems. This may occur because the spin diffusion is itself mediated by segmental displacements which carried the quasi-particles between successive flip-flops. When the segmental diffusion is more confined, as would be expected at high concentrations, the value of D_{SD} might also be expected to decrease. This decrease in segmental mobility might be offset by a more rapid flip-flop process once the concentration becomes sufficiently high that dipolar interaction strengths significantly increase, thus explaining the presence of noticeable spin diffusion effects in the molten state.

Conclusion

We show here, in the case of semidilute polymer solutions, that the mechanism for spin diffusive migration of magnetization is one in which the quasi-particles are largely confined to the path of the single polymer in which they originate, possibly escaping to neighboring chains in longer times than those used in the present measurements. Evidence for this hypothesis is provided by the dependence of quasi-particle mean-squared displacements as $t^{1/2}$ and by the persistence of the spin diffusion contribution in a sample where interchain migration is suppressed. We note that the effect of concentration upon the observed spin diffusion effect is consistent with the model of quasi-particle migration being mediated by segmental displacements. It is possible that a careful analysis of spin diffusion effects in such polymer systems could provide new insight regarding segment−segment collisions and especially in separating the respective contributions of interchain and intrachain interactions.

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