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Analysis of Polymer Dynamics by NMR Modulated Gradient Spin Echo

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Summary: NMR modulated gradient spin echo method, which allows the quantification of polymer segmental displacement via the measurement of the velocity autocorrelation, requires the formulation of theoretical predictions in the frequency domain in order to test their validity. We worked out the velocity autocorrelation spectrum of the segmental motion according to the Rouse and the tube/reptation model to compare it to the experimental results obtained by the new NMR technique. The analysis of polybutadiene shows the segmental velocity autocorrelation spectrum typical for the reptation-like motion of polymer in a ''tube''. The measurement of bulk water indicates a kind of Rouse motion in a network of hydrogen bonds.

Keywords: gradient spin echo; nuclear magnetic resonance; polymer; reptation/tube model; rouse model; segmental motion; velocity correlation spectrum

Introduction

Elucidation of the nature of complex polymer dynamics on a molecular level is of major importance in understanding the behavior of polymeric materials. Dynamic behavior of polymer molecules in a melt appears to be an extremely complex problem. Due to the high density of polymer melts, it is difficult to formulate an explicit theory even on larger intramolecular length scales. Therefore the discussion is usually based on highly simplified models such as the Rouse[1] and the tube/reptation model.[2,3] De Gennes coined the term ''reptation'' for this snake-like wriggling of the chain under Brownian motion. These theories neglect all details of the chain structure and are consequently only applicable to length scales on which the polymer appears as a highly flexible chain with universal properties. Mathematical simplicity and a dependence on a very small number of free parameters attributes to the popularity of this model. However, the model remains controversial because of the bold a priori assumptions and the manner in which these assumptions are used to avoid the complexity of intermolecular correlations in the many-body dynamics. In particular, reptation represents a mean field approach, focusing on the behavior of a single chain in a matrix of surrounding chains whose influence is subsumed into a topologically constraint. The reptation theory predicts a rich complexity in the anomalous segment diffusion, involving transitions between families of different regimes characterized by time dependencies of the mean squared segmental displacements (MSD) that have no overall experimental verification so far.

NMR Measurement of the Velocity Autocorrelation Spectra

Methods of nuclear magnetic resonance (NMR) provide coefficients of self diffusion, D, in polymer melts or solutions either indirectly through analysis of spin relaxation data or directly by monitoring the way in which the spin echo signal responds to the applied magnetic field gradient. The

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pulsed gradient spin echo (PGSE) and its variant of stimulated gradient spin echo, measures directly the MSD in the direction of the magnetic field gradient of spin bearing particles in a time interval between two pulses via the loss in phase coherence among the moving spins. The diffusive motion is reflected in a decrease of the spin echo amplitude, which is a function of the gradient strength and self-diffusion constant[4]. Typically, for high molecular weight polymers, $D \approx 10^{-15}–10^{-12}$ m^2 s^{-1}, and the time over which diffusion takes place in PGSE experiment is within the range $10^{-3}–3$ s, giving the measured root of MSD in the range 100–450 nm. The analysis of molecular motion by PGSE requires that the molecular displacement during the application of the gradient pulse has to be shorter than the characteristic lengths of motion, which is almost impossible to satisfy for PGSE measurement of dense polymers at the present state of the art. However, the PGSE method is not unique and other sequences of gradient and radio-frequency (RF) pulses are possible that detect the molecular motion in a different manner. Here we refer to the method named the modulated gradient spin echo (MGSE) with the sequence of RF-pulses and magnetic field gradient waveforms that periodically modulate the spatial distribution of spin phase. It turns out the accumulated time dependent spin phase a natural related to the velocity autocorrelation spectrum (VAS) of molecular translation motion.[5] The method gives the spin echo attenuation in the form

$$\beta(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} q(\omega,\tau) \frac{D_z(\omega)}{\omega^2} q^*(\omega,\tau)\, d\omega, \tag{1}$$

where VAS is defined by[6]

$$D_z(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \langle \Delta v_z(t) \Delta v_z(0) \rangle e^{-i\omega t} dt. \tag{2}$$

Here $\Delta v_z(t) = v_z(t) - \langle v_z(t) \rangle$ is the component of the velocity fluctuation in the direction of the effective magnetic field gradient $\mathbf{G}_{\text{eff}}$ (z-axis in our case). Periodic spin phase modulation creates the spin dephasing with the spectrum $q(\omega,\tau) = \gamma \int_0^\tau G_{\text{eff}} e^{i\omega t} dt$ that has a narrow peak at the modulation frequency. Thus, by changing the modulation frequency, we can sample VAS by this method.[7] The pulsed-gradient version of the MGSE method has already been used to study molecular flows and self-diffusion in porous media,[8–11] but the inductance of gradient coils limits the modulation frequencies to below 1 kHz. For this reason, the technique does not attract a lot of attention. For instance, in porous media, it cannot explore the part of VAS characteristic for restricted diffusion in pores smaller than $1\,\mu m$. Recently, we revealed[12] that a standard NMR Carr-Purcell-Meiboom-Gill sequence of π-RF pulses[13] behaves as a MGSE method, when applied simultaneously with a constant magnetic field gradient. This combination creates alternating spin dephasing in the pace of applied π-RF pulses giving the spectrum that has a peak at $\omega_m = \frac{\pi}{T_m}$, where T_m is the time interval between the π-RF pulses. Without the need to switch the magnetic field gradient, this technique overcomes the high-frequency deficiency of the pulsed MGSE technique by enabling VAS measurement to beyond 100 kHz. The resulting spin echo attenuation:[14]

$$\beta(\tau) = \frac{8\gamma^2 G^2 \tau}{\pi^2} \frac{D_z(\omega_m)}{\omega_m^2} \tag{3}$$

is proportional to VAS at the modulation frequency $1/T_m$. VAS gives MSD through the relation $\langle [z(t) - z(0)]^2 \rangle = \frac{4}{\pi} \int_0^\infty \frac{D_z(\omega)}{\omega^2} (1 - \cos(\omega t)) d\omega$.

MGSE method acts as a filter with an adjustable detection window into the frequency domain of spin translation dynamics by sampling only molecular motion that is in pace with the spin phase modulation. The method is unique in a clear discrimination of fast diffusion-like motion from slow collective one, e.g. flow or convection in fluids. However, its application for the study of polymer dynamics requires knowledge of velocity autocorrelation function of polymer segmental motion in the frequency domain as follows.

Rouse Model

While considering large-scale properties of polymer, there is no need to trace all sections of a macromolecule. We can study motion of a polymer in terms that are more general by choosing the points characterizing the spatial arrangement, sufficiently wide to neglect any stereo-chemical restriction of the orientation relative to each other. In the Rouse model[1] the length of chain section separating the neighboring points exceeds that of the Kuhn segment. It means that there is no mutual orientation correlation; merely the linear order of segments is retained. The treatment is based on the Langevin equation in the inertia-free approximation, where the effective intramolecular interactions between the segments are approximated by entropic harmonic interactions, reflecting the Gaussian character of the large-scale chain conformation. In this model the entropic spring constant and the friction coefficient of connected Kuhn segments of lenght b are $K = \frac{3k_B T}{b^2}$ and $\zeta = 6\pi\eta a_h$ respectively. Here k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the medium surrounding the segment, and a_h is the hydrodynamic radius of the segments. This model leads to a simple expression for the dynamics parameters, where the one dimensional MSD of s-th chain segment[15,16] is expressed as a sum over the m Rouse modes

$$\langle \Delta x^2 \rangle_{R,m} = 2D_{coil}\left(t + \tau_s \sum_{p=1}^{p=m} \frac{m^2}{p^2}\left(1 - e^{-\frac{tp^2}{m^2\tau_s}}\right)\right). \tag{4}$$

Here $D_{coil} = \frac{k_B T}{N\xi}$ is the diffusion coefficient of the chain center of mass. $\tau_s = \frac{b^2}{3\pi^2 D_{coil}}$ is the segmental, minimum relaxation time, which is related to the relaxation time of p-th Rouse mode $\tau_p = m^2\tau_s p^{-2}$. Here the number of modes m depends on the number of chain links. This model neglects the hydrodynamic interaction appearing because of solvent entrainment during motion of polymer chain. Each moving unit of a long flexible molecule induces in the surrounding solvent a velocity field that reacts on the motion of other segments. The Zimm model takes into account the long-range hydrodynamic interaction that couples the Rouse modes resulting into the relaxation times of modes as $\tau_p = m^2\tau_s p^{-3/2}$. However, the Rouse model is appropriate for dense polymers with screened hydrodynamic interactions. Detailed justification of this model for polymer melts is given in the reference.[17] In the case of large number of modes, $m \gg 1$, the continuum limit of Eq. 4 gives the analytical form of the Rouse MSD

$$\langle \Delta x^2 \rangle_{R,m} = 2D_{coil}\left(t + m\tau_s\left(\mathrm{e}^{-t/\tau_s} + \sqrt{\frac{\pi t}{\tau_s}}\mathrm{Erf} \times \left(\sqrt{\frac{t}{\tau_s}}\right) - 1\right)\right) \tag{5}$$

The Fourier transform of Eq. 5 gives the power spectrum of particle displacement fluctuation $I(\omega)$ that is related to VAS as $D(\omega) = \omega^2 I(\omega)$ giving the VAS of segmental motion according to the Rouse model as

$$D(\omega)_{R,m} = D_{coil}\left[1 + m\sqrt{\frac{\tau_m\omega}{8}}\left(\tan^{-1}\left(1 + \sqrt{\frac{2}{\tau_m\omega}}\right) - \tan^{-1}\left(1 - \sqrt{\frac{2}{\tau_m\omega}}\right) + \coth^{-1}\left(\frac{1 + \tau_m\omega}{\sqrt{2\tau_m\omega}}\right)\right)\right] \tag{6}$$

Figure 1 shows its plot that starts at $D(0) = D_{coil}$ and goes initially with the $\sqrt{\omega}$-dependence to end up with the asymptotic plateau $D(\infty) = D_{coil}(1 + m^2)$ at high frequencies, which is a consequence of the inertia-free approximation of the Langevine equation. Certainly, the spectrum of the velocity autocorrelation function will approach zero at very high

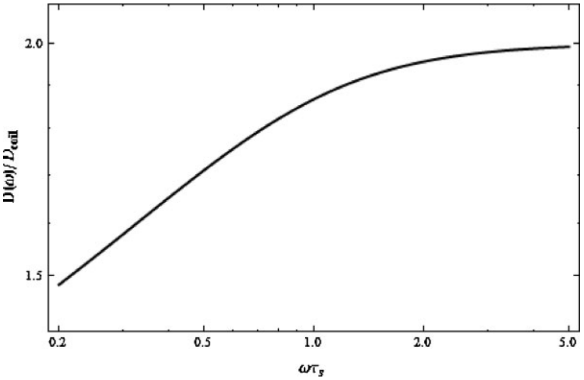

Figure 1.
Velocity autocorrelation spectrum of polymer segmental motion according to the Rouse model.

frequencies, if one takes into account the contributions from inertia term in the Rouse model. The assumption of infinite number of Rouse modes, $m \to \infty$, which is commonly used to get $\langle \Delta x^2 \rangle \sim \sqrt{t}$ dependence, leads to an infinite VAS at high frequencies. Computer simulation of the time dependence of the Rouse segmental velocity correlation function,[18] roughly agrees with the time dependence obtained with the Fourier transformation of VAS, Eq. 6.[19]

Reptation-tube Model

For long chains (high molecular-weight polymers), the presence of entanglements leads to the well-known reptation mechanism[2,3] in which, due to strong inter-chain interactions, the motion of a particular chain is constrained within an imaginary tube formed by the surrounding matrix and defined by the overall contour of the chain under consideration. The reptation model takes into account the interpenetration of each polymer coil by a large number of neighboring chains resulting in the entanglement effects. Here, the segmental diffusion resembles snake like motion in a virtual tube formed by the entanglement points. Such motion of chain link among entangled macromolecules brings about three qualitatively different distinguishable regimes, corresponding to different time scales:

- At short times, topologic constraints do not affect the segmental motion on the scales smaller than the characteristic diameter of the tube, d, and the chain section between entanglements experiences a classical Rouse dynamics but with the restricted the number of modes k. The MSD is given by $\langle \Delta x^2 \rangle_{R,k}$.
- When segmental MSD reaches d^2, we cannot neglect the topological constraints any longer. Tube inhibits motion of a link in the direction perpendicular to the polymer primitive path, i.e. tube axis, but the motion along the tube continues in the Rouse mode. Because of the Gaussian statistics of the primitive path on the scale exceeding d, one dimensional analog of the Rouse motion along the tube gives MSD as $d\sqrt{\langle \Delta x^2 \rangle_{R,m}}$. Here, Rouse modes of the whole chain play role.
- When MSD is greater than the chain size, the first term of the Rouse motion in Eq. 4 dominates the self-diffusion of the chain as a whole.

A number of modified versions of the tube/reptation model have been suggested in the literature (cited and explained in the reference[15]). Here we are dealing with very simplified model, in which the segmental MSD changes from the Rouse type of motion $\langle \Delta x^2 \rangle_s = \langle \Delta x^2 \rangle_{R,k}$ at short times into constrained MSD along the tube $\langle \Delta x^2 \rangle_s = d\sqrt{\langle \Delta x^2 \rangle_{R,m}}$, and then into $\langle \Delta x^2 \rangle_s = 2D_{coil}t$ at long times. By adjusting the five parameters: D_{coil}, characteristic time τ_m, number of modes of the entangled chain section k, number of modes of the whole polymer m, and the diameter of tube d, we can get the overall time dependence just by using Eq. 5. Its evolution from one regime of motion into another is shown in Figure 2. By the Fourier transform of MSD of different regimes of motion, we can obtain VAS of entangled polymer[19] as in the case of Rouse model. Proper parameter adjustment gives VAS of entangled polymer by piecewise bonding of VAS of different regimes as shown in Figure 3.

Experimental Part

Despite the many successes and widespread popularity of the reptation theory, the debate regarding its validity has continued for a number of reasons. The reasons concern the difficulty in finding an experimental technique capable of measuring MSD with the necessary range of time and distance scales. Neutron scattering experiments have provided access at distances below and just beyond the tube diameter, while NMR field gradient measurements have revealed anomalous diffusion just below the polymer end-to-end to displacements as shown by the measurement in semidilute solutions of high molar mass polystyrene.[20,21] However,

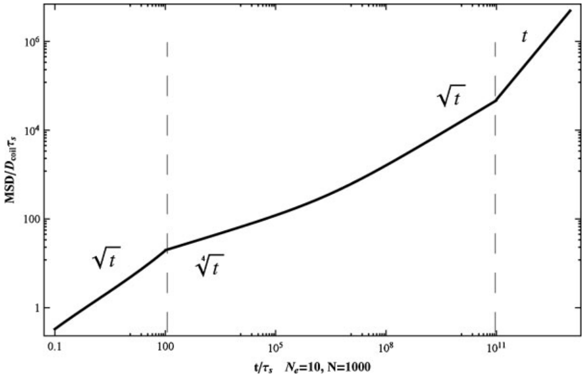

Figure 2.
Time dependence of segmental mean squared displacement of an entangled polymer chain calculated with the use of Eq. 5.

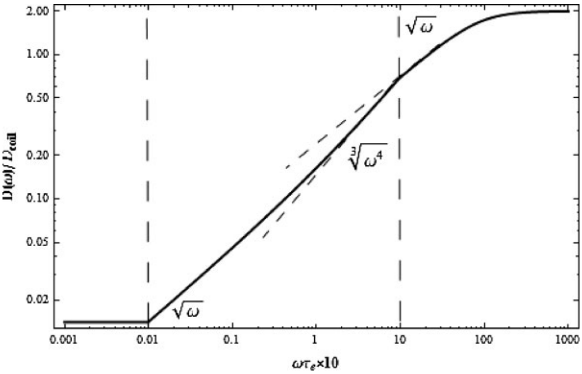

Figure 3.
Segmental velocity autocorrelation spectrum of an entangled polymer chain.

estimating segment diffusion with the aid of the tube/reptation model based on such data leads to unrealistic predictions. The predicted segment displacements tend to be much too large.[15] In the paper,[22] the formation of spin-echoes in the Carr-Purcell-Meiboom Gill NMR experiment on rubbery polybutadiene, which contains 99% cis-l,4 double bonds, has been studied as a function of inter-pulse spacing. The decay of magnetization during the CPMG pulse sequence diverged strongly from the decay of magnetization observed in free precession, despite an extremely uniform external magnetic field. Such differences between the FID and the responding echoes train in a CPMG sequence was first reported in a study of molten polyethylene.[23] Kimmich[15] suggested that the local field inhomogeneities within the sample that arise from the presence of voids in the bulk sample lead to this difference. Thus, authors in reference[22] explain the observed dependence of CPMG signals on the inter-pulse spacing by a sort of restricted diffusion in a tube as capillary. However at that time, they were not aware that the applied sequence directly provides VAS of polymer segmental motion as we demonstrate here. Figure 4 shows the plot of their data as a function of reciprocal time of RF-pulse spacing. This is the velocity autocorrelation spectrum of polybutadiene that decreases from almost linear ν-dependence at frequencies close to 5 kHz into $\sqrt{\nu}$-dependence at about 1 kHz. As shown in Figure 3, this behavior is typical for the diffusive reptation-like motions in a tube. However, the spectrum drop at 500 Hz, which is bigger than the experimental error, could indicate motion described by n-renormalized Rouse models,[16,17] in which the decay of normal mode autocorrelation functions differs for the long- and short-wave modes.

In the MGSE measurement of self-diffusion in gel systems, we intended to use VAS of water for the purpose of calibration at first. The obtained VAS of water exhibits a very distinct low-frequency decrease in the range below 2 kHz as shown in Figure 5. Identical measurements of other liquids: nitrobenzene, toluene and ethanol that yielded a flat VAS in this low frequency range, rule out an eventual systematic error. We ruled out possibility of water heating by a high duty cycle of RF pulses by performing the measurements with RF-pulse trains of different duration obtaining identical frequency dependencies. On Figure 5, the low frequencies part VAS of water at 4 °C and 20 °C have nearly

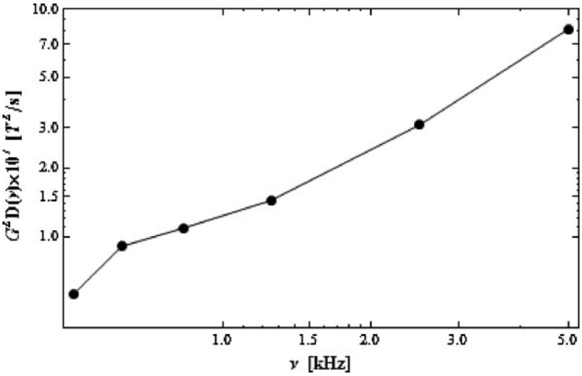

Figure 4.
By considering the CPMG measurements of BR1220 polybutadiene from the reference[22] as the measurement with the MGSE method (CPMG and internal gradients), VAS of polybutadiene at 380 K has a frequency dependence similar to that of the diffusive reptation-like motions of entangled polymer in a "tube". Deviation at low frequency might be related to the nonexponential behavior of the mode relaxation times.[17] Experimental error is about 5%.

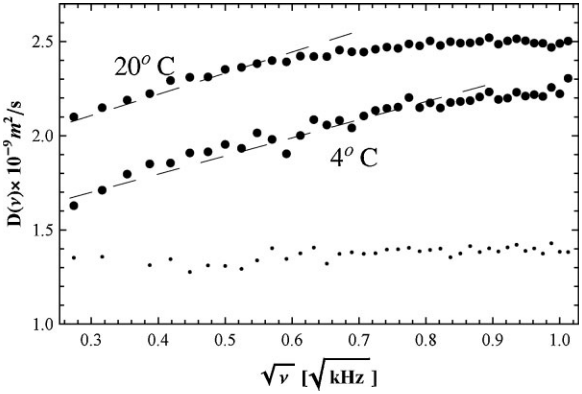

Figure 5.
Low frequency part of water velocity correlation spectra at 20^o C and at 4^o C, measured by MGSE technique, show $\sqrt{\nu}$-dependence that speaks of polymer like motion in the hydrogen bond network of water. Measurements of ethanol at 20°C (small dots) are for comparision.

$\sqrt{\nu}$-dependence. According to Eq. 6, this may indicate that a chainlike structure is formed in water with the dynamics similar to polymer Rouse normal modes. Recent dielectric measurement of water[24] also shows an anomalously slow Debye-like relaxation process, which is believed to be caused by a collective motion of hydrogen-bonded structures similar to polymer-like-dynamics. According to Eq. 6, a steeper slope of $D(\sqrt{\nu})$ at $4\,^\circ$C compared to that at $20\,^\circ$C speaks about the longer chains of connected water molecules at low temperatures.

Conclusion

The new NMR technique of MGSE, which can provide data on polymer chain translational motion on time scale to about a few μs by measuring the spectrum of segmental velocity autocorrelation, is expected to be an important tool for the investigation of polymer dynamics. Analysis of measurement on polybutadiene shows the frequency dependence that is typical for the reptation-like motion of the polymer in a tube, while the result of measurement of bulk water opens an interesting question about the dynamics within the network-like structure of hydrogen bonds.

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