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Chain dynamics in entangled polymers: Power laws of the proton and deuteron spin-lattice relaxation dispersions

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Chain modes of entangled polymer melts can directly be probed in a frequency range 10^2 Hz $< \nu < 10^8$ Hz with the aid of field-cycling proton or deuteron relaxometry. The frequency dispersion of proton spin-lattice relaxation universally shows crossovers between the power laws $T_1 \propto \nu^{0.5 \pm 0.05}$ (region I), $T_1 \propto \nu^{0.25 \pm 0.05}$ (region II), and $T_1 \propto \nu^{0.45 \pm 0.05}$ (region III) from high to low frequencies. Regions I and II are identified as limits of a theory based on the renormalized Rouse model assuming intrasegment dipolar interactions. Region III does not appear in distinct form in the deuteron T_1 dispersion of perdeuterated chains. It is inferred that proton relaxation in region III is influenced by intersegment interactions which are negligible with deuterons. A corresponding formalism is given. The comparison with the experimental data suggests some multi-chain correlation of the displacement dynamics. © 1998 American Institute of Physics.
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I. INTRODUCTION

Proton and deuteron field-cycling NMR relaxometry¹ of melts of entangled polymers reveals different power laws of the frequency dependence of the spin-lattice relaxation time T_1 in a range of 10^2 Hz $< \nu < 10^8$ Hz (in combination with conventional high-field methods).^{2,3} In our previous papers we have shown that these power laws reflect the characteristics of collective chain dynamics.³⁻⁵

At frequencies $\omega \ll \tau_s^{-1}$, where τ_s^{-1} is the fluctuation rate within a Kuhn segment, the following crossovers of the proton T_1 dispersion have been found with decreasing frequency: $T_1 \propto \omega^{0.5 \pm 0.05}$ (region I), $T_1 \propto \omega^{-0.25 \pm 0.05}$ (region II), $T_1 \propto \omega^{-0.45 \pm 0.05}$ (region III). Note that none of these power laws fits to de Gennes' $\nu^{3/4}$ prediction of 1971.⁶

The crossover frequencies depend on the polymer species and the temperature. Figure 1 shows the T_1 frequency dispersion of a polybutadiene melt as an example where all three regions appear in our frequency window with the same sample albeit at different temperatures.

In our previous work we have elucidated that the power laws in regions I and II can be derived from the renormalized Rouse theory⁷ anticipating that *intrasegment* dipolar spin interactions dominate.^{4,5} However, the power law of region III could not be explained on this basis. In the present study we demonstrate experimentally and theoretically that *intersegment* spin interactions become important at low frequencies as well (typically $\nu < 10^5$ Hz), and that the power law found in region III is an effect of the particularly slow fluctuations intersegment dipole-dipole interactions are subject to.

In the experiments to be described in the following the frequency dependencies of proton and deuteron spin-lattice relaxation of polymers and their perdeuterated counterparts of equivalent chain lengths are compared. Proton relaxation is dominated by dipole-dipole coupling. That is, there are

contributions from intra- as well as intersegment dipole pairs. This is in contrast to deuteron relaxation which essentially is a single-particle mechanism: It is governed by the coupling of the nuclear quadrupole moments to the local (intrasegment) electric field gradients. Note that our study refers to relaxation of deuterated chains rather than of undeuterated chains diluted in a deuterated matrix.⁸

II. MATERIALS AND INSTRUMENTS

With one exception the samples were purchased from Polymer Standard Services, Mainz, Germany or Polyscience, Eppelheim, Germany. The polydispersities of undeuterated 1,4-polybutadiene (PB_H) with weight-averaged molecular masses $M_w = 65500$ and $M_w = 400000$ were specified as $M_w/M_n = 1.01$. The partially deuterated counterpart (PB_D, $M_w = 360000$, $M_w/M_n = 1.04$) was a gift from S. Hafner, MPI Mainz. Comparative studies of intra- and intersegment effects were also carried out with perdeuterated polyethyleneoxide (PEO_D, $M_w = 460\,000$, $M_w/M_n < 1.4$) and undeuterated polyethyleneoxide (PEO_H, $M_w = 438\,000$, $M_w/M_n < 1.2$), respectively. All samples were kept in vacuum over several days before use in order to remove any volatile constituents. Especially with PEO samples the uptake of atmospheric humidity may influence the segmental friction coefficient, although the qualitative behavior of the chain modes is not affected to our experience.

Apart from conventional high-field NMR spectrometers, two homemade field-cycling instruments suitable for ¹H and ²H relaxometry were used for the examination of the low-field spin-lattice relaxation dispersion. The ²H field-cycling relaxometer is operated with a oil-cooled copper magnet coil with a 23.5 mm room temperature bore. The inductivity is 3.2 mH. The magnetic-field homogeneity within the sample volume of 1 to 1.5 cm³ is better than $\pm 10^{-4}$ of the nominal field value. The zero ("earth") field in the magnet coil was

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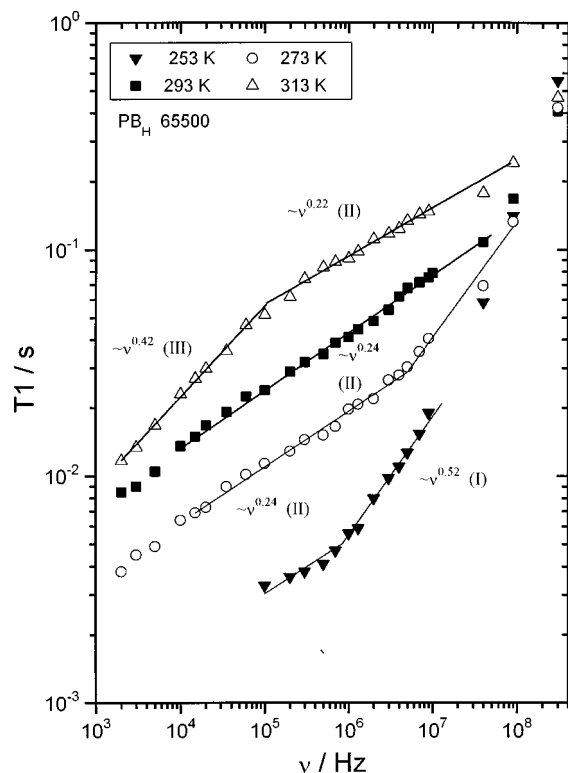


FIG. 1. Frequency dependence of the proton spin-lattice relaxation time of polybutadiene melts ($M_w = 65500$) at various temperatures. Regions I, II and III of the proton spin-lattice relaxation (Ref. 3) are indicated. The data above about 3×10^7 Hz are influenced by fluctuations within the Kuhn segments.

compensated by correction coils. The detection flux density is 1.5 T corresponding to 60 MHz proton or 9 MHz deuteron resonance frequency. Switching the field down, the relaxation interval is reached within $\pm 10\%$ in 1.5 ms. Corresponding to the field homogeneity, the detection field is stabilized within $\pm 10^{-4}$ of the resonance value in 2.5 ms after triggering the field rise. These specifications permitted us (i) to measure low-field relaxation times even shorter than 1 ms and (ii) to accumulate signals in the phase sensitive detection mode. The latter is a crucial prerequisite for deuteron field-cycling relaxometry.

The total accessible Larmor frequency ranges are 10^3 Hz $< \nu < 3 \times 10^8$ Hz for protons and 3×10^2 Hz $< \nu < 4 \times 10^7$ Hz for deuterons. The lower limits depend on the spin-interaction induced local fields within the samples, of course. Within the experimental error, all relaxation curves were found to decay monoexponentially over at least one decade.

III. EXPERIMENTAL RESULTS

Figures 2 and 3 show the proton and deuteron spin-lattice relaxation dispersions of polyethylene oxide and polybutadiene. In the deuterated cases there is no crossover from region II to III as observed at about 10^5 Hz with proton relaxation. This suggests that region III represents a limit in which intersegment dipole-dipole interactions come into play in addition to the intrasegment contributions. We also note that the deuteron T_1 dispersion tends to be slightly

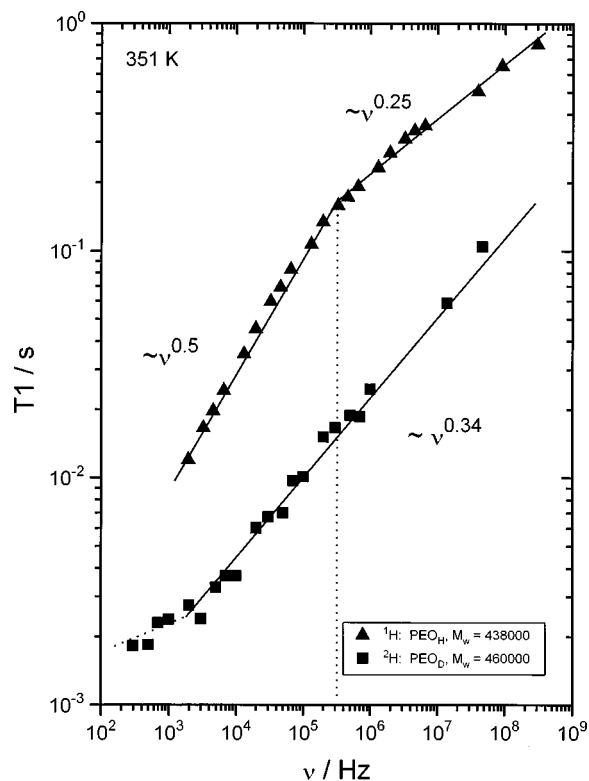


FIG. 2. Frequency dependencies of the proton and deuteron spin-lattice relaxation times of polyethyleneoxide PEO_H and PEO_D , respectively. The vertical dotted line indicates the crossover between regions II and III. The deuteron data below 3×10^3 Hz are affected by the crossover to the low-field case of nuclear quadrupole resonance.

steeper than in the proton region II case. The variation of the deuteron T_1 dispersion slope at very low frequencies ($\nu < 10^4$ Hz) is attributed to the crossover from the high- to the low-field nuclear quadrupole resonance case. The low-frequency plateau arising on these grounds has no relevance for chain dynamics.

IV. THEORETICAL DESCRIPTION

Let us now discuss the influence of intersegment dipole-dipole interactions on the proton spin-lattice relaxation dispersion. In general, the spin-lattice relaxation rate mediated by dipolar coupling is¹

$$R_1 \equiv \frac{1}{T_1} = \frac{9}{8} \gamma_p^4 \hbar^2 \sum_{\ell} [J_{k\ell}^{(1)}(\omega) + J_{k\ell}^{(2)}(2\omega)]. \quad (1)$$

The subscript ℓ runs over all dipoles interacting with the reference dipole indicated by the subscript k . The intensity functions $J_{k\ell}^{(1)}(\omega)$ and $J_{k\ell}^{(2)}(2\omega)$ are given as the Fourier transforms of the autocorrelation functions of the spatial terms of the spin interaction Hamiltonian,

$$G_{k\ell}^{(m)}(t) = d_m \left\langle \frac{Y_{2,m}^*(\varphi_{k\ell}(t), \vartheta_{k\ell}(t))}{r_{k\ell}^3(t)} \times \frac{Y_{2,m}(\varphi_{k\ell}(0), \vartheta_{k\ell}(0))}{r_{k\ell}^3(0)} \right\rangle (m=1,2). \quad (2)$$

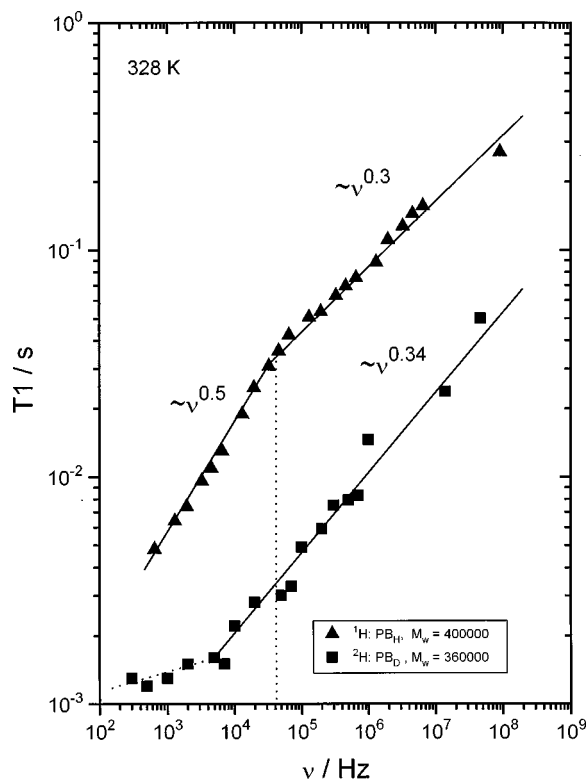


FIG. 3. Frequency dependencies of the proton and deuteron spin-lattice relaxation times of polybutadiene PB_H and PB_D, respectively. The vertical dotted line indicates the crossover between regions II and III. The deuteron data below 5×10^3 Hz are affected by the crossover to the low-field case of nuclear quadrupole resonance.

These functions of the second-order spherical harmonics, $Y_{2,1}$ and $Y_{2,2}$, depend on the polar coordinates, $r_{k\ell}$, $\varphi_{k\ell}$, $\vartheta_{k\ell}$ of the vector connecting the dipoles k and ℓ . The constants are $d_1 = 8\pi/15$ and $d_2 = 32\pi/15$.

The total spin-lattice relaxation rate consists of contributions arising from intra- and from intersegment interactions, that is, $R_1 = R_1^{\text{intra}} + R_1^{\text{inter}}$. The intersegment part may be characterized by effective intersegment dipolar correlation functions of dipole k given as the sum over all intersegment contributions

$$G_{\text{inter}}^{(m)}(t) = \sum_{\ell \neq k} G_{k\ell}^{(m)}(t) \quad (m=1,2). \quad (3)$$

The subscript ℓ addresses a nuclear dipole on a polymer segment neighboring to the “tagged segment” on which the “tagged nucleus” k is residing. In the continuum limit these functions read

$$G_{\text{inter}}^{(m)}(t) = d_m \rho_s \int d^3r g(r(0)) \times \left\langle \frac{Y_{2,m}^*(t)}{r^3(t)} \frac{Y_{2,m}(0)}{r^3(0)} \right\rangle \quad (j=1,2), \quad (4)$$

where ρ_s is the spin number density, and r is the distance of a intersegment dipole–dipole pair. The intersegment pair correlation function may be approached by

$$g(r) \approx \begin{cases} 0 & \text{if } r \leq \sigma \\ 1 & \text{otherwise} \end{cases}. \quad (5)$$

The nearest neighbor distance of intersegment dipoles is designated by σ . The number density of dipoles “external” to the tagged segment thus is $\rho_s g(r)$.

Let us now refer to a coordinate frame with axes parallel to those of the laboratory frame but with the origin fixed at the position of the tagged dipole k . We define the initial distance vector to the “external” dipole ℓ , $\mathbf{r}_0 \equiv \mathbf{r}(0)$. In a time t the distance vector becomes

$$\mathbf{r}(t) = \mathbf{r}_0 + \tilde{\mathbf{r}}(t), \quad (6)$$

where $\tilde{\mathbf{r}}(t)$ is the displacement vector of the “external” dipole ℓ in the frame moving along with the position of dipole k .

The initial distance, $r_0 \equiv r(0)$, is a natural measure for the length scale on which non-negligible values of the correlation function $G_{\text{inter}}^{(m)}(t)$ can be expected. Clearly, reasonable values of r_0 are between the nearest-neighbor distance σ and the limit where dipole–dipole interaction becomes negligible anyway. On the other hand, the ensemble average in Eq. 4 becomes smaller and smaller with increasing root mean squared (rms) relative displacements of dipole ℓ in the interval t . The relevant range is hence restricted to $\sqrt{\langle \tilde{r}^2(t) \rangle} < r_0$.

The autocorrelation function in Eq. 4 may consequently be approached by the ansatz

$$\left\langle \frac{Y_{2,m}^*(t)}{r^3(t)} \frac{Y_{2,m}(0)}{r^3(0)} \right\rangle \approx \left| \frac{Y_{2,m}(0)}{r_0^3} \right|^2 P(t) = \frac{1}{r_0^6} P(t), \quad (7)$$

where $P(t)$ is the probability that dipole ℓ is in a spherical volume $V \propto r_0^3$ around its initial position after a time t , i.e., that the relative displacement of nucleus ℓ obeys $\tilde{r}(t) < r_0$. In the limit $\langle \tilde{r}^2(t) \rangle \ll r_0^2$, one expects $P(t) \approx 1$. In the opposite limit, $\langle \tilde{r}^2(t) \rangle \gg r_0^2$, the probability $P(t)$ decays according to $P(t) \approx r_0^3 / \langle \tilde{r}^2(t) \rangle^{3/2}$, where the denominator is proportional to the volume of a sphere of a radius equal to the relative rms displacement $\langle \tilde{r}^2(t) \rangle^{1/2}$. For the latter limit we have assumed that the probability density for finding $\tilde{r}(t) < \sqrt{\langle \tilde{r}^2(t) \rangle}$ is roughly constant. This ansatz obviously implies that the local segment displacements are *isotropic* as anticipated in the Rouse⁹ and renormalized Rouse theories.⁷

The two limiting expressions for $P(t)$ are already implied in

$$P(t) \approx \frac{r_0^3}{[r_0^2 + \langle \tilde{r}^2(t) \rangle]^{3/2}}. \quad (8)$$

Inserting Eqs. 5 and 8 into Eq. 4 and expressing the mean squared segment displacement $\langle \tilde{r}^2(t) \rangle$ relative to the tagged segment by the actual, laboratory frame mean squared segment displacement $\langle r_s^2(t) \rangle = \frac{1}{2} \langle \tilde{r}^2(t) \rangle$, leads to

$$\begin{aligned}
 G_{inter}^{(m)}(t) &\approx d_m \rho_s \int_0^\infty \frac{1}{r_0^6} \frac{r_0^3}{[r_0^2 + 2\langle r_s^2(t) \rangle]^{3/2}} g(r_0) r_0^2 dr_0 \\
 &= d_m \rho_s \int_0^\infty \frac{r_0^3}{r_0 [r_0^2 + 2\langle r_s^2(t) \rangle]^{3/2}} dr_0 \\
 &\approx \frac{d_m \rho_s \ln[2\langle r_s^2(t) \rangle / \sigma]}{\langle r_s^2(t) \rangle^{3/2}}.
 \end{aligned} \quad (9)$$

Here we have assumed that the mean squared displacements of different segments are independent from each other for simplicity. However, a detailed comparison of the quantitative T_1 values in region III shows that some correlation exists. That is, $\langle r_s^2(t) \rangle > \frac{1}{2} \langle \tilde{r}^2(t) \rangle$. This important finding will be analyzed in more detail in a forthcoming paper.¹⁰

The logarithmic term in Eq. 9 varies slowly with time so that this correlation function scales as

$$G_{inter}^{(m)}(t) \approx \frac{d_m \rho_s}{\langle r_s^2(t) \rangle^{3/2}}. \quad (10)$$

In our previous work⁵ two expressions for the mean-squared segment displacement in the low-mode number limit were derived:

$$\langle r_s^2(t) \rangle \approx 0.18 \frac{b^2}{\sqrt{\psi}} \left(\frac{t}{\tau_s} \right)^{3/8} \quad \text{and} \quad \langle r_s^2(t) \rangle \approx 0.2b^2 \left(\frac{t}{\tau_s \psi} \right)^{2/5}, \quad (11)$$

where b is the Kuhn segment length and ψ is a dimensionless parameter. Inserting these power laws into Eq. 10 and evaluating Eq. 1 for the intersegment contribution suggests

$$T_1^{inter} \propto \nu^{0.4 \dots 0.44}. \quad (12)$$

It is now evident that deuteron spin-lattice relaxation which is of an entirely intrasegment nature cannot show any crossover from region II to region III. On the other hand, proton spin-lattice relaxation reflecting intra- as well as intersegment contributions reveals distinct regions II and III as the limits where the intra- and intersegment rates dominate, respectively. Intersegment interactions dominate at low frequencies because they are fluctuating more slowly than intrasegment interactions. The origin of such displacements are segment displacements over relatively large distances. At high frequencies, these fluctuations virtually do not contribute so that the relaxation mechanism essentially is of an intrasegment nature.

V. DISCUSSION

The comparison of proton and deuteron field-cycling relaxometry data shows that intersegment dipole-dipole interactions influence the proton spin-lattice relaxation dispersion of entangled-polymer melts. This is the basis for the explanation of dispersion region III which revealed itself in our previous proton relaxometry studies.

The results are reasonably well accounted for on the basis of the renormalized Rouse theory. That is, all three T_1 frequency dispersion regions discovered so far in isotropic melts of entangled polymers are in full accordance with predictions derived from this concept.

These conclusions are of interest for two reasons: First, it was hitherto tacitly assumed that the spin-lattice relaxation dispersion of polymers is a matter of *intra*segment spin interactions in the whole frequency range, whereas it is now evident that this holds true only in the upper Larmor frequency range. Second, the intersegment relaxation contribution is characteristic for the type of chain dynamics in a different way than that of intrasegment relaxation because interchain correlations play a role. Information on this basis is therefore expected to be decisive in tests of polymer theories.¹¹ It also appears that nuclear magnetic relaxation dispersion would be an ideal field for molecular dynamics studies which provides access to longer and longer time scales.¹²

In a forthcoming paper we will present the twice-renormalized Rouse theory^{13,10} which provides an even more precise understanding of the power laws which became evident in field-cycling relaxometry studies. Further attention will be paid to the fact that the slope of the deuteron relaxation data is somewhat steeper than that of the protons in region II. Actually the twice-renormalized Rouse theory predicts a frequency dependence $T_1 \propto \omega^{1/3}$ for intrasegment spin interactions in that region as observed in our deuteron relaxation experiments.

An apparent shortcoming of the renormalized as well as of the twice-renormalized Rouse theories is that they cannot account for the viscoelastic plateau of stress relaxation. These theories are single-chain concepts where concerted multi-chain dynamics is not considered explicitly. On the other hand, it is an unproven hypothesis underlying most polymer dynamics theories so far that single-(tagged)-chain relaxation can in principle imply all information relevant for the dynamic behavior of an entangled polymer matrix.

One of the conclusions of this work is that polymer dynamics is subject to concerted interchain effects which cannot be inferred from single-chain theories. Stress relaxation intrinsically probes concerted chain dynamics, whereas deuteron field-cycling relaxometry reflects processes single segments are suffering. The problem is that multi-chain theories are not available at present. On the other hand, it still is an open question whether single-chain theories can account for both classes of phenomena at one time in principle.

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- ¹R. Kimmich, *NMR: Tomography, Diffusometry, Relaxometry* (Springer-Verlag, Berlin, 1997).
- ²H. W. Weber and R. Kimmich, *Macromolecules* **26**, 2597 (1993).
- ³R. Kimmich, N. Fatkullin, H. W. Weber, and S. Stapf, *J. Non-Cryst. Solids* **172–174**, 689 (1994).
- ⁴N. Fatkullin, R. Kimmich, and H. W. Weber, *Phys. Rev. E* **47**, 4600 (1993).
- ⁵N. Fatkullin and R. Kimmich, *J. Chem. Phys.* **101**, 822 (1994).
- ⁶P. G. de Gennes, *J. Chem. Phys.* **55**, 572 (1971).
- ⁷K. S. Schweizer, *J. Chem. Phys.* **91**, 5802 (1989).
- ⁸J. Collignon and H. Sillescu, *J. Polym. Sci., Polym. Lett. Ed.* **18**, 669 (1980).
- ⁹P. E. Rouse, *J. Chem. Phys.* **21**, 1272 (1953).
- ¹⁰N. Fatkullin and R. Kimmich (in preparation).
- ¹¹M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
- ¹²S. W. Smith, C. K. Hall, and B. D. Freeman, *J. Chem. Phys.* **104**, 5616 (1996).
- ¹³N. Fatkullin, Thesis (second dissertation), University of Kazan, 1995.