Microscopic Dynamics and Topological Constraints in Polymer Melts: A Neutron-Spin-Echo Study

D. Richter,[1] B. Ewen,[2] B. Farago,[1] and T. Wagner[2]

[1]*Institut Laue-Langevin, 38042 Grenoble, France*
[2]*Max-Planck-Institut für Polymerforschung, 6500 Mainz, Federal Republic of Germany*
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We have studied the dynamic self- and pair-correlation function on appropriately labeled polydimethylsiloxane melts. For small decays of the scattering function or for small values of the Rouse scaling variable both the results for self and pair correlations are in very good agreement with the Rouse model. For larger values, strong deviations from Rouse dynamics are found indicating the importance of topological constraints. However, no indication for the existence of an intermediate length scale corresponding to the tube diameter of the reptation concept is observed.

One of the major still unsolved problems in the dynamics of polymers concerns the nature of the molecular motion in dense systems. Intuitively it is clear that topological constraints mutually imposed on each other by the different moving chains must play a decisive role in determining the motional characteristics of the chains. The most popular model in this area is the reptation model which describes the topological hindrance in terms of a tube around the contour of a given chain. Chain motion is then only possible inside a spatially fixed tube, the lifetime of which may reach macroscopic times.[1,2] While viscoelastic theory based on such a reptation concept was very successful to describe rheological properties,[3,4] microscopically the situation is much less clear. Theoretically, one expects a crossover from Rouse relaxation at times shorter than that which a chain segment needs to equilibrate across the tube diameter, to a so-called local reptation regime where density fluctuation equilibrates along the fixed tube. The most important feature of this microscopic reptation concept is the introduction of a new intermediate length scale in between the chain dimension and the elementary length of a polymer segment. Up to now microscopic dynamic studies of chain relaxation revealed the basic features of Rouse relaxation (characteristic frequency $\Omega_R \sim Q^4$) although deviation in the spectral line shape appeared to be evident.[5,6]

In this paper we present a systematic study of the dynamic structure factor for polymer motion in melts. For the initial relaxation of the scattering function for both pair and self correlations we find an excellent agreement with Rouse dynamics. For stronger relaxation pronounced deviations from Rouse behavior are observed. The measured slower relaxation may be attributed to the presence of topological hindrance. However, other than assumed by the tube models, the data bear no evidence for the existence of a new intermediate length scale such as the tube diameter or the entanglement distance.

The theoretical description of chain motion in polymer melts distinguishes three different time regimes separated by corresponding crossover times τ_s and τ_t.

(i) At short times ($t < \tau_s$) the chains do not realize entanglement constraints and their motion is controlled by random thermal and entropic forces. In this Rouse regime the mean-square displacement of a chain segment increases proportionally to the square root of time. In the Gaussian approximation the segmental self-correlation function relates directly to the mean-square segment displacement yielding a particularly simple intermediate scattering function[7]

$$S_{\text{self}}(Q,t) = \exp[-Q^2(W\sigma^4 t/9\pi)^{1/2}]. \quad (1)$$

Thereby Q is the momentum transfer during scattering, σ denotes the segment length, and $W = 3kT/\zeta_0\sigma^2$, where ζ_0 is a segmental friction coefficient, k is Boltzmann's constant, and T is the temperature. The pair-correlation function of a Rouse chain describing the interferences between the scattering from different segments is more complicated.[7] We note, however, that S_{self} scales with the universal "Rouse" variable $u = Q^2(W\sigma^4 t)^{1/2}$. Besides the size of the chain R_g, there exists only *one* length scale, namely, the length of the chain segment σ.

(ii) At intermediate times ($\tau_s < t < \tau_t$) the viscoelastic data from long chain molecules show that the dynamic modulus exhibits a plateau regime indicating elastic behavior. This elasticity may be understood in terms of a transient polymer network, the mesh size of which is given by the distance between entanglements or topological constraints. The most famous approach modeling these topological constraints is the reptation model. It assumes that these constraints restrict the chain motion to a tube along the chain contour.[1] At intermediate times in the so-called local reptation regime,[2] the chain relaxes within the spatially fixed tube. Using the Doi-Edwards theory, which generalizes the reptation concept to a theory of viscoelasticity, the tube diameter can be evaluated from essentially the plateau modulus[8] $d_T^2 = \frac{4}{5} \times (6R_g^2/M)(\rho LkT/G_N^0)$, where G_N^0 is the plateau

modulus, ρ is the polymer density, M is the molecular mass, and L is Avogadro's number. For polydimethylsiloxane (PDMS), e.g., this consideration yields $d_T \sim 50$ Å. Thus there is considerable lateral freedom for the chain motion. The crossover time τ_s from the Rouse to the local reptation regime may be estimated by taking the slowest Rouse relaxation time for a chain whose end-to-end distance R_E corresponds just to the tube diameter[9] $\tau_s = d_T^4/2W\sigma^4\pi^2$. Concerning the scattering function, since the tube diameter is a new dynamic length scale, it is expected to invalidate the scaling with the Rouse variable u. In the local reptation regime the density fluctuations of a given chain equilibrate within the fixed tube. Consequently, the spatial segmental positions stay correlated and the scattering function does not decay completely but contains a time-independent contribution related to the size of the tube. Neglecting the short-time Rouse regime, de Gennes has calculated the coherent scattering function for local reptation:[2]

$$S(Q,t) = \left[1 - \frac{Q^2 d_T^2}{36}\right] + \frac{Q^2 d_T^2}{36} \exp\left[\frac{u^2}{36}\right] \mathrm{erfc}\left[\frac{u}{6}\right]. \quad (2)$$

Equation (2) shows explicitly that $S(Q,t)$ contains a time-independent part which is related to the tube diameter and is calculated to second order in $d_T Q$.

An alternative approach to treat topological constraints was recently proposed by Ronca:[10] He describes the elastic interaction between different chains in dense systems by introducing a memory term into the Langevin equation for chain motion, the kernel of which is related to the relaxation modulus of the polymer ensemble. This *Ansatz* is also able to reproduce the main experimental results and has the future virtue that it allows a calculation of the scattering function in the crossover regime where the short-time Rouse behavior transforms into entanglement controlled motion.

(iii) For long times $(t > \tau_t)$, where τ_t is the disentanglement time, the polymer leaves its tube and the memory on the initial tube is lost. Then all intersegment correlations vanish and $S(Q,t)$ decays to zero. This time regime is outside the reach of neutrons.

Our neutron scattering investigations were performed on PDMS, a polymer which combines a very low monomeric friction coefficient ζ_0 with very high flexibility.[11] Two samples were prepared: (i) a melt from deuterated PDMS molecules $(M_w = 10^5, M_w/M_n \simeq 1.6)$ labeled at random positions along the chain. These polymers permit the investigation of the self-correlation function since the labeled sections (8 protonated for on the average 80 deuterated monomers) are small enough to be seen as a single unit at the momentum transfer of the experiment and, on the other hand, are large enough to create sufficient coherent scattering necessary for the spin-echo experiment. (ii) A deuterated melt $(M_w = 1.5 \times 10^5, M_w/M_n \simeq 1.1)$ containing 12% protonated polymers of the same molecular weight. The molecular

weight of both samples was well above the entanglement molecular weight of $M_c = 21\,000$ for PDMS.[12]

The experiments were carried out at the spin-echo spectrometer IN11 at the Institut Laue-Langevin, covering a Q range $0.02 \leq Q \leq 0.15$ Å^{-1}. Apart from resolution corrections neutron spin-echo spectroscopy measures directly the real part of the intermediate scattering function $S(Q,t)/S(Q,0)$, the time being proportional to the applied Larmor precession field H.[13] In a first experiment we measured at a neutron wavelength $\lambda = 8.56$ Å achieving a resolution of 17 neV ($1/e$ decay). Figure 1 presents spin-echo results for the self- and pair-correlation function from PDMS at 100 °C. The data are plotted versus the scaling variable of the Rouse model $u = Q^2(W\sigma^4 t)^{1/2}$. The solid lines present the results of a fit with the appropriate Rouse self- and pair-correlation functions,[7] the only fit parameter being the "Rouse parameter" $W\sigma^4$. For both correlation functions we observe excellent agreement with Rouse dynamics. This concerns the Q as well as the time dependence: The characteristic frequencies of both sets of data follow the required Q^4 dependence; the line shape of the self-correlation function agrees well with the predicted $t^{1/2}$ power law [Eq. (1)]. Within experimental accuracy the Rouse parameters obtained from the two measurements coincide [self-correlation: $W\sigma^4 = (1.75 \pm 0.15) \times 10^{13}$ Å^{4}s^{-1}; pair correlation: $W\sigma^4 = (1.85 \pm 0.05) \times 10^{13}$
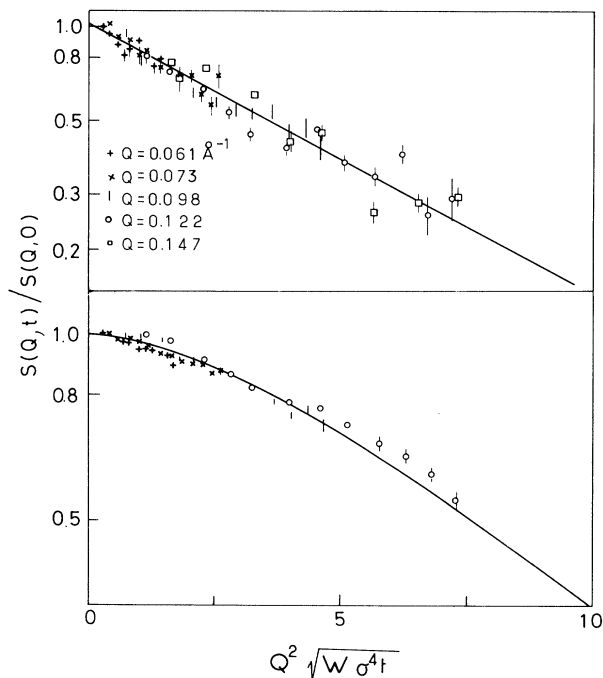

FIG. 1. Upper part: Neutron-spin-echo data for the self- and pair-correlation function obtained from PDMS melts at 100 °C. The data are scaled to the universal variable of the Rouse model. The symbols used refer to the same Q values in both parts of the figure.

$\text{Å}^4\text{s}^{-1}$]. The segmental friction coefficient $\zeta_0/\sigma^2 = (8.9 \pm 0.7) \times 10^5$ dyn/cm^3 derived from these microscopic data agrees well with the viscoelastic result $\zeta_0/\sigma^2 = 7.1 \times 10^5$ dyn/cm^3.[14]

In order to understand why the data presented up to now do not show any influence of entanglement constraints, we estimate the crossover time τ_s using the viscoelastically determined tube diameter $d_T = 50$ Å and the measured Rouse parameter. We obtain $\tau_s = 18$ ns somewhat larger than the experimentally covered time regime $0.35 \leq t \leq 14$ ns. Another estimate may be obtained from high-frequency measurements of dynamic modulus of PDMS performed at room temperature.[15] Rescaling the measured crossover frequency between the plateau modulus and the high-frequency Rouse regime with the ratio of the temperatures and friction coefficients, we find $\tau_s = 50$ ns also outside of our measuring range.

Using a longer neutron wavelength $\lambda = 10.94$ Å (Fourier time $t \sim \lambda^3 H$) in a second experiment we extended the experimental time range to $t_{max} = 40$ ns. Simultaneously we accelerated the polymer relaxation by heating to 200 °C. The combined measures resulted in an increase of the time scale by 1 order of magnitude. At 200 °C from mechanical data τ_s is estimated to be 20 ns while the theoretical estimate gives 7 ns. Both values

of τ_s are well within the extended experimental time range.

Figure 2 presents the characteristic frequencies $\Omega = \hbar/12 Q^4 W\sigma^4$ (Ref. 7) obtained from a fit of the data at short times ($t < 10$ ns) with the Rouse model. The inset in Fig. 3 displays the measured spectra for small values of the Rouse scaling variable u. Both figures demonstrate that at short times or small values of the scaling variable the data again agree very well with simple Rouse dynamics. For the Rouse parameter we find $W\sigma^4 = (4.2 \pm 0.1) \times 10^{13}$ Å^{4}s^{-1}. These figures further show that the experimental Q range is well within the universal regime where deviation due to local potentials are of no importance. Figure 3 displays the results obtained over the full experimental time range again using the scaling presentation. The solid line in the upper part of Fig. 3 shows the prediction of the Rouse model based
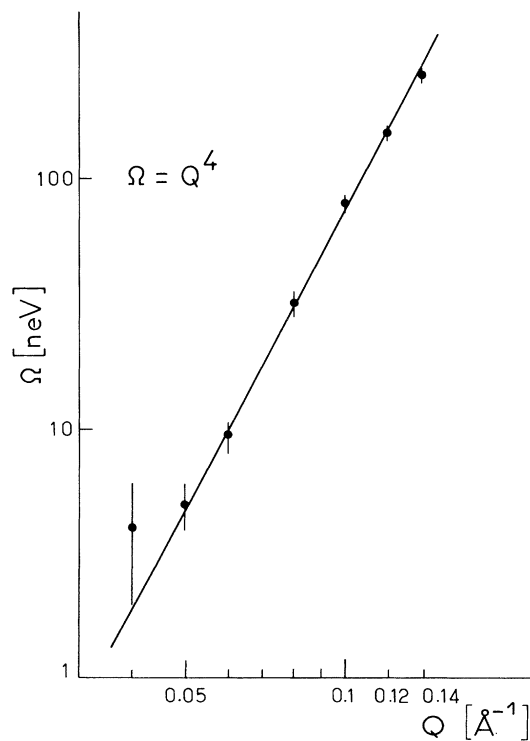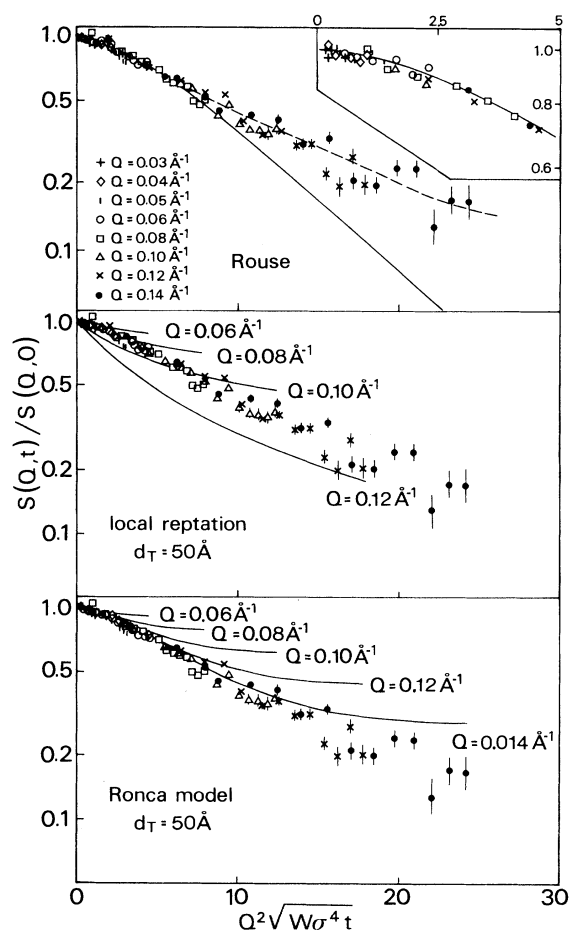

FIG. 2. Characteristic Rouse relaxation rate Ω obtained from the PDMS melt at 200 °C in the short-time regime ($t < 20$ ns). The solid line indicates the theoretical Q^4 power law.

FIG. 3. Neutron-spin-echo results from PDMS at 200 °C displayed in a scaling plot. Upper part: Comparison with the Rouse model, solid line; the dashed line serves as a guide to the eye. Inset: Behavior of the relaxation function at small values of the scaling variable. Middle part: Comparison with the local reptation model (Ref. 2) [Eq. (2)]. Lower part: Comparison with the generalized Rouse model (Ref. 11).

on the short-time behavior. While for small u we observe good agreement with the Rouse model, at higher u we see systematic deviations towards slower relaxation. Thus, qualitatively, we find additional hindrance to the polymer motion as we would expect from topological constraints. We note, however, that apparently the scaling with $Q^2(W\sigma^4 t)^{1/2}$ prevails. Thus, without applying any further model, we may state that our data bear no evidence for the existence of a further dynamic length which necessarily must destroy the Rouse scaling. In order to underline this result more quantitatively we compare the data with microscopic models. The middle part of Fig. 3 compares the model prediction of the scattering function for local reptation [Eq. (2)] with experimental results. Thereby, we have fixed the tube diameter to $d_T = 50$ Å and used the Rouse parameter determined at short times. As we see, model predictions and experimental results are incompatible. In particular, for different Q's the data do not split into different branches. As we have already mentioned earlier this Q-splitting in the model prediction originates from the additional length scale d_T. Furthermore, we observe that the model does not contain the short-time Rouse behavior. This makes it inapplicable in the crossover range between the two dynamic regimes.

The only model calculation treating explicitly the scattering function in the crossover range is Ronca's generalized Rouse model.[10] This model leads to a temporal chain localization on a length scale d_T which may be identified with the tube diameter or the distance between entanglements. At the bottom of Fig. 3 we compare the prediction of the Ronca model with our data fixing again the tube diameter to 50 Å and keeping the Rouse parameter obtained at short times. For small values of $Q^2(W\sigma^4 t)^{1/2}$ the model describes well the Rouse dynamics which for higher values of the scaling variable slows down and crosses over to a Q-dependent plateau level. Thus, the Ronca model depicts the crossover from Rouse to entanglement controlled dynamics. However, again as a consequence of the additional dynamic length d_T it predicts strong deviations from scaling with the Rouse variable—a prediction which experimentally is not confirmed.

Recent molecular-dynamics simulations on polymer melts exhibit a pronounced crossover in the time dependence of the mean-square displacement from a Rouse-type $t^{1/2}$ to a reptation-type $t^{1/4}$ behavior.[16] These calculations indicate that finite-size effects may obscure the reptation dynamics in a coherent scattering experiment. However, other than in these simulations, our chains were about 20 times longer than the average distance between entanglements $(M_E = 8100)$.[8] Therefore, the end sections can be considered as small compared to the large chain regions which, following the tube concept, should be safely trapped in the tube. For that same reason effects of constraint release should be negligible.[17] In the way that our data show the severe influence of topological constraints they are not contradictory to interdiffusion results,[18] orientation relaxation experiments on center labeled chains,[19] or recent total reflection experiments[20] which also manifest the importance of these constraints. Those experiments, however, do not test for the existence of an intermediate dynamic length scale such as the tube diameter which can only be observed directly in a dynamic experiment probing the appropriate length and time scales.

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