Direct Microscopic Observation of the Entanglement Distance in a Polymer Melt

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Using neutron spin-echo spectroscopy and rheometry, we investigated the melt dynamics of poly(ethylene-propylene) alternating copolymers. The experiments show that beyond a certain length scale the relaxation of density fluctuations within a given chain is strongly reduced. The presence of this intermediate dynamic length scale implies the existence of a well-defined entanglement distance confirming the essential assumption of the reptation concept. Its value is found to be in excellent agreement with the entanglement distance obtained from the rheological measurement.

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The most characteristic feature in the dynamics of long-chain polymer melts is the observation of a broad plateau regime in the dynamic shear modulus $G(t)$, where—$G(t)$ being independent of time—stress and strain are proportional.[1] In this time regime the polymer melt behaves like a rubber, where the elasticity arises from the entropy elasticity of the chains between the permanent crosslinks. Similarly, the plateau regime in uncrosslinked melts is explained by the assumption of long-lived topological constraints mutually imposed by the other interpenetrating chains. In analogy to the rubber, these entanglements act as temporary crosslinks. The entanglement crosslinks appear to be mainly of geometrical nature, being determined by chain contour length density and segment length of the Gaussian chains.[2] The celebrated reptation theory of viscoelasticity assumes that large-scale transverse motions are forbidden mandating snakelike motion confined in a tube along the chain profile.[3,4] The tube diameter d_T, an intermediate length between the segment length and the chain end-to-end distance, is identified as the distance between entanglements. In spite of the importance of this new dynamic length to viscoelasticity, it has never been observed directly although attempts in this direction have been made.[5-7]

Here, using polymers which have tailored to match the accessible time and momentum-transfer range of neutron spin-echo spectroscopy (NSE), we present the first direct microscopic observation of this intermediate dynamic length scale. Comparison with rheological measurements shows good agreement with an interpretation in terms of the Doi-Edwards theory.[4-8]

If the chains could intersect freely, the chain dynamics would be described as thermal motion damped via a friction coefficient ζ_0. In this so-called Rouse model, the diffusing chain segment performs a random walk on the random chain profile. This convolution of two processes leads to a mean-square segment displacement $\langle r^2(t)\rangle \cong \sigma^2(Wt)^{1/2}$, with $W=3kT/\zeta_0\sigma^2$ being the Rouse rate and σ being the segment length.[9] Besides the overall chain dimension, σ is the only length scale in the problem. Consequently, the time-dependent intermediate scattering function $S(Q,t)$ for internal chain motion is a function of only *one* variable $u=Q^2\sigma^2(Wt)^{1/2}$, where Q is the momentum transfer during scattering. Explicit expressions for the Rouse dynamic structure factors are available.[9] At short times we recently found excellent agreement with this Rouse picture for polydimethylsiloxane (PDMS).[7] On polytetrahydrofuran (PTHF) Higgins and Roots[6] observed a strong retardation of the chain relaxation compared to the Rouse structure factor. We also observed this effect at longer times in PDMS.[7] However, neither experiment confirmed the major characteristic of the reptation model, i.e., the existence of an intermediate dynamic length scale corresponding to the tube diameter. Finally, recent molecular-dynamics simulations presented evidence for the reptation mechanism in a computer experiment.[10] As we shall see in the following, the present work has confirmed these earlier perspectives on reptation[6,7,10] and firmly established the existence of the all-important intermediate dynamic length scale.

The presence of a second dynamic length scale d_T changes the scaling behavior of $S(Q,t)$. The entanglement distance or the tube diameter adds an additional dynamic length scale and is expected to cause systematic Q-dependent deviations from the Rouse scaling behavior. In the framework of reptation de Gennes derived an explicit first-order expression for $S(Q,t)$:[11]

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

$S(Q,t)$ describes the equilibration of density fluctuations along the tube (local reptation) neglecting decay due to Rouse modes of a spatial extent smaller than the tube diameter. The important feature of Eq. (1) is the factor Qd_T which introduces a new length scale. Because of the tube constraints, $S(Q,t)$ only partially decays to a certain Q-dependent fraction. The remaining "elastic" part is a consequence of long-living segment-segment correlation due to the tube confinement. The elastic part actually decays only for times longer than a terminal time τ_t after which the chain has lost its memory of its original tube.

For a quantitative analysis of scattering data originating from the crossover regime between short-time Rouse motion and local reptation, it is necessary to include the initial Rouse motion which was neglected by de Gennes. The only model in the literature providing an explicit expression for the dynamic structure factor in this regime is Ronca's effective-medium model.[12] In the framework of the self-consistent approach of Hess[13] and the reptation model, Ronca's model is a simplification using an *ad hoc Ansatz* for the time-dependent friction. Nevertheless, Ronca's formalism belongs to the class of reptation models.[10] Finally, Ronca's explicit calculation also allows one to theoretically establish the range of Qd_T for which the splitting of $S(Q,t)$ could be observed. According to these calculations, deviations from scaling are to be expected at least up to $Qd_T \leq 7$. This result agrees well with the computer simulations of Kremer, Grest, and Carmesin,[10] where splitting was observed in a range $2.9 \leq Qd_T \leq 6.7$. As we shall see, the Qd_T range covered in our experiment was $2.9 \leq Qd_T \leq 6.7$, well within the above limits.

In order to be compatible with the experimentally accessible Q-t regime of NSE ($t < 40$ nsec, $Q > 0.02$ Å^{-1}), it was important to find a thermally stable linear polymer combining a high plateau modulus (short entanglement distance), high flexibility, and a low monomeric friction coefficient. Hydrogenation of 1,4 polyisoprene (PI) yields an alternating copolymer of poly(ethylene-propylene) (PEP) with the required properties. Hydrogenation increases the plateau modulus of PI by nearly a factor of 3, $G_N^0(\mathrm{PI}) = 0.44\times10^7$ dyn/cm^2, $G_N^0(\mathrm{PEP}) = 1.22\times10^7$ dyn/cm^2 at 25 °C.[14] This change is the largest so far seen via the saturation of a polydiene to a polyolefince structure. Using the Doi-Edwards theory of viscoelasticity we have[8]

$$d_T^2 = \frac{4}{5}\frac{\langle R_E^2\rangle}{M}\frac{\rho N_a kT}{G_n^0}, \tag{2}$$

where $\langle R_E^2\rangle$ is the mean-square end-to-end distance, M is the molecular weight, ρ is the polymer density, and N_a is Avogadro's number. Equation (2) yields $d_T = 36$ Å for PEP at 25 °C.[14] The segment length of PEP at 500 K is 7 Å indicating high flexibility. Finally, using the Vogel-Fulcher viscosity parameters of Gotro and Graessley[14] in the Bueche approximation[15] we estimate a monomeric friction coefficient of $\zeta_0 = 1.9\times10^{-9}$ dyn sec/cm at 500 K. The corresponding Rouse rate $W = 2.2\times10^{10}$ sec^{-1} assures high mobility.

Four samples were prepared by hydrogenation (or deuteration) of linear 1,4 polyisoprene. Sample I was a fully deuterated matrix used for background measurements, sample II was a deuterated matrix containing 10% protonated species, and sample III consisted of a deuterated matrix containing 30% of a triblock copolymer with identical segment lengths where the center block was protonated. Finally, sample IV was another deuterated polymer used for measurements of the plateau modulus. The use of partially deuterated mixtures allowed us to monitor single-chain dynamics in the bulk. The polymerization and the subsequent hydrogenation and deuteration are described elsewhere.[16,17] The resultant PEP alternating copolymers were found via D and H NMR spectroscopy to be > 99.4% saturated. The molecular weights and polydispersities are given in Table I. Size exclusion chromatography inspections after the prolonged heat treatment during the neutron spin-echo experiments show no indication of polymer degradation.

The neutron spin-echo experiments were performed using the NSE spectrometer IN11 at the Institut Laue-Langevin in Grenoble.[18] At an incident neutron wavelength of $\lambda = 11.3$ Å we accessed a time regime of $0.5 < t < 37$ nsec at an energy resolution ($1/e$ decay) of 5 neV. Figure 1 presents the measured resolution and background-corrected intermediate scattering function for the homopolymer at 492 K and compares them with selected results from the triblock polymer at 492 K and the homopolymer at 523 K. All observed scattering

TABLE I. Parameters characterizing the different polymers, and values for entanglement distance and monomeric friction coefficients obtained from the various fits.

				Ronca's model		de Gennes' model
Sample	$10^{-4}M_w$	M_w/M_n	T (K)	d_T (Å)	$10^9\zeta_0$ (dyn sec/cm)	d_T (Å)
d_{10}/h_{10} PEP(II)	8.6(h_{10})	1.02	492	47.5 ± 0.4	3.1 ± 0.1	49.6 ± 0.9
d_{10}/h_{10} PEP(II)	8.5(d_{10})	1.02	523	51.3 ± 0.5	2.5 ± 0.1	53.4 ± 1.0
PEP triblock(III)	8.2	1.02	492	47.1 ± 0.7	4.2 ± 0.2	49.2 ± 0.9
d_{10} PEP(IV)[a]	17.0	1.03	500	43	1.9	(Rheology)

[a] This sample was used for the rheological measurements.

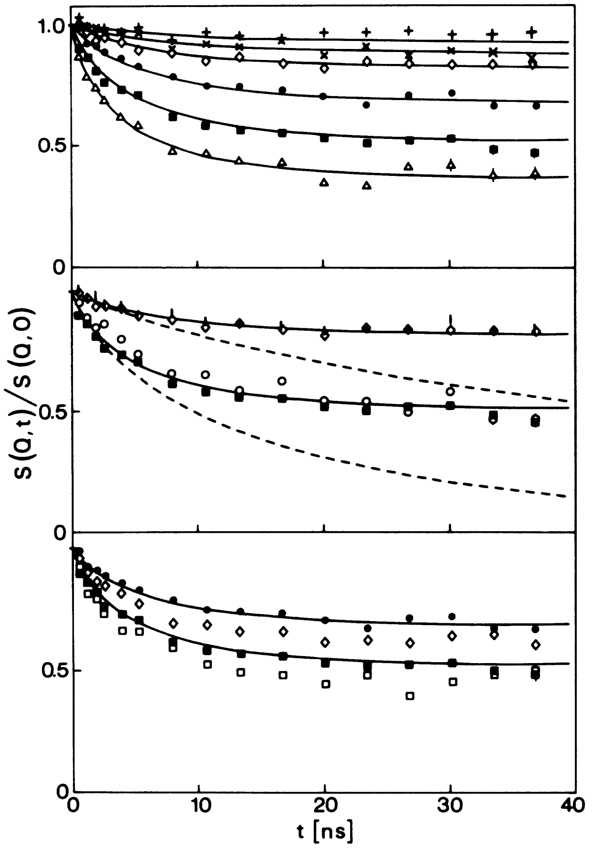

FIG. 1. Neutron spin-echo results from the homopolymer and the triblock copolymer samples. Upper part: homopolymer (sample II) at 492 K. (+, $Q=0.058$ Å^{-1}; ×, $Q=0.068$ Å^{-1}; ◇, $Q=0.078$ Å^{-1}; ●, $Q=0.097$ Å^{-1}; ■, $Q=0.116$ Å^{-1}; △, $Q=0.135$ Å^{-1}). Middle part: Comparison of the relaxation spectra obtained from the homopolymer and the triblock copolymer at $Q=0.078$ Å^{-1} (|) and $Q=0.116$ Å^{-1} (○). The dashed lines indicate the expected intermediate scattering function for Rouse relaxation. Lower part: Comparison of the obtained spectra from the homopolymer at 492 and 523 K (◇, $Q=0.097$ Å^{-1}; □, $Q=0.116$ Å^{-1}). The solid lines in all parts of the figure represent the result of a joint fit with the Ronca model to the data from the homopolymer at 492 K.

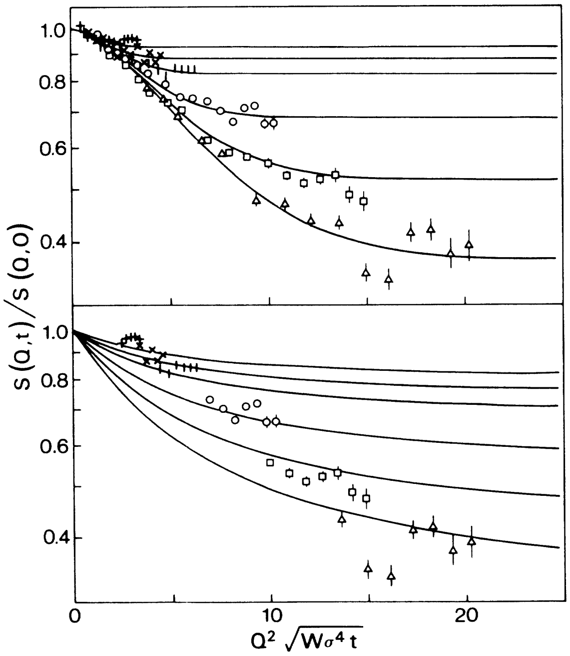

FIG. 2. Rouse scaling representation of the PEP data at 492 K. Upper part: solid lines represent the Ronca model; lower part: solid lines show the prediction of local reptation. (+, $Q=0.058$ Å^{-1}; ×, $Q=0.068$ Å^{-1}; |, $Q=0.078$ Å^{-1}; ○, $Q=0.097$ Å^{-1}; □, $Q=0.116$ Å^{-1}; △, $Q=0.135$ Å^{-1}).

functions are characterized by an initial decay followed by a plateau regime in time. The observation of an "elastic" or nondecaying contribution to $S(Q,t)$ at long times is the central result of our experiment. For comparison, the dashed lines in the middle part of Fig. 1 display the dynamic structure factor for pure Rouse relaxation exhibiting the same initial decay. Besides some small deviations in the initial decay the comparison between the results from homopolymer and triblock shows very similar relaxation behavior. In particular, the long-time plateau for both polymers is identical indicating the same constraints for both polymers; for these samples end effects are of no importance. On the other hand, the comparison of the measurements on the homopolymer at 492 and 523 K indicates a reduction of the constraints with increasing temperature, in addition to a faster initial decay due to more rapid motion, the plateau regime at long times is shifted towards lower values.

Figure 2 presents the homopolymer data at 492 K in a scaling form. The data were fitted to both the effective medium and the local reptation theory. Both are plotted versus the Rouse variable $u=Q^2(W\sigma^4 t)^{1/2}$. The upper part presents the fit with Ronca's effective-medium model. In contrast to previous experimental results,[5-7] the data do not scale with u but split into Q-dependent plateau levels. Rouse-like scaling is only observed for the initial rapid decay. The Ronca model (solid lines in the upper part of Fig. 2) represents an excellent description of the experimental data reproducing experimental line shape, the relatively sharp crossover, and the Q dependence of the long-time plateau. The results for the model parameters are given in Table I. The lower part of Fig. 2 presents a fit with the local reptation model to the long-time tails of the measured spectra ($t > 17$ nsec). We omitted the initial Rouse-like decay which is not included in the theory and used the Rouse rate obtained in the Ronca fit.[19] Though the long-time plateau is less developed than in the effective-medium model, the fit provides satisfying agreement with the data (for results, see Table I). Finally, the internal consistency of the fitting procedure was further tested by fitting tube diameters at different Q values separately. Within the experimental accuracy no Q dependence of the tube diameter could be detected.

From Table I we observe that the entanglement distance increases with temperature. This effect is opposite to that expected in the framework of the Eq. (2). That is, using $G_N^0 = \frac{4}{5}(\rho/M_e)N_a$ (M_e denotes molecular weight in between entanglement; as a purely geometrical quantity M_e should not depend on T) in Eq. (2) we find $d_T^2 = \langle R_E^2 \rangle M_e/M$ which should contract with temperature.

In order to compare with rheological results and to avoid temperature extrapolation of existing low-temperature data, we studied the plateau modulus of sample IV at 500 °C using a Rheometrics System 4. A form of the Kramers-Kronig relation $G_N^0 = (2/\pi)\int_{-\infty}^{+\infty} G''(\omega)\, d\ln\omega$ (Ref. 20) was used to determine G_N^0. The value obtained is 9.3×10^6 dyn/cm^2. Employing Eq. (2) a tube diameter or entanglement distance of 43 Å is evaluated. This value compares very well with the 47 Å measured by NSE on the microscopic scale. Again we note that the rheological data show an increase of d_T with T in contrast to Eq. (2). If we scaled the room-temperature value for the tube diameter in PDMS ($d_T = 61$ Å) in a similar fashion to 200 °C, we would obtain a new value of about 80 Å, too large to be measured with current NSE techniques. Finally, the PEP monomeric friction coefficient comes out to be 50% bigger than the rheological one obtained from the Bueche approximation. Considering the long extrapolations required for the rheological data, this agreement is satisfying.

In conclusion, we have observed clear microscopic evidence for the existence of a well-defined intermediate length scale that drastically limits the relaxation of density fluctuations of a given polymer chain. Furthermore, this microscopic length scale is found to be in excellent agreement with the segment entanglement distance obtained from rheological measurements assuming the reptation model. Our work confirms the essential *Ansatz* of the elegant reptation dynamics of de Gennes.

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