Crossover from Rouse dynamics to the α-relaxation in poly(vinyl ethylene)

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Abstract. By means of neutron spin echo (NSE) we have explored the dynamics of poly(vinyl ethylene) on length scales covering Rouse dynamics and below. The results establish the simultaneous existence of a generic sublinear diffusion regime which underlies the α-process in addition to the Rouse process. Both regimes are separated by a well-defined dynamic crossover. From that the size of the Gaussian blobs making up the Rouse model is determined directly. The glassy dynamics may thus be identified with subdiffusive motions occurring within these Gaussian blobs.

Keywords. Dynamics in glass-forming polymers; α-relaxation; chain dynamics; quasi-elastic neutron scattering.

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1. Introduction

Polymers show features typical for glass-forming systems and for interconnected objects. On the one hand, the structural (α) relaxation in polymers, which is observed directly at the structure factor peak [1–3], is subject to the same universalities as found for glass-forming materials in general: stretching of the relaxation function, time–temperature superposition, etc [1]. For a large number of polymers, in the time range around the structural relaxation time τ_s [4], the self-correlation function $S_{\text{self}}(Q,t)$ was found to be

- stretched in time, i.e., it shows the functional form of a Kohlrausch–Williams–Watts (KWW) function:

$$S_{\text{self}}(Q,t) = A(Q)\exp\left[-\left(\frac{t}{\tau_w}\right)^{\beta}\right]. \tag{1}$$

Here, $A(Q)$ accounts for microscopic motions and assumes the form of a Debye Waller factor, β is the stretching exponent (usually $0.4 \leq \beta \leq 0.6$) and τ_w is the characteristic time that depends on Q (momentum transfer) and temperature;

- and Gaussian in space:

$$S_{\text{self}}(Q,t) = A(Q)\exp\left[-\frac{Q^2\langle r^2(t)\rangle}{6}\right], \tag{2}$$

thus being directly related to the mean square displacement $\langle r^2(t)\rangle$.

These simultaneous observations imply that the atoms within a polymer perform sublinear diffusion with a mean-square displacement $\langle r^2(t)\rangle \approx t^{\beta}$ [5–10].

On the other hand, the chain character of polymers leads the universal entropy-driven (Rouse) dynamics to prevail at intermediate scales, where local potentials have ceased to be important and entanglements are not yet active. A key signature of the Rouse motion is the sublinear evolution of the segmental mean-square displacement $\langle r^2(t)\rangle \approx t^{1/2}$. The Rouse dynamics distinguishes polymers from simple glass-forming systems, where the decaging process is followed by translational diffusion of the whole molecule.

Recently, molecular dynamics simulations [11] as well as mode coupling theory calculations [12] on coarse-grained polymer models (bead and spring models) show the existence of a plateau in the early stages of $\langle r^2(t)\rangle$ after the initial ballistic regime. This proves that the 'cage effect' also exists for polymers. However, as $\langle r^2(t)\rangle$ increases above the plateau, instead of a continuous crossover to simple diffusion, an extended subdiffusive regime ($\langle r^2(t)\rangle \approx t^x, x \approx 0.5$–0.6) is found. This difference was related to the Rouse dynamics of polymer chains. Furthermore, quasi-elastic neutron scattering experiments on glass-forming polymeric liquids taken at high Q were interpreted in terms of Rouse motion [13].

In real polymers it is clear that the precondition of Gaussian beads can only be fulfilled on large scales. Then, the question arising is: Is it possible to experimentally clarify the independent existence of a generic dynamic regime of sublinear diffusion associated with the α-process apart from the Rouse process?

Here we present a neutron spin echo (NSE) investigation on poly(vinyl ethylene) (PVE). These results, that are previously reported in ref. [14], have allowed for the first time to clearly distinguish between two separated dynamic regimes of sublinear diffusion. The data display a well-developed crossover from the sublinear diffusion regime of the α-relaxation dynamics to the Rouse regime representing the universal chain dynamics. The observed crossover establishes the existence of an independent α-relaxation power law regime well-separated from the Rouse dynamics. This allows a direct atomistic identification of the Gaussian blob underlying the Rouse model – the crossover length amounts to $\approx$20 Å. Within this blob the sublinear diffusion representing the α-relaxation takes place [14].

2. Experimental

Deuterated and protonated PVE samples (weight-averaged molecular weights $M_{\mathrm{w}} = 80$ kg/mol for both and polydispersities better than 1.02) were synthesized by anionic polymerization. Two correlation functions were accessed in this study: (i) the single chain dynamic structure factor $S_{\mathrm{chain}}(Q,t)$ – the normalized Fourier-transformed pair correlation function of the segments within one chain and (ii) the self-correlation function $S_{\mathrm{self}}(Q,t)$, originating from the proton self-motion. $S_{\mathrm{chain}}(Q,t)$ was measured on a deuterated matrix containing 10% protonated chains at the NSE instrument IN15 (ILL, Grenoble). The Q-range covered was $0.07 \leq Q \leq 0.2$ Å^{-1} and the dynamic range $2 \leq t \leq 40$ ns. On the other hand, $S_{\mathrm{self}}(Q,t)$ was obtained on a fully protonated sample at the NSE spectrometer at the FRJ-2 reactor in Jülich. A time range of $0.01 \leq t \leq 22$ ns was accessed in the Q-range $0.07 \leq Q \leq 0.4$ Å^{-1}. Both kinds of experiments were performed at 418 K (about 150 K above the glass transition).

3. Theory: The Rouse model

The Rouse model [15] treats the dynamics of a Gaussian chain (bead and spring model) in a heat bath. Thereby, it implicitly assumes that on the considered length and time-scales only entropic restoring forces drive the dynamics. At scales $QR_0 \gg 1$, where R_0 is the chain end-to-end distance, the normalized single chain dynamic structure factor $S_{\mathrm{chain}}^{\mathrm{Rouse}}(Q,t)$ can be written as a function of a scaling variable $x = Q^2\sqrt{W\ell^4 t}$, which combines spatial and temporal scales [15]:

$$S_{\mathrm{chain}}^{\mathrm{Rouse}}(x) = \int_0^\infty \mathrm{d}s \exp\left[-s - \frac{x}{3\pi}\int_0^\infty \frac{\cos\left(\frac{6ys}{x}\right)}{y^2}\left(1 - \exp\left(-y^2\right)\right)\mathrm{d}y\right]$$

(3)

with $W = 3k_{\mathrm{B}}T/\zeta\ell^2$, the elementary Rouse frequency. W is the ratio of the entropic force, $3k_{\mathrm{B}}T/\ell^2$, and the friction coefficient ζ. $\ell^2 = C_\infty \ell_0^2$ is the mean square segment length, where C_∞ is the characteristic ratio and ℓ_0 the bond length. The validity of the Rouse approach is limited to long scales by topological constraints leading to reptation and to short scales by the microscopic details of the chemical polymer structure.

In the standard Rouse theory the intermediate incoherent scattering function is given by

$$S_{\mathrm{self}}^{\mathrm{Rouse}}(Q,t) = A(Q)\exp\left[-\left(\frac{W\ell^4}{9\pi}Q^4 t\right)^{1/2}\right].$$

(4)

In the Q-regime considered, the prefactor $A(Q)$ is close to 1. In comparison with eq. (1), $S_{\mathrm{self}}^{\mathrm{Rouse}}(Q,t)$ has the form of a KWW function with $\beta^{\mathrm{Rouse}} = 0.5$ and

$$\tau_w^{\mathrm{Rouse}} = \frac{9\pi}{W\ell^4}Q^{-4}.$$

(5)

It is also easy to deduce that $S_{\text{self}}^{\text{Rouse}}(Q,t)$ also fulfills the Gaussian approximation (eq.(2)) with the mean squared displacement given by

$$\langle r^2(t)\rangle^{\text{Rouse}} = 2\sqrt{\frac{W\ell^4 t}{\pi}}. \tag{6}$$

4. Results and discussion

Figure 1 shows $S_{\text{chain}}(Q,t)$ from the PVE melt measured at IN15. The solid lines display a fit with the Rouse dynamic structure factor (eq. (3)). For $Q < 0.11$ Å^{-1} the data follow the Rouse prediction well. Above this value the measured data decay less than that predicted by the Rouse model. In order to quantify the deviations, individual fits with eq. (3) to all data were performed revealing the Rouse variable $W\ell^4$. This turns out to be Q-dependent for $Q \geq Q_R = 0.11$ Å^{-1} [14]. Similar deviations from the Rouse model have been previously reported for other polymers [16–18].

The PVE chain dynamics is thus Rouse-like for $Q < Q_R$. In such a regime, the self-motion corresponds to a Gaussian sublinear diffusion as predicted by this model and the characteristic time for self-motion is obtained through eq. (5). We
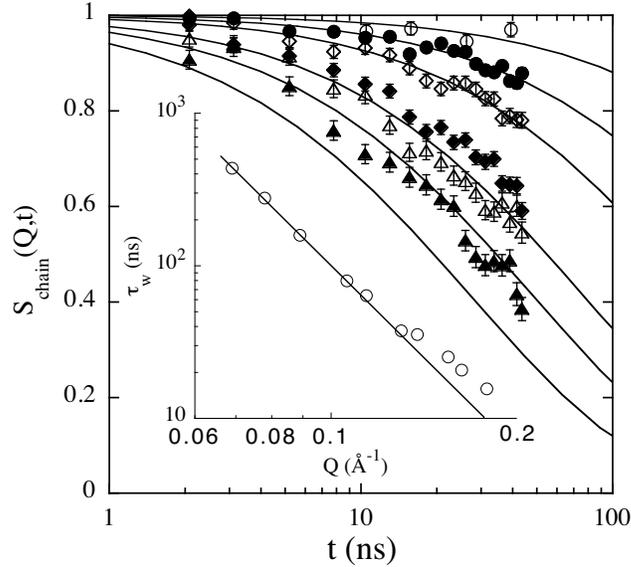

Figure 1. $S_{\text{chain}}(Q,t)$ obtained for PVE at $Q = 0.07$, 0.09, 0.11, 0.14, 0.16 and 0.18 Å^{-1} (top to bottom). The solid lines are the prediction of the Rouse model with $W\ell^4 = 2800$ Å^4/ns. Inset: Q-dependence of the characteristic time for the self-motion deduced from the values of $W\ell^4$ as obtained from individual fits of $S_{\text{chain}}(Q,t)$ to the Rouse model. The line shows the Rouse prediction for the Q-dependence of $\tau_w^{\text{Rouse}}(Q)$.

may take the time at Q_R, $t_R = \tau_w^{\text{Rouse}}(Q_R) \approx 100$ ns, as representative for the Rouse time-scale. From eq. (6), at t_R we have $\langle r^2(t_R) \rangle \approx 600$ Å^2. For $Q \geq Q_R$, we can calculate the characteristic time for self-motion from the effective description performed on $S_{\text{chain}}(Q,t)$ in terms of the Rouse model also by applying eq. (5). The above-obtained values for $W\ell^4(Q)$ lead to the times depicted in the inset of figure 1. As can be seen, this variable also reflects the deviations from universal Rouse dynamics at large Q's.

Up to this point, the information presented about the self-motion in PVE has been deduced from the application of the Rouse model to the coherent data corresponding to $S_{\text{chain}}(Q,t)$. However, with the Jülich NSE measurements we have *direct* access to the proton self-motions. Figure 2a shows the experimental $S_{\text{self}}(Q,t)$ data obtained on the protonated sample. With these data at hand, we can answer the key question: Is there another Gaussian subdiffusive regime at length scales shorter than that of the Rouse dynamics? In this case, also for $Q > Q_R$ it should be possible to construct a Q-independent $\langle r^2(t) \rangle$ following $\langle r^2(t) \rangle = -6 \ln[S_{\text{self}}(Q,t)]/Q^2$ (eq. (2)). Figure 2b shows that this is indeed the case. For $Q \geq 0.20$ Å^{-1} a nearly perfect collapse of the experimental data into a single curve is obtained. The time dependence of the such determined $\langle r^2(t) \rangle$ can be well-described by a power law with an exponent of 0.5 (solid line). Thus, for $t < t_R$ the data reveal a subdiffusive regime which is obviously distinct from the Rouse process, though it is characterized by the same exponent $\beta = 0.5$. For comparison we have included in figure 2b the mean squared displacement from the Rouse motion (eq. (6)) towards longer times. Both regimes differ by the prefactor governing the magnitude of $\langle r^2(t) \rangle$.

The early subdiffusive regime is indeed relevant for the α-relaxation. Two time-scales may be invoked in order to define the time range where the α-relaxation dynamics evolves: (i) the structural relaxation time τ_s and (ii) the time needed by a proton to move as far as the average interchain distance d. Measurements of $S(Q)$ [14] reveal that the first (intermolecular) peak is located at $Q_{\max} = 0.9$ Å^{-1}. The value determined for τ_s from the decay of the dynamic structure factor at $Q_{\max}$ gives $\tau_s = 0.1$ ns [14]. This value lies well within the subdiffusive regime – the proton moves about 4 Å during τ_s. On the other hand, the average interchain distance $d = 2\pi/Q_{\max} \approx 7$ Å is covered in about 1 ns (see figure 2b). This time is just in the middle of the time range where sublinear diffusion is observed.

The crossover between the Rouse regime and the subdiffusive α-regime becomes clear if we focus on the Q-dependent characteristic relaxation times. We note that the correlation functions $S_{\text{chain}}(Q,t)$ and $S_{\text{self}}(Q,t)$ are different and that their direct comparison is not possible. However, we may easily relate the characteristic times corresponding to the self-motions: (i) A fit of the $S_{\text{self}}(Q,t)$ to eq. (1) with $\beta = 0.5$ (see solid lines in figure 2a) reveals τ_w directly in both regimes. (ii) From the effective description of $S_{\text{chain}}(Q,t)$ in terms of the Rouse model we already know the associated incoherent time-scales (inset of figure 1). Figure 3 presents the Q-dependent relaxation times obtained from both approaches. Removing the Q^{-4} dependence expected for both the Rouse as well as for the α-regime will lead to a plateau in the variable $\tau_w Q^4$. This is indeed observed for both regimes: the plateau at $Q < 0.11$ Å^{-1} corresponds to Rouse dynamics, while the plateau at higher Q reflects the Gaussianity in the α-relaxation region. The two regimes are separated
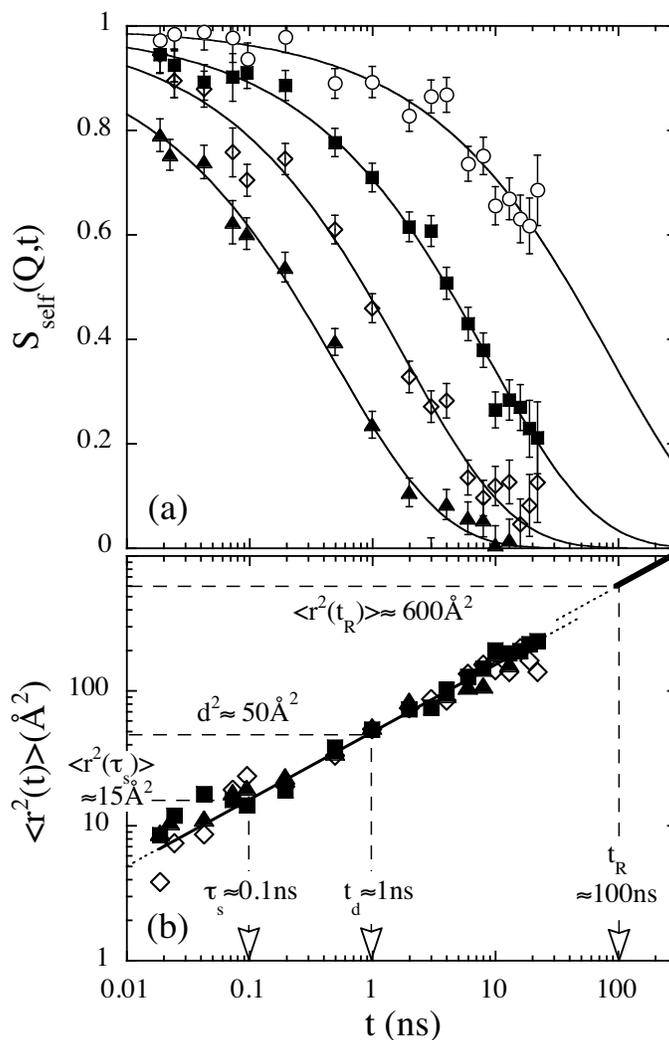
Figure 2. (a) $S_{\text{self}}(Q,t)$ at $Q = 0.1$, 0.2, 0.3 and 0.4 Å^{-1} (top to bottom). Solid lines are KWW fits with $\beta = 0.5$. (b) Mean square displacement of the protons obtained from the measured $S_{\text{self}}(Q,t)$ at $Q > Q_R$. Symbols are as in (a). The solid line represents $\langle r^2(t) \rangle \propto t^{0.5}$. The dashed lines mark the characteristic times and lengths discussed in the text. The thick solid line in the upper right corner displays the $\langle r^2(t) \rangle$ in the Rouse regime ($\langle r^2(t) \rangle^{\text{Rouse}}$, eq. (6)). The two dotted lines extrapolate into the crossover regime.

by a step occurring around $Q_{\text{cross}} \approx 0.13$ Å^{-1}. We note that the results from a direct measurement of $S_{\text{self}}(Q,t)$ in the low Q regime agree very well with those deduced from the Rouse description of $S_{\text{chain}}(Q,t)$, demonstrating the consistency of the results obtained. Finally, we have tested the sensitivity of the step-like shape
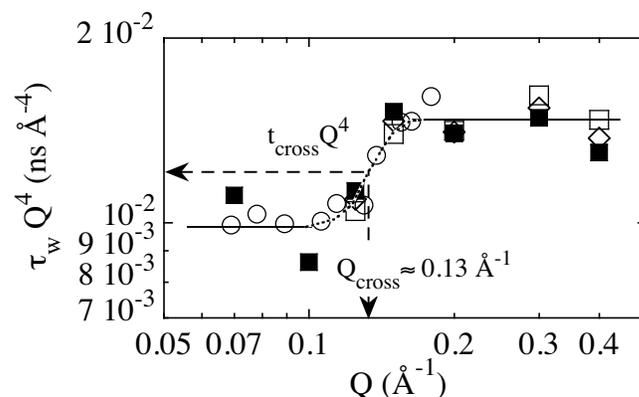
Figure 3. Q-dependence of $\tau_w Q^4$ from the description of $S_{\text{self}}(Q, t)$ with a KWW function with $\beta = 0.5$ (black squares), 0.52 (rhombs) and 0.55 (squares), and from the description of $S_{\text{chain}}(Q, t)$ in terms of the Rouse model (circles).

of the crossover by varying the β-parameter of the fit with eq. (1), thereby remaining within the limits dictated by figure 2b ($\beta_{\max} = 0.55$). An increase of β has little effect on the size and the shape of the crossover, as can be seen in figure 3.

The determination of the crossover at $Q_{\text{cross}} \approx 0.13$ Å^{-1} allows to define a crossover length scale $\ell_{\text{cross}} \approx \pi/Q_{\text{cross}} = 24$ Å. This length scale may be identified with the size of a Gaussian blob underlying the Rouse model. For PVE this corresponds to ten monomers or twenty bonds for the Gaussian blob [14]. For distances along the chain longer than this size, the Gaussian bead and spring model works and we obtain Rouse dynamics. For smaller scales, we observe the internal dynamics within the Gaussian blobs reflecting the α-relaxation.

5. Conclusions

For a PVE polymer melt we have established the existence of a generic dynamic regime in between the decaging process and the Rouse motion. This regime, characterized by sublinear diffusion [5,7], is well-separated from the Rouse process. It evolves from the motion of the atoms within the polymer which are subject to specific intra- and inter-molecular forces and can be identified with the dynamical process relevant for the glassy character of the polymer. The coarse grained molecular dynamics simulation and mode coupling theory calculations based on bead and spring models [11,12] do not reveal this subdiffusive α-regime, which appears to relate to the internal dynamics within the Gaussian blobs. Given the rather general observation of a subdiffusive regime in polymer melts [5–10,13], our result on the well-defined crossover indicates that the phenomenon is of general nature.

Acknowledgements

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