

## Molecular View on Supramolecular Chain and Association Dynamics

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The chain and association dynamics of supramolecular polymer ensembles decisively determines their properties. Using neutron spin echo (NSE) spectroscopy we present molecular insight into the space and time evolution of this dynamics. Studying a well characterized ensemble of linearly associating telechelic poly(ethylene glycol) melts carrying triple H-bonding end groups, we show that H-bond breaking significantly impacts the mode spectrum of the associates. The breaking affects the mode contributions and *not* the relaxation times as was assumed previously. NSE spectra directly reveal the so far intangible H-bond lifetimes in the supramolecular melt and demonstrate that for both the microscopic and the macroscopic dynamics of the supramolecular ensemble the instantaneous average of the  $M_w$  distribution governs the system response at least as long as the Rouse picture applies.

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The investigation of the structure and dynamics of supramolecular polymer systems is a strongly expanding field. Polymers functionalized with reversible linkers form an emerging class of polymers that offer superior properties compared to their nonassociating counterparts. They open opportunities for advanced materials with qualities such as self-healing or responsiveness [1]. H bonding as the linker is directional and has the advantage of a tunable selective strength by self- and heterocomplementarity [2,3]. Bioactivity combined with biocompatibility, e.g., for functional tissues, is well achieved using multiple H bonds [4].

The properties of associating polymers relate to their thermodynamic equilibrium structure and most importantly to the dynamics of the chains and the associates determined by the inherent H-bond dynamics as well as their interplay. Experimentally, the association dynamics of H-bonding systems was mainly studied in solution [5,6], or very low molecular weight melts [7]. Direct experiments on supramolecular polymer melts, on the other hand, are very difficult [8]. After early treatments of the stress relaxation employing a Poisson renewal model [9] in entangled living associating systems by Granek and Cates [10], detailed theoretical approaches on the dynamics of associating polymers—closer to the here investigated case—were reported, e.g., by Stukalin and Freed [11]. Using the Poisson renewal approach for Rouse chains they presented explicit results for the complex viscosity and the dielectric response from the chain end-to-end vector. If scission rates are comparable to the structural chain relaxation times, both approaches predict that the interplay between chemical and structural relaxation strongly affects the stress relaxation and accelerates it. In a recent paper, Watanabe *et al.* evaluated the viscoelastic response of nonentangled

transiently binding unimer blocks with one (hydrogen) bonding group each within the realm of the Rouse model [12]. They find the ratio between Rouse relaxation (of a unimer chain) and the association or dissociation time to be the key parameter separating regimes with distinct dimer and unimer response and apparent unimer response in the case of fast exchange.

Recently, we investigated associating telechelic poly(ethylene glycol) (PEG) melts with heterocomplementary diaminotriazine and thymine (DAT and Thy, respectively) functional groups that form triple H bonds [13]. Using different labeling schemes, small angle neutron scattering proved exclusively linear chain aggregation. Furthermore, pulsed field gradient nuclear magnetic resonance (PFG NMR) and viscosity measurements revealed that Rouse dynamics [14] prevailed even though the associated chains are well in the entanglement regime [15]. Rouse dynamics is known to be valid for sufficiently short linear polymer chains. All interchain interaction can be lumped to segmental friction, and no specific topological interaction effects are seen. The combination of static and dynamic results demonstrated an underlying chain length distribution characteristic of random, position independent association or dissociation (e.g., polycondensation) reactions [16]. The observation of overall Rouse dynamics implied a short lifetime  $\tau_b$  of the hydrogen bond; i.e., long multiblock associates do not persist long enough to exhibit topological constraint effects. However, as in all earlier studies of associating polymer melts the quantitative determination of  $\tau_b$  remained elusive.

Using this very well characterized supramolecular polymer melt, here we present a neutron spin echo (NSE) study addressing both the chain and the association dynamics.

This enabled a direct microscopic determination of the bond dissociation time  $\tau_b$  through its signature in the spectral response and provided insight into the molecular mechanism: scission shows itself in a reduction of the mode contributions; the density of instances where supramolecular relaxation modes prevail are diminished exponentially with the ratio of the mode relaxation time  $\tau_p$  and the chain dissociation time  $\tau_b/M$ , where  $M$  is the degree of association of the considered supramolecular chain. This is the basis of our empirical ansatz to adopt the description of Rouse dynamics to the present problem. Thus, the commonly employed approach of an effective mode relaxation rate adding the rates of the respective modes and scission events does not apply for the single chain structure factor (as seen by NSE spectroscopy) of the supramolecular melt.

The supramolecular melt was prepared by solution blending and subsequent drying under high vacuum conditions of equal amounts (volume fraction  $\Phi_{1-4} = 1/4$ ) of all four well monodisperse ( $M_w/M_n = 1.03$ ) building blocks: Thy-h-PEG-Thy, Thy-d-PEG-Thy, DAT-h-PEG-DAT, and DAT-d-PEG-DAT with molecular weights of 2.2, 2.7, 2.3, and 2.7 kg/mol respectively. This leads to a random scattering contrast that results in a zero average of all interferences between scattering contributions from different blocks. The synthesis and characterization of the different compounds are described elsewhere [15]. The neutron spin echo experiments at three temperatures (353, 373, and 450 K) were performed at the Institute Laue Langevin in Grenoble [17,18]. Figure 1 presents the obtained dynamic structure factors  $S(Q, t)/S(Q)$  at  $T = 373$  K; all experimental data are presented in Fig. 2.

In order to arrive at an unambiguous data analysis we take advantage of the ample prior knowledge about the system. From our earlier study we know that the chain

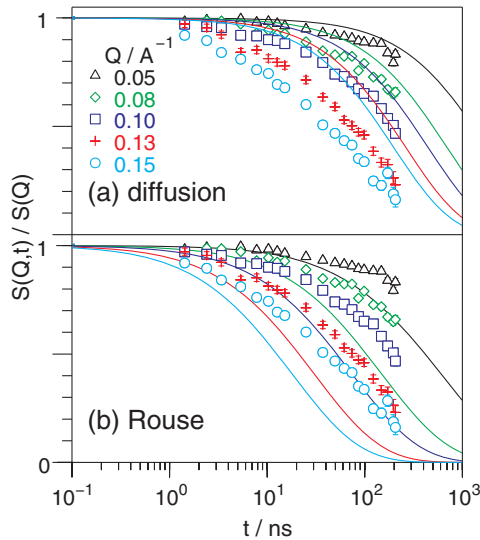


FIG. 1. NSE data at 373 K compared to  $S(Q, t)_{\text{diff}}$ , the pure diffusion contribution in part (a), and in part (b) the prediction of the unmodified (unbreakable chain) as described in the text.

length distribution is of the Flory polycondensation type:  $w(M) = MP^{M-1}(1-P)^2$  with  $P = 1 - 1/M_{\text{agg},n}$  with average aggregation numbers  $M_{\text{agg},w}$  consistently determined by small-angle neutron scattering, PFG NMR, and rheology [13]. From PFG NMR and viscosity measurements the overall Rouse behavior of the ensemble was established, where the diffusion coefficient results from the weight average over chain association numbers  $M$  of the diffusion contributions  $D_R(M) = D_b/M$  with  $D_b$  the diffusion coefficient of the building block with  $N_b$  segments.

In a first step we analyze to what extent the distribution of translational diffusion coefficients describes the data. To account for the aggregation we average over contributions from chains with different aggregation numbers. For the average diffusion coefficient we get

$$D_{\text{av}} = \sum_{M=1}^{\infty} w(M) D_R(M). \quad (1)$$

Table I presents  $M_{\text{agg},n}$  and  $D_{\text{av}}$  for our system. For  $T = 373$  K in an exemplary way Fig. 1(a) displays the predicted structure factor

$$S(Q, t)_{\text{diff}}/S(Q) = \sum_{M=1}^{M_{\text{max}}} w(M) e^{-D_R(M)Q^2 t}. \quad (2)$$

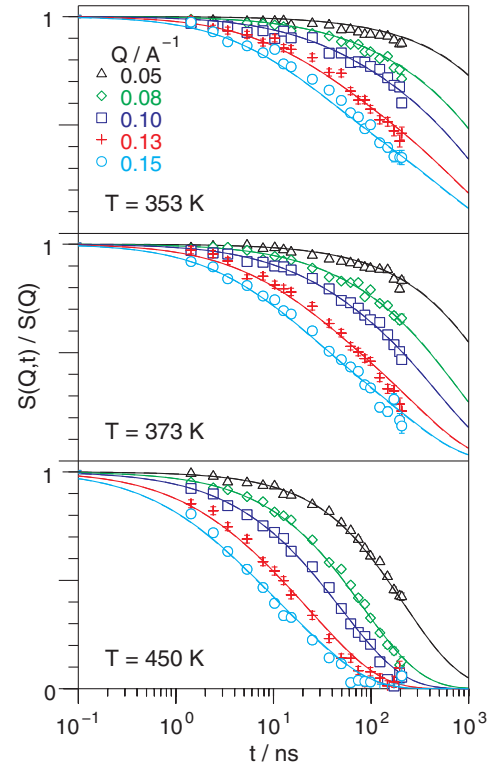


FIG. 2. NSE data for three different temperatures. The solid lines represent the result of the model fitting, where only one parameter, the bond breaking time  $\tau_b$ , was fitted.

TABLE I. Model parameters to describe the NSE data for three temperatures. \* indicates the fitted values. Errors include the contribution from systematic effects due to 3% uncertainties in  $Wl^4$  and  $M_{\text{agg},n}$ .

$T$ (K)	$\tau_b$ (ns)	$\tau'_c(M_{\text{agg},n})$ (ns)	$\tau_R^b$ (ns)	$M_{\text{agg},n}$	$Wl^4(\text{\AA}^4\text{ns}^{-1})$	$D_{\text{av}}(\text{\AA}^2\text{ns}^{-1})$	$D_{\text{NMR}}(\text{\AA}^2\text{ns}^{-1})$
353	835* $\pm$ 135	128	70	7.5	4560	0.13	0.13
373	383* $\pm$ 60	85	43	5.5	7427	0.29	0.31
450	32.7*( $\pm$ 4)	15	10	3.2*( $\pm$ 0.013)	33601	2.24	

While for the two lowest scattering wave vectors  $Q$  in the long time limit the diffusional description roughly matches the observation, it is obvious that the measured data cannot be described in this way. There are significant further relaxation channels that have to be ascribed to internal dynamics.

The following description is based on the standard Rouse model expressed by the explicit summation over the mode contributions [14]. To account for the distribution we average over contributions  $w(M)$  from chains with aggregation numbers  $M$ . With the end-to-end distance of the building block  $\langle R_c^2 \rangle = N_b l^2$  with  $l$  the effective bond length,  $Wl^4$  the usual Rouse rate parameter, and  $N = MN_b$ , the mode relaxation times for mode numbers  $p$  follow  $\tau_p = l^4 / \{2Wl^4[1 - \cos(\pi p/N)]\} \simeq (Nl^2)^2 / (Wl^4 \pi^2) p^{-2}$ , where the Rouse diffusion constant is  $D_R = Wl^4 / (3Nl^2)$ . Then, the normalized intermediate scattering function  $S(Q, t)/S(Q)$  as measured by the NSE experiments follows from our model function

$$S(Q, t) = \sum_{M=1}^{M_{\text{max}}} w(M) \left( \sum_{n=h}^{h+N_b} \sum_{m=h}^{h+N_b} e^{-Q^2 \Phi_{n,m}^{N=MN_b}(t)} \right) \quad (3)$$

with

$$\begin{aligned} \Phi_{n,m}^N(t) = D_R t + \frac{|n-m|l^2}{6} + \frac{2Nl^2}{3\pi^2} \sum_{p=1}^N \frac{1}{p^2} (1 - e^{-t/\tau_p}) \\ \times \cos\left(\frac{\pi p n}{N}\right) \cos\left(\frac{\pi p m}{N}\right) e^{-\tau_p/\tau_c}. \end{aligned} \quad (4)$$

The random labeling situation is taken into account by restricting the sums over the beads ( $n, m$ ) to the region of one single selected labeled building block starting at bead  $h$ . For efficiency of the computation only one representative position  $h \simeq N/4$  was used and  $M_{\text{max}} \simeq 5M_{\text{agg}}$ .

In the second step of the data analysis we assume an infinite lifetime of the aggregates (unbreakable chain limit) and compare the data with the prediction of the full Rouse model including all internal relaxations. Figure 1(b) displays the outcome again for  $T = 373$  K. At first glance the result is surprising: even though by H-bond breaking a further relaxation channel is opened, the plain Rouse model alone overpredicts severely the decay of  $S(Q, t)/S(Q)$ . Seemingly, not all Rouse modes contribute equally to the

observed structure factor and the bond breaking dynamics significantly changes the mode spectrum in a nontrivial way.

In the earlier approach of Stukalin and Freed [11] aiming at the stress relaxation in macromolecular associates, the mode contributions to the relaxation rate were augmented by the bond breaking rate leading to effective relaxation rates of  $1/\tau_{p,\text{eff}} = 2/\tau_p + 1/\tau_c(M)$ , where  $\tau_c(M)$  is the characteristic time of scission for an aggregate of size  $M$ . Inspecting Fig. 1(b), it is clear that any increase of the mode relaxation beyond the plain Rouse rates will make the disagreement with the NSE data even worse.

Thus, the mechanism behind the dynamics as seen in the dynamic structure factor must be different: a significant contribution to the chain relaxation by a mode  $p$  only occurs if the mode relaxes before the chain breaks at  $\tau_c(M)$ . For the single chain relaxation, breaking means instantaneous loss of the restoring entropic forces that were transmitted by the bond. Thus, the driving force for the corresponding relaxation is lost and it slows down. The faster diffusion of the residues is already accounted for by the equilibrium size distribution. Whenever a chain breaks, somewhere else a chain is formed, but without internal stresses at the moment of formation. Because of its halt when the restoring force is lost on average a  $p$  mode only contributes with the probability  $e^{-\tau_p/\tau_c(M)}$ . Thus, the main effect of bond breaking, which is visible in the pair correlation function, changes the mode amplitudes that are affected by the probability of survival, rather than the mode relaxation times.

As a third step we include this phenomenon as a key ingredient for our description of the bond breaking dynamics in the aggregated chain. The amplitude modification mathematically is performed by the inclusion of the  $e^{-\tau_p/\tau_c(M)}$  factor at the end of Eq. (4). We identify the time  $\tau_c(M)$  with the effective chain lifetime. It is related to the bond lifetime  $\tau_b$  by multiplying the rate of breaks by the number of transient bonds ( $M-1$ ). For the  $M$ -chain lifetime this yields  $\tau_c = \tau_b/(M-1)$ . The complete loss of the mode contribution, even if, e.g., only one chain end separates, is probably a too extreme assumption. In order to account for this, we correct by a factor proportional to the spacing between modes:  $\tau'_c = \tau_c(M)/(1 - 1/2p)$ . This correction leads to a 20% change in  $\tau_b$ .

$\tau_b$  is the only free parameter to be fitted; all other values for  $l, Wl^4, N_b$  are known from independent sources [15,19];

the aggregation numbers  $M_{\text{agg},n}$  are known for the two lower temperatures [15] and extrapolated (and as an exception fitted). The solid lines in Fig. 2 display the fitting results and show an extraordinary good agreement with the experiment. Fitting only one parameter, the theory describes the chain and association dynamics nearly perfectly and at the same time is in complete agreement with all structural and macroscopic dynamic data [15]. Table I presents the obtained bond breaking times  $\tau_b$ , the lifetimes of an average associate  $\tau'_c(M_{\text{agg},n})$ , the average aggregation numbers  $M_{\text{agg},n}$ , the literature values for the Rouse rates  $Wl^4$ , as well as the resulting average translational diffusion coefficients  $D_{\text{av}}$  in comparison to the NMR data  $D_{\text{NMR}}$ .

Figure 3 displays an Arrhenius plot of the bond breaking time  $\tau_b$  and of the lifetime of the average aggregate  $\tau'_c(M_{\text{agg},n})$ . For the activation energies  $E_a$  we find 45 and 30 kJ/mol, respectively. The prefactor for the bond breaking time is 0.2 ps and is well in the order of what would be expected for an attempt frequency ( $5 \times 10^{12}$  Hz). The H-bond activation energy is higher than that of the association constant 38 kJ/mol [15] describing the thermodynamic equilibrium. Seemingly a small activation is necessary to break the bond. With the entropy contribution [15] of  $73.4 \text{ J/mol K}^{-1}$  a complexation energy  $\Delta G_{298}^0 = 16 \text{ kJ/mol}$  may be obtained, which is close to  $\Delta G_{298}^0 = 14 \text{ kJ/mol}$  obtained with the empirical expression for the hydrogen bonded complex stability given in Ref. [20]. Using this and assuming a good correspondence between the increments in free energy and activation energy we may infer  $\Delta E_a \approx 10\text{--}20 \text{ kJ/mol}$  per H bond [20] and as a consequence about 2 orders of magnitude acceleration or retardation of bond breaking rates upon addition or removal of one hydrogen bonding site in the stickers. A few

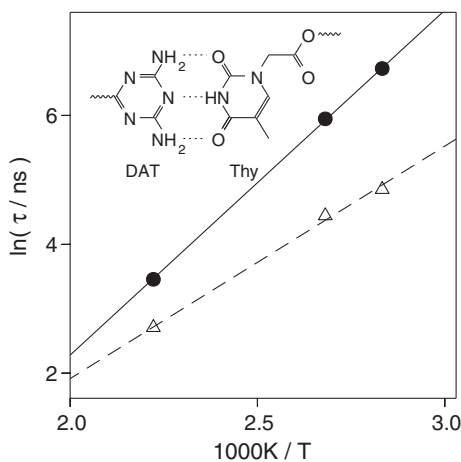


FIG. 3. Temperature dependencies of the bond breaking time  $\tau_b$  (circles) and the lifetime of an average aggregate  $\tau'_c(M_{\text{agg},n})$  (triangles). The inset in the upper left illustrates the sticker groups with the H-bond pairing.

attempts to determine the characteristic time scale of H-bond breaking in supramolecular compounds are described in the literature. In early work [21,22] on linearly associating functionalized short ureidopyrimidinone spacers a second dielectric relaxation peak termed  $\alpha^*$  relaxation was related to the mean lifetime of the hydrogen bonded spacers. Experiments on low-molecular weight Thy-DAP (diamidopyridine) hydrogen bonded liquids revealed dynamical signatures of H bonds manifesting themselves in a weak decoupling between mechanical relaxation and dielectric Debye relaxation, which was ascribed to the dissociation and recombination of H-bonded groups [7,23]. However, both the mechanism as well as the time scale remained unclear.

The NSE results also allow us to rationalize the observation of nearly perfect Rouse dynamics within the supramolecular polymer ensembles as concerns diffusion and viscosity: Table I displays the Rouse times  $\tau_b^R \approx \tau_e$  of the building blocks. For a PEG melt these are close to the entanglement times  $\tau_e$ . The lifetimes  $\tau'_c(M_{\text{agg},n})$  of the average aggregates are of the same order explaining thereby the inability of the ensemble to build up topological constraints. Rather than being affected by accelerated Rouse modes, the viscosity and diffusion are mirroring the Rouse response of the instantaneous equilibrium thermodynamic distribution of the ensemble.

The slowing down of the relaxation compared to simple Rouse dynamics originates from the loss of the relaxation channels provided by the lower modes of long chains that become inactive upon chain breaking. The breaking of a long chain disrupts the drag force from the other part of the long chain and the corresponding contribution to the relaxation motion stops. It is the different time correlation of the corresponding chain segments that influences  $S(Q, t)$ . If a mode vanishes due to chain breaking the correlator comes to a halt. Thus, its average relaxation amplitude is reduced. This view is corroborated by the excellent description of the measured  $S(Q, t)$  by the corresponding model over the whole wave vector–time range with only one adjustable parameter, namely, the characteristic bond breaking time scale.

Finally, we have presented a direct measurement of the so far intangible lifetime of supramolecular polymer aggregates in the melt together with the associated H-bond breaking times. In treating long entangled giant micelles employing the Poisson renewal approach, Granek and Cates [10] remarked, without elaborating on it, that this approach would fail in the Rouse limit, since long wavelength Rouse modes are more affected by the renewal process than high modes. Our experiments prove this idea and our model elucidates the detailed mechanism. The approach of Stukalin and Freed [11] assuming an acceleration of (chain mediated) stress relaxation contributions beyond mode relaxation for Rouse chains by bond breaking, i.e., acceleration, is clearly different from our results,

which show retardation due to loss of internal chain stresses upon breaking.

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