Supporting Information for:

A Critical Approach to Polymer Dynamics in Supramolecular Polymers

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Table of Contents:

Appendix 1. Arm retraction.[S1,S2]

This model often used for graft and star polymers and is based on the tube model. The stress relaxation has three contributions, Rouse-like motions, arm retraction and reptation, therefore:

$$G(\mathrm{t}) = G_{\mathrm{retraction}}(\mathrm{t})+ G_{\mathrm{reptation}}(\mathrm{t})+ G_{\mathrm{Rouse}}(\mathrm{t}) \qquad (1)$$

The fraction of the stress relaxing by arm retraction can be expressed as:

$$G_{\mathrm{retraction}}(\mathrm{t}) = \int_0^{x_d} dx \frac{dG(\Phi(x))}{dx} \exp\left(-t/\tau(x)\right) \qquad (2)$$

with 0 ≤ x ≤ 1, the fractional distance from the free end of a chain to the middle of the chain. Here in case of linear polymer the chain is considered a two-arm star polymer with equal arm size. X_d is the crossover between the arm retraction time scales and reptation. The volume fraction Φ of unrelaxed material is given by $\Phi(x) = 1 - x$.

This means in case of graft polymers the stress relaxation starts from the outermost segments of the arms and by time the deeper segments of the chain relax first via Rouse-like motions and contour length fluctuations (CLF) and then via reptation. After the arms are relaxed, the backbone relaxes in a dilated tube as the relaxed arms can act as a solvent.

The retraction is an activated process and depends on the length of the chain. For small fluctuations closer to the chain ends, the branches perform a Rouse-like motion along the primitive path and the early retraction time $\tau_{ae}(x_a)$ ($\tau_{be}(x_b)$ for the backbone) is considered. Whereas for deeper segments an activated fluctuation is needed to overcome the unfavorable entropy effects. Therefore, at longer times $\tau_{al}(x_a)$ is considered. The transition to an activated relaxation time, occurs at a certain value of the coordinate x_a and the potential $U(x_a)$ becomes effective. The arm relaxation time can be expressed as:

$$\tau_a(x_a) = \frac{\tau_{ae}(x_a)e^{U_a(x_a)}}{1 + \tau_{ae}(x_a)e^{U_a(x_a)}/\tau_{al}(x_a)} \qquad (3)$$

And the backbone relaxation can be calculated using:

$$\tau_{bb}(x_{bb}) = \frac{\tau_{be}(x_b)e^{U_b(x_b)}}{1 + \tau_{be}(x_b)e^{U_b(x_b)}/\tau_{bl}(x_b)} \qquad (4)$$

Appendix 2. Modified time marching algorithm and hindered fluctuations (by van Ruymbeke et al.).[S3]

For the detailed description of the model we refer the reader to the original theory.[S3] Here briefly the modification of the theory to the supramolecular systems is discussed.

The relaxation modulus of the supramolecular system follows the basic mechanism for the linear covalent chains:

$$\frac{G(t)}{G_N^0} = \Phi(t)\Phi_{CR}^{\alpha}(t) + \Phi_{Rouse}(t) \qquad (1)$$

Where $\Phi(t)$ is the chain survival probability or unrelaxed fraction of the tube. $\Phi_{CR}^{\alpha}(t)$ is the global tube relaxation (e.g: based on constraint release (CR) motions). $\Phi_{Rouse}(t)$ is the contribution of the low frequency Rouse-like motions and α is the dilution exponent.

The relaxation of the chain within a tube starts from the free end of the polymer chain (x=1) towards the center (x=0) assuming the polymer chain is a 2-arm star polymer. Therefore, the relaxation occurs using contour length fluctuations (CLF) as well as reptation:

$$\Phi(t) = \int_0^1 \varphi_{reptation}(x,t).\varphi_{fluctuation}(x,t)dx \qquad (2)$$

The Rouse-like dynamics at high frequencies follows the basic Rouse-like relaxations limited by sticker association-dissociations. Therefore, the Rouse contribution in equation 1, can be calculated based on sticky Rouse model as follows:

$$\Phi_{Rouse}(t) = \frac{5}{4Z}\left[\sum_{j = z_{app} + 1}^{N} exp\left(\frac{-j^2t}{\tau_R}\right) + \sum_{j = Z}^{Z_{app}} exp\left(\frac{-j^2t}{\tau_{S.R}}\right)\right] \qquad (3)$$

where $(\frac{j^2}{\tau_R})^{-1}$ is the Rouse relaxation time in the absence of the stickers and $(\frac{j^2}{\tau_R})^{-1}$ is the Rouse-relaxation time for longer segments after dissociation of the stickers:

$$\tau_R = \tau_e Z^2 \qquad (4)$$

and

$$\tau_{S.R} = \tau_{sticker} {Z_{app}}^2 \qquad (5)$$

where τ_e and $\tau_{sticker}$ are the Rouse relaxation time of an entanglement and the association lifetime of stickers, respectively.

Finally, the number of entanglements has contributions from chain entanglement (Z) and the number of stickers along the chain (N_s):

$$Z_{app} = Z + N_s \qquad (6)$$

The model considers both the fluctuations and reptation but is modified to take into account the extra friction or extra penalty arising from stickers. Due to the presence of the stickers the CLF of the chains slows down to the rhythm of the sticker association/dissociations.

In the extra penalty approach, the stickers along the chain start to blink after which a portion of the chain is free to fluctuate and relax the stress. Of course, the chain ends have more time to fluctuate as one end is free of constraints. Therefore, the relaxed fraction of the chain via (hindered) fluctuations can be expressed as:

$$\varphi_{fluctuation}(x,t) = \exp\left(-\frac{\Delta t(x,t)}{\tau_{fluc}(x,t)}\right) \qquad (7)$$

where $\Delta t(x,t)$ is the accumulated time during which a segment x could fluctuate.

On the other hand, in the extra friction approach the linear associative polymer is considered like a comb-like polymer. Therefore, an extra friction comes from the side groups (whether it is a sticker or side branch in comb-polymer) and the total friction is expressed by:

$$\xi_{\mathrm{total}} = N_i \xi_0 + \frac{2(i-1)kT\tau_{sticker}}{a^2} \qquad (8)$$

where ξ_0 is the monomeric friction, N_i is the number of mobile monomeric units at mode i, and a is the tube diameter. It has to be pointed out that no tube dilation exists unlike comb polymers in which the relaxation of the branches leads to a solvent-like effect and consequent tube dilation.

Similarly, reptation has contributions from the entanglements and the stickers leading to the equation 9 as follows:

$$\tau_{\mathrm{rept}} = 3\tau_e Z^3 \varphi_{active}^{a}(t) + \frac{2N_s\tau_{sticker}}{\pi^2}\varphi_{active}^{2a}(t) \qquad (9)$$

where $\varphi_{active}(t)$ is the fraction of the polymer not yet relaxed by fluctuations.

Appendix 3. Modified mean-field percolation theory of Rubinstein and Semenov (by Chen et al.).[S4]

For the detailed description of the theory it is encouraged to refer to the paper by Chen et al.[S4] This theory based on the chemical sol-gel transition with a few modifications. The gel point is predicted from the growth of the sol, generation by generation to an infinite size:

$$p_c = {}^{1}/(N-1) \qquad (1)$$

where N is the functionality, N–1 corresponds to the available (potential) functionalities and the extent of gelation can be expressed by:

$$\varepsilon = {}^{(p-p_c)}/_{p_c} \qquad (2)$$

with p being the degree of reaction. Depending on different values of ε a regime can be defined. For ε = -1 the behavior of an unentangled polymer is predicted by $G' \sim \omega^n$ (where n = 0.5 and 1 before and after the Rouse relaxation time). Therefore:

$M_X = M_0 N_X$ (3) the precursor chain molecular weight

$R_X = N_X^{1/2} b$ (4) the precursor chain size

$\tau_X = \tau_0 N_X^2$ (5) the precursor chain Rouse relaxation time

with b the segmental size, N_X the number of segments, M_0 the segment molecular weight, and τ_0 the relaxation time of one segment.

If $-1 < \varepsilon < -\varepsilon_{\mathrm{G}}$, clusters are formed via mean-field (MF) percolation and the Rouse relaxation of the cluster leads to $G' \sim \omega^1$ before the terminal relaxation (ε_{G} is the extent of the reaction at Ginzburg point).

For the third regime $-\varepsilon_{\mathrm{G}} \leq \varepsilon < -\varepsilon_{\mathrm{c}}$ where MF and critical percolation (CP) apply in shorter and longer times than $\tau_{\mathrm{X}} N_{\mathrm{X}}$ and $G' \sim \omega^n$ with n = 1 and 0.67 for MF and CP, respectively.

In the fourth regime where $-\varepsilon_{\mathrm{c}} \leq \varepsilon < \varepsilon_{\mathrm{c}}$, a time called "effective breakup time" is taken into account. The effective breakup time is defined as the time the cluster takes to breakup into two comparable clusters after the stickers are broken (after that sticker lifetime is reached). Since there is a competition between the cluster dissociation time ($\tau_{\mathrm{life}} = \tau_{\mathrm{s}} \varepsilon$) and cluster relaxation time ($\tau_{\mathrm{char}} = \tau_{\mathrm{X}} |\varepsilon|^{-3}$), comparing τ_{life} and τ_{char} one can calculate τ_{c} as:

$$\tau_{\mathrm{c}} = \tau_{\mathrm{x}}^{1/4} \tau_{\mathrm{s}}^{3/4} \qquad (\text{if } -\varepsilon_{\mathrm{c}} \leq \varepsilon < \varepsilon_{\mathrm{c}}) \qquad (6)$$

with τ_{s} being the sticker lifetime. For 1 < ε sticky-Rouse model applies.

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