Discussion of paper by M. E. Shivokhin, T. Narita, L. Talini, A. Habicht, S. Seiffert, T. Indei, and J. D. Schieber, entitled 'Interplay of entanglement and association effects on the dynamics of semidilute solutions of multisticker polymer chains'

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Gun Woo Park: Is there any way to decompose stress tensor into the contributions of entanglement and stickers? If so, it might be helpful to visualize relaxation modulus in Fig. 4 with individual autocorrelation part and cross-correlation part of each contribution.

For instance, the stress tensor can be rewritten in position vector rather than connector vector Q. In this replacement, the stress tensor might be decoupled into (a) pure entanglement point contribution, (b) pure sticker point contribution, and (c) cross terms. Then the stress autocorrelation gives a pair of (a,a), (b,b), and the sum of other correlations.

Answer: No, this does not seem possible. We do not know how to write the stress as a sum over these different components in order to do this—it's not a clean separation.

Gun Woo Park: Concerning the lifetime of associated stickers (τ_L) and free stickers (τ_f): I am not sure about the influence of τ_f is on the model prediction. In Fig. 7, for instance, the terminal region is postponed by decreasing τ_f (purple lines). Is it due to the fact that decreasing the lifetime of the free stickers will increase the crosslinking ratio r_c?

Answer: r_c (β_{st}) never changes. But the number of cross-links (associated stickers) per chain increases with decreasing τ_f. That slows down reptation.

Johan Mattsson: For the surface fluctuation specular reflection technique (SFSR) do you need to do any special accounting for surface effects in order to determine G^*, since the material close to the surface can be different from the bulk? What about the existence of a gradient in G^* values at the surface?

Answer: You definitely need surface tension. The characteristic vertical length of the measurement is given by the beam radius: it means that SFSR probes the average properties over $\sim$50 μm, i.e., for most systems, it corresponds to bulk properties.

Michael Rubinstein: What is the amplitude of the surface wave compared to, e.g., tube diameter?

Answer: The roughness of a surface is of a few angstroms for liquids with usual surface tensions. The equipartition theorem implies that all spatial modes of the surface are thermally excited. However, by using the specularly reflected part of the laser beam (whose size can be tuned by changing the focal length of the lens we use), we measure mainly the contribution of modes whose wavelengths are close to the beam size. This is because we do not measure a variation of the height of the surface but of its local slope. In our experiments, the beam size is 55 μm. The measurement scale is therefore much larger than any length of the polymer, even though the surface fluctuations are much smaller.

Michael Rubinstein: Do you account for self-association of chains?

Answer: No.

Michael Rubinstein: How do you take into account the possible change in β?

Answer: β is the equilibrium entanglement activity, and is kept constant always, even during nonlinear flow. This assumption guarantees that nonequilibrium conformation distributions will always return to equilibrium in the absence of flow. However, we should point out that we considered only the equilibrium relaxation modulus for the present model.

Evelyne van Ruymbeke: You say that the polydispersity of the sample in molar mass is not taken into account, which does not allow quantitative prediction. But do you think this is the most important? To me, the polydispersity in association and free lifetimes play a role even larger.

Answer: Polydispersity in molar mass plays an important role in entangled polymers. On the other hand, polydispersity in τ_L is also important in associating polymers because τ_L determines the peak position in G'' and the longest relaxation time is determined by the number of stickers per chain and τ_L. For entangled associating polymers, polydispersity in τ_f should be also important as expected from Fig. 7. It is difficult to answer which effect is the most important for entangled associating polymers. But at least in our material, polydispersity in molar mass should be the largest. That's why we pointed out it.

Evelyne van Ruymbeke: You seem to adjust only one parameter, the ratio of association for free time. But should you not consider these two times as two independent parameters? What is it happening if you multiply these two times by a constant? I would expect that it affects the balance between disentanglement/disassociation mechanisms?

Answer: We have three fundamental time scales: τ_L, τ_f, and τ_K. The ratio of the first two is determined by equilibrium thermodynamics. That leaves a single, independent ratio. However, we assume that τ_K is much faster than everything else. For convenience, we did not make it much faster, but the physics underlying other assumptions are consistent with that. As a result, our predictions are not so sensitive to that ratio. Finally, we see that the disentanglement rates are determined largely by disassociation. Or course, the question is correct, in general, and systems could conceivably be built where the second ratio comes into play.

Jorge Ramirez: You showed that entanglements and stickers are not additive in their effects. But, does the model include the idea that when a sticker dissociates, it may return to the same place and stick again?

Answer: We assume perfect relaxation on dissociation, i.e., no return.

Evelyne van Ruymbeke: You don't seem to account for loops. Are loops important? Do they contribute to the modulus?

Answer: Yes, they should probably be included at lower concentrations especially. But this is a simple single-chain model. Loops should be included in a self-consistent way, and we haven't yet considered it.