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Barbara Gold: Have you done dielectric measurements in order to determine the sticker lifetime?

Answer: We did do one test, but the temperature was too low to detect the dynamics of the reversible bonds within the experimental frequency window. But indeed, this is something we are planning to do in the near future.

Ralph Colby: Is there an inconsistency? The activation energy is 125 kJ/mol, so >50 kT, so it should be slow and sticky. But this is not consistent with the fraction of associated end-groups.

Answer: Indeed, if we consider the very long association time of the metal-ligand complexes, the proportion of associated stickers at any time *t* should be very close to 1, which is not what we found from our analysis. This is due to the fact that adding the stoichiometric amount of metal ion does not seem to be enough to allow all the ligands to find a free ion and participate to the network. Therefore, we suspect a non-negligible proportion of arms to behave as dangling ends due to this lack of ions available in their surroundings, and not because of the dynamics of the reversible bonds. This assumption is validated by the figure here below, which shows the relaxation moduli of the sample Star160k+Cu, with different amounts of Cu^{2+} ions (the stoichiometric amount = 0.5 eq.): by adding an excess of metal ions, the fraction of dangling arms relaxing at high frequency significantly decreases (Fig. 1).

Therefore, in the model, we have to account for this possible population of free arms found at stoichiometric amount of ions. This is done through the parameter p_{ass}, which is the only real fit parameter of the model.

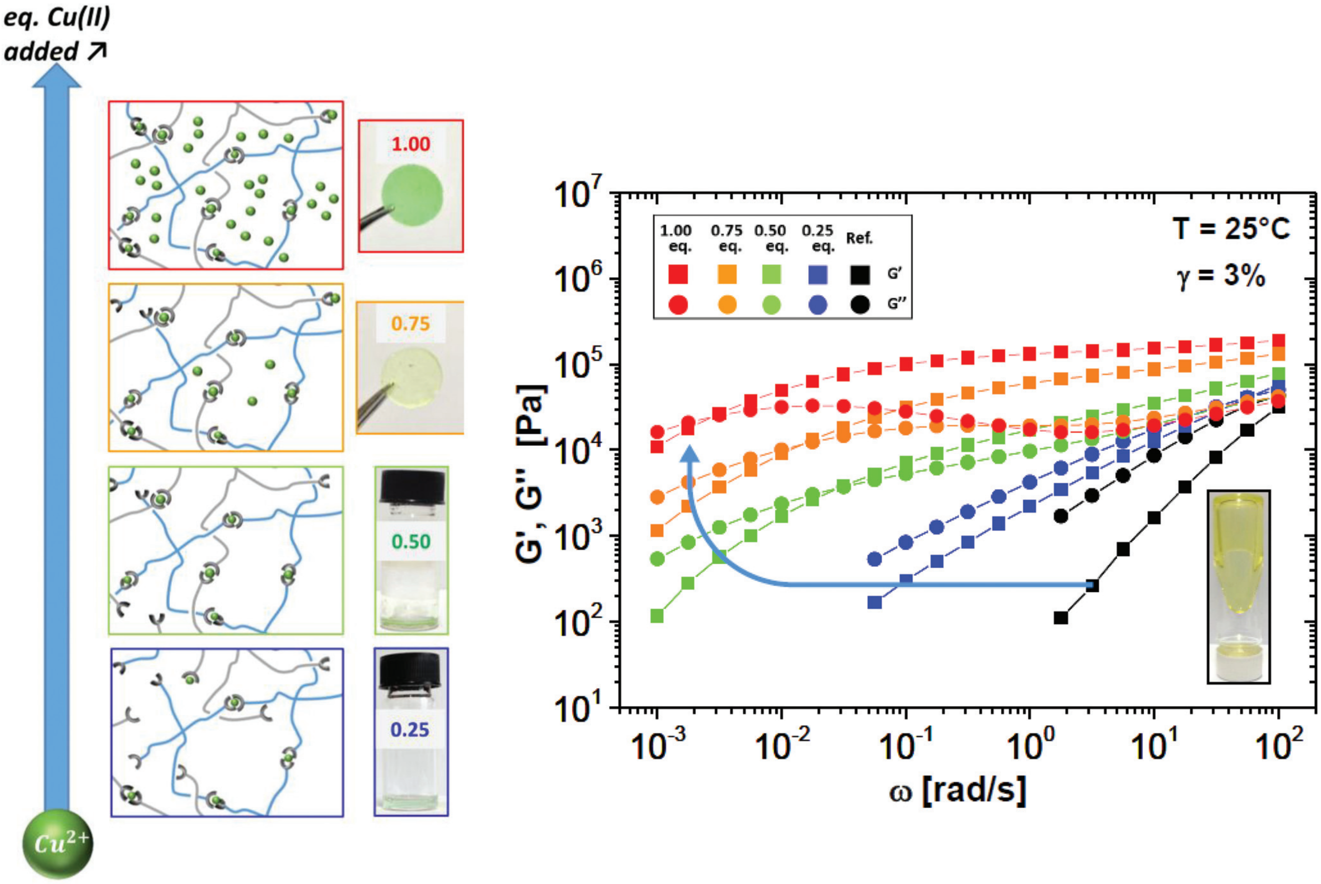

FIG. 1. Relaxation moduli of Sample Star160k+Cu, containing different amounts of cupper ions (the stoichiometric amount = 0.5 eq.), at 25 °C, and cartoon representing these different networks.

Jeremy Brassinne, comment to R. Colby's remark: In the particular case of Cu(II), we could expect a large fraction of five-coordination complexes, i.e., Cu(II) monoterpyridine dichloride, because the d^9 electronic configuration of the metal cation is stabilized by a second-order Jahn–Teller effect. This is another way to explain the large fraction of dangling arms.

Answer: It must be noted that similar results were obtained with the other metal ions, such as cobalt or zinc.

Sanat Kumar: Can you predict the concentration of ions for entanglements to dominate stickers in stress relaxation?

Answer: In all cases, the star arms are very long and the density of the stickers is low compared to the entanglement density. Thus, we expect the level of plateau modulus to be dominated by the entanglements, with a value only slightly higher than the entanglement plateau modulus (160 kPa). This is indeed verified (see Fig. 2). We also expect that the stress relaxation takes place as soon as the star arms are able to disentangle. If the concentration of ions is low, the stars will assemble into simple architectures, such as pom-pom or comb architectures and these supramolecular assemblies will be able to relax as covalent architectures (thus fully governed by the entanglements) as long as their relaxation time is shorter than the dissociation time of the metal-ligand complexes. But at larger concentration of ions, the terminal relaxation is influenced by both association and entanglement dynamics since the arms must first dissociate, then disentangle in order to relax. In order to determine the relative importance of these processes, one should compare their corresponding characteristic times, which requires knowing the association time of the complexes as a function of the ion concentration. This is something we have not studied up to now.

Michael Rubinstein: What about a sticker coming back to the same partner, i.e., relax a bit of the arm, then return to the same partner without relaxing all entanglements? The concentration of free ends per entanglement volume is not high.

Answer: Indeed, the probability of a free end to detach and to come back to the same partner should be quite high. In the case studied here, since the relaxation time of a free arm (∼0.01 s) is very short compared to the terminal relaxation time of the telechelic stars, we didn't consider the possibility of the arms to only partially disentangle before coming back to the same (or even to a different) sticker. The assumption according to which the chain ends must associate and dissociate several times in order to fully disentangle is the assumption we followed in a previous work [1] for describing the dynamics of very long telechelic star molecules. Figure 2 presents the results obtained with this model, for sample Star250k+Co. The parameters τ_{as} and τ_{free}, which are fit parameters, represent the average time during which a sticker is associated or free, respectively. While a reasonable agreement can be reached, we could not rationalize the values used for these two parameters and we could not use the same parameters for the different samples. Also, we had to use relatively small values of τ_{free} (∼the Rouse time of an entanglement segment, τ_e) in order to ensure several association/dissociations of the stickers before the full arm relaxation, which does not seem realistic. Therefore, we didn't follow this approach (Fig. 2).

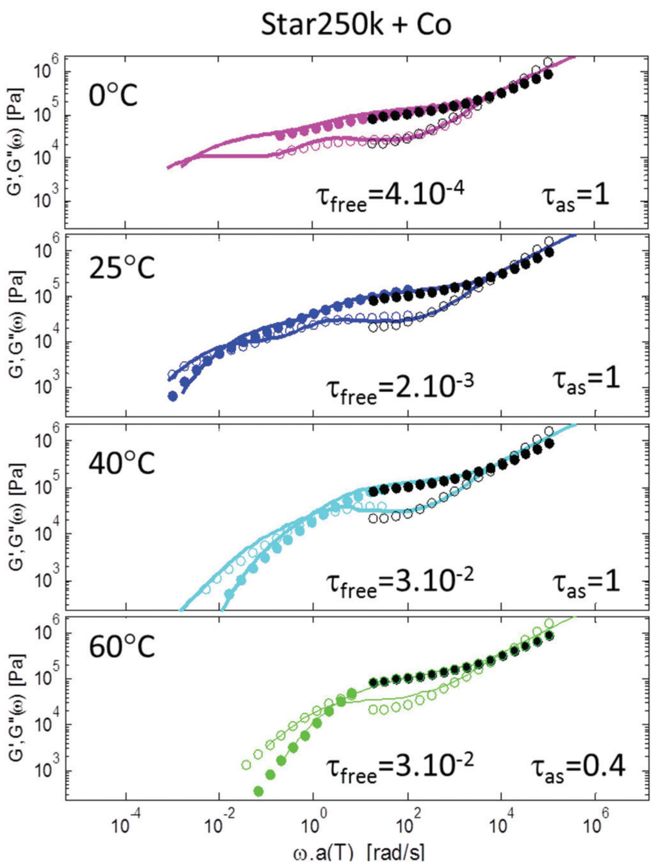

FIG. 2. Comparison between experimental (symbols) and theoretical (continuous curves) relaxation moduli for Sample Star250k+Co, containing 0.5 eq. of ions, at different temperatures. The theoretical curves have been obtained, based on the approach proposed in [1].

Daniel Read: If you return to the same partner, there would be some residual stress even after all entanglements are relaxed, i.e., the same stress as for unentangled stars returning to the same partner.

Answer: Indeed. This is an interesting idea. We should explore it further.

Jeremy Brassinne: How the authors explain the fact that metal-containing samples relax differently from the reference sample at the limit of high temperatures (see, e.g., Fig. 11), at which the sticker is expected to become "invisible"? Is thus the choice of the same shift factors as the blank appropriate to shift the viscoelastic data of the supramolecular polymers?

Answer: Obviously, 80 °C is not high enough to fully erase the influence of the stickers. Still, one can observe that the difference between the viscoelastic properties of the neat sample and of the telechelic sample is decreasing as temperature is raised.

Yes, using the same shift factors makes sense. They have the same T_g and same segmental dynamics.

Salvatore Coppola: What is the average distance between two "neighbor ions"?

Answer: It would depend on the length of the arm.

Michael Rubinstein interjected: But there are many overlapping arms. A quick estimate suggests that ions are about a tube diameter apart on average.

Hiroshi Watanabe: If we focus on a single arm, if it changes partners does the network relax? What is the effect of tension unbalance (that becomes important when we think about the ensemble of arms)?

Michael Rubinstein answered: It relaxes to kT per strand if you return to the same partner, because it eventually relaxes the tube, but keeps the connectivity as in unentangled networks. If you get a new partner you eventually relax the whole network.

Ameur Louhichi: Concerning the parameter p_{ass}, the fraction of associated stickers: Is it possible to calculate it from the stickers' plateau using rubber elasticity? If the elastically active chain has a molar mass of $2M_{\mathrm{n}}$ (2arms), so one can calculate the ideal plateau if all stickers are active (no loops allowed), then compare the experimental plateau with this ideal value.

Answer: Yes, indeed. However, for our materials this does not work since the plateau is strongly dominated by the entanglements. Also, the "second" plateau is not well defined (we observe a slow decrease of G' with decreasing the frequency). But somehow, this is what the model is doing: determining p_{ass} in order to correctly capture the two plateaus.

Reference

[1] van Ruymbeke, E., D. Vlassopoulos, M. Mierzwa, T. Pakula, D. Charalabidis, M. Pitsikalis, and N. Hadjichristidis, "Rheology and structure of entangled telechelic linear and star polyisoprene melts," Macromolecules **43**(9), 4401–4411 (2010).