Discussion of paper by J. Brassinne, A. Cadix, J. Wilson and E. van Ruymbeke, entitled ‘Dissociating sticker dynamics from chain relaxation in supramolecular polymer networks – The importance of free partner!’

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Zuowei Wang: For the low molecular weight polymers, what happens if you increase the number of metal ions? Do you observe a similar effect as when decreasing the number of ligands?

Answer: The effect of metal content was not systematically screened within the entire polymer library, but an increased dynamics is expected to be observed at higher ion contents.

Michael Rubinstein: Is the time of removing each sticker the same (i.e., time from 3 to 2 and from 2 to 1 stickers)? Do most ions have the full complement of saturated stickers? Perhaps the effects of neighboring chains will be important.

Answer: Even if the bonding energy might be similar or increasing with the formation of bis- and tris-complexes, there might be indeed an increasing energy penalty to be considered that is associated with the formation of saturated complexes due to steric hindrance between the neighboring chains. We assume the formation of tris-complexes given the high association constant, but a clear differentiation might be difficult to achieve experimentally since mono-/bis-/tris-complexes essentially have identical signature in spectroscopy, for example. Advanced characterizations might be thus required, maybe with labeling.

Charles-Andre Fustin: Do you think you could observe the same behavior with bis-complexes, compared to tris-complexes?

Answer: The same behavior would be expected, but it is difficult to predict since there is a fundamental difference between networks held together by bis-complexes compared to tris-complexes. Indeed, three stickers allow keeping the percolated network properties even if one sticker dissociates.

James Wilson: We could try using the same polymer with another metal, able to link only two chains, in order to see the effect.

Answer: Indeed, we could try to favor bis-complexes, but the related association strength will also be affected, so it will be difficult to compare. Also, the formation of nonsaturated bis-complexes with the metal cation will open a pathway for the associative ligand exchange mechanism. Via this mechanism, a free sticker can displace a bound sticker and relaxation might be thus observed even under a low concentration of free partners (i.e., at stoichiometry).

Daniel Read: What about keeping the stoichiometry fixed by adding some short chains (this might have interesting effects on the chain and sticker exchange dynamics, whilst keeping all ions saturated)?

Answer: This would be interesting, and we could prepare mixtures to change the potential network structures.

Ralph Colby: What about the effects of hydrated counteranions? We often use Gaussian to compute the effects of steric crowding on the binding energies which could be important since there are three anions and three stickers around each trivalent cation.

Answer: We did not investigate the effect of the counterions but it might be indeed of interest to compute such effect on the stability of the metal–ligand crosslinks, and to relate this on the rheology of the gels if variations are observed.

Ralph Colby: Your Fig. 15 suggests a very simple way to evaluate the association lifetime at any temperature. First apply strain amplitude 10 (1000%) for 1 min and then start a time sweep at 1 Hz with strain amplitude 0.1 (10%) and watch the rehealing of the transient network. Probably some sigmoidal function can determine the time scale of rehealing? Do you think such a protocol could be done and be useful for supramolecular polymers?

Answer: This protocol is indeed useful and applied in some studies. Here, attempts were made to evaluate the recovery kinetics of our hydrogels by strain pulses. In this test, the shear strain was abruptly varied from 10% to 5000% and backward and the evolution of storage and loss moduli was monitored with time. Fast responses were recorded during both breaking and recovery event. Therefore, the timescale of reassociation cannot be extracted from the recovery in storage modulus.

Our current efforts are now dedicated to the investigation of the nonlinear rheology via orthogonal superposition rheometry. Our initial results suggest that the nonlinear rheology of these samples include both shear-induced creation and destruction of metal–ligand bonds. Our hope is that we could clearly differentiate these two processes and their dynamics using this advanced characterization.

From the SUPOLEN team (anonymous): As shown, the relaxation behavior depends on the amount of metal ions and thus in the presence of mono, bis, and tris-complexes. What is the relationship between this behavior and the relative values of the three association constants (K1, K2, and K3)? For example, would the same behavior be observed if K3 is largely superior to K2 and K1?

Answer: Unfortunately, we didn't estimate the theoretical fractions of mono-, bis-, and tris-complexes as a function of the metal-to-ligand ratio because we didn't assess the value for the equilibrium constants, neither experimentally nor from the literature. Otherwise, this would indeed allow establishing how the rheological behavior of the gel evolves with these fractions.

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By analogy with similar complexes, the three association constants should be high and should follow the relative order K1 < K2 < K3, each being at least one order of magnitude higher than the previous. The fraction of mono- and bis-complexes in the media should be thus very low compared to tris-complexes, at least at the stoichiometric balance. When an excess of metal ions is added, the equilibria are slightly shifted in favor of nonsaturated complexes.

It is not excluded that the fractions of mono- and bis-complexes stay very low and that most of the excess of metal ions simply remains free in solution if the tris-complexes are very well favored (K3 largely superior to K2 and K1). These free cations can act as transient carriers that immediately stabilize the free ligand in the form of monocomplexes and thus open an enhanced pathway for the ligand exchange process by lowering the activation energy of the hopping process.

From the Supolen team (anonymous): Is it possible to determine a critical distance between stickers at which the observed relaxation behavior is obtained? How is this distance dependent on the complex lifetime?

Answer: We didn't determine it experimentally, but it is possible after the synthesis of a larger library of associating polymers with varying amounts of stickers. An effect of the chain length is also expected since the observed relaxation is rather a matter of the number of active stickers per chain.

This distance may be independent of the complex lifetime as long as it stays relatively long. The observed relaxation is indeed most probably due to the relaxation of chains, dangling ends, or finite size aggregates, which has nothing to do with the sticker lifetime. A clear answer would however require more experimental data on at least two different metal ions, since it remains difficult to predict the complex behavior of the gel.