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Hiroshi Watanabe: Fluctuation of crosslinking points in gels/rubbers is known to reduce the equilibrium modulus below the modulus for an idealized case shown in Eq. (1). Is there any possibility that the observed difference between n_{stoic} and n_{eff} ($<n_{\text{stoic}}$) at 60 °C is due to this fluctuation effect?

Answer: Yes, along with elastically ineffective strands and chain entanglements, fluctuations of crosslink points may also partly explain the differences between n_{stoic} and n_{eff}. For example, consider the classical phantom model that allows for crosslink fluctuations, but also allows chains to cross one another. The elastic modulus of the phantom model is

$$E_{ph} = 3\upsilon_{eff}kT(1 - f/2),$$

which is a factor of exactly $f/(f-2) = 3$ softer than that of E_x, from the affine model [Eq. (1)].

Equation (4) assumes that the stress relaxation rate is identical to the chemical dissociation rate. However, the stress relaxation requires the network strand motion (decay of strand orientational anisotropy), and this assumption is valid *only when* the strand motion is much faster than the chemical dissociation (as is the case for rather dilute hydrophobically modified urethane-ethoxylate associative polymers solutions, for example).

Hiroshi Watanabe: Is there any information about the relative magnitude of the rates of the chemical dissociation and chain motion in the poly(caprolactone) (PCL) network examined?

Answer: The dynamics for network strand motion in the amorphous melts are believed to be much faster than chemical dissociation. We did not study this explicitly. However, the literature [1] reported the relaxation modulus of similarly crosslinked gels from PCL prepolymers to be $G = S$ t-n with the most similar gel ("PCL2" in their paper) having experimentally determined values of $n = 0.91$ and $S = 5.1 \times 10^{-1}$ Pa s^n. These values indicate very fast relaxation of PCL compared to the timescales shown in our Figs. 3 and 5.

Flanco Zhuge: As explained with Eqs. (5)–(10), knowing E′, you determine the fraction of associated groups, p, based on Eqs. (5) and (6), which allows determining K_{eq}, based on Eq. (9).

Could you do the opposite, i.e., measuring the equilibrium constant K_{eq} in order to determine the (real) T-dependence of the fraction p?

Answer: Yes, one would simply need to measure the temperature dependence of K_{eq} to get the temperature dependence of the extent of conversion p. This can normally be done by spectroscopy. However, in some cases, the equilibrium constant is difficult to measure spectroscopically because binding groups are too dilute or are not accessible. I think there is a need for a model system that one can determine K_{eq} both spectroscopically and mechanically to further validate the central idea of our paper.

Charles-Andre Fustin: It is mentioned in the paper that some stars are coupled by disulfide bridges. Such bonds can also be reversible, but their dynamics are probably different from the main Diels–Alder (DA) bonds. Is there a signature of these additional reversible bonds in the different experiments?

Answer: We noticed that the molecular weight and polydispersity increased when the triacrylates were converted to trithiols (see supplementary material). Therefore, we expect some oxidation of thiols to form some S-S coupled stars. The resulting S–S bonds can exchange with unreacted thiols. Unreacted thiols were observed using Elman's reagent, but could not be quantified. Therefore, we expect the amount of

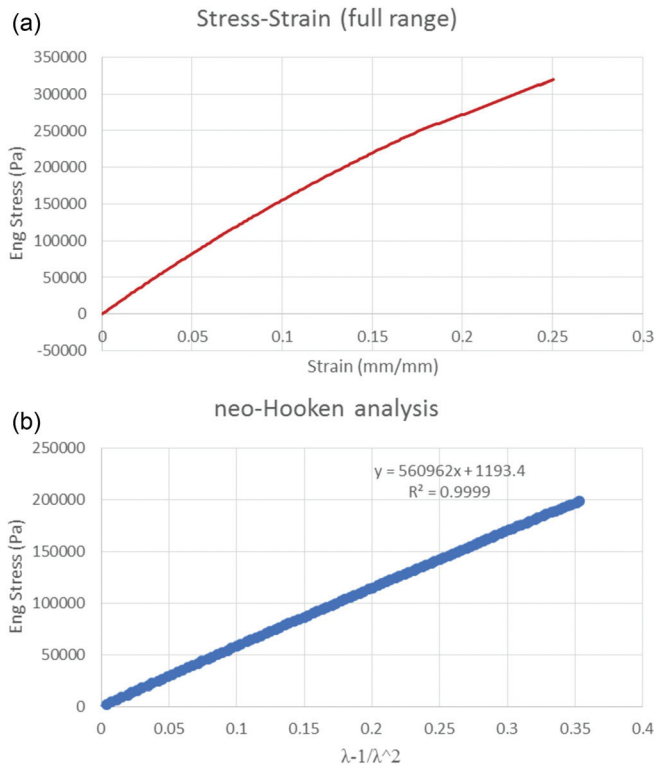

FIG. 1. Stress strain relationship of thermoreversible DA network, PCL-5.5 kDa. Data were acquired using a slow strain rate (∼1%/s).

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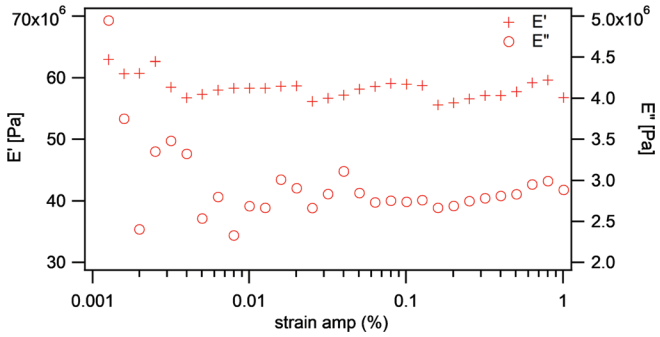

FIG. 2. Strain sweep from dynamic mechanical analysis of PCL-5.5 kDa. The oscillation frequency is 1 Hz, and the temperature is 60 °C.

disulfide exchanges to be small compared to the DA exchanges. The DA exchange response occurs on similar time-scales as that reported in the literature. From our raw mechanical data, it would be difficult, or even impossible, to discern the effects of disulfide exchange from DA exchange. That is a shortcoming of our chosen chemistry.

Evelyne van Ruymbeke and Dimitris Vlassopoulos: What is the strain amplitude above which the response is nonlinear? And what is the influence of these large deformations on the stress level? Since the curves are normalized (for example, in Fig. 3 or 5), it is difficult to determine whether the response is weakly or strongly nonlinear.

Answer: First, as shown in Fig. 1, the stress-strain data acquired at a slow rate ($\sim 0.01\ s^{-1}$) show that stress is quite linear beneath 8% strain. The engineering stress of the DA network studied in the manuscript at 60 °C is also shown. The same data follow the neo-Hookean model very well, i.e., stress is linear against $(\lambda - 1)/\lambda^2$ over the entire range of λ (0%–25% strain). The nonlinearity of the neo-Hookean model could be used to determine "weak" versus "strong" nonlinearity.

In oscillatory strain experiments, the strain amplitude was first varied to ensure experiments are conducted in the linear viscoelastic regime. The data in Fig. 2 show the DA network's "strain sweep". E' and E'' remain fairly constant at small strain amplitudes up to 1%. Experiments were performed at strain amplitudes $<1\%$, typically around 0.1% strain. Large amplitude oscillatory strain would be interesting to consider in the future.

Peter Olmsted: I find it very interesting that the DA bond breakage is so unaffected by stress. Can this be modified to introduce some stress-sensitivity into the bonds?

Answer: We also found it interesting that we did not see bond breakage induced by stress. However, we only looked at a relatively low stress range where stress was too low to influence the DA bonds. We do expect to see DA breakage at higher stresses. Yes, we suspect it would be possible to modify the DA equilibria by using carefully placed substituents, if that is what you are thinking. Another approach would be to replace the reversible covalent bonds with softer bonds such as reversible hydrogen bonds such as the ureidopyrimidinones.

Reference

[1] Izuka, A., H. Winter, and T. Hashimoto, "Molecular weight dependence of viscoelasticity of polycaprolactone critical gels," Macromolecules **25**, 2422–2428 (1992).