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**Daniel Read:** Is time-temperature superposition principle (TTS) really working for your material? Visually, it appears there is a region between the two plateaus where the curves don't quite match up. Did you try plotting the data in (for example) the van Gurp–Palmen representation (tan $\delta$ vs $G^*$) which would show up regions where TTS might fail.

**Johan Mattsson:** Is the rheology master curve constructed properly? What about thermorheological complexity? This will affect the reliability of the data in the intermediate frequency regime.

**Answer:** We don't state, that our system is thermorheologically simple, but we state that it can be treated in very good approximation as thermorheological simple. We proved that the activation energy of group dissociation (28.5 kJ/mol) is one order of magnitude lower than the activation energy of the alpha-process (110 kJ/mol), which therefore dominates the systems behavior. Thus, the applicability of time-temperature superposition is a physical, well-founded approach. Of course, the effect of group activation still exists, which leads not to a perfect, but still a very good level of overlap in the region between the two plateaus (the frequencies at which group activation becomes visible) (see Fig. 13 of the publication). Therefore, also in the van-Gurp–Palmen representation, no breakup of the TTS becomes visible.

The rheological master curves are constructed by using a two dimensional residual minimization carried out via a cubic spline interpolation. The horizontal and vertical shift factors are determined by this best-fit procedure, leading to mathematically well-constructed master curves and thus reliable rheological activation times. We would like to stress the experimental fact that a direct measurement of $G^*(\omega)$ over a time range at the reference temperature is in perfect agreement with the modulus of a TTS-shifted curve.

**Hiroshi Watanabe:** The dielectric relaxation data may be affected by the dissociation/reassociation times due to the dipole moment correlation. But dielectric relaxation occurs only when the dipole loses its orientational memory, and no dielectric relaxation occurs if a sticker associates again with its original partner and recovers its initial dipole orientation. Then, what is the mechanism of dielectric relaxation observed at frequencies much higher than those for viscoelastic relaxation?

**Answer:** The reason why the dielectric relaxation and the rheological relaxation process introduced by the supramolecular groups arises at different time scales is that both methods are triggered by different processes as explained in the following:

The dielectric signal arises from the pure group opening: The dipole moment of a dimeric complex which consists of two associated groups equals zero due to its centrosymmetric, oriented structure. As soon as the groups dissociate, the absolute value of the dipole moment takes on a time dependent finite value and the $\alpha^*$ process is observed. Thus, as mentioned by Professor Watanabe, dielectrics is not sensitive to the reassociation with an old or also a new partner, but reveals the averaged sticker lifetime $\tau_{bond}$ [1].

To become rheologically active a strand has to relax mechanically, a process for which pure bond opening (leading to dielectric response) is not sufficient. Following the model of Rubinstein and coworkers [2], our prediction is that as soon as a complex breaks up, an opened sticker starts to explore its surrounding volume by a random walk, which brings it quickly and several times (J) returns back to its old binding partner where it stays over and over bonded for $\tau_{bond}$ (rheological inactive). Only finding a new binding partner during the time the sticker is opened $\tau_{open}$ allows the connected strand to relax mechanically and a rheological relaxation process is observed.

Thus, the reason why we and other groups applying dielectrics and rheology to comparable systems observe different dielectrical and rheological relaxation times introduced by supramolecular groups is that both methods are sensitive for a different signal. As explained above, dielectrics detects the pure bond lifetime $\tau_{bond}$ while rheology detects the (2–3 order of magnitude slower) rheological activation time $\tau_{rheo} = J^*\tau_{bond} + \tau_{open}$.

**Laurence Ramos:** In the small-angle neutron scattering (SANS) profile [3], how could you distinguish a $Q^{-4}$ slope due to bubbles from one due to phase separation?

**Answer:** Based on the following results we anticipate that the $Q^{-4}$ slope arising in the low $Q$-range arises from microscopic air bubbles inside the sample material or a very small amount (0.02 vol. %) of chains affected by clustering:

A $Q^{-4}$ scaling is typical for Porod scattering, which means scattering arising from a smooth two-dimensional surface (e.g., air bubbles). As the sample material becomes more and more viscous and elastic by increasing the amount of functional groups, it is very plausible that some microscopic air bubbles remain trapped in the material, even under the high vacuum conditions ($p < 10^{-3}$ mbar) which we apply to the supramolecular samples for four days to remove

solvent residues and as much microscopic air bubbles as possible.

Nevertheless, one could argue, that the observed forward scattering could result from clusters obeying a spherical shape. As mentioned in the synthesis part of our publication the functionalization with supramolecular groups was undertaken separately for the protonated and the deuterated base polymer. After completion of the Alder-ene reaction, both stock solutions were mixed (95 mol. % protonated and 5 mol. % deuterated to provide a favorable contrast for the neutrons) and the solvent was removed properly. Therefore, the observed scattering pattern at low $Q$-values could result from the contrast between a certain amount of clustered hydrogenous to clustered deuterated functionalized chains.

The volume fraction $\Phi$ of clustering chains can be estimated by a simple approach: The scattering contrast between clustering hydrogenous and deuterated polyisoprene (PI) chains amounts to $(\Delta\rho)^2 = 4.4 \times 10^{21}\,cm^{-4}$. The size of a cluster is represented by the spherical volume $V = 4\pi(R_{cluster})3/3$ from which the intensity $I_{cluster} = \Phi \times V \times (\Delta\rho)^2$ results, depending on the volume fraction $\Phi$ of clustering chains inside the total scattering volume. In its most intense manifestation (for 4 mol. % stickers), we observe from our SANS curves: $I_{cluster} = (0.8 \times 10^{-3})^{-1}\,cm^{-1}$ occurring at a characteristic length scale $R\_cluster = Q_{cluster}^{-1} = (1.5 \times 10^{-3})^{-1}\,Å$. $\Phi = 0.02$ vol. % follows from this case of maximal observed forward scattering.

Furthermore, strong clustering would lead to a perturbation of the random walk statistics of the Gaussian chain structure. To exclude this unfavorable side effect the persistence of the Gaussian chain structure was proven by fitting the supramolecular SANS curves with a random phase approximation using a Gaussian form factor [3]. The fits clearly evidence an undisturbed random walk statistics, proving that the Gaussian chain structure remains unaffected by the supramolecular groups, which leads to the conclusion that only a very small amount of chains (0.02 vol. %) could be affected by clustering.

**James Wilson:** Is there any impact on chain flexibility coming from the shift of the internal double bond to an external one during alder ene functionalization?

**Answer:** We have proven by SANS measurements [3] that for temperatures well above the glass transition temperature the jump of the double bond does not modify the chain statistics and therefore also does not influence the chain flexibility.

However, we detect by differential scanning calorimetry measurements that the supramolecular side groups reduce the segmental flexibility at the glass transition temperature and slightly above.

Observations:

- The specific glass transition temperature $T_g$ increases linearly with the degree of functionalization. This well-known effect is related to increasing intermolecular chain interactions due to the supramolecular groups, therefore reducing segmental mobility.
- Enthalpy recovery effects which are reflected by an endothermic peak slightly above $T_g$. Generally, even if the

nature of this phenomenon is still under debate, this effect is attributed to thermally activated structural rearrangements from a former thermal nonequilibrium (e.g., introduced by isothermal annealing below $T_g$) to an equilibrium state. We observe that the effect of enthalpy recovery decreases for an increasing amount of functional groups/chain. Thus we conclude that the segmental mobility is decreased by the implementation of physical crosslinks, reducing the ability of the chain segments to undergo structural rearrangements.

One might think, that these effects could as well be triggered by the change in the microstructure as mentioned in the question. Nevertheless we detect all effects described in the following also for covalently crosslinked networks, in which the microstructure is not affected by the peroxidic crosslinking process (as proven by nuclear magnetic resonance).

Following the shift of the internal double bond to an external one during Alder-ene functionalization plays at the most a subordinated role for the chain flexibility. What decreases the chain flexibility is the high amount of associated groups with very long lifetime around $T_g$, which makes them comparable to covalent crosslinks at $T_g$.

**Dimitris Vlassopoulos:** In relation to the master curves and potential thermorheological simplicity, how did you determine the vertical shift factors when constructing the stress relaxation master curves? This shift factor should only depend on the density.

**Answer:** As mentioned earlier, the rheological master curves are constructed by using a two dimensional residual minimization carried out via a cubic spline interpolation. The computed values of $b_T$ ranged between $1 < b_T < 1.1$ for $T < T_{ref,TTS}$ and $0.85 < b_T < 1$ for $T > T_{ref,TTS}$ for all investigated samples. For the linear reference system as well as for the supramolecular networks, we observe a nearly identical, in a good approximation linear, decrease of $b_T$ for increasing temperature and therefore decreasing density.

Thus we conclude that the horizontal shift factors only mirror the temperature dependent density changes for the PI used as base polymer and is not influenced by the functional groups.

**Salvatore Coppola:** How about the sensitivity of the results to humidity? It is sensible to expect that such polar materials might absorb humidity and, if so, this might change the rheological and dielectric response. And about chemical stability?

**Answer:** We used PI as base polymer for our sample system which was backbone functionalized with 4-phenyl-urazole. PI is known to be hydrophobic, so we expect no sensitivity of humidity from this side. By comparing the infrared traces of the unfunctionalized reference and the supramolecular sample systems, which had been exposed to air and therefore also to humidity for some hours, we see no fingerprint of absorbed water molecules. Thus there is no evidence that the polar groups in our system lead to humidity sensitivity.

In general, we protect our samples against any external deleterious influences. After the synthesis process, the

samples are stored under a protecting argon atmosphere in the fridge at $-18\,^\circ$C. For all methods, the measurements are carried out under inert gas. By reproducing measurement results [fourier-transform infrared spectroscopy (FTIR), dielectrics, rheology, and differential scanning calorimetry (DSC)] derived from freshly synthesized samples with some years old samples, we are certain that the samples are chemical stable under the mentioned conditions.

**Quan Chen:** In using FTIR, should the obtained association-dissociation ratios change with temperature? How does this also appear in rheology?

**Answer:** Yes, the association-dissociation ratios are temperature dependent as shown by our FTIR analysis (see Fig. 11 in our publication). As mentioned in the publication, rheological measurements were carried out for temperatures ranging from 228 to 333 K. At 228 K around 90% of the groups are associated on average, while this amount decreases to around 80% at 333 K. All rheological measurements were undertaken in the regime in which the majority (80%–90%) of the groups is associated on average. As we expect, the ratio of opened to closed groups influences the rheological activation time, this may be a possible reason why, in the region at which group activation becomes visible, not to a perfect, but still a very good level of overlapping is observed in the rheological master curves (see Fig. 13 of the publication).

**Johan Mattsson:** This polymer has a dipole-moment component along the chain and you will thus be able to observe chain modes directly in dielectric spectroscopy and you see this in your data for the pure polymer without stickers. You would expect to see the chain-modes dielectrically also for the polymers with stickers, the chain mode spectrum might be modified by the stickers

and/or you might observe two separate relaxation modes. The observed additional relaxation you see for the polymers with stickers is very broad, does it consist of two modes? If you try to analyze it using two modes, how does that change the results? It would be interesting to plot up the temperature dependent normal mode relaxation time for the pure polymer in the plot to see how it compares to the effective temperature dependent relaxation time observed from fitting the broad extra relaxation component using a single broad relaxation.

**Answer:** Yes, we are able to see the normal mode relaxation in our systems. As shown in Fig. 1, it is covered more and more by conductivity with increasing amount of groups/chain.

We can state that the spectrum in the normal mode region is modified by the stickers. Nevertheless, there is no hint for an "additional" mode for the normal mode relaxation, as stated by the questioner. However, the normal mode relaxation for the polymers with stickers is very broad. Up till now, we did not analyze the normal mode spectrum further, but we plan to do it in the near future.

Indeed "it would be interesting to plot up the temperature dependent normal mode relaxation time for the reference system to see how it compares to the effective temperature dependent relaxation time observed from fitting the broad extra relaxation component using a single broad relaxation." We are working on that and started to transform the real part $\varepsilon(f)$ of the complex dielectric function $\varepsilon^*(f)$ by Kramers–Kronig relation into its imaginary part $\varepsilon''(f)$. That should give us the advantage to analyze the normal mode spectrum without the inconvenient signal of normal mode conductivity.
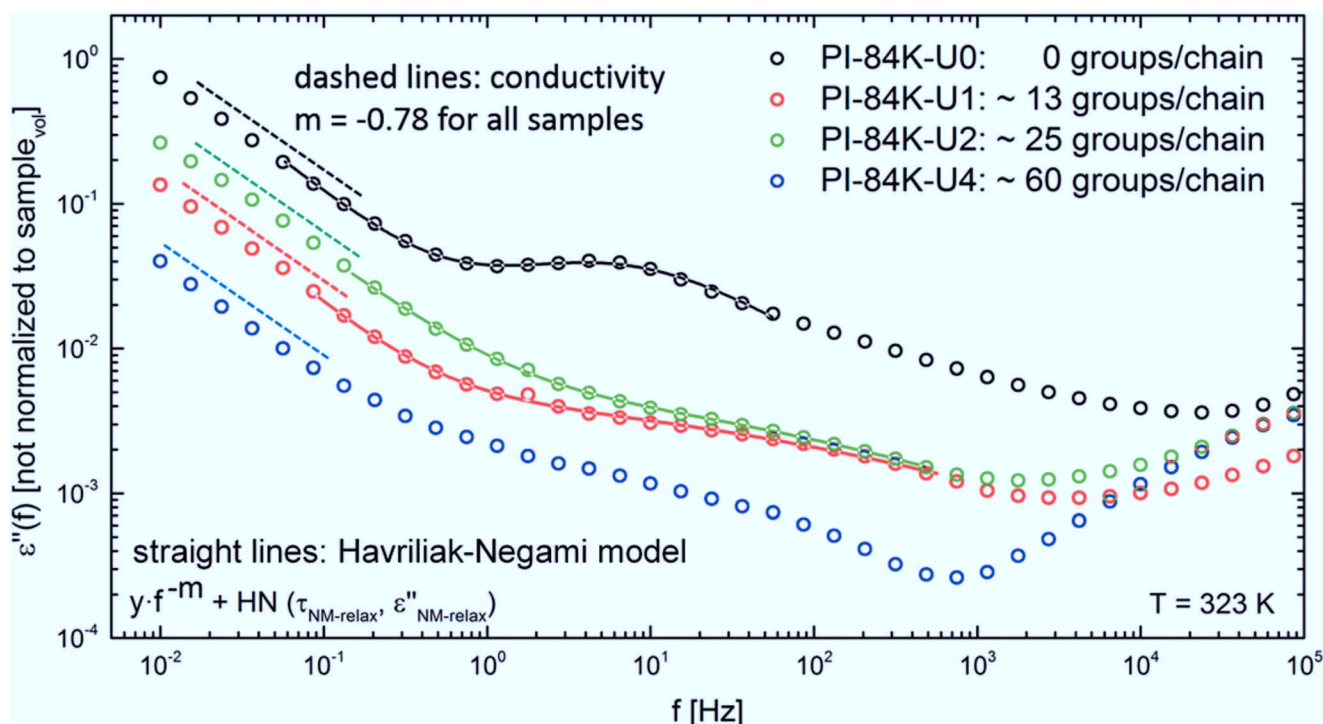


**FIG. 1.** Conductivity and normal mode relaxation of the transient model system measured at $T = 323$ K. Straight lines represent fits according to one Havriliak–Negami relaxation (normal mode) plus additional conductivity term.

**Ashwinikumar Sharma:** Today, we have lot of DSC instruments with capability of having various cooling and heating rates like hyper DSC, Flash DSC, etc. Is it possible to overcome the enthalpy recovery effect by use of such DSC instruments?

**Answer:** In general, thermal equilibrium states which express itself in enthalpy recovery effects can be introduced into amorphous polymers by cooling slowly through the glass transition zone (which cooling rate is needed exactly to introduce this effect depends on the system) or vice versa by isothermal annealing close to $T_g$ after fast quenching from the rubbery to the glassy state. By subsequent reheating with moderate rates (10–40 K/min) one observes the typical endothermic peak slightly above $T_g$ in the DSC traces. If one avoids both of these above-mentioned scenarios, one can prevent the systems from being in a state out of thermal equilibrium. Another thing one can do, if one is not interested in enthalpy recovery effects, is to measure the glass transition during the cooling process, as enthalpy recovery effects will only be observed in the reheating process.

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