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# Discussion of paper by A. Louhichi, A. R. Jacob, L. Bouteiller and D. Vlassopoulos, entitled 'Humidity affects the viscoelastic properties of supramolecular living polymers'

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**Daniel Read:** Is there a difference between working at fixed humidity (i.e., water vapor pressure) and with a fixed number of "chain stoppers" added to the solution? You have to be careful because these are actually different ensembles (grand canonical vs canonical). In order to keep a fixed amount of humidity, you need to add one molecule of $H_2O$ each time one of them is used as chain stopper, but if you simply have a fixed number of chain stoppers, then each time one is used it is removed from the solvent and it is possible for all chain stoppers to be used up. What were the assumptions used in the theory for calculating chain lengths?

**Answer:** We agree and there should be a difference given the different ensembles, especially before a steady state is reached. Concerning the experiment, the relative humidity (RH) is kept constant within the resolution of our method. The water consumption is very low, below that in the chamber which is kept at the required level for the target RH by means of the $P_2O_5$ drying material (see also discussion in the paper).

**Ralph Colby:** I always thought Ducouret's result that relaxation time scales as the 0.77 power of concentration c (and you report the same exponent) made sense if the contour length L were independent of c. The reptation time would then scale as the 3/2 power of c and then the geometric mean of the breaking time and reptation time scales as the 3/4 power of c. You provide a nice explanation here that humidity might control and restrict L, so do you think your finding (and Ducouret's finding) suggests that L is in fact independent of c for these bis-ureas?

**Answer:** Yes, we totally agree. The presence of humidity will control L as shown in the paper. We have in fact back-calculated the concertation dependence of the Bisurea monomer (EHUT) growth from the experimental results ($\tau_t \sim C^{0.77}$) and found that the average length exhibits a very weak dependence on the concentration, i.e., $L \sim C^{0.02}$, which is much weaker than $C^{0.5}$ proposed by Cates. This indeed justifies the above scaling law.

As we state in the paper, the disagreement of the experimental terminal relaxation time scaling with concentration with Cates prediction ($\tau_t \sim C^{1.25}$) is attributed to the assumption of $L \sim C^{0.5}$ in the model of Cates, which is a mean field approximation, and may not hold true for all the living polymer systems [1].

For completeness, whereas the above nearly-independence of L on concentration confirms the scaling of the terminal relaxation time with concentration, in agreement with your comment, we should note that the concentration independent growth of the bis-ureas assemblies could be also a result of the very high polydispersity (which may reach a value of 6) expected for this system as reported by Simic *et al.* [2].

**Hiroshi Watanabe:** Does $H_2O$ stay on the end of the tubules, or does it move around?

**Answer:** In principle, it competes for sites so it should break the micelle.

**Hiroshi Watanabe:** But if it can actually move then it's not strictly a stopper, and it could lead to different species with different length distributions.

**Answer:** The chain stoppers in general will strictly stop the growth of the chains at a certain critical EHUT concentration $C_t$. This critical concentration decreases with increasing the ratio between chain stopper monomers and the EHUT monomers as shown in Fig. 1 [2].

In this view, we attributed the humidity effect on the linear viscoelastic properties to a kind of incomplete chain stopper effect for the EHUT assemblies because we are studying one single EHUT concentration at the time, hence, water molecules will shorten some of the long chains without actually stopping their growth when we increase this specific concentration.

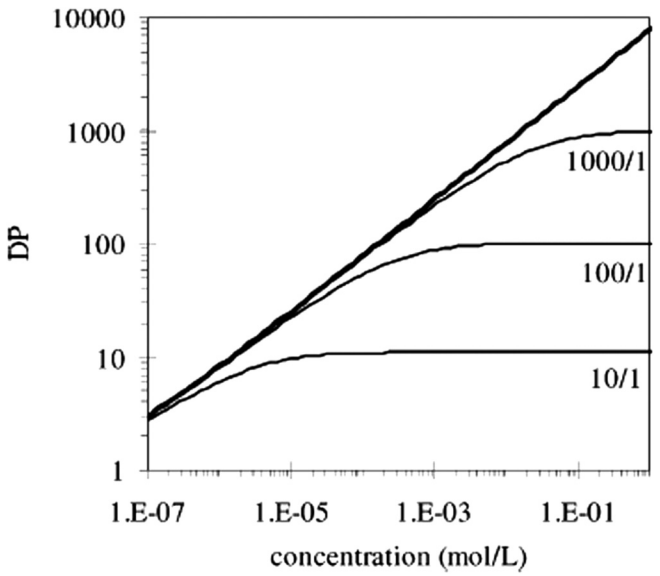



**FIG. 1.** Calculated number-average degree of polymerization for a supramolecular polymer (bold curve) and for 1000/1, 100/1, and 10/1 EHUT monomer/chain stopper mixtures (plain curves) vs monomer concentration. The association constant is $6 \times 10^{-7}$ l mol$^{-1}$.

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Nevertheless, the water molecules stuck to one EHUT assembly will be part of the equilibrium of this system; hence, the assemblies can still break and reform but in the presence of chain stoppers the worms are shorter which makes them relax faster.

**Lynn Walker:** What if you saturate the dodecane with $H_2O$? Do you know the saturation level of dodecane to test this?, i.e., does a "saturation point" exist defined by a constant density of water (so this amount cannot increase further)?

**Answer:** Probably, very short chains will be obtained. There will be a competition between self-assembly and chain-stopper effect in the saturated solvent.

It has been reported that the saturation level of Dodecane with water is 65 ppm by wt in [3]. Note that in our case we measured about 13 ppm in wt; however, it is not certain that the EHUT/Dodecnae solution will have the same saturation level. We expect that it may be higher because of the hygroscopic nature of the EHUT assemblies.

**Leo Gury:** Can you compare with other solvents, in order to find one without moisture effects?

**Answer:** This can be done, though it is not obvious given that moisture is in the environment and one message from this work is that one needs to measure under conditions of reduced ambient humidity. Note also that we have chosen dodecane for rheological reasons (e.g., reduced volatility, measurable but not too high viscosity).

In addition, as mentioned in the paper, water has a very low solubility in dodecane and in nonpolar solvents in general (see the previous comment); hence, it is disregarded as a primary source of moisture. However, the hygroscopic EHUT assemblies will anyway absorb water molecules from the surrounding environment regardless the low polarity of the solvent. This is why working in truly dry conditions was needed despite the fact of all the drying precautions during the sample preparation.

**Charles-Andre Fustin:** To stop a chain, you actually need to block both chain ends. Thus, if you block only one chain end, the chain should still continue to grow. Do you think these defects at the chain extremities should affect the rheology?

**Answer:** Yes, we think this may affect the rheology. However, as we mentioned above (see answer to Professor Watanabe's question), here we address the chain stopper-like effect considering one concentration at the time. So, we can't really talk about growth without changing the concentration and by keeping the ratio stoppers/EHUT constant at each concentration.

**Evelyne van Ruymbeke:** Is there any branching in the living micelles which are created?

**Answer:** We didn't observe any branching effect on the rheology (at least) of the concentrations studied in this work. Also in the concentration range studied there is no report of branching in the literature. We may try to concentrate more to see if we will induce some branching or not.

But then, how do you explain the strain hardening?

**Answer:** It is not necessary to have branching for shear hardening to occur. We speculate that hardening reflects a coupling of stretching and breakage and note that it has also been observed in solutions of associating polymers [4–6]

Of course, branching will increase the number density of elastically active chains, hence, increasing the modulus (when we look at the start-up data in stress vs strain). But this explanation was brought by Berret *et al*. [4] to explain the shear thickening in the steady state after the stress overshoot which was attributed to the breakup of the bonds; hence, they can change configuration from intra (elastically nonactive) to inter (elastically active).

Finally, shear banding arises early before reaching the stress peak but this need to be quantified. Strong shear bonding for this system have been already elucidated in previous work by Van der Gucht *et al*. [7], in the steady state regime after the overshoot.

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