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Ralph Colby: The combination of dielectric and mechanical spectroscopies is very powerful. However, it is not quite clear in your paper how the time scales of your supramolecular combs compare from these two spectroscopies. Maybe you can make a plot of the temperature dependence of the time scales for arm retraction and for terminal relaxation that are obtained by these two methods? That would really help the reader understand not only how they compare but what temperature ranges can be studied for these two vital time scales.

Answer: Since we could not show all experimental data in this work, some evidences are missing indeed. The comparison with microscopic times from the dielectrics and rheology was virtually perfect for the backbone PBO but these can be easily detected like, e.g., the Rouse time in the break of the slopes from $-1/4$ to $-1/2$. The supramolecular functionalized polymers are more complicated but also there a comparison was reasonably good, although less obvious. However, we think that a comparison with retraction times is not as accurate as well since the arms are too short to show clear effects of this process.

Dimitris Vlassopoulos: The analogy to "permanent combs" is very interesting and convincing and so is the link to "nonassociating blends," which have been examined in great detail in the literature. On the other hand, the analysis is based on the assumption of equidistributed branches along the backbone, as clearly stated in the paper. Whereas this is reasonable and has been discussed in the literature and to some degree justified for permanent combs (e.g., Ref. 30), two questions arise: (i) What would be the consequences of a departure from this assumption on the rheological properties? (ii) Is it possible with the present system (and with the help of complementary techniques, maybe spectroscopic) to test this by producing transient combs with nearly equidistributed branches and with very asymmetric distribution? I note that the latter relates to the so-called dispersity in macromolecular architecture which has been addressed for synthetic branched polymers (combs, stars).

Answer: We have made some thoughts about it in due course of the work. As the work was performed on model materials which had to be synthesized from the monomer up to the functionalized material and nothing was known before about the microscopic time scales and their dependence on the thymine/DAT modification, we found out that indeed some more and additional molecular weights and backbone functionalization degrees would have been very welcome. This was impossible at the time of preparing these investigations. However—to answer your first question—we don't expect a large effect associated with the "equidistant" assumption in the evaluation of the rheological data: the volume fraction of arm material would not change, behave identically for dilution effects and only some long-time processes related to the branch point dynamics might have been slightly different. Those, however, as well as the dependence along the backbone toward the center are treated on a very modest level of sophistication. To your second question, we must repeat that this would mean a lot of extra work which is in principle possible but was not performed for the sake of reducing as good as possible extra difficulties in the neutron scattering evaluation. The latter could describe the association very well in a preaveraged fashion and has led to reasonable equilibrium constants.

Evelyne van Ruymbeke: The hierarchical relaxation of the branches and the backbone of the comb polymers are not clearly visible, due to the relatively short length of the backbone. Indeed, since the backbone volume fraction is around 25 wt. % (see Table II), at times longer than the relaxation time of the branches, the effective molar mass between two (unrelaxed) entanglement is around $8/0.25 = 32$ kg/mol. Thus, taking into account the dilution effect of the branches, the backbone PBO40k is not entangled anymore, while the backbone PBO80k only contains 2.5 effective entanglements. This explains why these samples show Rouse-like relaxation at low frequencies, rather than reptation-like relaxation.

Therefore, I wonder if it is possible, from the synthesis point of view, to use a longer backbone in order to ensure backbone-backbone entanglements and consequently, to enhance their slow relaxation, compared to the relaxation of the branches? The difficult point is that on one hand, the length of the branches must be increased in order to increase their relaxation time and clearly observe the advantage of the reversible bonding, while on the other hand longer branches also means larger dilution effect. Maybe targeting few but long branches is the way to proceed?

Answer: Indeed the present system could have been configured better if we would have had the knowledge that we now have, before at the time of preparing the base polymers, deciding on the H and D labeling, where to place thymine and diaminotriazine better. Longer arms and backbone would have been decisive for a better microscopic separation of retraction and bonding times. I agree that the enhanced dilution effect caused by arms molecular weight could be compensated by the decrease of the number of arms. So

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from the chemical point of view I see nothing against your proposal, except for the samples availability and the starting of a new characterization process. We have however unpublished data on bi-functionally modified arms that create transient networks that corroborate the present time scales fully. These are also measured in a combined rheology/dielectric spectroscopy/small angle x-ray and neutron study and which we hope to publish in the next months as well.