A molecular view on supramolecular chain and association dynamics

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The chain and association dynamics of supramolecular ensembles decisively determines their properties. In this talk I present a combined analysis of small angle neutron scattering, linear rheology, pulsed field gradient nuclear magnetic resonance and neutron spin echo experiments on the structure and dynamics of well-defined telechelically modified poly(ethylene glycol) (PEG) in the bulk. PEG was functionalized with directed hetero complementary hydrogen bonding end groups, thymine (Thy) diaminotriazine (DAT). The polarity of the backbone polymer is comparable to the end groups and avoids clustering of the groups that is often observed in hydrophobic environments. Their linear association behaviour in the melt state was investigated on the microscopic/molecular level as a function of temperature. By means of a selective labelling scheme that should ideally lead to the formation of alternating hydrogenous-deuterated building block sequences, if the hydrogen bonding reaction is exclusively hetero-complementary. I show that the Thy/DAT association is dominant and that Thy/Thy homo-association is approximately three times less probably. From the Q-dependence of a multiblock RPA structure factor, the linear association in the melt is confirmed and quantified. Furthermore, the diffusion and viscosity study reveals simple Rouse dynamics of the supramolecular polymer chains with molecular weight much larger than the entanglement mass M_e. The Rouse like dynamics of the long supramolecular chains indicates short life-time hydrogen-bonds of the end groups. The results are an excellent agreement with the related poly-condensation theory. Using neutron spin echo (NSE) spectroscopy I present further molecular insight in the space-time evolution of this dynamics. I show that the hydrogen bond breaking significantly impacts the mode spectrum of the associates. Their breaking affects the mode contributions and <u>not</u> the relaxation times as was assumed previously. The NSE spectra directly reveal the so far intangible H-bond-lifetimes in the supramolecular melt and demonstrate that for both, the microscopic and the macroscopic dynamics of the supramolecular ensemble the instantaneous average of the molecular weight distribution governs the systems response as least as long as the Rouse picture applies.

References:

Association behaviour, diffusion and viscosity of end-functionalized supramolecular poly(ethylene glycol) in the melt state
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Macromolecules **48**, 8933 (2015)

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submitted