

Studies of the influence of isomer structure of additives on the phase transition of thermo-responsive Poly(N-isopropylacrylamide) microgels

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Our work investigates the effects of different additives such as structural isomers of Hydroxybenzaldehyde (HBA) on the phase transition behaviour of a Poly(N-isopropylacrylamide)/N,N'-Methylenebisacrylamide (PNiPAM/BIS) microgel (0.9 wt%) with 5.4 mol% crosslinker-content. Different methods such as NMR Spectroscopy, Differential Scanning Calorimetry (DSC), Turbidimetry, Isothermal Titration Calorimetry (ITC) and Dynamic Light Scattering (DLS) are used to determine the characteristic Volume Phase Transition Temperature (VPTT), transition widths and critical concentrations of cosolutes.

The homopolymer of PNiPAM already has been studied by Hofmann et al. in the presence of various aromatic additives.[1] Now the influence of *ortho*-, *meta*- and *para*-HBA (10 mM) on the VPTT on a PNiPAM microgel has been determined systematically and compared to a homopolymer. Those model drug substances caused a shift of the VPTT to lower temperatures, which could be observed by all utilized techniques. Furthermore, as a result from temperature dependent ¹H-NMR spectra, this work proves the existence of an incorporated species of the additives at $T > VPTT$. A quantification of those incorporated species was also possible by using reference solutions of the additives in absence of polymer. By investigation of the transverse relaxation times T_2 of the aldehyde protons using the Carr-Purcell-Meiboom-Gill sequence (CPMG), local dynamics below and above the collapse temperature of the microgel (Fig. 1) were clarified:

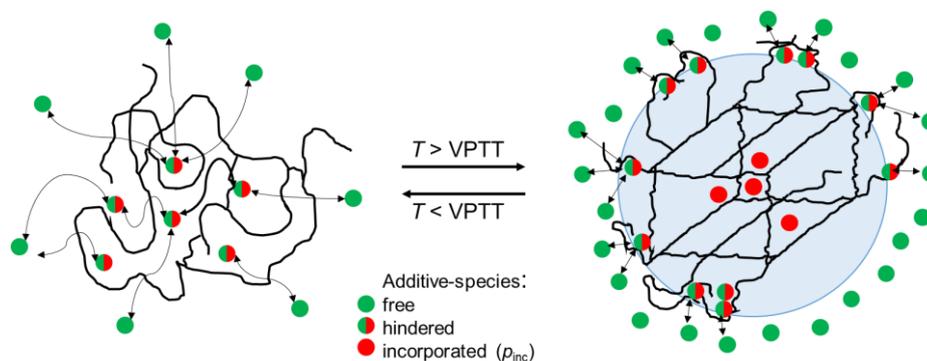


Figure 1. Illustration of local additive dynamics (sites) inside and outside the PNiPAM microgel at different temperatures by interpreting the obtained monoexponential spin-echo decays and transverse relaxation times T_2 of temperature dependent NMR measurements.

In the microgel a freely moving, a hindered and a completely incorporated species of the additive were identified. Also the influence of the substitution pattern of HBA and Dihydroxybenzene (DHB) on the VPTT of further acrylamide polymers has been studied.

Currently, ongoing studies investigate the influence of further additives by varying the size of the aromatic π -system and by the use of additives exhibiting hydrogen-bridge acceptor/donor properties.

[1] C. H. Hofmann, M. Schönhoff, *Colloid Polym Sci* 2012, 290, 689.