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NMR STUDY ON POLYMER-SOLVENT INTERACTIONS IN SOLUTIONS OF THERMORESPONSIVE POLYMERS

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It is well known that some polymers, including poly(vinyl methyl ether) (PVME), poly(*N*-isopropylacrylamide) (PIPAAm) and poly(*N*-isopropylmethacrylamide) (PIPMAAm), exhibit in aqueous solutions a lower critical solution temperature (LCST), i.e., they are soluble at lower temperatures, but heating above the LCST results in phase separation. Here we report some results on hydration and other polymer-solvent interactions as obtained with D₂O solutions of PVME and other thermoresponsive polymers using NMR methods.

For D₂O solutions of PVME ($c = 2\text{-}10$ wt %) ¹H NMR relaxation measurements revealed that a certain portion of water molecules is bound in phase-separated globular-like structures, i.e., mesoglobules.¹ The residence time of the bound HDO is 1.2 ms. Also in D₂O solutions of PIPAAm and PIPMAAm ($c = 5$ wt %), a part of the HDO is bound in globular-like structures. With increasing time, a slow release of the bound water from the respective mesoglobules was observed in all cases, with the rate decreasing in the order PVME>PIPMAAm>PIPAAm.² For highly concentrated PVME/D₂O solutions ($c = 20\text{-}60$ wt %) the residence time of bound HDO is 2.1 s and no release of the bound water was detected even after 70 h. A similar behaviour as described above for water, we also observed for ethanol (EtOH) in PVME/D₂O/EtOH solutions. For $c = 20$ wt %, the correlation times of the bound EtOH were 2-3 times longer compared with free EtOH. Taking into account that EtOH inhibits phase separation³, an important role of the arrangement of water molecules in the phase transition process follows from the obtained results.

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