

Title: The Study of Dynamic Behaviour and Interactions During the Temperature-Induced Phase Separation in Polymer Solutions

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Abstract: ^1H and ^{13}C high-resolution NMR spectroscopies were used for the phase separation investigation in three types of polymer solutions: i) poly(*N*-isopropylmethacrylamide)/ D_2O /ethanol with or without negatively charged comonomer sodium methacrylate, ii) random copolymers poly(*N*-isopropylmethacrylamide-*co*-acrylamide) in D_2O , D_2O /ethanol and D_2O /acetone and iii) D_2O solutions of polymer mixtures poly(*N*-isopropylmethacrylamide)/poly(*N*-vinylcaprolactam). For i) cononsolvency effect and influence of temperature on the phase separation was studied. Differences between mesoglobules formed as a consequence of cononsolvency effect and of temperature were found. While inside the cononsolvency-induced mesoglobules no bound ethanol molecules were detected, in the mesoglobules formed by the effect of temperature ethanol molecules were present. The charge introduced into the polymer chains strenghtens polymer-solvent interactions. For ii) mesoglobules were found to be rather porous and disordered. Acrylamide sequences and surrounding short isopropylmethacrylamide sequences are hydrated and mobile, while sufficiently long isopropylmethacrylamide sequences are dehydrated with reduced mobility. For iii) phase transitions of both polymers were detected. The phase-separated poly(*N*-vinylcaprolactam) was sedimenting in the order of hours. Lower critical solution temperature of poly(*N*-vinylcaprolactam) shifts to lower temperatures with both the increasing polymer concentration and poly(*N*-vinylcaprolactam) content. Solvent T_2 shortens after the poly(*N*-vinylcaprolactam) phase separation, after the poly(*N*-isopropylmethacrylamide) separation no further shortening was observed.

Keywords: Phase Separation, Polymer Solution, Cononsolvency, ^1H and ^{13}C NMR Spectroscopy