

Supplementary Information

Co-nonsolvency of PNiPAM at the transition between solvation mechanisms

I. Bischofberger^{**}, D. C. E. Calzolari and V. Trappe^{*}

University of Fribourg, Department of Physics, CH-1700 Fribourg

*** current address: University of Chicago, Department of Physics, Chicago, IL 60637*

The distinct temperature dependence of the PNiPAM dimensions in respectively the low and high X -regime is not limited to the microgels discussed in the paper. As shown in the Figure below, the temperature dependence of the dimensions of linear PNiPAM exhibits the same features as that of the microgels. For $X < X^*$ the radius of gyration R_g exhibits a strong dependence on temperature T , which is set by the relative distance of the temperature to the lower critical solution temperature, $\Delta T = T_c - T$. For $X > X^*$ the PNiPAM dimensions are insensitive to temperature upon approach of T_c , independent of whether the phase transition is characterized by a lower or upper critical solution temperature.

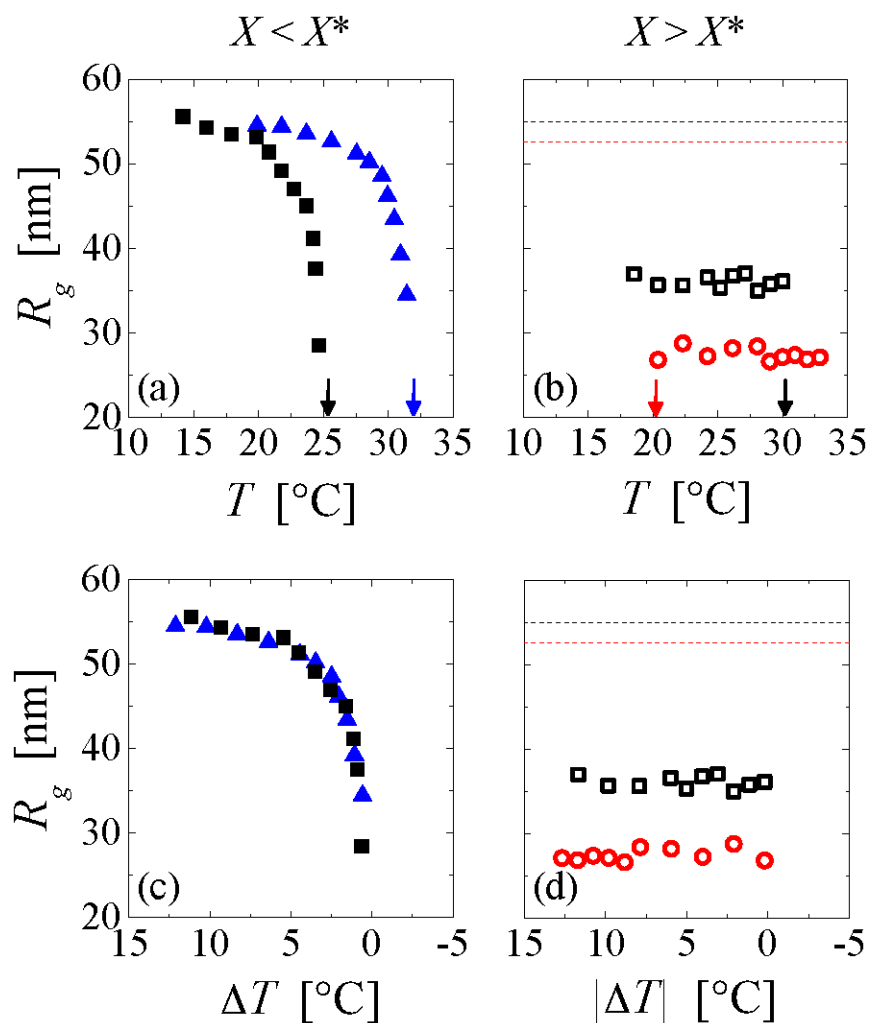


Figure S1. Radius of gyration R_g of a linear PNiPAM with $M_v = 465\,500$ g/mol and $M_w/M_n = 4.9$ at a concentration of $c = 10^{-3}$ g/ml. (a) Temperature dependence of R_g in the low X -regime for $X=0$ (full triangles) and $X_{MeOH}=0.08$ (full squares). The PNiPAM chains exhibit a coil-to-globule transition that coincides with the LCST denoted by arrows. Beyond the LCST the PNiPAM chains aggregate; this precludes measurements of the fully collapsed state. (b) Temperature dependence of R_g in the high X -regime for $X_{MeOH}=0.44$ (open squares) and $X_{EtOH}=0.33$ (open circles). The approach to the critical solution temperature T_c is independent of temperature. The radii in the water/alcohol mixtures are smaller than those in the pure alcohols,

which are denoted as dotted lines (black: methanol, red: ethanol). (c) In the low X -regime, R_g evolves with respect to the reduced temperature $\Delta T = T_c - T$. (d) In the high X -regime, the approach to T_c is qualitatively similar for both type of transitions, that characterized by a LCST and that characterized by an UCST.