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Communication

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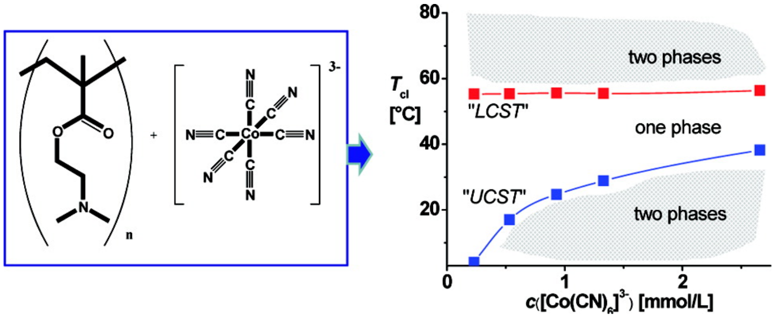

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Tuning the Thermoresponsiveness of Weak Polyelectrolytes by pH and Light: Lower and Upper Critical-Solution Temperature of Poly(*N,N*-dimethylaminoethyl methacrylate)

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Thermoresponsive polymers exhibit a change in the solubility upon heating or cooling. Water-soluble polymers often exhibit a lower critical solution temperature (LCST), that is, phase separation occurs upon raising the temperature. Examples are poly(*N*-isopropyl acrylamide) or poly(vinyl methyl ether).[1,2] In contrast, an upper critical solution temperature (UCST) behavior, that is, demixing on cooling, is often observed for solutions in organic solvents.[3] There are only a few examples of water-soluble polymers that exhibit both an LCST and a UCST. Examples are poly(vinyl alcohol)[4] and triblock copolymers of, for example, polyglycidol and poly(propylene oxide).[5] Concentrated poly(vinyl methyl ether) mixtures with water as the minority component show an additional UCST transition below 0 °C.[6] The opposite behavior is reported for poly(ethylene oxide), showing a UCST above the reported LCST (above 100 °C under pressure).[7] However, there is no way to adjust critical temperatures over a wide range.

We recently reported that the LCST-type cloud points of linear and star-shaped PDMAEMA can be easily adjusted by pH ($\mathrm{p}K_{\mathrm{a,app}} \approx 6$ for the protonated polybase).[8] At high pH, when the polymer is almost uncharged (degree of neutralization < 2% at pH 9),[8] the cloud points of PDMAEMA behave as for uncharged polymers.[9] At lower pH, however, the weak polyelectrolyte PDMAEMA starts to carry charges by protonation, enhancing the solubility in water. Concomitantly the cloud points are shifted to higher temperatures.

Here we present the first observation of a UCST behavior of a typical LCST polymer, poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA), in the presence of small quantities of trivalent counterions. This behavior is similar to the UCST behavior reported by Jia et al. for micelles consisting of an inner core of protonated poly(2-vinyl pyridine), where the core is connected by redox-sensitive divalent counterions.[10] Moreover, we demonstrate that both LCST and UCST can be adjusted independently over a wide temperature range and the UCST-like cloud point can even be manipulated by UV light.

We monitored the cloud points of aqueous solutions of PDMAEMA by turbidimetry (for experimental details, see Supporting Information). In all cases reported here the UCST-type cloud points were lower than the LCST transitions, and a one-phase region intervenes. As seen in Figure 1, the UCST-type cloud points appear by adding small amounts of the trivalent counterion hexacyanocobaltate(III) $[\mathrm{Co(CN)_6}]^{3-}$ (other multivalent counterions like $[\mathrm{Fe(CN)_6}]^{4-}$ show a similar effect). The more trivalent counterions are present, the higher the cloud points of the lower miscibility gap. This is found at practically constant ionic strength and constant pH. At the same time the LCST-type cloud points are hardly affected by the presence of $[\mathrm{Co(CN)_6}]^{3-}$. This behavior is observed for both linear and star-shaped PDMAEMA. The region of full miscibility is narrowed for star-shaped PDMAEMA (for synthesis see ref 11) owing to the higher molecular weight compared to the linear polymer.[8] Hence, effects caused by the different architecture of the polymers cannot be excluded.

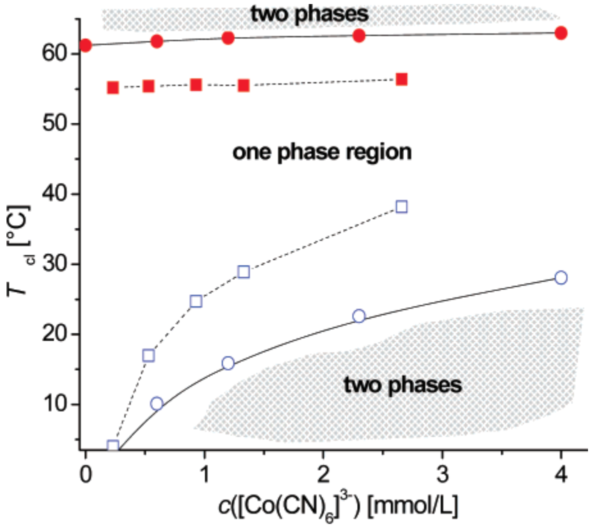

Figure 1. Dependence of the cloud points, T_{cl}, of aqueous PDMAEMA solutions (0.1 g/L in buffer of pH 8 + 0.1 N NaCl) on the $[\mathrm{Co(CN)_6}]^{3-}$ concentration (titrated 0.0166 N $\mathrm{K_3[Co(CN)_6]}$ into 25 mL of PDMAEMA solution) for linear $\mathrm{PDMAEMA_{100}}$ (circles) and star-shaped $(\mathrm{PDMAEMA_{170}})_{18}$ (squares); closed symbols assign LCST-type cloud points, open ones refer to cloud points of the UCST-behavior (the lines are a guide to the eye).

As shown earlier, the cloud points of the LCST behavior can be adjusted by the pH of the buffer.[8] Now the UCST can be adjusted by addition of trivalent counterions (Figure 1).

The effect of pH on both UCST and LCST at constant concentration of counterions and polymer is shown in Figure 2. The UCST-type cloud point disappears at high pH. This is due to the fact that the electrostatic interaction between the almost uncharged polymer and the trivalent ions must vanish at high pH. This indicates that the electrostatic interaction of counterions with the polymer induces the UCST behavior: the multivalent counterions connect different polymer molecules, leading to precipitation at low temperatures. The interactions weaken and the bridges break at higher temperatures. This could be also one reason for the negligible influence of the trivalent ion on the LCST-type cloud points. On the other hand, the introduction of charges stabilizes the homogeneous phase as shown recently. Hence, the phase behavior seen when introducing trivalent ions results from the competition of two effects: (i) The stabilization of the homogeneous phase by charges and (ii) the destabilization through the bridges

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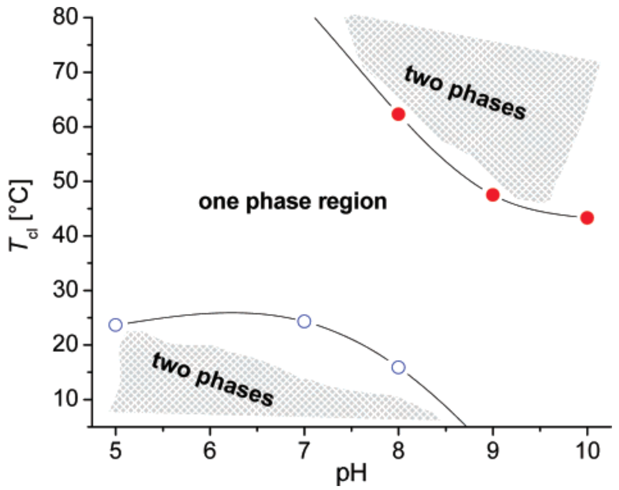

Figure 2. Dependence of the UCST- (open symbols) and LCST-type (full symbols) cloud points on pH (0.1 g/L $PDMAEMA_{100}$; 1.2 mmol/L $[Co(CN)_6]^{3-}$; 0.1 N NaCl); the lines are a guide to the eye.

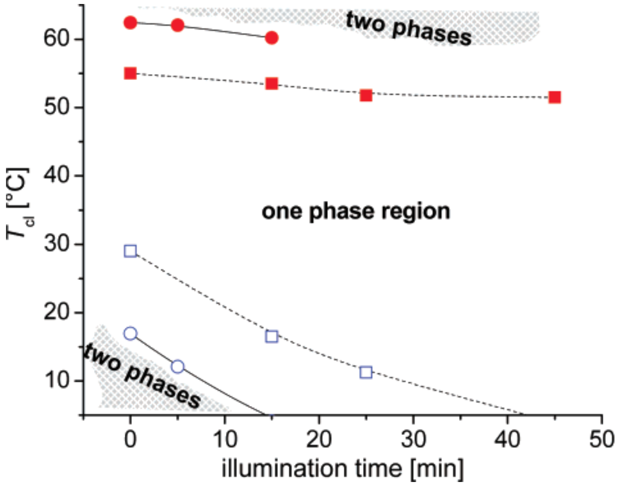

Figure 3. Tuning of the UCST-type (open symbols) and LCST-type (closed symbols) cloud point by UV illumination (λ = 300−400 nm); 0.1 g/L $(PDMAEMA_{170})_{18}$ (squares) and $PDMAEMA_{100}$ (circles) in pH 8 buffer, 0.1 N NaCl and 1.3 mmol/L $[Co(CN)_6]^{3-}$; the lines are a guide to the eye.

introduced by trivalent ions. However, an excess of the number of trivalent charges compared to those on the polymer was always needed to obtain an UCST behavior. This might be due to the unfavorable equilibrium between multivalent counterions freely dissolved in bulk solution and counterions bridging the weakly charged polyelectrolyte. This is in contrast to the behavior of strongly charged polymer stars in the presence of multivalent counterions.[12]

We have shown earlier that photosensitive counterions $[Co(CN)_6]^{3-}$ can induce a conformational change in polyelectrolyte stars upon illumination besides a change in their solubility.[12] The counterion reduces its valency from trivalent to divalent by ligand exchange after excitation with UV-light, owing to photoaquation (exchange of one cyanide ligand with water).[13] Since the interaction and the bridging abilities of the counterions with the weak polyelectrolyte are very much dependent on the valency, we expect a photoinduced tuning of the UCST (and in less extent of the LCST). In contrast to other more tedious techniques to modify the thermoresponsive properties (e.g., incorporation of light sensitive monomers into the polymer),[14,15] the present observations demonstrate that the thermosensitive behavior can be switched in a much easier fashion.

Indeed, we are able to switch off the UCST-behavior again by UV illumination as seen in Figure 3. The UCST-type cloud point decreases below the accessible temperature range after 45 min of UV illumination (photoinduced dissolution). The divalent $[Co(CN)_5H_2O]^{2-}$ ions developed by illumination of the solution are less efficient to bridge the polymer chains. The influence of illumination on the LCST is less pronounced, since multivalent counterions have only a minor effect here (Figure 1).

All effects mentioned in this Communication were only observed in buffered solutions containing a considerable amount of salt (ionic strength ≈ 0.1 mol/L). The thermoresponsive effects are more complicated in buffer-free solution, since the various parameters cannot be varied independently from each other. In fact, pH increases in the presence of multivalent counterions (counterions stabilize the protonated form of PDMAEMA and act as a cobase). Evidently, a shift of the pH has a considerable influence on the cloud points. Thus, we did not observe an UCST behavior in the absence of buffer. In the absence of additional monovalent ions the electrostatic repulsion of the charged polymer is dominant. However, the LCST-type cloud point is at that stage very much dependent on the concentration of multivalent counterions. This point is in need of further elucidation.

In conclusion, the phase behavior of a weak polyelectrolyte can be changed in a well-defined manner by introducing trivalent counterions: A UCST is induced in addition to the LCST already present. Photoswitching the valency of the counterions from trivalent to divalent can be used to undo this change. Hence, we presented a novel way to change the thermodynamics of polymer solutions by light.

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Supporting Information Available: Experimental procedures, concentration dependences. This material is available free of charge via the Internet at http://pubs.acs.org.

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