

**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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**Introduction**

Water-soluble polymers often show a lower critical solution temperature (LCST), i.e. phase separation at rising temperatures, e.g. poly(*N*-isopropyl acrylamide) (PNIPAAm) or poly(vinyl methylether).<sup>1,2</sup> Another example of LCST-polymers is poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA). PDMAEMA is a useful polymer to study the effects of charges on the LCST, since it is a weak cationic polyelectrolyte. The thermoresponsive properties of the polybase PDMAEMA can then be altered by slight changes in *pH* and salinity as well. In contrast, an upper critical solution temperature (UCST) behavior, i.e. demixing on cooling, is often observed for solutions in organic solvents. In contrast, polybetaines often have a UCST in water.<sup>3</sup>

We report on the investigation of the LCST-properties of a well defined set of star-shaped PDMAEMA. The results are compared to those obtained with linear polymers. For details of synthesis and characterization we refer to an earlier paper.<sup>4,5</sup> In addition we present the first observation of an UCST behavior of the typical LCST polymer PDMAEMA. It can be induced in presence 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.<sup>6</sup> 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 switched by UV light.

Some rare examples of water-soluble polymers with both LCST and UCST are poly(vinyl alcohol)<sup>7</sup> and triblock copolymers of e.g. polyglycidol and poly(propylene oxide).<sup>8</sup> In all reported examples there is no feasible possibility to easily adjust critical temperatures over a wide range.

**Experimental**

**Materials.** The polymer's preparation and characterization are described in previous papers (i.e. for linear PDMAEMA<sub>100</sub> or star-shaped (PDMAEMA<sub>170</sub>)<sub>18</sub> – a star with 18 arms and a degree of polymerization per arm  $DP_{arm} = 170$ ).<sup>4,5</sup> Potassium hexacyanocobaltate(III) K<sub>3</sub>[Co(CN)<sub>6</sub>] and sodium chloride NaCl were purchased from Aldrich. The buffer solutions were delivered by Riedel-de Haën (*pH* 8 sodium borate / hydrochloric acid buffer type 33547), Merck (*pH* 9 boric acid / potassium chloride / sodium hydroxide buffer type 9461) and VWR Titrimorm (*pH* 7 potassium dihydrogen phosphate / disodium hydrogen phosphate buffer 32 096.291; *pH* = 10 boric acid buffer).

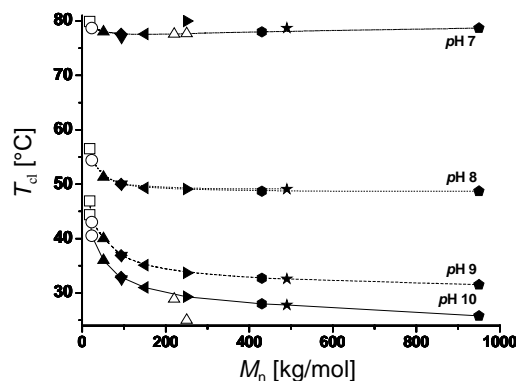
**Sample Preparation.** All aqueous solutions (usually 0.1 g/L) were prepared by dissolution of the respective amount of PDMAEMA in 25 mL of buffer by vigorous stirring (ionic strength of all buffers in the order of 0.05 mol/L). In presence of multivalent counterions, the ionic strength was adjusted by NaCl (0.1 mol/L) in order to dominate the ionic strength in relation to the inherent salt of the buffer solutions. A K<sub>3</sub>[Co(CN)<sub>6</sub>] solution of same ionic strength (0.016 mol/L) was titrated to the respective solutions in order to adjust the cobaltate concentration. The prepared solutions were degassed by applying vacuum (50 - 100 mbar) for 15 min at room temperature to minimize bubble formation during heating.

**Cloud point determination.** The determination of the cloud points was achieved by turbidity measurements using a titrator (Titrand 809, Metrohm, Herisau, Switzerland) equipped with a turbidity sensor ( $\lambda_0 = 523$  nm, Spectrosense, Metrohm). In addition, a temperature sensor (Pt 1000, Metrohm) was

used. The temperature program (1K / min) was run by a thermostat (LAUDA RE 306 and Wintherm\_Plus software), using a home-made thermostatable vessel. We defined the cloud point as the intercept of the tangents of the transmittance-temperature dependence at the onset of turbidity.

**Results and Discussion**

**LCST-Behavior of PDMAEMA.** We start the discussion at high *pH*  $\geq 9$ , where the stars are almost uncharged. Here the cloud points decrease monotonously with increasing molecular weight irrespective of arm length and arm number. Therefore all cloud points seem to fit one "master curve" (Figure 1).



**Figure 1.** Cloud points,  $T_{cl}$ , at 0.1 g/L of linear and star-shaped PDMAEMA in dependence of molecular weight,  $M_n$ , (□: PDMAEMA<sub>108</sub>; ○: PDMAEMA<sub>133</sub>; ▲: (PDMAEMA<sub>100</sub>)<sub>3,1</sub>; ▼: (PDMAEMA<sub>160</sub>)<sub>3,7</sub>; ◆: (PDMAEMA<sub>110</sub>)<sub>5,4</sub>; ◀: (PDMAEMA<sub>170</sub>)<sub>5,6</sub>; ▶: (PDMAEMA<sub>170</sub>)<sub>9,5</sub>; ●: (PDMAEMA<sub>240</sub>)<sub>11</sub>; ★: (PDMAEMA<sub>170</sub>)<sub>18</sub>; ◆: (PDMAEMA<sub>240</sub>)<sub>24</sub>; △: PDMAEMA<sub>1400</sub> and PDMAEMA<sub>1600</sub> prepared by free radical polymerization); the lines are a guide to the eye.

We have shown that classical Flory-Huggins theory for linear polymers<sup>9</sup> seems to describe the positions of the cloud point in dependence of the molecular weight adequately irrespective of architectural details.<sup>5</sup> Even linear PDMAEMA with a rather high molecular weight does not deviate much from the curve in Figure 1. In conclusion, the Flory approach in terms of a temperature-dependent  $\chi$  parameter seems to well describe the thermoresponsive behavior of PDMAEMA at high *pH*.

At decreasing *pH* the PDMAEMA stars will be more and more charged. This is also reflected in the shift of the phase boundary to higher temperatures as expected.<sup>10,11</sup> In addition, the cloud points do not fit to one monotonous "master curve" any more (especially at *pH* = 7). Furthermore, the cloud points are now located in a rather narrow window between 77 and 80 °C, i.e. they are nearly independent of degree of polymerization *DP*. A contribution to the deviations at low *pH* might be attributed to the architecture and the resulting counterion confinement. Moreover, at low *pH* the charge density (ionization) starts to have an influence on the observed cloud points.

**UCST and LCST Behavior of PDMAEMA.** We monitored the cloud points of aqueous solutions of PDMAEMA in presence of trivalent counterions. This lead to the appearance of UCST-type cloud points. In all our investigated cases the UCST-type cloud points were lower than the LCST transitions, i.e. having a temperature window with full miscibility. As seen in Figure 1, the UCST-type cloud points appear with increasing concentration of hexacyanocobaltate(III) [Co(CN)<sub>6</sub>]<sup>3-</sup> as a trivalent counterion. The more trivalent counterions present, the higher the cloud points of the lower miscibility gap. Note that this is true at practically constant ionic strength and constant *pH*. At the same time the LCST-type cloud points are hardly affected by the presence of [Co(CN)<sub>6</sub>]<sup>3-</sup>. This behavior is observed for both linear and star-shaped PDMAEMA

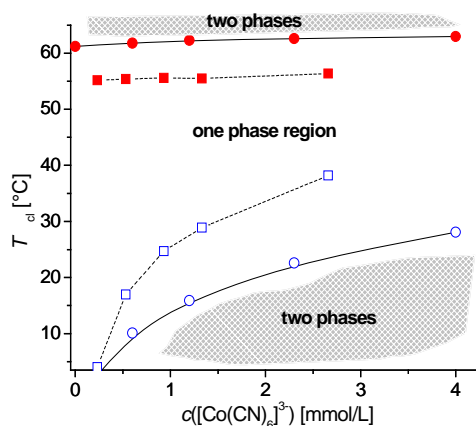


Figure 2: Dependence of the cloud points,  $T_{cl}$ , of aqueous PDMAEMA solutions (0.1 g/L in buffer of pH 8 + 0.1 n NaCl) on the  $[\text{Co}(\text{CN})_6]^{3-}$  concentration (titrated 0.0166n  $\text{K}_3[\text{Co}(\text{CN})_6]$  into 25 mL PDMAEMA solution) for linear PDMAEMA<sub>100</sub> (circles) and star-shaped (PDMAEMA<sub>170</sub>)<sub>18</sub> (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).

After adjusting the LCST of PDMAEMA<sup>5</sup> the UCST can be adjusted by addition of trivalent counterions (Figure 2).<sup>16</sup> Therefore this is a novel system in which the thermoresponsive properties can be adjusted in a facile manner.

Increasing pH causes both UCST-type and LCST-type cloud points to decrease when keeping constant concentration of counterions and polymer. Then the UCST-type cloud point shifts below the accessible temperature range 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. Therefore the LCST-type cloud points are hardly affected by the presence of trivalent counterions.

We have to note that all effects mentioned in this preprint were only encountered in buffered solutions, containing inherently a considerable amount of salt (ionic strength  $\sim 0.05$  mol/L). The thermoresponsive effects are more complicated in buffer-free solution, since conditions cannot be varied independently.

**Light Sensitivity of the cloud points.** We have shown earlier that photosensitive counterions  $[\text{Co}(\text{CN})_6]^{3-}$  can induce a conformational change in polyelectrolyte stars upon illumination besides a change in their solubility.<sup>12</sup> The counterion reduces its valency from trivalent to divalent by ligand exchange after excitation with UV-light.<sup>13</sup> Since the interaction and the bridging abilities of the counterions with the weak polyelectrolyte are very much dependent on the valency, we expect a photo-induced 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),<sup>14, 15</sup> 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 developed divalent  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  ions 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 3).

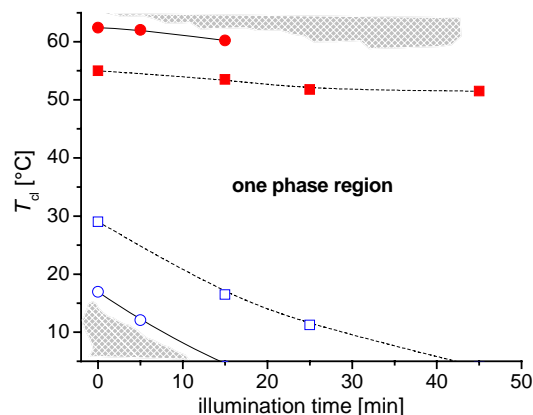


Figure 3: Tuning of the UCST-type (open symbols) and LCST-type (closed symbols) cloud point by UV-illumination ( $\lambda = 300 - 400$  nm). 0.1 g/L (PDMAEMA<sub>170</sub>)<sub>18</sub> (squares) and PDMAEMA<sub>100</sub> (circles) in pH 8 buffer, 0.1 n NaCl and 1.3 mmol/L  $[\text{Co}(\text{CN})_6]^{3-}$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

## Conclusions

Multivalent counterions induce in buffered aqueous solutions of poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) a UCST-behavior. This happens in addition to PDMAEMA's known LCST-Behavior, which is hardly affected by the presence of multivalent counterions.

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