

# Nanoblossoms: Photoinduced Stretching and Photoinduced Dissolution of Polycation Stars by Switching the Charge of Counterions

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## INTRODUCTION

Polyelectrolytes consist of highly charged polymeric macroions that carry charges on each repeating unit.<sup>1,2</sup> Dispersed in water or solvents with high dielectric constant these counterions will partly dissociate. A certain fraction, however, will be closely correlated to the macroion because of its high electric field. This strong correlation of the counterions to the macroion in dilute aqueous solution must lead to a marked osmotic pressure within branched macroions. As a consequence of this, the arms of the polyelectrolyte star must be strongly stretched.<sup>3-6</sup> If salt is added to the solution, the electrostatic interaction is more and more screened.<sup>7</sup>

Replacing monovalent counterions by e.g. trivalent ones should lead to a marked decrease of the osmotic pressure. As a consequence of this, polyelectrolyte stars should collapse in solutions of multivalent counterions, again in direct analogy to the collapse of polyelectrolyte brushes when replacing monovalent counterions by counterions of higher valency.<sup>8</sup>

We show that the conformation of star polyelectrolytes in aqueous solution can be manipulated by UV-light: Using the photochemical reaction of hexacyanocobaltate(III)  $[\text{Co}(\text{CN})_6]^{3-}$ , trivalent counterions are irreversibly converted into divalent ones.<sup>9,10</sup> In this way the number of counterions is raised significantly in order to balance the charge of the macroion. We demonstrate that this effect can be used to induce the transition of star polyelectrolytes from a collapsed to a stretched state. In this way we present a novel way of manipulating single molecules in solution by light.

## EXPERIMENTAL

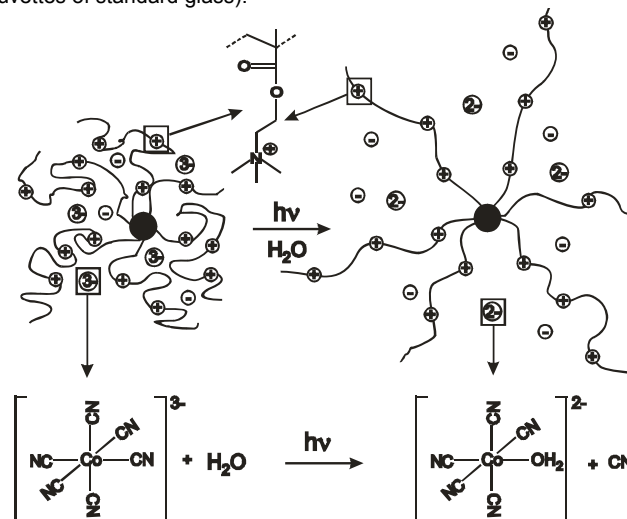
**Materials.** The synthesis and characterization of anionic and cationic polyelectrolyte stars using multifunctional ATRP initiators were reported in earlier publications.<sup>5,7</sup> Here we used a star-shaped poly[[2-(methacryloyloxy)ethyl] trimethylammonium iodide] (PMETAI) with an arm number  $f_n = 18$  (number average; PDI in arm number distribution  $\approx 1.4$ ) and a number-average degree of polymerization per arm  $P_n(\text{arm}) = 170$  (PDI of arms = 1.2). The formula of the star polymer is assigned as (PMETAI<sub>170</sub>)<sub>18</sub>. Potassium hexacyanocobaltate(III)  $\text{K}_3[\text{Co}(\text{CN})_6]$  was purchased by Aldrich, whereas potassium tetracyanonickelate(II)  $\text{K}_2[\text{Ni}(\text{CN})_4]$  was purchased from ABCR and used as received.

**Sample Preparation.** The samples for DLS measurement were prepared by slow addition (titration rates from 0.008 to 0.15 mL/min; added volume increment around 0.02 mL) of freshly prepared aqueous  $\text{K}_3[\text{Co}(\text{CN})_6]$  (0.0167 M) or  $\text{K}_2[\text{Ni}(\text{CN})_4]$  (0.0333 M) solutions to a polyelectrolyte solution (100 mL) of 0.5 g/L (PMETAI<sub>170</sub>)<sub>18</sub> with the same ionic strength (adjusted with NaCl; 0.1 M) as the metalate solutions. For this purpose we used a titrator (Titrando 809, Metrohm, Herisau, Switzerland) equipped with a turbidity sensor (wavelength = 523 nm, Spectrosense, Metrohm). The same setup was also used for turbidimetric titrations (without any sample removal). We assumed negligible dilution during addition of metalate solution, as only up to three ml were added to a starting volume of 100 ml. The samples were kept at room temperature for about one day, then they were filtered in a flow box for measurements by dynamic light scattering using Millipore Nylon filters with a pore size of 0.45  $\mu\text{m}$ . Exposure to direct sunlight was avoided.

**Dynamic Light Scattering (DLS)** was performed at 24 °C using an ALV DLS/SLS-SP 5022F compact goniometer system with an ALV 5000/E correlator and a He-Ne laser ( $\lambda = 632.8 \text{ nm}$ ; Peters ALV, Langen, Germany). The intensity fluctuations were detected at 90°. By

means of CONTIN analysis of the intensity autocorrelation functions the intensity weighted hydrodynamic radii were derived from the collective diffusion coefficients by the Stokes-Einstein relation. Prior to the light scattering measurements the sample solutions were filtered using Millipore Nylon filters with a pore size of 0.45  $\mu\text{m}$ .

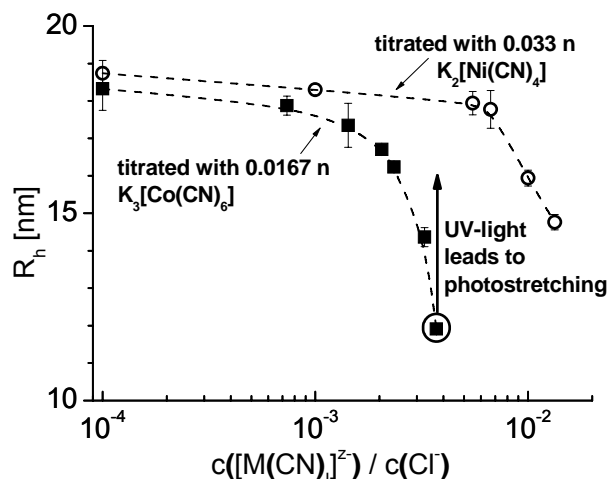
**Irradiation.** The mixtures were irradiated using a Honle UVAHAND 250<sub>H1/BL</sub> lamp (310 W), operated with black light filter, which transmits light of wavelengths between 310 and 400 nm. IR radiation was attenuated with a water flow filter. The samples were placed 7 cm away from the lamps surface. No special care was taken for the transmittance of the glassware used (small glass vials, VWR, and cuvettes of standard glass).



**Figure 1.** Scheme of the structure of the polyelectrolyte star and the photochemical reaction (photoaquation) leading from trivalent to divalent ions

## DISCUSSION

Fig. 1 displays an exemplary structure of the cationic star polymer used. The details of the synthesis and characterization of these systems have been given elsewhere.<sup>7</sup> On average, it has 18 arms and a degree of polymerization per arm of 170, yielding the abbreviation (PMETAI<sub>170</sub>)<sub>18</sub>.



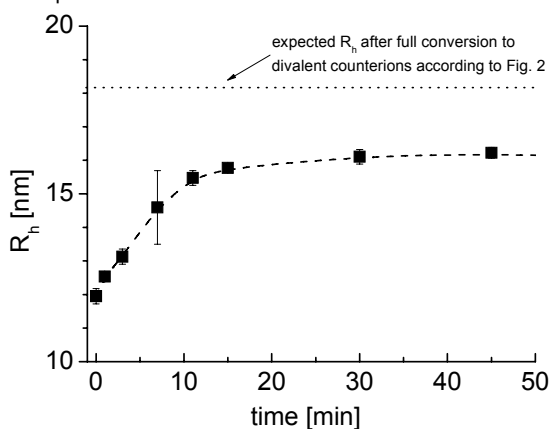
**Figure 2.** Change of the hydrodynamic radius of the cationic star polyelectrolyte (0.5 g/L of (PMETAI<sub>170</sub>)<sub>18</sub>) in dilute aqueous solutions with same ionic strength (0.1 M NaCl) but different ratios of mono- to multivalent salt; the dashed lines are a guide to the eye

As for the counterions we chose cyanometalates with high complexation equilibrium constants, like the quadratic planar tetracyanonickelate(II) ( $[\text{Ni}(\text{CN})_4]^{2-}$ ) and octahedral hexacyanocobaltate(III)

([Co(CN)<sub>6</sub>]<sup>3-</sup>). Both do not change their structure at moderate pH-values. Only the cobaltate is able to undergo photoaquation (i.e. exchange of cyano ligand with water) when irradiated with UV-light (see Fig. 1).<sup>9, 10</sup> This effect will be used for a photochemical switching of the star polyelectrolytes in solution as already sketched in Fig. 1.

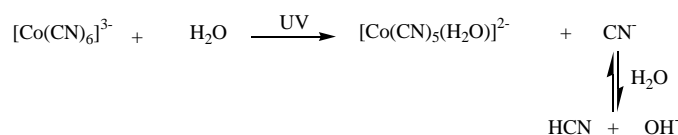
We first discuss the overall dimensions of the star polyelectrolyte in dilute aqueous solution. Fig. 2 displays the hydrodynamic radius of the star polyelectrolyte when monovalent salt is gradually replaced by divalent or by trivalent salt. Note that the ionic strength was kept constant at 0.1 M in all cases. There is a strong exchange of the monovalent counterions by a smaller number of the multivalent ones. This leads to a pronounced drop in osmotic pressure within the star and to a partial retraction of the arms. Hence, the overall dimensions of the star polyelectrolytes in solution are expected to become considerably smaller as seen from the decrease of the hydrodynamic radius.

The influence of counterion charge at constant ionic strength is shown in Fig. 2. For both the divalent as well as for the trivalent counterions, a marked decrease of the overall dimensions is seen, as expected. In particular, a rather small fraction of trivalent counterions is already sufficient to lead to a collapse of the star polyelectrolyte in solution. The divalent tetracyanonickelate(II) ([Ni(CN)<sub>4</sub>]<sup>2-</sup>) counterion, however, needs a higher counterion concentration for a marked decrease of the dimensions as compared to trivalent counterions, e.g. [Co(CN)<sub>6</sub>]<sup>3-</sup>. Since divalent counterions bear a lower charge the charge compensation and ion exchange takes place at higher counterion concentration. At sufficiently high counterion concentrations both systems enter a two-phase region, yielding a polyelectrolyte-rich gel-like precipitate and a virtually polymer-free aqueous phase. The onset of precipitation for the system used for Fig. 2 occurs, as obtained by turbidimetric titration, at a concentration of trivalent counterions about 4 · 10<sup>-3</sup> mol/L (i.e. c([Co(CN)<sub>6</sub>]<sup>3-</sup>)/c(Cl<sup>-</sup>) ≈ 4 · 10<sup>-3</sup>). Precipitation starts close to the point where all charges of the polyelectrolyte star are compensated with trivalent counterions. The large majority of the trivalent counterions is expected to be located inside the collapsed stars. Hence, the correlation of the star polyelectrolytes by the trivalent ions leads to a net attractive force between the polymers. A similar observation has already been made for spherical polyelectrolyte brushes in presence of trivalent counterions.



**Figure 3.** Photoinduced stretching measured by DLS of 0.5 g/L (PMETA)<sub>170</sub> in 0.1 n NaCl in presence of 3.7 · 10<sup>-3</sup> mol/L K<sub>3</sub>[Co(CN)<sub>6</sub>] in dependence of illumination time

We finally turn to the photo-switching of the conformation of the polyelectrolyte stars in solution. Fig. 2 demonstrates that at constant concentration of multivalent counterions the degree of contraction depends sensitively on the valency of the counterions. Hence, changing the valency of the counterion by an external stimulus from trivalent to divalent should lead to a marked increase of the overall dimensions. The trivalent hexacyanocobaltate(III) counterion can be changed to a mixture of divalent aquapentacyanocobaltate(III) and monovalent cyanide ions by the so-called photoaquation of the cyanocobaltate:



To demonstrate the photo-switching of star polyelectrolytes by change of the valency of the counterions, we adjust the concentration of the trivalent hexacyanocobaltate(III) counterions in order to achieve a collapsed state (indicated by encircled sample in Fig. 2). Shining UV light on this solution, the hydrodynamic radius  $R_h$  is indeed increasing as is seen from Fig. 3. Like the petals of a flower the arms can be stretched again by illumination as the trivalent counterions are transformed to divalent counterions. In this way the star polyelectrolytes can be viewed upon as “nanoblossoms”. Note that the decrease in ionic strength due to transformation of trivalent to divalent counterions is negligible because of the excess of NaCl that determines the ionic strength.

Fig. 3 shows that the final state expected for total conversion of the trivalent ions to divalent ones cannot be reached (18 nm; see Fig. 2) even after prolonged irradiation. After longer irradiation  $R_h$  starts to decrease again which may be traced back to the cleavage of the cores of the stars. Photoaquation produces hydroxide ions directly inside the star by the protonation of cyanide which may cleave off the arms.

The same mechanism as described for photostretching can be used for photoinduced dissolution. In order to demonstrate this, mixtures of 0.5 g/L (PMETA)<sub>170</sub> in 0.1 n NaCl and 5.9 · 10<sup>-4</sup> n K<sub>3</sub>[Co(CN)<sub>6</sub>] were prepared by direct mixing. A precipitate of aggregated counterion-polyelectrolyte complexes was immediately formed as one is already in the two-phase region for trivalent counterions. The amount of trivalent cobaltate was adjusted that way that after complete conversion to divalent cobaltate one would still expect almost noncollapsed polyelectrolyte stars (see Fig. 2). On the way to those noncollapsed polyelectrolytes the aggregation disappears by UV-irradiation. This was seen by complete re-dissolution of the precipitate after 45 min UV-irradiation, while the mixture turns slightly yellow due to [Co(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>2-</sup>.

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