

Nanoblossoms: Light-Induced Conformational Changes of Cationic Polyelectrolyte Stars in the Presence of Multivalent Counterions

Felix A. Plamper,[†] Andreas Walther,[†] Axel H. E. Müller,^{*,†} and Matthias Ballauff^{*,‡}

Makromolekulare Chemie II, Physikalische Chemie I, and Bayreuther Zentrum für Kolloide und Grenzflächen, Universität Bayreuth, D-95440 Bayreuth, Germany

Received October 26, 2006; Revised Manuscript Received December 4, 2006

ABSTRACT

We analyze the structure of star-shaped polyelectrolytes in the presence of di- and trivalent counterions, and we use the gained knowledge to manipulate the polyelectrolyte's conformation by light. By applying dynamic light scattering and atomic force microscopy, we demonstrate that, at constant ionic strength, the arms of the cationic polyelectrolyte retract when adding multivalent counterions. Adding trivalent hexacyanocobaltate(III) ions leads to a collapse of the polyelectrolyte star even at low concentrations. This is shown by analysis of the star polyelectrolytes in solution as well as in the adsorbed state on mica surfaces. Considerably higher salt concentrations are necessary to obtain the same contraction of the polyelectrolyte star if the divalent tetracyanonickelate(II) ions are used. Sufficiently high multivalent counterion concentration leads finally to the precipitation of the polymer from the solution. We demonstrate that we can switch a polyelectrolyte star from the collapsed to the expanded state by transforming the trivalent hexacyanocobaltate(III) ions into a mixture of mono- and divalent ions by UV light. Thus, these collapsed stars react to light like "nanoblossoms". Moreover, polyelectrolyte stars precipitated through addition of the trivalent hexacyanocobaltate(III) ions can be redissolved by irradiation with light (photoinduced dissolution). Hence, the conformation and interaction of star polyelectrolytes can be switched by light. Possible applications of this novel way of manipulating polymers are discussed.

Strong polyelectrolytes are highly charged polymeric macroions.^{1,2} The number of charges, which are usually placed on each repeating unit along the polymer chain, is irrespective to pH. The counterions of the polyelectrolyte will partly dissociate from the polyion when dispersed in water or solvents with high dielectric constant. A certain fraction, however, will be closely correlated to the macroion because of its high electric field. For linear polyelectrolytes, this strong binding of counterions has been termed counterion condensation and can be determined directly by the much reduced osmotic activity of the counterions.³ For more complicated architectures as, e.g., star polyelectrolytes or layers of densely grafted polyelectrolytes (polyelectrolyte brushes), this correlation has been predicted to be much stronger, leading to a confinement of the order of 90%.^{4–7} This strong correlation of the counterions to the macroion in dilute aqueous solution must lead to a marked osmotic pressure within the macroion.^{5,6,8,9} As a consequence of this, the arms of the polyelectrolyte star must be strongly stretched. If salt is added to the solution, the electrostatic interaction is more and more screened. Hence, at sufficiently high salt concentration, the stretching of the arms of the star

polyelectrolyte will be greatly diminished and the conformation of the macroion should be comparable to the solution structure of uncharged star polymers.¹⁰ This behavior can be directly compared to the well-studied cases of polyelectrolyte brushes, where long polyelectrolyte chains are densely grafted to planar or spherical surfaces.^{11,12}

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 higher valent counterions.¹³ To the authors' best knowledge, no experimental work has been published on star polyelectrolytes in the presence of trivalent counterions. Practically all available experimental studies refer to systems having monovalent counterions.

Here we present the first analysis of star polyelectrolytes¹⁰ in the presence of di- and trivalent counterions. We show that the conformation of star polyelectrolytes in aqueous solution can be manipulated by UV light: by using the photochemical reaction of hexacyanocobaltate(III) $[\text{Co}(\text{CN})_6]^{3-}$, trivalent counterions are irreversibly converted into divalent ones (Figure 1).^{14,15} 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

* Corresponding authors. E-mail: axel.mueller@uni-bayreuth.de (A.H.E.M.); matthias.ballauff@uni-bayreuth.de (M.B.).

[†] Makromolekulare Chemie II.

[‡] Physikalische Chemie I.

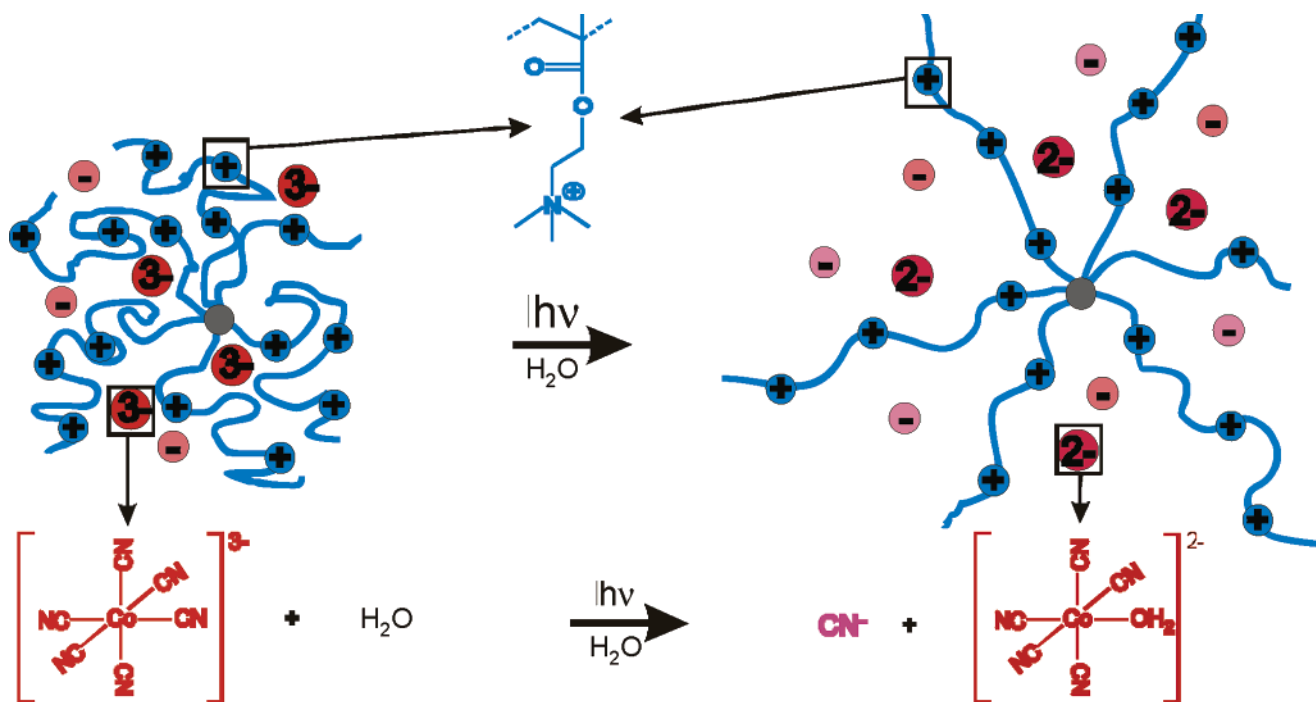


Figure 1. Scheme of the structure of the polyelectrolyte star and the photochemical reaction (photoaquation) leading from trivalent to divalent ions.

induce the transition of star polyelectrolytes from a collapsed to a stretched state through a photochemical reaction. In this way, we present a novel way of manipulating single molecules in solution by light.

Experimental Section. Materials. The synthesis and characterization of cationic polyelectrolyte stars were reported in an earlier publication.¹⁰ 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 ≈ 1.4) and a number-average degree of polymerization per arm $P_n(\text{arm}) = 170$ (PDI of arms = 1.2). In our previous publication, the nonquaternized precursor was denominated as 58A. The formula of the star polymer is assigned as (PMETAI₁₇₀)₁₈. Potassium hexacyanocobaltate(III) K₃[Co(CN)₆] was purchased by Aldrich, whereas potassium tetracyanonickelate(II) K₂[Ni(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 mL/min to 0.15 mL/min; added volume increment around 0.02 mL) of freshly prepared aqueous K₃[Co(CN)₆] (0.0167 M) or K₂[Ni(CN)₄] (0.0333 mol/L) solutions to a polyelectrolyte solution (100 mL) of 0.5 g/L (PMETAI₁₇₀)₁₈ with the same ionic strength (adjusted with NaCl; here 0.1 N) as the metalate solutions. For this purpose, we used a titrator (Titrand 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 1 day, then they were filtered in a flow box for measurements

by dynamic light scattering. Exposure to direct sunlight was avoided.

Dynamic light scattering (DLS) was performed at 24 °C using an ALV DLS/SLS CGS-8FW compact goniometer system with an ALV 5000/E correlator and a He–Ne laser ($\lambda = 632.8$ 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 μm .

Atomic Force Microscopy (AFM). For sample preparation, the polyelectrolyte was first dissolved in a 0.1 N NaCl aqueous solution (0.5 g/L (PMETAI₁₇₀)₁₈). For the samples with trivalent counterions, additionally 0.37 mmol/L [Co(CN)₆]³⁻ were present. All samples were dialyzed against pure water, then diluted by factor 100 with pure water and finally deposited onto freshly cleaved mica by spin-coating at 2000 rpm. A multimode AFM instrument (Digital Instruments, Santa Barbara, CA) was operated in tapping mode using an E-Scanner. SuperSharpSilicon SFM-Sensors (SSS–NCHR-10, Nanosensors) with a typical tip radius of 2 nm, spring constant of 10–130 N/m, and resonance frequency of 204–497 kHz were used for imaging. All measurements were performed at very soft tapping conditions to minimize structural changes of the previously deposited star-shaped polymers. The images were acquired at settings when it was just possible to obtain a meaningful height image by decreasing the amplitude set point (ca. 1.9 V, depending on the individual measurement and setup), leading to tapping conditions where the SFM tip just touches the substrate

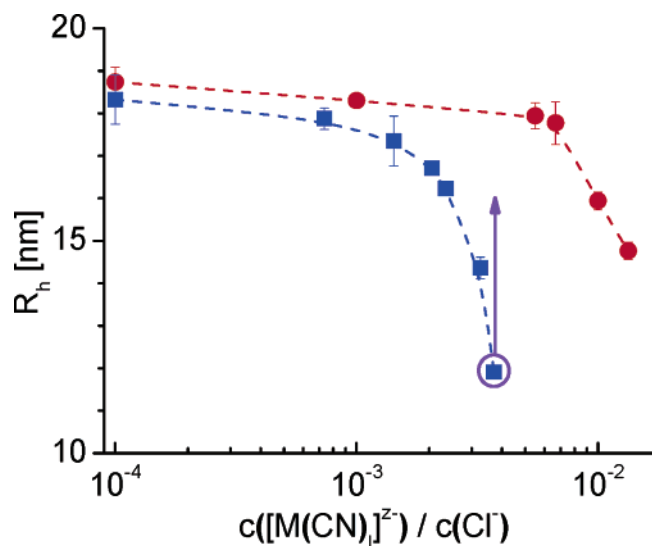


Figure 2. Change of the hydrodynamic radius of the cationic star polyelectrolyte (0.5 g/L of (PMETAI₁₇₀)₁₈) in dilute aqueous solutions with same the ionic strength (0.1 N NaCl) but different ratios of mono- to multivalent salt; circles: titrated with 0.033 mol/L divalent K₂[Ni(CN)₄]; squares: titrated with 0.0167 mol/L trivalent K₃[Co(CN)₆]; the arrow demonstrates the principle of photostretching (see Figure 4); the dashed lines are a guide to the eye

sufficiently. Additionally, the imaging was done at very low scan speeds (0.1–1 Hz) to minimize lateral forces exerted by the SFM tip to the sample. These parameters correspond to very soft SFM tapping conditions, minimize scan artefacts, and lead to the most reliable height data. Off-line data processing was done using the Nanoscope software 6.12r1.

The mixtures were irradiated using a Honle UVAHAND 250_{H1/BL} lamp (310 W), operated with a black light filter, which transmits light of wavelengths between 310 and 400 nm. IR radiation was diminished 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).

Results and Discussion. Figure 1 displays the structure of the cationic star polymer used in this study. The star-shaped polyelectrolyte, whose formula was assigned as (PMETAI₁₇₀)₁₈, bears 18 arms (number average) and a number-average degree of polymerization per arm of 170. The details of the synthesis and characterization of these systems have been given elsewhere.¹⁰

As for the counterions, we chose cyanometalates with high complexation equilibrium constants, K_c (log K_c in the range of 30), like the quadratic planar tetracyanonickelate(II) ([Ni(CN)₄]²⁻) and octahedral hexacyanocobaltate(III) ([Co(CN)₆]³⁻). Both do not change 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 Figure 1).^{14,15} This effect will be used for a photochemical switching of the star polyelectrolytes in solution, as already sketched in Figure 1.

We first discuss the overall dimensions of the star polyelectrolyte in dilute aqueous solution. Figure 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 mol/L in all cases. If only the Debye length would be the decisive parameter, the hydrodynamic radius would not change with increasing cyanometalate concentration. However, there is a strong exchange of the monovalent counterions by a smaller number of the multivalent ones.¹³ 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 depicted in Figure 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)₄]²⁻) counterion, however, needs a higher counterion concentration for a marked decrease of the dimensions as compared to trivalent counterions, e.g., [Co(CN)₆]³⁻. Because 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 Figure 2 occurs, as obtained by turbidimetric titration, at a concentration of trivalent counterions about $4 \cdot 10^{-4}$ mol/L (i.e., $c([Co(CN)_6]^{3-})/c(Cl^-) \approx 4 \cdot 10^{-3}$). Precipitation starts close to the point where the number of nominal charges of the polyelectrolyte star is matched with the number of charges originating the added trivalent counterions. Thus the large majority of the trivalent counterions is expected to be located inside the collapsed stars. But as soon as most of the star's charges are compensated with trivalent counterions, net attractive forces between the polymers prevail because excess counterions are able to bridge different stars. A similar observation has already been made for spherical polyelectrolyte brushes in presence of trivalent counterions.¹³

The marked collapse of cationic star polyelectrolytes in solution when replacing mono- by multivalent counterions can also be demonstrated by the study of the interaction of these polyelectrolytes with solid surfaces. Atomic force microscopy (AFM) is the method of choice, as has been demonstrated in early work on spherical polyelectrolyte brushes¹⁶ and on charged dendrimers.¹⁷ On the left-hand side of Figure 3, we see adsorbed (PMETAI₁₇₀)₁₈ without trivalent counterions. The cores of the stars (height around 2.5 nm) and its arms or several arms are clearly visible. Occasionally, some single polymer chains or some triarm stars are visible. It is not clear if this fraction is already present in the sample or if those fragments develop due to adsorption effects on mica (no evidence of detached fragments was found in a previous study¹⁰). The right-hand side of Figure 3 displays the image of the same star polyelectrolyte in presence of [Co(CN)₆]³⁻. Now the arms only appear as a corona around the core, which assumes a globular shape. No single arms

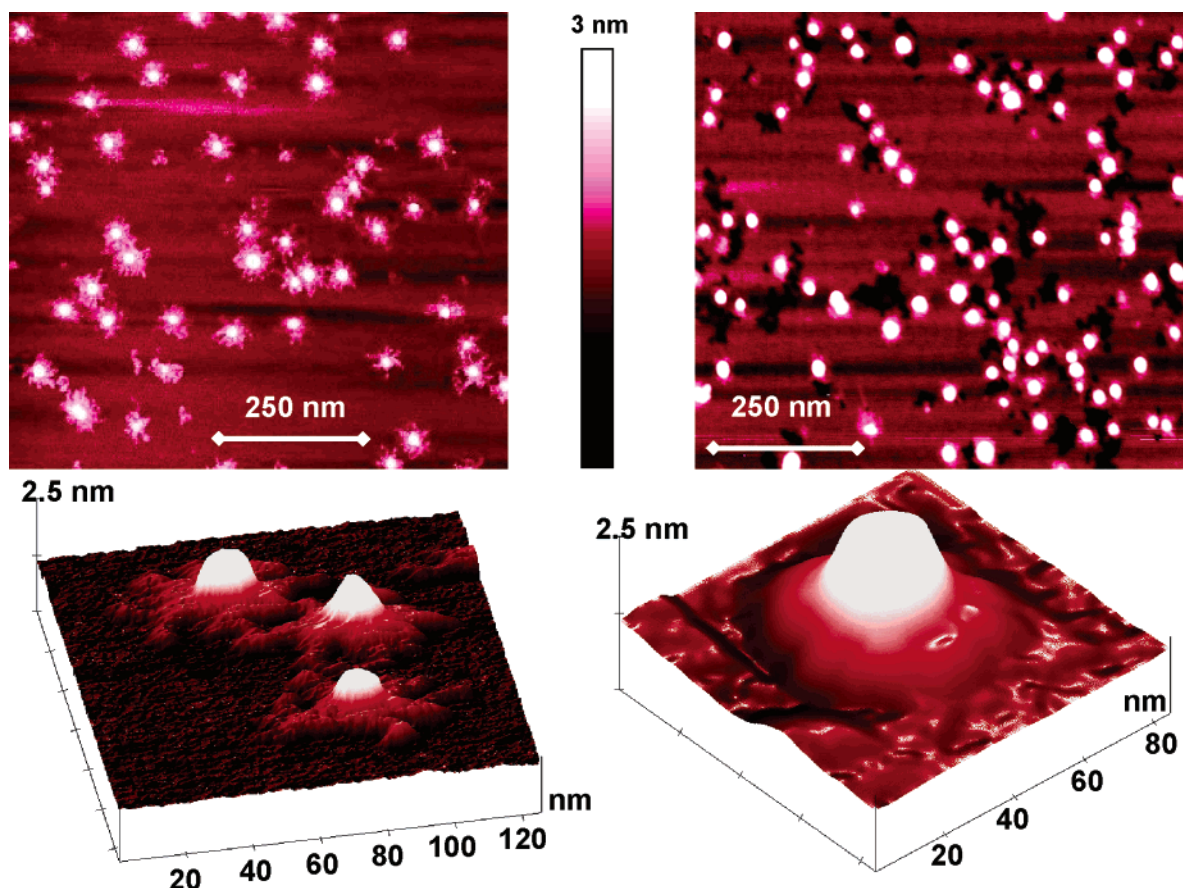
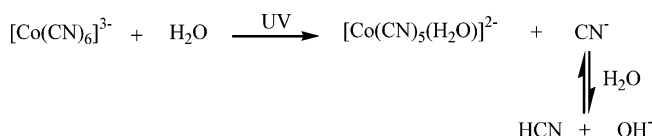


Figure 3. AFM height images of spin-coated solutions of (PMETA₁₇₀)₁₈ (~0.005 g/L) on mica (left-hand side: without added trivalent counterion, dialyzed against pure water from 0.1 N NaCl solution; right-hand side: dialyzed against pure water from 0.1 N NaCl and 3.7·10⁻⁴ mol/L [Co(CN)₆]³⁻; bottom: enlarged 3D representations).

can be seen anymore, as is expected for a collapsed conformation of the polyelectrolyte star. Before deposition of the samples on mica, excess salt was removed by dialysis in both cases. This helps to avoid the formation of salt crystals on the surface, which hampers the visibility of the stars. Because of the strong interaction of the trivalent counterions with the branched polyelectrolyte, the multivalent counterions are preferentially confined within the star and thus not removed by dialysis, as seen in Figure 3.

We finally turn to the photoswitching of the conformation of the polyelectrolyte stars in solution. Figure 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:^{14,15}



To demonstrate the photoswitching 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 Figure 2). By shining UV light on this solution, the hydrodynamic radius R_h is indeed increasing, as is seen from Figure 4. Like the petals of a flower, the arms can be stretched again by illumination as the trivalent

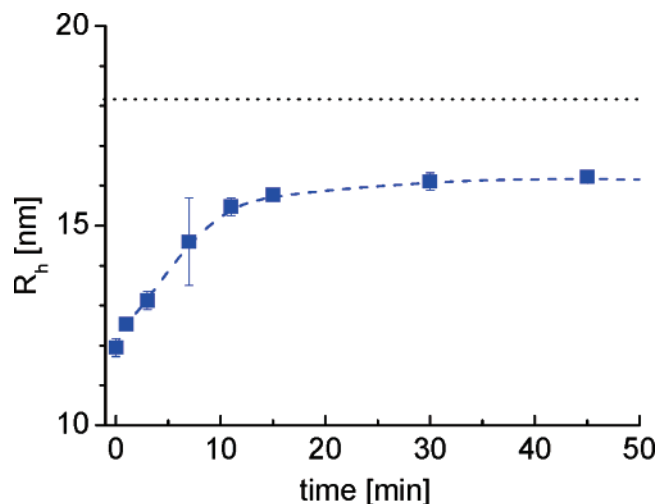


Figure 4. Photoinduced stretching measured by DLS of 0.5 g/L (PMETA₁₇₀)₁₈ in 0.1 N NaCl in the presence of 3.7·10⁻⁴ mol/L K₃[Co(CN)₆] in dependence of illumination time; the dotted line depicts the hydrodynamic radius of (PMETA₁₇₀)₁₈ in 0.1 N NaCl with 3.7·10⁻⁴ mol/L divalent [Ni(CN)₄]²⁻.

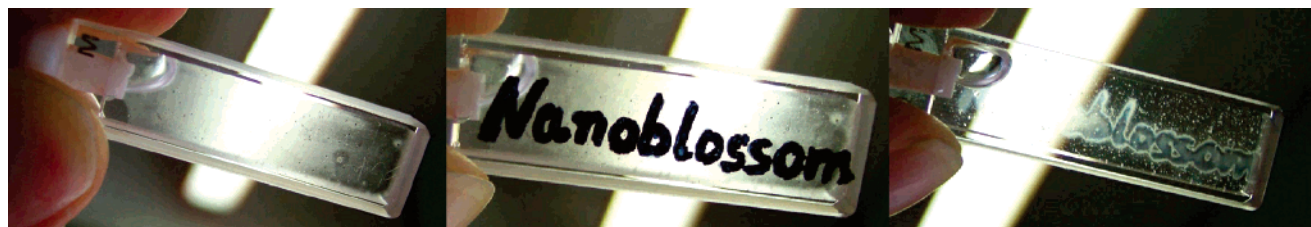


Figure 5. Left-hand side: mixture of 0.5 g/L (PMETA_{I70})₁₈ in 0.1 N NaCl and $5.9 \cdot 10^{-4}$ mol/L $K_3[Co(CN)_6]$ 1 day after mixing (precipitate has settled along the walls of the glass vial); center: same mixture with mask; right-hand side: after 25 min, UV irradiation mask was wiped away and photoundissolved complex was left behind.

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.

Figure 4 shows that the final state expected for total conversion of the trivalent ions to divalent ones cannot be reached (18 nm; see Figure 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. To demonstrate this, mixtures of 0.5 g/L (PMETA_{I70})₁₈ in 0.1 N NaCl and $5.9 \cdot 10^{-4}$ mol/L $K_3[Co(CN)_6]$ 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, so that after complete conversion to divalent cobaltate, one would still expect almost uncollapsed polyelectrolyte stars (see Figure 2). On the way to those uncollapsed polyelectrolytes, the aggregation disappears by UV irradiation. This was seen by complete redissolution of the precipitate after 45 min of UV irradiation, while the mixture turns slightly yellow due to $[Co(CN)_5H_2O]^{2-}$. Figure 5 shows photographs of the mixture before and after partial photodissolution.

These new effects described in this paper might be used and optimized for applications like use in waterborne photoresists. Especially, the compact structure of the star-polymers could lead to defined patterns in lithography. In principle, the photomanipulation of polyelectrolytes can be applied to all branched polyelectrolyte architectures. Thus the photoinduced expansion of polyelectrolyte chains grafted on, e.g., latex particles, could lead to photofreezing of a concentrated latex suspension. Therefore, the viscosity of polyelectrolyte solutions can be manipulated by light. These effects will be of interest in our future research.

Conclusion. We demonstrate a novel way to manipulate the conformation of polyelectrolytes by changing the charge of counterions by light. Further, we present the first study on the collapse of star polyelectrolytes in presence of di- and trivalent ions. The pronounced shrinkage of the dimensions of the cationic polyelectrolyte star in presence of di-

and trivalent counterions could directly be observed by DLS and AFM. Star polyelectrolytes collapsed by the trivalent hexacyanocobaltate(III) ions can be reopened again by UV light (“nanoblossoms”). We demonstrated that this transition is due to the photoaquation reaction transforming the trivalent hexacyanocobaltate(III) ions into a mixture of the divalent aquapentacyanocobaltate(III) and monovalent cyanide ions. Possible applications of this photoswitching could be related for example to photoresists or systems with light-responsive viscosity.

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft (DFG) within SFB 481 and by Fond der Chemischen Industrie (FCI). We acknowledge Alexander Schmalz for his help in finding the photoactive complex, Yu Mei, Manuela Schumacher, Markus Ruppel, and Markus Burkhardt for the help with dynamic light scattering and photography, and Frauke Pfeiffer for her help with the UV lamp.

References

- (1) Katchalsky, A. *Pure Appl. Chem.* **1971**, 26, 327.
- (2) Mandel, M. *Encycl. Polym. Sci. Eng.* **1987**, 11, 739.
- (3) Manning, G. S. *J. Chem. Phys.* **1969**, 51, 924.
- (4) Pincus, P. *Macromolecules* **1991**, 24, 2912.
- (5) Jusufi, A.; Likos, C. N.; Lowen, H. *Phys. Rev. Lett.* **2002**, 88, 018301.
- (6) Jusufi, A.; Likos, C. N.; Löwen, H. *J. Chem. Phys.* **2002**, 116, 11011.
- (7) Borisov, O. V.; Zhulina, E. B. *Eur. Phys. J. B* **1998**, 4, 205.
- (8) Guo, X.; Ballauff, M. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2001**, 64, 051406.
- (9) Plamper, F. A.; Becker, H.; Lanzendörfer, M.; Patel, M.; Wittemann, A.; Ballauff, M.; Müller, A. H. E. *Macromol. Chem. Phys.* **2005**, 206, 1813.
- (10) Plamper, F.; Schmalz, A.; Penott-Chang, E.; Jusufi, A.; Ballauff, M.; Müller, A. *Macromolecules* **2006**, submitted.
- (11) Rühle, J.; Ballauff, M.; Biesalski, M.; Dziezok, P.; Gröhn, F.; Johannsmann, D.; Houbenov, N.; Hugenberg, N.; Konradi, R.; Minko, S.; Motornov, M.; Netz, R. R.; Schmidt, M.; Seidel, C.; Stamm, M.; Stephan, T.; Usov, D.; Zhang, H. *Adv. Polym. Sci.* **2004**, 165, 79.
- (12) Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühle, J. *Polymer Brushes*; Wiley VCH: Weinheim, 2004.
- (13) Mei, Y.; Lauterbach, K.; Hoffmann, M.; Borisov, O.; Ballauff, M.; Jusufi, A. *Phys. Rev. Lett.* **2006**, 97, 158301.
- (14) MacDiarmid, A. G.; Hall, N. F. *J. Am. Chem. Soc.* **1953**, 75, 5204.
- (15) Wrigton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, 93, 5254.
- (16) Mei, Y.; Wittemann, A.; Sharma, G.; Ballauff, M.; Koch, T.; Gliemann, H.; Horbach, J.; Schimmel, T. *Macromolecules* **2003**, 36, 3452.
- (17) Pericet-Camara, R.; Papastavrou, G.; Borkovec, M. *Langmuir* **2004**, 20, 3264.

NL0625269