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COMMUNICATION TO THE EDITOR

e-Micellization: Electrochemical, Reversible Switching of Polymer Aggregation

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On-demand switching of amphiphiles has become increasingly important. Beside the use of stimuli like pH or salinity,[1−4] light has been exploited as an external stimulus, which can be easily controlled.[5−7] Recently, Matyjaszewski et al. demonstrated that the hydrophobic character of diblock copolymers can be influenced by light, allowing the reversible generation of micelles.[8] In our previous paper, the light-induced disintegration of micelles of bishydrophilic copolymers was achieved by the valency change of bridging and photosensitive counterions.[9] In the latter case, the associating forces between the polyelectrolyte chains of the copolymer weakened upon illumination. The same principle holds true for star-shaped and linear cationic polyelectrolytes, which phase-separated from aqueous solutions upon addition of hexacyanocobaltate(III).[10,11] The valency decrease of the cobaltate upon illumination led to a photoinduced dissolution of the polyelectrolyte complex. A similar principle will be applied for the electrochemical formation and disintegration of micelles as described in this Communication.

Low molecular weight surfactants bearing redox-sensitive moieties are known for more than 20 years.[12,13] They allowed the reversible micellization by oxidation and reduction. However, an electrical switch is to our best knowledge unknown for the reversible induction of micellization of polymers so far. Only limited advances have been made on that field. Two examples are given by block copolymers bearing electroactive constituents (like polyaniline). They allowed a change in the size of aggregates upon changing the potential.[14,15] However, the hydrophobic character of one of the blocks was kept in all cases. Full control over aggregation of polymers using electrochemical means is still an undiscovered field and could lead to a plethora of applications in nanoscience, controlled release or phase transfer catalysts demands, surfactant engineering, membrane technology, and so on. This development might exceed the success of thermosensitive polymers. In the latter case, full solubility and immiscibility are obtained at different temperatures, allowing the reversible formation of micelles of block copolymers with temperature.[16−21] This is in contrast to conventional surfactants, which can also show macroscopic phase separation from water, though the amphilicity is mostly retained.[22−24] Hence, electrosensitive systems would benefit from the ease of use of electricity in cases, where variations in temperature, pH, and light or addition of reactants are inappropriate. In addition, electricity can be accurately controlled both in potential and in current. Further, it can be operated by just a conventional electrical switch, like turning on light at home.

The use of electroactive counterions in tuning the interaction with oppositely charged polyelectrolytes was introduced recently.[25,26] In both cases hexacyanoferrates were adsorbed onto electrodes, which were covered with polyelectrolyte layers. Changes in potential lead to changes in contact angle or in thickness of the polyelectrolyte layer. It is also known that chemical redox agents allow the formation or decomposition of (cross-linked) polymer micelles in different solvents.[20,27−29] In this Communication, the former concept is extended to bulk solutions and united with the latter concept. This allows then the facile manipulation of micellization ranging from unimers to vesicles by just operating an electrical switch.

We chose a miktoarm star polymer consisting of one poly(ethylene oxide) (PEO) and on average 2−3 shorter poly{[2-(methacryloyloxy)ethyl]trimethylammonium chloride} (PMOTAC) arms (see Scheme 1 and Schemes S1 and S2, Supporting Information). PMOTAC is a water-soluble, strong polyelectrolyte, which phase-separates in the presence of multivalent anionic counterions. The star-shaped architecture of the PMOTAC moiety was chosen due to the expected sharp onset of micellization upon addition of multivalent counterions. First, intramolecular complexation takes place within the branched structure before the counterions bridge different stars (after saturation of one star).[10] The PEO ensures the solubilization of the polymer even in the aggregated state. The polymer was synthesized by atom transfer radical polymerization (ATRP) of a PEO and dipentaerythritol-based macroinitiator, aiming for five PMOTAC grafts. The overall formula was determined to PEO$_{114}$-(PMOTAC$_{40}$)$_{2.5}$, indicating the PMOTAC arm number (number-average; $f_a = 2.5$) and the number-average degree of polymerization for the PEO arm ($P_n = 114$) and for one PMOTAC chain ($P_n = 40$). The synthesis and detailed characterization are explained in the Supporting Information.

The electrochemical experiments were performed in mixtures of hexacyanoferrate(III) (ferricyanide) and hexacyanoferrate(II) (ferrocyanide). In order to prevent large potential changes during the redox reactions, an initial state was chosen, where we had mixtures of ferri- and ferrocyanide in a ratio 7/3. Therefore, the complexing abilities of both ions were investigated by light scattering titration of hexacyanoferrate mixtures to a 0.1 g/L solution of miktoarm stars in 0.1 M NaCl. The ionic strength of the titrant was adjusted to be close to 0.1 M, using 0.0166 M $[\mathrm{Fe(CN)_6}]^{3-/4-}$. The result of two titrations is shown in Figure 1. The intensity of the scattered light hardly changes at the beginning of the titration, first indicating the predominant complexation of counterions within each star.[10] At a certain point the intensity of scattered light increases due to the bridging between different stars, caused by an excess of multivalent counterions. This happens at somewhat higher concentrations as needed for the stoichiometric compensation of all charges of the polyelectrolyte with the charges of the hexacyanoferrates. Interestingly, the onset of micellization is more abrupt and happens at lower hexacyanoferrate concentrations for mixtures with higher content of hexacyanoferrate(III) (see Table S2, Supporting Information). This is contradictory to the expectations, assuming stronger interactions with the polyion for the higher charged counterions. It was shown that trivalent hexacyanocobaltate(III)

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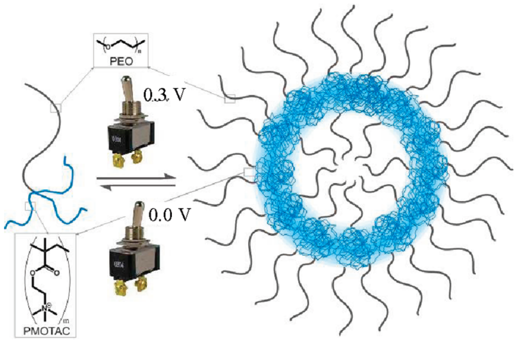
Scheme 1. Self-Assembly Due to Electrolysis of Hexacyanoferrates



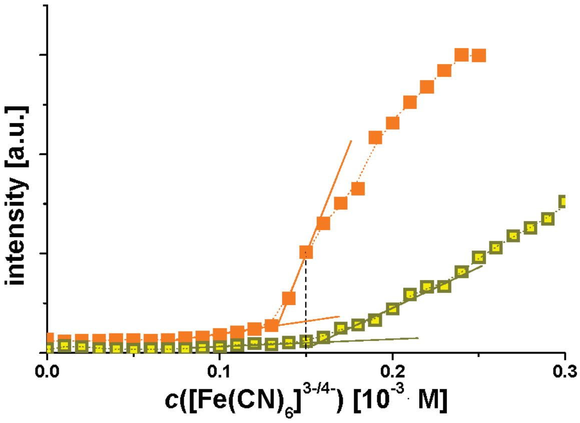


Figure 1. Intensity of scattered light (measured at scattering angle 173°) of PEO$_{114}$-(PMOTAC$_{40}$)$_{2.5}$ solution (0.1 g/L in 0.1 M NaCl) in dependence of [Fe(CN)$_6$]$^{3-/4-}$ concentration (24 °C); the dotted lines are a guide to the eye, whereas straight lines extract onset of micellization (see Table S2, Supporting Information); dashed line refers to switching process mentioned in the text; orange curve: c([Fe(CN)$_6$]$^{3-}$)/c([Fe(CN)$_6$]$^{4-}$) = 7/3; yellow curve: c([Fe(CN)$_6$]$^{3-}$)/c([Fe(CN)$_6$]$^{4-}$) = 3/7.

counterions are more capable of forming insoluble polymer complexes compared to divalent tetracyanonickelate(II).[10] However the same unexpected trend in the interaction of hexacyanoferrates with cationic polyelectrolyte brushes was found before.[25] These ion specific interactions were discussed on the basis of the weaker polarizability of the higher charged ferrocyanide. Nevertheless, both hexacyanoferrates possess different complexing abilities with PMOTAC, allowing the facile formation and disintegration of micelles. The ratio between both ions can be changed by electrolysis, since the ferrocyanide is a tetravalent anion which can be reversibly oxidized to the trivalent hexacyanoferrate(III). This is also true in the presence of the complexing miktoarm star (for cyclovoltametric measurements see Supporting Information). The switching of the micellization can be performed under different conditions. For instance, a mixture containing 0.1 g/L PEO$_{114}$-(PMOTAC$_{40}$)$_{2.5}$ and 0.15 mM [Fe(CN)$_6$]$^{3-/4-}$ in an original molar ratio of c([Fe(CN)$_6$]$^{3-}$)/c([Fe(CN)$_6$]$^{4-}$) = 3/7 should still be without any micelles (see dashed line in Figure 1). However, reversing the ratio would lead to the formation of micelles. Switching can be performed also at lower iron concentration, as a 0.13 mM [Fe(CN)$_6$]$^{3-/4-}$ solution (c([Fe(CN)$_6$]$^{3-}$)/c([Fe(CN)$_6$]$^{4-}$) = 7/3) would be on the direct onset of micellization. Further oxidation would proceed into the micellar state, whereas reduction would favor unimers (see Table S2, Supporting Information). We choose the latter conditions for most of our measurements in order to minimize electric current.

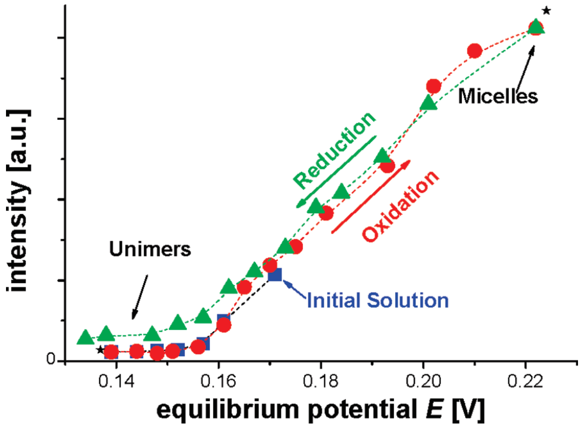


Figure 2. Intensity of scattered light (measured at 173°) of PEO$_{114}$-(PMOTAC$_{40}$)$_{2.5}$ solution (0.1 g/L, c_0([Fe(CN)$_6$]$^{3-}$)/c_0([Fe(CN)$_6$]$^{4-}$) = 7/3, 0.13 mM [Fe(CN)$_6$]$^{3-/4-}$, 0.1 M NaCl; 50 mL) in dependence of equilibrium potential (against SCE, 24 °C); the dashed lines are a guide to the eye; (■) first reduction with total −140 mC (at −0.05 V); (●) oxidation with total 280 mC (0.35 V); (▲) second reduction with total −280 mC (−0.05 V); asterisk refers to Figure 4.

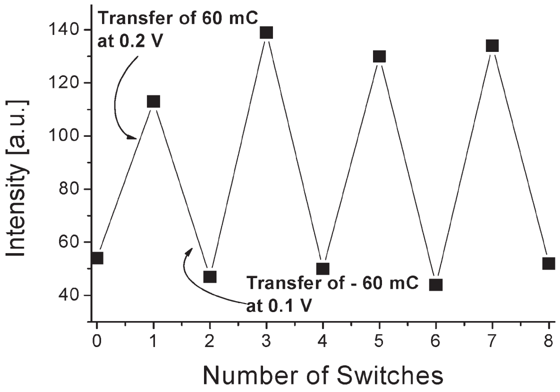


Figure 3. Intensity of scattered light (measured at 173°) of PEO$_{114}$-(PMOTAC$_{40}$)$_{2.5}$ solution (0.1 g/L, c_0([Fe(CN)$_6$]$^{3-}$)/c_0([Fe(CN)$_6$]$^{4-}$) = 7/3, 0.13 mM [Fe(CN)$_6$]$^{3-/4-}$, 0.1 M NaCl; 50 mL) in dependence of number of redox cycles.

In order to obtain effective variations in the molar ratio of trivalent to tetravalent ions, the anode reaction was separated from the cathode reaction by use of a very simple cell setup employing a glass frit (see Scheme S3, Supporting Information). The most probable reactions on the counterelectrode are chlorine or hydrogen evolution and are neglected for further discussion.

The electroswitching was usually performed with 50 mL polymer solution (0.1 g/L PEO$_{114}$-(PMOTAC$_{40}$)$_{2.5}$; 0.1 M NaCl) controlling the amount of exchanged charge (in total, ±140 mC with respect to initial solution). This treatment changes the ratio c([Fe(CN)$_6$]$^{3-}$)/c([Fe(CN)$_6$]$^{4-}$) = 7/3 to roughly 9/1 for oxidation with 140 mC or to 5/5 when reducing with −140 mC. The equilibrium potential of the above-mentioned initial solution is close to 0.17 V (against saturated calomel electrode, SCE). After transfer of ±140 mC, the equilibrium potential E of the oxidized or reduced solution changes to ~0.22 or ~0.14 V, respectively. Therefore, the oxidations and reductions could be performed as gently as just using 0.25 or 0.10 V, respectively. Mostly, the constant potential at 0.35 or −0.05 V was used for our measurements. One example is given in Figure 2, where the intensity of scattered light is plotted against equilibrium potential. It is obvious that the oxidation leads to larger aggregates. In contrast, the intensity of scattered light levels off during reduction, indicating a solution with minor or negligible aggregation. The time needed for complete oxidation (from E = 0.14 to 0.22 V) was about 35 min and for reduction 20 min (basically the same time was needed for a control experiment transferring −280 mC in the absence of polymer). These values are determined by our setup

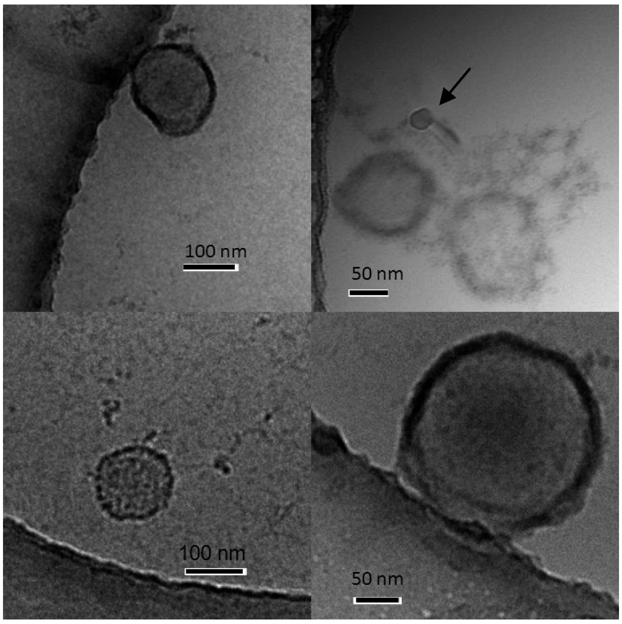


Figure 4. Cryo-TEM images of PEO_{114}-$(PMOTAC_{40})_{2.5}$ solution (vitrified from 25 °C; 0.1 g/L, $c_0([Fe(CN)_6]^{3-})/c_0([Fe(CN)_6]^{4-}) = 7/3$, 0.13 mM $[Fe(CN)_6]^{3-/4-}$, 0.1 M NaCl) after oxidation with 140 mC (with respect to original solution—see upper right asterisk in Figure 2; 50 mL; at 0.35 V); arrow assigns possible contamination on surface of vitrified water.

(e.g., limited surface of the electrode and the limited potential used) and can be certainly shortened considerably by suitable engineering of the equipment.

As seen in Figure 2, the reduction and oxidation traces superimpose nicely. Therefore, the equilibrium potential can be used as an indicator or even as a calibration tool for the current state of aggregation. The slight deviations from totally parallel behavior might be attributed to some side reactions (e.g., traces of oxygen, adsorption of polymer, dust; for discussion of possible polymer decomposition during switching see Supporting Information). But also the direct transfer of a certain amount of charge during consecutive reduction and oxidation steps leads to a fairly good reproducibility (see Figure 3). This allows quick and reproducible switching of the micellar state.

The structure of the aggregates can be observed by cryogenic transition electron microscopy (cryo-TEM; Figure 4). In the oxidized state, the polymer assembles into unilamellar vesicles (size distribution in radius typically between 30 and 120 nm). This is in accordance with dynamic light scattering (DLS), which showed a unimodal size distribution with an average hydrodynamic radius $\langle R_h \rangle_z \approx 70$ nm (Figure S7 and discussion in the Supporting Information). In the reduced state, DLS shows predominantly much smaller structures ($\langle R_h \rangle_z \approx 10$ nm), which are believed to originate from unimers. Cryo-TEM gives a more detailed picture of the self-assembled polymer. It is even seen by some of the images that vesicles are on the stage of being formed. The transition occurs via fuzzy elongated structures as seen in Figure 4 (top right). It is also expected in our case that the transitions of micellization occur via formation of spherical star-shaped micelles, wormlike micelles, and finally vesicular aggregates (at certain conditions coexistence is possible), as it was shown for micellar structures based on block copolymers.[30] Therefore, an electrochemical tailoring of the aggregate morphology appears possible along with changes in the polymer concentration and will be investigated in more detail in future.

In conclusion, a facile way of switching the micellization of star-shaped polymer based on PEO and PMOTAC is presented. The formation of vesicles could be demonstrated at low concentration of hexacyanoferrates by changing the ratio of ferri- and ferrocyanides during electrochemical oxidation or reduction. The oxidized form hexacyanoferrate(III) (ferricyanide) is a better complexing agent toward PMOTAC compared to ferrocyanide, leading to the aggregation of the copolymer. The reproducibility between different oxidation and reduction cycles is good. After all, the concept, as it is introduced in this paper, can be applied to many other polyelectrolyte systems. Beneficially, the tedious (co)polymerization of electrosensitive monomers is omitted at the same time. This opens up plenty of applications, where easy manipulation of aggregation is required by just operating an electrical switch.

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Supporting Information Available: Experimental data, synthesis, characterization of polymer, effect of concentration, and further electrochemical experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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