Environment-sensitive stabilisation of silver nanoparticles in aqueous solutions

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We describe the preparation and characterisation of inorganic–organic hybrid block copolymer silver nanoparticles via the preparation of spherical multi-responsive polymeric micelles of poly(N-methyl-2-vinyl pyridinium iodide)-block-poly(ethylene oxide), P2MVP 38-b-PEO211, and poly(acrylic acid)-block-poly(isopropyl acrylamide), PAA55-b-PNIPAAm88 in the presence of AgNO3. Hence, the P2MVP and PAA segments were employed to fix Ag+ ions within the micellar core (25 °C) or shell (60 °C), while the PEO segments ensured spontaneous reduction of Ag+ ions into metallic Ag, as well as colloidal stabilisation. Spherical and elongated composite core–shell (–corona) nanoparticles (CNPs) were formed containing several small, spherical silver nanoparticles within the micellar core or shell. As the co-assembly of the oppositely charged copolymers into micelles is electrosstatically driven, the CNPs can be destabilised by, for example, addition of simple salts, i.e., the CNPs are stimuli responsive. CNP size and morphology control can be achieved via the preparation protocol. For example, heating to 60 °C, i.e., above the PNIPAAm LCST, results in core–shell–corona CNPs with the Ag-NPs situated in the aggregate shell.

1. Introduction

The preparation of stable, monodisperse metallic nanoparticles has been topic of active research for many years. Nowadays, many researchers also employ polymer-assisted fabrication routes to prevent the particles from undergoing self-aggregation and chemical reactions; that is, to overcome stability problems related to the high surface energy of inorganic nanoparticles [1,2]. Metal precursors (or preformed nanoparticles) may be loaded or ‘trapped’ into already formed polymeric micelles, but alternatively, they may also be used to induce micellisation of the otherwise soluble block copolymers [2–6]. Via nucleation and growth processes within the composite nanoparticles (CNPs), the initially formed primary metal atoms may further aggregate into clusters, resulting in either one single colloid per micellar core or into several small colloids within a micellar core [7]. Recently, also bimetallic colloids have been formed in solution [8]. In general, the formation of the metal nanoparticles from the metal precursor typically involves the addition of a reducing agent (e.g., LiAlH4, NaBH4, H2-N-NH2, LiEt3H, or H2) and semiconductor nanoparticles can be obtained by addition of H2S to the metal precursors to form metal sulfides [1–3,6,9,10]. Various applications have been suggested for the resulting hybrid organic–inorganic particles, including their potential as quantum dots (i.e., fluorescent nanoparticles) [1,8,9], catalysts [1,6,11], particle growth modifiers [5,12], and MRI contrast agents [13–15].

In aqueous solutions, electrostatically driven co-assembly of charged copolymers and oppositely charged metal precursors gives rise to the formation of so-called complex coacervate core micelles (C3Ms) [16], also known as polyion complex (PIC) micelles [17], block ionomer complexes (BIC) [18], and interpolyelectrolyte complexes (IPEC) [19]. Examples include Au- and Pt-NP formation in aqueous mixtures of P2VP-b-PEO and a wide variety of Au and Pt-NP precursors [6,20], comiscellisation of γ-Fe2O3 and PTEA-b-PAAm [13], and La(OH)3-NP formation in aqueous solutions containing La3+ ions and PAA-b-PAAm copolymers [5,21,22]. Inspired by the spontaneous formation of silver nanowires in the presence of PMAA-b-PEO [4], i.e., without addition of a reducing agent, and the numerous studies on NP formation in the presence of P2VP and P4VP-containing copolymers (exhibiting a rather high affinity for many metal precursors due to the formation of coordination bonds between the metal ions and the pyridinium segments [6,7,23]), we decided to study Ag-NP formation in C3Ms consisting of poly(N-methyl-2-vinyl pyridinium iodide)-block-poly(ethylene oxide), P2MVP 38-b-PEO211 and poly(acrylic acid)-block-poly(isopropyl acrylamide), PAA55-b-PNIPAAm88. As suggested by Zhang et al. [4], the presence of PEO should ensure the spontaneous reduction of Ag+ to Ag through oxidation of the oxyethylene groups, while the polyelectrolyte segments should coordinate with the Ag+ ions, so that the C3Ms may serve as a template for the spontaneous formation of silver nanoparticles.
In a previous publication [24], we have shown that micelles of P2MVP<sub>38</sub>-b-PEO<sub>211</sub> and PAA<sub>55</sub>-b-PNIPAAm<sub>88</sub> are responsive to a number of experimental parameters, such as pH, ionic strength, and temperature. The C3Ms reversibly associate and dissociate upon cycling the ionic strength of the solution through the so-called “critical ionic strength” (corresponding to the ionic strength above which micelles can no longer be detected), which is approximately 105 mM for this particular system [24]. Upon raising the temperature from 25 °C to 60 °C, the C3Ms undergo a structural transition from core–shell C3Ms at T = 25 °C with the polyelectrolyte blocks in the core to a core–shell–corona system at T = 60 °C with the polyelectrolyte blocks in the shell. In the present contribution, we will demonstrate that the responsive nature of complex coacervate core micelles renders them an attractive candidate for polymer-assisted fabrication and stabilisation of silver nanoparticles (Ag-NPs). We will show that the size and location of Ag-NPs within the micellar carrier can be controlled through preparation of the complexes at various temperatures as these are coupled to distinct morphologies of the micelles and hence, different loci of the polyelectrolyte segments to which the Ag-NPs are coordinated. Furthermore, we will show that a controlled release of Ag-NPs is easily achieved through the addition of a simple monovalent salt NaNO<sub>3</sub>.

In the following, we will refer to the silver nanoparticles with the abbreviations (Ag-)NPs, to the micellar carriers as (complex coacervate core) micelles, C3Ms, or carriers, and to the combination of Ag-NPs and C3Ms as hybrid organic–inorganic nanoparticles and composite nanoparticles (CNPs).

2. Materials and methods

2.1. Materials

Poly(N-methyl-2-vinyl pyridinium iodide)-block-poly(ethylene oxide), P2MVP<sub>38</sub>-b-PEO<sub>211</sub> (M<sub>n</sub> = 13 kg mol<sup>−1</sup>) has been synthesised by sequential anionic polymerisation [25,26] (polydispersity index, PDI ~ 1.01), followed by quaternisation with methyl iodide (degree of quaternisation ~89%). Poly(acrylic acid)-block-poly(isopropyl acrylamide), PAA<sub>55</sub>-b-PNIPAAm<sub>88</sub> (M<sub>n</sub> = 14 kg mol<sup>−1</sup>) has been synthesised by RAFT (PDI ~ 1.10), according to a procedure described elsewhere [24,27]. All polymers and other chemicals were used as received, without further purification. Chemical structures are given in Scheme 1 [Subscripts correspond to the degree of polymerisation].

2.2. Sample preparation

Aqueous polymer stock solutions were prepared by dissolution of known amounts of polymer into Milli-Q water to which NaNO<sub>3</sub> was added to obtain [NaNO<sub>3</sub>] = 1 mM, followed by a pH-adjustment to pH = 7.7 ± 0.1 using 0.1 and 1.0 M NaOH and HNO<sub>3</sub>. The stock solutions were mixed in a 1:1 ratio of chargeable groups; i.e., at a mixing fraction, f<sub>c</sub>, of 0.5. For pH = 7.7, this mixing fraction corresponds to the so-called preferred micellar composition (PMC) [24]. The mixing fraction, f<sub>c</sub>, is defined as the ratio between the number of positively chargeable monomers and the sum of the numbers of positively and negatively chargeable monomers, i.e.,

\[ f_c = \frac{[n_+]}{[n_+] + [n_-]} \]

The control samples A, B, and C were prepared by mixing the filtered P2MVP<sub>38</sub>-b-PEO<sub>211</sub> and PAA<sub>55</sub>-b-PNIPAAm<sub>88</sub> stock solutions (1 × over a 0.45 μm Schleicher and Schuell filter). The samples D, E, F, and K were prepared by mixing the filtered P2MVP<sub>38</sub>-b-PEO<sub>211</sub> and PAA<sub>55</sub>-b-PNIPAAm<sub>88</sub> stock solutions, followed by addition of an excess of AgNO<sub>3</sub> (e.g., [Ag<sup>+</sup>] ≫ [P2(M)VP<sup>−</sup>]), and centrifugation for at least 20 min at 13,000 rpm, to remove the precipitated AgI formed through complexation of Ag<sup>+</sup> with the P2MVP<sup>−</sup> counterions, i.e., Ag<sup>+</sup>−P2MVP<sup>−</sup>. The supernatant was decanted into a vial and AgNO<sub>3</sub> was again added in excess (e.g., [Ag<sup>+</sup>] ≫ [P2(M)VP<sup>−</sup>]). Now, no more precipitation is observed, indicating that in the previous step all I<sup>−</sup> counterions have been replaced by NO<sub>3</sub><sup>−</sup> counterions. The control samples A, B, and C without silver ions, and the samples D, E, F, and K with silver ions were placed in the fridge (A, D, K) or in a programmable thermostated bath. Silver-containing P2MVP<sub>38</sub>-b-PEO<sub>211</sub> stock solutions for samples H and J were prepared by addition of AgNO<sub>3</sub> to the filtered P2MVP<sub>38</sub>-b-PEO<sub>211</sub> stock solution, followed by the same procedure as used in the preparation of samples D, E, and F to get rid of the insoluble salt AgI. The stock solutions of P2MVP<sub>38</sub>-b-PEO<sub>211</sub> and PAA<sub>55</sub>-b-PNIPAAm<sub>88</sub> for the control samples G and I without silver ions, and for the samples H and J with silver ions were placed in the fridge (G, H) or in the thermostated bath (I, J). Sample B was heated from 25 °C to 60 °C with a rate of 0.03 °C min<sup>−1</sup> while the samples C, E, F, and the stock solutions for the samples I and J were kept at 33 °C for 24.5 h, followed by heating from 33 °C to 60 °C in ~25 min. The P2MVP<sub>b</sub>-PEO<sub>211</sub> and PAA<sub>b</sub>-PNIPAAm<sub>88</sub> stock solutions for samples G, H, I, and J were mixed at T = 25 °C (G, H) and 60 °C (I, J) one full day after storage in the fridge or the thermostated bath. A concentrated NaNO<sub>3</sub> solution was added to samples C and F ~36 h after their preparation. A summary of the preparation protocol of the various samples is given in Table 1.

2.3. Dynamic light scattering (DLS)

Dynamic light scattering measurements have been performed on (1) an ALV light scattering instrument equipped with an ALV-5000/60 × digital correlator and a Lexel 85 400 mW argon ion laser operated at a wavelength of 514.5 nm, on (2) an ALV light scattering instrument equipped with an ALV-5000 digital correlator and a Spectra Physics 2000 1 W argon ion laser operated at a wavelength of 514.5 nm, and on (3) an ALV light scattering instrument equipped with an ALV-5000 digital correlator and a 100 mW DPSS laser operated at a wavelength of 532 nm. In all three setups, a refractive index matching bath of filtered cis-decalin

Scheme 1. Chemical structure of the polymers used in this study. (Left) Poly(acrylic acid)-block-poly(isopropyl acrylamide), PAA<sub>55</sub>-b-PNIPAAm<sub>88</sub>; (right) poly(N-methyl-2-vinyl pyridinium iodide)-block-poly(ethylene oxide), P2MVP<sub>38</sub>-b-PEO<sub>211</sub>. Note that 38 denotes the sum of the number of quaternised and non-quaternised monomers (~11%). The numbers beside the brackets denote the degree of polymerisation.
the last sample preparation step, kept at 60°C in between storage and blotting, the temperature was carefully controlled using (1) a Haake F8-C35 thermostat, (2) a Haake F3-K thermostat, and (3) a Haake Phoenix II-C25P thermostat. The second-order correlation function, \( C_g(t) \), was recorded 5 times per angle, \( \theta \), at \( \theta = 90^\circ \) or at 19 angles (35° < \( \theta < 135^\circ \), increments of 5°) to evaluate the angular dependence of the diffusion coefficient, \( D \). DLS experiments have been analysed using the method of cumulants. The diffusion coefficient extrapolated to zero angle, \( D^0 \), has been obtained from the slope in a plot of the average frequency, \( f \) versus \( q^2 \) and has been calculated into a hydrodynamic radius, \( R_h^0 \) via the Stokes–Einstein equation.

2.4. Cryogenic transmission electron microscopy (cryo-TEM)

Cryo-TEM observations were carried out on 100 K on a Philips CM12 Microscope operating on at 120 kV. Samples were prepared on Quantifoil grids (R2/2, 200 mesh grids with a pattern of 2 μm holes in a support film) using the Vitrobot. Images were taken under low dose conditions. For details see [28]. Samples A, D, H, K, and AgNO3 containing P2MVP38-b-PEO211 solution for sample H were blotted at \( T = 25^\circ \)C. Samples B, E, I, and J, and AgNO3 containing P2MVP38-b-PEO211 solution for sample J were blotted at \( T = 60^\circ \)C. In between storage and blotting, the temperature was carefully kept at 60°C. Blotting was performed at least 96 h after the last sample preparation step, i.e., either mixing of the (Ag-containing) P2MVP38-b-PEO211 and PAA55-b-PNIPAAm88 stock solutions (samples A, B, G, H, I, and J) or addition of AgNO3 to the preformed C3M solutions (samples D, E, and K).

3. Results and discussion

3.1. Micelle formation in the absence of AgNO3

As reported previously, spherical micelles (\( R_h^0 = 13.6 \text{ nm} \)) are formed spontaneously in aqueous mixtures of P2MVP38-b-PEO211 and PAA55-b-PNIPAAm88 at \( T = 25^\circ \)C [24]. They appear to be in coexistence with a (small) number of (large) aggregates, as a ‘fast’ and a ‘slow’ mode is observed in dynamic light scattering (DLS) experiments. From static light scattering (SLS) experiments, the C3Ms were found to consist of about 16 cationic and 11 anionic copolymers. Upon addition of NaNO3, the C3Ms were found to swell until above \( \sim 105 \text{ mM} \) NaNO3 micelles could no longer be detected. Temperature-induced aggregation was observed upon raising the temperature from 25°C to temperatures above the LCST of PNIPAAm (\( \sim 33^\circ \)C). Aggregate size and mass were found to be dependent on temperature, and for fast scan rates (>0.3 °C min\(^{-1}\)), on scan rate and history. The aggregate structure at 60°C was found to be of the ‘core–shell–corona’ type, i.e., the aggregates consist of a PNIPAAm core, surrounded by a coacervate shell, stabilised by a PEO corona. Cryo-TEM images on the control samples A (\( T = 25^\circ \)C) and B (\( T = 60^\circ \)C), i.e., in the absence of AgNO3, are presented in Fig. 1. The greyish dots in Fig. 1a, corresponding to the micellar cores of the core–shell C3Ms in sample A \( (T_r = T_s = 25^\circ \)C), are many smaller (\( R < 4 \text{ nm} \)) than those observed in Fig. 1b \( (R ≈ 16 \text{ nm} \)), corresponding to the aggregate core (and possibly shell) of the core–shell–corona micelles in sample B, which was heated from 25°C to 60°C with a rate of 0.03°C min\(^{-1}\) shortly after mixing the polymer stock solutions.

3.2. Nanoparticle formation within preformed C3Ms

Upon addition of AgNO3 to the preformed C3Ms depicted in Fig. 1a so that \( [\text{Ag}^+]/[\text{P2MVP}] \geq 1 \), precipitation occurs, as an insoluble AgI salt is formed due to complexation of Ag\(^+\) with I\(^-\) ions (see materials and methods section). After removal of this precipitate, further addition of AgNO3 does not result in precipitation. In analogy to the coordination of Ag\(^+\) with PMMA segments and Au and Pt-NP precursors with P2VP segments in aqueous mixtures of PMAA-b-PEO/Ag\(^+\) [4] and P2VP-b-PEO/Au and Pt-NP precursors [6,20], silver ions are now selectively incorporated into the C3M cores as they contain pyridinium and acid groups. This results in the spontaneous (that is, without the addition of a reducing agent) formation of silver nanoparticles within the C3Ms, as manifested by a gradual yellowish/reddish coloration of the Ag-containing solutions in samples D and K (Fig. 2). In the cryo-TEM images, we observe tiny dark dots corresponding to silver nanoparticles.
(R < 4 nm) and larger greyish spots corresponding to the C3M cores (Fig. 3). Clearly, there is quite some variation in particle size, aggregation state, and shape. In both images, (near) spherical, as well as elongated (open arrows), worm-like structures can be observed. Besides, there is a non-negligible amount of approximately spherical objects of considerably higher (circles) and lower (closed arrows) contrast than average. These results are in agreement with the DLS measurements, where \(R_{\text{h},90}/C_{176}\) was found to be larger for samples D and K than for sample A (Table 1). Moreover, deviations from linearity are observed in \(R_h\) versus \(q^2\) in the low-\(q\) region (cumulant analysis of DLS results), which are caused by the presence of a (small) number of large (loose) aggregates as observed

![Fig. 1](http://doc.rero.ch)

**Fig. 1.** Cryo-TEM images of a 1:1 mixture of P2MVP28-b-PEO211 and PAA65-b-PNIPAAm88 at: (a) \(T = 25^\circ\text{C}\) (sample A) and (b) \(T = 60^\circ\text{C}\) (sample B). The black circles indicate core–shell C3Ms in sample A and core–shell–corona micelles in sample B.

![Fig. 2](http://doc.rero.ch)

**Fig. 2.** Pictures of samples A–K, taken over 10 days after micellisation. The sample codes correspond to those given in Table 1. Ag-NP formation is manifested by a yellowish/reddish coloration of the Ag-containing samples, being samples D, E, F, H, J, and K. Precipitation of the Ag-NPs is observed after addition of NaNNO\(_3\) to raise \([\text{NaNNO}_3] > I_c\) (sample F), while no precipitation is visible for \([\text{NaNNO}_3] = 1\text{ mM}\) (sample E). (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

![Fig. 3](http://doc.rero.ch)

**Fig. 3.** Cryo-TEM images of a 1:1 mixture of P2MVP28-b-PEO211 and PAA65-b-PNIPAAm88 in the presence of AgNO\(_3\) at \(T = 25^\circ\text{C}\). The sample was blotted: (a) ~8 days (sample D) and (b) ~7 days (sample K) after addition of AgNO\(_3\). Circles and closed arrows indicate approximately spherical objects of considerably higher (circles) and lower (arrows) contrast than average. Several elongated, worm-like structures are indicated with open arrows. Note that the two samples are very similar, although they correspond to a 24 h difference in Ag\(^+\) addition. Note that – on the contrary – these images are very different from those obtained for samples prepared at 60 °C as shown in Fig. 5.
is in agreement with the results of Zhang et al., who observed Ag-objects (circles). The slow kinetics and random Ag-NP distribution mostly found at the periphery of the larger and darker spherical within the micellar cores of about 8 nm in diameter, they are particle size. While the Ag-NPs appear to be randomly distributed 0.3 nm (sample K), while after 52 h, ing time after Ag+ addition, indicating the existence of a maximum absolute difference in particle size becomes smaller with increas-

2.9 nm. The particles continue to grow for several days, but the

Table 1 shows that, 3 days after C3M formation, the

R_h,90 increases with increas-

ing time after Ag+ addition. As observed for the CNPs at T = 25 °C, R_h,90 increases with increasing time after Ag+ addition.

3.3. Nanoparticle formation after premixing Ag+ and P2MVP-b-PEO

Fig. 4. Cumulant results. (a) F as a function of q^2 and (b) R_h,90 as a function of q^2 for (A) sample A, 3 days after C3M formation in absence of Ag+, (O) sample D, 3 days after C3M formation, ~52 h after addition of Ag+, (□) sample K, 3 days after C3M formation, ~29 h after addition of Ag+, and (+) sample J, 6 days after addition of Ag+ to the P2MVP_38-b-PEO_211, stock solution, and ~64 h after C3M formation.

The NP induced increase in R_h,90 is a rather slow process, occurring on a timescale of several days. For example, about 3 days after C3M formation and 29 h after addition of Ag+, R_h,90 = 23.8 ± 0.3 nm (sample K), while after 52 h, R_h,90 = 64.2 ± 1.0 nm (sample D). About 7 days after C3M formation, and 132 h after addition of Ag+, R_h,90 = 93.1 ± 2.6 nm, while after 155 h, R_h,90 = 104.8 ± 2.9 nm. The particles continue to grow for several days, but the absolute difference in particle size becomes smaller with increasing time after Ag+ addition, indicating the existence of a maximum particle size. While the Ag-NPs appear to be randomly distributed within the micellar cores of about 8 nm in diameter, they are mostly found at the periphery of the larger and darker spherical objects (circles). The slow kinetics and random Ag-NP distribution is in agreement with the results of Zhang et al., who observed Ag-NP formation within an aging time of 5 h in the PMAA-b-PEO/Ag+ system. Contrary to their system, where the formation of smooth silver nanowires was observed after ~54 h of aging, we do not ob-

serve aggregation into clusters of continuous Ag-NPs. Still, some elongated, worm-like objects containing several separated Ag-NPs are clearly observed. One might hypothesise that NP formation at a different f, may lead to the incorporation of a larger number of metal nanoparticles.

The encircled aggregates in Fig. 3 resemble the objects found in sample E (Fig. 5), where the first stages of NP formation take place at 33 °C, as the sample was kept at 33 °C for 23 h, followed by heating from 33 °C to 60 °C in ~25 min. Here, most objects appear spherical with R ~ 7–10 nm, containing small NPs on the periphery, confirming the core–shell–corona structure of P2MVP_38-b-PEO_211 and PAA_55-b-PNIPAM_88 aggregates at elevated temperatures. As Ag+ coordinates with the PAA and/or P2(M)VP monomers in the coacervate layer, the NPs should be formed at the periphery of the core, i.e., in the shell of the core–shell–corona particles, where they are indeed observed. The cryo-TEM images suggest that the cores of the CNPs of sample E are smaller than those of sample B, i.e., 14–20 nm instead of ~32 nm, in agreement with our previous findings on aqueous mixtures of P2MVP_38-b-PEO_211 and PAA_55-b-PNIPAM_88 in the absence of Ag+, where quick heating to 60 °C resulted in smaller particle sizes [24]. However, Table 1 shows that, 3 days after C3M formation, the R_h,90 of CNPs (sample E, F) are larger than those of the aggregates without Ag-NPs (sample B, C). A tentative explanation might be that there is an increased tendency for secondary aggregation in the Ag-containing samples due to the oxidation of the oxyethylene groups. As observed for the CNPs at T = 25 °C, R_h,90 increases with increasing time after Ag+ addition.

Fig. 5. Cryo-TEM image of sample E, AgNO_3 was added to a 1:1 mixture of P2MVP_38-b-PEO_211 and PAA_55-b-PNIPAM_88, followed by storage at 33 °C for 23 h and consecutive heating from 33 °C to 60 °C in ~25 min. The sample was blotted at T = 60 °C for ~7 days after addition of AgNO_3. The inset is a schematic representation of a core–shell–corona particle containing one silver nanoparticle in the shell.
served for Ag-NP formation after C3M formation, premixing of Ag+ with P2MVP38-b-PEO211 before C3M formation results in CNPs with larger $R_{h,90}/C_{176}$ than the corresponding C3Ms without Ag-NPs (i.e., compare $R_{h,90}$ of samples H and G, and those of samples D, K, and A).

When C3M formation occurred at $T = 60 \degree C$ after premixing of Ag+ and P2MVP38-b-PEO211 (Sample J, Fig. 7b), i.e., after formation of PAA55-b-PNIPAAm88 micelles with a hydrophobic PNIPAAm core and a negatively charged PAA corona, large aggregates of $R \sim 16 \text{ nm}$ are observed, as in the control sample I (Fig. 7a) in absence of Ag+, and in addition tiny dark spots corresponding to Ag-NPs, larger and darker than in samples D, K, and A. Contrary to those samples, there is a considerable amount of Ag-NPs that appear not to be associated with the aggregate cores, i.e., they are not found within or on the periphery of the objects, but are seemingly 'free'. This is in agreement with the observation of (partial) macroscopic precipitation in sample J, as the free Ag-NPs, i.e., without stabilisation by polymer micelles, are colloidally unstable.

### 3.4. Environment-sensitive stabilisation

In the previous sections, we have shown that composite nanoparticles (CNPs) consisting of two oppositely charged block copolymers P2MVP38-b-PEO211 and PAA55-b-PNIPAAm88 and Ag-NPs are formed spontaneously, i.e., without addition of a reducing agent, in aqueous solutions. We have demonstrated possibilities to tune the size of the Ag-NPs, the size and shape of the composite nanoparticles, and the location of the Ag-NPs within the CNPs. Key parameters are the temperature at which the CNPs are prepared and the order of mixing of the individual components. At room temperature, upon addition of Ag+ after comicellisation of the block copolymers, the resulting core–shell CNPs contain...
several small Ag-NPs in the micellar core of spherical and worm-like micelles (samples D and K). Upon premixing Ag⁺ and P2MVP₉₋₈-PEO₂₁₁, followed by addition of this solution to the PAAS₉₋₈-B-PNIPAAm solution, the resulting CNPs are of comparable size, but now nearly all objects are spherical and hardly any elongated, worm-like structures are observed (sample H). When the C3Ms formed at room temperature are heated to T = 60 °C in the presence of Ag⁺, the resulting core–shell–corona CNPs are larger and contain several Ag-NPs in the micellar shell (sample E). Upon premixing Ag⁺ and P2MVP₃₋₅-PEO₂₁₁, and addition of this solution to a PAAS₃₋₅-B-PNIPAAm solution at T = 60 °C, i.e., containing preformed PAAS₃₋₅-B-PNIPAAm micelles (sample J), similar core–shell–corona CNPs are formed containing larger Ag-NPs, in coexistence with a considerable amount of non-associated ‘free’ Ag-NPs, leading to (partial) macroscopic precipitation.

In the previous sections, we have characterised the thermo-sensitivity of the complexes of Ag-NP, PAAS₃₋₅-B-PNIPAAm and P2MVP₃₋₅-PEO₂₁₁ and utilised this feature to prepare CNPs of different size and shape containing several Ag-NPs within their core or shell. As the complexes are formed by virtue of electrostatics (Coulombic attraction and entropy gain through counterion release), they are also pH and salt-sensitive [16,24,29–31]. The former arises from the weak (annealed) nature of the PAA segments; that is, their charge is dependent on pHe. As a consequence, we can destabilise the CNPs by addition of a sufficiently large amount of acid, such as HCl, or salt, such as NaNO₃. To demonstrate this environment-responsive character, we have prepared two identical samples E and F, containing a colloidally stable mixture of Ag⁺, P2MVP₉₋₈-PEO₂₁₁, and PAAS₉₋₈-B-PNIPAAm. To one of these samples, sample F, we have added a large amount of NaNO₃ such that the ionic strength of the solution: Ag-NP release from the CNPs upon exposure of hydrophilic surfaces to a solution of Ag-NP containing CNPs [32].

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4. Conclusion

We have reported on the formation of silver containing composite nanoparticles (CNPs) consisting of silver nanoparticles (Ag-NPs), poly(N-methyl-2-vinyl pyridinium iodide)-block-poly(ethylene oxide), P2MVP₉₋₈-PEO₂₁₁ and poly(acrylic acid)-block-poly(isopropyl acrylamide), PAAS₉₋₈-B-PNIPAAm. Both the Ag-NPs and the CNPs from spontaneously upon mixing of the double hydrophilic block copolymers in the presence of silver ions; that is, without the addition of a reducing agent such as NaBH₄. We have demonstrated possibilities to achieve control over the size of the Ag-NPs, the size and shape of the CNPs, and the location of the Ag-NPs within the CNPs. Spherical and elongated CNPs were observed. Ag-NPs were found to colocalise with the polyelectrolyte blocks within the CNPs. Temperature could be used to trigger a structural transition from a core–shell structure at T = 25 °C to a core–shell–corona structure at T = 60 °C, translocating the Ag-NPs from the micellar core in the former into the micellar shell in the latter. The most uniform and well-defined CNPs were obtained by premixing Ag⁺ and P2MVP₃₋₅-PEO₂₁₁ at room temperature prior to addition of this solution to a solution of PAAS₃₋₅-B-PNIPAAm at T = 25 °C (sample H). Finally, we have shown that the colloidal stability of the CNPs is dependent on the ionic strength of the solution: Ag-NP release from the CNPs can easily be triggered by addition of a simple salt, such as NaNO₃.

In summary, this work shows that complex coacervate core micelles can be regarded as a promising candidate for polymer-assisted synthesis and stabilisation of silver nanoparticles. Future work might be directed towards the potential application of such CNPs as environment-sensitive silver quantum dots and as antimicrobial agents in antifouling surface coatings that can be prepared upon exposure of hydrophilic surfaces to a solution of Ag-NP containing CNPs [32].

References


