



# Colloidal stability of zwitterionic polymer-grafted gold nanoparticles in water



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## ABSTRACT

We investigate the colloidal stability of gold nanoparticles (AuNPs) coated with zwitterionic sulfobetaine polymers in aqueous solution. Zwitterionic polymers with different molar masses, synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization of *N,N*-dimethyl(methacrylamido propyl)ammonium propanesulfonate (SPP) exhibit a well known Upper Critical Solution Temperature (UCST) in water, i.e., phase separate at low temperature. The colloidal stability of gold nanoparticles grafted with PSPP was studied as a function of the temperature. The effects of the molar mass of the grafted polymers, the salt concentration, and the presence of free polymer chains in solution were investigated. UV–vis spectroscopy and dynamic light scattering measurements show that whatever the molar mass of the grafted polymer, the nanoparticles never aggregate at low temperature in pure water. However, a reversible thermal-driven aggregation process of the gold nanoparticles is observed in presence of free polymer chains in solution and explained by a depletion process.

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## 1. Introduction

During the last decade, metallic nanoparticles and especially gold nanoparticles (AuNPs) have received tremendous interest in diverse application fields such as biomedical labeling [1,2], drug delivery [3,4], photothermal therapy [5] and catalysis [6], mainly due to a combination of their unique physical and chemical properties. For most of these applications, a grafted polymer layer is required which act as a protecting shell against aggregation processes, non-specific interactions and which can be functionalized for targeting. Among ligands used to stabilize gold nanoparticles, zwitterionic polymers which are composed of an equal number of positive and negative charges appear to be hopeful [7]. This interest for this type of ligands lies in the remarkable anti-fouling properties, i.e., resistance to cell, bacteria and protein adsorption, exhibited by zwitterionic functions as a result of their strong hydration [8]. These excellent properties actually make zwitterion-based materials the ideal candidate for biomedical applications maybe better than well-known poly(ethylene glycol) [9] or oligo(ethylene glycol) [10]. However, some hydrophilic

zwitterionic polymers tend to precipitate in water as the temperature decreases, a property related to the UCST (Upper Critical Solution Temperature) behavior, which comes from Coulombic interactions between positive and negative charges located either on the same repeat unit or between different repeat units of the polymer chain (intra or interchain interactions) [11–13]. Such behavior mainly depends on the structure, molar mass and concentration of the zwitterionic polymer. One may wonder if the thermoresponsive property of zwitterionic polymers used as ligands for nanoparticles may be disturbing for colloidal stability.

In the literature, most of the studies regarding the properties of thermosensitive polymer-coated gold nanoparticles reported to date concern polymers exhibiting a LCST (Lower Critical Solution Temperature) behavior such as poly(*N*-isopropylacrylamide) poly(-NiPAM) [14], poly(*N*-vinyl caprolactam) poly(VCL) [15], ethylene oxide oligomers of different lengths [16], or statistical copolymers based on ethylene oxide and propylene oxide groups [17]. In many cases, it was observed that, when the temperature increases above the phase transition temperature, the decrease of the solvent quality induces a collapse of the polymer leading to an aggregation of the polymer-coated AuNPs and a shift of the Surface Plasmon Resonance SPR towards longer wavelengths. In general, the thermoresponsive behavior is totally reversible and the influence of many

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parameters on the phase transition temperature such as AuNPs concentration and size, ligand composition, has been studied.

On the other hand, very few studies on the influence of the temperature on the stability of UCST polymer-coated nanoparticles (including gold) have been reported. Dong et al. studied the effect of the temperature, salt, concentration and solvent on the behavior in water of silica nanoparticles coated by poly(*N,N'*-dimethyl(methacrylate ethyl)ammonium propanesulfonate) (PSPE) [18]. They found that PSPE-coated silica nanoparticles aggregate when the temperature decreases meaning that the SPE polymers exhibit an UCST behavior. They also observed that the aggregation–dissociation process of poly(SPE)-grafted silica particles is not totally reversible, meaning that the thermal-driven processes of aggregation and dissociation are distinct, difference explained by a possible rearrangement of the polymer-coated silica particles due to intra and interchain interactions. Using the same zwitterionic polymers on polystyrene latex particle, Polzer et al. observed a solubility change of the polymer corona as a function of the temperature and salt establishing the UCST behavior of PSPE polymers in aqueous solution. However, no temperature induced aggregation is reported in their study [19]. Housni et al. reported the preparation of gold nanoparticles coated with a block copolymer composed of poly(ethylene oxide) and poly(*N,N'*-dimethyl(methacrylate ethyl)ammonium propanesulfonate) [20]. The zwitterionic polymer block which constitutes the inner layer on the AuNP surface exhibits a phase transition with the temperature. On the other hand, no aggregation occurs due to the steric protection of the poly(ethylene oxide) outer layer.

In this work, the behavior and the colloidal stability of sulfobetaine polymer-coated gold nanoparticles in aqueous solution was investigated. First, a series of zwitterionic polymers, poly(*N,N'*-dimethyl(methacrylamido propyl)ammonium propanesulfonate) (PSPP), with different molar masses were synthesized by RAFT polymerization using 4-cyanopentanoic acid dithiobenzoate as RAFT agent. The advantage of the RAFT polymerization is twofold: (i) it allows to control the molar mass of the synthesized polymers which is an important parameter for the study of thermosensitive behavior of polymer solutions. (ii) The end-group of 4-cyanopentanoic acid dithiobenzoate allows, after the cleavage of the dithiobenzoate function to obtain a thiol function which constitutes a good anchor for the gold nanoparticle surface. In the first stage, the phase diagrams of the zwitterionic polymers were determined in pure water before their grafting on gold nanoparticles. Then, the behavior of zwitterionic polymer-coated AuNPs (AuNP@PSPP), prepared by ligand exchange, was investigated in aqueous solution. The effects of the average molar mass of the grafted polymers, the salt concentration, the temperature and the presence of free polymer chains in solution were studied. We found that the AuNP@PSPP do not exhibit a thermal-driven aggregation in pure water but show a reversible aggregation in presence of an excess of free polymer chains in solution. With these results, we aimed at a deeper understanding of the colloidal behavior of gold nanoparticles coated by zwitterionic polymer chains in aqueous solution.

## 2. Experimental part

### 2.1. Materials

*N,N'*-Dimethyl(methacrylamido propyl)ammonium propane-sulfonate (SPP) was donated from RASCHIG GmbH, Germany. 2,2'-Azobis(2-amidinopropane) dihydrochloride (V50), hydrogen tetrachloroaurate(III) (HAuCl<sub>4</sub>), sodium citrate tribasic dehydrate, sodium borohydride (NaBH<sub>4</sub>) were purchased from Sigma–Aldrich. All products were used as received. The RAFT agent, 4-cyanopenta-

noic acid dithiobenzoate, was synthesized as reported in Ref. [21]. Ultrapure deionized water (MilliQ, Millipore, France) was used in the experiments.

### 2.2. Synthesis

#### 2.2.1. Zwitterionic polymers

The zwitterionic polymers, PSPP, were synthesized by RAFT polymerization in water at 70 °C in the presence of 4-cyanopentanoic acid dithiobenzoate as RAFT agent. In a typical experiment (Table 1, PSPP40K), SPP monomers (2 g, 6.9 mM) and RAFT agent (14 mg, 0.05 mM) were dissolved in 150 mL of water in a 500 mL round-bottom flask. The content was stirred under N<sub>2</sub> atmosphere during 40 min. Then, V50 (500 µL, 2 g/L) was added and the reaction was performed during 16 h at 70 °C. The polymers were purified by dialysis in Spectra Por membranes (cutoff 12–14 kg/mol) against pure water during one week and finally freeze dried.

#### 2.2.2. Gold nanoparticles (AuNPs)

Citrate stabilized AuNPs of diameter 17 nm were synthesized using the standard citrate reduction method. Briefly, 1 mL of a HAuCl<sub>4</sub> solution (25 mM) was added to 100 mL of water. The solution was boiled and then 5 mL of trisodium citrate solution at 1% in weight was added under vigorous stirring. After 20 min of boiling, the solution was allowed to cool to room temperature. Water volume was then completed to 100 mL. Citrate AuNPs solutions were concentrated 4 times by centrifugation and stored at 4 °C.

#### 2.2.3. Zwitterionic polymer-protected gold nanoparticles (AuNP@PSPP)

Zwitterionic polymer-protected gold nanoparticles were prepared by ligand exchange procedure. 2 mL of PSPP aqueous solution at 1 wt% (1 eq) was mixed, under stirring, with a freshly prepared NaBH<sub>4</sub> solution (3 eq) during 30 min in order to cleave the dithiobenzoate end group and obtain thiol group at the end of the polymer chain. The disappearance of the characteristic pink color of the RAFT agent was observed during this reaction. Then, 2 mL of citrate stabilized gold nanoparticles (~4 nM) were added into the functionalized polymers under stirring for 1 h at 25 °C. First, the zwitterionic polymer-grafted gold nanoparticles were purified three times by centrifugation/redispersion cycles (18,600g, 10 min) at 40 °C to remove the polymer excess. Afterwards, they were purified by dialysis in Spectra Por membranes (cutoff 12–14 kg/mol) against pure water until the conductivity of the solution reached 6–7 µS/cm. They are noted AuNP@PSPP followed by the weight-average molar mass of PSPP used.

#### 2.2.4. Mixture of AuNP@PSPP and free polymer chains

The mixtures of AuNP@PSPP and free PSPP polymer chains were directly prepared in the UV–vis spectrophotometer at 50 °C under stirring (400 rpm). For instance, 1 mL of AuNP@PSPP with a nanoparticle concentration of about 2 nM was mixed with 1 mL of a 2 wt% aqueous polymer solution in order to obtain a solution of AuNP@PSPP in 1 wt% of free PSPP chains.

### 2.3. Characterization

#### 2.3.1. SEC

The number-average molar mass ( $M_n$ ), the weight-average molar mass ( $M_w$ ), and the dispersity ( $\bar{D} = M_w/M_n$ ) were determined by size exclusion chromatography (SEC) in 0.5 M NaNO<sub>3</sub> aqueous solution at 25 °C and at a flow rate of 1 mL/min using a Viscotek SEC system equipped with three SHODEX OHPack columns SB-806M HQ (13 µm, 300 × 8 mm). All polymers were injected at a concentration of 2 mg/mL after filtration through a 0.2 µm pore-size membrane. The absolute molar masses of the samples were

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