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Temperature-induced adsorption and optical properties of an amphiphilic diblock copolymer adsorbed onto flat and curved silver surfaces

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ABSTRACT

Temperature-induced adsorption of a thermoresponsive amphiphilic copolymer, containing poly(*N*-isopropylacrylamide), on citrate-capped silver nanoparticles and planar silver surfaces has been studied with the aid of quartz crystal microbalance with dissipation monitoring (QCM-D) and dynamic light scattering (DLS). The results clearly show that both the amount of adsorbed copolymer and thickness of the adsorbed layer increase strongly at temperatures above the lower critical solution temperature (LCST). These findings are ascribed to enhanced hydrophobicity of the polymer and higher affinity for polymer adsorption at elevated temperatures and formation of intermicellar structures of the copolymer. The values of the layer thickness calculated from QCM-D data are practically identical to the values for the hydrodynamic thickness from DLS. This result suggests that the adsorbed layer is compact with few tails protruding out into the bulk. The surface plasmon peak for silver is observed at all temperatures, and the maximum is red-shifted with increasing temperature, which is attributed to an increase of the localized refractive index as more polymer chains are adsorbed onto the silver particles.

1. Introduction

Controlling the surface properties of colloidal materials, such as gold and silver nanoparticles, is a most important research field [1–4] encompassing studies in the pharmaceutical, semiconductor, biosensor, biological, and medical areas. Polymer coating of noble metal nanoparticles and planar surfaces is one method to modify the surface features, with the polymer type determining the final characteristics of the interfaces. To prevent aggregation of metal nanoparticles, various types of polymeric stabilizers are used such as poly(vinyl pyrrolidone) [5], poly(vinyl alcohol) [5], chitosan [6–8], and cellulose derivatives [9] as well as amphiphilic copolymers [10].

Copolymers that have constituent blocks with different affinities for their surroundings exhibit amphiphilic properties, and they may self-organize or self-assemble at interfaces and in solution to minimize contact between less compatible parts [11]. This behavior can be exploited to alter the characteristics of surfaces and to enhance solubility in solution. Especially strong candidates for this purpose are copolymers that are capable of reacting adaptively and reversibly to changing environmental stimuli [12–15], such as temperature and pH. Poly(*N*-isopropylacrylamide) (PNIPAAM) is a polymer endowed with such properties [16,17], and it has been the object of a vast number of publications and is still today among the most investigated stimuli-responsive polymers in the fields of pharmaceutical sciences and biomedical engineering [11,18–20]. An aqueous solution of this polymer is characterized by a phase separation upon heating, and the system exhibits a lower critical solution temperature (LCST) at about 32 °C [21]. However, it has recently been shown that in the low molecular weight range [22] the LCST or the cloud point depends on the length of the chain and the concentration of PNIPAAM. The LCST is a result of the entropy gain for the dehydration of the amide moieties with increasing temperature, and the phase transition temperature can be modulated by copolymerization with more hydrophilic or hydrophobic monomers.

In this work, we have focused our attention on a temperature-responsive diblock copolymer [23], comprised of methoxy-poly(ethylene glycol) (MPEG) as the hydrophilic block and PNIPAAM is the hydrophobic part at elevated temperatures. This PNIPAAM-based copolymer has previously been synthesized [23] in our laboratory and it has the following composition: $MPEG_{53}$-*b*-$PNIPAAM_{113}$. This copolymer forms intermicellar structures at intermediate temperatures and contraction of the species occurs at higher temperatures [15,23,24].

The aim of this paper is to gain insight into the effect of temperature on the adsorption features of this copolymer onto

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citrate-capped silver nanoparticles as well as planar silver surfaces. Silver nanoparticles are known for their unique optical properties determined by the collective oscillations of electron density termed plasmons [25]. The surface plasmon resonance of silver nanoparticles is determined by factors such as particle size, shape, interparticle distance, and dielectric environment [26–28]. Currently, very little is known about the effect of temperature on the adsorption of this type of thermally-responsive copolymer onto noble metal surfaces, as well as how the surface plasmon peak is affected by the coating from this type of copolymer.

In this work, we have focused our attention on the properties of $MPEG_{53}$-b-$PNIPAAM_{113}$ layers physisorbed to citrate-capped silver substrates. To gain structural information on these polymer layers, we combined UV–visible absorbance measurements with quartz crystal microbalance (QCM) [29] experiments. Additionally, the hydrodynamic layer thickness and adsorption kinetics on silver particles have been monitored by dynamic light scattering (DLS). Both QCM and DLS are capable of providing information about the kinetics of adsorption and thickness of the adsorbed polymer layer. However, the two techniques are sensitive to different aspects of the process, and hence a comparison may lead to a better understanding of the mechanisms. The QCM is sensitive to any adsorbed mass, and this method probes a combination of the acoustic impedance and thickness. The calculated layer thickness from this technique is sensitive to trains and loops and also entrapped water, while DLS monitors the hydrodynamic thickness of the adsorbed layer and is governed [30] by the polymer tails.

2. Experimental

2.1. Materials and solution preparation

The uncharged diblock copolymer $MPEG_{53}$-*b*-$PNIPAAM_{113}$ was synthesized via an atomic transfer radical polymerization (ATRP) in aqueous media according to a procedure described elsewhere [23]. The weight-average molecular weight M_w = 17,200 and the polydispersity index M_w/M_n = 1.1 were both determined by asymmetric flow field-flow fractionation (AFFFF) [23]. The composition of the polymer was determined by means of ^{1}H NMR and AFFFF methods; the number of MPEG groups is 53 and the number of repeating NIPAAM units in the PNIPAAM block is 113 [23].

The spherical silver nanoparticles were purchased from Ted Pella, Inc., Redding, USA. The particles have a narrow size distribution and they are covered with a citrate-layer, which make them stable (more than 1 month) against aggregation in aqueous solutions. The size of the particles was measured by DLS and the hydrodynamic radius of the particles was found to be ca. 30 nm. The silver particles are negatively charged because of the surrounding citrate-layer and with the aid of a Malvern Zetasizer the zeta potential of the particles was determined to be approximately −50 mV.

The polymer concentration was fixed at 0.1 wt.% in all experiments and the polymer solutions were prepared by weighing in the components and then stirring the solutions for 3 days at ambient temperature to ensure that the solutions were homogeneous.

2.2. Ultraviolet–visible absorbance

The absorption spectra were collected using a temperature-controlled Helios Gamma (Thermo Spectronic, Cambridge, UK) spectrophotometer, over wavelengths from 330 nm to 600 nm. The apparatus is a single beam UV–visible spectrophotometer and equipped with a temperature unit (Peltier plate) that gives a good temperature control over an extended temperature interval and time. The instrument can scan a wavelength range from 190 nm to 1100 nm and is computer controlled through a homemade program. The results from the spectrophotometer will be presented in terms of the absorbance. At each temperature, the silver particle/$MPEG_{53}$-*b*-$PNIPAAM_{113}$ mixture was allowed to equilibrate for 3 h before the measurement was conducted.

2.3. Quartz crystal microbalance with dissipation monitoring (QCM-D)

The amount of copolymer adsorbed onto planar citrate-covered silver surfaces was acquired on a QCM-Z500 supplied by KSV Instruments Ltd., which monitors the reduction in vibration frequencies of a piezoelectric crystal when it is exposed to adsorbing species. The silver-coated quartz crystals were cleaned by immersion and ultrasonication in a freshly prepared 0.5 M solution of NaOH for approximately 15 min, followed by 15 min of ultrasonication in ethanol. Finally the crystals were rinsed with Milli-Q water and dried under a stream of N_2 gas. The performance of the experiments as well as the analysis of the data has been described in detail previously [9,31]. From the QCM-D technique a direct measure of the adsorbed mass of polymer and associated water on the surface is determined, and the thickness of the layer can be estimated from a model in the accompanying software [9,32].

2.4. Dynamic light scattering

The dynamic light scattering experiments were conducted with the aid of an ALV/CGS-8F multi-detector compact goniometer system, with eight off fiber-optical detection units, from ALV-GmbH, Langen, Germany. The beam from a Uniphase cylindrical 22 mW He–Ne-laser, operating at a wavelength of 632.8 nm with vertically polarized light, was focused on the sample cell (10-mm NMR tubes) through a temperature-controlled cylindrical quartz container (with two plane-parallel windows), vat the temperature constancy being controlled to within ±0.01 °C with a heating/cooling circulator, which is filled with a refractive index matching liquid (*cis*-decalin). The polymer solutions were filtered through a 5.0 μm filter (Millipore) directly into precleaned NMR tubes.

In the dilute concentration regime probed in this study, the scattered field obeys Gaussian statistics and the measured intensity correlation function $g^2(q,t)$, where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the wavevector, with λ, θ, and n being the wavelength of the incident light in a vacuum, scattering angle, and refractive index of the medium, respectively, can be related to the theoretically amenable first-order electric field correlation function $g^1(q,t)$ by the Siegert relationship $g^2(q,t) = 1 + B|g^1(q,t)|^2$, where B is usually treated as an empirical factor.

In this study, a nonexponential behavior of the autocorrelation function was observed, and in accordance with previous DLS studies on colloidal particles [33–36] a stretched exponential function was employed in the analysis of correlation function data to allow deviations from a single exponential behavior

$$g^1(t) = \exp\left[-\left(\frac{t}{\tau_{fe}}\right)^{\beta}\right] \tag{1}$$

where τ_{fe} is some effective relaxation time and β ($0 < \beta \leqslant 1$) is a measure of the width of the distribution of relaxation times. The values of β were always close to 0.8 during the adsorption process. The mean relaxation time τ_f is given by

$$\tau_f = \frac{\tau_{fe}}{\beta}\Gamma\left(\frac{1}{\beta}\right) \tag{2}$$

where $\Gamma(1/\beta)$ is the gamma function of β^{-1}. The correlation functions were analyzed with a nonlinear fitting algorithm to obtain best-fit values of the parameters τ_{fe} and β appearing on the right-hand side of Eq. (1). A fit was considered satisfactory if there were