Colloid Polym Sci (2004) 282: 1146–1149
DOI 10.1007/s00396-004-1048-9

SHORT COMMUNICATION

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Influence of polyelectrolyte multilayer adsorption on the temperature sensitivity of poly(*N*-isopropylacrylamide) (PNiPAM) microgels

Received: 31 October 2003
Accepted: 19 December 2003

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Abstract The electrophoretic mobility and temperature-dependent particle size of poly(*N*-isopropylacrylamide) (PNiPAM) microgels after alternating adsorption of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS) have been determined. First a PNiPAM-co-acrylic acid (AAc) shell was added to the PNiPAM microgel, then PDADMAC and PSS were adsorbed alternately. The studies of the electrophoretic mobility revealed charge reversal when a polyelectrolyte (PE) layer was adsorbed. Particle size measurements revealed a strong influence of polyelectrolyte adsorption on the temperature-dependent particle swelling. The strong influence of the adsorbed polyelectrolyte on the particle size is in contrast to polyelectrolyte multilayer adsorption on rigid particles.

Keywords PNiPAM microgel · Thermosensitive · Polyelectrolyte adsorption · Layer-by-layer

Introduction

The alternating adsorption of polyelectrolytes (PE) with opposite charges to form polyelectrolyte multilayers (PEM) has been studied intensively [1, 2, 3, 4, 5]. Besides formation on planar substrates [1], the encapsulation of colloidal templates has also been performed [2, 6, 7]. In both cases the alternating adsorption, also called the layer-by-layer (LbL) technique, is based on the electrostatic attraction between the charged surface of the substrate and the oppositely charged adsorbate [4]. Overcompensation due to tails and loops of the polyelectrolyte results in charge reversal and allows for the adsorption of several layers [8]. The LbL technique is therefore a valuable preparation method, which has the potential to alter the properties of particles by modifying the surface and to prepare core-shell as well as hollow particles [9].

To our knowledge only rather rigid interfaces have been used as substrates for polyelectrolyte multilayer adsorption, which has the advantage that the properties of the substrate are not affected by the adsorbed layer. In this contribution we report the preparation of PEM-coated particles employing soft poly(*N*-isopropylacrylamide) (PNiPAM) microgels as an alternative type of substrate with respect to the rigid templates used elsewhere.

PNiPAM microgels are internally cross-linked spherical particles with colloidal dimensions which show temperature-sensitive behavior in the form of a drastic volume phase transition at the lower critical solution temperature of PNiPAM in water at ca. 32 °C [10]. Due to its temperature sensitivity PNiPAM has attracted considerable interest in recent years [11]. It has also been employed for the preparation of hybrid particles via the adsorption of PNiPAM chains on colloidal silica particle surfaces [12], which allows the phase transition in a confined geometry to be investigated.

Recently, the variability of microgel properties has been enhanced by the preparation of core-shell particles [13, 14]. Lyon and coworkers synthesized multiresponsive core-shell microgels comprising a PNiPAM core and a copolymer shell consisting of a PNiPAM-co-poly(acrylic acid) copolymer. The charges incorporated into the microgel's shell strongly influence the temperature sensitivity of the microgel particles.

In this contribution we describe the influence of adsorbed polyelectrolytes on the properties of PNiPAM microgels. In order to ensure a high affinity between microgel surface and polyelectrolyte, the surface charge of the microgels was increased by synthesizing a PNiPAM/poly(acrylic acid) (PAAc) shell in analogy to the work by Lyon and coworkers [13].

Afterwards, poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS) were adsorbed consecutively on the template by means of the LbL approach. The success of PEM formation was monitored using laser Doppler electrophoresis (LDE) to measure the electrophoretic mobility and by dynamic light scattering (DLS) to determine the particle size. Due to the soft nature of the microgels, electrostatic interactions between the particle and the polyelectrolyte may affect the particle properties.

Experimental

Materials

N,N'-methylenebis(acrylamide) (BIS) and sodium dodecyl sulfate (SDS) were purchased from Fluka. Poly (sodium 4-styrenesulfonate) (PSS), $M_w = 70{,}000$ g mol^{-1}, poly(diallyldimethylammonium chloride) (PDADMAC), $M_w = 100{,}000$–$200{,}000$ g mol^{-1}, acrylic acid (AAc), and *N*-isopropylacrylamide (NiPAM) were purchased from Aldrich. Sodium chloride (NaCl), disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4{\cdot}12H_2O$), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$), and potassium peroxodisulfate (KPS) were purchased from Merck. Water was ion exchanged to a specific resistance of $\rho \geq 18$ MΩ cm (Milli-Q) and filtered through a 0.2-μm filter.

PNiPAM microgel synthesis

The PNiPAM core microgel was prepared via free radical emulsion polymerization as reported previously [15, 16]. The surface charge density was increased by synthesizing an additional microgel shell prepared with a 9:1:0.5 ratio of comonomers (NiPAM:AAc:BIS). PNiPAM core solution (25 ml) was diluted with 25 ml deionized water in a 100-ml three-neck bottle equipped with a mechanical stirrer, reflux condenser, thermometer, and gas inlet. The solution was heated to 70 °C and flushed with nitrogen for 40 min while stirring at 200 rpm. For the microgel shell, 0.43 g NiPAM, 0.025 g AAc, 0.033 g BIS, 0.025 g SDS, and 0.023 g KPS were diluted in 50 ml deionized water. The reaction was started by adding 10 ml of the shell solution to the core solution. Every 10 min a further 5 ml of shell solution was added and the reaction was conducted for a further 5 h under a nitrogen stream with constant stirring at 200 rpm. The dispersion was passed through glass wool in order to remove particulate matter and further purified by three centrifugation cycles (30, 20, and 15 min) (Beckmann L8-55 M, rotor 70.1) at 50,000 rpm and 25 °C [13].

Preparation of polyelectrolyte multilayers

A 1:100 diluted dispersion of microgels (3 ml) was added to 6 ml of an aqueous 1 mg ml^{-1} PDADMAC or PSS solution containing 0.5 M NaCl. The solution was mixed for 20–30 min on a Staudinger wheel. The products were separated from the excess polyelectrolytes using two centrifugation cycles at 50,000 rpm and 25 °C, decantation, and redispersion in 3 ml solvent [17]. While during the first centrifugation cycle water was used to redisperse the precipitate, during the second cycle a 0.0008 N phosphate buffer was used. The latter was prepared by dissolving 3.581 g (0.02 mol) disodium hydrogen phosphate dodecahydrate and 1.56 g (0.02 mol) sodium dihydrogen phosphate dihydrate in 100 ml water and further dilution of 2 ml of the stock solution with water to 1 l, to give a 0.0008 N phosphate buffer solution.

The electrophoretic mobilities of the bare and coated microgels were measured using LDE (Brookhaven Instr., Zeta-Plus). Particle sizes were determined by DLS experiments on the highly diluted samples (Milli-Q water) using an ALV goniometer connected to a digital ALV 5000E autocorrelator. Scattered light was detected at 90° with an integration time of 60 s. Particle sizes were calculated from cumulant fits. The samples were allowed to equilibrate for 25 min at each temperature for measurements with increasing temperature and 30 min for decreasing temperatures.

Results and discussion

First a PNiPAM microgel with enhanced surface charge density (sample AS1), serving as template, was synthesized by seed-and-feed polymerization of NiPAM/AAc onto a PNiPAM core [13, 14, 15, 16]. Then a polycation, PDADMAC, was adsorbed on the substrate (sample AS1-L1) and afterwards the polyanion PSS was adsorbed on the charge-reversed particle (sample AS1-L2). The adsorption was conducted with excess polyelectrolyte according to the methods described by Caruso et al. [17]. Centrifugation was used to remove the excess polyelectrolyte from the microgel product. In the last

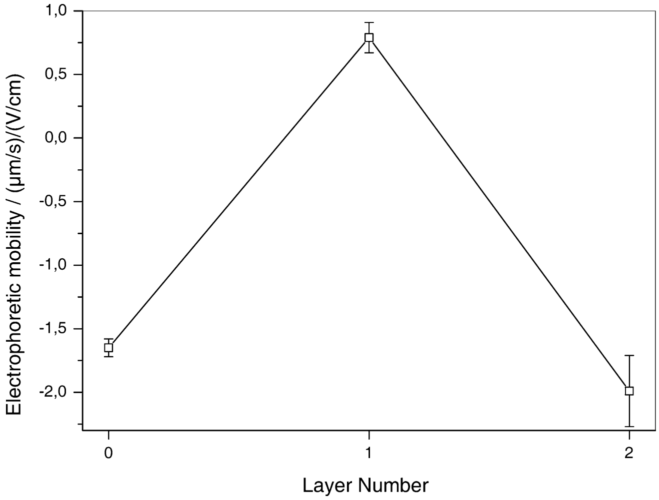

Fig. 1 Electrophoretic mobility as a function of polyelectrolyte adsorption for PDADMAC/PSS-coated negatively charged PNiPAM/AAc core-shell microgels. Layer number 1 corresponds to PDADMAC deposition and number 2 to PSS deposition

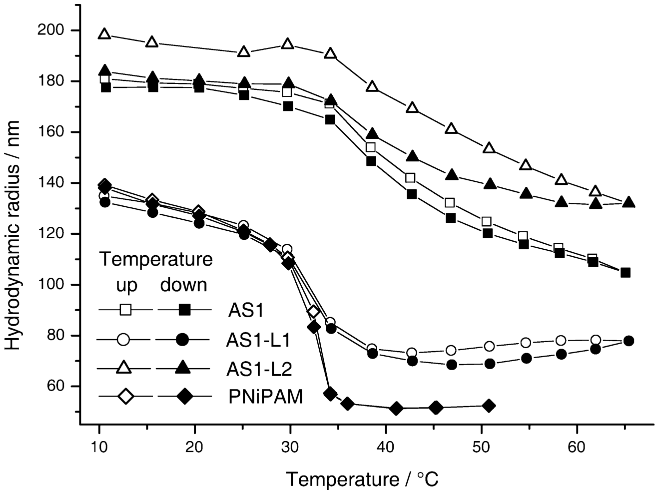

Fig. 2 Temperature-dependent hydrodynamic radius of the microgels with 0, 1, and 2 adsorbed PE layers, in 0.0008 N buffer. A temperature program with increasing, then decreasing temperature was conducted

centrifugation cycle the microgel was redispersed in 0.0008 N phosphate buffer, providing reproducible conditions at pH = 6.5 and an ionic strength of $I = 0.0036$ for further measurements.

Figure 1 shows the electrophoretic mobility of samples AS1, AS1-L1, and AS1-L2. The sign of the particle charge reverses with every adsorbed polyelectrolyte layer, such that AS1 and AS1-L2 have net particle charges of the same sign, while AS1-L1 has an opposite net particle charge. The result is consistent with electrophoretic measurements of PEM adsorbed on rigid particles [17]. The experiments therefore indicate that the multilayers prepared on soft templates have a similar character to multilayers adsorbed on rigid substrates.

Figure 2 shows the temperature-dependent hydrodynamic particle radius of four samples, namely the PNiPAM core microgel, the core-shell microgel AS1, and the microgels with adsorbed polyelectrolytes AS1-L1 and AS1-L2. Drastic changes of the particle sizes can be observed in all cases at the lower critical solution temperature (LCST) of PNiPAM between 30 and 35 °C. However, the absolute particle sizes, the temperature-dependent particle size change, and the reversibility of the measurements with increasing and decreasing temperatures show obvious differences between PNiPAM, AS1, AS1-L1, and AS1-L2.

In contrast to the core PNiPAM microgel, the sample AS1 exhibits a less sharp transition at the LCST and the particle size change extends over a wide range without reaching a distinct plateau. This observation is consistent with the results of Lyon et al. for a system equivalent to AS1 [13] and is due to the electrostatic interaction in the copolymer shell. Secondly, and most important, the particle size is much bigger as compared to that of the PNiPAM microgel, which again is a consequence of the enhanced swelling caused by the charges in the shell.

Contrarily to AS1, AS1-L1 shows a very different behavior. First, a sharp transition at 33 °C between two plateau regions above and below the LCST is observed. Second, and most important, the microgel size after the adsorption of the polycation is much smaller as compared to the size of parent core-shell microgel AS1. In fact, at low temperatures the size is very similar to that of the PNiPAM core microgel, i.e., before the PNiPAM-co-PAAc shell was attached. Apparently the charged shell collapsed when the polycation was added, similar to polyelectrolyte complex formation. This could indicate that the polyelectrolyte is partially adsorbed inside the microgel's shell. At higher temperatures AS1-L1 is smaller than AS1 but bigger than the PNiPAM core. This clearly shows the different behavior of polyelectrolyte adsorption onto microgels as compared to polyelectrolyte adsorption onto rigid interfaces. The adsorption of the second polyelectrolyte layer leads to an increase of the hydrodynamic radius, as expected.

As can be seen in Fig. 2, the particle size of sample AS1-L2 at 10 °C was different at the end of the measurement than at the beginning of the heating/cooling cycle. Figure 3 shows additional measurements obtained after different annealing processes. The second measurement followed immediately after the first. The third was performed after 2 days, while the sample was stored at room temperature. Finally, the fourth measurement was conducted after allowing the sample to sit at 70 °C for 4 days. The data show that the first measurement results in major alteration of the particle. Extended time periods under harsher conditions lead only to rather small changes. Apparently the first heating cycle already

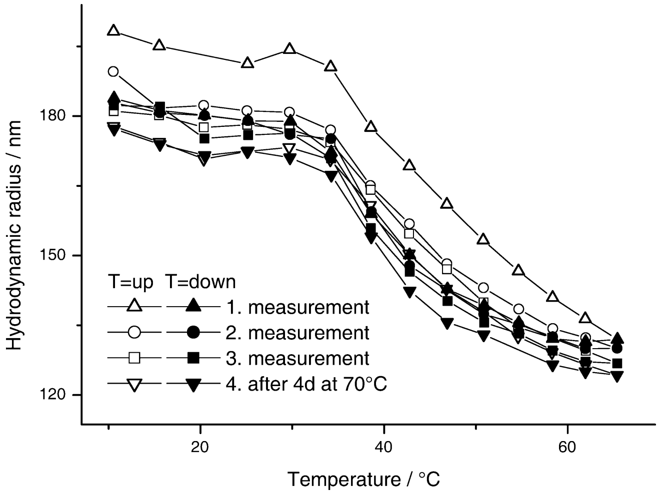

Fig. 3 Influence of thermal history on hydrodynamic radius of sample AS1-L2. Four measurements with the same sample were conducted. The second measurement followed immediately after the first. The third measurement was conducted after storing the sample for 2 days at room temperature. Finally the fourth measurement was conducted after annealing the sample for 4 days at 70 °C

induced a reorganization of the polyelectrolyte chains that leads to a different hydrodynamic radius.

The different particle sizes obtained after the polyelectroyte adsorption steps and the different hysteresis behavior in the heating/cooling cycles indicate the strong influence of the charge conditions on the swelling behavior. It is beyond the scope of this communication to fully clarify the swelling properties, and to this end it is not possible to discuss whether the size increase of sample AS1-L2 as compared to that of AS1-L1 is caused only by the adsorbed polymer layer or whether the configurations of the PDADMAC chains and of the microgel are also affected. Nevertheless, the results clearly reveal the strong influence of polyelectrolyte adsorption on the temperature-dependent swelling of PNiPAM microgels.

Conclusions

The data presented here demonstrate the tremendous influence of polyelectrolyte adsorption on the properties of charged, temperature-sensitive microgels. The first step, i.e., the adsorption of an oppositely charged polyelectrolyte, has especially strong effects, indicating complex formation that leads to a collapse of the shell; thus the segment density must increase strongly. This can have consequences for various applications of such smart materials. Temperature-sensitive polymers can be used for applications in very different fields, such as catalysis, biotechnology, and controlled drug release. Here polyelectrolyte adsorption will be a convenient tool to control the microgel properties, especially functionality and permeability of the surface. These opportunities will be explored in the future.

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