Linearly thermoresponsive core–shell microgels: Towards a new class of nanoactuators

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ABSTRACT

In this study we present novel core–shell microgels, with a shell made of poly(*N-n*-propylacrylamide) (pNNPAM) and a core consisting of poly(*N-iso*-propylmethacrylamide) (pNIPMAM), exhibiting a unique linear temperature response. The effect is produced by the large LCST gap of 23 °C between the shell- and the core-forming polymer. We demonstrate that the shell exhibits a temperature induced de-swelling process that is almost independent of the swelling properties of the core. Furthermore the active collapse of the shell forces a collapse of the core (which is known as the so-called "corset-effect"). In a region between 25 °C and 41 °C the response of the particles is directly proportional to the temperature. Moreover, the core properties were systematically varied, revealing the possibility to linearly change the magnitude of the linear swelling. Hence, these particles are very promising as piezo-like linear nano-actuators.

1. Introduction

Actuator materials undergo a change of their spatial dimensions upon application of an external stimulus. Up to now one can find a great diversity of actuators that fullfill the requirements to react on electric fields, magnetic fields, pressure or temperature. Besides commercially established products (bimetal stripes, thermoelements, piezo ceramics) we like to refer to promising artificial responsive materials, like thin-film multiferroics, which can be specifically designed to have a strong magnetoelectric coupling [1]. Soft condensed matter provides alternative strategies to realize responsive materials. For example polymer matrix embedded carbonnanotube composites can be synthesized to show a photo-induced mechanical actuation [2].

In general, the obtained response may be irreversible or reversible and the actuator may only work under equilibrium or non-equilibrium conditions. However, actuator-design for nano-scale applications is still a demanding task since only few systems, like piezo-materials, are capable to linearly change their size in a well defined manner. On the way to new actuators one needs to face challenges like predictability of the response and very often the macroscopic dimensions of the made materials make it difficult to fullfill the requirements of nanoscopic devices. Additionally, the manufacturing process can be rather complex and therefore cost-intensive.

Smart materials are systems that exhibit the characteristics described above. They comprise a built-in responsivity under equilibrium conditions and in the case of colloidal hydrogel particles (microgels) the dimensions are in a range of several hundred nanometers. Microgels have been intensively studied in the last 25 years because of their great potential with respect to applications such as photonic materials, intelligent substrates, or carriers for catalytic and biotechnological applications [3–5]. Besides their broad applicability, such systems can also serve as models to study complex phenomena, like glass transitions in colloids [6]. The properties and applications of microgels were reviewed in several articles during the last decade [7–11]. Recently, the complexity of the synthesized systems increased because multi-compartment particles exhibit the possibility of having a specific particle surface, whereas the interior can be individually modified to incorporate additional desired functionalities [12,13].

In this contribution we report a novel design strategy of thermoresponsive core–shell colloids which leads to a responsivity where the size is linearly coupled to the applied temperature. We think this material is of particular interest because its unique responsive behavior might be advantageous regarding new actuator designs and responsive coatings.

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Thermoresponsivity in the context of polymers in aqueous solutions is a well known phenomenon. The most intensely studied thermoresponsive polymer is poly(*N-iso*-propylacrylamide) (pNI-PAM), which exhibits a lower critical solution temperature (LCST) at ca. 32 °C [14,15]. Recently, we have shown that in microgels this phase transition temperature can be taylored in a linear way using copolymerization of *N*-alkylacrylamide derivatives [16]. In the present study a core−shell system, consisting of two different temperature-responsive polymers was prepared and characterized. Such kind of systems can be accessed using copolymerized microgels of NIPAM with AAc (acrylic acid) as core particles with a crosslinked pNIPAM shell as was shown by Jones et al. [17,18]. However, copolymerization with non- or less thermoresponsive materials significantly alters the overall thermoresponsive properties. In the case of AAc, the phase transition of the NIPAM based system is broadened due to the incorporated charges. Additionally, one observes a second phase transition step in the region of the LCST of AAc at moderate pH values (pH ∼ 8) [19,20]. A structurally related system was introduced by Richtering et al. [21]. Within their study they have chosen pNIPAM and its derivative pNIPMAM (poly(*N-iso*-propylmethacrylamide)) where the magnitude of the phase transition is conserved but shifted. They mainly focused on systems where the polymer in the shell exhibits a larger LCST (pNIPMAM: 44 °C [22]) compared to the LCST of the pNIPAM cores [23−29]. The inverse system was less intensely studied despite the fact that this system shows the so-called "corset-effect". This terminology indicates the strong interplay between thermodynamic and mechanical properties of the shell with the core material which is also part of the discussion in the mentioned studies above [17,18,25−28].

In this study we present novel responsive core−shell microgels based on *N-iso*-propylmethacrylamide (NIPMAM) as core material and *N-n*-propylacrylamide (NNPAM) (LCST = 21 °C) forming the shell (see Fig. 1) [22,30]. Thus, the LCST-gap between both materials was significantly increased ($\Delta = 23$ °C) compared to the known systems in literature. It is remarkable, that the combination of both relevant factors, namely the strong interplay between the low-LCST shell and the high-LCST core, as well as the large LCST-gap results in a *linear* swelling behavior. In addition, we present the synthesis of core−shell systems containing cores that exhibit varying swelling properties. The shell properties were kept constant which allowed us to systematically study the influence of core-properties on the overall core−shell characteristics.
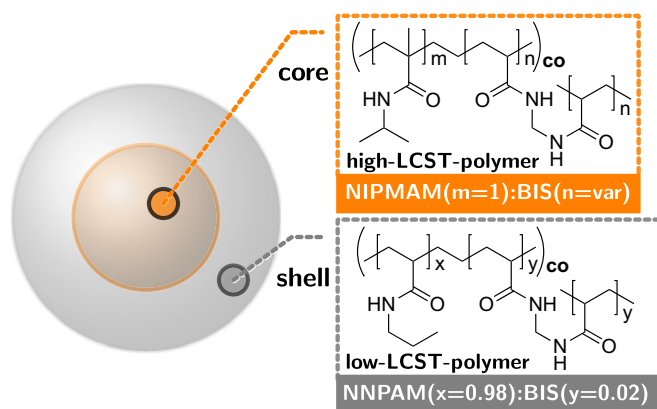
2. Experimental

2.1. Shell monomer synthesis

N-n-propylacrylamide was synthesized following a classical Schotten−Baumann reaction described by Hirano et al., using acryloyl chloride (97%, Aldrich, USA), triethylamine (99%, Grüssing, Germany), propylamine (99%, Fluka, USA) and methylene chloride (p. A.) as solvent [30].

2.2. Synthesis of core−shell microgels

A seeded growth two-step protocol was followed to build up the core−shell system [17]. First of all, pNIPMAM core-particles were synthesized (0.1 mol/L, in water, 400 rpm, 4 h at 70 °C) and purified by 5 successive ultracentrifugation and re-dispersion steps. The corresponding feeding ratios of monomer (*N-iso*-propylmethacrylamide, 97% purity, Aldrich, USA), crosslinker monomer (*N,N'*-methylenebisacrylamide, 99%, Sigma Aldrich, USA), initiator APS (ammonium peroxodisulfate, 98%, Sigma−Aldrich, USA) and surfactant (sodium dodecyl sulfate, analytical grade, Serva, Germany) are listed in Table 1. Every water-based synthesis was conducted in Milli-Q water (Millipore, Merck KGaA, Germany) with a resistance of 18 MOhm cm and a TOC-value of <10 ppb. Then 150 mL of a 0.15 wt.% of the corresponding seed-particle dispersion were equilibrated at synthesis conditions, as described for the core-particle synthesis, and subsequently coated with NNPAM (0.70 g) and BIS (0.0175 g) using SDS (0.048 g) and APS (0.093 g), which resulted in a shell with a nominal crosslinker content of 1.8 mol%. After synthesis the same purification steps were followed as described before.

2.3. Determination of temperature dependent swelling curves

Angular dependent photon correlation spectroscopy (PCS) measurements were performed using a light scattering goniometer system equipped with a multiple τ digital correlator (ALV-5000/E, ALV-GmbH, Langen, Germany) combined with an Argon-Ion LASER $\lambda = 514.5$ nm (Spectra Physics Stabilite 2017, Newport Corp., USA).

The swelling curves were measured at a fixed scattering angle of $\theta = 60°$ using a solid-state LASER (TOPTICA Photonics AG, Germany) at a wavelength of $\lambda = 661.8$ nm and a fast correlator (ALV-6010, ALV-GmbH, Langen, Germany) with a thermostated bath (Haake Phoenix II, Thermo Scientific). All measurements were taken with samples at a concentration of $7.5 \cdot 10^{-4}$ wt.% in cylindrical Quartz cuvettes (Hellma GmbH & Co. KG, Germany) with an outer diameter of 10 mm. The samples were brought to equilibrium at constant thermal conditions for 15 min prior to the measurement. The visualized datapoints are average results of at least 5 individual measurements.

Fig. 1. Visualization of the studied core−shell systems. The core consists of pNIP-MAM (LCST ≈ 44 °C in water) with varying nominal crosslinker contents between 2 mol% and 20 mol%, while the shell polymer is pNNPAM (≈21 °C) with a constant crosslinker content of 1.8 mol%.

Table 1
Overview of the feeding ratios used for the core particle synthesis. The abbreviations NIPMAM, BIS, SDS and APS stand for the monomer *N-iso*-propylmethacrylamide, the crosslinker monomer *N,N'*-methylenebisacrylamide, the surfactant sodium dodecyl sulfate and the initiator ammonium peroxodisulfate.

Sample[a]	c(NIPMAM)$_{core}$	m(BIS)$_{core}$	c(SDS)$_{core}$	c(APS)
C (2 mol%)	0.0819 M	0.0379 g	0.0011 M	0.0027 M
C (5 mol%)	0.0819 M	0.0947 g	0.0011 M	0.0027 M
C (7.5 mol%)	0.0819 M	0.1422 g	0.0011 M	0.0027 M
C (10 mol%)	0.0819 M	0.1894 g	0.0011 M	0.0027 M
C (12.5 mol%)	0.0819 M	0.2370 g	0.0011 M	0.0027 M
C (15 mol%)	0.0819 M	0.2841 g	0.0011 M	0.0027 M
C (20 mol%)	0.0819 M	0.3788 g	0.0011 M	0.0027 M

[a] The sample name indicates the nominal crosslinker concentration in mol%.