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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 nanoactuators.

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 nanoscale 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) (pNIPAM), 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.

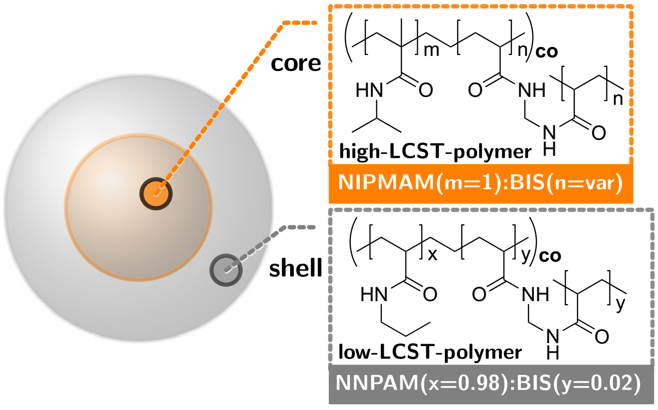

Fig. 1. Visualization of the studied core–shell systems. The core consists of pNIPMAM (LCST ≈ 44 °C in water) with varying nominal crosslinker contents between 2 mol% and 20 mol%, while the shell polymer is pNNPAM (≈21 °C) with a constant crosslinker content of 1.8 mol%.

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.

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]	$c(\mathrm{NIPMAM})_{\mathrm{core}}$	$m(\mathrm{BIS})_{\mathrm{core}}$	$c(\mathrm{SDS})_{\mathrm{core}}$	$c(\mathrm{APS})$
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%.

Photon correlation spectroscopy is well suited to determine the hydrodynamic properties of microgels [31]. Since our systems show monomodal particle size distributions, we have treated our data with a third order cumulant analysis which was first introduced by D. E. Koppel. In this method the normalized field autocorrelation function is expanded in a MacLaurin series thus giving us, amongst others, the first cumulant which corresponds to the relaxation rate Γ [32]. All temperature dependent measurements were carried out at a fixed scattering angle of 60°. This is appropriate because angular-dependent measurements revealed the purely diffusional nature of the observed relaxation at this angular position. The hydrodynamic radius is related to the relaxation rate via the Stokes–Einstein equation:

$$R_\mathrm{h} = \frac{k_\mathrm{B}T}{6\pi\eta\frac{\Gamma}{q^2}} \qquad (1)$$

with $q = 4\pi n/\lambda \sin(\theta/2)$ being the magnitude of the scattering vector, the thermal energy $k_\mathrm{B}T$, the viscosity η and the refractive index of the solvent n.

2.4. Electron microscopy of dried microgels

Concentrated particle suspensions were previously spin-coated on Si-wafers (1000 rpm), dried and sputtered with a 1.3 nm thick Pt-layer (Sputter Coater 208HR, Cressington, UK). The measurements were carried out using a FE-SEM instrument (Gemini 1530, Zeiss, Germany) with an acceleration voltage of 3 kV (Inlens-detector).

3. Results and discussion

The first step on the route to core–shell microgels was the synthesis of pNIPMAM based cores. A series of seven core-particles with different amounts of crosslinker (*N,N′*-methylenebisacrylamide; BIS) was synthesized via a precipitation polymerization technique. The hydrodynamic radii of these core-particles were studied in a temperature range between 10 °C and 60 °C using photon correlation spectroscopy (see Fig. 2). The observed behavior is similar to the results found for pNIPAM particles [33]. Increasing the amount of incorporated crosslinker leads to a diminishing swelling capability of the microgels. Additionally, a broadening of the volume phase transition is observed. Both effects are a result of an increasing network rigidity and larger fraction of non-responsive polymer material (pure crosslinker based polymer) in the microgel. More details about the influence of crosslinker content on the phase transition of the microgels can be found in the supplementary material (Fig. S1).

In the second synthesis step differently cross-linked pNIPMAM microgels were used as seeds for a seeded growth precipitation polymerization to grow a pNNPAM shell around the cores [17]. We kept the shell properties constant via fixed synthesis protocols as well as fixed monomer feeds. The synthesis was performed at elevated temperatures to avoid shell-monomer diffusion inside the collapsed cores [17,18,21,25–28]. Due to the described procedure, the corresponding shell polymer covers preferentially the core surface and thereby an interpenetration of shell material into the core is reduced and only a small interpenetration layer is obtained [25,26].

As a next step we also studied the influence of temperature on the hydrodynamic core–shell radius. The behavior of the core–shell system is significantly changed in contrast to the unperturbed core system. In Fig. 3a a sketch of the temperature induced transitions of the core–shell microgels is shown. This totally reversible swelling/deswelling process of the new particles can be subdivided into three distinct regions of different behavior. As an example the corresponding plot of the hydrodynamic radius for a core–shell microgel with 10 mol% cross-linker in the core is shown and discussed (Fig. 3b).

In region I, we observe a nonlinear decrease of the particle size with increasing temperatures up to 25 °C. This behavior indicates the occurrence of a typical collapse of the shell forming pNNPAM, which exhibits its transition around 21 °C. Above this transition temperature, water becomes a bad solvent for the shell material which initiates the shrinking process. At temperatures larger than 25 °C the regular phase transition of the shell material is finished.

Region II points to the temperature window where the hydrodynamic radius of the microgel is linearly changing with temperature. In detail, this linear relation is found in a temperature range between 25 °C and 41 °C ($\Delta T \approx 15°$ C). It is the intermediate temperature range between the two LCST values of the core and shell material, respectively.

The synthesis is performed at elevated temperatures (80 °C) thus the shell material covers fully collapsed seeds. Because of the presence of the shell-“corset”, the core material cannot retain its original shape at temperatures lower than its own phase transition temperature. At each point in the swelling curve the core is mechanically stressed due to the presence of the shell and vice versa. Thus the shell actively compresses the core, which retains its shape simply due to its network elasticity and its osmotic modulus. Upon increasing temperature, the pNIPMAM solubility successively

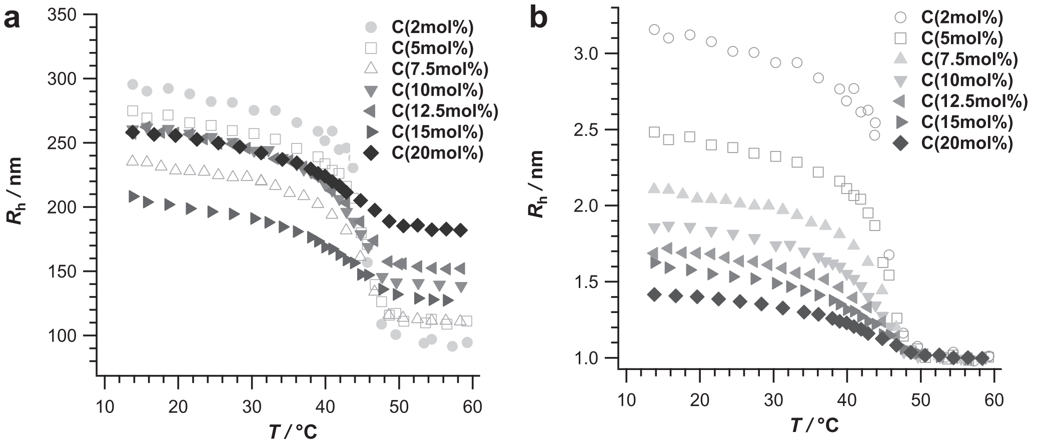

Fig. 2. Swelling behavior of microgels. a, Hydrodynamic radius R_h as a function of temperature T for different pNIPMAM core systems containing nominally different crosslinker contents. b, Normalized radius for the same systems as in a, with the fully collapsed state as reference condition.

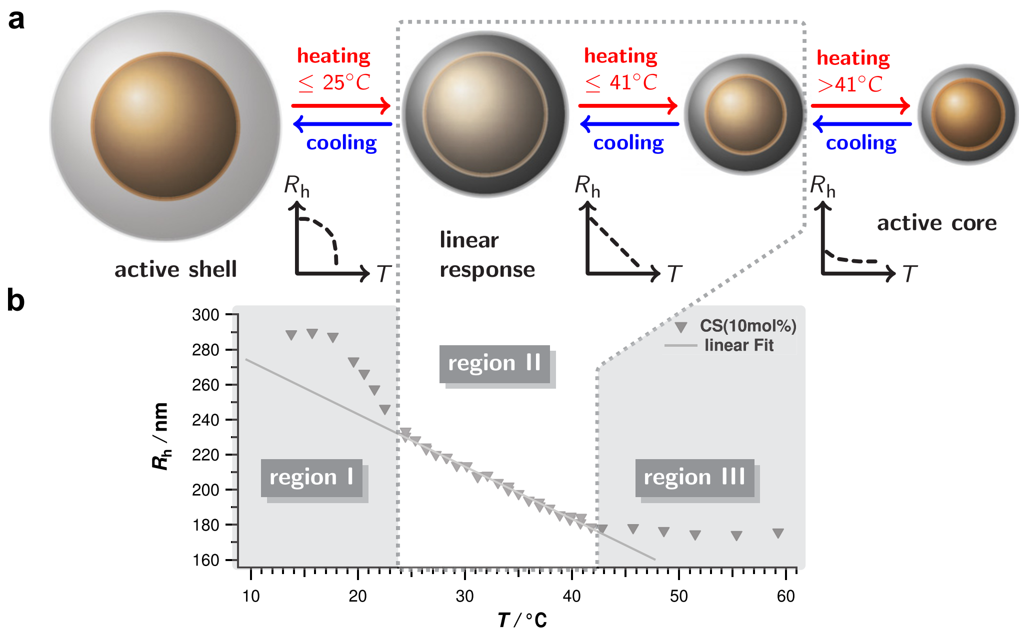

Fig. 3. Linear temperature response. a, Schematic illustration of a core–shell microgel which undergoes three regions of different swelling behavior (completely reversible process). b, Corresponding classification of previously mentioned regions in an exemplary $R_h(T)$-diagram of a core–shell microgel system with 10 mol% cross-linked cores. In region I we find a restricted shell collapse, while region II covers the linear swelling behavior. Region III indicates the occurrence of an active core collapse.

decreases while the active compression of the shell is still present. As a result, the microgel shrinks with increasing temperature. Since this change in size is linear, we propose that this effect can be related to the polymer–solvent interaction parameter, which is in a first approximation inversely proportional to the temperature for temperatures below the phase transition ($\chi \propto T^{-1}$) [34,35].

Finally region III corresponds to an active collapse of the core inside the core–shell microgel, because we reach the transition temperature of the core material. However, due to the “corset-effect” the compression of the core is already in an advanced stage and only a small change in terms of particle size is observed in this region.

We verified the linear swelling behavior for all synthesized core–shell microgels. Taking a closer look at the normalized radius of the particles in Fig. 4a it is obvious that the magnitude of the slope of the linear fit increases with decreasing crosslinker concentration in the core. From a qualitative point of view this trend is reasonable because the mechanical properties of the core should have a significant influence on the core–shell particle properties. Theoretical models like the Flory–Rehner theory underline this trend as well, since the thermodynamic phase behavior of a neutral gel can be described by two terms for the osmotic pressure inside the gel, namely mixing and elastic contributions [34]. In Fig. 4b we demonstrate that the slope k, which captures the radial swelling capability, is directly proportional to the core crosslinker content as well. Thus from a quantitative point of view we determined the key parameter, namely the core crosslinker content, that can be utilized to directly tune the responsive behavior of the core–shell particles. To our knowledge such a response in combination with an easily accessible tuning parameter has not been found before for any thermoresponsive system. This behavior could e.g. be exploited to produce materials serving as linear actuators on a nm scale. The desired magnitude of

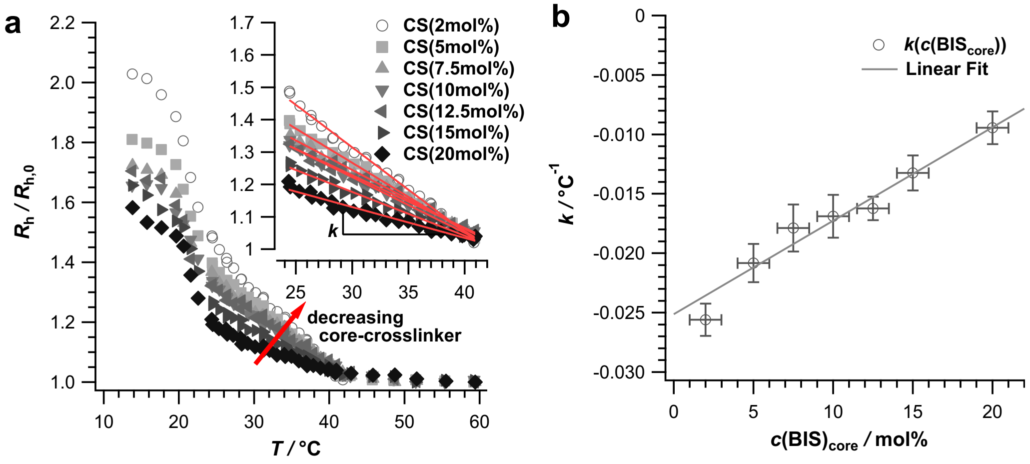

Fig. 4. Influence of the core-crosslinker. a, Temperature dependence of the normalized radius with the fully collapsed condition as a reference (Inset: magnified view on region II where the solid lines indicate linear regressions). b, Corresponding slopes k within region II for different core-crosslinker contents (y-error: as obtained from the fit, x-error: ±1 mol%). The solid line again indicates a linear regression.

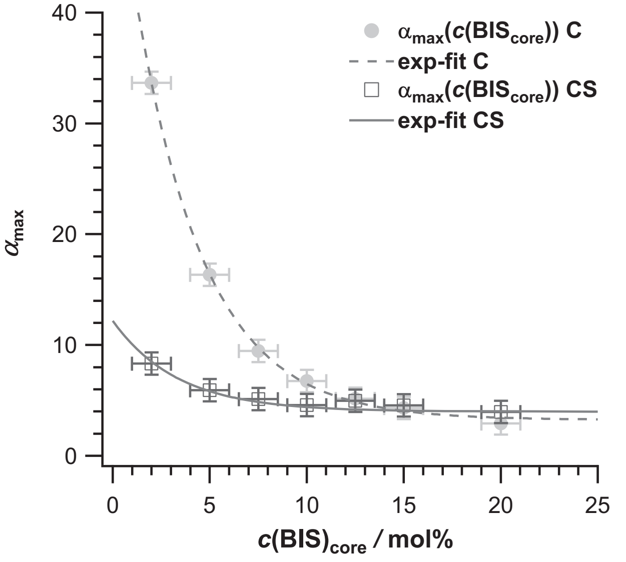

Fig. 5. Swelling capability of the microgels. Maximum swelling coefficient for differently cross-linked cores and the corresponding core–shell systems. The lines indicate equally weighted exponential fits.

mechanical response can be realized by simply changing the core crosslinker content.

In the present work the number of different crosslinker contents was sufficiently large to allow a more detailed analysis of the relationship between the maximum swelling ratio α_{max} and the crosslinker content. α_{max}, which is the maximum hydrodynamic volume normalized to the corresponding fully collapsed state, decreases with increasing BIS molar ratio (see Fig. 5). This decreasing maximum swelling capacity can be described by a single exponential decay and is accompanied by a broadened phase transition. Furthermore, the observed exponential trend can be also found for the corresponding core–shell particles. It is remarkable that the decay constant is identical within the standard deviation for the parameter sets of the core particles and the corresponding core–shell particles. The computed baseline parameters slightly deviate from each other. Only the amplitude is significantly different between both systems. In other words it can be stated that there is also a significant influence of the core crosslinker content on the swelling capability of the microgels. This trend is consistent for both types of particles, we conclude that the core determines the swelling behavior of the core–shell system.

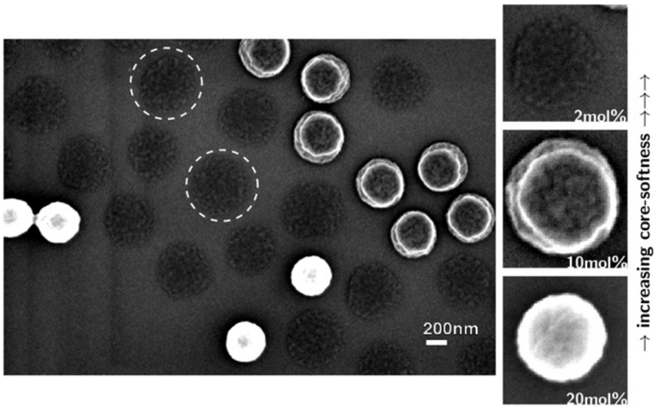

Fig. 6. Shape retention of dried particles. SEM-micrograph of a mixture of three core–shell particles with different core-crosslinker contents (2 mol%, 10 mol% and 20 mol% BIS) dried on a Si-wafer and sputtered with a 1.3 nm thick layer of Pt. The softness of the particles, which can be related to the brightness and contrast, is decreased for those systems that contain cores with larger amounts of crosslinker (scale bar: 200 nm). Additionally the morphology is significantly changed which can be also seen from the magnifications on the right side (no scale bar given). Hence, already in the dry state the interaction between core and shell is obvious.

Similar results can be found for dried mixtures of different core–shell particles which were studied using SEM (Fig. 6b). This method captures surface dependent properties and therefore the particles tend to have enhanced contrast the more crosslinker the cores contain. Upon drying, soft spheres (microgels with low crosslinker contents) exhibit a flat "pancake"-like structure where we obtain only low contrast and brightness levels relative to the substrate, whereas harder spheres retain their spherical shape having high contrast and brightness [36,37]. We were able to confirm these correlations by reference measurements of the individual particles on different substrates (see supplementary material Fig. S3). This already indicates the same trend as was shown for the light scattering results, where the core–shell system was significantly influenced by the core properties. Furthermore the drying patterns of the particles deviate significantly from each other. However, SEM only shows the differences in qualitative way.

4. Conclusion

In conclusion this study presents the synthesis of non-NIPAM based core–shell microgels. It was found that the combination of distinct monomers for core and shell leads to a new system class with extraordinary linear swelling properties. In our study, every single core–shell microgel exhibits a region of at least $\Delta T = 15\ ^\circ C$, where the hydrodynamic radius was linearly dependent on the temperature. This is a result of the enhanced "corset-effect" realized due to the use of two polymers with largely different LCST. Moreover, we demonstrate how differently cross-linked cores influence the overall core–shell swelling behavior in bulk solutions. In more detail, it was shown that the magnitude of the linear response may be tuned, again in a linear manner, over a wide range by simply changing the crosslinker content of the employed cores.

We like to point out that this system class is a very promising candidate for two types of applications. Since the transition of the shell material occurs around room temperature, the introduced core–shell microgels exhibit a dense shell at temperatures above 25 °C. This addresses to their usability as model systems, which can fill the gap between hard-spheres and fuzzy, soft colloids. Additionally, we think this system class is of immediate relevance with respect to actuator design in general, where a simple control and predictability of the responsive behavior is advantageous.

Future studies include small angle neutron scattering with the goal to determine the temperature dependent shell/core density- and size-ratio which are essential to verify our current understanding for the involved physical processes and to develop a suitable theoretical model.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2012.10.001.

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