Role of Anionic Surfactants in the Synthesis of Smart Microgels Based on Different Acrylamides

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ABSTRACT: We investigated the influence of two anionic surfactants, namely, sodium dodecyl sulfate and sodium decyl sulfate, on acrylamide-based microgels consisting of N-n-isopropylacrylamide. In this context, the main focus was on the influence of surfactant addition on the size of the microgels. The surfactant was added to the reaction mixture before or during the polymerization at different points in time. Microgels were characterized via photon correlation spectroscopy and atomic force microscopy. All results were compared to those for other non-NIPAM-based microgels. One of the most prominent anionic surfactants for microgel synthesis is SDS. The main aim of this study was the investigation of the influence of SDS on the synthesis of NnPAM microgels. Therefore, we synthesized NnPAM microgels in the presence of different amounts of SDS. Moreover, we also used sodium decyl sulfate (SDeS), aiming at scrutinizing changes in the obtained particle properties caused by the different lengths of the alkyl chain of the surfactant. The results for PnPnAM microgels are compared to the data for PNIPAM and PNIPMAM particles.

INTRODUCTION

Several acrylamide-based microgels exhibit changes in size triggered by external stimuli such as temperature and pH, for instance. This interesting behavior granted them the name smart microgels.1–5 Because of their stimulus response, they are considered in a lot of different applications, ranging from the biomedical field6–9 to photonics10–15 surface modification,16,17 and as nanoparticle containers18,19 or for drug uptake and release.20,21 More detailed information can be found in recent reviews.22–25

Especially, in the context of applications concerning optical properties of hybrid systems, it is important to control and tune the size of the microgels during the synthesis. A very distinguished example for this was given by Serpe et al. They described the design of etalons from gold-coated substrates.26 Additionally, tuning the particle size of acrylamide microgels broadens their scope of applicability.2 In 1993, Pelton et al. have shown how the size of the microgels based on poly(N-isopropylacrylamide) (PNIPAM) can be influenced by the addition of sodium dodecyl sulfate (SDS).27 For particles based on poly(N-isopropylmethacrylamide) (PNIPMAM), the influence of several surfactants on the size of the obtained colloidal microgels was studied by von Nessen et al.28 Recently, we started to study microgels based on the monomer N-n-propylacrylamide (NnPAM). This monomer yields microgels that show a very sharp and steep change in size upon changes in temperature30 and might therefore be used for making more precise sensors compared to those from the other mentioned systems. From a physical chemistry point of view, this steep change in size might indicate a discontinuous phase transition in these microgels. However, this issue will be addressed in a different work. Moreover, NnPAM can be copolymerized with NIPMAM, leading to a tunability of the phase transition temperature between 21 °C (lower critical solution temperature (LCST) of PNnPAM) and 44 °C (LCST of PNIPMAM).29 Because of these promising properties, it is of interest to achieve size control also in the synthesis of these non-NIPAM-based microgels. One of the most prominent anionic surfactants for microgel synthesis is SDS. The main aim of this study was the investigation of the influence of SDS on the synthesis of NnPAM microgels. Therefore, we synthesized NnPAM microgels in the presence of different amounts of SDS. Moreover, we also used sodium decyl sulfate (SDeS), aiming at scrutinizing changes in the obtained particle properties caused by the different lengths of the alkyl chain of the surfactant. The results for PnPnAM microgels are compared to the data for PNIPAM and PNIPMAM particles.

RESULTS AND DISCUSSION

Influence of Surfactant on the Particle Size. We used photon correlation spectroscopy to study the swelling behavior and the size of PnPnAM microgels prepared in the presence of increasing amounts of SDS between 0 and 2.08 mM. All SDS concentrations were far below the bulk critical micelle concentration (cmc) value of SDS.31 These results were subsequently compared to the behavior of PNIPAM and PNIPMAM microgels.

Figure 1 shows some exemplary swelling curves of the obtained PnPnAM microgels. These swelling curves are very similar to those of other responsive microgels,28,32 but in...
contrast, the transition is very steep and sharp. Especially, the PNnPAM microgels synthesized without surfactant show a very rapid change in the hydrodynamic radius. The broadening of phase transition for higher SDS concentrations could indicate a different cross-linker distribution. However, PNnPAM microgels might exhibit a discontinuous phase transition. Such a behavior is not yet observed in other microgels.

We observed a decrease in particle radius from 150 to 30 nm in the collapsed state (see Figure 2). The relation between PNnPAM particle size and surfactant concentration was similar to the results previously published for PNIPAM and PNIPMAM microgels, with a remarkably great difference in the reduction of the hydrodynamic radius. We synthesized PNIPAM and PNIPMAM microgels under identical conditions to compare the influence of SDS on the particle size in the collapsed state.

Whereas the radius of PNnPAM microgels decreased by around 81% upon addition of increasing amounts of SDS, the size reduction for PNIPAM microgels was 70%. The size reduction for PNIPMAM microgels was only about 53%. In addition, it should be noted that for SDS concentrations of 0.69 and 2.08 mM PNnPAM nanogels were obtained despite the fact that the “classical” Pelton synthesis was used and no functionalized comonomers were added.

We assume that the structural difference between the side chains of PNIPAM, PNIPMAM, and PNnPAM gives rise to a more pronounced influence of the surfactant on the stabilization of the precursor particles during an early stage of microgel formation. Due to the higher hydrophobicity of small PNnPAM oligomer chains compared to that of PNIPAM, the stabilization of the mentioned precursors starts at lower chain lengths of the oligomers. Therefore, the number of growing particles in the early stage of the process is probably substantially higher for PNnPAM compared to that for PNIPAM and PNIPMAM microgels. Consequently, the resulting particles are smaller. This assumption is confirmed when the influence of smaller amounts of surfactant is studied. The effect of SDS is modest for PNIPAM microgels at low concentrations, for example, 0.17 mM, whereas PNnPAM microgels become significantly smaller in the presence of 0.17 mM SDS.

Given the results for the influence of SDS on the hydrodynamic radius of PNnPAM microgels, we expected the same trend for the addition of SDeS to the microgel reaction mixture. The results are plotted in Figure 3. The influence of SDeS on the particle size was, taking the lower surface activity of SDeS into account, equal to the effect of SDS addition. The inferior surface activity of SDeS can be quantified by comparing the cmc of SDeS with that of SDS (33 vs 8.3 mM). It was not possible to normalize the particle size when the surfactant concentrations are divided by the cmc, though. The reason for this is that the addition of large amounts of SDeS, which lead to

Figure 1. Swelling curves of PNnPAM microgels synthesized in the presence of different SDS concentrations (squares, 0 mM; circles, 0.17 mM; triangles, 0.69 mM; and diamonds, 2.08 mM).

Figure 2. Hydrodynamic radius of fully collapsed PNIPMAM (squares), PNIPAM (circles), and PNnPAM (triangles) microgels as a function of SDS concentration present during the microgel synthesis. The hydrodynamic radius was measured and calculated via angle-dependent photon correlation spectroscopy.

Figure 3. Hydrodynamic radius of fully collapsed PNnPAM (circles) and PNIPAM (squares) particles as a function of surfactant concentration during the synthesis: SDS (filled symbols) and SDeS (hollow symbols).
particles comparable in size with the particles synthesized with the rather moderate SDS concentrations, causes a substantially higher ionic strength in the batch synthesis. This also influences the particle size, as it leads to a higher aggregation rate in the early synthesis phase. Therefore, we obtain smaller particles when SDS is used as a surfactant in emulsion polymerization.

**Influence of the Moment of Surfactant Addition.** Up to this point, the presented results focused on the influence of anionic surfactants on the formation and swelling behaviors if the surfactant is added before the initiation of polymerization. However, it is well known that the process of microgel formation has different steps. It is still under investigation at which stage of microgel formation the surfactant has the greatest influence. Two possibilities appear to be most likely. The first possibility is the stabilization of early precursor particles as mentioned above due to the surface activity of anionic surfactants. The second possibility is the action of a surfactant at a later stage of the reaction, where the surfactant molecules influence the interfacial tension between the growing microgel particles and the monomer solution and control the incorporation of monomer units and small oligomer chains. We investigated these phenomena by adding SDS during the synthesis of PNPnPAM at different times in point. As shown before, NnPAM has a polymerization velocity comparable to that of NIPAM. The particle formation seems to be finished after approximately 20 min. Therefore, we choose the following points in time for the addition of SDS during the synthesis: 15, 30, 60, 90, 120, 210, 300, and 900 s.

The resulting particle dispersions were investigated by angle-dependent photon correlation spectroscopy. The averaged relaxation rates, $\Gamma$, which were obtained for the eight different synthesis batches, are plotted versus the square of the magnitude of the scattering vector, $q$, in Figure 4. For a system with only one population of particles in solution, a linear dependence between $\Gamma$ and $q^2$ should be detected (see eq 2). Even for the sample in which SDS was added 15 s after initiation, a slight deviation from the expected linear dependence is observed. This effect increases for the following points in time, and the maximal deviation is reached when SDS is added 210 s after starting the polymerization. Hence, it is evident that the addition time of SDS has a drastic influence on the obtained results. Addition of SDS after 300 and 900 s seems to have a minor influence on the resulting particles compared to that at the previous points in time. We conclude that the influence of SDS during the aggregation phase in the early synthesis procedure is more important than the influence of the surface tension during the growth of the collapsed microgel particles.

The influence of SDS is very pronounced for the addition time points from 30 up to 210 s as during this period initiation and oligomer formation occur and precursor particles are formed. SDS stabilizes the oligomers to new precursor particles at lower chain lengths and also the precursor particles that were formed before the surfactant addition because of a high surface charge. Therefore, we expect two types of particles in the reaction mixture differing in size. A small particle species, representing the precursors that were formed after the addition of SDS at lower chain lengths, and a large particle species, representing the precursors that were formed before the SDS addition and were stabilized by SDS after their collapse. Concerning the time point of SDS addition, the fraction of the second particle species should be higher when the interval between initiation and SDS addition is increased. To verify this assumption, we used atomic force microscopy (AFM). As an example, Figure 5 shows the AFM height profiles for the representative addition times 60, 120, and 300 s. The obtained results confirm the idea that addition of SDS at different time points during the synthesis leads to the formation of two particle species, as we obtain two noticeably different particle sizes in the AFM images for the addition times of 60 and 120 s. The nucleation phase seems to have been completed early in the synthesis process, as there is only one species left in the AFM images of the PNPnPAM microparticles with an addition time of 300 s.

The data clearly reveal the importance of SDS addition during the nucleation process of the PNPnPAM microgel synthesis. The size distribution of the resulting particles is controlled by the time interval between initiation of the reaction and SDS addition. To investigate the influence of SDS on the secondary particle growth later during the synthesis process, we analyzed the size of the second particle species, which seems to be formed before SDS has a crucial influence on particle nucleation. The particle size of these microparticles was extracted from the height profiles of the AFM measurements and can be compared to the particle sizes obtained from an analogous surfactant-free synthesis. Figure 6 shows the results we obtained for SDS addition during the synthesis. Clearly, the interfacial tension of the growing particles plays an important role for the particle size as well. The particle size of PNPnPAM microparticles obtained upon addition of SDS is substantially smaller compared to that of the particles obtained by surfactant-free synthesis (solid line in Figure 6). After an addition time of 120 s, a plateau is reached. Even if the particle nucleation phase has been completed before the addition of

![Figure 4. Relaxation rates of PNPnPAM microgels against the square of the magnitude of the scattering vector. The microparticles synthesized with SDS addition to the proceeding reaction after the mentioned times.](Image 354x473 to 534x749)
SDS, the particle size is only about one-third of the size that the particles have when no SDS is added during the polymerization. A possible explanation for the limit in size might be the assembly of surfactant molecules on the microgel surface or in the microgel (see Supporting Information). The surface charge of the growing particles is increased, and small oligomer chains and monomers cannot be adsorbed onto the particles. Therefore, significant amounts of water-soluble, small polymers are produced as side products, by chain termination reactions. These small polymer chains were not found to precipitate during the reaction. The resulting water-soluble polymers can be analyzed during the purification process by a gravimetric determination of the mass of PNnPAM in the supernatant of the first centrifugation cycle. Compared to that in PNIPAM, in the reaction mixture of the PNnPAM particles a higher amount of water-soluble un-crosslinked polymer is present at the end of the synthesis. This is in accordance with the results we obtained for the volume phase transition temperature (VPTT) shift and the particle size because the interaction of surfactant molecules and microgel particles is stronger for PNnPAM. Consequently, the influence of SDS on the size of PNIPAM particles after the nucleation phase seems to be less pronounced or even does not exist.

To confirm our observations, we studied the influence of SDS and SDeS on the VPTT of premade microgels. The VPTT of the purified particles changes upon addition of anionic surfactant. These changes can be described by a master curve, which we obtained by normalization of VPTT data by the surfactant cmc (see Supporting Information).

Figure 5. AFM images of PNnPAM microgels synthesized with SDS addition after 60 s (top), 120 s (middle), and 300 s (bottom). Additionally, the respective height profiles of the measured particles (denoted z-value) are given as a function of the measured x direction. The images were recorded in tapping mode.
Figure 6. Particle size of PNNPAM microgels that were synthesized by adding SDS during the synthesis at the points in time given on the t axis. The particle sizes were obtained from AFM height profiles as shown in Figure 5.

■ EXPERIMENTAL SECTION

Materials. NIPAM (97%; Sigma-Aldrich, Munich, Germany) and NIPMAM (97%; Sigma-Aldrich Munich, Germany) were recrystallized from n-hexane. Acryloyl chloride (98%; Sigma-Aldrich Munich, Germany), n-propylamine (99%, Fluka; Buchs, Switzerland), triethylamine (99%; Grüssing, Filsam, Germany), dichloromethane (p.a.), ammonium persulfate (≥98%; Sigma-Aldrich Munich, Germany), N,N′-methylenebisacrylamide (99%; Sigma-Aldrich Munich, Germany), SDS (≥99%; Sigma-Aldrich Munich, Germany), and SDeS (≥99%; Sigma-Aldrich Munich, Germany) were used without purification. Water was purified using an Arium pro VF system (Satorius Stedim Systems GmbH, Göttingen, Germany). The synthesis of NnPAM was described elsewhere.39,40

Synthesis of Microgels. All microgels were synthesized via precipitation polymerization following the first published PNIPAM microgel synthesis.38 All syntheses were performed in a 250 mL three-neck flask equipped with a reflux condenser, a mechanical stirrer, and a nitrogen inlet. The respective monomers (total amount, 11.55 mmol) and the cross-linker (N,N′-methylenebisacrylamide (BIS), 0.6 mmol, 5.4 mol%) were dissolved in 150 mL purified water. After heating up to 70 °C, the solution was purged with nitrogen for 1 h. The respective surfactant was added 10 min before the initiation of polymerization. In the case of SDS, concentrations of 0, 0.17, 0.35, 0.69, 1.11, 1.68, and 2.08 mM were used. The employed SDeS concentrations in the synthesis were 1.11, 3.75, 7.5, and 12.5 mM. Furthermore, samples were prepared, in which SDS was added shortly after the initiation. The exact addition times were 15, 30, 60, 90, 120, 210, 300, and 900 s. After the initiation, the reaction mixture was stirred for 4 h at 70 °C, then cooled to room temperature, and stirred overnight.

The resulting microgels were cleaned by five consecutive centrifugation, decantation, and redispersion cycles using purified water. After the first centrifugation cycle, the supernatant of each synthesis batch was dried and the remaining mass was analyzed gravimetrically.

PCS Measurements. Particle sizes were determined using photon correlation spectroscopy applied to highly diluted samples (c ≤ 0.001 wt %).

Measurements of the particle size as a function of temperature were performed using a diode laser (wave length, $\lambda = 661.4$ nm; Toptica Photonics, Graefelfing, Germany) and an ALV-6010 multiple- r-digital correlator (ALV-GmbH, Langen, Germany). We used a scattering angle of 60° to avoid the observation of internal contributions. At higher scattering angles, one may also approach the form factor minimum, which is typically in the range of 90° for microgels. The scattered light was collected by a single-mode fiber connected to the photomultiplier tubes of an ALV detection unit, and the temperature was controlled by a thermostated decaline bath. At each temperature, the samples were allowed to equilibrate for 20 min.

The hydrodynamic radii in the collapsed state were determined via angle-dependent PCS measurements with an ALV goniometer setup using an argon ion laser ($\lambda = 514.5$ nm; Spectra Physics 2017, Darmstadt, Germany) operated with a constant output power and an ALV-5000/E multiple-r-digital correlator (ALV-GmbH, Langen, Germany). In all cases, the obtained time-correlation functions of the scattered intensity were converted into field correlation functions, $g^\prime(t)$, using the SIEGERT relation.

The different $g^\prime(t)$ curves were subsequently analyzed using inverse Laplace transformations by means of CONTIN.39 This is based on the following description of $g^\prime(t)$.

$$g^\prime(t) = \int G(\Gamma) \exp(-\Gamma t) d\Gamma$$ (1)

Hence, Laplace inversion yields the relaxation rate distribution $G(\Gamma)$ and average relaxation rate $\overline{\Gamma}$. The average relaxation rate, $\overline{\Gamma}$, can be plotted versus $\theta^2$, leading to a linear dependence with the translational diffusion coefficient as slope.

$$\overline{\Gamma} = D \cdot q^2$$ (2)

The magnitude of the scattering vector, $q$, can be described by

$$q = \frac{4\pi n}{\lambda} \sin \left( \frac{\theta}{2} \right)$$

with refractive index $n$ of the solvent and scattering angle $\theta$.

Deviations from the linear behavior might indicate additional dynamic contributions to the decay of $g^\prime(t)$ curves by several different particle species, rotation, or internal modes, for instance.41

AFM. AFM measurements were performed on a nanoscope III microscope (Digital Instruments, now Bruker, Karlsruhe, Germany) at room temperature in tapping mode. The cantilevers (Tap300 Al-G; Budget Sensors, Innovative Solutions Bulgaria Ltd., Sofia, Bulgaria) had a radius of ≤10 nm, a frequency of 300 kHz, and a spring constant of 40 N/m. For sample preparation, a silicon wafer (Siegert Wafer GmbH, Aachen, Germany) was coated with 50 μL of a diluted microgel suspension and dried at room temperature in the air.

■ CONCLUSIONS

This study shows the influence of anionic surfactants on the precipitation polymerization process of PNNPAM microgels. In the first part, we focused on the particle size. Good control of the PNNPAM particle size was achieved by changing the SDS or SDeS concentrations. At high amounts of surfactants, nanogels were obtained. The results were compared to the data obtained for homologous microgels based on PNIPAM and NIPMAM. We found that the influence of anionic surfactants on the formation of PNNPAM microgels is stronger than for PNIPAM and NIPMAM particles. This can be explained by the very strong interaction between the amphiphilic surfactant molecules and the PNNPAM particles. In the early reaction
phase, smaller particles with a substantially lower surface charge can be stabilized. In addition, there is a significant interaction between SDS and the growing particles during the secondary growth phase that limits the size of PNnPAM microgels. The difference between the n-propyl group and the isopropyl group in the side chains seems to have a crucial influence on the hydrophobicity of the resulting particles. Not only the chemical structure of the monomers but also the chain length of the anionic surfactant and hence the strength of surface activity play an important role in the interaction between the surfactant and the microgel during and after the synthesis.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00424.

Addition of SDS and SDeS to preemc microgels (PDF)

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Pelton, R. Temperature-sensitive aqueous microgels. Adv. Colloid Interface Sci. 2000, 85, 1–33.
(2) Nayak, S.; Lyon, L. A. Soft Nanotechnology with Soft Nanoparticles. Angew. Chem., Int. Ed. 2005, 44, 7686–7708.
(3) Saunders, B. Microgel particles as model colloids: Theory, properties and applications. Adv. Colloid Interface Sci. 1999, 80, 1–25.
(4) Imaz, A.; Forcada, J. N-vinylcaprolactam-based microgels: Synthesis and characterization. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 2510–2524.
(5) Fernández-Nieves, A.; Fernández-Barbero, A.; Vincent, B.; de las Nieves, F. J. Reversible Aggregation of Soft Particles. Langmuir 2001, 17, 1841–1846.
(6) Sigolaeva, L. V.; Gladyr, S. Y.; Gelissen, A. P. H.; Mergel, O.; Perguson, D. V.; Kurockin, I. N.; Plamper, F. A.; Richter, W. Dual-Stimuli-Sensitive Microgels as a Tool for Stimulated Spongelike Adsorption of Biomaterials for Biosensor Applications. Biomacromolecules 2014, 15, 3735–3745.
(7) Sung, B.; Kim, C.; Kim, M.-H. Biodegradable colloidal microgels with tunable thermosensitive volume phase transitions for controllable drug delivery. J. Colloid Interface Sci. 2015, 450, 26–33.
(8) Wang, H.; Helwa, Y.; Rempel, G. L. Preparation of polycrylamide based microgels with different charges for drug encapsulation. Eur. Polym. J. 2013, 49, 1479–1486.
(9) Uhlig, K.; Wegener, T.; He, J.; Zeiser, M.; Bookhold, J.; Dewald, I.; Godino, N.; Jaeger, M.; Hellweg, T.; Fery, A.; Duscht, C. Patterned Thermoresponsive Microgel Coatings for Noninvasive Processing of Adherent Cells. Biomacromolecules 2016, 17, 1110–1116.
(10) Contreras-Cáceres, R.; Sánchez-Iglesias, A.; Karg, M.; Pastoriza-Santos, I.; Pérez-Juste, J.; Pacifico, J.; Hellweg, T.; Fernández-Barbero, A.; Liz-Marzán, L. M. Encapsulation and Growth of Gold Nanoparticles in Thermoresponsive Microgels. Adv. Mater. 2008, 20, 1666–1670.
(11) Farooqi, Z. H.; Siddiq, M. Temperature-Responsive Poly(N-isopropylacrylamide-Acrylamide-Phenyboronic Acid) Microgels for Stabilization of Silver Nanoparticles. J. Dispersion Sci. Technol. 2015, 36, 423–429.
(12) Dulle, M.; Jaber, S.; Rosenfeldt, S.; Rudalescu, A.; Förster, S.; Mulvany, P.; Karg, M. Plasmonic gold–poly(N-isopropylacrylamide) core–shell colloids with homogeneous density profiles: A small angle scattering study. Phys. Chem. Chem. Phys. 2015, 17, 1354–1367.
(13) Karg, M.; Jaber, S.; Hellweg, T.; Mulvany, P. Surface plasmon spectroscopy of gold-poly-N-isopropylacrylamide core-shell particles. Langmuir 2011, 27, 820–827.
(14) Das, M.; Sanson, N.; Fava, D.; Kumacheva, E. Microgels loaded with gold nanorods: photothermally triggered volume transitions under physiological conditions. Langmuir 2007, 23, 196–201.
(15) Hantrischel, N.; Zhang, F.; Eckert, F.; Pich, A.; Winnik, M. A. Poly(N-vinylcaprolactam-co-glycidyl methacrylate) aqueous microgels labeled with fluorescent LaF3:Eu nanoparticles. Langmuir 2007, 23, 10793–10800.
(16) Wiedenair, J.; Serpe, M. J.; Kim, J.; Masson, J.-F.; Lyon, L. A.; Mizakoff, B.; Kranz, C. In-situ AFM studies of the phase-transition behavior of single thermoresponsive hydrogel particles. Langmuir 2007, 23, 130–137.
(17) Schmidt, S.; Hellweg, T.; von Klitzing, R. Packing density control in P(NIPAM-co-AAc) microgel monolayers: effect of surface charge, pH, and preparation technique. Langmuir 2008, 24, 12595–12602.
(18) Pich, A.; Lu, Y.; Boyko, V.; Richter, S.; Arndt, K.-F.; Adler, H.-J. P. Thermosensitive poly(N-vinylcaprolactam-co-acetoacetoxyethyl methacrylate) microgels. 3. Incorporation of polypyrrole by selective microgel swelling in ethanol–water mixtures. Polymer 2004, 45, 1079–1087.
(19) Pich, A.; Karak, A.; Lu, Y.; Ghosh, A. K.; Adler, H.-J. P. Preparation of Hybrid Microgels Functionalized by Silver Nanoparticles. Macromol. Rapid Commun. 2006, 27, 344–350.
(20) Bradley, M.; Vincent, B.; Burnett, G. Uptake and release of anionic surfactant into and from cationic core-shell microgel particles. Langmuir 2007, 23, 9237–9241.
(21) Bradley, M.; Vincent, P. Poly(vinylpyrridine) core/poly(N-isopropylacrylamide) shell microgel particles: their characterization and the uptake and release of an anionic surfactant. Langmuir 2008, 24, 2421–2425.
(22) Hertle, Y.; Hellweg, T. Thermoresponsive copolymer microgels. J. Mater. Chem. B 2013, 1, 5874.
(23) Pich, A.; Richtering, W. Microgels by Precipitation Polymerization: Synthesis, Characterization, and Functionalization. In Chemical Design of Responsive Microgels, 2010th ed.; Pich, A., Albrecht, K., Eds.; Springer-Verlag: Berlin, 2011; Vol. 234, pp 1–37.
(24) Wiedenair, J.; Richter, M.; Hellweg, T.; von Klitzing, R.; Hertle, Y. Responsive Microgels at Surfaces and Interfaces. Z. Phys. Chem. 2015, 229, 1225–1250.
(25) Richtering, W.; Saunders, B. R. Gel architectures and their complexity. Soft Matter 2014, 10, 3695.
(26) Sorrell, C. D.; Carter, M. C. D.; Serpe, M. J. Color Tunable Poly(N-isopropylacrylamide)-co-Acrylic Acid Microgel-Au Hybrid Assemblies. Adv. Funct. Mater. 2011, 21, 425–433.
(27) McPhee, W.; Tam, K. C.; Pelton, R. Poly(N-isopropylacrylamide) Latices Prepared with Sodium Dodecyl Sulfate. J. Colloid Interface Sci. 1993, 156, 24–30.
(28) von Nessen, K.; Karg, M.; Hellweg, T. Thermoresponsive poly-(N-isopropylmethacrylamide) microgels: Tailoring particle size by interfacial tension control. Polymer 2013, 54, 5499−5510.

(29) Wedel, B.; Zeiser, M.; Hellweg, T. Non NIPAM Based Smart Microgels: Systematic Variation of the Volume Phase Transition Temperature by Copolymerization. Z. Phys. Chem. 2012, 226, 737−748.

(30) Wedel, B.; Hertle, Y.; Wrede, O.; Bookhold, J.; Hellweg, T. Smart Homopolymer Microgels: Influence of the Monomer Structure on the Particle Properties. Polymers 2016, 8, 162.

(31) Mukerjee, P.; Mysels, K. J. Critical Micelle Concentrations of Aqueous Surfactant Systems; NBS Publications, 1971.

(32) Kratz, K.; Eimer, W. Swelling properties of colloidal poly(N-isopropylacrylamide) microgels in solution. Ber. Bunsen-Ges. Phys. Chem. 1998, 102, 848−854.

(33) Wu, X.; Pelton, R. H.; Hamielec, A. E.; Woods, D. R.; McPhee, W. The kinetics of poly(N-isopropylacrylamide) microgel latex formation. Colloid Polym. Sci. 1994, 272, 467−477.

(34) Wu, C.; Zhou, S. Effects of surfactants on the phase transition of poly(N-isopropylacrylamide) in water. J. Polym. Sci., Part B: Polym. Phys. 1996, 34, 1597−1604.

(35) Tam, K. C.; Ragaram, S.; Pelton, R. H. Interaction of Surfactants with Poly(N-isopropylacrylamide) Microgel Latexes. Langmuir 1994, 10, 418−422.

(36) Mears, S. J.; Deng, Y.; Cosgrove, T.; Pelton, R. Structure of Sodium Dodecyl Sulfate Bound to a Poly(NIPAM) Microgel Particle. Langmuir 1997, 13, 1901−1906.

(37) Hirano, T.; Nakamura, K.; Kamikubo, T.; Ishii, S.; Tani, K.; Mori, T.; Sato, T. Hydrogen-bond-assisted syndiotactic-specific radical polymerizations of N-alkylacrylamides: The effect of the N-substituents on the stereospecificities and unusual large hysteresis in the phase-transition behavior of aqueous solution of syndiotactic poly(N-n-propylacrylamide). J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 4575−4583.

(38) Pelton, R. H.; Chibante, P. Preparation of aqueous latices with N-isopropylacrylamide. Colloids Surf. 1986, 20, 247−256.

(39) Provencher, S. W. CONTIN: A general purpose constrained regularization program for inverting noisy linear algebraic and integral equations. Comput. Phys. Commun. 1982, 27, 229−242.

(40) Berne, B. J.; Pecora, R. Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics; Dover Publications: Newburyport, 2013.