Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 6829–6833 **6829**
DOI: 10.1021/ma100422e

Cononsolvency of Poly(*N*,*N*-diethylacrylamide) (PDEAAM) and Poly(*N*-isopropylacrylamide) (PNIPAM) Based Microgels in Water/Methanol Mixtures: Copolymer vs Core–Shell Microgel

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Received February 23, 2010; Revised Manuscript Received June 30, 2010

ABSTRACT: The cononsolvency effect on the swelling of different stimuli-sensitive microgels was investigated in water/methanol mixtures. Poly(*N*,*N*-diethylacrylamide) (PDEAAM) and poly(*N*-isopropylacrylamide) (PNIPAM) homopolymer microgels, a PDEAAM-core–PNIPAM-shell microgel, and a poly(*N*,*N*-diethylacrylamide-*co*-*N*-isopropylacrylamide) (P(DEAAM–NIPAM)) microgel have been synthesized. The core–shell and the copolymer microgel have similar compositions; the PDEAAM core of the PDEAAM-core–PNIPAM-shell particle contributes 80% to the total mass, and the copolymer consists of 75% DEAAM and 25% PNIPAM. They were characterized with dynamic light scattering (DLS) and small-angle neutron scattering (SANS). Microgels containing PNIPAM show the cononsolvency effect, and the particle size reaches a minimum at a methanol fraction of $x_{\mathrm{methanol}} = 0.2$. Moreover, in core–shell microgels, the cononsolvency effect can be limited to one compartment of the particle. A core–shell microgel with a PDEAAM core and PNIPAM shell reveals a sharp surface at $x_{\mathrm{methanol}} = 0.2$; i.e., the PNIPAM shell is collapsed, and the PDEAAM core is swollen in the solvent mixture. The results demonstrate how responsive swelling properties of such polymers in solvent mixtures can be tuned via microgel morphology. Core–shell microgels provide new opportunities for encapsulation of guest molecules.

Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) and poly(*N*,*N*-diethylacrylamide) (PEDAAM) microgels are known to be temperature sensitive and have been analyzed widely in recent years.[1,2] The sensitivity is related to interactions of the polymer with the solvent. Especially H-bonds play an important role in hydrophobic and hydrophilic interactions in the polymer–solvent system. Temperature sensitivity is due to a weakening of the intermolecular polymer–solvent hydrogen bonds upon heating the solution. The polymer–solvent interaction dominates below the volume phase transition temperature (VPTT); therefore, polymers are solvated and microgels are strongly swollen. Under these conditions the solvent acts as a good solvent. Upon heating the solution the hydrogen bonds between the polymer and the solvent become weaker; above the VPTT the intramolecular polymer–polymer interactions are dominant, and microgels collapse. The properties render such polymers a simplified model system for the cold and pressure denaturation of proteins.[3−6]

Copolymer microgels have been investigated as well; however, few studies involve nonionic comonomers where the interaction is not dominated by electrostatic interaction.[7,8] P(DEAAM–NIPAM) copolymer microgels were first synthesized and analyzed by Keerl and Richtering[9] and reveal an outstanding VPTT behavior. The VPTT of these nonionic copolymers displays a nonideal dependence on composition and can be even lower than the VPTT of the pure components. A minimal VPTT of 20 °C was found for copolymers with a nearly equimolar PDEAAM/PNIPAM ratio. The depression of the VPTT is caused by a strong increase of intramolecular hydrogen bonds in the copolymer. NIPAM has a secondary amide group and thus is able to act as a hydrogen bond donor and acceptor; in contrast, DEAAM has a tertiary amide group which can only act as hydrogen bond acceptor. NMR measurements show that NIPAM and DEAAM are statistically distributed along the polymeric chain. Therefore, a NIPAM unit can build strong hydrogen bonding with a DEAAM unit in close proximity.[9−11]

Core–shell microgels of stimuli-responsive polymers have been prepared, and the mutual influence of core and shell on their respective swelling leads to special behaviors that can e.g. be detected by scattering methods and calorimetry.[12−18] A core–shell microgel synthesized with the same monomers as a copolymer will display different properties due to the spatial separation of the repeating units inside a microgel particle. For example, a PDEAAM-core–PNIPAM-shell system does not reveal a VPTT depression like the corresponding copolymer does. In core–shell systems, the different repeating units are locally separated in the core and the shell, respectively, and hence intramolecular H-bonding between the different units in shell and core is unlikely. However, the connected networks of core and shell can influence each other by mechanical forces leading e.g. to shell restricted swelling.

The collapse of a microgel can be induced not only by temperature but also by the composition of the solvent. For example, methanol and water are both good solvents for PNIPAM, but certain mixtures of both are bad solvents for the same polymer. This effect is named cononsolvency. Cononsolvency was found not only in water/methanol mixtures but also in other water/organic solvent mixtures.

There are numerous publications about the cononsolvency of linear PNIPAM,[19−27] which shows a strong cononsolvency effect in several water/solvent mixtures. Also, some publications about linear PDEAAM[28,29] and copolymers of PNIPAM and a second

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monomer[29] were published in the recent years. For other thermosensitive polymers the cononsolvency effect was also described.[30] However, there are only few reports on cononsolvency of PNIPAM and PNIPAM–copolymer microgels.[31-33] To the best of our knowledge, there are no reports on cononsolvency of either PDEAAM or core–shell microgels. Moreover, cononsolvency of microgels has, to the best of our knowledge, never been studied with SANS experiments before.

Recently, linear PDEAAM and linear P(DEAAM–NIPAM) copolymers were analyzed in different water/methanol mixtures by Maeda and Yamabe.[29] They found that the cloud point temperature (T_{cp}) of copolymers with a PNIPAM content more than 20% is reduced in certain water/methanol mixtures; for PDEAAM-rich copolymers and PDEAAM they found an increase in T_{cp} with higher methanol content. The origin of cononsolvency has been discussed considering various possible contributions.[22,23,30] It was e.g. proposed that the polymer collapse can be attributed to the formation of water/methanol complexes.[22] In addition, specific solvation effects might be relevant: In water-rich solvents, the polymer is solvated by the interaction with water molecules and polymer–solvent interactions dominate. When methanol is added, water can build clathrate-like structures with methanol because solvent–solvent interactions are favored; this will lead to a decrease of water molecules at the polymer and as a consequence to a less solvated polymer. At a certain methanol fraction all water (previously solvating the polymer) is bound in structures with the methanol. This leads to a reduced solvatization of the polymer with water, and therefore polymer–polymer interactions become dominant. In the case of a PNIPAM microgel this causes a collapse of the microgel particle. Adding further methanol leads to a reswelling when the polymer is solvated by excess of methanol.[23,32]

Furthermore, the influence of cooperativity involved with competitive hydrogen bonding between the polymer and the two solvents has been discussed recently.[24]

In this contribution we analyzed the behavior of PNIPAM, PDEAAM, a PDEAAM-core–PNIPAM-shell microgel, and a P(DEAAM–NIPAM) copolymer microgel with similar monomer content as the core–shell particle in different water/methanol mixtures. The swelling properties were investigated by means of dynamic light scattering and small-angle neutron scattering. Microgel systems are distinctly different from linear macromolecules as microgels are colloidally stable even in the collapsed state. In addition, as already mentioned above, microgels provide the opportunity of compartmentalization, i.e., a spatial separation of different repeating units inside the particles, and e.g. copolymers and core–shell microgels with the same total composition but different internal structure—and thus different properties—can be prepared. Investigating the cononsolvency effect with copolymer microgels provides new insights into the hydrophobic and hydrophilic interactions in such polymers that are also of interest for controlled uptake and release.

Experimental Section

Materials. *N*-Isopropylacrylamide (NIPAM), *N,N*-methylenebis(acrylamide) (BIS), sodium dodecyl sulfate (SDS), and potassium peroxodisulfate (KPS) were obtained from Sigma-Aldrich. *N,N*-Diethylacrylamide (DEAAM) was procured from Polysciences Germany. Deuterium oxide and methanol-d_4 were purchased from Deutero, Germany. Methanol was purchased from VWR. Doubly distilled Milli-Q water was used during the synthesis and for the preparation of the DLS samples. All materials were used as received.

Microgel Synthesis. Synthesis details were described previously.[9] The synthesis of the homo- and copolymer microgels was carried out in a 500 mL round-bottomed flask in a N_2 atmosphere under constant stirring at a temperature of 80 °C. A total monomer feed of 25 mmol of monomer was dissolved in 125 mL of doubly distilled water. 5 mol % *N,N*′-methylenebis(acrylamide) (BIS) as cross-linker and 1.7 mol % sodium dodecyl sulfate (SDS) as emulsifier were added. After degassing the mixture for 1 h with nitrogen the mixture was heated under stirring. The reaction was started with 1 mol % potassium peroxide sulfate (KPS) and proceeded for 6 h at 80 °C under constant nitrogen flow and stirring. The contents of the two repeating units in the copolymer microgel were determined with ^{13}C NMR by comparing the integrals of the isopropyl groups (NIPAM) and the ethyl groups (DEAAM). The contents in the microgel hardly differ from the contents in the feed.

The core–shell microgel was synthesized via a two-step process with the above-described procedure.[14] The core was synthesized as described above; after thoroughly cleaning with centrifugation the core solution was diluted with doubly distilled Milli-Q water. The core was stabilized in water with a small amount of SDS, and the shell synthesis was carried out as described above. The PDEAAM core contributes 80% and the PNIPAM shell 20% to the total mass of the core–shell particles as was confirmed by NMR. All microgels were cleaned by three cycles of centrifugation and redispersion in doubly distilled Milli-Q water.

Dynamic Light Scattering (DLS). To prevent multiple scattering, highly diluted solutions were prepared and were filtered through a 0.8 μm filter to remove dust. The time-dependent intensity was measured with an ALV-5000 goniometer at a laser wavelength of 633 nm. The measurements were taken at three different angles (45°, 60°, and 90°) at 10 °C. Viscosities and refractive indices of the solvent mixtures were taken from the literature.[34] Diffusion coefficients were calculated from the second-order cumulant, and the hydrodynamic radii were calculated with the Stokes–Einstein equation. The size change is fully reversible for all microgels, which was checked with a temperature-dependent measurement in water.

Small-Angle Neutron Scattering (SANS). Dispersions of 0.2 wt % polymer microgel in deuterium oxide, methanol-d_4, and deuterium oxide/methanol-d_4 mixtures with methanol-d_4 fractions of $x_{\text{methanol-}d_4} = 0.2, 0.35$, and 0.5 were measured at the instrument D11 at ILL in Grenoble, France. The wavelength was 0.6 nm, and the temperature was 12 °C. The scattering curve was calculated from intensities measured at detector distances of 1.2, 8, 20, and 39 m. The magnitude of scattering vector is given by $q = 4\pi \sin(\theta)/\lambda$, where 2θ is the scattering angle and λ is the neutron wavelength. Data were corrected for background scattering and calibrated on an absolute scale by incoherent water scattering according to the standard procedures at the ILL.[35]

Results and Discussion

Dynamic Light Scattering (DLS). Figure 1 displays results from DLS. The relative hydrodynamic radius R_h^* is plotted vs solvent composition for the different microgels. To determine the change in the hydrodynamic radii of the different microgels, the ratios

$$R_h^* = \frac{R_{\text{h-mixture}}}{R_{\text{h-water}}}$$

were calculated. In Table 1 the hydrodynamic radii (R_h) of the polymer microgels in water at 10 and 45 °C and in methanol at 10 °C are summarized.

The two homopolymer microgels show a very different behavior: the swelling of PNIPAM microgel is strongly affected by the content of methanol in the solvent mixture as has been reported previously.[32,33] However, PDEAAM is nearly insensitive to the solvent composition. Obviously, the different substitution pattern of the amide group influences the competitive hydrogen bonding between polymer and solvent molecules tremendously.

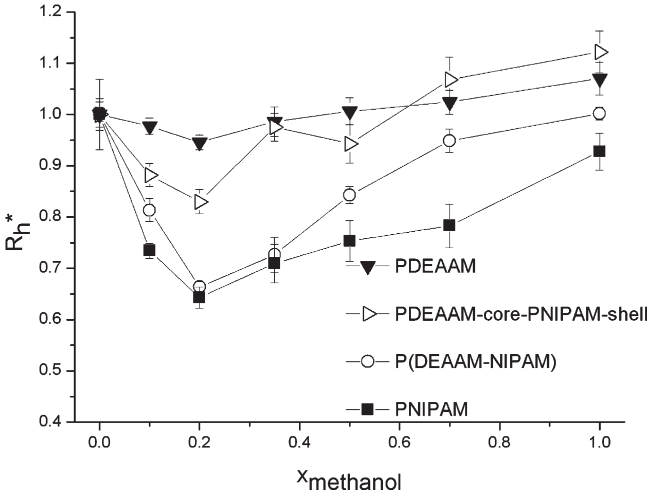

Figure 1. DLS measurements: relative radii of PNIPAM, PDEAAM, a P(DEAAM−NIPAM) copolymer, and a PDEAAM-core−PNIPAM-shell microgel in different water/methanol mixtures.

Table 1. Hydrodynamic Radii of the Microgels in Water below and above Their VPTT and in Methanol

	R_h/nm		
	water, 10 °C	methanol, 10 °C	water, 45 °C
PNIPAM	71	72	33
PDEAAM	87	93	39
P(DEAAM−NIPAM)	154	143	82
PDEAAM-core−PNIPAM-shell	229	252	117

The PDEAAM-core−PNIPAM-shell microgel (core contributing 80% of the total microgel mass, shell 20% mass fraction) is also sensitive to the solvent composition; however, the effect is smaller as compared to the copolymer microgel with similar total composition.

Obviously, PDEAAM is nearly insensitive to the solvent composition and different than PNIPAM; the size of the PDEAAM microgel in methanol is bigger than in water. Apparently, methanol is a better solvent for PDEAAM than water, and this strongly reduces the cononsolvency effect.

Small-Angle Neutron Scattering (SANS). A collapse of the particles as a function of the solvent composition could also be determined by SANS. The scattering intensity was measured over a broad range of momentum transfer q and analyzed with a form factor model developed previously.[36] This model takes into account the inhomogeneous cross-link density of such microgels and provides information on the microgel size and the smooth decay of the segment density at the microgel surface. In this model the microgels are described by a central region with homogeneous density; this "core" has a dimension of $R_{box} = R - 2\sigma_{Surf.}$. Up to this radius the cross-link density profile of the microgel can be described with a box model. The decrease of the cross-link density near the microgel surface is described with σ_{Surf}. At a radius of R the profile has decreased to the half of the core density, and the profile approaches zero at $R_{SANS} = R + 2\sigma_{Surf}$, which thus can be described as the total size of the particle. R_{SANS} is in general smaller as compared to the hydrodynamic radius R_h as SANS is less sensitive to dangling chains as compared to DLS.

For a better comparison of the different microgels, the solvent-dependent change of the size is described by the ratio

$$R^*_{SANS} = \frac{R_{SANS\text{-}mixture}}{R_{SANS\text{-}D_2O}}$$

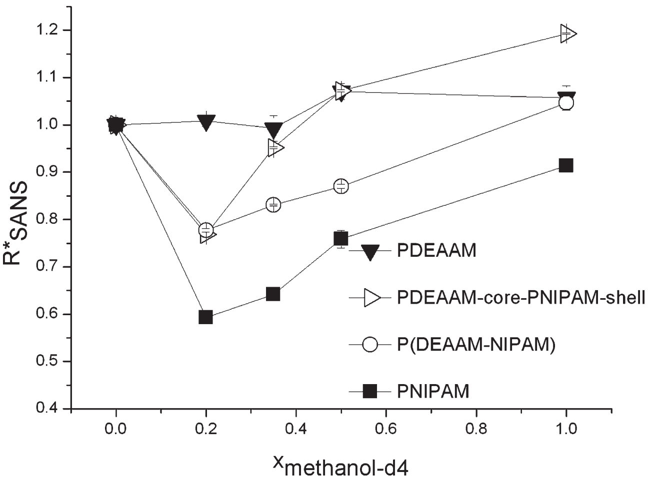

Figure 2. Relative radii R^*_{SANS} of PNIPAM, PDEAAM, a P(DEAAM−NIPAM) copolymer, and the PDEAAM-core−PNIPAM-shell particle in different deuterium oxide/methanol-d_4 mixtures.

The change of the relative radii R^*_{SANS} is pictured in Figure 2, and the results are in good agreement with the DLS data. The cononsolvency effect is strongest at a methanol mole fraction of $x_{methanol\text{-}d_4} = 0.2$ for all microgels including the core−shell microgel and PNIPAM. Again, PDEAAM shows a different behavior.

In Figure 3 the scattering curves for the homopolymers in the pure solvents deuterium oxide and methanol-d_4 are shown. The scattering curves for PNIPAM are very similar over wide q range, which means that the particle has similar size and structure in deuterium oxide and methanol-d_4. However, the scattering curves for PDEAAM differ slightly, which displays different sizes for the PDEAAM particle in the two pure solvents. It was observed that the radius R_{SANS} of the PDEAAM particle in methanol-d_4 is slightly bigger than in deuterium oxide, which was also visible in DLS (see Figure 2).

The lines in Figures 3 and 4 display the fit of the form factor model described above[36] to the experimental data, and a very good agreement is observed. The fit results are summarized in Table 2. For almost all microgels the value of σ_{surf} shows a similar dependency on the solvent composition as the radius R_{SANS}. It has a minimum at $x_{methanol\text{-}d_4} = 0.2$, and the value of σ_{surf} is very small, indicating that the surface chains are collapsed and the microgel has the structure of a sphere with homogeneous density profile. However, PDEAAM is the sole exception: its radius R_{SANS} and σ_{surf} hardly change with the methanol content. The σ_{surf} values in deuterium oxide and methanol-d_4 are similar, but the radius R_{SANS} in methanol-d_4 is slightly higher, indicating the methanol-d_4 as the better solvent.

Figure 4 shows normalized SANS data of PNIPAM, PDEAAM, P(DEAAM−NIPAM) copolymer, and the PDEAAM-core−PNIPAM-shell microgel in a deuterium oxide/methanol-d_4 mixture with a methanol fraction of $x_{methanol\text{-}d_4} = 0.2$. The curve of the PDEAAM is typical of a swollen microgel, whereas the PNIPAM and copolymer samples reveal scattering curves of collapsed microgels. In contrast to the PDEAAM curve, the PNIPAM and the copolymer curve in Figure 4 have more distinct minima. The minima of the scattering curve of the PDEAAM-core−PNIPAM-shell particle are less pronounced. The radii R_{SANS} and the value of σ_{surf} are the smallest at a methanol-d_4 fraction of $x = 0.2$ for PNIPAM and the copolymer, but this is not the case for PDEAAM. The P(DEAAM−NIPAM) copolymer and the

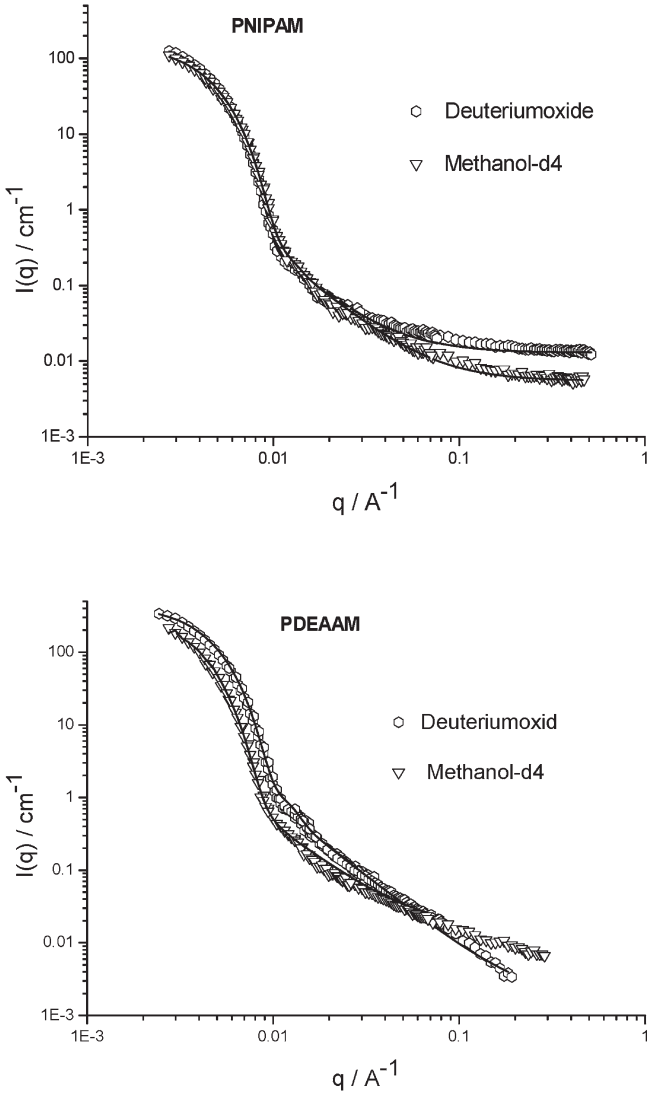

Figure 3. SANS data for the homopolymers in pure deuterium oxide and in pure methanol-d_4 at 12 °C.

PDEAAM-core–PNIPAM-shell particle have a similar total composition but different internal structure, which is already observable in the different scattering curves.

The SANS data analysis for the P(DEAAM–PNIPAM) copolymer clearly shows that the microgel deswells in deuterium oxide/methanol-d_4 mixtures as compared to the pure solvents. However, the value of σ_{surf} in the solvent mixture with $x_{\text{methanol-}d_4} = 0.2$ is still rather high, indicating that the microgel is not collapsed and still has a fuzzy surface with dangling chains.

The scattering curve of the core–shell microgel was fitted with two different form factor models, namely, the above-mentioned standard model for microgels with a fuzzy corona[36] and with a model for core–shell microgels.[18] The two fits hardly differ (data not shown); apparently, the PNIPAM-shell is too thin in order to lead a core–shell structure that can be detected by SANS. Nevertheless, the analysis of the scattering curve provides important information on the structure of the PDEAAM-core–PNIPAM-shell microgel. A value of $\sigma_{\mathrm{surf}} = 3.6$ nm was obtained at $x_{\text{methanol-}d_4} = 0.2$ and $x_{\text{methanol-}d_4} = 0.35$. Thus, the density profile decays rather steeply, indicating that the small PNIPAM shell is collapsed as it would be expected from the behavior of pure PNIPAM. The relative variation of R with solvent composition is smaller than for σ_{surf}, which further indicates that the PDEAAM core is in the swollen state.

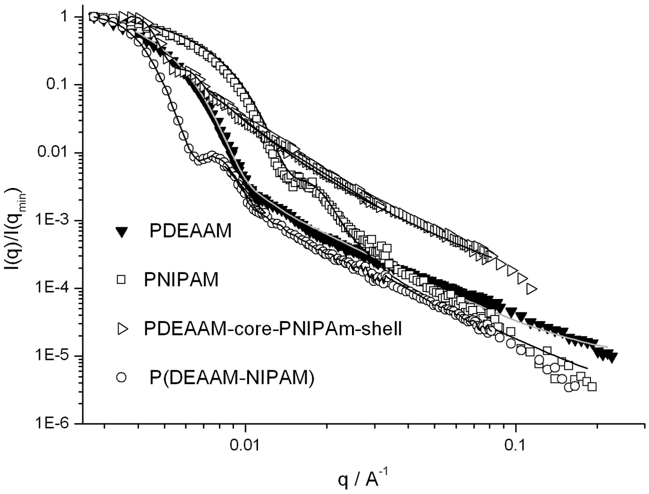

Figure 4. SANS data of PNIPAM, PDEAAM, P(DEAAM–NIPAM) copolymer, and the PDEAAM-core–PNIPAM-shell microgel in methanol-d_4/deuterium oxide mixture with $x = 0.2$ methanol-d_4 fraction at 12 °C.

Table 2. Fit Results for the Microgels in Different Solvents and Solvent Mixtures at 12 °C

	R [nm]	σ_{surf} [nm]	R_{SANS} [nm]	R^*_{SANS}
PNIPAM				
deuterium oxide	38.9	15.4	69.7	1
$x_{\text{methanol-}d_4} = 0.2$	29.8	5.7	41.3	0.59
$x_{\text{methanol-}d_4} = 0.35$	32.7	6	44.7	0.64
$x_{\text{methanol-}d_4} = 0.5$	35.3	8.8	52.9	0.76
methanol-d_4	36.3	13.7	63.7	0.91
PDEAAM				
deuterium oxide	40	14.1	68.2	1
$x_{\text{methanol-}d_4} = 0.2$	38.8	15	68.8	1.01
$x_{\text{methanol-}d_4} = 0.35$	43.4	12.1	67.7	0.99
$x_{\text{methanol-}d_4} = 0.5$	43.8	14.6	73	1.07
methanol-d_4	43.5	14.3	72.1	1.06
P(DEAAM–NIPAM) (copolymer)				
deuterium oxide	80	17	114	1
$x_{\text{methanol-}d_4} = 0.2$	67.2	10.2	87.6	0.77
$x_{\text{methanol-}d_4} = 0.35$	77.5	15.5	108.5	0.95
$x_{\text{methanol-}d_4} = 0.5$	84.2	19	122.2	1.07
methanol-d_4	89.2	23.4	136	1.19
PDEAAM-core–PNIPAM-shell (microgel)				
deuterium oxide	158.5	15.4	189.3	1
$x_{\text{methanol-}d_4} = 0.2$	140	3.6	147.2	0.78
$x_{\text{methanol-}d_4} = 0.35$	150	3.6	157.2	0.83
$x_{\text{methanol-}d_4} = 0.5$	152.5	6.1	164.7	0.87
methanol-d_4	157.4	20.4	198.2	1.05

The different behavior of the core–shell microgel as compared to the corresponding copolymer can also be seen when the size at $x_{\text{methanol-}d_4} = 0.2$ is compared with collapsed state in water at 45 °C. The data in Table 1 show that all microgels give a ratio of $R_{\mathrm{h}}(45\ ^{\circ}\mathrm{C})/R_{\mathrm{h}}(10\ ^{\circ}\mathrm{C}) \approx 0.5$; i.e., microgels deswell to half of their size when the collapse is induced by temperature. For the core–shell microgel $R^*_{\mathrm{h}} = 0.83$ was found at $x_{\text{methanol-}d_4} = 0.2$, whereas $R^*_{\mathrm{h}} = 0.65$ was obtained for the P(DEAAM–NIPAM) copolymer. Thus, from DLS and SANS one can conclude that the core–shell microgel has a swollen PDEAAM core and a collapsed PNIPAM shell at $x_{\text{methanol-}d_4} = 0.2$.

The DLS and the SANS data show that PNIPAM and the P(DEAAM−NIPAM) copolymer are sensitive to the composition of the solvent, while PDEAAM reveals hardly not a cononsolvency effect. The influence of solvent composition on microgel size was measured by DLS and SANS; both techniques show a minimum in size for a methanol fraction of $x_{\text{methanol}} = 0.2$, in agreement with literature reports on PNIPAM.[22−24,32,33] Further increase of the methanol fraction leads to reswelling of the particle. The form factor analysis of the SANS data provides additional information on the structure, especially of the microgel surface, as shown in Figures 3 and 4. The sharper the minimum of a scattering curve, the less fuzzy is the surface of the microgel.

For all microgels a change of the radii R_{SANS} with the change of the methanol content in the solvent mixture can be observed. The different behavior of the un-cross-linked PDEAAM homopolymer in water/methanol mixtures as compared to PNIPAM was discussed by Maeda and Yamabe[29] in terms of (i) the different hydrogen-bonding pattern of secondary and tertiary amides and (ii) the solvation of the alkyl groups. For PDEAAM a balance of two opposing effects, namely a destabilization of the polymer solution when water in the H-bond C=O···H−O−H is replaced by methanol and a stabilization due to a favorable solvation of the alkyl groups by methanol as compared to H_2O, leads to a reduction of hydrophobic interaction.

The different architecture of microgels as compared to linear macromolecules provides further opportunities to modify the solution behavior. Cross-linking constrains chain conformations, and the radial variation of cross-link density inside the microgel leads to a particle morphology with a fuzzy surface. SANS can be used to probe the different swelling properties of the cross-linked inner part and the corona.

Most important is the possibility to prepare core−shell microgels. Our results show that the cononsolvency effect can be limited to one compartment in PDEAAM-core−PNIPAM-shell microgels, which provides new opportunities for encapsulation of guest molecules.

Conclusions

PDEAAM and PNIPAM homopolymer, a P(DEAAM−NIPAM) copolymer, and a PDEAAM-core−PNIPAM-shell microgels were synthesized and investigated by means of DLS in different water/methanol and SANS in different deuterium oxide/methanol-d_4 mixtures. All PNIPAM-containing microgels display the cononsolvency effect. The particle size reaches a minimum at a methanol fraction of $x_{\text{methanol}} = 0.2$ according to SANS and DLS. The PDEAAM microgel hardly shows a cononsolvency effect while pure PNIPAM shows a strong effect.

The cononsolvency effect can be limited to one region in a PDEAAM-core−PNIPAM-shell microgel. SANS data show that this core−shell microgel reveals a sharp surface at $x_{\text{methanol}} = 0.2$; i.e., the PNIPAM shell is collapsed, and the PDEAAM core is swollen in the solvent mixture. The results demonstrate how responsive swelling properties of such polymers in solvent mixtures can be tuned via copolymerization and microgel morphology.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for financial support and Ralf Schweins, ILL, for his help during the SANS experiments.

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