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Temperature Sensitive Copolymer Microgels with Nanophase Separated Structure

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Abstract: Small-angle neutron scattering data from a thermosensitive copolymer microgel consisting of *N*-isopropylacrylamide (PNIPAM) and *N*-isopropyl*meth*acrylamide (PNIPMAM regions) were analyzed using a new form factor model. The neutron scattering data display an exceptional shape of the scattering curve at the transition temperature of the microgel indicating an additional characteristic length scale inside the microgel. A new form factor model with a nanophase separated internal morphology was derived which describes the experimental scattering very well. At the transition temperature of the copolymer, which is in between the transition temperatures of the two components, the copolymer microgel particles consist of collapsed PNIPAM domains and swollen PNIPMAM regions. The results demonstrate that a one-pot synthesis can lead to a highly sophisticated material with phase separated domains on a microscopic length scale.

Introduction

"Smart", i.e., stimuli-responsive microgels have found useful applications in different areas such as coatings, medicine, carrier materials for drugs, enzymes, and catalysts.[1−5] The most intensively studied thermosensitive system is poly-*N*-isopropylacrylamide (PNIPAM) that exhibits a volume phase transition temperature (VPTT) of 32 °C in water.[6] The responsive characteristics can be modified by either copolymerization[7] or advanced polymer architecture; especially core−shell microgels have been investigated recently.[8−12] Because of the chemical versatility and physical properties of PNIPAM-based microgels, particle design has continued to attract attention for potential applications and thus the accurate determination of the structure of microgel particles is required to improve their usage in areas where precise structural manipulation is needed.[13−18]

Scattering experiments can provide detailed information on the structure of the entire microgel.[19−21] Two different form factor models are well established for describing microgels with an inhomogeneous segment density according to the reaction parameters and microgels with a core−shell structure. The internal structure is closely connected to the synthesis conditions.[22,23]

A common way to prepare microgels is the so-called precipitating microgel polymerization which is in detail described by Pelton.[6] In contrast to one-pot syntheses normally used for the preparation of homopolymer or copolymer microgels, microgels with core−shell architecture are synthesized in a two-step synthesis where first a cross-linked core is synthesized and cleaned and then a cross-linked shell is polymerized on top of the core-microgel. By means of small-angle neutron scattering (SANS), it was, e.g., possible to correlate the microgel structure with the reaction parameters and the mutual influence of core and shell swelling.[10,23]

In this contribution we present SANS results on a copolymer system consisting of nearly equimolar amounts of *N*-isopropyl-

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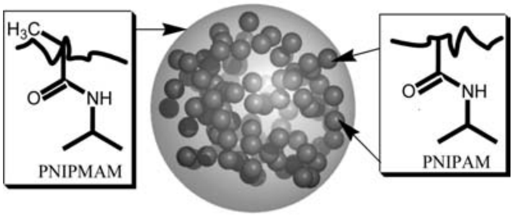
Scheme 1. Schematic Drawing of the Internal Nanophase Separated "Dirty Snowball" Structure at the Transition Temperature of the PNIPMAM−PNIPAM−Microgel[a]



[a] The fuzziness of the microgel particles is not illustrated. The parameters $R_{large} = 100$ nm, $R_{small} = 10$ nm, and $n = 100$ small particles are in agreement with the fit results. The scheme allows a transparent three-dimensional view into the proposed structure, illustrated with the fading gray color of the continuous phase. The dark gray nanophases are located randomly inside the continuous phase.

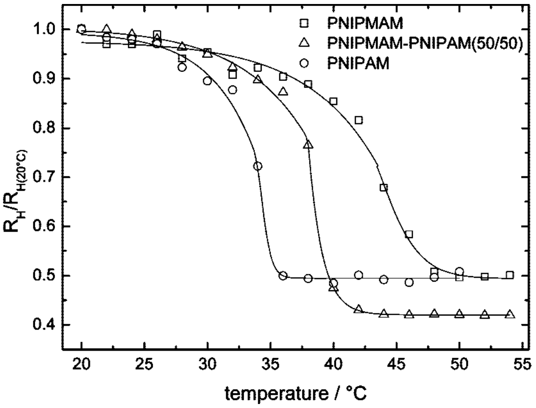


Figure 1. Temperature dependence of the size of two homopolymers PNIPMAM and PNIPAM and the copolymer microgel PNIPMAM−PNIPAM(50/50). Hydrodynamic radii are normalized to the radii at 20 °C in D_2O. Lines are used as guide to the eye.

*meth*acrylamide and *N*-isopropylacrylamide (named as PNIPMAM−PNIPAM(50/50)). This one-pot synthesis with two chemically similar monomers (differing only in the additional α-methylgroup of the backbone of the NIPMAM compound) results in an unexpected internal microgel structure which could be best described by a new form factor for particles with a nanophase separated internal morphology. Particles which consist of several domains with different densities as schematically illustrated in Scheme 1 are sometimes termed as "dirty snowball".

Experimental Section

N-Isopropylmethacrylamid (NIPMAM: Aldrich), *N*-isopropylacrylamide (NIPAM: Acros Organics), sodium dodecyl sulfate (SDS: Fluka), potassium peroxodisulphate (KPS: Merck KGaA), and cross-linker *N*,*N'*-methylenebisacrylamide (BIS: Merck KGaA) were used as received. Water for all purposes was bidistilled Milli-Q water.

The cross-linked copolymer microgel was synthesized via free radical dispersion polymerization. In brief, the synthesis was performed in a 250 mL vessel equipped with a mechanical stirrer, thermometer, a reflux condenser, and a nitrogen inlet. The two monomers (1.965 g NIPAM and 2.208 g NIPMAM), 0.075 g BIS, and 0.075 g SDS were dissolved in 150 mL of water at 75 °C and purged with nitrogen at least for 1 h. Polymerization was initiated by adding 0.15 g of KPS (dissolved in 10 mL degassed water at room temperature) and added to the monomer mixture. Polymerization was carried out for 6 h at 75 °C, a constant gas stream, and constant stirring of 330 rpm. The reaction mixture was allowed to reach room temperature under stirring overnight. The dispersion was filtered through glass wool and was purified three times by repeated ultracentrifugation (30 min, 50 000 rpm) and decantation of the supernatant, and the precipitate was redispersed in bidistilled water. A Sorvall Discovery 90SE ultracentrifuge with a T865 rotor was used for the centrifugation at 20 °C.

Dynamic light scattering measurements were performed with an ALV goniometer and a laser wavelength of 633 nm. The samples were highly diluted in D_2O ($c < 0.01$ wt%) to prevent multiple scattering and filtered through a 0.8 μm filter to remove dust. The scattered light was detected at a scattering angle of 40°, and hydrodynamic radius $R_H(T)$ values have been calculated from second-order cumulant fits via Stokes−Einstein equation. Heating and subsequent cooling cycles have been performed. The particle size change is fully reversible.

SANS experiments were performed at the D11 beam line at the Institut Laue-Langevin (ILL) in Grenoble, France. A neutron wavelength with 6 Å was used. The data were collected on a ^{3}He detector with 64×64 pixels of 10×10 mm^2 size. The maximum accessible scattering vector modulus (q) range was covered by three detector distances of 2.5, 10.0, and 36.7 m. The scattering vector modulus is given by $q = 4\pi \sin(\theta)/\lambda$ where 2θ is the scattering angle and λ is the neutron wavelength. The incoherent scattering of water at detector distances of 2.5 and 10 m was used for absolute intensity calibration. The microgels were investigated at mass concentrations of 0.1 wt% in D_2O. The temperature was controlled by an external thermostat. Data were corrected for background scattering and calibrated on an absolute scale by incoherent water scattering according to the standard procedures at the ILL.

Results and Discussion

The nanophase separated form factor model contains domains with higher segment densities which can be caused by different functionalities of the reacted monomers inside one particle. This multidomain model describes perfectly the internal structure of the PNIPMAM−PNIPAM(50/50) copolymer microgel as will be shown in this work.

The temperature dependent size of two homopolymer microgels and the PNIPMAM−PNIPAM(50/50) copolymer is displayed in Figure 1. PNIPAM has a transition temperature of 34 °C in heavy water; the transition temperature of PNIPMAM is ca. 44 °C. The transition temperature of the PNIPMAM−PNIPAM(50/50) copolymer microgel is 38 °C and thus in between the VPTTs of the corresponding homopolymers. A similar phase transition behavior was reported before for linear PNIPMAM−PNIPAM copolymers and could indicate that PNIPMAM−PNIPAM copolymers display ideal behavior[24] in contrast to other copolymer systems.[25,26]

However, an unusual structure of the copolymer microgel was found using SANS. Experimental SANS intensities of the PNIPMAM−PNIPAM(50/50) copolymer microgel are plotted in Figure 2. Three different data sets were analyzed: one in the swollen state (20 °C), one in the transition region (38 °C), and one in the collapsed state (53 °C). An unusual shape is observed for the scattering profile of the copolymer microgels at 38 °C; an additional broad bump in the intermediate q range is observed (marked with an arrow in Figure 2). This unusual intensity bump after the third minimum indicates the presence of an additional characteristic length scale inside the microgel.

The PNIPMAM−PNIPAM(50/50) copolymer microgel was prepared in a one-pot synthesis; thus it is unlikely that a

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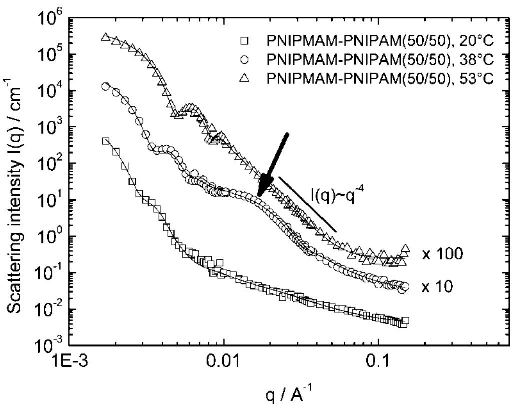

Figure 2. SANS scattering data and fits of the copolymer PNIPMAM−PNIPAM(50/50) in D_2O in the swollen state (20 °C), during the collapse (38 °C) and in the collapsed state (53 °C). Note that two of the curves were shifted vertically.

core−shell structure was built *in situ*. In fact, core−shell microgels containing PNIPAM and PNIPMAM have been investigated before. In those cases, the core−shell morphology was deliberately obtained via a two-step (seed and feed) polymerization process and the structure was determined and confirmed by SANS.[10,19,27]

The PNIPMAM−PNIPAM(50/50)−copolymer microgel in the swollen state at 20 °C and the fully collapsed state at 53 °C can be well described with the same form factor model for homogeneous spheres with a graded surface that is suitable for PNIPAM and PNIPMAM microgels.[23] However, no reasonable fit could be obtained in the transition region at 38 °C with this model due to the additional bump of the scattering intensity. It was also not possible to fit the SANS data at 38 °C with a previously established form factor model for core−shell microgels.[10,19]

To interpret the scattering data, we developed a "dirty snowball" model; i.e., we propose that the copolymer microgel consists of two different regions: phases with a higher density consisting of (mainly) PNIPAM which is in the collapsed state at 38 °C ($\text{VPTT}_{\text{PNIPAM}} = 34$ °C!) and a matrix with a lower density consisting of (mainly) PNIPMAM which is still in the swollen state at 38 °C. Scheme 1 illustrates schematically the proposed nanophase separated structure of the PNIPMAM−PNIPMAM−copolymer at the transition temperature. Two different phases are located inside one microgel particle; the darker particles (dark gray) are PNIPAM-rich domains (collapsed at 38 °C) and a continuous phase (slightly gray) which is the PNIPMAM-rich phase (swollen at 38 °C). Please note that the scheme does not illustrate the fuzzy surface of the microgel.[23]

The scattering of this "dirty snowball" object can be calculated using as a starting point the Debye formula for a collection of monodisperse spheres.[28] There are n smaller spherical domains (PNIPAM) within the large spherical particle (continuous phase, PNIPMAM). In the following equation, the contrast in terms of excess scattering length density of phase one (continuous phase) relative to water is called $\Delta\rho_1$. The contrast between the domains and the phase between the domains is called $\Delta\rho_{int}$. Note that $\Delta\rho_{int} = \Delta\rho_2 - \Delta\rho_1$ is the contrast between the PNIPMAM ($\Delta\rho_1$) and the PNIPAM ($\Delta\rho_2$) domain scattering length densities.[27] The normalized scattering amplitude of a spherical domain with radius R_i

$$P(q) = \sum_{i,j} \Delta\rho_1 \Delta\rho_j V_i V_j A_i(q) A_j(q) \frac{\sin(qr_{ij})}{qr_{ij}} = \Delta\rho_1^2 V_{particles}^2 P(q)_{particles} + n\Delta\rho_{\text{int}}^2 V_{PNIPAM}^2 P(q)_{PNIPAM} + 2\Delta\rho_1\Delta\rho_{\text{int}} V_{particles} V_{PNIPAM} A(q)_{particles} A(q)_{PNIPAM} \sum_i \frac{\sin(qr_{center,i})}{qr_{center,i}} + \Delta\rho_{\text{int}}^2 V_{PNIPAM}^2 P(q)_{PNIPAM} \sum_{i,j,PNIPAM\text{ only}} \frac{\sin(qr_{ij})}{qr_{ij}} \quad (1)$$

and volume V_i is designated $A_i(q)$ (with $A_i(q = 0) = 1$). The parameter r_{ij} is the distance between the centers of the spherical domains or the center of the particle, and the indices i and j are associated with these. With this, the Debye equation gives for the form factor $P(q)$ where the terms with self-correlation and cross correlations are taken out separately and where the indices "*particles*" and "*center*" are introduced for the embedding particle itself and its center. In addition the index "*PNIPAM*" is used for the small spherical domains.

The single sum in the third term can be approximated by the scattering amplitude of the embedding particle, if n (number of small particles) is large and the distribution of the domains is homogeneous. The double sum in the fourth terms can under the same assumptions be approximated by the form factor of the embedding particle. With the correct normalization, the form factor becomes

$$P(q) \approx \Delta\rho_1^2 V_{particles}^2 P(q)_{particles} + n\Delta\rho_{\text{int}}^2 V_{PNIPAM}^2 P(q)_{PNIPAM} + 2n\Delta\rho_1\Delta\rho_{\text{int}} V_{particles} V_{PNIPAM} P(q)_{particles} A(q)_{PNIPAM} + n(n-1)\Delta\rho_{\text{int}}^2 V_{particles}^2 P(q)_{PNIPAM} P(q)_{particles} = \Delta\rho_1^2 V_{particles}^2 P(q)_{particles} + \Delta\rho_{\text{int}}^2 V_{PNIPAM}^2 P(q)_{PNIPAM} (n + n(n-1)P(q)_{particles}) + 2n\Delta\rho_1\Delta\rho_{\text{int}} V_{particles} V_{PNIPAM} P(q)_{particles} A(q)_{PNIPAM} \quad (2)$$

or

$$P(q) = P(q)_{particles}(\Delta\rho_1^2 V_{particles}^2 + \Delta\rho_{\text{int}}^2 n (n-1) V_{PNIPAM}^2 P(q)_{PNIPAM} + 2n\Delta\rho_1\Delta\rho_{\text{int}} V_{particles} V_{PNIPAM} A(q)_{PNIPAM}) + n\Delta\rho_{\text{int}}^2 V_{PNIPAM}^2 P(q)_{PNIPAM} = P(q)_{particles}(\Delta\rho_1 V_{particles} + n\Delta\rho_{\text{int}} V_{PNIPAM} A(q)_{PNIPAM})^2 + n\Delta\rho_{\text{int}}^2 V_{PNIPAM}^2 P(q)_{PNIPAM}(1 - P(q)_{particles}) \quad (3)$$

At this stage, the form factor amplitudes entering the expressions are not fully specified. For a radial (scattering length) density distribution of homogeneous particles with the radius R, the profile is described by a simple box profile and the form factor amplitude is

$$A(q) = \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3} \quad (4)$$

Microgels have a graded interface due to a faster consumption of cross-linker molecules than of monomer during synthesis,[29] and therefore another form factor amplitude has to be used. Assuming a symmetric profile consisting of a piecewise parabolic profile, the form factor can be calculated analytically.[10,23] In this case

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$$A(q)=\frac{4\pi}{V}\left[\left(\frac{R}{\sigma^2}+\frac{1}{\sigma}\right)\frac{\cos(q(R+\sigma))}{q^4}+\left(\frac{R}{\sigma^2}-\frac{1}{\sigma}\right)\frac{\cos(q(R-\sigma))}{q^4}-\frac{3\sin(q(R+\sigma))}{q^5\sigma^2}-\frac{3\sin(q(R-\sigma))}{q^5\sigma^2}+\frac{2\cos(qR)}{q^5\sigma^2}+\frac{6\sin(qR)}{q^5\sigma^2}\right] \quad (5)$$

where V is the volume of the particle, R is the distance from the center of the particle to the midpoint of the profile, and σ describes the width of the interface of the particle. The volume is given by

$$V=4\pi\left(\frac{R^3}{3}+\frac{R\sigma^2}{6}\right) \quad (6)$$

The final model expression includes size polydispersity using a Gaussian distribution, a Lorentzian to describe the polymer-like scattering from the internal structure, a constant to describe background scattering, and corrections for the instrumental smearing.[30] The model was fitted to experimental data using least-squares methods.[31] To reduce the number of fit parameters in the model, several parameters could be fixed during the fitting like the mass of the particle and apparent specific densities ρ of the homopolymers. The temperature dependent density data of PNIPAM and PNIPMAM were taken from previous studies.[23,27]

When deriving the form factor it was assumed that the internal domains were randomly distributed. However, if they are correlated and repel one another, an internal structure factor $S(q)$, which can account for these effects, has to be introduced.[32] In the present case, the "dirty snowball" form factor was extended by an additional internal hard sphere structure factor to account for possible correlations between domains inside one microgel particle. This results in the mixed term ($\Delta\rho^2_{int}n$-$(n-1)V^2_{PNIPAM}\ P(q)_{PNIPAM}\mathrm{P}(q)_{particle}$) in eq 3 being multiplied by the structure factor. However, the fitting of our experimental data revealed no influence of the structure factor on the intensity profile. This indicates that the PNIPAM domains are randomly distributed inside the PNIPMAM phase.

The form factor is composed of several contributions describing the scattering and interference from the different constituents of the particles. These constituents exhibit a marked variation of SANS contrast depending on temperature. In general, the overall contrast of the particles in SANS experiments can be changed through use of mixtures of H_2O and D_2O as used in conventional contrast variation techniques. In the case of the PNIPMAM−PNIPAM(50/50) copolymer microgel, the difference in neutron scattering density of the components of the particles is mainly due to the variation of the scattering length densities of the two monomers when their densities change with temperature. The contrast between the PNIPAM domains and PNIPMAM phase reaches the maximum value at 38 °C, the transition temperature of the copolymer. The scattering length density of the collapsed PNIPAM domains is higher than that of the swollen PNIPMAM domain which makes it possible to distinguish the two domains without a special contrast variation technique. Thus an important parameter in the dirty snowball model is the excess contrast $\Delta\rho_{int} = \Delta\rho_2 - \Delta\rho_1$ between the two phases. Figure 2 reveals that this new model expression describes the data at 38 °C very well.

The results obtained by the fitting procedure are summarized in Table 1. The scattering curves in the swollen state and collapsed state of the microgel can be fitted with the form factor model for microgels with an outer graded surface; thus there are no results for the PNIPAM domains in Table 1 at 20 and 53 °C.

Table 1. Summary of the Parameters Obtained by Fitting the Experimental *I*(*q*)[a]

	PNIPMAM−PNIPAM(50/50)						
T (°C)		*R* (nm)	σ (nm)	σ_{poly} (%)	ϕ_{poly} (°)	R_{SANS} (nm)	R_H (nm)
20	entire particle	86	68	15	0.07	222	254
38	PNIPMAM	92	35	10	0.14	162	197
	PNIPAM	11	1	19	0.54		
53	entire particle	89	3	8	0.51	95	107

[a] The radius R_{SANS} was calculated by $R_{SANS} = R + 2\sigma$ with σ as the smearing of the surface and R as the radius of the box profile. σ_{poly} denotes the relative particle size polydispersity. ϕ_{poly} describes the radial polymer volume fraction. R_H is the hydrodynamic radius obtained by dynamic light scattering. More details can be found in the text.

The SANS analysis provides detailed information on the microgel structure in this intermediate state: the overall number n of small PNIPAM domains is ∼100. The polymer volume fraction inside the particle, $\phi_{poly}(r)$ at $r = 0$ nm, increases dramatically with increasing temperature and was determined to $\phi(0)_{poly,PNIPMAM,38\ °C} = 0.14$ for PNIPMAM and to $\phi(0)_{poly,PNIPAM,38\ °C} = 0.54$ for the PNIPAM domains; similar results were reported before for microgels in the swollen (PNIPMAM) and in the collapsed (PNIPAM) state.[23,27]

The relative particle size polydispersity σ_{poly} is nearly temperature independent. In general, the structure of microgels can be described as follows: A highly cross-linked microgel is characterized by a constant box profile up to $R_{box} = R - 2\sigma$. The cross-linking density decreases with increasing distance to the center described by σ, and at R the profile has decreased to half the microgel density. The overall size obtained by SANS is approximately given by $R_{SANS} = R + 2\sigma$ where the profile approaches zero. R_{SANS} is slightly smaller than the hydrodynamic radius R_H obtained by DLS.[23] The total radius R_{SANS} of the swollen PNIPMAM domain was determined to be 162 nm ($R_{PNIPMAM} = 92$ nm, smearing of the surface $\sigma = 35$ nm) and is in good agreement with the DLS results on the hydrodynamic radius ($R_H = 197$ nm). R_H is expected to be larger due to dangling chains at the microgel surface which contribute to the hydrodynamic radius but hardly contribute to the static scattering intensity. The radius of the small particles is determined to be 11 nm with $\sigma = 1$ nm. The smearing of the surface σ decreases with increasing temperature which is typical for a microgel system. PNIPMAM is still in the swollen state, the smearing of the surface is high, PNIPAM is collapsed, and the smearing is low; thus the small particles behave like homogeneous spheres with a "hard" surface. At 38 °C the mass in the collapsed domains is ca. 25% of the total particle mass, and thus not all of the PNIPAM segments are in the collapsed state. Apparently chains with short PNIPAM blocks do not participate in the collapsed domains.

Analysis of the SANS data reveals a rather special structure of the copolymer microgel. Various factors during the polymerization influence copolymer microgel structures like, e.g., a difference in reactivity of monomers and cross-linker or phase separation of the different subdomains.[22,33] Related to the present work is that of Higuchi et al., who recently reported several

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microphase separated structures in nanoparticles consisting of different amounts of polystyrene and polyisoprene, depending on the copolymerization ratios. They could show that the solubility parameter of each compound controls the structure of the so-called Janus-type particles.[34,35] The structures were visualized with dark field scanning transmission microscopy.

Duracher et al. studied the kinetics of PNIPMAM polymerizations. They could show that the formation of the PNIPMAM particles is slower as compared to the PNIPAM particles.[36] This can be related to the additional methyl group in the NIPMAM backbone. The analysis of the PNIPMAM−PNIPAM(50/50) copolymer structure in the present work indicates that domains with different monomer sequences are built inside the microgel. A slightly different reactivity might lead to an inhomogeneous distribution of PNIPAM and PNIPMAM inside the microgel. The cross-propagation reactions which are related to steric hindrance or chain transfer reactions with tertiary PNIPMAM radicals may account for the inhomogeneity as well. The cross-linker distribution should also be considered in this respect, since chain transfer in PNIPMAM-rich phases may effectively undo some of the cross-links in this phase to permit improved mobility of the PNIPAM domains to form these nanophase separated domains. However, it does not lead to core−shell or core−corona structures that were discussed in other microgel systems.[37]

The sequences of repeating units along the network chains cannot be determined with SANS. Here NMR studies would be helpful but not trivial with the monomers used, and such a study is beyond the scope of this contribution. The formation of collapsed domains can be caused by the monomer sequence within the network strands and/or a local microphase separation. In this context it is important to note that the phase behavior of PNIPAM and similar polymers is due to highly cooperative hydrogen bonding.[38,39] Apparently, this favors the formation of collapsed domains in the copolymer microgel. These domains are randomly distributed, and consequently the hydrodynamic radius shows only one transition. Thus the PNIPMAM−PNIPAM copolymer microgels have a distinctly different structure and properties as compared to core−shell microgels with the same polymers.

Conclusions

We have presented neutron scattering data of a PNIPMAM−PNIPAM(50/50) copolymer system at three different temperatures in the swollen state, at the transition temperature, and at the collapsed state. The phase transition behavior was investigated by means of light scattering, and the transition temperature of the cross-linked microgel was determined to be 38 °C. The small-angle neutron scattering data at the transition temperature displayed an unusal shape for a copolymer which was prepared in a one-pot synthesis: An extra bump was observed in SANS indicating an unexpected additional characteristic length scale inside the microgel. A novel form factor model has been developed which is very well suited for analyzing scattering data of a copolymer system with an internal nanophase separated "dirty snowball" structure. The copolymer system consists of different domains of PNIPAM and PNIPMAM. At 38 °C, the PNIPAM domains ("dirt") are collapsed, and the PNIPMAM domains ("snowball") are still in the swollen state.

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