Communication

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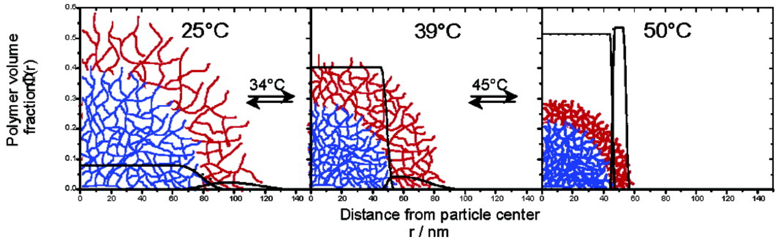

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Structure of Multiresponsive “Intelligent” Core−Shell Microgels

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Environmentally responsive microgels have been subjects of great interest in past years due to their versatile applications. Such microgels are sometimes termed “intelligent” since their properties allow them to be tailor-made to react in a specific way to the environment. The most intensively studied thermosensitive polymer is poly-*N*-isopropylacrylamide (PNIPAM), which exhibits a lower critical solution temperature (LCST) of 34 °C.[1,2] Chemically cross-linked PNIPAM microgels reveal a drastic particle size decrease upon heating in aqueous solution. The responsive characteristics can be modified by either co-polymerization or advanced polymer architecture, and especially core−shell microgels have been investigated recently.[3,4] Such an advanced microgel architecture can give rise to unique particle properties since one can assume that core and shell de-/swelling mutually influence.[5−7] Indeed, dynamic light scattering (DLS) experiments probing the hydrodynamics size of the entire particle, as well as fluorescence studies[8,9] probing the core−shell interface, have demonstrated a mutual influence of core and shell swelling.

Scattering experiments can provide more detailed information of the internal structure of the entire microgel.[10−12] In this contribution, we present small-angle neutron scattering (SANS) results on doubly temperature-sensitive microgels realized by a core−shell structure of two thermosensitive polymers with different LCSTs. Recently, we reported emulsion polymerization and properties of PNIPAM *core*−PNIPMAM *shell* microgels, where PNIPMAM is poly-*N*-isopropylmethacrylamide with a LCST of 44 °C.[7] These particles show a two-step shrinking process of hydrodynamic radius R_h upon heating in aqueous solution (Figure 1). The transitions at 34 °C and 44 °C are assigned to core and shell collapse, respectively. In the analysis of the SANS data, a new general form factor model is employed for describing the particles with core−shell morphology.

Experimental scattering curves at three temperatures corresponding to the fully collapsed (50 °C), partially collapsed (39 °C), and fully swollen (25 °C) states are plotted in Figure 2. Experimental details are given elsewhere.[13] Porod scattering ($I(q) \sim q^{-4}$) is observed at 50 °C in the intermediate q-range of $q = \sim 0.02-0.06$ Å^{-1}, indicating the presence of a sharp interface, whereas the slope is slightly smaller at 39 °C. Counterintuitive on first sight is the shift of the mimimum toward higher q-values with decreasing temperature from 50 to 39 °C, indicating a particle size decrease contradictory to DLS results.

The radial (scattering length) density distribution of homogeneous particles with the radius R is well described by a box profile. Microgels have a graded interface due to a faster consumption of cross-linker molecules than of monomer during synthesis.[10,14] Consequently, the structure of core−shell microgels has to be described by a profile with two boxes of widths W_{core} and W_{shell}, a graded outer surface, and an additional interface accounting for interpenetration of core and shell polymer networks, as depicted in Figure 3.

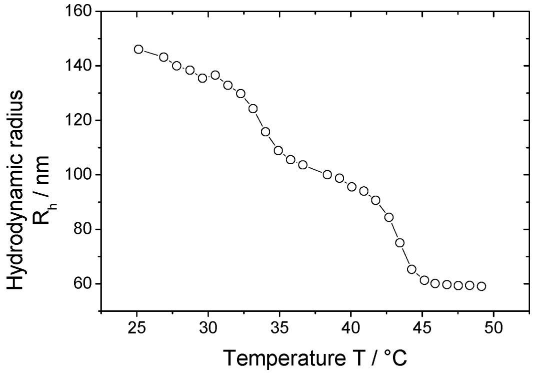

Figure 1. Temperature dependence of the hydrodynamic radius R_h of a PNIPAM *core*−PNIPMAM *shell* microgel in D_2O. Mass ratio core/shell = 1:0.7, cross-link density in core, 1.4, in shell 5 mol %.

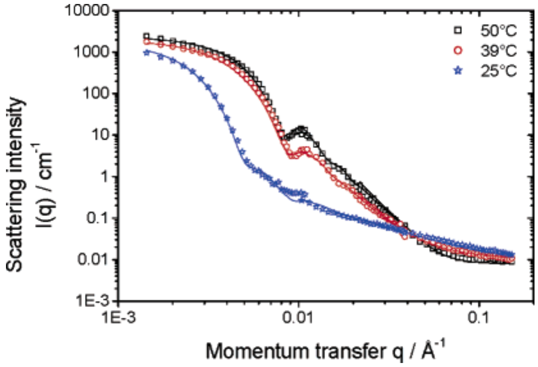

Figure 2. Experimental SANS scattering profiles at 25, 39, and 50 °C. Lines show the fits. Note the shift of the minimum toward higher q-values with decreasing temperature from 50 to 39 °C.

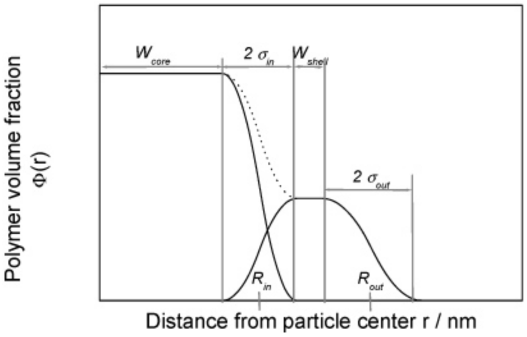

Figure 3. Schematic density profile used to model scattering data from core−shell systems. The core is characterized by a box with width W_{core} and an interface with a width of $2\sigma_{\text{in}}$ accounting for core and shell interpenetration. The shell is described by a box of width W_{shell} and a surface profile of $2\sigma_{\text{out}}$. The dotted line shows the total density profile.

The scattering amplitude of a core−shell particle can be described by

$$A(q) = \Delta\rho_{\text{shell}} V_{\text{shell}} \Phi(q, R_{\text{out}}, \sigma_{\text{out}}) + (\Delta\rho_{\text{core}} - \Delta\rho_{\text{shell}}) V_{\text{core}} \Phi(q, R_{\text{in}}, \sigma_{\text{in}}) \quad (1)$$

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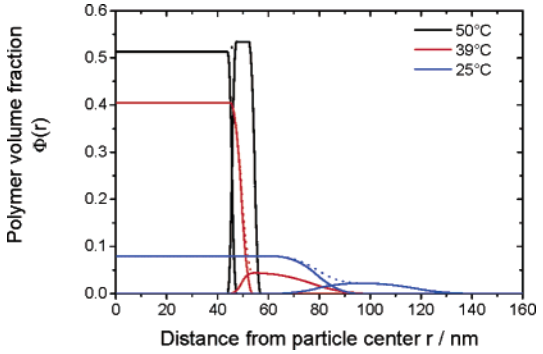

Figure 4. Radial density profiles of a core−shell microgel at 25, 39, and 50 °C. Dotted lines represent the total of core and shell profiles.

where $\Delta\rho_{\rm shell}$ and $\Delta\rho_{\rm core}$ are the excess scattering length densities of shell and core, respectively. $V_{\rm shell}$ and $V_{\rm core}$ are the partial volumes of the polymer in the shell and in the core, respectively, and $\Phi(q,R,\sigma)$ is the normalized Fourier transformation of a particle with half-width radius R and with a width of the interface given by σ. If the radial profile is described with a symmetric form based on a parabolic shape,

$$\rho(r) = 1 \qquad r \le (R-\sigma) \tag{2a}$$

$$\rho(r) = 1 - \frac{1}{2}\frac{[(r-R)+\sigma]^2}{\sigma^2} \qquad (R-\sigma) < r \le R \tag{2b}$$

$$\rho(r) = \frac{1}{2}\frac{[(R-r)+\sigma]^2}{\sigma^2} \qquad R < r \le (R+\sigma) \tag{2c}$$

$$\rho(r) = 0 \qquad r > (R+\sigma) \tag{2d}$$

the Fourier transformation can be done analytically, leading to

$$\Phi(q,R,\sigma) = \frac{1}{V_{\rm n}}\Bigg[\left(\frac{R}{\sigma^2}+\frac{1}{\sigma}\right)\frac{\cos(q(R+\sigma))}{q^4} - \frac{3\sin(q(R+\sigma))}{q^5\sigma^2} + \left(\frac{R}{\sigma^2}-\frac{1}{\sigma}\right)\frac{\cos(q(R-\sigma))}{q^4} - \frac{3\sin(q(R-\sigma))}{q^5\sigma^2} + \frac{2\cos(qR)}{q^5\sigma^2} + \frac{6\sin(qR)}{q^5\sigma^2}\Bigg] \tag{3}$$

where $V_{\rm n} = (R^3/3 + R\sigma^2/6)$ and $V = 4\pi V_{\rm n}$ is the volume of a particle with the radial profile $\rho(r)$ (eq 2). The parameters $R_{\rm in}$ and $R_{\rm out}$ in the expression for the amplitude are related to the parameters $W_{\rm core}$ and $W_{\rm shell}$ in Figure 2 by $R_{\rm in} = W_{\rm core} + \sigma_{\rm in}$ and $R_{\rm out} = W_{\rm core} + 2\sigma_{\rm in} + W_{\rm shell} + \sigma_{\rm out}$. Similar profiles were considered by Kerker[15] using Lorenz−Mie theory for light scattering, and some examples of form factors were calculated numerically. Our calculations are performed within Rayleigh−Debye theory and result in relatively simple closed expressions (eq 3).

The model includes the following additional features: (i) polydispersity of the size in terms of Gaussian distribution, (ii) a Lorentzian to describe the polymer-like scattering from the internal structure of microgels, (iii) smearing of the model expression due to the instrumental resolution, and (iv) incoherent background scattering.[16]

The analysis of SANS data provides the radial density profile (see Figure 4). At 50 °C the microgel structure is described by two boxes of similar volume fractions of 51 and 53%, a narrow interface, and relative size polydispersity of 8%. The total radius is in good agreement with DLS results. As the temperature is above the LCSTs of both polymers, core and shell are both in a fully collapsed state. Significant changes are observed at 39 °C, where the temperature is between the LCSTs of the core and shell polymers. The shell is found to be highly swollen, with a low volume fraction of 4.4% and a fuzzy surface of $2\sigma_{\rm out} = 46$ nm. The interface $\sigma_{\rm in}$ has increased from 1.7 to 4.4 nm, and the core volume fraction has decreased to 41%. When the temperature is further decreased, also a highly swollen core with a volume fraction of 8% and a broad $\sigma_{\rm in} = 16$ nm is observed.

Decreasing the temperature below 44 °C leads the shell to swell in radial and tangential directions. The radial growth directly contributes to an increase of particle size, whereas swelling in the tangential directions leads to mechanical strains at the core−shell interface. As the shell is interpenetrated with the collapsed but flexible core network, these strains can be released by stretching the core and core−shell interface, leading to increased core dimensions (characterized by $R_{\rm in}$ and $\sigma_{\rm in}$) as compared to those at 50 °C. At temperatures below 34 °C, the dimensions of the core in the core−shell system are smaller as compared to the naked core (i.e., without shell). The size of the pure core microgel was determined independently and was found to be $R_{\rm in} + 2\sigma_{\rm in} = 122$ nm.[13] This clearly demonstrates that in the core−shell microgel at 25 °C, the shell restricts full swelling of the core. Thus, compared to the naked core, the core of the core−shell particles is *expanded at intermediate temperature* and *compressed at low temperature* due to the swelling properties of the shell.

From the scattering point of view, the change of temperature can be regarded as a contrast variation. At the intermediate temperature, Figure 4 shows the volume fraction of the shell decreased by a factor of 10 at 39 °C. As the contrast changes in the same manner, the scattering profile is mainly determined by the scattering from the core, which is smaller than the entire particle at 50 °C. Thus we can explain the shift of the mimimum to high q.

The use of the SANS technique thus provides a more detailed insight into the internal structure of “intelligent” PNIPAM *core*−PNIPMAM *shell* microgels than is possible by DLS. The analysis of SANS data from microgels with different compositions provides quantitative information on the mutual influence of core and shell swelling and will be reported elsewhere.[13] The particle properties can be controlled by the core−shell mass ratio as well as by the cross-link density in the core and shell.[7]

In conclusion, a novel universal form factor has been introduced which is very well suited for analyzing scattering data of core−shell/core−corona systems. The simple form used for the radial profile allows the form factor expressions to be calculated in analytical form. The model is quite general, as it allows analysis of both core−shell particles with diffuse and sharp interfaces. In the case of the doubly thermosensitive microgel investigated in this study, detailed information on the mutual influence of the temperature-dependent swelling of core and shell is obtained.

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