Influence of Polymerization Conditions on the Structure of Temperature-Sensitive Poly(*N*-isopropylacrylamide) Microgels

Stefanie Meyer and Walter Richtering*

Institute of Physical Chemistry, RWTH Aachen University, D-52056 Aachen, Germany

Received October 29, 2004
Revised Manuscript Received December 16, 2004

Introduction

Aqueous mixtures of poly(*N*-isoproplyacrylamide) (PNiPAM) are of growing interest mainly due to their temperature-sensitive solubility in water.[1,2] Linear PNIPAM macromolecules display a coil-to-globule transition when the lower critical solution temperature of ca. 32 °C is approached; macroscopic gels display strong shrinking upon heating, and a volume phase transition is found. Similar behavior is observed with colloidally dispersed PNIPAM microgels,[3] the hydrodynamic radius of which decreases strongly at elevated temperatures. Because of this strong temperature sensitivity, several applications of such PNIPAM microgels have been discussed.

In most experimental studies the size of microgel particles is characterized by means of dynamic light scattering albeit it is well-known that static light scattering can provide more detailed information via the analysis of the full form factor (see e.g. refs 4 and 5). Even if the full form factor is not accessible, the ρ parameter, which is the ratio of radius of gyration and hydrodynamic radius, gives additional information on the particle structure.[6]

Furthermore, it is commonly assumed that the PNIPAM particles not only have spherical shape but that the internal structure is homogeneous. However, kinetic investigations revealed that in batch polymerizations the methylenebis(acrylamide) cross-linker is consumed faster than is the NIPAM monomer.[7] This suggests that the particles prepared in batch methods will have a nonuniform morphology. Adsorption studies of microgels prepared in batch and semibatch emulsion polymerization have been interpreted with a different internal structure of the microgel particles.[8] Structural inhomogeneities inside PNiPAM microgels were studied by Guillermo et al. with nuclear magnetic resonance.[9] They distinguished different structural regions by their different proton mobility detected through magnetic relaxation rates. Furthermore, a comparison of radius of gyration and hydrodynamic radius showed that PNIPAM microgels do not follow homogeneous sphere behavior in the swollen state at low temperatures but only approach homogeneous sphere properties at temperatures above the transition temperature.[10] However, to the best of our knowledge, a more direct investigation of the different morphology of PNIPAM microgels prepared in batch and semibatch conditions based on scattering data is lacking.

Recently, it was demonstrated that a form factor model that does not assume a sharp particle surface describes very well the experimental small-angle neutron scattering (SANS) data at all temperatures over an extensive range of scattering vector q.[11] The overall particle form as well as the internal structure of the microgel network is described by the model. The influence of temperature is revealed by the radial density profiles and clearly showed that the segment density in the swollen state is not homogeneous but gradually decays at the surface. The density profile reveals a box profile only when the particles are collapsed at elevated temperatures. In this study we used the same model to analyze data from static light scattering (SLS) experiments that are much easier to perform as compared to SANS. Different microgel samples have been prepared in batch and semibatch polymerization and investigated in dilute aqueous solution at different temperatures.

* Corresponding author. E-mail: richtering@rwth-aachen.de.

Experimental Section

N,*N*′-Methylenebis(acrylamide) (BIS) and sodium dodecyl sulfate (SDS) were purchased from Fluka. *N*-Isopropylacrylamide (NiPAM) was purchased from Aldrich. The general synthesis and purification procedure of PNiPAM microgels via free radical emulsion polymerization were reported previously.[12] Static light scattering experiments at high dilution, 0.01% (w/w), have been performed with a computer-controlled modified FICA goniometer (SLS Systemtechnik) with a helium−neon ion laser at a wavelength of $\lambda_0 = 632.8$ nm. A refractive index increment $dn/dc = 0.162$ mL/g was used at 25 °C.[13] The form factor analysis was performed with software developed by J. S. Pedersen, University of Aarhus. Typical errors for the three parameters of interest are $\Delta R/R = 0.02$, $\Delta\sigma_{poly}/\sigma_{poly} = 0.15$, and $\Delta\sigma_{surf} = 2$ nm.

Results and Discussion

Three different reaction procedures have been used for the preparation of PNiPAM microgels. First two samples, Pni01and Pni02, were prepared in batch processes similar to samples that have been investigated before.[11] In a second series, 20% of the total cross-linker content was given to the reaction solution at the beginning of the reaction and 80% of the cross-linker was added continuously over a period of 15 or 30 min, respectively (sample code V15 and V30). Third, microgels were synthesized by starting with a cross-linker to monomer mixture that contained 20% of the total cross-linker and 40% of the total monomer amounts. The rest, i.e., 80% of cross-linker and 60% of the monomer, were added continuously over 30 min (sample codes VM). Compositions of the different preparations are summarized in tables given in the Supporting Information. After purification, dilute solutions of the microgels in H_2O have been investigated by light scattering.

Particle interactions can be neglected in highly dilute solutions, and the angular dependence of the scattering intensity is described by the particle form factor $P(q)$, where q denotes the magnitude of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, with wavelength λ and scattering angle θ. For homogeneous spheres the form factor is given as[14]

$$P_{hom}(q) = \left(\frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3}\right)^2 \qquad (1)$$

For microgel particles prepared in a batch process a higher degree of cross-linking density is expected inside the particle than outside due to the different reaction

10.1021/ma047776v CCC: $30.25
Published on Web 01/29/2005

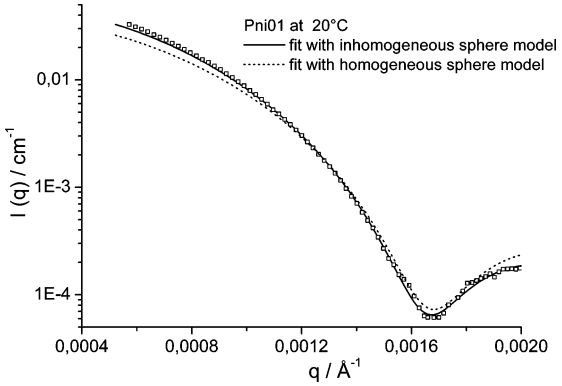

Figure 1. Static light scattering data from dilute solution of the batch sample Pni01 in H_2O together with fits with form factor models of polydisperse homogeneous and inhomogeneous spheres.

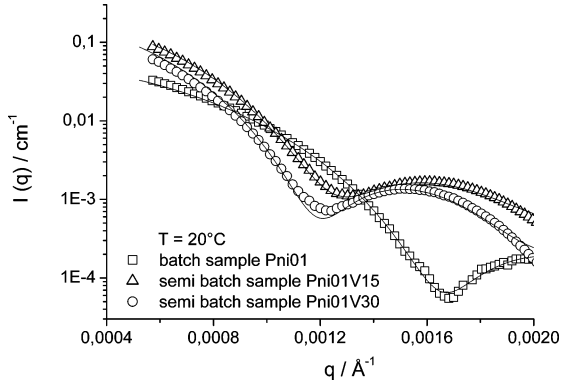

Figure 2. Static light scattering data from dilute H_2O solutions of the batch sample Pni01 and the semibatch samples Pni01V15 and Pni01V30 and fits with a polydisperse inhomogeneous sphere model.

kinetics of cross-linker and monomer.[7] This leads to a fuzziness of the particle surface, which has to be included in a realistic model. Pedersen and co-workers assumed that the fuzziness can be accounted for by convoluting the radial box profile with a Gaussian.[11] In reciprocal space the convolution is just a product yielding the form factor $P_{\mathrm{inho}}(q)$ that describes scattering from a monodisperse sphere with an interface that gradually decreases at the sphere surface as an error function. The form factor is

$$P_{\mathrm{inho}}(q) = \left[\frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3}\exp\left(-\frac{(\sigma_{\mathrm{surf}}q)^2}{2}\right)\right]^2 \quad (2)$$

where σ_{surf} denotes the width of the smeared particle surface. A similar approach was applied by Svaneborg et al.[15,16] to describe the scattering of block copolymer micelles. The model assumes that the core of the microgel exhibits a higher degree of cross-linking density which is characterized by the radial box profile up to a radius of about $R_{\mathrm{box}} = R - 2\sigma_{\mathrm{surf}}$. The subsequent decrease in cross-linking density is described by σ_{surf}, and the profile has decreased to half the core density at R. At $R_{\mathrm{SLS}} = R + 2\sigma_{\mathrm{surf}}$, the profile approaches zero, and thus, the overall size of the particle obtained by static scattering is approximately given by R_{SLS}.

To consider size polydispersity of the particles, we assume the number distribution with respect to the particle radius R to be a Gaussian function

$$D(R,\langle R\rangle,\sigma_{\mathrm{poly}}) = \frac{1}{\sqrt{2\pi\sigma_{\mathrm{poly}}{}^2\langle R\rangle^2}}\exp\left(-\frac{(R-\langle R\rangle)^2}{2\sigma_{\mathrm{poly}}{}^2\langle R\rangle^2}\right) \quad (3)$$

with $\langle R\rangle$ describing the average particle radius and σ_{poly} denoting the relative particle size polydispersity. Stieger et al. employed small-angle neutron scattering (SANS) to investigate the microgel structure. SANS probes structural features also at very high q values where fluctuations of the network also contribute to the scattering intensity, and these contributions were taken into account with a Lorentz function. Since light scattering does not reach such high q values, network fluctuations need not to be considered in the present investigation.

Figure 1 displays the angular-dependent light scattering intensity of batch sample Pni01 at 20 °C together with curves from fitting the form factor of polydisperse homogeneous and polydisperse inhomogeneous spheres to the experimental data. In agreement with Stieger et al., we find that the microgel particles prepared in a batch process cannot satisfactorily be described by homogeneous spheres when they are in the highly swollen state at low temperature. A comparison of SLS data and fits with the inhomogeneous sphere model obtained at 20 °C from samples prepared in batch and semibatch processes is shown in Figure 2.

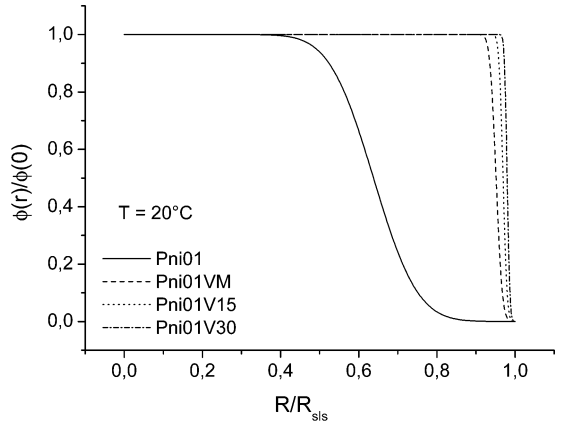

Figure 3. Normalized density profile of PNIPAM microgels in H_2O at 20 °C. From left to right: batch sample Pni01 (solid line) and semibatch samples Pni01VM (dashed line), Pni01V15 (dotted line), and Pni01V30 (dash-dot line).

After the model is fitted to experimental data, the amplitude of the form factor can be calculated as the terms inside the square brackets in eq 2. A numerical Fourier transformation leads to the radial density profile of the particle providing useful information about the structure of the particle. Normalized radial density profiles of different samples at 20 °C are shown in Figure 3. Obviously, microgels prepared under semibatch conditions reveal a much sharper decay of the segment density as compared to the sample prepared in a batch reaction. The fit results are summarized in Table 1.

The fuzziness of the density decay in the outer regions of the microgel particles is characterized by the parameter σ_{surf}, and the results clearly demonstrate that the inhomogeneity of the microgels prepared under semibatch conditions is much smaller as compared to microgels synthesized in a simple batch reaction. However, the data indicate that the size polydispersity increased slightly. One can assume that a more sophisticated reaction procedure as e.g. starved-feed conditions could

Table 1. Results from the Form Factor Analysis

sample	T/°C	σ_{poly}/%	R/nm	σ_{surf}/nm	R_{SLS}/nm
Pni01	21	8	268	41	350
	26	6	256	40	336
	30	6	232	27	286
Pni01V15	19	11	344	5	354
	26	11	310	4	318
	30	11	277	3	283
Pni01V30	19	9	370	3	376
	26	10	337	2	341
	30	9	301	2	305
Pni01VM	19	13	415	6	427
	26	10	348	4	356
	30	10	304	3	310

further improve the homogeneity of PNIPAM microgels. Finally, the tabulated values show that the overall size $R_{SLS} = R + 2\sigma_{surf}$ of the microgels Pni01V15 and Pni01V30 prepared in a semibatch reaction is not much higher as compared to the sample from the batch polymerization although the form factor minimum in Figure 2 revealed a rather strong shift to lower q. The form factor of homogeneous spheres with radius R has a first minimum at the q-position $Rq_{min} = 4.493$. The extended inhomogeneous sphere form factor has a minimum at the same Rq_{min} value where R corresponds the distance form the particle center at which the relative segment density has decayed to $^1/_2$. For homogeneous spheres $R_{SLS} = R$ since $\sigma_{surf} = 0$, whereas $R_{SLS} = R + 2\sigma_{surf}$ for inhomogeneous spheres. Thus, the overall size of the microgels, the form factor of which is shown in Figure 2, is very similar although the form factor minimum of the batch microgel sample is at higher q. The observation that the overall size is very similar indicates that a semibatch reaction leads to a smaller fraction of linear chains, which are not connected to a microgel particle. Results from a second series of samples that reveal the same trends as discussed here are provided as Supporting Information.

Conclusions

PNIPAM microgels have been prepared under different polymerization conditions, namely batch or semibatch. The structure of the microgel particles was investigated by means of static light scattering, and an inhomogeneous sphere model developed recently by Pedersen and co-workers was used to analyze the experimentally determined form factor. The combination of static light scattering measurements with the direct modeling approach utilizing this form factor model provides a convenient tool for a quantitative investigation of the structure of microgels. More detailed information is obtained as compared to the commonly applied dynamic light scattering. The results demonstrate that a semibatch reaction process leads to microgels with a homogeneous morphology in contrast to a simple batch polymerization. This is in agreement with kinetic studies of Wu et al.[7]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft. We are greatly indebted to Jan Skov Pedersen, University of Aarhus, Denmark, for the development of the form factor model.

Supporting Information Available: Tables with detailed compositions of polymerization reactions as well as results of the form factor analysis of additional samples. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(2) Pelton, R. *Adv. Colloid Interface Sci.* **2000**, *85*, 1.
(3) Pelton, R. H.; Cibante, P. *Colloids Surf.* **1986**, *20*, 247.
(4) Schnablegger, H.; Glatter, O. *J. Colloid Interface Sci.* **1993**, *158*, 228.
(5) Hansen, J. C.; Merie, D.; Honerkamp, J.; Richtering, W.; Horn, F. M.; Senff, H. *J. Colloid Interface Sci.* **1999**, *215*, 72.
(6) Burchard, W. *Adv. Polym. Sci.* **1983**, *48*, 1.
(7) Wu, X.; Pelton, R. H.; Hamielec, A. E.; Woods, D. R.; McPhee, W. *Colloid Polym. Sci.* **1994**, *272*, 467.
(8) Zhang, J.; Pelton, R. *Langmuir* **1999**, *15*, 8032.
(9) Guillermo, A.; Addad, J. P. C.; Bazile, J. P.; Duracher, D.; Elaissari, A.; Pichot, C. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 889.
(10) Senff, H.; Richtering, W. *Colloid Polym. Sci.* **2000**, *278*, 830.
(11) Stieger, M.; Richtering, W.; Pedersen, J. S.; Lindner, P. *J. Chem. Phys.* **2004**, *120*, 6197.
(12) Senff, H.; Richtering, W. *J. Chem. Phys.* **1999**, *111*, 1705.
(13) Senff, H. PhD Thesis, University of Freiburg, Germany, 1999.
(14) Rayleigh, L. *Proc. R. Soc. London, Ser. A* **1911**, *84*, 25.
(15) Svaneborg, C.; Pedersen, J. S. *Phys. Rev. E* **2001**, *64*, 10802.
(16) Pedersen, J. S.; Svaneborg, C. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 158.

MA047776V