Investigation on the structure of temperature-responsive $N$-isopropylacrylamide microgels containing a new hydrophobic crosslinker

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Investigation on the structure of temperature-responsive \( N \)-isopropylacrylamide microgels containing a new hydrophobic crosslinker

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**Abstract:** Temperature-responsive poly\((N\)-isopropylacrylamide\) microgels crosslinked with a new hydrophobic chemical crosslinker were prepared by surfactant-mediated precipitation emulsion polymerization. The temperature-responsive property of the microgel and the influence of the crosslinker on the swelling behaviour was studied systematically by light scattering and small-angle X-ray scattering (SAXS). The radius of gyration (\( R_g \)) and the hydrodynamic radius (\( R_h \)) of the microgels decreased with increase in temperature due to the volume-phase transition from a swollen to a collapsed state. The ratio of \( R_g / R_h \) below the transition temperature was lower than that of hard-spheres due to the lower crosslinking density of the microgels.

The SAXS data were analysed by a model in which the microgels were modelled as core-shell particles with a graded interface. The model at intermediate temperatures included a central core and a more diffuse outer layer describing pending polymer chains with a low crosslinking density. In the fully swollen state, the microgels were modelled with a single component with a broad graded surface. In the collapsed state, they were modelled as homogeneous and relatively compact particles. The polymer volume fraction inside the microgel was also derived based on the model.

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**PUBLIC INTEREST STATEMENT**

Temperature-responsive microgels are crosslinked polymer particles that can respond to external changes in external temperature. These materials have become the focus of research interest in materials science owing to their interesting properties. The most widely studied temperature-responsive microgel system is based on poly\((N\)-isopropylacrylamide\) (PNIPAM). The PNIPAM microgel dispersion in water exhibits a volume-phase transition around 32°C. The swelling of the microgel can be influenced by the type and amount of crosslinker present, and the quantification of the amount of polymer present in the microgel is rather tedious. In this work, we use a hydrophobic crosslinker in the synthesis of PNIPAM microgels and show by using scattering methods, the quantification of important molecular parameters of the microgels as function of external temperature. The methods and model described in this work can be extended to other stimuli-responsive microgel systems.
and was found to increase with increase in the temperature as a result of collapse of the microgel to compact particles. The polymer volume fraction in the core of the microgel in the collapsed state was about 60% which is higher than that of similar microgels crosslinked with hydrophilic and flexible crosslinkers.

Subjects: Physical Sciences; Materials Chemistry; Polymers & Plastics

Keywords: microgels; SAXS; light scattering; core-shell particles

1. Introduction

In recent years, colloidal dispersions of microgels have gained considerable research attention in various engineering and biomedical fields (Deen, Alsted, Richtering, & Pedersen, 2011; Karg & Hellweg, 2009; Stieger, Richtering, Pedersen, & Lindner, 2004). These materials have been studied extensively in relation to theoretical studies of soft condensed matter and in applied areas such as material science for applications in drug delivery systems, cosmetics and special coatings. A polymer microgel is a chemically crosslinked latex particle that is swollen by a good solvent. Depending on the type of monomers used in the synthesis of microgels, they can be tuned to vary their physical properties in response to changes in external environment (external stimuli) (Deen, Quah, Mah, & Loh, 2013; González, Elvira, & Román, 2005; Peppas, Bures, Leobandung, & Ichikawa, 2000). These systems are called the “smart” or “stimuli”-responsive microgels. A wide variety of external stimuli have been studied and these include pH, temperature, inorganic salts, electric field, magnetic field, pressure, etc. Among the fascinating family of smart microgels, the temperature-responsive microgel colloids have attracted much attention due to their common properties with water soluble polymers and water insoluble polymer latexes (Deen et al., 2013; Frank & Lauterbur, 1993; González et al., 2005; Pelton, 2000; Peppas et al., 2000; Tanaka, 1981; Wong, Gaharwar, Müller-Schulte, Bahadur, & Richtering, 2008).

Some of the interesting temperature-responsive microgels are based on monomers such as N-acryloyl piperidine (Hoshino, Sakoi, Kawaguchi, & Ohtsuka, 1987), N-vinylcaprolactam (Imaz & Forcada, 2010), N-vinylisobutyramide (Serizawa, Chen, & Akashi, 1998), N-acryloyl pyrrolidine (Kawaguchi, Hoshino, & Ohtsuka, 1986), N-isopropylmethacrylamide (Wong & Richtering, 2008) and N-isopropylacrylamide (NIPAM) (Balliauf & Lu, 2007; Das, Zhang, & Kumacheva, 2006; Hoare & Pelton, 2004, 2008; Kuckling, 2009). Among the monomers used in the synthesis of temperature-responsive microgels, NIPAM is the most widely studied owing to its excellent properties. In water and in the presence of a suitable chemical crosslinker, it undergoes rapid free-radical polymerization to give high molar mass polymer poly(N-isopropylacrylamide) (PNIPAM) (McPhee, Tam, & Pelton, 1993). The aqueous PNIPAM microgel colloidal dispersions exhibit a volume-phase transition around 32°C. This phase transition corresponds to the lower critical solution temperature (LCST) of the uncrosslinked polymer (Gilányi, Varga, Me száros, Filipcsei, & Zrínyi, 2000; Kuckling, 2009; McPhee et al., 1993).

In the case of PNIPAM microgels, much research focus has been given to the factors that affect the swelling and shrinking properties in response to variation in external temperature. Such studies are important to achieve a well-controlled targeted drug delivery system, chemical sensors, actuators, etc. (Gilányi et al., 2000; McPhee et al., 1993; Peppas et al., 2000). The internal structure of the microgel particles plays an important role in controlling the swelling properties. The microgel structure during transition from the swollen state to the collapsed state is still a matter open for debate (Gilányi et al., 2000; Guillermo et al., 2000; Saunders & Vincent, 1999; Shibayama, Tanaka, & Han, 1992; Stieger et al., 2004). The type and amount of chemical crosslinker used during the synthesis of microgels has a great impact on the final morphology and hence the swelling properties (Deen, Quah, Mah, & Loh, 2012; Pich, Lu, & Adler, 2003; Varga, Gilányi, Mészáros, Filipcsei, & Zrínyi, 2001). PNIPAM microgels crosslinked with N,N-methylene bisacrylamide (MBA) is the most widely studied system. MBA is hydrophilic in nature and contains flexible chemical structural units (Deen et al., 2012; Gilányi et al., 2000; Guillermo et al., 2000; Kuckling, 2009; McPhee et al., 1993; Pich et al., 2003; Saunders & Vincent, 1999; Shibayama et al., 1992; Varga et al., 2001; Zha et al., 2002).
In this work, thermo-responsive microgels of PNIPAM were prepared using a new hydrophobic and structurally rigid crosslinker, 1,4-diacryloyl piperazine (DAP) by precipitation emulsion polymerization at 70°C. The purpose of this work is to study the structure of microgels crosslinked with hydrophobic crosslinker and to understand the structural variation during the temperature-dependent collapse transition by means of light scattering and small-angle X-ray scattering (SAXS) techniques. This study will contribute in the development of microgels with controlled swelling properties for targeted applications.

2. Experimental

2.1. Materials
All chemicals and solvents were purchased from Sigma-Aldrich unless otherwise mentioned. NIPAM was purified by recrystallization in toluene/hexane (60:40 v/v) solvent mixture. Acryloyl chloride, piperazine, triethylamine, 4,4-azobis(4-cyanovalelic acid), sodium dodecyl sulphate (SDS) and acetonitrile were used as received.

2.2. Synthesis of crosslinker, 1,4-diacryloyl piperazine
Acryloyl chloride (200 mmol, 18.10 g) and triethylamine (200 mmol, 18.0 g) were dissolved in 400 ml of acetonitrile in a 2 l round bottom flask. The mixture was gently stirred and the flask was placed in an ice-bath. To this solution, anhydrous piperazine (197 mmol, 17.0 g) dissolved in 200 ml of acetonitrile was added dropwise from a pressure equalizing funnel over a period of 1 h. After the complete addition of acryloyl chloride, the reaction mixture was allowed to equilibrate to room temperature. The mixture was further stirred for about 3 h. The precipitated triethylamine hydrochloride salt was filtered, and the filtrate was concentrated to an approximate volume of 100 ml on a rotary evaporator. The concentrated filtrate was cooled in a freezer (−18°C, 2 days) to crystallize the product as white crystals. The crystals were filtered under nitrogen and were further purified by recrystallization in acetonitrile (Yield: 70%, mp: 67°C). \( ^1 \)H NMR chemical shifts (ppm): \( \text{CH}_2=\text{C}– (6.37–6.45, \text{cis proton, doublet of doublet, } J = 16.77 \text{ Hz}), \text{CH}_2=\text{C}– (5.67–5.78, \text{trans proton, doublet of doublet, } J = 10.11 \text{ Hz}), \text{CH}_2=\text{CO}– (6.52–6.67, \text{doublet of doublet}), \text{CO}–\text{N(CH}_3_2)– (3.66, broad singlet, 8 protons). The structure of the monomer and crosslinker is shown in Figure 1(A).

2.3. Synthesis of crosslinked PNIPAM microgels
The PNIPAM microgels crosslinked with DAP were prepared by surfactant aided emulsion polymerization in water at 70°C using the method reported by Senff and Richtering (1999) as follows: NIPAM (7.0 g), DAP (0.20 g) SDS (0.8 g) were dissolved in 470 ml of water in a three-neck round bottom flask fitted with a condenser, a nitrogen-inlet tube and a glass-outlet tube. Under constant magnetic stirring (1,000 rpm), the reaction mixture was maintained at 70°C and purged with nitrogen gas in order to remove the dissolved oxygen. After 30 min, 0.14 g of KPS dissolved in 30 ml of water and purged...
with nitrogen gas was added to the reaction mixture. The reaction mixture turned turbid in about 30 min after the addition of KPS solution. Polymerization was conducted at 70°C for 7 h followed by air cooling. The large particulates were removed by filtration through glass wool, and the microgel dispersion was purified by extensive dialysis followed by freeze-drying.

2.4. Static and dynamic light scattering

The light scattering measurements were performed on a commercially available instrument (ALV, Langen, Germany) consisting of an ALV/CGS-8F goniometer equipped with an ALV-6010/EPP multi-tau digital correlator. The instrument is equipped with ALV static and dynamic enhancer with fibre-splitting at 632.8 nm for operation in the pseudo-cross correlation mode using two avalanche photo diodes as the detection unit. The light source was a He–Ne diode laser of wavelength 632.8 nm (JDS Uniphase) with a power output of 25 mW. The incident light was vertically polarized with respect to the scattering plane and the light intensity was regulated with a software controlled ALV/8-steps beam attenuator.

The samples for the light scattering measurements were prepared by weight on an analytical balance by dissolving the required PNIPAM microgels in Millipore water. The aqueous samples were clarified by filtering at least three times through syringe filters (pore size = 0.5 micron) into clean cylindrical glass cells. The samples were allowed to equilibrate at 23°C for 24 h prior to the measurement. Triple-distilled and filtered water was used for background corrections and filtered toluene was used for the absolute normalization of laser light intensity. The scattering intensity was measured in the angular range from 15° to 160° in intervals of 5°.

The static light scattering (SLS) data were analysed using the Zimm approximation (Zimm, 1948) to obtain the characteristic molecular and thermodynamic parameters as,

\[
\frac{KcR(q)}{R(q)} = \frac{1}{M_w} \left( 1 + \frac{1}{3} \left( \frac{R_g^2}{q^2} \right) \right) + 2A_2c \quad (1)
\]

where \(q\), \(K\), \(c\), \(R\), \(M_w\), \(R_g\), and \(A_2\) are the scattering vector modulus, optical constant, concentration of the microgel, excess Rayleigh ratio, weight-average molar mass, the ensemble average square of the radius of gyration and the second-virial coefficient, respectively. The scattering vector modulus \(q\) and the optical constant \(K\) are defined by the following respective equations,

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

\[
K = \frac{4\pi^2 n^2}{\lambda^2 N_A} \left( \frac{dn}{dc} \right)^2 \quad (3)
\]

where \(n\), \(\lambda\), \(N_A\), and \(dn/dc\) are the solvent refractive index, wavelength of laser light (632.8 nm), angle between the direct and scattered beam, Avogadro’s constant and the change in refractive index with concentration of the microgels, respectively.

In the dynamic light scattering (DLS), the intensity-time correlation function \(g_2(t)\) was measured which is expressed as,

\[
g_2(t) = A \left( 1 + \beta |g_1(t)|^2 \right) \quad (4)
\]

where \(t\), \(A\), \(\beta\), and \(g_1(t)\) are the time, baseline, coherence factor and normalized electric field-time correlation functions. This is related to the line-width distribution \(G(\Gamma)\) as,

\[
g_1(t) = \int_0^\infty G(\Gamma)e^{-\Gamma t} d\Gamma \quad (5)
\]
The normalized intensity-time correlation functions were measured at a scattering angle of 90° for 10 min at each temperature of interest. The correlations were analysed by Laplace inversion using CONTIN (Provencher, 1982) to obtain the hydrodynamic radius ($R_h$) by the Stokes–Einstein relation as,

$$R_h = \frac{k_B T}{6\pi\eta D}$$  \hspace{1cm} (6)

where $k_B$, $T$, $\eta$, and $D$ are the Boltzmann constant, absolute temperature, solvent viscosity and diffusion constant, respectively.

2.5. Small-angle X-ray scattering

SAXS measurements (high-resolution) of the microgel of concentration 1 wt % were performed at the Aarhus University SAXS facility (Pedersen, 2004). The NanoSTAR instrument (Bruker AXS) which is optimized for solution scattering uses a rotating anode as the X-ray generator and multilayer parabolic Gobel mirrors for monochromating the X-rays. The configuration of the instrument in the high-resolution (low-$q$) configuration provides a range of scattering vector moduli $q$ from 0.004 to 0.22 Å$^{-1}$ with a flux of about $10^6$ photons per second. In this configuration, the sample-to-detector distance was fixed at 106.70 cm. The X-ray beam was collimated using three small pinholes viz. 0.5 mm of source pinhole, 0.15 mm of defining pinhole and 0.5 mm of anti-scatter pinhole in front of the sample. The diameter of the beam-stop was 2.0 mm. The scattered X-rays were recorded on a two-dimensional position sensitive HiSTAR gas detector.

The microgel sample in water was placed in a home-built reusable quartz capillary sealed with stainless steel caps and O-rings. Measurements at various temperatures were performed by placing the capillary in a thermostated block that was controlled by Peltier element (Anton-Paar, Graz). Water was measured as background (solvent) and subtracted from the sample measurements. Water measured at 20°C was used for absolute normalization of the intensity.

2.6. Theory and data fitting

The SAXS experiments provide information on the intensity distribution $I(q)$ in reciprocal space as a function of scattering vector modulus or momentum transfer $q$. In order to extract the valuable real space information on the system from the SAXS data, a relevant model has to be used. The SAXS experimental data of the microgels in water was fitted using a model described by Stieger et al. (2004). In this model, the microgel structure is described by an average spherical form factor with a graded interface, a Lorentzian $I_{\text{fluct}}(q)$ describing the polymer scattering from the internal structure of microgels and a constant term $\text{const}_{\text{back}}$ describing the residual background. This is given as,

$$I(\langle q \rangle) = N\Delta\rho^2 \int_0^\infty D(R, \langle R \rangle, \sigma_{\text{poly}}) \times V_{\text{poly}}(R)^2 P_{\text{inho}}(q, R) dR dq + I_{\text{fluct}}(q) + \text{const}_{\text{back}}$$  \hspace{1cm} (7)

where $I$ is the scattering intensity, $N$ is the number density of particles, $\Delta\rho$ is the scattering length density difference between the polymer and solvent, $V_{\text{poly}}$ is the volume of polymer in a microgel, $\sigma_{\text{poly}}$ is the relative particle polydispersity and $\langle R \rangle$ is the average radius of the particle. $P_{\text{inho}}$ is the form-factor for microgels with fuzzy surface which is expressed as,

$$P_{\text{inho}}(q) = \left[ \frac{3}{(qR)^4} \left( \sin(qR) - qR \cos(qR) \right) \times \exp \left( -\frac{(\sigma_{\text{surf}}q)^2}{2} \right) \right]^2$$  \hspace{1cm} (8)

where $\sigma_{\text{surf}}$ is the width of the smeared particle surface.
A Gaussian distribution was used for describing the size polydispersity of the radius of microgels as,
\[
D\left(R, \langle R \rangle, \sigma_{\text{poly}}\right) = \frac{1}{\sqrt{2\pi\sigma^2(R)^2}} \exp\left(-\frac{(R - \langle R \rangle)^2}{2\sigma^2_{\text{poly}}(R)^2}\right)
\]
(9)
where \( \langle R \rangle \) is the average radius of the particle.

The fits were performed on absolute scale and the normalization of the model was performed as described by Stieger et al. (2004). Excess electron density and SAXS contrasts were calculated as function of temperature from the reported density. The number average molar mass of the particles were calculated for each temperature. As this value has to be conserved during the fitting of data, it was used as a constraint.

The SAXS data are influenced by instrumental smearing. This was included in the analysis by smearing the model intensities by the instrumental resolution function (Pedersen, Posselt, & Mortensen, 1990) for which the parameters were determined by estimating the width of the direct beam on the detector (Pedersen, 1993). Radial volume fraction of polymer distributions for the average particles were calculated by Fourier transforming the model scattering amplitude for the average particles (Arleth, Xia, Hjelm, Wu, & Hu, 2005) and \( z \)-average values for the radius of gyration of the model was calculated for comparison with the corresponding values determined from the Zimm analysis of the SLS data.

3. Results and discussion

3.1. Synthesis of microgels

The microgels were synthesized using the hydrophobic crosslinker 1,4-diacryloylpiperazine by precipitation emulsion polymerization at 75°C which is well above the LCST of PNIPAM. Upon addition of the free-radical initiator, the reaction mixture turned opaque and finally became turbid indicating the formation of microgels. During polymerization at this temperature, the crosslinker reacts more rapidly and is consumed faster than NIPAM. This leads to the formation of microgels with heterogeneous internal structure due to non-uniform distribution of crosslinker in the radial direction (Deen et al., 2011; Senff & Richtering, 1999; Varga et al., 2001). As a result the microgels results in core-shell morphology and is illustrated in Figure 1(B). The surfactant concentration was fixed at 2.8 mM. The presence of SDS in the emulsion polymerization of microgels increases the colloidal stabilization against flocculation of precursor particles and lowers the size of primary particles as the number of particles increases. High SDS concentration would shift the system closer to a good-solvent condition with significant impact on the structure of the microgels (Andersson & Maunu, 2006; McPhee et al., 1993; Wu, Pelton, Tam, Woods, & Hamielec, 1993).

3.2. Characterization of microgels by light scattering below the LCST

The molecular and thermodynamic parameters of the microgels in water at 23°C were measured by SLS and DLS techniques. SLS measurements enabled the determination of the weight-average molar mass \( (M_w) \), the radius of gyration \( (R_g) \) and the second-virial coefficient \( (A_v) \), whereas DLS gives the hydrodynamic radius \( (R_h) \) of the microgels.

At this temperature which is below the LCST of PNIPAM, the microgels are in their fully swollen state and the following values were determined according to the Zimm approximation, \( M_w = 2.7 \times 10^8 \text{ g mol}^{-1} \), \( R_g = 94 \text{ nm} \), \( R_h = 132 \text{ nm} \) and \( A_v = 7.14 \times 10^{-9} \text{ mol dm}^{-3} \text{ g}^{-2} \). The Zimm plot for the microgel dispersion in water at 23°C is shown in Figure 2. The microgels have a very high molar mass as a result of emulsion polymerization. Emulsion polymerization in general, leads to polymers with very high molar mass and this has been reported for various systems (Deen et al., 2011; Senff & Richtering, 1999; Varga et al., 2001).
3.3. Influence of temperature on structural changes of microgels and the role of crosslinker

The effect of temperature on the collapse of the microgels was measured both by light scattering and SAXS techniques. The intensity-time correlations as function of temperature are shown in Figure 3. The correlations shift towards the left with increase in temperature and a single decay mode is observed at all measured temperatures indicating a monomodal distribution of microgels. The shift of the correlation to shorter time reflects the shrinking of microgel from its fully swollen state ($T < \text{LCST}$) (Gao & Frisken, 2003). In the fully swollen state, the microgel experiences a slower diffusion rate exhibiting a large decay time. The decay time is related to the diffusion of microgels by the expression,

$$\frac{1}{\tau} = D_m q^2$$  \hspace{1cm} (10)

where $D_m$ is the collective translational diffusion coefficient and $q$ is the magnitude of the scattering vector. In the collapsed state ($T > \text{LCST}$), the microgels owing to its small size diffuses faster leading to the observed shorter decay time.

The change in $R_g$ as function of temperature for the microgels is shown in Figure 4. A decrease in $R_g$ with increase in external temperature is clearly evident reflecting the thermo-responsive property.
of the microgels. At 20°C, which is far below the LCST of PNIPAM, the microgels show a maximum \( R_h \) of 119 nm which corresponds to the fully swollen size. In the temperature region 30-35°C, which corresponds to the transition temperature region of PNIPAM, the microgels show a considerable size reduction due to the discrete volume-phase transition (Tanaka, 1981). Above the transition temperature (\( T > \text{LCST} \)), the \( R_h \) of the microgels is 57 nm. This reduction in the size of the microgels from the fully swollen state amounts to a twofold decrease.

Above the LCST, the microgels are most likely to be stabilized against aggregation by electrostatic repulsion between the fractional anionic surface groups arising from the polymerization initiator (potassium peroxodisulfate) fragments (Deen et al., 2011; Senff & Richtering, 1999; Stieger et al., 2004). Further, the concentration of the microgels in water for the light scattering measurements was only 0.01 wt %. In this very low concentration regime, a macroscopic phase separation was not observed.

The temperature induced phase transition of the microgels can be accounted based on the chemical structure of the monomer/crosslinker and Gibbs' free energy relationship (Flory & Rehner, 1943) as,

\[
\Delta G = \Delta H_m - T \Delta S_m
\]

where \( \Delta H_m \), \( \Delta S_m \), and \( T \) are the enthalpy of mixing, entropy of mixing and temperature, respectively.

The core of the microgels contains PNIPAM which is a temperature-sensitive polymer and the crosslinker. Based on the chemical structure of the polymer, the –CONH– groups are hydrophilic and readily forms hydrogen bonds with water molecules and the –CH(CH₃)₂ groups are hydrophobic in nature. The crosslinker is a diamide with two carbonyl (CO) groups each of which is linked to a tertiary nitrogen. Although a hydrophilic nature is expected for this molecule, in contrast, it is hydrophobic in nature due to the presence of the heterocyclic ring that contains four methylene groups.

At \( T < \text{LCST} \), the strong hydrogen bonding between the hydrophilic groups and water overcomes the unfavourable free energy related to the exposure of hydrophobic groups to water leading to a fully swollen state of the microgels with a large average \( R_h \). As the temperature is increased, water becomes a poor solvent leading to increased interaction between the hydrophobic groups of the polymer and crosslinker. At \( T > \text{LCST} \), the hydrophobic interactions become dominant leading to an
entropy-driven collapse of the polymer chains (Feil, Bae, Feijen, & Kim, 1993). Such transitions are usually referred as the coil-to-globule type transition of linear polymers. During the collapse of the polymer, the heat capacity of the system also decreases sharply and such volume-phase transition is well documented in the literature for various stimuli-responsive polymer systems (Chilkoti, Chen, Stayton, & Hoffman, 1994; Feil et al., 1993; Gan, Gan, & Deen, 2000; Schild, 1992).

The change in the radius of gyration $R_g$ for the microgels as function of temperature was also measured and is shown in Figure 5. The $R_g$ decreases with increase in temperature and the trend is similar to that of $R_h$ change. The $R_h$, however, is larger than $R_g$ for microgels due to the dangling chains that are hardly detected by SLS but contribute to the diffusion coefficient. In the temperature region 30–31.3°C a sharp decrease is clearly evident. For a very small variation in temperature of 1.3°C, a large change in $R_g$ of about 19% is observed reflecting the temperature-responsive collapse of the microgels.

Combining the experimental data measured by SLS and DLS, the structural information of microgels can be obtained. The ratio $R_g/R_h$ defined as the shape factor is a sensitive tool for monitoring the changes in the density profiles of the microgels (Arleth et al., 2005; Senff & Richtering, 2000; Stieger et al., 2004). A plot of the shape factor as function of temperature is shown in Figure 6. The shape factor...
factor values are in the range between 0.728 and 0.981 for temperatures below and above the LCST, respectively. In the case of monodisperse hard spheres of constant polymer density, the shape factor is equal to 0.775, while in the case of random polymer coils it varies between 1.50 and 1.78 based on thermodynamic solvent quality (good solvent or poor solvent conditions).

Below the LCST, the shape factor of the microgels is smaller than that of the hard spheres as observed in Figure 6. These small values are typical for swollen microgels of low crosslink density (Gilányi et al., 2000; Varga et al., 2001). Due to this low crosslink density, the microgels contain a dense inner core and an outer less dense surface layer (corona). At low crosslink density, the length of polymer chains dangling on the surface of the crosslinked core increases.

The structural morphology of the microgels is determined by the ratio of the length of dangling polymer chains to the radius of crosslinked core. This ratio is strongly dependent on the distribution and the type of chemical crosslinker in the microgels. In general, the structure of microgels can be varied by varying the extent of crosslinking (Lin, Chiu, & Lee, 2005; Varga et al., 2001).

Near the LCST of microgels (32°C), a drop in the value of shape factor is clearly observed in Figure 6. This is attributed to the large fluctuations in the system close to the LCST which leads to an apparent increase in polydispersity and this effect has been observed for PNIPAM microgels crosslinked with MBA which is a hydrophilic crosslinker (Arleth et al., 2005; Deen et al., 2011). This lower value further indicates a non-uniform internal structure of the microgel above the transition temperature where it is in a collapsed state.

3.4. SAXS investigation on the temperature induced structural changes of the microgels

The SAXS data along with the fit (solid line) for the microgels below, at, and above the LCST is shown in Figure 7. A very large change in the scattering intensity with temperature is clearly observed. The forward scattering is higher at temperatures below the LCST, due to the large excess electron density of the PNIPAM microgels. A large size difference of the microgels at various temperatures is also clearly evident from the forward scattering intensity and the Guinier region. In addition, the Porod power-law scattering is beyond $q = 0.012 \text{ Å}^{-1}$ and is also observed above the LCST. At 25°C ($T < \text{LCST}$) the microgels are in a fully swollen state and contributes significantly to polymer scattering. At 40°C ($T > \text{LCST}$) the microgels are in a collapsed and compact state with a sharp interface.

The model fits the experimental data very well at all temperatures as shown in Figure 7, and the fit parameters obtained are summarized in Table 1. The $\chi^2$ which represents the quality of fit to the experimental scattering data are 1 and below. The relative polydispersity ($\sigma_{rel}$) above the LCST was 33% which is higher than the values reported for larger PNIPAM microgels with MBA as crosslinker. The fuzziness of the microgel surface described by $\sigma_{surf}$ decreases as the temperature is increased.

Below the LCST (25°C) the $\sigma_{surf}$ is 14.2 nm and around the LCST (30°C) it decreases to 13.1 nm. Above the LCST (32°C), the surface of the microgel sharpens and $\sigma_{surf}$ significantly drops to 2.2 nm. This corresponds to a density profile which resembles a box profile of a homogeneous sphere. Interestingly, only a small decrease of the radius of microgel is observed when the temperature is increased from 30 to 40°C. It can thus be concluded that the swelling (changes in structural parameters of the outer region) is dominated by the swelling of the outer regions of the microgels. The core of the microgel exhibits a higher crosslinking density than the outer region due to the presence of crosslinker, and its type and amount does play a role in controlling the overall swelling.

The overall radius of the microgels obtained by SAXS is smaller than the hydrodynamic radius $R_h$ obtained by DLS. This is attributed to the few dangling polymer chains that are attached to the surface of microgels. These dangling polymer chains contribute to the hydrodynamics of the microgels. The concentration of these chains is not high to be detected by SAXS.
Figure 7. SAXS scattering profiles of the microgel dispersion in water at various temperatures. The solid lines represent fits according to Equations 7–9.

Table 1. Microgel parameters obtained by fitting the experimental SAXS data according to the model

| Temperature (°C) | R (nm) | σ_{surf} (nm) | σ_{rel} | ϕ_{poly} | χ²   |
|-----------------|--------|---------------|---------|----------|------|
| 15              | 80.4   | 14.2          | 0.12    | 0.09     | 1.08 |
| 25              | 64.0   | 14.2          | 0.14    | 0.17     | 0.76 |
| 30              | 51.0   | 13.1          | 0.21    | 0.27     | 1.09 |
| 35              | 33.8   | 2.2           | 0.33    | 0.61     | 0.83 |
| 40              | 33.1   | 0.5           | 0.33    | 0.67     | 0.98 |
The radial volume fraction profiles of the average microgels determined using Equations 7–9 is shown in Figure 8. At 20°C, the microgels are in a fully swollen state with a broad graded outer surface. The volume fraction of polymer in the core of the microgel is about 15% at 20°C, while at 40°C the volume fraction in the core increases to 60%.

The amount of polymer in the core is higher than that reported for PNIPAM microgels crosslinked with a flexible and hydrophilic crosslinker MBA (Stieger et al., 2004; Varga et al., 2001). This increase in volume fraction of the core is attributed to the chemical nature of the crosslinker.

The stiff and hydrophobic crosslinker tries to push much of the water from the core of the microgel during collapse. Hydrophilic crosslinkers tend to increase the swelling of gels while hydrophobic crosslinkers reduces the amount of swelling. Although the crosslink density is an import factor that influences swelling, the nature of crosslinker is another factor to be considered. The swelling behaviour can thus be controlled by using a stiff and hydrophobic crosslinker at low crosslinking density. Hence the type and amount of crosslinking density greatly affects the morphology and swelling characteristic of microgels (Amalvy et al., 2004; Gürdağ & Kurtulus, 2010; Mathur, Moorjani, & Scranton, 1996; Sahiner, Godbey, McPherson, & John, 2006; Varga et al., 2001).

4. Conclusion

In this study, we have investigated the structure and temperature-responsive properties of PNIPAM microgels crosslinked with a stiff chemical crosslinker at low crosslinking density. The dynamics of collapse of the microgels as a function of temperature were characterized by light scattering and SAXS in the high-resolution set-up. Below the LCST, the shape factor of the microgels was smaller than that of hard spheres due to low crosslinking density. The volume fraction of polymer in the core of the microgels above the LCST was about 60%. This increase in volume fraction of polymer in the core compared to microgels crosslinked with hydrophilic crosslinker is attributed to the chemical nature of the new crosslinker. Hence the swelling behaviour of microgels can be significantly altered by chemical nature of the crosslinker. Responsive microgels with controlled swelling pattern can be achieved even at low crosslinking density by using a stiff and hydrophobic chemical crosslinker.
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