Characterisation of monodisperse poly(*N*-isopropylacrylamide) microgel particles

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Poly(*N*-isopropylacrylamide) microgel particles prepared by emulsion polymerisation in the presence of anionic surfactant have been investigated in different media in the swollen and collapsed state by static and dynamic light scattering measurements. The microgel latex was found to be highly monodisperse. The particle scattering function fits well to the theoretical function of a sphere. The hydrodynamic diameter of the particles is significantly higher than the diameter calculated from the measured radius of gyration for a sphere of constant density. The discrepancy was interpreted by a core/shell structure of the microgel particles. If the particles are in the collapsed state the two kinds of diameter coincide with each other, indicating that the microgel particles are compact spheres. In the globular state the gel still has 39% (w/w) water content. The particles bear a small surface charge resulting in a long-range electrostatic interaction between the particles in an aqueous environment. It was observed for the first time that at a sufficiently low ionic strength the aqueous microgel particle system undergoes an ordered/disordered phase transition.

Introduction

Several studies have been reported in the last decade on smart materials capable of varying their physical properties in response to environmental changes.[1] In particular stimuli-responsive hydrogels, which can change their swelling and shrinking in response to external stimuli, have become noteworthy intelligent materials that can be tailored to a variety of biomedical and engineering applications. The discovery of a discontinuous volume phase transition in gels, which is often called a collapse transition, has rendered such soft materials technologically useful.[2] The stimuli that have been investigated to induce changes in polymer gels are diverse, and they include temperature, pH, solvent and ionic composition, electric field, light intensity and an introduction to specific molecules. These gels can be utilised in mechanical devices or controlled release delivery and separation systems.[3] In particular, pulsatile drug release (on–off release) has attracted much attention recently.

Poly(*N*-isopropylacrylamide) hydrogel, abbreviated as PNIPAM gel, is one of the most frequently studied temperature responsive hydrogels. PNIPAM gels have negative thermosensitivity, *i.e.* they exhibit a remarkable shrinking with increasing temperature. A non-continuous collapse transition takes place around 34 °C. These gels are often used to immobilise enzymes and as carriers of certain functional groups important for biochemical or biomedical applications.[4] The gels are heated either by a surrounding heat source or internally by an electromagnetic field to control the degree of swelling and thus the release rate. In order to achieve a well controlled drug release (or uptake) it is of great importance to control the swelling and shrinking kinetics. The structure of the microgel particles also plays an important role in the swelling properties. Theories of microgel swelling assume a uniform crosslink density; however, the mechanism of micro-gel formation suggests an inhomogeneous inner particle structure.[5] The question of the inner particle structure has not yet been settled:[6] only a few controversial experimental results dealing with the topic are available. In an early study on PMMA microgels[7] Nieuwenhuis and Vrij calculated different particle diameters from the radius of gyration (static light scattering) and from the diffusion coefficient (dynamic measurements), from which it could be concluded that the segment density in the microgel spheres is not distributed homogeneously. More recently Wu *et al.*[8] calculated the same diameter of PNIPAM microgel particles from static and dynamic light scattering, leading to the opposite conclusion.

The aim of this work was to characterise the shape, structure and electrical properties of PNIPAM microgel particles, important parameters in both the swelling and colloidal behaviour of these systems.

Experimental

Preparation of PNIPAM microgel beads

For the preparation *N*-isopropylacrylamide (NIPAMM), methylene bisacrylamide (BA), ammonium persulfate (APS) and sodium dodecyl sulfate (SDS) were used. These chemicals were provided by Aldrich and were used for the preparation without further purification. Our procedure was based on the method developed by Wu *et al.*[9] 7 g of NIPAMM, 0.7 g of BA and 94 mg of SDS were dissolved in 470 ml of distilled water. The temperature of the reactor was kept at 60 °C and the solution was intensively stirred. In order to remove oxygen, nitrogen gas was purged through the solution for 30 min. Then 0.14 g of APS dissolved in 30 ml of water was mixed with the solution, followed by intensive stirring for 4 h. The PNIPAM latex was purified from unreacted monomers and surfactant by dialysis against distilled water for 4 weeks.

Static and dynamic light scattering measurements

Static and dynamic light scattering measurements were performed by means of Brookhaven dynamic light scattering equipment consisting of a BI-200SM goniometer and a BI-9000AT digital correlator. An argon-ion laser (Omnichrome, model 543) operating at 488 nm wavelength and emitting vertically polarised light was used as the light source. The signal analyser was used in the real-time 'multi tau' mode. In this mode the time axis was logarithmically spaced over a time interval ranging from 0.1 µs to 0.1 s and the correlator used 218 time channels. The pinhole was 100 µm.

Time averaged scattered light intensities were measured at scattering angles from 20 to 155° at different microgel concentrations. The reduced scattering intensities R_ϑ were calculated according to standard procedures using benzene as reference with a known absolute scattering intensity (3.86×10^{-5} cm^{-1}). The volume-corrected scattering intensities of the benzene varied by less than $\pm 2\%$ in the angular range from 20 to 155°, demonstrating the good calibration of the instrument. A back scattering correction was also applied for the asymmetrically scattering microgel samples.

The microgel samples were cleaned of dust particles by filtering through a 0.8 µm pore-size sintered glass filter.

Data analysis

In the dynamic light scattering experiments the intensity–intensity correlation function $g_2(\tau)$ was measured (homodyne method), and was converted into the normalised electric field autocorrelation function $g_1(\tau)$ by means of the Siegert relation:

$$bg_1^2(\tau) = [g_2(\tau) - A]/A \qquad (1)$$

where A is the experimentally determined baseline and b ($0 < b < 1$) is a constant that depends on the number of coherence areas seen by the detector. $g_1(\tau)$ is related to the distribution of relaxation rates $G(\Gamma)$ through a Laplace transformation:

$$g_1(\tau) = \int_0^\infty G(\Gamma)\exp(-\Gamma t)\mathrm{d}\Gamma \qquad (2)$$

where Γ is the relaxation rate. Since the recovery of $G(\Gamma)$ from the experimentally determined $g_1(\tau)$ is an ill-posed problem, several numerical methods have been developed for the analysis of the measured autocorrelation function. In this work we used the cumulant expansion, which gives reliable results in the case of a narrow distribution of Γ. This method has the advantage of getting $\bar{\Gamma}$ and $\mu_2 = \int (\Gamma - \bar{\Gamma})^2 G(\Gamma)\mathrm{d}\Gamma$ (the so-called first and second cumulants) without any knowledge about $G(\Gamma)$.

If the intensity fluctuation of the scattered light is due to the translational motion of the particles the mutual diffusion coefficient can be calculated from the mean relaxation rate as

$$D_{\mathrm{m}} = \bar{\Gamma}/q^2 \qquad (q \to 0) \qquad (3)$$

where $q = (4\pi n/\lambda_0)\sin(\vartheta/2)$, n is the refractive index of the solution, λ_0 is the wavelength of the incident light in a vacuum and ϑ is the scattering angle. The diffusion coefficient, D_0, is determined by the following relation:

$$D_{\mathrm{m}}(c) = D_0(1 + k_{\mathrm{s}} c) \qquad (c \to 0) \qquad (4)$$

in which c is the particle concentration and k_{s} is a constant. In case of spherical particles D_0 is related to the hydrodynamic diameter of the particles d_{h} through the Stokes–Einstein relation

$$D_0 = \frac{kT}{3\pi\eta d_{\mathrm{h}}} \qquad (5)$$

where k is the Boltzmann constant, T is the temperature and η is the viscosity of the medium.

Static light scattering data are usually analysed in terms of the classical Zimm equation, yielding the weight averaged molecular weight (M_{w}), the z-mean of the square of the radius of gyration (ρ_z^2) and the second virial coefficient (A_2) as the result of the analysis

$$\frac{Kc}{R_\vartheta} = \frac{1}{M_{\mathrm{w}}}\left(1 + \frac{q^2}{3}\rho_z^2\right) + 2A_2 c \qquad (c \to 0,\ \vartheta \to 0) \qquad (6)$$

where $K = [2\pi n_0(\mathrm{d}n/\mathrm{d}c)]^2 N_{\mathrm{A}}^{-1}\lambda_0^{-4}$, c is the concentration of the particles, $\mathrm{d}n/\mathrm{d}c$ is the refractive index increment and N_{A} is the Avogadro number.

The angular dependence of the reduced scattering intensity often contains further information on the particle shape. In general R_ϑ can be given in the following form for monodisperse system

$$R_\vartheta = KcMP_\vartheta S_\vartheta \qquad (7)$$

where P_ϑ is the particle scattering function (characteristic for the particle shape) and S_ϑ is the structure factor (determined by the particle–particle interactions).

More detailed discussions on light scattering theory are available in several textbooks.[10–12]

Electrokinetic measurements

The electrophoretic mobility of the microgel particles was determined by laser Doppler electrophoretic equipment (Malvern Zeta Sizer, Version PCS). The measurements were performed at well defined ionic strengths of 5×10^{-4} and 1×10^{-3} M adjusted by NaCl solution. The gel was found to be negatively charged. The electrophoretic mobility was $(-1.45 \pm 0.046) \times 10^{-4}$ and $(-0.903 \pm 0.035) \times 10^{-4}$ cm^2 V^{-1} s^{-1} at 5×10^{-4} and 1×10^{-3} M ionic strength, respectively. The mobility of the ion-exchanged gel particles was -2.05×10^{-4} cm^2 V^{-1} s^{-1}. At 1×10^{-3} M NaCl concentration practically the same mobility (-1.0×10^{-4} cm^2 V^{-1} s^{-1}) was measured by Snowden et al.[13] on PNIPAM latex particles prepared with carboxy initiator.

Determination of the analytical charge

The total analytical charge of the gel particles was determined by conductometric titration of the latex with NaOH solution. Prior to the titration the microgel sample was purified by mixed bed anion–cation exchange,[14] in a similar method to that used in the case of latex dispersions for the elimination of ionic contaminants and to convert the latex into an acidic form. The charge of the microgel particles was found to be 1.6×10^{-6} mol negative charges per g dry gel.

Results and discussion

In Fig. 1 the unnormalized autocorrelation functions measured at 90° scattering angle are plotted for PNIPAM gel samples in methanol and water at 25 and 40 °C. The autocorrelation functions plotted against $q^2\tau$ were found to be independent of the scattering angle (measured at 20, 90 and 155°), indicating that in the delay time range investigated the intensity fluctuation originates from the translational motion of the gel particles. The $g_1(\tau)$ function was also independent of the gel concentration in the very dilute concentration range investigated (from 1×10^{-5} to 2×10^{-4} g cm^{-3}); therefore, the extrapolation of D_{m} to $c = 0$ to determine D_0 was omitted [eqn. (4)].

The cumulant analysis of the autocorrelation functions indicates an extremely narrow size distribution of the gel particles. The second cumulant yields $p = 0.02 \pm 0.01$ polydispersity. The gel particles can be well characterised with a single relaxation time or diffusion coefficient. In Table 1 the diffusion coefficients in different media and the hydrodynamic diam-
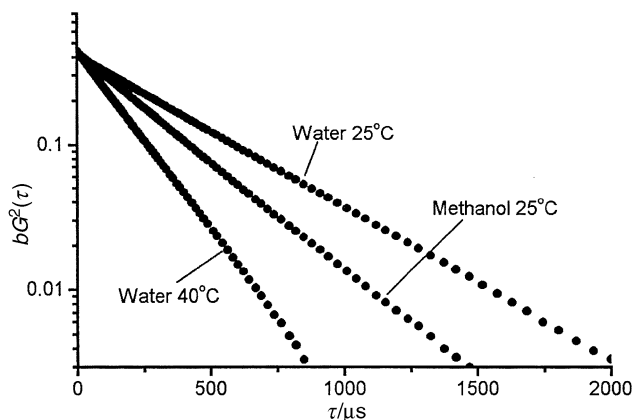
Fig. 1 Autocorrelation functions of the PNIPAM microgel latex in different media.

eters of the gel particles d_h calculated from eqn. (5) are collected.

The hydrodynamic diameter of the microgel particles was also calculated from viscosity measurements by means of the following relation:

$$[\eta] = 2.5 \frac{V_h N_A}{M} = \frac{2.5\pi N_A}{6M} d_h^3 \qquad (8)$$

where $[\eta]$ is the intrinsic viscosity and V_h is the hydrodynamic volume of the particles. $[\eta]$ ($= 15.6 \pm 0.3$ cm^3 g^{-1}) was determined by a capillary viscosimeter at 25 °C in the presence of 0.1 M NaCl to eliminate the electroviscous effect. The η_{sp}/c vs. c relation was linear in the concentration range measured from 3×10^{-3} to 1.7×10^{-2} g cm^{-3}, from which η_{sp}/c was extrapolated to $c = 0$ to determine $[\eta]$. The dilute latex solution behaves as a Newtonian liquid, as confirmed by stress vs. shear rate measurements with a HAAKE RheoStress RS100 rheometer. The hydrodynamic diameter from the viscosity measurement was found to be $d_h = 224$ nm. This value is in good agreement with that measured by dynamic light scattering (within 5%).

At room temperature in aqueous medium the microgel particles are in a swollen state. Increasing the ionic strength by dissolving salts does not influence the size of the particles considerably (Table 1). This suggests that the PNIPAM gel is electrically neutral, as expected from its chemical structure, and its swelling characteristics are governed by non-electrostatic interactions. The slight decrease (2%) in diameter in the presence of 0.1 M NaCl can be attributed to a change of solvent quality rather than to electrostatic interactions. However, electrokinetic measurements show that the PNIPAM gel particles are electrically charged. Since the ionic strength of the aqueous medium does not influence the swelling of the particles it can be expected that the electrical charges are located in the surface layer and the core of the particles is neutral. Evidence of this electric structure will be given below.

In water the PNIPAM gels have a lower critical temperature[15] (around 34 °C) at which the gel network collapses. Because of this effect, on increasing the temperature to 40 °C the diameter of the gel particles significantly decreases from 240 to 140 nm, corresponding to an 80% change in the volume of the particles.

When the medium of the microgel latex is changed from water to methanol or ethanol, the particles swell further, indicating that methanol and especially ethanol is a better solvent for the PNIPAM polymer than water at 25 °C. McPhee et al.[5] and Crowther and Vincent[16] showed that the PNIPAM gel latex first collapses and then swells again with increasing alcohol concentration.

In Fig. 2 a Zimm plot of the static light scattering data is given for PNIPAM gel in methanol at 25 °C. The scattered light intensity shows a very strong dependence on the scattering angle and is almost independent of the gel concentration. Similar Zimm plots were found when the medium was water.

The strong angular dependence of the scattering data gives an opportunity for the analysis of the shape of the microgel particles on the basis of eqn. (7). The application of this equation is justified by the dynamic light scattering measurements that indicated highly monodisperse microgel samples. The experimental P_ϑ functions can be determined by extrapolating Kc/R_ϑ to zero particle concentration (when $S_\vartheta = 1$).

In Fig. 3 an experimentally determined P_ϑ function (in water at 25 °C) is shown together with three theoretical ones for different particle shapes (monodisperse spheres, coils and rods, respectively).
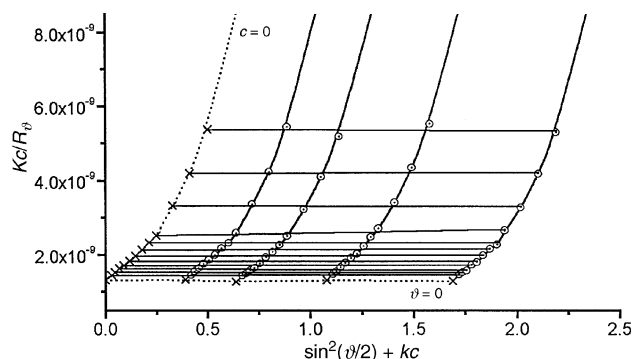
Fig. 2 Zimm plot of the PNIPAM microgel latex in methanol at 25 °C.
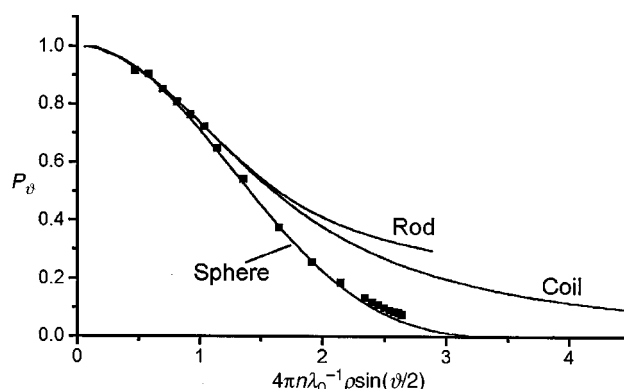
Fig. 3 Comparison of the experimental P_ϑ function calculated from static measurements in methanol at 25 °C with the theoretical ones for different particle shapes.

Table 1 Diffusion coefficient and hydrodynamic diameter of the microgel particles in different media

Medium	$D_0/10^8$ cm^2 s^{-1}	d_h/nm
Water (25 °C)	2.037 ± 0.016	240.6 ± 1.8
2×10^{-3} M La(NO$_3$)$_3$ (25 °C)	2.032 ± 0.024	240.5 ± 2.9
0.1 M NaCl (25 °C)	2.074 ± 0.011	235.5 ± 1.3
Water (40 °C)	4.857 ± 0.091	140.4 ± 2.4
Methanol (25 °C)	2.973 ± 0.033	270.1 ± 3.1
Ethanol (25 °C)	0.957 ± 0.016	424.7 ± 7.2

$$P_\vartheta(X) = \left(\frac{3}{X^3} \{ \sin(X) - X \cos(X) \} \right)^2$$

$$\left(\text{for spheres}; \ X = q\sqrt{\frac{20}{12}} \rho_z \right) \quad (9a)$$

$$P_\vartheta(X) = \left(\frac{2}{X^4} \{ \exp(-X^2) + X^2 - 1 \} \right)$$

$$(\text{for coils}; \ X = q\rho_z) \quad (9b)$$

$$P_\vartheta(X) = \frac{2}{X} \int_0^X \frac{\sin Z}{Z} \, dZ - \left(\frac{2}{X} \sin \frac{X}{2} \right)^2$$

$$(\text{for rods}; \ X = q\sqrt{12}\,\rho_z) \quad (9c)$$

The theoretical curves were calculated using the radius of gyration (ρ_z) determined from the Zimm diagram. As Fig. 3 shows, the measured P_ϑ function fits the P_ϑ function of spheres well, though there is a small but increasing deviation at larger angles. A possible explanation of this small discrepancy will be discussed below.

In order to improve the evaluation of the static light scattering measurements we applied a fitting procedure in which eqn. (7) was directly fitted to the experimental data. In this fitting procedure closed analytical P_ϑ and S_ϑ functions for well defined particle shapes (spheres and coils) were used. The applied S_ϑ functions

$$S_\vartheta = 1 - 2A_2 Mc \qquad (\text{sphere}) \quad (10a)$$

$$S_\vartheta = 1 - 2A_2 M P_\vartheta c \qquad (\text{coil}) \quad (10b)$$

were based on the assumption that strong long-range interactions did not exist among the particles. Reasonable fits could be reached only for spheres. The results of the calculations are summarised in Table 2, while an example for the fitted data is given in Fig. 4 (in water at 25 °C). In the third row of Table 2 the diameter of the gel particles, d, calculated
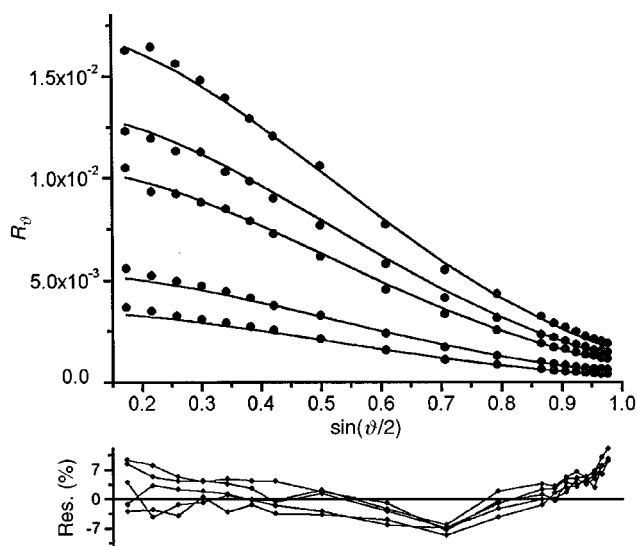

Fig. 4 Fitting of experimental data (water, 25 °C) to eqn. (7) in the case of spheres.

from the experimental radius of gyration for a sphere of constant density is given. d is called here the "optical" particle diameter in order to distinguish it from the hydrodynamic diameter (d_h) listed in the last row of the table. At 25 °C the optical diameter of the particle is significantly smaller than that of the hydrodynamic one both in methanol and water. On the other hand in these cases systematic deviations could be observed between the measured and fitted R_ϑ curves (Fig. 4). According to electron micrographs the microgel particles have spherical symmetry; consequently, these deviations must reflect that the local density of the polymer within the gel particles is not constant. One may suppose a radially decreasing density function, or a crosslinked core with a higher density and a looser shell around it. The latter supposition is more rational because, depending on the degree of crosslinking, longer or shorter polymer strands, which can freely conform in good solvent, are expected to cover the surface of the particle. However, when the gel network collapses due to the stronger segment–segment interactions above the critical temperature, the microgel particles form a compact sphere. This is reflected by the measurements performed at 40 °C, where the hydrodynamic and 'optical' size of the gel particles practically coincide with each other and the systematic deviation between the measured and fitted R_ϑ function also vanishes. Nieuwenhuis and Vrij arrived at a similar conclusion from static and dynamic light scattering measurements concerning the structure of polymethylmethacrylate microgel particles in benzene.[7]

By combining the results of the static and dynamic measurements the mean polymer segment density in the microgel particles was calculated. At 25 °C in water the mean polymer concentration within the hydrodynamic particle volume ($M/N_A/V_h$) is 0.13 g cm^{-3}. At 40 °C in the collapsed state it is 0.66 g cm^{-3}. In order to calculate the water content of the gel particles the specific volume of the polymer in the latex was determined from density measurements of the latex as a function of the latex concentration. The density measurements were performed by the oscillating capillary method using an AP PAAR density measuring cell. The specific volume of the PNIPA was found to be 0.862 and 0.877 cm^3 g^{-1} in water at 25 and 40 °C, respectively. At 40 °C in the collapsed state the particles still contain 39% (w/w) water. Whu et al.[8] estimated a significantly higher (70%) water content of the collapsed gel at 35 °C.

The second virial coefficient is around zero in methanol: the particles are in a pseudo-ideal state where the excluded volume effects are compensated by attractive forces acting between the particles. In water A_2 has a small positive value, which means that the overall interactions between the particles are repulsive. This is an apparent contradiction to the conclusion that can be drawn from the decrease of both the hydrodynamic and optical particle size when the medium is changed from methanol to water. The latter suggests that A_2 should be negative in water if it is zero in methanol. However, A_2 characterises the interactions between the gel particles as colloid entities and not those of the polymer segments, which govern swelling. An extra force, repulsive in nature, must act between the particles in water. Since the microgel particles are electrically charged in aqueous medium the electrical interactions can account for the repulsion and for the positive second virial coefficient.

Table 2 Results of static light scattering measurement on PNIPAM microgel in different media

Medium	ρ/nm	d/nm	$A_2/10^{-7}$ mol cm^3 g^{-2}	$M/10^8$ g mol^{-1}	d_h/nm
Methanol (25 °C)	81.5 ± 0.5	210.3 ± 1.3	−5.1 ± 4.2	5.69 ± 0.08	270.1 ± 3.1
Water (25 °C)	73.6 ± 0.3	190.0 ± 0.7	8.5 ± 2.3	5.86 ± 0.07	240.6 ± 1.8
Water (40 °C)	55.6 ± 0.2	143.6 ± 0.6	—	—	140.4 ± 2.4

For small potentials the relation between surface charge density σ and surface potential ϕ_0 can be approximated as[17]

$$\sigma = \varepsilon \kappa \phi_0 \left(1 + \frac{1}{\kappa a}\right) \tag{11}$$

where ε is the static permittivity of the medium, κ is the Debye–Hückel inverse screening length and a is the particle radius. If we apply eqn. (11) for the hydrodynamic particle ($a = d_h/2$ and ϕ_0 is the electrokinetic potential) then the electrokinetic charge or surface charge density of the hydrodynamic particle can be estimated. The electrokinetic potential is -11.45 mV at 1 mM ionic strength, which yields 0.09 μC cm^{-2} (corresponding to 10^3 charges per particle) charge density. This charge density is very small, generally one order of magnitude larger for polystyrene latex particles and two magnitudes larger for ionic surfactant micelles. The surface charge density of the hydrodynamic particle calculated from the analytical charge of the particle is 0.08 μC cm^{-2}. The analytical and hydrodynamic charges of the particles practically fall in the same range. If the charges were distributed inside the gel particle (in its bulk) the electrokinetic charge should be much smaller than the analytical one because most of the charges would be screened inside the particles. Therefore, it can be concluded that the charges originating from the initiator[18] are at the surface of the particles, probably on the terminal groups of free polymer chains located in the surface layer.

This result also explains why the ionic strength of the aqueous medium does not influence the swelling of the microgel particles but plays an important role in the particle–particle interactions. This was proved by Snowden et al. by stability measurements on gel particles.[13] The latex can not be flocculated by electrolytes at room temperature due to the steric stabilization[19] and/or the negligibly small van der Waals attractive forces acting between the very loose gel particles. At 40 °C, when the particles shrink due to the increased segment density, the dispersion forces are strong enough to flocculate the microgel latex by adding electrolytes.

If the microgel particles are monodisperse and electrically charged it can be predicted that due to the long range electrostatic interactions the dilute microgel latex may undergo an ordered/disordered phase transition under appropriate conditions. This prediction was checked by decreasing the ionic strength, thus increasing the effective length of the electrical interparticle interactions of the latex dispersion by means of ion exchange. It was found that at a certain stage of the ion exchange process an ordered crystalline phase formed in the microgel sample showing iridescence which is typical of ordered structures if the interparticle distance is comparable to the wavelength of the visible light. The characteristic colour spectrum of the ordered phase changes with the temperature.

In some respects the liquid crystalline microgels differ from ordinary latexes of compact particles, e.g. from polystyrene (PS) latex. While the ordered phase of the PS latex is microcrystalline, in the microgel latex the formation of huge single crystals of several millimetre in size can be observed. The crystals are very labile. Small mechanical disturbances, e.g. a gentle shaking of the test tube, are enough to destroy them, then in the resting tube the crystals slowly reform. This lability can be explained by the very weak electrostatic interactions that result from the very small surface charge density. The amount of the ordered phase strongly depends on the temperature. At 10 °C in a 1.7% microgel latex visually the total volume of the ion-exchanged sample is in the ordered state. At 25 °C about 1/10 of the sample height from the bottom is filled with crystals and at around 27–28 °C (still below the lower critical solution temperature of PNIPAM) the ordered phase completely disappears.

Another difference between the microgel and a PS latex is that while the ordered PS latex can be concentrated (and dried out) and the system still keeps its ordered structure, the ordered microgel exists only in a certain concentration range. If we gradually concentrate the ordered microgel latex, (for example, by carefully evaporating the solvent) the particles are pressed to each other and since the gel particles may be easily deformed they fill the entire volume, loosing their individuality from the optical and kinetic points of view. The compressed system can be considered as a macroscopic gel rather than a microgel latex. However, in the dried microgel latex the individuality of the particles is retained, and the latex again shows the two-dimensional ordered structure investigated by transmission and scanning electron microscopy.[19–21]

Acknowledgement

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