

Novel microgel-particle colloids: the detailed characterisation of the layer structure and chain topology of silica:poly(NIPAM) core–shell particles

N. Hatto^{a,*}, T. Cosgrove^a, M.J. Snowden^b

^a*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*

^b*University of Greenwich, Wellington St., Woolwich, London SE18 6PF, UK*

Received 26 September 1999; received in revised form 10 December 1999; accepted 13 December 1999

Abstract

A monodisperse core–shell microgel has been synthesised in which silica provides the core (average diameter 1367 Å), and poly(NIPAM) the cross linked shell. Transmission Electron Microscopy and Photon Correlation Spectroscopy (PCS) measurements have confirmed the existence of a thick polymer layer. PCS measurements have shown that the hydrodynamic thickness of the layer is ~2450 Å at 25°C, collapsing to 600 Å when heated to 70°C. Small-angle neutron scattering (SANS) experiments on the core–shell microgels show a high volume fraction near the surface and suggest an exponential volume fraction profile. PCS and SANS measurements have also been used to measure the de-swelling of the layer with change in temperature and the results are compared with classical microgel particles. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Core–shell; Small-angle neutron scattering; *N*-isopropylacrylamide

1. Introduction

Poly-*N*-isopropylacrylamide (poly(NIPAM)) is a water soluble polymer which can form monodisperse colloidal microgel particles [1–3] when synthesised using surfactant-free emulsion polymerisation. A microgel particle is a cross-linked latex particle which is swollen in a good solvent, and much work has been focused on the preparation and properties of poly(NIPAM) microgels [4,5]. These microgels are swollen at room temperature, but being thermosensitive, the microgel particles collapse as the temperature is increased above 32°C [6,7] (the Lower Critical Solution Temperature—LCST). Thermally induced deswelling also occurs for poly(NIPAM) macrogels [8]. The growth mechanism within the microgel particles results in a non-uniform distribution of cross-linker [9], whereas the preparation of macrogels result in a more homogeneous network structure. Polystyrene latex spheres with a poly(NIPAM) microgel layer or anchored cross-linked poly(NIPAM) chains, have previously been prepared [10–14]. Dingenouts et al. [14] investigated the volume transition in PS-core(800 Å)/poly(NIPAM)-shell particles using small-angle X-ray scattering (SAXS). In that system, a small amount of poly(NIPAM) is included in the synthesis of

the core and is located in a thin shell at the surface, providing a means of fixing the gel layer. They observed a change in layer thickness from 320 Å in the swollen state at 25°C to 180 Å after shrinking by a continuous volume transition.

SANS has been used previously to study the collapse of microgels and microgel structure by fitting the gel structure to a Porod Law–Lorentzian combination. The parameter of interest is the correlation length, ξ , which is a measure of the size of the cross-linked regions. Mears et al. [15] reported a value of ξ as 18 Å for their microgel particles which had a hydrodynamic diameter of 1440 Å. In this paper we examine thermosensitive core–shell particles which comprise of a silica core and a poly(NIPAM) shell and compare our results to classical microgel particles.

2. Experimental

2.1. Sample preparation

The water used throughout this synthesis was purified using ion exchange (MilliQ–Millipore). The silica particles were synthesised “in house” using the Stober method [16]. 108 ml of tetraethyloxysilicate (Aldrich) was added quickly to a clean flask containing 2.5 l ethanol, 67 ml ammonia and 92 ml of water. The solution was stirred continuously for

* Corresponding author. Tel.: +44-0117-928-9941.

E-mail address: n.b.hatto@bris.ac.uk (N. Hatto).

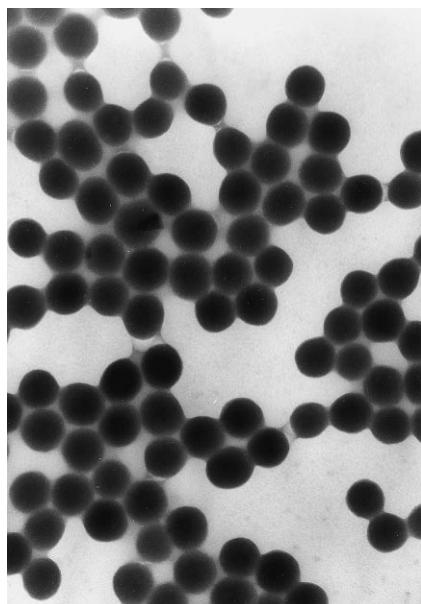


Fig. 1. TEM of silica particles coated with poly(NIPAM) “(photograph supplied)”.

24 h. A 1% dispersion of the resulting silica was dialysed against MilliQ water, and then used as a seed for the subsequent emulsion polymerisation of the cross-linked polymer microgel. The emulsion polymerisation was carried out in a 500 mL round-bottomed flask fitted with a reflux condenser, a stirrer and a nitrogen supply. The initiator, potassium persulphate (Aldrich), was dissolved in 400 ml of the 1% silica dispersion which had been degassed and heated to 70°C in an oil bath. *N*-isopropylacrylamide and *N,N*-methylenebisacrylamide (Aldrich) were dissolved in 100 ml of the 1% silica dispersion at room temperature. This solution was then added to the reaction flask. The reaction was allowed to proceed for 6 h at 70°C. The oil bath was then switched off, and the reaction mixture allowed to cool overnight. Nitrogen was passed over the reaction mixture for the duration. The core-shell particles were centrifuged several times at 8000 rpm for 30 min. The particles were then re-dispersed in MilliQ water.

The final dispersion had a volume fraction of 1.33% with respect to the silica particles which was obtained through a series of dry weight analyses.

2.2. Techniques

The hydrodynamic radius of the core-shell particles was measured using a Malvern Zetasizer 1000 spectrometer, which uses a laser that operates at 6330 Å. The measurements were made over a temperature range of 25–65°C.

The transmission electron micrographs were obtained using a Phillips EM430 operating at 250 kV. The samples were placed on copper grids, which had graphite-supporting films. Excess water was removed with a tissue and the sample then left to dry in air for a few minutes.

The SANS experiments were performed using the LOQ instrument at the ISIS facility, Rutherford Appleton Laboratory, Didcot, UK. Samples were measured in 1 mm path length “banjo” cells. The effective Q range was 0.009–0.249 Å⁻¹. A scattering length density, sld of 3.73×10^{-6} Å⁻² was obtained for the bare silica particles by making scattering measurements at different D₂O/H₂O ratios [17]. The scattering from the systems described were then studied as a function of temperature, to measure the exclusion of solvent and resulting change in the structure of the adsorbed gel layer as the poly(NIPAM) layer collapses.

2.3. Scattering theory

With the core matched in sld to that of the solvent, only scattering from the layer was observed. The subsequent SANS data was reduced using the Colette programme at the ISIS facility, which corrects the data for transmission and scattering from the cell.

The gel layer was characterised by using model mathematical functions which describe the volume fraction of the gel layer. The analysis was carried out using the equations developed by Crowley [18,19] and the data was fitted using a non-linear least-squares analysis [18,20]. The scattering from the layer, $I(Q)_{\ell\ell}$, is given by Eq. (1):

$$I(Q)_{\ell\ell} = \frac{6\pi(\rho_{\ell} - \rho_s)^2 \phi_p}{Q^2 r_0} \left| \int_0^t \phi(z) \exp(iQz) dz \right|^2 + I_{\text{inc}} + \tilde{I} \quad (1)$$

where $\phi(z)$ is the volume fraction of the polymer at a distance z normal to the surface and t is the maximum extent of the layer. ϕ_p is the volume fraction of the particles, r_0 is the radius of the particles, ρ_s and ρ_{ℓ} are the scattering length densities of the solvent and layer, respectively. I_{inc} is the scattering due to the incoherent background, \tilde{I} is the scattering due to spatial concentration fluctuations within the layer. Q is the momentum transfer vector of the neutrons, which is related to the scattering angle (ϑ) and the wavelength (λ) of the neutrons by:

$$Q = \left(\frac{4\lambda}{\pi} \right) \sin\left(\frac{\vartheta}{2} \right) \quad (2)$$

For an adsorbed homopolymer layer, the fluctuations would be expected to vary as $\tilde{I}(Q) \sim Q^{-4/3}$ [21]. It was not however possible to fit these with a fluctuation term and the results presented had ignored this contribution. This is an approximation, but as the data scatter very strongly at low Q , this approach is not unreasonable.

3. Results and discussion

Fig. 1 shows an electron micrograph of the microgel particles. Inevitably, particle coalescence occurs when the sample is dried onto the supporting grid, but a gel layer is still very much in evidence. An approximate indication of

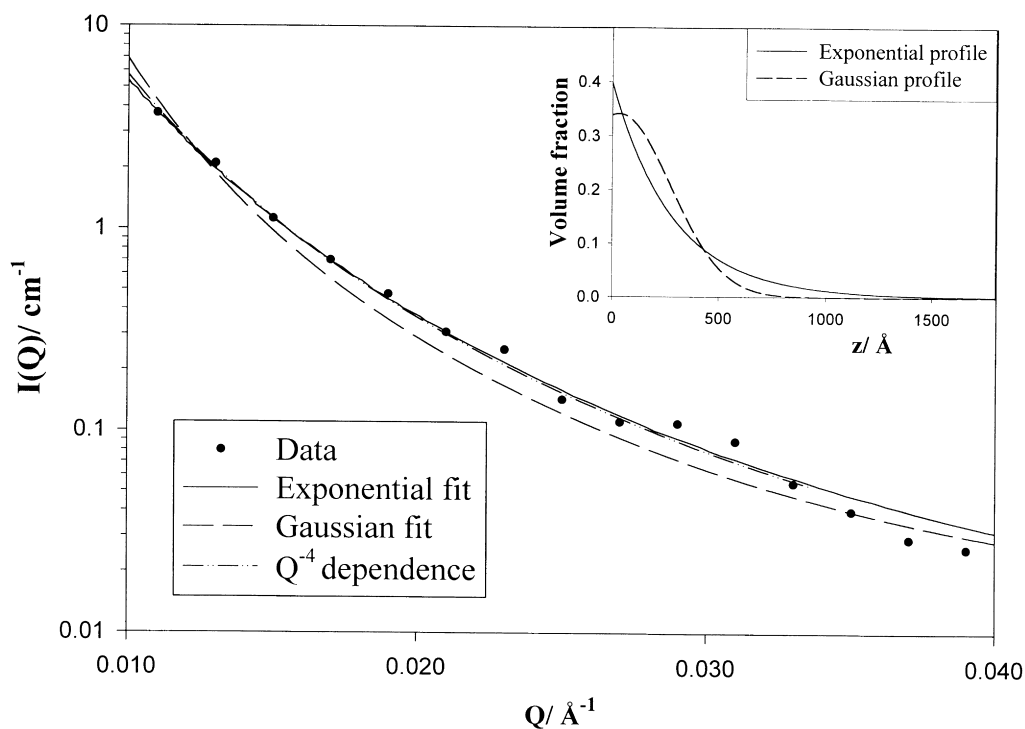


Fig. 2. Scattering from poly(NIPAM) layer at 40°C plus fits and profiles.

the thickness of the totally collapsed gel layer can be obtained from the electron micrograph, and gave an approximate thickness of $122 \pm 5 \text{ \AA}$. This would correspond to an adsorbed amount (Γ) of $15.4 \pm 1.0 \text{ mg/m}^2$.

Fig. 2 shows the intensity data obtained from the SANS experiments carried out when the silica core was matched in

sld to the solvent mixture. The data has a pronounced Q^{-4} structure at high Q with a tendency to a lower Q dependence at low Q .

This is clearly indicative of a very thick layer with virtually no surface Guinier regime [18,19]. The data were fitted with exponential and Gaussian models for the volume

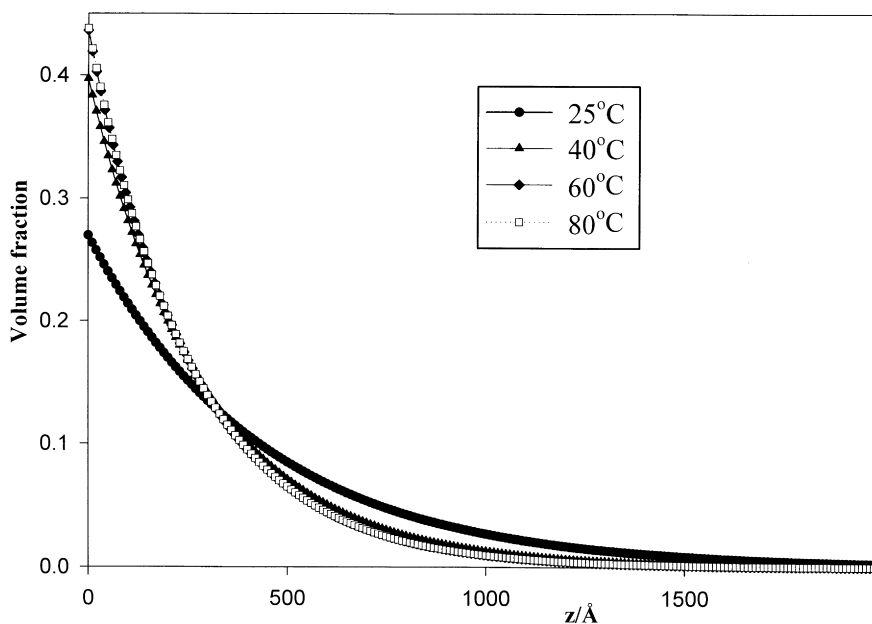


Fig. 3. Layer profiles as a function of temperature (Gaussian profiles).

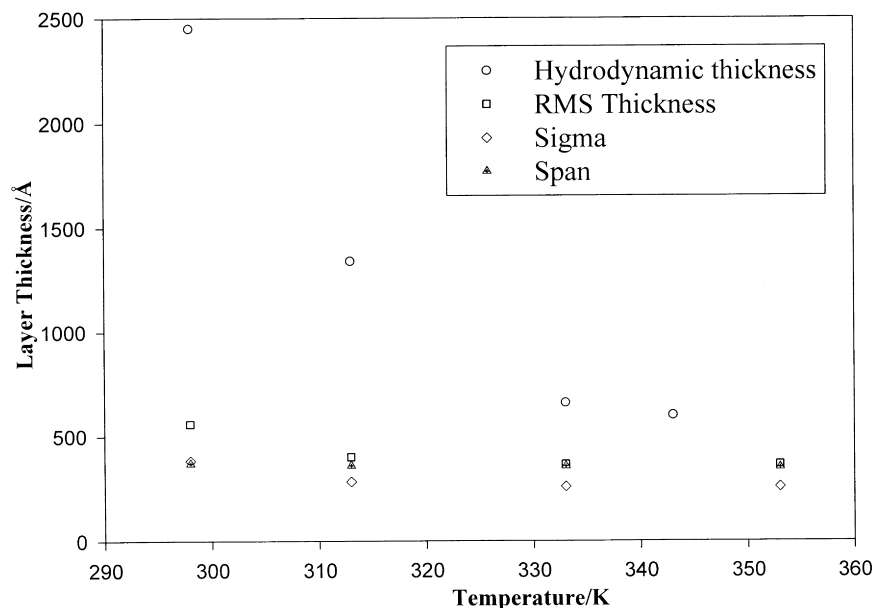


Fig. 4. Layer thickness as a function of temperature (PCS data).

fraction profile of the layer using Eq. (1). Fig. 2 shows the fits obtained by these two functional forms and the resulting profiles. Of the two functions used to fit the data the exponential yielded the best fit with the lowest χ^2 parameter. A physically adsorbed layer is also best characterised using an exponential function. The layer however, is quite dense with an average volume fraction of 19% and an RMS layer thickness of $400 \pm 18 \text{ \AA}$. An adsorbed amount (Γ) of $14 \pm 1.0 \text{ mg/m}^2$ was found by fitting the scattering from the layer at 80°C . These values are much greater than one would obtain simply from an adsorbed homopolymer. The value for the collapsed layer was used to fit the data for the other temperatures.

Fig. 3 shows the subsequent exponential profiles of the layer as the temperature is increased. The layer thickness varies most on traversing the LCST (32°C), with very little change occurring with further heating, especially from 60 to 80°C . The volume fraction increases at the silica surface as the layer collapses, but at 80°C the collapsed layer still contains as much as 60% water [22].

Fig. 4 shows the hydrodynamic layer thickness as a function of temperature, obtained using PCS. These measurements give a greater layer thickness compared to the profiles in Fig. 3, as the diffusion of the gel/particle is determined by the longest tails evident in the layer structure: these are too dilute to be detected by SANS. The PCS measurements do however follow the same trend, and collapse to roughly the span of the volume fraction profile (taken when the volume fraction is less than 10^{-3}). The figure also includes the RMS thickness and the second moment, σ . As the layer collapses the hydrodynamic thickness approaches the measured span indicating the collapse of the tail region.

4. Conclusions

We have successfully synthesised thermosensitive core-shell particles which comprise of a silica core and a poly (NIPAM) shell. They behave in a similar way to microgel particles with the layer collapsing on heating as evidenced by change in both the hydrodynamic and RMS layer thickness.

Acknowledgements

The authors gratefully acknowledge Dr S. Davies, Schlumberger, and the EPSRC (UK) for the financial support of a CASE award, and the EPSRC (UK) for beam time at ISIS. We also thank Dr S. King (Rutherford Appleton Laboratories, Didcot, UK).

References

- [1] Baker WO. *Ind Engng Chem* 1949;41:511.
- [2] Staudinger H, Husemann E. *Ber* 1935;54:73.
- [3] Schild HG. *Prog Polym Sci* 1772;17:163.
- [4] Murray MJ, Snowden MJ. *Adv Colloid Interface Sci* 1995;54:73.
- [5] Saunders BR, Vincent B. *Adv Colloid Interface Sci* 1999;80:1.
- [6] Pelton RH, Pelton HM, Morphesis A, Rowell RL. *Langmuir* 1989;5:816.
- [7] Shibayama M, Tanaka T. *Adv Polym Sci* 1993;1:109.
- [8] Shibayama M, Tanaka T. *J Chem Phys* 1992;9:6829.
- [9] Wu X, Pelton RH, Hameilec AE, Woods D, McPhee W. *Colloid Polym Sci* 1994;272:467.
- [10] Kiminta OMD, Luckham PF, Lenon S. *Polymer* 1995;25:4827.
- [11] Makino K, Yamamoto S, Fujimoto K, Kawaguchi H, Oshima HJ. *J Colloid Interface Sci* 1994;166:251.
- [12] Okubo M, Ahmad H. *Colloid Polym Sci* 1996;274:112.

- [13] Kratz K, Eimer W. *Ber Bunsen-Ges Phys Chem* 1998;102:848.
- [14] Dingenouts N, Norhausen C, Ballauf M. *Macromolecules* 1998;31:8912–7.
- [15] Cosgrove T, Mears S, Deng Y, Pelton R. *Langmuir* 1997;13(7):1901.
- [16] Stober W, Fink A, Bohn E. *J Colloid Interface Sci* 1968;26:62.
- [17] Ottewill RH, Goodwin JW, editors. *Colloid dispersions* London: Royal Society of Chemistry, 1982. p. 143.
- [18] Crowley TL. D.Phil. thesis, University of Oxford, 1984.
- [19] Barnett KB. Ph.D. thesis, University of Bristol, 1986.
- [20] Fleer GJ, Cohen Stuart MA, Scheutjens JM, Cosgrove T, Vincent B. *Polymers at interfaces*. London: Chapman and Hall, 1993.
- [21] Auvray L, de Gennes PG. *Europhys. Lett.* 1986;2:647.
- [22] McPhee W, Chiu Tam Kam, Pelton R. *J Colloid Interface Sci* 1993;24:156.