Colloidal Microgel Systems: Phase Transition Properties in Aqueous Solution of Poly(*N*-isopropylacrylamide)

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A reversible phase transition, in aqueous solution, of the colloidal poly(*N*-isopropylacrylamide) microgel system with an excess specific heat capacity maximum at 307.7 K (in the concentration range 0.05–0.5% m/m) is observed using high sensitivity differential scanning calorimetry (HSDSC); the thermodynamic parameters and turbidimetric changes associated with this transition are reported.

The physical properties of poly(*N*-isopropylacrylamide) [poly(NIPAM)] microgel systems have received considerable attention in the recent literature. Studies reported include the reversible flocculation of the dispersion[1,2] and uptake and release characteristics particularly with regard to the absorption of polymers[3] and also much smaller molecules including heavy metal ions.[4] All of the foregoing behaviour is attributable to the poly(NIPAM) microgel shrinking reversibly when heated in water. Though the extent of the volume change associated with the transition can be measured by dynamic light scattering[1] none of the thermodynamic parameters associated with the phase transition for a colloidal dispersion of poly(NIPAM) have, as yet, been reported. For microgel systems, solution phase properties are of crucial importance since changes in conformation/size/hydration characteristics as a function of temperature are not only of fundamental scientific interest but also of technological importance in *e.g.* enhanced oil recovery processes.[5]

Poly(NIPAM) microgel particles were prepared by the free-radical polymerisation of NIPAM in water at 70 °C, in the presence of *N,N'*-methylenebisacrylamide [$(CH_2{=}CHCONH)_2CH_2$; from BDH Chemicals] as a cross-linking agent, following the procedure described by Pelton and Chibante.[6] After extensive dialysis against distilled water, transmission electron micrographs showed the particles to be monodisperse spheres having a mean diameter of 380 ± 28 nm.

The temperature dependence of the particle diameter of poly(NIPAM) microgel was determined turbidimetrically using a Lambda 2 (Perkin–Elmer) spectrophotometer connected to a programmable temperature scanning water-bath at a scan rate of 1 K min^{-1}. The temperature in the measuring cell was monitored using a platinum thermocouple temperature probe. The turbidity of the dispersion (0.1% m/m) was measured against distilled water in the range 20–50 °C. Fig. 1 shows the change in turbidity at 547 nm as a function of temperature, for both heating and cooling scans. The maximum transition temperature obtained from the first derivative plot is 34.2 °C. On cooling, the microgels re-expand to their original size. The decrease in particle diameter with increasing temperature is a consequence of the increase in the Flory[7] interaction parameter (χ) for poly(NIPAM) in water with increasing temperature. This facilitates more polymer–polymer contacts; hence the particles contract, forcing out solvent from the interstitial spaces.

The theory and practice of high-sensitivity differential scanning calorimetry (HSDSC) is well documented.[8,9] The technique has been widely used to study directly the thermodynamic parameters associated with *e.g.* conformational/denaturation/melting/dehydration transitions of naturally occurring[10] and synthetic polymers.[11] The phase transitions exhibited by poly(NIPAM) are shown in Fig. 2, and the associated thermodynamic parameters are given in Table 1. Calorimetric measurements were carried out using a Microcal MC-2D ultrasensitive DSC (MicroCal Inc Northampton, MA, USA). Data acquisition and analysis was carried out using the DA2 software package, supplied by the

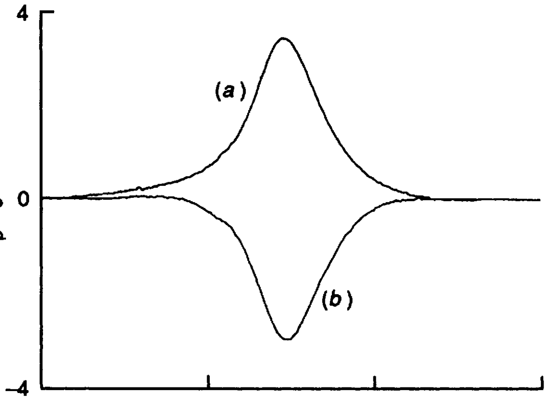

Fig. 2 Temperature dependence of the partial specific heat capacity of the colloidal poly(NIPAM) microgel system in double deionised water at a concentration of 0.5% (m/m). The HSDSC recording shows the heating, endothermic, (*a*) and subsequent cooling, exothermic scan, (*b*) of the microgel (30 and −30 K h^{-1} respectively).

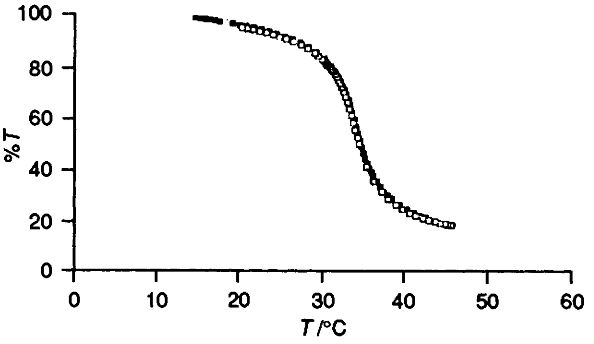

Fig. 1 The turbidity of a 0.1% dispersion of poly(NIPAM) at 547 nm as a function of temperature, (■) heating and (□) cooling at 60 and −60 K h^{-1} respectively

Table 1 Microcalorimetrically recorded thermodynamic parameters[a] for the poly(NIPAM) microgel using a scan rate of 0.5 K min^{-1} in water at a concentration of 0.5% (m/m)

Thermodynamic parameter	Value
T_m	307.7 K (34.5 °C)
ΔH_{cal}	20.8 J g^{-1}
ΔH_{VH}	508 kJ mol^{-1}
$\Delta H_{VH}/\Delta H_{cal}$	25 000
$\Delta T_{\frac{1}{2}}$	4.8 °C
$C_{p,max}$	3.4 J g^{-1} K^{-1}

[a] T_m is the temperature at which the excess heat capacity of the transition is a maximum ($C_{p,max}$); $\Delta T_{\frac{1}{2}}$ is the width of the transition in °C at $\frac{1}{2}C_{p,max}$; ΔH_{cal} is the calorimetric enthalpy of the transition and ΔH_{VH} is the van't Hoff enthalpy.

manufacturer. The transitions shown in Fig. 2 were obtained after baseline subtraction but have not been treated or artificially smoothed in any other way. Interestingly the transition, at a scan rate of 0.5 K min^{-1}, is quite symmetrical. It is also reversible in that the heating endotherm and cooling exotherm are, within experimental error, almost identical. This reversibility indicates that the process or processes occurring during the transition are fast in relation to the time-scale of the experiments. Furthermore the first and second heating scans of the same sample were superimposable. The fact that the phase transition of the microgel does not involve kinetic limitations, at least at the macroscopic level, is further substantiated by the identity of the T_m (the temperature at the maximum value of the excess specific heat capacity, $C_{p,max}$) as a function of concentration of microgel between 0.05 and 0.5% (m/m) and with varying scan rate between 10 and 60 K h^{-1}. Excellent correlation exists between the transition temperatures measured by turbidimetric analysis and HSDSC. As a macroscopic technique HSDSC does not usually give any direct information as to the molecular process(es) occurring during a phase transition. However, initial HSDSC observations indicate that the process(es) occurring involve water and may include desolvation during the heating scan. This hypothesis is supported by the fact that at a scan rate of 10 K h^{-1} the T_m of the colloidal microgel increases in D_2O by approximately 1.5 °C compared to the T_m in H_2O. The ratio of ΔH_{VH} (the van't Hoff enthalpy, which reflects the width of the transition) to ΔH_{cal} (the calorimetric enthalpy of the transition) represents the base molar unit which, in this case, has a value of approximately 25 000. For hydrogels three types of phase transitions have been reported:[12] thermoswelling type (expansion with temperature), thermoshrinking type (collapse with temperature) and the third is the 'convexo' type, a mixture of the thermoswelling and thermoshrinking types. The transition reported herein for poly (NIPAM) is of the thermoshrinking type arising from the affinity of NIPAM monomers for water.[1,2]

A number of interesting facets emerge concerning the presently reported work. It is, as far as we know, the first instance in which HSDSC has been used to study the dilute aqueous solution properties of a colloidal microgel. As such it invites direct comparison with results obtained for the phase transition properties of NIPA macrogels reported by Otake *et al.*[12] They prepared cylindrical gel rods (1.6 mm diameter and 20 mm length) which were immersed in water until equilibrium was reached. Subsequently thermodynamic properties were examined using DSC. Although the T_m reported for some samples are very similar to the T_m values obtained in the present study, ΔH_{cal} values were several orders of magnitude smaller. Furthermore at a scan rate of 30 K h^{-1} the transitions did not, from the published data, appear symmetrical.

Further studies in our laboratory are in progress in order to elucidate the molecular basis of the phase-transition phenomenon observed in colloidal microgels using NMR, FT-IR, Raman, densitometric, low-angle X-ray scattering techniques and further HSDSC studies. The interest will, in part, relate to the nature of the monomer used to produce the microgel and the relationship of the experimentally derived thermodynamic parameters to the structure of the microgels in aqueous and non-aqueous solutions. Finally, detailed studies are currently in hand to investigate and account for small but significant changes in excess heat capacity values (ΔC_p^d) which may occur at other scan rates and/or concentrations for the microgel between pre- and post-transition temperature values using HSDSC.

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References

1 M. J. Snowden and B. Vincent, *J. Chem. Soc., Chem. Commun.*, 1992, **16**, 1103.
2 M. J. Snowden, N. Marston and B. Vincent, *Colloids Surf.*, 1994, in the press.
3 M. J. Snowden, *J. Chem. Soc., Chem. Commun.*, 1992, 803.
4 M. J. Snowden, D. Thomas and B. Vincent, *Analyst*, 1993, **118**, 1367.
5 M. J. Snowden, B. Vincent and J. C. Morgan, *UK Pat.*, GB2262117A, 1993.
6 R. H. Pelton and P. Chibante, *Colloids Surf.*, 1986, **20**, 247.
7 P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953.
8 S. C. Cole and B. Z. Chowdhry, *TIBTECH.*, 1989, **7**, 11.
9 J. M. Sturtevant, *Ann. Rev. Phys. Chem.*, 1987, **38**, 463.
10 P. L. Privalov and S. J. Gill, *Adv. Protein Chem.*, 1989, **39**, 191.
11 J. K. Armstrong, J. Parsonage, B. Chowdhry, S. Leharne, J. Mitchell, A. Beezer, K. Löhner and P. Lagner, *J. Phys. Chem.*, 1993, **97**, 3904.
12 K. Otake, H. Inomata, M. Konno and S. Saito, *Macromolecules*, 1990, **23**, 283.