INTERROGATION OF POLY (N-ISOPROPYLACRYLAMIDE-BISACRYLAMIDE) MICROGEL NANOPARTICLES BY RAMAN SPECTROSCOPY

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Abstract: Uniquely, Raman spectroscopy has been used to investigate the volume phase transition of microgels as well as structural differences between colloidal and freeze dried microgels.

Microgels-sometimes referred to as "intelligent" (capable of reacting to a wide range of environmental stimuli) materials-are intra-molecularly cross-linked supramolecular polymeric colloidal dispersions [1]. Because of their porous 'sponge-like' open-network structure they can undergo reversible de-swelling/swelling (i.e. a volume phase transition; VPT) either isothermally (e.g. as a function of pH) and/or as a function of temperature [2]. Raman spectroscopy has been used, herein, for the first time, to investigate both the VPT properties and the structural differences between an aqueous colloidal dispersion and freeze- dried poly (N-isopropylacrylamide/ N, N'-methylenebisacrylamide) [poly(NIPAM/BA)] microgel samples.

Anionic [poly(NIPAM/BA)] microgels (10 wt% cross-linker density) with terminal -SO₃⁻ groups were synthesized (by surfactant-free emulsion polymerization) and purified as described previously [3].

The Raman spectral profiles, in the 2600-3800 cm⁻¹ region, for the poly(NIPAM/BA) microgels as a function of temperature are shown in Fig. 1. A plot of Raman intensity of the 2948 cm⁻¹ vibrational band (due to C-H stretching modes) versus temperature allows the VPT temperature to be determined as having a value of \sim 34°C. This value is in accord with that obtained by other techniques including e.g. high sensitivity differential scanning calorimetry [5]. In addition a plot (not shown) of the ratio of the area of the bands due to C-H stretching modes, between 2820 and 3027 cm⁻¹, (A₁) to that of the water band(s), between 3040 and 3730 cm⁻¹, (A₂) *versus* temperature shows a marked discontinuity at \sim 35°C. The values of A₁/A₂ are in themselves noteworthy because they *appear* to indicate that the change in the conformation of the microgel occurs more slowly than the expulsion of water from the interstitial spaces of the microgel i.e. that the two events occur sequentially rather than concomitantly. Obviously this is an oversimplification in relation to the complex physico-chemical behaviour of microgels [4]. Nevertheless, this observation is important in terms of the kinetics/mechanism of the VPT of the microgel and would be difficult to ascertain so easily using alternative analytical techniques.



Fig. 1.Raman spectra, as a function of temperature, of aqueous dispersions of poly(NIPAM/BA) microgels in the 2600-3800 cm⁻¹ obtained using 632.8 nm exciting radiation from a helium-neon laser.

Other wavenumber regions of the Raman spectra (not shown) of aqueous dispersions and freeze-dried poly(NIPAM/BA) microgel samples obtained from the same synthetic batch have also been examined. A reversible change in conformation and /or secondary structure is indicated by the C=O (1640 cm⁻¹) stretching and N-H (1552 cm⁻¹) bending vibrational bands which undergo a significant reproducible wavenumber shift, by ~14 cm⁻¹, between the freeze-dried and aqueous microgel dispersions. Such changes/differences would not be easily discernible using other analytical techniques.

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