Thermotropic Color Changing Nanoparticles Prepared by Encapsulating Blue Polystyrene Particles with a Poly-*N*-Isopropylacrylamide Gel

Bing Yuan, Douglas A. Wicks

School of Polymers and High Performance Materials, The University of Southern Mississippi, Hattiesburg, Mississippi 39406

ABSTRACT: Water-dispersed thermotropic nanoparticles with core-shell structures were synthesized by the *in situ* polymerization of a lightly crosslinked shell of poly(*N*-isopropylacrylamide) [poly(NIPAM)] onto blue polystyrene cores. At room temperature, the thermal responsive outer shell is hydrophilic and is in a fully swollen gel state; but as the temperature is raised above 31°C, it becomes increasingly hydrophobic and eventually collapses as the temperature reaches the lower critical solution temperature (LCST) of the poly(NIPAM). Passing through the LCST has a drastic effect on the color of the latex solution, which exhibited an intense blue color at room temperature and gradually pales or lightens as the temperature is raised above 31°C. Analysis using spectroscopic and dynamic light scattering techniques showed that it is a reversible process. Microscopy evaluation of samples dried by the evaporation of water at temperatures above and below the LCST revealed that the swollen/collapse state of the polymer shell influenced the morphology of the dry state. Drying at room temperature resulted in thin films in which only particles of sizes corresponding to the polystyrene core are clearly seen in the microscopy images; but for samples prepared above the LCST, the images revealed a morphology made of much larger particles with diameters of 400–500 nm. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 446–452, 2007

Key words: emulsion polymerization; hydrogels; thermoresponsive; nanoparticles; poly(*N*-isopropylacrylamide)

INTRODUCTION

Poly(*N*-isopropylacrylamide) [poly(NIPAM)] is a water-soluble polymer that has gained lots of attention in the past 20 years because of its thermal response properties.[1] In aqueous solution, poly(NIPAM) exhibits a lower critical solution temperature (LCST) between ∼ 30 and 35°C that results in a reversible transformation from a hydrophilic polymer to one that is hydrophobic as the solution temperature is raised above the LCST. With an LCST close to normal body temperature, the thermosensitive nature of poly(NIPAM) has resulted in a wide number of investigations for potential use in drug delivery systems.[2–12] Several investigations have involved incorporating poly(NIPAM) into aqueous core-shell nanoparticles, for which a diverse thermally responsive properties can be obtained.[13–18]

Polymers have been extensively investigated for use in systems to modify the transmission of light or an attenuate of color and chroma with change in temperature. Many of the systems investigated are based on polymer-based gels that contain thermoresponsive dyes[19] or dispersed liquid crystalline phases.[20] Among these, best known are the thermotropic liquid crystalline compounds that can change transmissivity as they pass through a thermal transition from one phase to another. Liquid crystalline compounds often show thermochromic responses derived from the change in molecular order.[21] Acrylamide-based hydrogels have used the LCST to impart a thermotropic response, with the transition to the collapsed form attenuating transmission through light scattering.[22]

In this study, we examine a thermotropic response imparted by encapsulating a colored polymeric nanoparticles with a thick, lightly crosslinked poly (NIPAM). These materials are prepared using blue colored, carboxy-functional polystyrene particle as the core, followed by encapsulation through a precipitation polymerization of NIPAM. Because of the LCST of the outer shell and the concurrent drastic change in refractive index, the resulting nanoparticle solutions exhibit a change of color from deep blue at

room temperature to a much lighter pastel blue as the temperature is increased above the LCST.

EXPERIMENTAL

Material

Materials used in this work include styrene (Alfa Aesar), methacrylic acid (Aldrich), sodium dodecyl sulfate (Sigma), potassium persulfate (Aldrich), sodium metabisulfite (Aldrich), ammonium persulfate (Acros Organics), Triton X-405 nonionic surfactant (Dow Chemical), N-isopropylacrylamide (NIPAM, Polysciences), N,N′-methylenebisacrylamide (MBA, Polysciences), and Neozapon Blue 807 dye (a water-insoluble copper phthalocyanine dye, BASF). All chemicals were used as received. Deionized water was used throughout the research.

Preparation of polystyrene core by miniemulsion polymerization

A monomer solution comprised 36.8 g styrene, 2 g methacrylic acid, and 1.2 g Neozapon Blue 807 was added to a 140 mL of distilled water containing 0.4 g SDS and 0.6 g Triton X-405. After mechanically stirring for 10 min at a speed of 400 rpm, the emulsion was homogenized at 18,000 rpm with an Ultra Turrax T18 homogenizer (IKA) for 20 min.

The resulting miniemulsion was transferred to a 500-mL kettle equipped with a paddle stirrer, a nitrogen bubbler, and a reflux condenser. While stirring at 150 rpm, the emulsion was heated under nitrogen to 45°C, using a water bath. An initiator solution of 0.4 g potassium persulfate and 0.25 g sodium metabisulfite in 10 g water was then added to the reactor at 0.1 mL/min using a KDS model 200 syringe pump (KD Scientific). After completion of the initiator feed, the polymerization was continued for another 5 h. Finally, initiator chaser solutions (0.10 g t-butyl hydroperoxide in 2 g water and 0.065 g sodium metabisulfite with 2 g water) were added separately to ensure complete monomer consumption. The resulting latex product was purified by dialysis against distilled water for 3 days to remove all the surfactants, ions and other initiator residues (using Spectra/Por 1 membrane tubing, molecular weight cut-off: 6–8000).

Preparation of poly(NIPAM) shell

To a 50-mL three-necked round-bottomed flask equipped with a mechanical stirrer, a nitrogen tube, and a reflux condenser, the following was charged: polystyrene core latex, which contained 0.5 g polymer solids (dilute to 2.5 wt % by adding DI water), 1.3 g NIPAM, and 0.06 g MBA. While stirring, the reactor was heated in a water bath to 65°C, followed by the dropwise addition of an initiator solution comprised 0.1 g ammonium persulfate in 2 g water. The polymerization was allowed to continue for 5 h at 65°C. The resulting product was purified by dialysis for 3 days using Spectra/Por 1 membrane tubing (molecular weight cut-off: 6–8000) against DI water to remove initiator residues, unreacted monomer, and other small molecules.

Characterization

^{1}H NMR spectra were recorded in D_2O using a temperature-controlled Mercury Innova 500 MHz spectrometer. Dynamic light scattering studies of the nanoparticles were conducted using Malvern Instruments Zetasizer Nano Series Instrument equipped with a 22 mW He–Ne laser operating at $\lambda = 632.8$ nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple τ digital correlator electronics system. Solution light transmission measurement was made using a DU-64 spectrophotometer at a wavelength of 630 nm with the temperature controlled by a water circulator. Atomic force microscopy (AFM) images were obtained in tapping mode using a standard RTESP silicon cantilever (length: 125 μm; spring constant: 20–80 N/m; and resonance frequency: ∼ 300 kHz) (VEECO probes, CA) in a Dimension 3000 scanning probe microscope (Digital Instruments). Transmission electron microscope (TEM) images were collected using a JEM 2100 electron microscope. To prepare samples for AFM and TEM experiment, the particles were diluted to 1/10,000 by weight. For the AFM measurement, one drop of the diluted solution was put on a glass slide and air dried at either ambient temperature or at 45°C. For TEM imaging, one drop of diluted latex was placed on a formvar-coated copper grid and allowed to dry at specified conditions.

RESULTS AND DISSUSSION

Core-shell polymer synthesis

In the first step of the process, a carboxy-functional blue polystyrene core was prepared using a miniemulsion technique. Attempts at using conventional emulsion polymerization were not successful because of the separation of the monomer and dye, resulting in large needlelike dye particles in the final latex. Miniemulsion polymerization is an effective method to incorporate the hydrophobic blue colorant into the polymer nanoparticles, as the polymerization occurs in the performed monomer droplets rather than through component diffusion to active micelles, as required in conventional emulsion
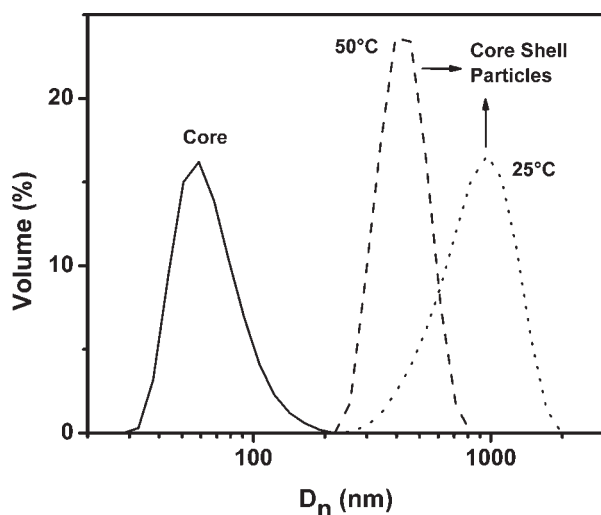
Figure 1 Hydrodynamic particle size of the polystyrene core and core-shell particles. Core-shell particle size measured at both 25 and 50°C.

polymerization. Hydrophobic copper phthalocyanine dyes have been used as costabilizers in several articles in miniemulsion polymerization of styrene.[23–25] After dialysis, the product of the miniemulsion polymerization was translucent and deep blue in color, dynamic light scattering measurements showed a unimodel size distribution with a peak of ~ 60 nm. Having only one particle size in the sample prepared by this miniemulsion indicates that the secondary nucleation of non-dye-containing particles did not take place during the polymerization. This was also confirmed by the consistent color of size-fractionated samples isolated by using a centrifuge.

The purified polystyrene particles were then used as the core material for the preparation of core-shell particles through the precipitation polymerization of NIPAM. Although the monomer is water soluble, the resulting poly(NIPAM) is insoluble in water at temperatures above its LCST between 30–35°C. With a reaction temperature of 65°C, as used here, the NIPAM begins to polymerize and precipitates on the surface of the core particles. Structural integrity of the core-shell particle was imparted by lightly cross-linking the shell with 5 wt % of a difunctional monomer, MBA. Success of the shell-preparation step is evidenced by the increase in particle size after NIPAM polymerization. The results of particle-size measurements are given in Figure 1. The polystyrene core before NIPAM polymerization was centered at 60 nm and after polymerization, a much larger, temperature-dependent particle size is found after the NIPAM polymerization. When measured at 25°C, a particle size of about 1000 nm is found, while at 50°C, the observed particle size is 430 nm. Only one particle size was found in the final product, indicating that no secondary nucleation occurred during

the second-step polymerization with complete incorporate polystyrene core.

The particle-size measurements give a first glimpse of the thermal-responsive nature of the core-shell polymer and may also give insight as to the homogeneity of the poly(NIPAM) shell. On a weight basis, the ratio of poly(NIPAM) to polystyrene based on feed would at be 2.7/1 and would not result in the large difference in particle size measured at 50°C if the NIPAM layer was homogenously free of water above its LCST. Assuming spherical particles, the effective particle volume (at 50°C) increases 360× after the second step indicating that there is a large volume of either entrapped or bound water accompanying the formation of the shell. When the temperature is reduced to 25°C, there is an additional ninefold increase in effective volume.

Visual effects

The color change of the final latex between 25 and 50°C temperature can be seen in Figure 2. The color of the left sample (25°C) is very blue with a color close to that of the original core but that on the right one (50°C) is much lighter. The color change is
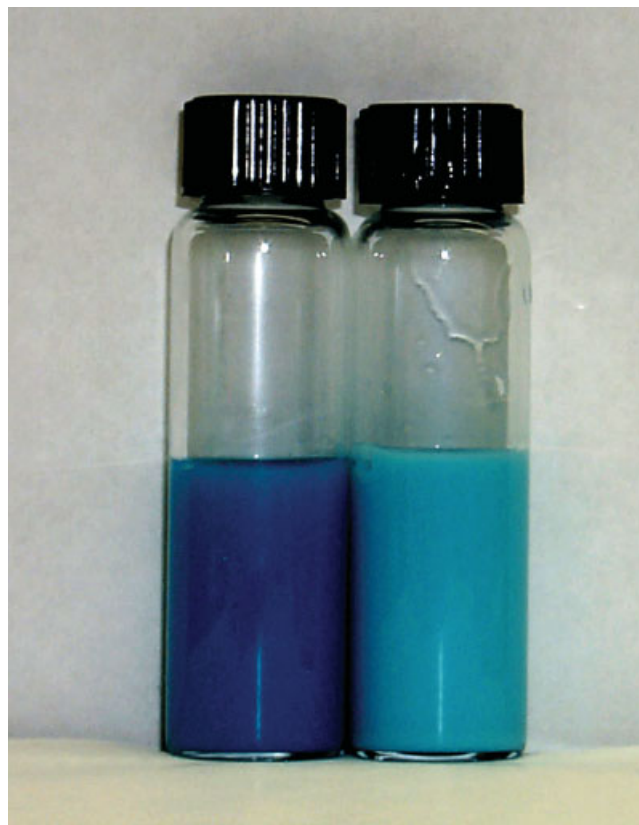

Figure 2 The effect of solution temperature on the color of the final product (left: 25°C, right: 50°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

reversible as temperature is cycled above and below the LCST. This thermochromic effect is most likely a result of changes in the refractive index of the shell below and above the LCST. Below the LCST, the poly(NIPAM) shell is fully swollen and appears transparent because of the lack of a dramatic change in refractive index with the water continuous phase. Above LCST, the shell collapses, leading to a refractive index difference between the shell and continuous phase resulting in increased light scattering. The presence of encapsulated water domains in the shell would magnify this effect by increasing the number of scattering interfaces.

Particle size and impact on solution turbidity

A more thorough evaluation of the relationship between particle size and temperature was performed to determine the shell LCST. As the solution temperature was increased incrementally from 25°C, the particle size essentially remains constant of 900 nm until reaching 31°C (Fig. 3). At that point, a rapid decrease in size is seen over a span of 6°–7° resulting in a particle size of 480 nm at 40°C. Beyond 40°C, the size continues to decrease at a much slower rate reaching 430 nm at 50°C.

An increase in solution turbidity, as measured by the reduction in transmittance at 630 nm, tracks inversely with changes in particle size (Fig. 4). As the temperature is increased above 30°C, there is a rapid drop in transmittance until 40°C where it once again stabilizes. Neither poly(NIPAM) or polystyrene has a significant absorption at the 630-nm wavelength. The Neozapon Blue 807 dye does absorb at 630 nm, but it is not temperature sensitive in this range. So, the transmittance changes measured is only dependent on the physical changes of the latex, particle sizes.
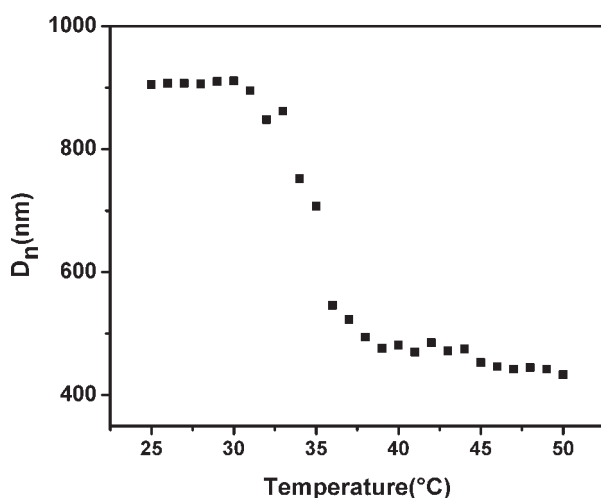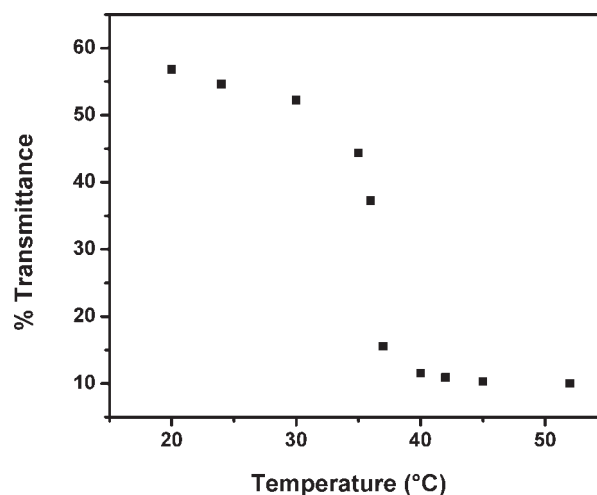

Figure 4 Transmittance of core-shell latex solution at 630 nm as a function of temperature.

The ^{1}H NMR spectra of the latex at different temperatures (Fig. 5) also support the observed color change being derived from scattering at the new polymer-continuous phase interfaces as the polymer passes through its LCST. There is a major reduction in signal intensity from the poly(NIPAM) at temperatures above LCST. The signal reduction and line broadening is attributable to a loss of mobility as the chains lose the solvation of water.

Microscopy

Quite surprisingly, the effects of the LCST carried over to dried samples of the particles that were prepared below and above LCST. All samples for AFM and TEM were prepared from a dilute dispersion (solution) at same concentration. The AFM and TEM
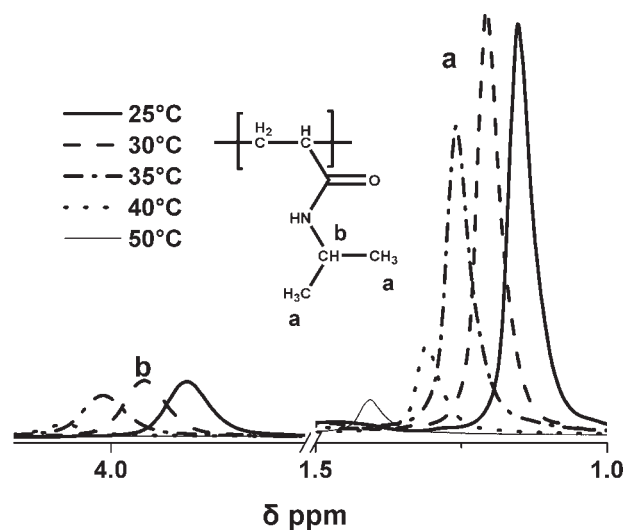

Figure 3 The particle size of core-shell nanoparticles as a function of temperature.

Figure 5 ^{1}H NMR spectra of the core-shell latex at temperature between 25 and 50°C.
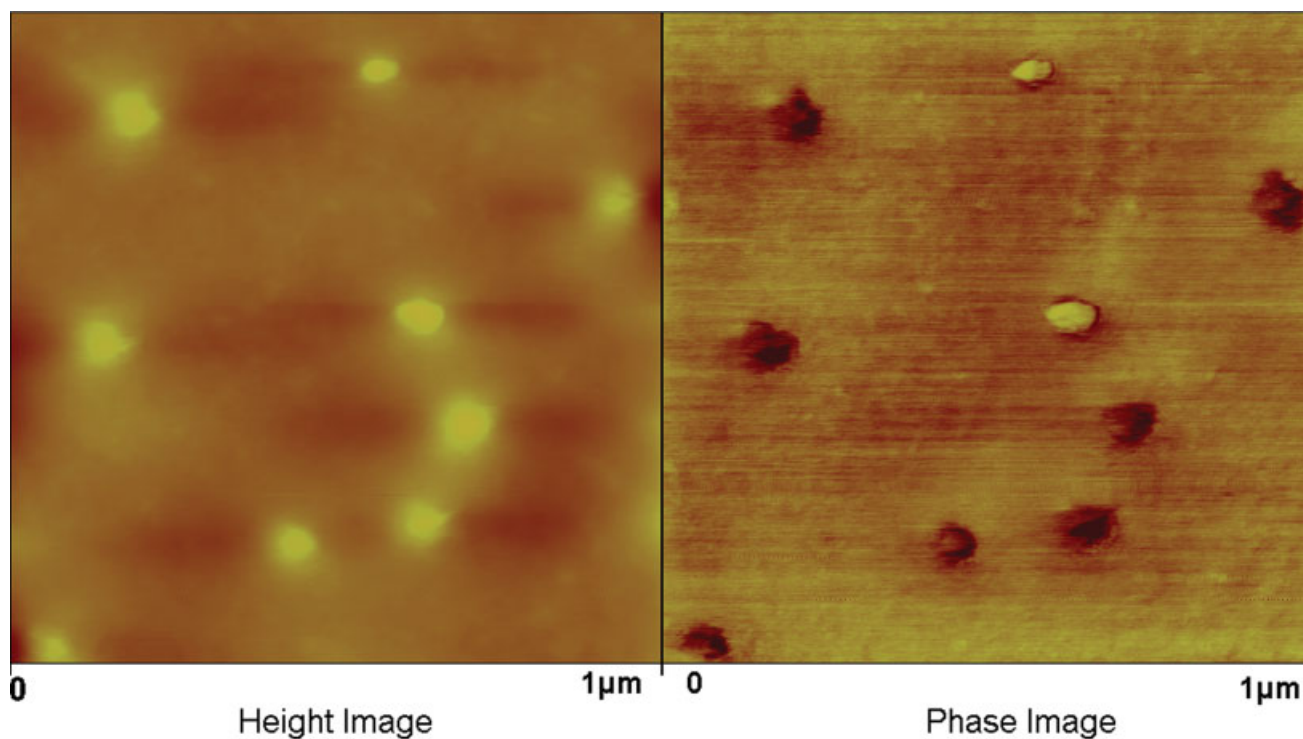
Figure 6 AFM height and phase images for the sample prepared by drying at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

images obtained for samples prepared at room temperature (Figs. 6 and 7) revealed that only small features with diameters of less than 100 nm are present. This particle size is roughly the same as the blue polystyrene particles used as the core for the NIPAM polymerization and bears no correlation to the

900-nm particles observed in solution by dynamic light scattering.

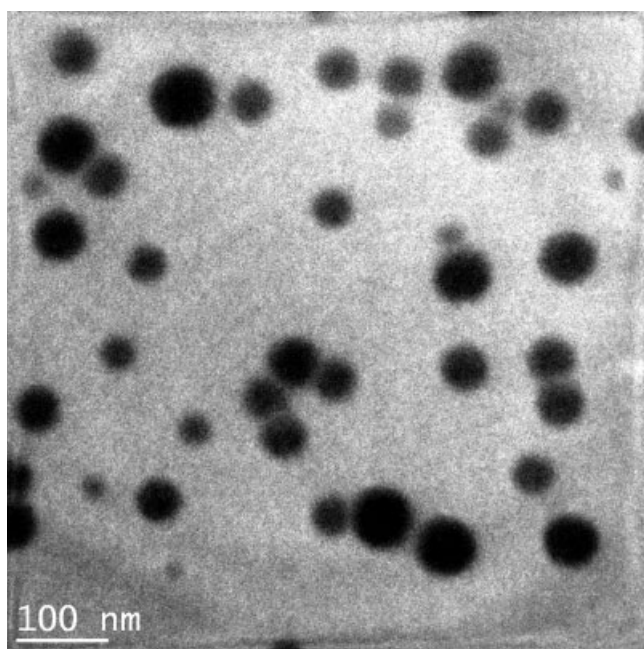The AFM image shown in Figure 8 is quite different. This image was obtained from a sample prepared by

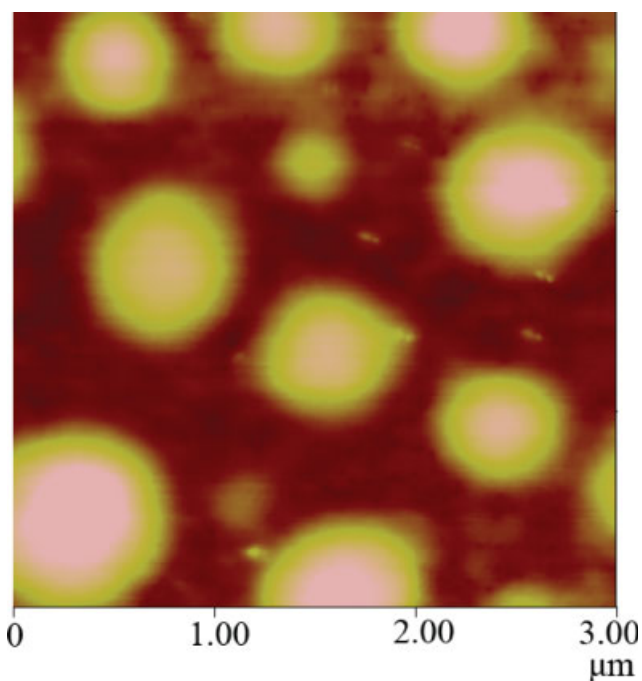**Figure 7** TEM image for the sample prepared by drying at room temperature.

Figure 8 AFM height image for samples prepared by drying at 45°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
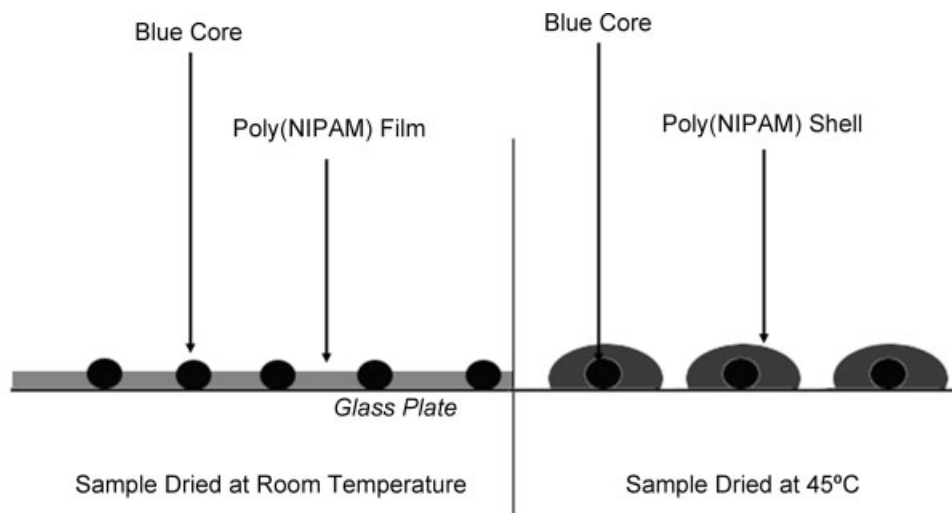
Figure 9 Illustration of dried particle morphology in samples dried below and above LCST.

drying at 45°C. The particle sizes observed in this sample are much larger than those found for samples prepared below the LCST, and are closer to those found in solution by dynamic light scattering measurement. The largest one's approach is 1 μm in size and the differences between such a size and that measured in solution may be a matter of measurement perspective or from a slight pancaking of the particle during the drying process.

The differences found in the dried samples reflect the differences in poly(NIPAM) solvation in water. At room temperature, the shell is in a fully swollen state with high mobility. As drying takes place, the hydrated outer shell is able to deform yielding even films with the polystyrene core particle distributed inside it. An illustration of the dried states formed at room temperature and 45°C are shown in Figure 9. For samples prepared at room temperature (left in Fig. 9), though the light crosslinking prevents full coalescence, what appears to be a smooth ''continuous'' phase is formed by the water-plasticized polymer shell. At a temperature higher than LCST, the thick poly(NIPAM) shell is collapsed around the core particles without the plasticizing effect of water solvation and morphology is retained and remains unchanged as the solution dries (right in Fig. 9).

SUMMARY

Thermally responsive colored nanoparticles were prepared by forming a thick, lightly crosslinked shell of poly(NIPAM) around a blue, 60-nm polystyrene core. These materials were found to exhibit a thermochromic response in solution because of changes in light scattering caused by the particles above and below the LCST of the shell. At temperatures below 30°C, the thick outer shell is highly solvated by

water resulting in an overall particle size of 900 nm. The hydrated shell, with a refractive index close to water, is transparent and allows the blue color of core particles to be seen. At temperatures above 31°C, blue color is lost as the refractive index of the collapsed shell no longer matches with the continuous phase.

Analysis of AFM and TEM images of dried samples prepared at room temperature, the poly (NIPAM) shell was not detected and only the PS core evident. For dry samples prepared at 45°C, AFM analysis revealed the presence of the large particles with an intact NIPAM shell in place. It is proposed that, at room temperature, the shell was solvated and extended to form a gel-like structure at room temperature, and upon drying formed an even continuous phase in film, leaving only the core particles to be detected by either TEM or AFM. For samples prepared above the LCST, the outer shell turns hydrophobic and shrinks around the core particles to form larger particles that are retained after the evaporation of water.

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