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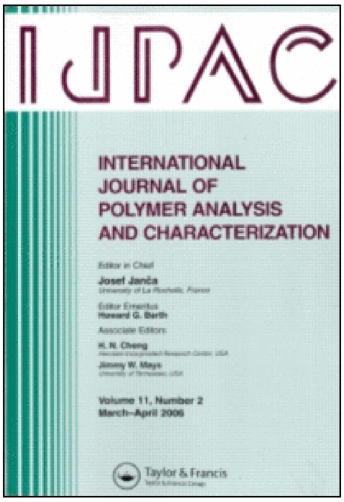

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Thermoresponsive Core Polystyrene-Shell NIPAm Microgels

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Abstract: We report the investigation of a colloidal crystal array (CCA) of thermoresponsive colloidal core-shell microgels prepared via the emulsion polymerization method using polystyrene (PS) as a hard core and N,N,-methylene(bisacrylamide) (BIS) as a cross-linker with acrylic acid (AA) as a co-monomer with a soft-shell morphology. In this work, PS/NIPAm colloidal core-shell microgels were prepared and characterized by Atomic Force Microscopy (AFM), particle size analyzer, and reflectance measurements. In situ measurement of reflectance with varying temperatures was carried out from 25° to 45°C using a special setup assembly with a temperature controller attached to the sample stand of the reflectance measurement instrument. PS core and PNIPAm shell morphology was confirmed by AFM analysis. The effect of varying mole of N-isopropylacrylamide (NIPAm) from 2.1 to 8.3 mmol while keeping the shell monomer ratio constant on the reflectance and particle size measurements with respect to temperature was investigated. The particle size increased as the NIPAm molar proportion was increased from 2.1 to 8.3 mmol. As expected, using more NIPAm led to an increase in the particle size and a thicker shell. A general trend was observed in the variation of reflectance wavelength peak decreasing with increase in temperature, allowing these novel CCA of PS/NIPAm microgels to be a potential core-shell microgel candidate for chemical sensor applications and optically tunable materials.

Keywords: Colloidal crystal array; Core-shell microgels; Polystyrene; Reflectance

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INTRODUCTION

Thermosensitive PNIPAm copolymers have been studied widely due to observation of a temperature-dependent volume phase transition.[1] Recently, significant attention has been given to colloidal microparticles based on this same material.[2] These can be obtained nearly monodispersed and can be prepared with a wide range of colloidal sizes. This particular polymer has been found to exhibit strong hydrogen bonding in aqueous solution, and it has also been shown to be highly temperature sensitive.[3,4] During the past three decades a large number of works[5–10] and also several reviews[11–13] on the subject of so-called intelligent macroscopic hydrogels were published. This class of hydrogel is of special interest due to the volume phase transition encountered in these systems, i.e., the collapse of the gel at the point where a certain temperature (lower critical solution temperature) (LCST)[14–16] or ionic strength[17] is reached. The first report on a hydrogel undergoing temperature-induced volume phase transition was published by Tanaka et al. in 1977.[18] Since then the number of investigations on this kind of smart material has been steadily growing. One of the most popular systems is made of NIPAm, which has a lower critical solution temperature of around 32°C. This organic monomer is typically cross-linked with N,N-methylenebisacrylamide (BIS) to build a three-dimensional network. The main difference between microscopic gels and their smaller counterparts lies in the response to external stimuli, which is much faster for the latter. This is due to the fact that the time constant of the swelling/deswelling process depends on the geometrical dimensions of the investigated gel, which was shown by Li and Tanaka.[19] This property makes microgels well suited for several applications such as sensor design[20–23] and drug delivery.[24–27]

Coating of colloidal particles with shells represents probably the simplest and most versatile strategy for increasing the diversity and complexity of a colloidal system.[28] First of all, formation of shells on colloidal particles may dramatically alter the charge, functionality, and reactivity of their surfaces and thus enhance the stability and compatibility of the core particles.[29] In principle, the properties (optical, mechanical, electrical, rheological, and catalytic) of core-shell particles can be tailored in a controllable fashion by independently altering the composition, dimension, and structure of the cores or shells.[28–30] Second, formation of shells on cores provides a natural vehicle to incorporate different materials into the same structure and thus to obtain hybrid, multifunctional colloidal particles.[31] Third, core-shell particles serve as the precursors to hollow structures that can be exploited to reduce the density of colloidal fillers and to save the use of precious materials by depositing them on inexpensive cores.[32] As a result of their unique features, core-shell particles have recently found use in a variety of applications. For example, core-shell particles with their shells optically matched to the suspending fluid have been explored as a good model system to investigate issues related to colloidal interaction and stabilizations.[33] Core-shell particles have also been demonstrated as a new class of building blocks to fabricate colloidal crystals with photonic properties different from those based on conventional plain particles.[34]

There is extensive literature exploring the diffraction properties of photonic crystals prepared through the use of crystalline colloidal self-assembly.[35,36] Colloidal crystal arrays (CCAs) form very highly charged, monodisperse colloidal particles dispersed in very low ionic strength aqueous media crystallize into cubic array structures. The strong electrostatic interactions between particles force the colloid to minimize the total system energy by arranging into either a face-centered cubic (FCC) or body-centered (BCC) crystalline array, depending on the particular number density and the strength of the repulsive interactions.[37,38] CCA lattice constants are typically on the order of hundreds of nanometers, so the array diffracts near-UV, visible, and near-IR light. CCA appears brightly colored and opalescent because of the diffraction of visible light.

There are several factors that govern the formation and orientation of colloidal crystals, such as the size, surface charge, and the ionic strength of the medium.[39,40] The lattice spacing in these systems usually exceed 100 nm, hence the dispersion efficiently diffracts visible light according to the Bragg diffraction equation[41] $n\lambda = 2n_{\mathrm{eff}} d \sin\theta$, where λ is the wavelength of diffracted light, n is the order of diffraction, d is the inter-planar spacing, n_{eff} is the effective refractive index of the dispersion, and θ is the Bragg angle. It has been shown that diffraction wavelengths from liquid colloidal dispersions can be tuned by varying the particle size, particle concentration, and Bragg angle.[42–44] It is this tunable characteristic of these crystal lattices, as depicted by Bragg's law, that has brought about the rapid movement towards their usage in optical devices.

In this article, we report the synthesis of a thermoresponsive core-shell microgel based on NIPAm using an acrylic acid shell and polystyrene as a core polymer by a free radical polymerization process with a varying molar quantity of NIPAm from 2.1 to 8.3 mmol while keeping the molar ratio of the monomer constant. First, core particles of polystyrene were reacted with NIPAm, acrylic acid, and BIS to prepare core-shell microgels. Core-shell particles were characterized by atomic force microscopy (AFM). AFM revealed spherical particle size, while photon correlation spectroscopy (PCS) further suggested that varying the quantity of NIPAm gives the core-shell particle a thicker shell and increased particle size. The effect of varying the ratio between the monomer and the cross-linker was also investigated with respect to particle size as a function of temperature. Real-time monitoring of reflectance with respect to varying temperature from 25° to 45°C demonstrated the characteristic feature of PNIPAM core-shell microgel as the reflectance peak shifted from right to left, making it a prospective candidate for chemical sensing.

EXPERIMENTAL SECTION

Materials and Methods

For the preparation of the CCA, we obtained OptiBind polystyrene microparticles (PS-MPs-Seradyn Inc, Ind., USA), which are uniformly sized (0.210 μ) stable colloids and were characterized to be monodispersed spheres. The specific gravity of polystyrene is 1.05 g/mL and the carboxyl content is 0.210 meq/g. The polystyrene colloidal spheres were centrifuged seven times. The final product is an iridescent opal-colored colloidal microgel. The gel mainly reflects light in the green to red region. The particles are supplied nominal 10% solids after dilution with distilled water form the original polymerization mixture. The stability of the colloids (i.e., maintaining spheres as separate particles) requires minimum amounts of surface negative charge. All reagents were purchased from Sigma-Aldrich unless otherwise noted. NIPAm was recrystallized from hexanes (J T Baker) and dried under vacuum prior to use. The ammonium persulfate (APS) was of Sigma Aldrich grade.

Synthesis of Core-Shell Microgels

Three samples, 1, 2, and 3, were prepared with various molar proportion of NIPAm, 2.1, 4.1, and 8.3 mmol respectively, with constant amounts of acrylic acid (AA) (0.1 mL) and BIS, as shown in Table I. NIPAm and BIS were mixed together in 100 mL water with a three-necked round-bottom flask, equipped with a condenser and a magnetic stirring bar. The solution was heated to 70°C with N_2 purge. A 3 mL PS solution, as core, was injected after the temperature had been stable for 1 h. Then 0.1 mL AA was injected 1 h later. After another hour, 0.02 g APS in 1 mL water was injected and the reaction was carried out for 4 h. Microgel was separated by filtration followed by repeated centrifugation at a relative centrifugal force of 5200 g for 70 min at room temperature. All preparation, results, discussion, and conclusion were based on sample 2.

Table I. Sample details

Sample	PS	NIPAm (mmol)	NIPAm/AA/ BIS (molar)	APS (g)
1	3 mL solution	8.3	100:10:1	0.02
2	3 mL solution	4.1	100:10:1	0.02
3	3 mL solution	2.1	100:10:1	0.02

Preparation of CCA

To prepare CCA, 0.03 g lyophilized dry core shell microgels were suspended into ~1.2 mL water. The colloid solution was centrifuged at a relative centrifugal force of 5200 g for 70 min, and then a certain amount of supernatant water was removed to reach a desired particle concentration. After being vibrated to a homogeneous state and left standing for ~12 h, the colloid was injected in between two glass covers separated by a ~0.3 mm thick double-sided sticky gasket that were placed on the temperature-controlled sample holder. The optical reflectance spectra were recorded immediately after injection.

Measurement of Reflectance

Real-time monitoring of reflectance (Ocean Optics USB 4000) was carried out as follows. The gasket was kept on the analyzer stand, which is connected to the temperature controller. As the analysis began, the temperature was varied with the help of the temperature controller, which helps prevent any error in recording the reflectance spectra. If the desired temperature is already maintained, i.e., sample transportation lag or sensor transportation lag is minimized, we could say almost zero error is achieved in recording the reflectance spectra of the samples at varying temperatures.

Measurement of Particle Size

Dynamic light scattering (DLS) (Beckman Coulter N5 Submicron Particle Analyzer) measurements were performed on a scattering instrument setup. Samples were prepared by suspending 0.1 mL of CCA latex in 20 mL of Milli-Q-water, followed by filtration through a 2 μm filter. To ensure data reproducibility, measurements were taken 25 min after the sample temperature was stabilized.

Atomic Force Microscopy Analysis (AFM)

One drop of the colloid was added to the surface of a glass substrate. AFM (Nano Surf Easy Scan 2) was used to observe the morphology after the sample dried. AFM analysis helped to confirm that the core-shell morphology showed the distinct appearance of a hard PS core surrounded by soft PNIPAm/AAc shell, as shown in Figure 4.

RESULTS AND DISCUSSION

We prepared temperature-sensitive microgel particles from NIPAm, BIS, and PS by the free radical emulsion polymerization method. A diluted solution of microgel particles was first concentrated by centrifugation followed by dilution of the sample to the desired concentration. The particle size of the colloid was measured by the dynamic light scattering method. The particle diffusion coefficient was obtained from the decay exponent of the correlation function of scattered light, and then the hydrodynamic radius (R_h) was calculated from the Stokes-Einstein equation. The results were provided as the histograms of scattered light intensity or mass versus fractions with various hydrodynamic radii. The sample was kept at a set temperature for ~20 min before measurement. The particle size of the microgels increased with increasing molar ratio of NIPAm.

From Figure 1, we can say that particle size decreases as the temperature increased from 25° to 45°C with various molar quantities of NIPAm in the range 2.1–8.3 mmol. As observed from Figure 1, particle size analysis was carried out for various quantities of NIPAm. Sample 1 contained 8.3 mmole NIPAm, and we can see that at 25°C the particle size is 1172 nm, which is due to the thick shell formation on the polystyrene core. On further increase in the temperature from 25° to 30°C, we observe that the particle size reduces sharply and remains between 900 to 1000 nm. For sample 2, where 4.1 mmole NIPAm was incorporated to prepare the core-shell microgel, a similar trend was observed, which can be seen in Figure 1. Sample 3, which contained the smallest amount of NIPAm, 2.1 mmole, showed the smallest particle size at room temperature and smallest particle size change as a function of temperature.

However, it had been shown in the literature that the exterior of the PS/NIPAm particles was composed mostly of the more hydrophilic PNIPAm due to some degree of the phase separation, while the center of the particle consists of the more hydrophobic polystyrene. PS/NIPAm graft copolymers have been reported earlier.[45,46] Further, it is a graft copolymerization reaction wherein PNIPAm chains are grafted onto

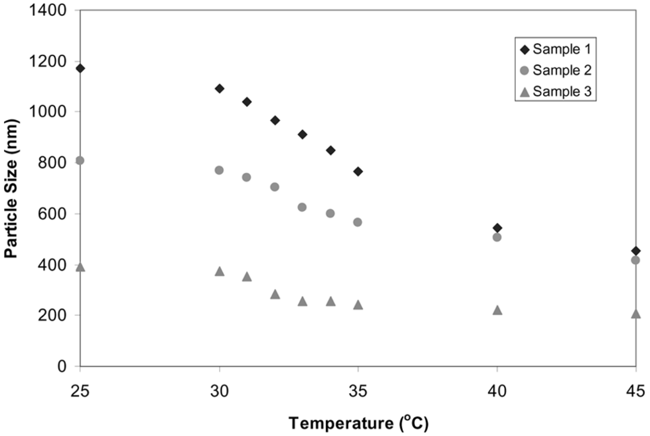

Figure 1. Particle size changes of samples 1–3 with a function of temperature.

polystyrene particles. We expect chemical interaction of sulfonate and carboxylate group available on polystyrene particles are used to anchor chains of PNIPAm. Therefore, it was proposed that this change in size is due primarily to the loss of water from the hydrated PNIPAm-rich periphery of the particles, while the spherical shape was effectively preserved as a result of the dense PS-rich core. This variation in size indicated the extent of surface flexibility that could be realized with these particles.

Colloids with a wide range of particle weight percentages were found to be able to form CCA, which shows various peak intensities at different wavelengths by varying the temperature from 25° to 45°C. In the reflectance spectra in Figure 2, a strong high wavelength and relatively broad peak was observed at 25°C. Bragg diffraction peaks are described in accordance with the Bragg diffraction equation:

$$m\lambda = 2nd \sin\theta$$

where m is the order of diffraction, λ is the wavelength in vacuum of the diffracted light, n is the average refractive index of the crystal inside, d is spacing between the diffracting lattice planes, and θ is the glancing angle between the incident light and the diffracting planes.

In this study, we have analyzed the effect of temperature on the reflectance wavelength of CCA. In Figure 2, at room temperature, the CCA prepared exhibited a wavelength at 522 nm as a sharp peak with a slight broad peak showing 235% intensity. Also, the diffraction peak shifted to lower wavelength with increasing temperature in the phase transition region of NIPAm around its low critical solution temperature (LCST) at ~31°C and weakened after 38°C. During the increases

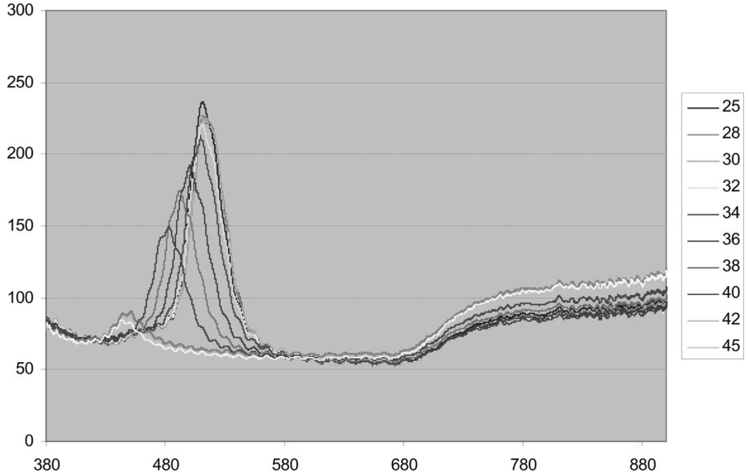

Figure 2. Real-time reflectance measurement of sample 2 with a function of temperature.

in temperature, water evaporation may have caused attractive capillary force between particle and convective particle flux, which overcame peak electrostatic repulsion and brought the particles closer. Therefore, the particles in this work organized into non-close packing CCA similar to noncharged spheres when particle concentration was forced up and was also capable of forming ordered close packing. Figure 2 suggests that upon the increase of the temperature, the volume of the microgel decreases. Since the particles as cross-linkers were covalently attached to surrounding PNIPAm polymer chains, the shrinkage of the particles does not take temperature-sensitive chains to move with them. As a result, the interparticle distance decreased with the temperature.

As shown in Figure 2 the sharp peak came from the Bragg diffraction from the periodic array of the microgel. The wavelength decreased from about 522 nm to 480 nm upon increasing the temperature from 25° to 45°C in excellent agreement for the temperature-sensitive microgel due mainly to a relatively higher concentration of NIPAm and PS-rich dense core. This wavelength shift from right to left plays an important role for sensors, actuators, and optical tunable materials. Since both the diameter of the microgel and particle size are small, the shift in wavelength should be fast in response to an external stimulus. Furthermore, because of the unique structure of particles as cross-linker, the long chains between particles may act as free liner polymer chains that have less friction for water molecules. It was clearly shown in Figure 3 that as the temperature increased from 25° to 45°C, the peak wavelength decreased; up to 36°C there is a linear relationship observed

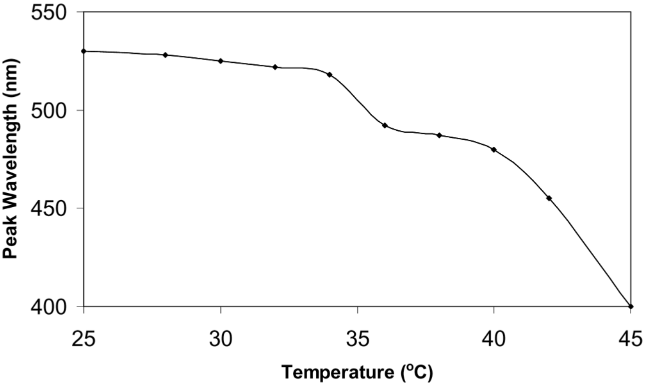

Figure 3. Effect of temperature on peak wavelength shift.

for the decrease in peak wavelength with increase in temperature, afterwards it decreased rapidly up to 45°C.

AFM measurements were conducted on sample 2 particles as shown in Figure 4. The spherical geometry of polystyrene was mostly preserved; the images reveal irregularities in the shape of the nanoparticles. These irregularities indicated the presence of the polymer coating on the polystyrene particles. This shrinkage possibly shows the thermosensitive behavior of the microgel, confirming that was due to crystal

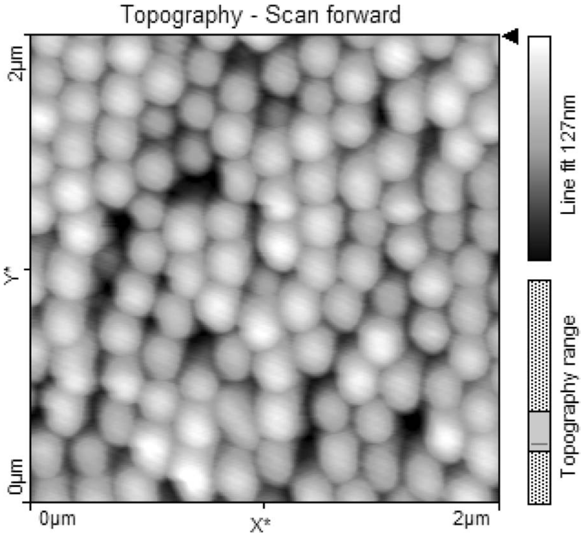

Figure 4. AFM image of sample 2.

lattice spacing and not because of driving the solvent out of the matrix. Furthermore, above LCST the effect of temperature change was negligible with respect to particle size. We observed a thermosensitive response of the microgel by varying the temperature from 25° to 45°C, showing a reflectance shift. A possible reason for the thermosensitivity could be that lightly cross-linked particles with a LCST could spontaneously form a crystalline colloidal array (CCA) via a simple temperature-cycling mechanism.

CONCLUSION

In this study it has been shown that a thermoresponsive, core-shell microgel can be prepared via free radical emulsion polymerization of a hard-core polystyrene and a soft-shell NIPAm and can be assembled into a colloidal crystal array with varying mole percentages of NIPAm and AAc. This simple temperature-sensitive core-shell colloidal microgel CCA caused the spontaneous formation of well-ordered CCA that displayed typical photonic phenomena. Core-shell morphology was mainly confirmed by AFM analysis showing the distinct appearance of PS core and PNIPAm shell. Such thermosensitivity was confirmed by further diffraction showing a reversible cycle. The main objective of this investigation was to report the temperature sensitivity of the microgel by measuring real-time reflectance, which was achieved successfully by setting up a special assembly of instrument sample stand, which was directly connected to the temperature controller preventing the loss of temperature variation during the measurement of the reflectance. NIPAm supported by hard-core PS could be affecting the mechanical strength of pure NIPAm gels, retaining spherical shape, which in turn provided a novel material. This thermoresponsive, colloidal core-shell microgel showed a peak reflectance wavelength of decreasing order from 522 nm to 480 nm with respect to increase in the temperature from 25° to 45°C, proving to be a prospective gel for future chemical sensors, actuator applications, and optical materials.

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