

Synthesis and Characterization of Thermosensitive Composite Microsphere Latex

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ABSTRACT: Monodisperse aqueous latex dispersions, prepared from mixtures of styrene, *N*-isopropylacrylamide, and *N,N'*-methylenebisacrylamide, were characterized. Thermosensitive composite microspheres with diameters greater than 1.0 μm , consisting of a polystyrene core and a poly(*N*-isopropylacrylamide) shell, were prepared. The morphology of the composite microspheres was observed with transmission electron microscopy, and the particle size of the composite microspheres was estimated with dynamic

light scattering. The thermosensitive properties of the composite microspheres were evaluated via the hydrodynamic size of the composite microspheres. The particle size of the composite microspheres decreased with increasing temperature. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 824–828, 2005

Key words: emulsion polymerization; polystyrene; morphology; stimuli-sensitive polymers

INTRODUCTION

Microgels composed of thermally sensitive polymers continue to attract attention because of their potential applications in numerous fields.^{1–3} Perhaps the most widely studied class of responsive polymers is temperature-responsive poly(alkylacrylamide)s, specifically poly(*N*-isopropylacrylamide) (PNIPAm).⁴ PNIPAm is very soluble in methanol and in cold water, and it has a lower critical solution temperature (LCST) at 31°C in water, which is very close to room temperature. Its related gels can undergo a volume change as large as 100 times upon an infinitesimal environmental change.⁵ Heskins and Guillet⁶ first reported the thermoreversible phase-transition phenomenon in 1968. Since then, the physical chemistry of thermosensitive polymers⁷ and ingenious applications^{8,9} of this phenomenon have been widely investigated with PNIPAm and *N*-isopropylacrylamide (NIPAm) copolymers.¹⁰

In the past decades, increasing attention has been paid to the preparation and characterization of thermally sensitive polymer particles, which were found to offer unique properties for many applications, especially in biology.^{11–13} Colloidal particles composed of a solid polymer core and a temperature-sensitive crosslinked polymer shell present interesting examples of micronetworks with a well-defined geometry. Thus, fixing the ends of crosslinked PNIPAm chains to

a solid polystyrene core defines one boundary of the micronetwork that stays constant during the transition.¹⁴ There has been a growing interest in responsive latices that possess a more advanced architecture and hence are multifunctional.^{15,16} Numerous responsive core-shell or core-corona particles have been synthesized.^{5,14,17–20} Polystyrene latices stabilized by PNIPAm were prepared by the free-radical polymerization of styrene (St) in the presence of PNIPAm.²¹ These latex particles, with the particle core composed of polystyrene and PNIPAm covered with a PNIPAm hydrogel layer, were expected to offer unique properties.^{17,22} In this article, we report on the preparation of thermosensitive composite microspheres with a polystyrene core and a PNIPAm shell and the particle size and thermosensitive properties of the resulting composite microspheres.

EXPERIMENTAL

Materials

St was distilled *in vacuo*, and the distilled St was refrigerated. All water was deionized and boiled under N_2 before use. NIPAm was purchased from Aldrich Chemical (NJ) and purified by recrystallization from a 1:1 mixture of toluene and hexane. All other chemicals, including potassium persulfate (KPS) and *N,N'*-methylenebisacrylamide (MBA), were used as received.

Preparation of the composite microspheres

Core-shell microspheres were prepared via aqueous free-radical, emulsifier-free emulsion polymerization

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under a nitrogen atmosphere. The polymerization was carried out as follows.

Poly(styrene-*co*-*N*-isopropylacrylamide) [poly(St-*co*-NIPAm)] seed

Water (68.0 mL) was added to a 250-mL, round-bottom, three-necked reactor equipped with a magnetic stirrer, a condenser, and a nitrogen inlet. St (5.8×10^{-2} mol), NIPAm (6.0×10^{-3} mol), and KPS (2.8×10^{-4} mol) were then added. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until the polymerization was finished. The mixture was stirred for 1 h. Then, the flask was placed in a 70°C oil bath. The reaction was carried out for 24 h.

Composite microspheres (I)

The poly(St-*co*-NIPAm) core emulsion (10.0 mL) was used as a seed, and KPS (3.0×10^{-5} mol) was added. The mixture was purged with nitrogen and was stirred for 1 h. Then, the flask was placed in a 70°C oil bath, and the reaction was allowed to proceed for 0.5 h. A solution of NIPAm (2.7×10^{-2} mol) and MBA (2.8×10^{-4} mol) in water (50.0 mL) was dripped for 2.5 h at 70°C. This reaction was carried out for 24 h at 70°C.

PNIPAm seed

Water (68.0 mL) was added to a 250-mL, round-bottom, three-necked reactor equipped with a magnetic stirrer, a condenser, and a nitrogen inlet. NIPAm (7.8×10^{-3} mol), MBA (3.7×10^{-4} mol), and KPS (1.7×10^{-4} mol) were then added. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until the polymerization was finished. The mixture was stirred for 1 h. Then, the flask was placed in a 70°C oil bath. The reaction was carried out for 24 h.

Composite microspheres (II)

The PNIPAm core emulsion (30.0 mL) was used as the seed, and water (25.0 mL), NIPAm (2.0×10^{-3} mol), and St (1.3×10^{-2} mol) were added. After the mixture was purged with nitrogen and was stirred for 2 h, the flask was placed in a 70°C oil bath, and KPS (5.6×10^{-5} mol) was added. The reaction was allowed to proceed at 70°C for 24 h.

Transmission electron microscopy (TEM)

To prepare an unstained specimen for TEM, we diluted the emulsion with deionized water. We placed a drop of this sample on a Formvar-coated copper grid

for 2 min, we removed the excess emulsion by touching a piece of filter paper to the drop, and we dried the grid in air. The TEM images were obtained at 80 kV with a JEOL (Tokyo, Japan) JEM 100 CxII instrument.

Dynamic light scattering (DLS)

The hydrodynamic radius (R_h) of the microspheres was measured by DLS. Emulsions were diluted with deionized water to obtain an appropriate concentration for the light scattering experiments and then were poured into a cuvette. The cuvette was set inside a sample holder. The holder was maintained at a desired temperature between 20 and 50°C. The diffusion coefficients (D) of particles in diluted dispersions were measured with a Inova 90 coherent argon laser (514.5 nm), a BI-200SM goniometer, and a BI-900AT multi- τ digital correlator (Brookhaven Instruments, Holtsville, NY) at a 90° scattering angle. R_h was calculated as follows:

$$R_h = k_B T / (6\pi\eta D) \quad (1)$$

where k_B , η , and T are the Boltzmann constant, solvent viscosity, and absolute temperature, respectively. The samples were not filtered before the measurements to prevent bias of the results by the exclusion of large particles.

RESULTS AND DISCUSSION

Preparation of the microspheres

The TEM photographs of the latex taken directly from the preparation are shown in Figure 1. The photographs show that the microspheres of poly(St-*co*-NIPAm) [Fig. 1 (a)] and I, consisting of a poly(St-*co*-NIPAm) core and a crosslinked (MBA) PNIPAm shell [Fig. 1 (b)], were spherical and monodisperse; the microspheres of crosslinked (MBA) PNIPAm [Fig. 1 (c)] were nearly spherical and monodisperse; and II [Fig. 1 (d)] was shaped like a silkworm cocoon, and there were some monodispersed small particles that may have been poly(St-*co*-NIPAm).

These results indicated that the emulsifier-free seeded emulsion polymerization in system I did not generate the second nucleation, and the polymerization proceeded in the corresponding seed particles. However, it did generate the second nucleation in system II.

The composite microspheres were synthesized by a two-stage reaction. The seed latices were synthesized in the first stage of the reaction. Then, the composite microspheres were formed in the second stage of the reaction. The morphology of the composite microspheres formed in this work with $K_2S_2O_8$ as the initiator could be explained as follows.

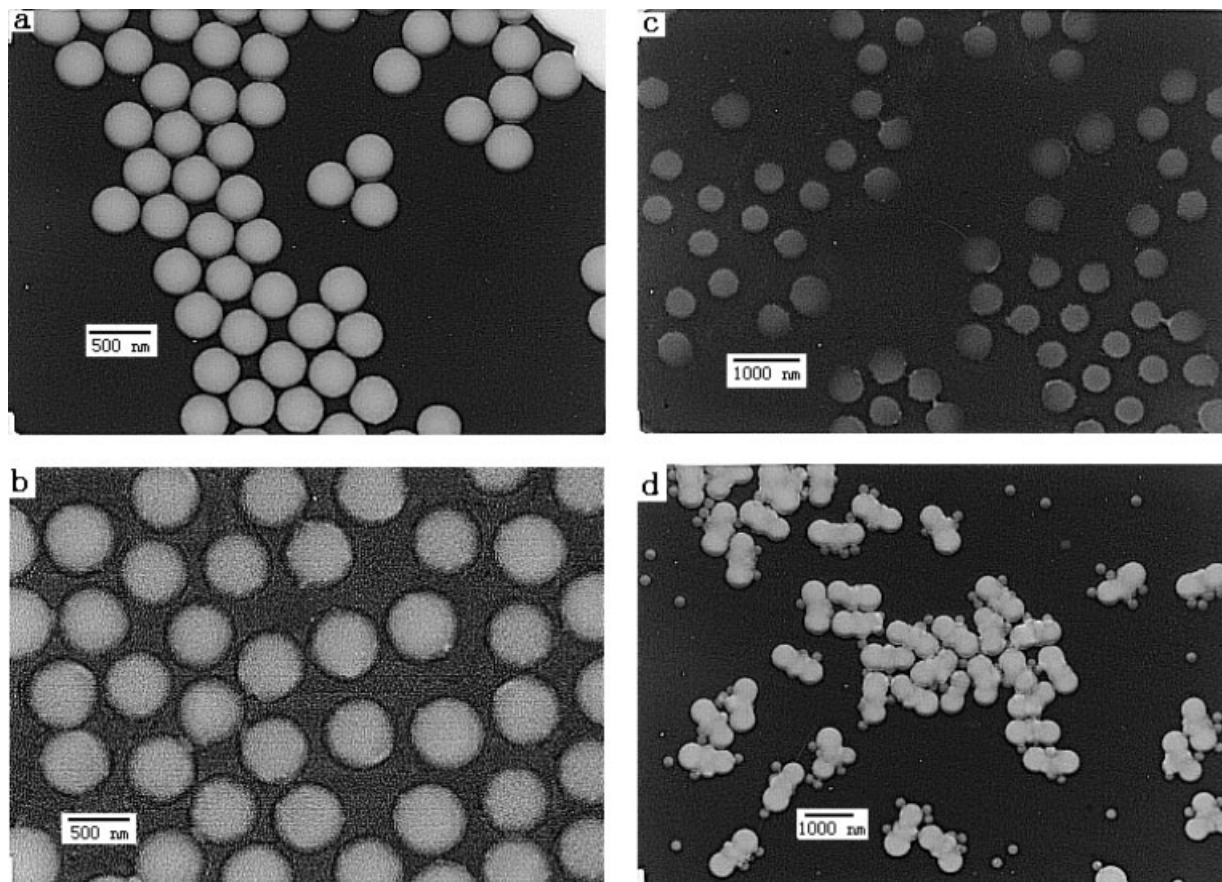


Figure 1 TEM micrographs of thermosensitive composite microspheres: (a) poly(St-co-NIPAm) seed latex, (b) composite microspheres (I), (c) PNIPAm seed latex, and (d) composite microspheres (II).

In system I, NIPAm and MBA were polymerized in the presence of poly(St-co-NIPAm) seed latices. After NIPAm and MBA were added, one part of NIPAm and MBA swelled into the shell region of the poly(St-co-NIPAm) seed latex microspheres by the stirring process, and another part of NIPAm and MBA dissolved in the aqueous medium. The initiator that was used in the second stage of the reaction was water-soluble $K_2S_2O_8$, so the hydrophilic SO_4^- group, which decomposed from $K_2S_2O_8$, anchored onto the surface of the seed latex particle and dissolved in the aqueous medium because the hydrophilic SO_4^- group liked to be close to the aqueous medium.²³ The polymerization in the second stage proceeded on the surface of the poly(St-co-NIPAm) seed latex to form a crosslinked (MBA) PNIPAm shell and in the aqueous medium to form an oligomer, but the oligomer was easily captured by the poly(St-co-NIPAm) seed latex microspheres. The NIPAm and MBA monomer that was in the aqueous medium diffused to the shell region to proceed to the second stage of the reaction. Therefore, I was formed.

In system II, NIPAm and St were polymerized in the presence of crosslinked (MBA) PNIPAm seed latices. After NIPAm and St were added, one part of

NIPAm swelled into the surface of the PNIPAm seed latex microspheres by the stirring process, but most of NIPAm dissolved in the aqueous medium; St formed monomer drops and dispersed in the aqueous medium. The hydrophilic SO_4^- group anchored onto the surface of the seed latex particle and dissolved in the aqueous medium. The copolymerization of NIPAm and St proceeded in the aqueous medium to form poly(St-co-NIPAm) particles. Moreover, NIPAm on the surface of the crosslinked (MBA) PNIPAm seed latex microspheres was polymerized. Some PNIPAm seed latex microspheres approached one part of the growing poly(St-co-NIPAm) particles to stabilize them. As a result, the poly(St-co-NIPAm) particles melted two or three crosslinked (MBA) PNIPAm seed latex microspheres to form silkworm-cocoon-shaped microspheres. The NIPAm and St monomer diffused to the poly(St-co-NIPAm) particles to proceed to the second stage of the reaction. Therefore, II was formed.

The number-average (D_n) and weight-average (D_w) diameters and the coefficient of variation (CV) were calculated from the results of TEM.^{24,25} Table I shows the values for D_n , D_w and CV obtained from TEM and the hydrodynamic diameter (D_h) of the microspheres obtained from DLS.

TABLE I
Diameters of the Microspheres

Sample ^a	TEM			DLS D_h (nm) ^b
	D_n (nm)	D_w (nm)	CV (%)	
Poly(St-co-NIPAm) seed latex	374	375	2.6	504
Composite microspheres (I)	609	612	4.2	1116
PolyNIPAm seed latex	518	530	8.5	1043
Composite microspheres (II)				1510

^a See the Experimental section.

^b Measured at 25°C.

At room temperature, the particles were swollen with water because PNIPAm was water-soluble. When a drop of the dilute latex was placed on a microscope grid, the monodisperse microspheres were pulled by surface tension forces to form familiar two-dimensional ordered arrays. Further drying caused the latex microspheres to shrink and form disks. Therefore, the diameters of the microspheres measured with TEM were smaller than those measured with DLS.

Thermosensitive properties

The hydrodynamic particle sizes of the microspheres were measured at various temperatures, and the results are shown in Figure 2. Figure 2(a) shows the hydrodynamic particle sizes of the microspheres transition for poly(St-co-NIPAm) microspheres and composite microspheres with a crosslinked (MBA) PNIPAm shell (I). The hydrodynamic microsphere size decreased with increasing temperature.

When the temperature of an aqueous PNIPAm solution is raised above the LCST, hydrophobic groups in the polymer form insoluble aggregates. This suggests that the microspheres collapsed because a hydrophobic interaction occurred between PNIPAm and polystyrene. The results indicate that the micro-

spheres shrank remarkably at 32°C, which was the LCST.

Figure 2(b) shows the hydrodynamic particle sizes of the microspheres transition for crosslinked (MBA) PNIPAm microspheres and II; similar results were obtained. A second peak, with a smaller particle size than the original peak, was observed in the histogram for II, but we did not use the peak in the calculation of the average composite microsphere size.

Small shifts in the LCST were observed for the composite microspheres in both cases. The LCST shifted to lower temperatures for I and to higher temperatures for II. This indicated that the properties of the composite microspheres were different from those of the seed latex particles.

CONCLUSIONS

Thermosensitive composite PNIPAm microspheres with diameters greater than 1.0 μm were prepared via aqueous free-radical, emulsifier-free emulsion polymerization. The results indicated that the emulsifier-free seeded emulsion polymerization of I, consisting of a poly(St-co-NIPAm) core and a crosslinked (MBA) PNIPAm shell, did not generate the second nucleation, and the polymerization proceeded in the corresponding seed particles. However, it generated the second nucleation in II, consisting of a crosslinked (MBA) PNIPAm core and a poly(St-co-NIPAm) shell, which was shaped like a silkworm cocoon. The thermosensitive properties of the composite microspheres were evaluated via the hydrodynamic size of the composite microspheres. The particle size of the composite microspheres decreased with increasing temperature. The results indicated that the microspheres shrank remarkably at 32°C, which was the LCST. The LCST shifted to lower temperatures for I and to higher temperatures for II.

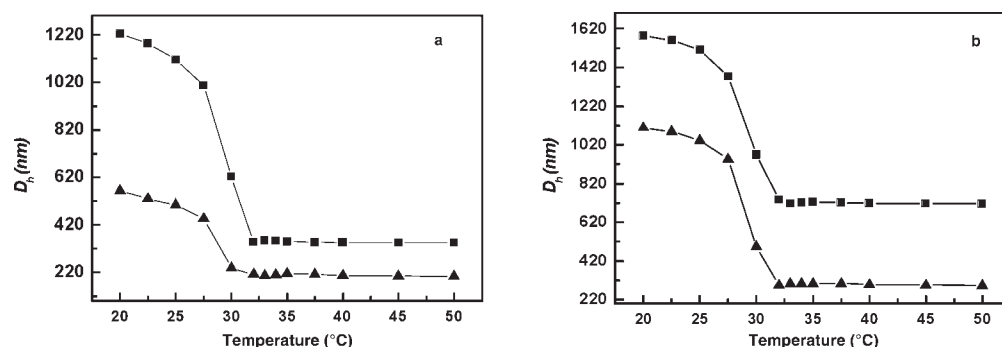


Figure 2 Effect of temperature on the hydrodynamic particle size: (a) (▲) poly(St-co-NIPAm) microspheres and (■) composite microspheres (I) with crosslinked (MBA) PNIPAm shells and (b) (▲) crosslinked (MBA) PNIPAm microspheres and (■) composite microspheres (II).

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