Dispersion of Polystyrene Inside Polystyrene-b-poly(N-isopropylacrylamide) Micelles in Water

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ABSTRACT: The addition of mixture of polystyrene-b-poly(N-isopropylacrylamide) (PS-b-PNIPAM) and polystyrene homopolymer (h-PS) in tetrahydrofuran dropwise into water leads to nanoparticles with a PS core and a thermally sensitive PNIPAM shell. The effects of the ratio of the homopolymer to copolymer and temperature on the formation and stabilization of the dispersion were investigated by using a combination of static and dynamic laser light scattering. PNIPAM shell continuously collapses as temperature increases in the range 20–40 °C. Such formed particles are stable even at temperatures much higher than lower critical solution temperature (LCST ~ 32 °C) of PNIPAM. Our results reveal that the area occupied per stabilizer is a constant. Such a model has been tested valid in several polymeric colloid systems. When a copolymer is dissolved in a solvent which is a nonsolvent for one block and a good solvent for the other, the copolymer may form micelles in solution. The micelles have the ability to solubilize homopolymer in solution and form stable dispersions, which have been studied both theoretically and experimentally. Theoretically, Viduna et al. studied the conformation of solubilized homopolymer chains and core-forming blocks by Monte Carlo Simulation. Izzo and Marques found that the maximum amount of solubilized homopolymer in 1 g of copolymer decreases with the polymerization index of the homopolymer. Experimentally, Tuzar et al. investigated the solubilization of two polybutadiene homopolymers and a triblock copolymer poly(styrene-b-polybutadiene-b-polystyrene) micelles with a high content of butadiene in the polybutadiene cores of polystyrene-b-polybutadiene-b-polystyrene micelles by light scattering. They found that the maximum amount of solubilized polybutadiene based on the weight of the copolymer was 60 wt %. Using laser light scattering, Quintana et al. studied the solubilization of polysobutylene by micelles of polystyrene-b-poly(ethylene/propylene) block copolymer in several selective solvents and found that the maximum of solubilized polysobutylene decreases with the polymerization index of the polysobutylene homopolymer. Besides the systems in organic solvents, aqueous systems have also been studied. Eisenberg et al. studied the formation of crew-cut aggregates from blends of polystyrene-b-poly(acrylic acid) diblock copolymer and polystyrene homopolymer in aqueous solution.

INTRODUCTION As an old issue, colloidal stabilization relates to phase behavior, structure, and properties of particulate suspensions. It is important in pharmacy, ceramics, paints, pigments, and other industries today. Because of the large attractive van der Waals’ interactions, colloids usually irreversibly aggregate. Generally, to stabilize colloidal dispersions, charged groups or short polymer chains are introduced to colloid surface, so that the interactions between the attractive van der Waals’ forces can be balanced by Coulombic or other steric-repulsive interactions. Recently, a so-called nanoparticle haloing strategy was introduced where colloids were stabilized by highly charged small nanoparticles. Such nanoparticles induce effective repulsion. Considering that the small nanoparticles, charged groups, polymer chains, and surfactants are stabilizers of colloids, quantitatively understanding the role of a stabilizer is important for controlling the colloidal stabilization. On the basis of the assumption that the hydrophobic tail of the stabilizer is on the surface of the particles, which is an idealized micelle structure, Antonietti et al. proposed a model, where the particle radius can be calculated with the weight ratio of emulsifier to polymer. Using a more simple model, Wu predicted that for a given dispersion, the particle surface area occupied per stabilizer is a constant. Such a model has been tested valid in several polymeric colloid systems. Besides small nanoparticles, charged groups, polymer chains, and surfactants, block copolymers can also be used as stabilizers. When a copolymer is dissolved in a solvent which is a nonsolvent for one block and a good solvent for the other, the copolymer may form micelles in solution. The micelles have the ability to solubilize homopolymer in solution and form stable dispersions, which have been studied both theoretically and experimentally. Theoretically, Viduna et al. studied the conformation of solubilized homopolymer chains and core-forming blocks by Monte Carlo Simulation. Izzo and Marques found that the maximum amount of solubilized homopolymer in 1 g of copolymer decreases with the polymerization index of the homopolymer. Experimentally, Tuzar et al. investigated the solubilization of two polybutadiene homopolymers and a triblock copolymer poly(styrene-b-polybutadiene-b-polystyrene) micelles with a high content of butadiene in the polybutadiene cores of polystyrene-b-polybutadiene-b-polystyrene micelles by light scattering. They found that the maximum amount of solubilized polybutadiene based on the weight of the copolymer was 60 wt %. Using laser light scattering, Quintana et al. studied the solubilization of polysobutylene by micelles of polystyrene-b-poly(ethylene/propylene) block copolymer in several selective solvents and found that the maximum of solubilized polysobutylene decreases with the polymerization index of the polysobutylene homopolymer. Besides the systems in organic solvents, aqueous systems have also been studied. Eisenberg et al. studied the formation of crew-cut aggregates from blends of polystyrene-b-poly(acrylic acid) diblock copolymer and polystyrene homopolymer in aqueous solution.
by static light scattering and transmission electron microscopy. Liu et al. reported a novel and simple approach to prepare micelles and hollow spheres through self-assembly of poly(e-caprolactone) homopolymer and a random copolymer with short poly(e-caprolactone) as side chains.

On the other hand, the synthesis and self-assembly of block copolymers with one thermosensitive block and one hydrophobic block have been reported. Among the thermosensitive polymers studied, poly(N-isopropylacrylamide) (PNIPAM) with a lower critical solution temperature (LCST) at ~32 °C has been extensively used. Cho et al. have synthesized diblock copolymer consisting of PNIPAM as hydrophilic block and poly(γ-benzyl l-glutamate) as hydrophobic block. The core-shell nanoparticles were obtained by the diafiltration method. The size of the nanoparticles was unchanged between 25 and 40 °C. While it was found that the size distribution of the nanoparticles was very large, Tenhu et al. have investigated the micellization behavior of series of amphiphilic diblock copolymers comprising PNIPAM as a thermosensitive block with hydrophobic blocks, either poly(styrene or poly(tert-butyl methacrylate). Micellar particles were formed when the length of the PNIPAM block was shorter and it was unexpected that the micellar particles were stable even at the temperature above LCST of PNIPAM. Recently, Hamley and coworkers have prepared poly(methyl methacrylate)-b-poly(N-isopropylacrylamide) amphiphilic block copolymers and studied the formation and stability of the micelles. They found that the micelles aggregated when the temperature was above LCST of PNIPAM. So far, solubilization of homopolymer by using these kinds of amphiphilic block copolymers with one thermosensitive block has received less attention.

In the present work, we have prepared polymeric colloids consisting of polystyrene-b-poly(N-isopropylacrylamide) (PS-b-PNIPAM) and polystyrene homopolymer (h-PS) in water, where PS blocks and h-PS are expected to form the core and PNIPAM blocks form the shell. The increase of the amount of h-PS leads to the increase in the size of the hydrophobic PS core, while the area stabilized by per hydrophilic PNIPAM is close to a constant. By using of a combination of static and dynamic laser light scattering, we have investigated the stabilization of the colloidal particles. Our objective is to understand the relation between the surface area per stabilizer and the stabilization of the dispersion in aqueous solution.

**EXPERIMENTAL**

**Sample Preparation**

Styrene was first washed three times with NaOH aqueous solution and then with water to remove the resultant salts and residual NaOH. Finally, styrene was distilled under reduced pressure over calcium hydride. N-isopropylacrylamide (NIPAM, Aldrich) was purified by recrystallization from a mixture of benzene and n-hexane. 4,4’-Azobisisobutyronitrile (AIBN; Fluka, 98%) were purified by recrystallization from ethanol. Tetrahydrofuran (THF) was distilled from a purple sodium ketyl solution. The details about the synthesis and characterization of PS-b-PNIPAM diblock copolymer can be found elsewhere. Molecular weight and molecular weight distribution (Mw/Mn) were determined by gel permeation chromatography (GPC) on a Waters 150C by use of monodisperse polystyrene as the calibration standard and THF as the eluent with a flow rate of 1.0 mL/min. PS-b-PNIPAM copolymer used contains 207 PS units and 357 PNIPAM units. The polydispersity index (Mw/Mn) is 1.17. Polystyrene homopolymer (h-PS, Shodex; Mw = 1.36 × 10^4 g/mol, Mw/Mn = 1.02) contains 131 PS units.

**Dispersion Preparation**

The micellization of PS-b-PNIPAM with a certain amount of h-PS was induced by adding 0.4 mL solution of PS-b-PNIPAM and h-PS in THF dropwise into 40 mL of deionized water under stirring at 20 °C. Such prepared dispersions were stabilized by the hydrophilic PNIPAM shell. The initial PS-b-PNIPAM concentration in THF solution was kept as 3.3 × 10^{-4} g/mL. The small amount of THF (1 wt %) introduced in the preparation was removed by evaporation under reduced pressure.

**Experimental**

**Sample Preparation**

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RESULTS AND DISCUSSION

Figure 1 shows that the average hydrodynamic radius ($R_h$) and average radius of gyration ($R_g$) of the dispersion as a function of the h-PS weight fraction ($f_{PS}$) which is defined as the ratio of the weight of h-PS ($W_{h-PS}$) to the total weight of h-PS and PS-b-PNIPAM ($W_{h-PS} + W_{PS-b-PNIPAM}$) at 25 °C. Our preliminary experiments demonstrated that PS dispersion is stable when $f_{PS} < ~33 \text{ wt }\%$. The introduction of more h-PS leads to macroscopic precipitation. This is because the hydrophilic PNIPAM blocks can only stabilize a certain surface area of the particles. Similarly, Tuzar et al. shows that the maximum amount of solubilized polybutadiene by a three-block copolymer poly(styrene-butadiene-styrene) was 60 wt % based on the weight of the copolymer, which means that the weight fraction based on the total weight of homopolymer and block copolymer was ~38 wt %. When the amount of polybutadiene homopolymer was higher than 38 wt %, the solution was unstable. Note that the zeta potential of the core-shell nanoparticles was slightly negative between $-6$ and $-3 \text{ mV}$, which is consistent with the value of PNIPAM grafted P(PNIPAM-co-styrene) core-shell nanoparticle ($-3.5 \text{ mV}$), indicating that the electrostatic interaction may contribute to some extent to the stability of the dispersion here. In comparison with the micelles formed only by PS-b-PNIPAM block copolymers, the addition of h-PS lead either ($R_h$) or ($R_g$) to increase slightly, suggesting an increase in the micellar dimensions and indicating that more h-PS have been accumulated and stabilized by PS-b-PNIPAM in each core-shell particle.

![FIGURE 1](image1.png)

**FIGURE 1** h-PS content ($f_{PS}$) dependence of average hydrodynamic radius ($R_h$), average radius of gyration ($R_g$) and their ratio ($R_g/R_h$) of core-shell particles ($h$-PS dispersion), where $f_{PS}$ is defined as $f_{PS} = W_{h-PS}/(W_{h-PS} + W_{PS-b-PNIPAM})$.

The structure of the particles can be better viewed in terms of $R_h/R_b$. It is known that for a uniform and nondraining sphere, $(R_h)/(R_b) = 0.78$; for a linear flexible random chain in a good solvent, $(R_h)/(R_b) = 1.5$. As $f_{PS}$ increases from 0 to 8.9 wt %, $(R_h)/(R_b)$ increases from 0.58 to 0.75. This is because the collapsed and dense PS core becomes larger, and the effect of the swollen PNIPAM shell on $(R_h)$ and $(R_b)$ decreases so that the particles become more uniform. Further increasing $f_{PS}$ from 8.9 to 32.8 wt % no longer varies $(R_h)/(R_b)$ because the particles tend to be uniform and nondraining. Namely, the addition of h-PS leads both $(R_h)$ and $(R_b)$ to increase but their ratio $(R_h)/(R_b)$ almost holds. Figure 2 shows that the apparent weight average molar mass ($M_w$) and the average density ($\rho$) of the dispersion increase with $f_{PS}$ further indicating that the core of the micelles becomes denser. Note that the maximum density (~0.25 g/mL) is still much lower than that of bulk PS or bulk PNIPAM (~1 g/mL). This is because that the PS chains in the core are unsolvated, i.e., the density of the PS core is close to that of the bulk PS (~1 g/mL), while the PNIPAM chains in the corona are highly solvated, which means that the density of the PNIPAM corona is much less than that of the bulk PNIPAM. Wu has reported that the densities of the PNIPAM microgel and PNIPAM linear chains in water at 30.0 °C are 0.021 and 0.0063 g/mL, respectively, which are smaller than the density of the core-shell nanoparticles due to the existence of the unsolvated PS core here.

![FIGURE 2](image2.png)

**FIGURE 2** Plots of the apparent molecular weight ($M_w$) and the average density of the micelles versus $f_{PS}$, where $(\rho)$ is defined as $\rho = M_w/(\frac{1}{3} \pi (R_h)^3 n_A)$.

Because h-PS and PS-b-PNIPAM polymer chains were mixed homogenously in THF solution, we can assume that the
composition of each micelle in aqueous solution is equal to that in original THF solution. From the composition of the micelles, $M_w$ of the nanoparticles, PS-b-PNIPAM diblock copolymer ($M_{PS-b-PNIPAM}$) and PS homopolymer ($M_{PS}$), we were able to calculate the average number of diblock copolymer ($N_b$) and PS homopolymer ($N_h$) inside each nanoparticle by using eqs 2 and 3,

$$N_b = \frac{[M_w \times (1 - f_{PS})/M_{PS-b-PNIPAM}]}{f_{PS}} \tag{2}$$

$$N_h = \frac{[M_w \times f_{PS}/M_{PS}]}{1} \tag{3}$$

Figure 3 shows that both $N_b$ and the ratio $N_h/N_b$ increase with $f_{PS}$. As more $h$-PS was trapped in the micelle, $N_h$ increases. Because of the increase in $N_h$, the dispersion $N_h$ also increase but for a small magnitude because the PS-b-PNIPAM is supposed to stabilize the surface of the dispersion. This is the reason that $N_h/N_b$ increases with $f_{PS}$.

Figure 4 shows that the scattering vector ($q$) dependence of the average line width ($\Gamma$). The linear ($\Gamma$) versus $q^2$ relation at different temperatures indicates that the micelles have an isotropic diffusive behavior.

Figure 5 shows that as the temperature increases, $\langle R_h \rangle$ gradually decreases, while $\langle R_g \rangle$ slightly decreases, i.e., the micelles undergo a continuous collapse transition. Such a continuous collapse transition has been observed for PNIPAM chains attached on polystyrene latex$^{34,35}$ and planar gold surface$^{36-38}$ The nonuniformity of the chains as well as the surface constraint were thought to be responsible for the continuity.$^{39-42}$ It is worth noting that crosslinked PNIPAM gels$^{43,44}$ and individual PNIPAM chains with narrowly distributed high molar mass$^{39}$ show a sharp volume change at $\sim 33$ °C. Note that double phase transition of PNIPAM chains has been reported by Tenhu et al. and Liu et al. Tenhu et al. prepared gold nanoparticles stabilized with two types of PNIPAMs via the "grafting to" approach and found the PNIPAM brushes with a grafting density of 0.42 nm$^2$/chain exhibit two separate phase transitions.$^{25}$ The PNIPAM segments in the inner zone undergo the first transition at lower temperature and PNIPAM segments in the outer zone show the second transition at higher temperature. Liu et al. synthesized silica nanoparticles grafted with...
PNIPAM brushes with a grafting density of ~2 nm²/chain and also found double thermal phase transition. We did not observe double phase transition maybe because of the relatively lower grafting density of PNIPAM chains in our experiments, which we will discuss later. It should be stated that there is no plateau at the temperature around 20 °C. This phenomenon has also been observed in the study of phase transition by laser light scattering and QCM, which may be explained as at this temperature the PNIPAM random coils or chains on the surface are still not fully hydrated and extended. Figure 5 also shows that $R_g$ of the PS dispersion stabilized with PS-b-PNIPAM decreases more slowly than that of PS-b-PNIPAM micelles. This is because the increase of PS weight in the dispersion makes the weight of PS dominant and the effect of the shrinking of PNIPAM play less importance on the decrease of $R_g$. This influence is much more obvious for the decrease of $R_h$ than that of $R_g$. To show clearly the effect of the temperature on the $R_h$, the data in Figure 5 have been replotted in Figure 6 in terms of percentage change in hydrodynamic radius. Figure 6 shows the temperature dependence of $R_h$ of the PS dispersion stabilized with PS-b-PNIPAM micelles at the temperature $T$ and 17.5 °C. Presumably, the PS core is unaffected by the change in temperature, the change in $R_h$ is because of the dehydration of the PNIPAM corona. $R_h$ increases from 61 to 72% with the increase in $f_{PS}$ from 0% to 32.8 wt %, which also indicates that the PNIPAM corona has less effect on hydrodynamic radius when $f_{PS}$ increases.

Our experimental results also show that the weight average molar masses of the micelles slightly change as the temperature increases, i.e., no aggregation occurs when PNIPAM corona collapses. In other words, the micelles are stable even at a temperature much higher than the LCST of PNIPAM. Such a phenomenon has been observed before. The stabilization of the dispersion can be explained in terms of viscoelasticity. The aggregation of the micelles is controlled by the average time of the collisions. Only when the collision time ($\tau_c$) is longer than the time ($\tau_0$) for a permanent chain overlapping entanglement between two approaching micelles, can they come into fusion. As PNIPAM chains consisting of the micelle corona are short, even at the temperatures below the LCST of PNIPAM, the tethered chains have much smaller contact area than the free chains. In other word, $\tau_c > \tau_0$, so that they have less chances to stick together. Meanwhile, the surface constraint prevents the grafted chains from complete dehydrating, further stabilizing the micelles. Note that Tang et al. shows that core-shell nanoparticles of poly(methyl methacrylate)-b-poly(N-isopropylacrylamide) diblock copolymers aggregate at ~32 °C, which may due to the relatively higher concentration (0.5 wt %) of the diblock copolymers compared with the concentrations (<5 x 10⁻⁶ g/mL) of the core-shell nanoparticles in our experiments.

Assuming the average hydrodynamic radius $R_h$ of the micelles at most collapsed state is equal to the average radius of the core of the micelle and the number of the PS-b-PNIPAM chains in the micelle can be obtained as shown in Figure 3, we can calculate that the surface area (s) occupied per PNIPAM chain is about 23 nm². However, the assumption that the hydrodynamic radius in the most collapsed state is equal to the average radius of the core of the micelle overestimate the size of the micelle core because we ignore the thickness of the collapsed PNIPAM corona. To obtain more accurate s, we have to estimate the thickness of the collapsed PNIPAM corona. By using a self-consistent field (SCF) developed by Milner et al., the height h of a brush is proportional to polymerization index. In addition, it has been shown by Brooks et al. that the hydrodynamic thickness of the PNIPAM brush ($M_n = 796,000, M_w/M_n = 1.26$) at the most collapsed state is ~100 nm. Note that the grafting density of their PNIPAM brush is 23 nm², which is similar to that of the PNIPAM brush here. The molecular weight of PNIPAM block is $4 \times 10^4$ g/mol. Therefore, the thickness of the PNIPAM brush at the most collapsed state can be estimated as ~5 nm. Then the s values can be recalculated and the data have been shown in Figure 7. From Figure 7 we know s is about 19 nm², which is independent of $f_{PS}$, i.e., for the micelles with or without the solubilized h-PS, each PNIPAM...
occupy a certain area. Such relation has been tested valid in polymeric nanoparticles stabilized by surfactant, ionic groups, and polymer chains. The present study further indicate such a relation is general for a stable polymeric particles manipulated by hydrophobic−hydrophilic interaction balance. Note that the value $s$ is higher than those reported by Tenhu et al.²⁵ and Liu et al.,⁴⁵ which maybe the reason we did not observe double phase transition.

**CONCLUSIONS**

Polystyrene dispersion can be stabilized by amphiphilic diblock copolymer PS-b-PNIPAM. The light scattering studies on the amount of hydrophobic $h$-PS as a function of temperature demonstrate that the particles are stable even at temperatures higher than LCST of PNIPAM. As temperature increases, PNIPAM shell continuously collapses in the temperature range 20–40 °C. The area occupied per hydrophilic PNIPAM chain on the hydrophobic PS core holds a constant independent of the amount of $h$-PS, and hence it is a critical parameter for stabilization of polymeric particles in water.

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**REFERENCES AND NOTES**