

Poly(methyl methacrylate)/Poly(*N*-isopropylacrylamide) Core-Shell Particles Prepared by Seeded Precipitation Polymerization: Unusual Morphology and Thermo-sensitivity of Zeta Potential*

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Abstract Poly(methyl methacrylate)/poly(*N*-isopropylacrylamide) (PMMA/PNIPAM) core-shell particles were synthesized by seeded precipitation polymerization of *N*-isopropylacrylamide (NIPAM) in the presence of PMMA seed particles. The anionic potassium persulfate was used as initiator, and acrylic acid as functional comonomer. It was shown that the weight ratio of the PNIPAM shell to the PMMA core can be greatly increased through continuous addition of NIPAM monomer at a relatively slow rate. PMMA/PNIPAM particles with different shell thickness were obtained by varying the amount of charged NIPAM monomers. These particles exhibited unique nonspherical core-shell morphology. PMMA core was partially coated by dense hair-like or antler-like PNIPAM shell depending on the shell thickness. The measurement of these particles' zeta potential at different temperatures showed that the absolute value of zeta potential unusually decreased as the particle size decreased with temperature.

Keywords: Core-shell particle; Thermo-sensitive; Seeded precipitation polymerization; Synthesis.

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INTRODUCTION

Among the various functional core-shell particles^[1, 2], the particles having glassy polymer core coated by thermo-sensitive polymer shell have attracted increasing attention in the recent years. Such particles have found diverse applications in different areas. For example, they can be used as the model systems for studying the crystallization and the flow behavior of concentrated colloidal suspensions, as the carrier systems for catalytically active metallic nanoparticles and enzymes, and so on^[3].

Poly(*N*-isopropylacrylamide) (PNIPAM) is a typical thermo-sensitive polymer with a lower critical solution temperature (LCST) of about 32 °C^[4]. The coating of PNIPAM onto a glassy polymer core, usually polystyrene (PS) or poly(methyl methacrylate) (PMMA), is generally accomplished by two different routes. One route is to graft PNIPAM chains (linear or branched) onto the polymer core, giving rise to the so-called hairy colloid particles^[5, 6]. The other route is to coat the PNIPAM shell by the seeded precipitation polymerization of NIPAM monomers (with crosslinker and usually a functional comonomer) in the presence of PS or PMMA core particles. For example, several research groups have reported the successful synthesis of PS/PNIPAM core-shell

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particles by seeded precipitation polymerization^[7–10]. In order to enhance the affinity between the shell and core polymers, a certain quantity of *N*-isopropylacrylamide (NIPAM) was added in the synthesis of PS seed particles. Thus, the seed particles used in these studies were in fact the copolymer of styrene and NIPAM. On the other hand, researchers have successfully prepared PMMA/PNIPAM core-shell particles by seeded precipitation polymerization of NIPAM on the PMMA seed particles with the existence of methyl methacrylate (MMA) monomer (the weight ratio of NIPAM to MMA was about 1.0)^[11, 12]. The use of MMA monomer in the seeded polymerization process aided in the formation of PNIPAM shell around PMMA core particles. In addition, other monomers such as anionic acrylic acid (AA) or cationic aminoethyl methacrylate hydrochloride were also copolymerized to the PNIPAM shell to endow it with additional functionalities.

In the present study, we demonstrate the synthesis of PMMA/PNIPAM core-shell particles by seeded precipitation polymerization of NIPAM on the PMMA seed particles. Differing from the literature mentioned above, we performed the seeded polymerization without the presence of MMA monomer. By varying the polymerization conditions, the PMMA/PNIPAM particles with different shell thickness were formed. These particles showed very unique core-shell morphology and thermo-sensitivity of zeta potential.

EXPERIMENTAL

Materials

NIPAM (Sigma Aldrich, Inc.) was recrystallized from hexane and dried under vacuum. MMA and AA monomers were distilled under a reduced pressure of nitrogen. Potassium persulfate (KPS, used as an initiator) was purified by recrystallization from water. *N,N*-Methylene bisacrylamide (MBA, Alfa Aesar, used as a crosslinker) was used as received. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., unless otherwise stated. Double-distilled water was used in all experiments.

Synthesis of PMMA Seed Particles

PMMA seed particles were prepared by soap-free emulsion polymerization within a 500 mL three-necked round bottom flask equipped with a mechanical agitator and a nitrogen inlet. MMA monomer (40.0 g), KPS (0.16 g) and water (260 mL) were charged into the flask, stirred (300 r/min) and purged with nitrogen for 30 min. Then the polymerization was initiated by transferring the flask into a 70 °C water bath. The polymerization was continued for 6 h. The obtained PMMA seed particles were purified by dialyzing against water for 3 days. The dialysate was changed every 12 h.

Synthesis of PMMA/PNIPAM Core-Shell Particles

PMMA/PNIPAM core-shell particles were synthesized by seeded precipitation polymerization of NIPAM in the presence of PMMA seed particles in a 250 mL three-necked round bottom flask equipped with a mechanical agitator and a nitrogen inlet. First, PMMA seed latex, KPS, AA (used as a functional comonomer) and water were charged into the flask and purged with nitrogen under stirring (300 r/min) for 30 min. Then, the flask was immersed into a 70 °C water bath and the oxygen-free aqueous solution of NIPAM and MBA was fed into the flask either batchwise or continuously under the blanket of nitrogen. After the monomer addition, the polymerization was further continued for 5 h. The resulted PMMA/PNIPAM core-shell particles were centrifuged, the supernatant decanted, and the white sediment redispersed in water. This centrifugation-decantation-redispersion operation was repeated for three times. The weight ratio of PNIPAM shell to PMMA core (shell/core) was determined by gravimetric method according to the following equation:

$$\text{Shell / core} = \frac{W_{\text{CS}} - W_{\text{s}}}{W_{\text{s}}} \times 100$$

where W_{CS} is the weight of PMMA/PNIPAM core-shell particles and W_{s} is the weight of PMMA seed particles. The detailed polymerization recipes for the synthesis of PMMA/PNIPAM particles are given in Table 1.

Table 1. Polymerization recipes for the synthesis of PMMA/PNIPAM core-shell particles by seeded precipitation polymerization and the typical properties for the particles obtained

Symbol	PMMA latex ^a (g)	KPS (g)	AA (mg)	NIPAM (g)	MBA (g)	H ₂ O (mL)	Monomer addition rate ^b (mL/min)	Shell/core ^c	OD ₁₆₅₆ / OD ₁₇₃₅	Shell thickness ^d (nm)
CS1	15.6	0.080	50	1.0	0.080	170	batch	0.30	0.285	123.9
CS2	15.6	0.080	50	1.0	0.080	170	1.0	0.46	0.382	229.8
CS3	15.6	0.080	50	1.0	0.080	170	0.7	0.61	0.564	271.8
CS4	15.6	0.080	50	1.0	0.080	170	0.5	0.65	0.758	309.5
CS5	15.6	0.056	35	0.7	0.056	170	0.5	0.48	0.438	250.7
CS6	15.6	0.024	15	0.3	0.024	170	0.5	0.23	0.119	80.2

^a Adjusted to contain 1.0 g solid polymer;^b The concentration of monomer solution was 5.0 wt%, which was prepared by dissolving NIPAM and MBA in appropriate amount of water;^c The weight ratio of PNIPAM shell to PMMA core, estimated by gravimetric method;^d Determined by DLS at 20 °C

Characterization

The hydrodynamic diameter (D_h) and zeta potential of particles were determined by dynamic light scattering (DLS) using a zeta potential analyzer (ZetaPlus, Brookhaven Instruments Corporation) equipped with a 15 mW solid state laser (678.0 nm) as light source. The scattered light was measured at the angle of 90° and collected by the autocorrelator. The measurements were made after allowing 5 min for sample equilibration at each temperature. Three successive runs were made on each sample.

The obtained PMMA/PNIPAM core-shell particles were observed by transmission electron microscopy (TEM) using a JEM-1200EXII microscope (JEOL). The latexes were sufficiently diluted with water and dropped onto a carbon film supported on a standard copper mesh grid. After being dried in a desiccator at room temperature, the specimens were examined by TEM at an accelerating voltage of 100 kV. On the other hand, the obtained PMMA seed particles were observed by scanning electron microscopy (SEM) instead of TEM since PMMA polymer is very prone to decompose under the strong irradiation of electron beam. After freeze-drying and sputter-coating with gold, the PMMA particles were examined by SEM (S-3400N, Hitachi) at an accelerating voltage of 20 kV.

Fourier transform infrared spectroscopy (FTIR) spectra were obtained on a Nicolet iS10 spectrometer using the pressed-KBr-pellet technique. The freeze-dried particles were used for FTIR analysis.

RESULTS AND DISCUSSION

PMMA seed particles were prepared by soap-free emulsion polymerization under the conditions specified in the experimental section. A typical SEM image of these particles is given in Fig. 1(a). The obtained PMMA particles were all perfectly spherical with featureless smooth surface. The hydrodynamic diameter (D_h) determined by dynamic light scattering (DLS) is 353.4 nm with a very narrow particle size distribution (PDI = 0.005). Figure 1(b) presents FTIR spectrum of PMMA seed particles. The characteristic absorption peaks due to the C=O stretching and CH₃ bending were observed at 1735 cm⁻¹ and 1394 cm⁻¹, respectively.

The prepared PMMA particles were used as seeds for the synthesis of PMMA/PNIPAM core-shell particles by seeded precipitation polymerization of NIPAM using AA as a functional comonomer and potassium persulfate (KPS) as an initiator. The detailed polymerization recipes are given in Table 1. The aqueous solution of NIPAM monomer and its crosslinker *N,N*-methylene bisacrylamide (MBA) was fed into the reactor either batchwise or continuously. For the batch monomer addition mode (CS1), the weight ratio of PNIPAM shell to the PMMA core (shell/core) was only 0.30 (Table 1). To increase the weight ratio of shell to core, we attempted to carry out the polymerization using the continuous monomer addition mode at various feeding rate while maintaining other parameters unchanged. As is clear from Table 1, CS2, CS3 and CS4 particles showed relatively high weight ratio compared to CS1 particles. Moreover, the slower the addition rate of monomer solution, the higher the ratio became. At the addition rate of 0.5 mL/min, the weight ratio of shell to core increased to 0.65.

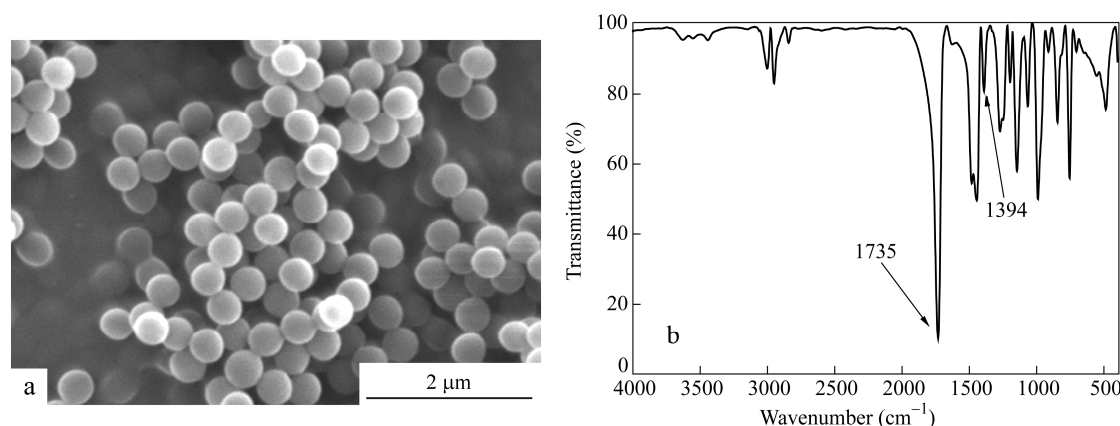


Fig. 1 (a) SEM image and (b) FTIR spectrum of PMMA seed particles prepared by soap-free emulsion polymerization

The FTIR spectra of CS1, CS2, CS3 and CS4 particles are presented in Fig. 2. As compared to PMMA seed particles (Fig. 1b), these PMMA/PNIPAM core-shell particles obviously displayed at least two new absorption peaks at 1656 cm^{-1} and 1550 cm^{-1} . These peaks can be assigned to the amide I band (mainly due to the C=O stretching vibration) and amide II band (a combination of the N—H bending vibration and C—N stretching vibration), respectively^[5, 13, 14]. From FTIR spectra, the ratio of optical density at 1656 cm^{-1} (OD_{1656}) to that at 1735 cm^{-1} (OD_{1735}) was calculated, and the results are given in Table 1. The OD_{1656}/OD_{1735} for CS1 particles was 0.285. In contrast, the CS2, CS3 and CS4 particles gave larger OD_{1656}/OD_{1735} in the range of 0.382–0.758, increasing with decreasing the monomer addition rate. The D_h of these core-shell particles was measured by DLS at 20 °C. From the DLS data of PMMA seed and PMMA/PNIPAM core-shell particles, the increment of particle's radius after seeded precipitation polymerization was calculated and expressed as shell thickness. As shown in Table 1, the shell thickness for CS1, CS2, CS3 and CS4 particles was 123.9, 229.8, 271.8 and 309.5 nm, respectively. This is a result consistent with those obtained from the analyses of weight ratio of shell/core and ratio of optical density.

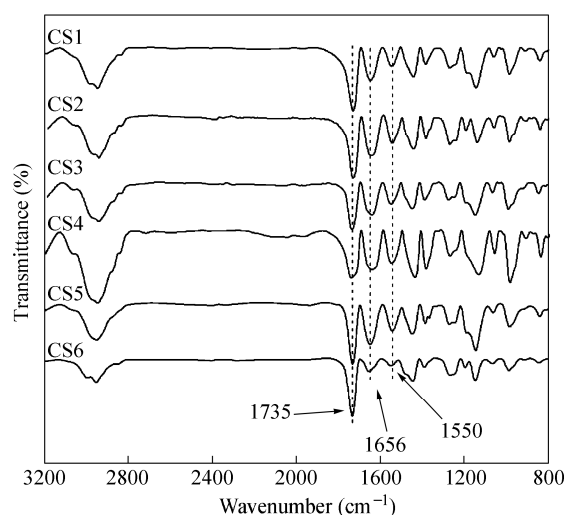


Fig. 2 FTIR spectra of PMMA/PNIPAM core-shell particles synthesized by seeded precipitation polymerization

The shell thickness, as well as the weight ratio of shell/core and OD_{1656}/OD_{1735} , can also be tuned by controlling the amount of second-stage monomer in the seeded precipitation polymerization. As specified in Table 1, The CS4, CS5 and CS6 particles were obtained by respectively charging 1.0, 0.7 and 0.3 g NIPAM

monomer into the reactor while keeping a constant addition rate at 0.5 mL/min. From the FTIR spectra (Fig. 2) and DLS data of these particles, the shell thickness and ratio of optical density were calculated. The results are shown in Table 1. It is clear that the decrease of NIPAM monomer from 1.0 g to 0.3 g significantly resulted in the decrease of shell thickness from 309.5 nm to 80.2 nm. At the same time, the weight ratio of shell/core was decreased from 0.65 to 0.23 and the OD_{1656}/OD_{1735} was decreased from 0.758 to 0.119.

The morphology of the PMMA/PNIPAM particles was examined by TEM. The samples for TEM observation were all prepared at room temperature, which is lower than the LCST of PNIPAM. Thus, these core-shell particles can well maintain the morphology of swollen state during dehydration process^[15]. Figure 3 displays the representative TEM images of CS6, CS5 and CS4 particles, in which PNIPAM domain has lower electron density and is relatively transparent. The TEM image of CS6 particles at lower magnification (Fig. 3a) indicates that the prepared particles still kept the high monodispersity in their size after the seeded precipitation polymerization. Figure 3(b) shows the close examination of CS6 particles at higher magnification. In contrast to the PMMA seed particles with smooth surface, the CS6 particles clearly showed a nonspherical morphology^[16, 17]. PNIPAM shell seemed to only partially coat the PMMA core and appeared as multiple dense hairs protruding out of the surface. As the addition amount of NIPAM increased to 0.7 g (CS5), the dense hairs became branched and looked like the antler of a male deer (Fig. 3c). As the addition amount of NIPAM further increased to 1.0 g (CS4), the antler-like morphology was still observable, especially at the particle periphery. However, the area of PMMA core surface covered by PNIPAM shell evidently increased (Fig. 3d).

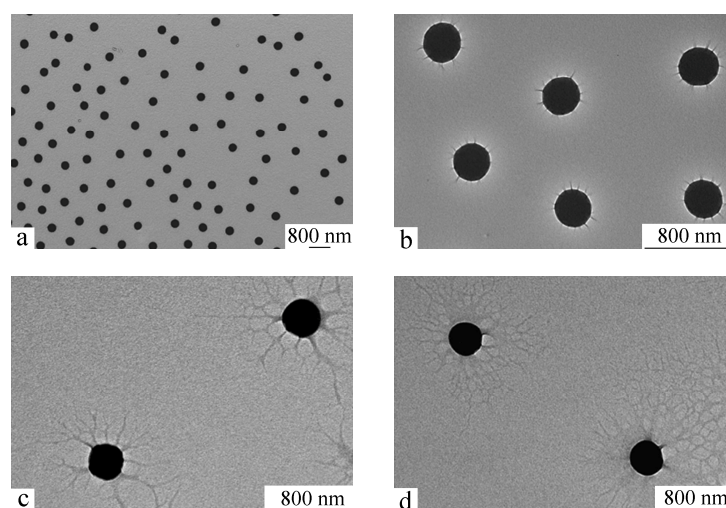


Fig. 3 TEM images of PMMA/PNIPAM core-shell particles synthesized by seeded precipitation polymerization: (a) and (b) CS6, (c) CS5 and (d) CS4 particles

The morphologies described above have not been reported before for the thermo-sensitive core-shell particles obtained by seeded precipitation polymerization, to the best of our knowledge. The particles with this kind of morphology indicate the presence of a large amount of space in the polymer hydrogel shell and more contacting area with the surrounding medium at the temperatures lower than the LCST of PNIPAM. We also dried the PMMA/PNIPAM particles at their fully shrunken state (at 50 °C) and examined them by TEM. As expected, the particles did not show the normal spherical morphology. In contrast, multiple dents were observed at the surface of particles (Fig. S1 in Electronic Supplementary Material). We believe that such uneven surface structure was formed while the antler-like PNIPAM shell collapsed towards the PMMA core surface during the drying process at 50 °C.

In this study, both the soap-free emulsion polymerization for the synthesis of PMMA seed particles and the seeded precipitation polymerization for the synthesis of PMMA/PNIPAM core-shell particles were initiated by

an anionic KPS initiator. In addition, a functional monomer AA was copolymerized to the PNIPAM shell in the seeded precipitation polymerization. Thus, the prepared PMMA/PNIPAM core-shell particles possess negative charge throughout the particles.

The zeta potential and D_h of PMMA/PNIPAM particles were investigated as a function of temperature in double-distilled water. As shown in Fig. 4, the D_h of the CS4 particles decreased continuously at the temperature range lower than 46 °C. Drastic decrease of D_h was observed at about 35 °C. In addition, the change in D_h was fully reversible towards the heating-cooling treatment. Over the four heating-cooling cycles (20–50 °C) we tested, the particle size and size distribution remained almost unchanged at both 20 °C and 50 °C (Fig. S2 in Electronic Supplementary Material). This indicates that the attachment of PNIPAM shell to PMMA core was strong enough to resist the temperature change in these measurements. As for the zeta potential measurement, the particles exhibited negative value at all temperatures as expected. However, the absolute value of zeta potential sharply declined when the temperatures increased from 20 °C to 36 °C regardless of that the shrinkage of thermo-sensitive hydrogel particles generally leads to an increment in the surface charge density and hence the absolute value of zeta potential^[18–20]. This anomalous thermo-sensitivity of zeta potential is probably attributable to the unique core-shell structure of CS4 particles. We speculate that, because of the antler-like morphology, the anionic charges distributed in the interior of PNIPAM shell and on the surface of PMMA core must have an important contribution to the measurement of zeta potential at lower temperatures. This part of anionic charges was screened due to the collapse and shrinkage of PNIPAM shell as the temperature increased, resulting in the decrease of the absolute value of zeta potential.

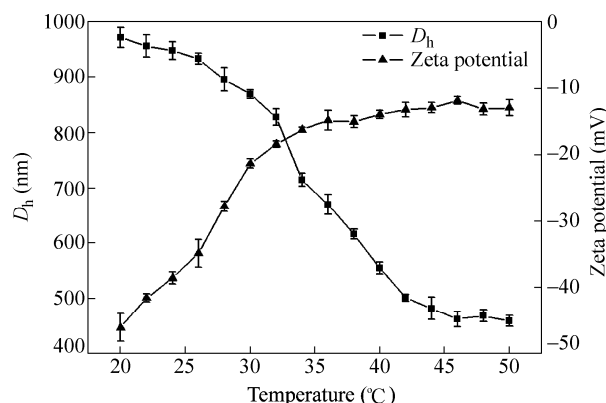


Fig. 4 Thermo-sensitivity of D_h and zeta potential of PMMA/PNIPAM particles (CS4)

CONCLUSIONS

In summary, we successfully synthesized PMMA/PNIPAM core-shell particles by seeded precipitation polymerization of NIPAM using PMMA particles as seed, anionic KPS as initiator and AA as functional comonomer. Different from the usual preparation of PMMA/PNIPAM particles in literature, we performed the polymerization in the absence of MMA monomer. PMMA/PNIPAM particles with different shell thickness were obtained by varying the amount of NIPAM added in the seeded polymerization process. These particles showed very unusual morphology and thermo-sensitivity of zeta potential.

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Electronic Supplementary Material

Poly(methyl methacrylate)/Poly(*N*-isopropylacrylamide) Core-Shell Particles Prepared by Seeded Precipitation Polymerization: Unusual Morphology and Thermo-Sensitivity of Zeta Potential

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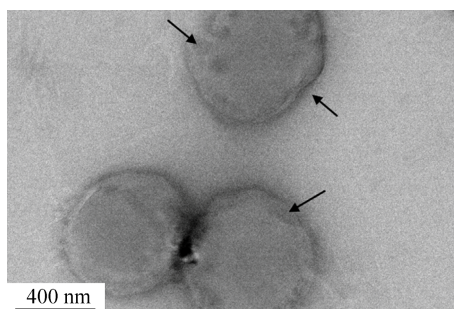


Fig. S1 TEM image of PMMA/PNIPAM core-shell particles (CS4)
The particles were dried at 50 °C. The arrows in the image indicate several indentations at the particle surface.

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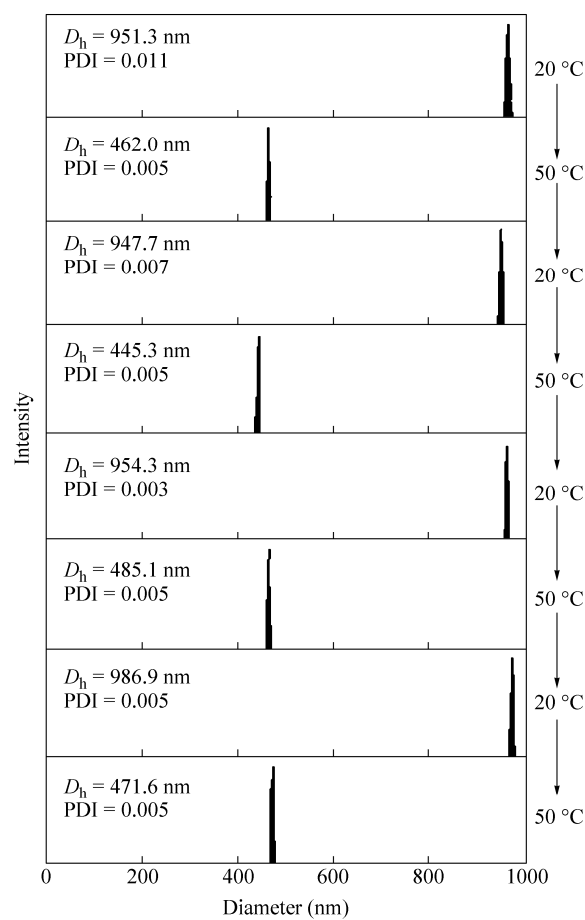


Fig. S2 The multimodal size distribution of PMMA/PNIPAM core-shell particles (CS4) over the four heating-cooling cycles (20–50 °C)
The particles were allowed to equilibrate at each temperature for 5 min before DLS measurements.