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ORIGINAL CONTRIBUTION

# Preparation of thermoresponsive core–shell polymeric microspheres and hollow PNIPAM microgels

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**Abstract** A reliable and efficient route for preparing thermoresponsive hollow microgels based on cross-linked poly(*N*-isopropyl acrylamide) (PNIPAM) was developed. Firstly, monodisperse thermoresponsive core–shell microspheres composed of a P(styrene (St)-*co*-NIPAM) core and a cross-linked PNIPAM shell were prepared by seeded emulsion polymerization using P(St-*co*-NIPAM) particles as seeds. The size of the P(St-*co*-NIPAM) core can be conveniently tuned by different dosages of sodium dodecyl sulfate. The thickness of the cross-linked PNIPAM shell can be controlled by varying the dosage of NIPAM in the preparation of PNIAPM shell. Then, hollow PNIPAM microgels were obtained by simply dissolving the P(St-*co*-NIPAM) core with tetrahydrofuran. The core–shell microspheres and the hollow microgels were characterized by transmission electron microscopy, dynamic light scattering, atomic force microscopy, and Fourier-transform infrared spectroscopy.

**Keywords** Core–shell polymeric microspheres · PNIPAM · Thermoresponsive · Hollow microgels

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## Introduction

Environmentally responsive microspheres that are sensitive to subtle environmental stimuli have attracted increasing interest in recent years due to their potential applications in controlled drug delivery [1–5], biosensing [6, 7], chemical separation [8, 9], catalysis [10, 11], etc. Among these smart materials, poly(*N*-isopropylacrylamide) (PNIPAM) is one of the most widely studied materials owing to its thermosensitivity. As the solution temperature increases, the polymer undergoes a volume phase transition at the lower critical solution temperature (LCST) which is about 32 °C [12].

In order to take advantage of the temperature-sensitive performance based on PNIPAM, various materials containing PNIPAM component have been prepared, including PNIPAM microgels [13–16], core–shell microspheres containing a PNIPAM shell [17, 18], hollow PNIPAM microcontainers [19], and so on. An interesting class of these thermoresponsive materials is monodisperse core–shell microspheres containing a PNIPAM shell. These kinds of core–shell microspheres are promising as supports in the biomedical field [20, 21], nanoreactor for preparing nanoparticles [22]. The thermoresponsive core–shell particles have also attracted interest as model colloids for a comprehensive study of the flow behavior of concentrated suspensions [23, 24]. Hitherto, various core–shell microspheres bearing a PNIPAM shell have been prepared such as polystyrene (PS)–PNIPAM core–shell microspheres [25–27], PMMA–PNIPAM core–shell microspheres [18, 21]. One outstanding advantage of the core–shell microspheres is that the properties can be conveniently controlled by altering the composition and structure of either the core or the shell. For example, if introducing functional monomer

to copolymerize with NIPAM or substituting common core polymer (typically PS and PMMA) with functional polymer, the properties are tuned and the applications are enlarged. Kawaguchi et al. [28] prepared poly(glycidyl methacrylate) (PGMA)–PNIPAM core–shell microspheres and used the thermoresponsive core–shell microspheres as template to synthesize gold nanoparticles. The epoxy groups of PGMA provided active points for the reaction and gold nanoparticles were synthesized in situ between the PGMA core and the PNIPAM shell. Lyon et al. [29] synthesized PNIPAM core–shell microgels of which either the core or the shell is copolymer of NIPAM and acrylic acid. These core–shell microgels are temperature and pH responsive.

Compared with core–shell microspheres, hollow PNI PAM microgels possess a centered void that endows the hollow microgels with potential applications in confined reaction vessels, drug carriers, and protective shield for bioactive materials. Up to now, several methods have been successfully developed to prepare hollow PNIPAM microgels. Sacrificial template method is the most common method for preparing hollow PNIPAM microgels. For example, Zha et al. [30] prepared PNIPAM microcontainers using silica particle templates. Removal of the silica core particles with hydrofluoric acid resulted in hollow PNIPAM microgels. Lyon et al. [31] designed a unique core–shell structure whose core and shell were cross-linked respectively by degradable cross-linker *N*,*N*′-(1,2-dihydroxyethylene) bisacrylamide (DHEA) and nondegradable cross-linker *N*,*N*′-methylenebisacrylamide (BIS). Degradation of the core by cleavage of the 1, 2-glycol bonds in DHEA with $NaIO_4$ left behind hollow microgels. Recently, Lyon et al. [32] prepared sub-50 nm hollow PNIPAM nanogels by in situ polymerization of NIPAM onto Au nanoparticles followed by dissolution of Au core with KCN. Zhang et al. [33] developed a novel route for preparing hollow PNIPAM microspheres from poly(ε-caprolactone) (PCL)–PNIPAM core–shell particles followed by removing the PCL core through biodegradation.

In this paper, we report a convenient method to prepare hollow PNIPAM microgels from P(styrene(St)-*co*-NIPAM)–PNIPAM core–shell microspheres. The preparation mainly includes two steps. Firstly, monodisperse P(St-*co*-NIPAM)–PNIPAM core–shell microspheres were prepared. Subsequently, the P(St-*co*-NIPAM) core was removed by tetrahydrofuran (THF). In this method, emulsion polymerization and physically dissolving process were employed. It is reliable and efficient. Additionally, the preparation of thermoresponsive hollow microgels can be performed in large scale.

## Experimental

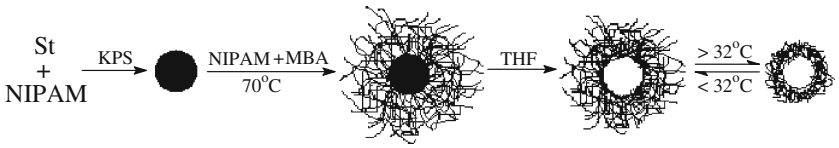
### Materials

St was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd and distilled under reduced pressure prior to use. NIPAM (97%) was obtained from Aldrich and recrystallized from hexane. BIS was purchased from Fluka and used as received. Sodium dodecyl sulfate (SDS; 99%) and potassium persulfate (KPS) were purchased from Fluka and used as received. THF was purchased from Sinopharm Group Chemical Reagent Co., Ltd and used as received. Well-deionized water was used in all experiments.

### Preparation of P(St-*co*-NIPAM)–PNIPAM core–shell microspheres

The polymerization was carried out in a 150-mL three-necked flask equipped with a nitrogen inlet, a stirrer, and a condenser. Firstly, P(St-*co*-NIPAM) core particles were prepared by emulsion polymerization. Briefly, 0.2 g of NIPAM and a certain amount of SDS (the concentration is below its critical micelle concentration (CMC)) were dissolved in 90 g of $H_2O$. Then, 1.8 g of styrene was added. The mixture was stirred at 350 rpm and nitrogen was bubbled into the mixture for 30 min. After the temperature increased to 70 °C, 0.16 g of KPS dissolved in 10 g of $H_2O$ was injected to initiate the polymerization.

The PNIPAM shell layers were fabricated on the P(St-*co*-NIPAM) cores by a seeded emulsion polymerization. When the above-mentioned reaction for the P(St-*co*-NIPAM) seeds had processed for 8 h, about 5 mL of sample was taken out for characterization. Then, 15 mL of aqueous solution containing defined amount of monomer NIPAM and cross-linker BIS was added in several shots to the reaction medium using a syringe. In this procedure, no additional KPS was added. The reaction was allowed to continue for another 4 h. The core–shell microspheres were purified by centrifugation, decantation, and redispersion in water, and the same cycle was performed for four times.




**Scheme 1** Schematic illustration of the preparation process of the P(St-*co*-NIPAM)–PNIPAM core–shell microspheres and the thermoresponsive hollow microgels

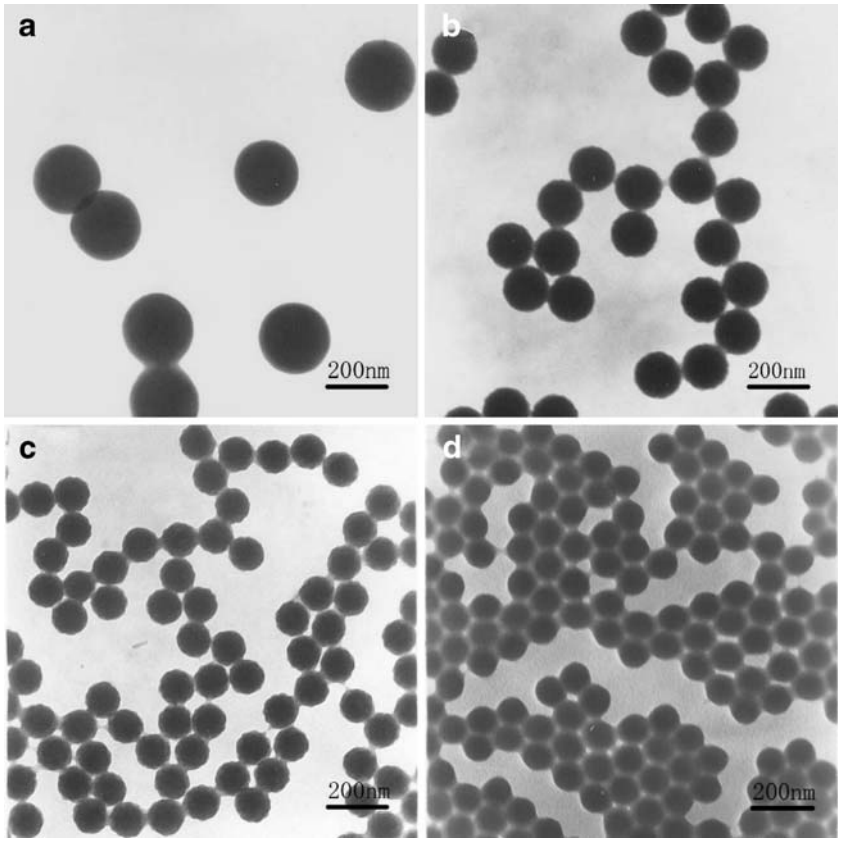



**Fig. 1** TEM images of P(St-*co*-NIPAM) core particles prepared with different dosages of SDS—**a** 0 g, **b** 0.03 g, **c** 0.06 g, **d** 0.10 g

### Preparation of hollow PNIPAM microgels

The hollow PNIPAM microgels were obtained by dissolving the P(St-*co*-NIPAM) core with THF. The as-prepared core–shell latex was centrifuged and then dissolved in THF. The mixture was stirred for 2 h and then treated by centrifugation, decantation, and redispersion in THF. The same cycle was performed for three times to completely remove the P(St-*co*-NIPAM) core. The resulting hollow PNIPAM microgels could be well dispersed in water.

### Characterizations

Transmission electron microscopy (TEM) images were obtained using a Hitachi H-600 transmission electron microscope operating at 250 kV. Diluted dispersions were placed onto carbon-coated copper grids and dried at room temperature.

Malvern Autosizer 4700 laser scattering spectrometer was used to determine the average hydrodynamic diameter ($D_h$) of the particles. The measurement angle was detected at 90°, and the samples were allowed to equilibrate at each temperature for 15 min before measurement.

Atomic force microscopy (AFM) experiments were performed using a Veeco–Digital Instruments Nanoscope IV AFM operating in tapping mode. Single crystal tips (Model: RTESP) were used. All the images were obtained under a scan rate of 0.25 Hz with 254 kHz drive frequency and 300 mV drive amplitude. The samples for AFM were prepared by casting a drop of diluted dispersion onto a smooth mica sheet, and the samples were allowed to dry at ambient temperature.

Fourier-transform infrared spectroscopy (FTIR) spectra of the specimen films on aluminium foil prepared from the solutions were recorded on a Nicolet Magna 550 spectrometer.

## Results and discussion

The preparation procedure of the core–shell microspheres and the thermoresponsive hollow microgels is schematically illustrated in Scheme 1. Firstly, monodisperse P(St-*co*-

**Table 1** Size of P(St-*co*-NIPAM) core particles obtained by DLS at 25 °C

| | Dosages of SDS | | | | |
|---|---|---|---|---|---|
| SDS (g) | 0 | 0.03 | 0.06 | 0.10 | 0.20 |
| $D_h$ (nm) | 268 | 241 | 182 | 130 | 43 |

In the systematic preparation of P(St-*co*-NIPAM) core particles, the dosages of St, NIPAM, and KPS were kept constant as 1.8 g, 0.2 g and 0.16 g, respectively. Only the dosage of SDS was varied.

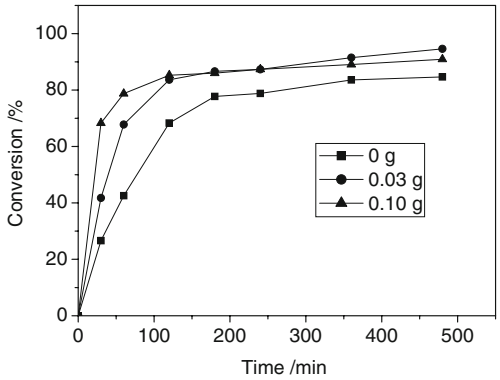



**Fig. 2** Conversion vs. time curves of polymerization of St and NIPAM with different dosages of SDS: (*filled squares*) 0 g; (*filled circles*) 0.03 g; (*filled triangles*) 0.10 g

NIPAM) core particles containing 90% styrene and 10% NIPAM were prepared by emulsion polymerization. Then, the core particles were used as seeds for the preparation of core–shell microspheres. Cross-linked PNIPAM shells were fabricated onto the seeds. At last, the cores were removed by THF and hollow PNIPAM microgels were obtained.

Figure 1 shows the TEM images of the P(St-*co*-NIPAM) core particles prepared with different SDS dosages. The SDS dosages were lower than the CMC of SDS solution (approximately 2.6 g/L). With each SDS dosage, monodisperse microspheres were obtained. With increasing the SDS dosage from 0 to 0.10 g, the particle size gradually decreased from 230 nm to less than 100 nm (measured from TEM images). The TEM images show that the size of P(St-*co*-NIPAM) core can be conveniently tuned by only changing the SDS dosage while the monodispersity is unaffected. In certain applications, especially in drug delivery systems [34], the control of size and distribution is very important for the microspheres to improve their performance. The preparation of monodisperse core particles is the precondition for sequently preparing well-monodisperse core–shell microspheres.

The sizes of the core particles obtained by dynamic laser scattering are listed in Table 1. The changing trend of the particle size characterized by DLS is in accord with the TEM images. As the dosage of SDS increases, the particle size decreases. When no SDS is added, the particle size is 268 nm. As the dosage of SDS increases to 0.20 g, the particle size decreases to 43 nm. The particle size at each SDS dosage obtained by DLS is larger than corresponding one measured from TEM images. It is understandable that the core particles contain 10% NIPAM, which creates a thin PNIPAM layer at the particle surface [35]. At low temperature, the thin PNIPAM layer swells in water while the microspheres shrink when observed under TEM. The PNIPAM component in the core particles also enhances the affinity to the hydrophilic shell and favors the formation of PNIPAM shell on the surface of the core.

PNIPAM shells were fabricated on the surface of the above-prepared P(St-*co*-NIPAM) core particles by using these particles as seeds. The addition of the mixture of NIPAM and BIS at different conversion of the seed has great influence on the morphology of the resulting micro-

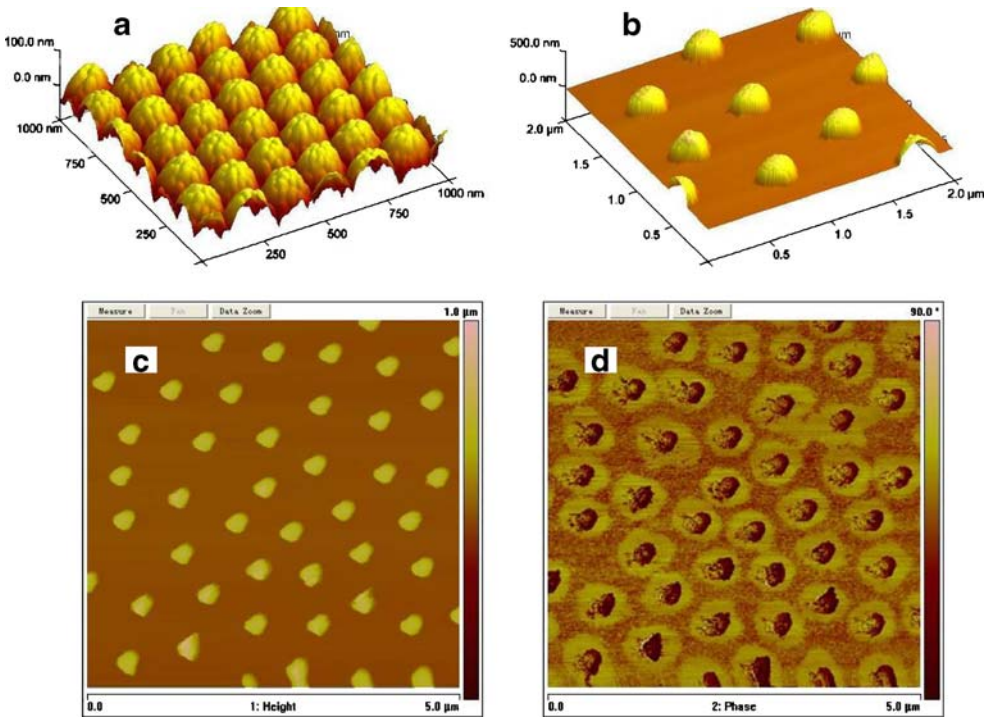



**Fig. 3** AFM images of P(St-*co*-NIPAM) seeds and P(St-*co*-NIPAM)–PNIPAM core–shell particles: **a** P(St-*co*-NIPAM) seeds; **b** 3-D image of the core–shell particles; (**c**) larger-scale image of the core–shell particles; **d** corresponding phase image of (**c**). For the shell preparation, the dosage of NIPAM is 2.0 g and the molar percentage of BIS is 10%

spheres [35]. The addition at high conversion made for perfect core–shell microspheres. To determine when the shot addition be performed for the synthesis of the PNIPAM shell, 3 mL of sample was withdrawn at regular time intervals during the preparation of the seeds and the conversion was determined gravimetrically. Figure 2 shows the conversion vs. time curves. The addition of SDS results in an obvious increase of the polymerization rate. With each SDS dosage, it requires less than 4 h to get a conversion plateau. We chose to add the aqueous solution of NIPAM and BIS when the polymerization had processed for 8 h at which time a high conversion of the seed had been obtained. For example, the conversion was almost completed (94.6%) for the reaction with 0.03 g of SDS. The following discussion is based on the core–shell microspheres whose cores were prepared with 0.03 g of SDS.

The preparation of PNIPAM shell was carried out at 70 °C, which was much higher than the LCST of the polymer. The "shell" monomer solution was added by several shots. In this method, the initial reaction manner was graft polymerization because of some residual living radicals on the surface of P(St-*co*-NIPAM) core [27]. Once a thin PNIPAM layer was formed, the later-formed polymer precipitated onto the seeds until the monomer was completely consumed. The successful formation of PNIPAM shell is demonstrated by the AFM images which are given in Fig. 3. For the P(St-*co*-NIPAM) seeds, the particles exhibit a raspberry-like structure reflecting a two-step polymerization mechanism [35, 36] which occurs and results in the formation of a rich-PNIPAM shell. Compared with the P(St-*co*-NIPAM) seeds, the shot-growth particles appear a smoother surface. Figure 3c and d present a larger-scale AFM image of the shot-growth particles and the corresponding phase image. From Fig. 3d, the core–shell structure is clearly observed. In Fig. 3c, the image exhibits the particles form an array with spaces between them. This is similar to the spontaneously array of PNIPAM microgels and particles with PNIPAM graft chains on the surface reported by Kawaguchi et al. [37]. They attributed the self-assembly to capillary forces between the particles and exclusive effect of PNIPAM.

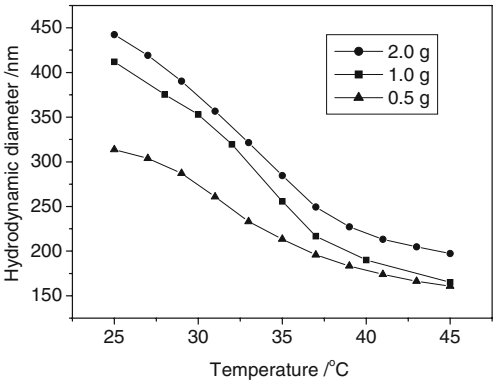



**Fig. 5** Hydrodynamic diameters of the core–shell particles prepared with different PNIPAM dosages. For all the samples, the molar percentage of BIS is 10%

The temperature sensitivity of the P(St-*co*-NIPAM)–PNIPAM core–shell microspheres was characterized by DLS. The hydrodynamic diameter vs. temperature of the core–shell particles prepared with different cross-linker contents is depicted in Fig. 4. The hydrodynamic diameter of the particles decreases with the increase of temperature from 25 to 45 °C, and a volume transition takes place at around 32 °C. With increasing the molar percentage ratio of the cross-linker (BIS) to the monomer (NIPAM) from 5% to 10% and 15%, the swelling ratio defined as $(D20\ °C/D45\ °C)^3$ decreases from 16.1 to 11.8 and 7.9. The cross-linked network confined the movement of the polymer chains. It is worth noting that the size distribution of the core–shell particles obtained from DLS keeps very narrow at each temperature. The narrow size distribution indicates that the formation of new PNIPAM microgels was avoided during the seeded polymerization. If there exist PNIPAM microgels in the latex, the size distribution of the particles must turn broad with the increase of temperature because

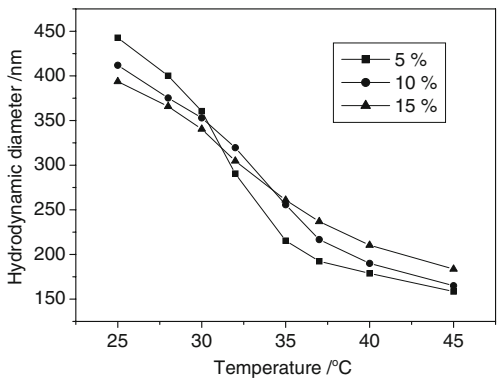



**Fig. 4** Hydrodynamic diameters of the core–shell particles prepared with different cross-linking density (molar percentage ratio of BIS–NIPAM). For all the samples, the dosage of NIPAM is 1.0 g

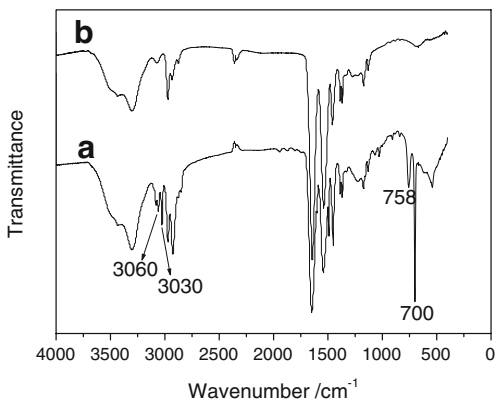



**Fig. 6** FTIR spectra of the core–shell particles **a** before and **b** after treated by THF

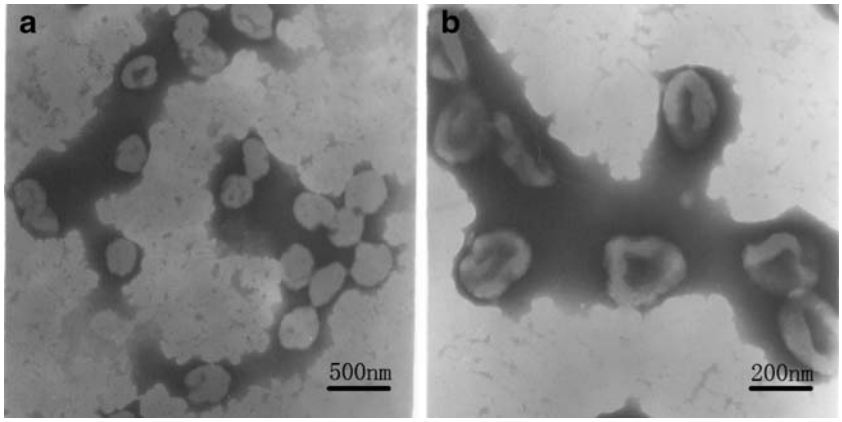



**Fig. 7** TEM images at different magnification of hollow PNIPAM microgels stained by phosphate tungstic acid. For the shell preparation, the dosage of NIPAM is 2.0 g and the molar percentage of BIS is 10%

PNIPAM microgels and P(St-*co*-NIPAM)–PNIPAM core–shell microspheres are different in the degree of shrinking.

The thickness of the cross-linked PNIPAM shell can be tuned by the dosage of NIPAM in the shell preparation. Figure 5 shows the hydrodynamic diameter vs. temperature of the core–shell microspheres prepared with different NIPAM dosages. With increasing the NIPAM dosage, the $D_h$ of the particles increases at each temperature. Taking at 25 °C for example, the $D_h$ of the core–shell microspheres prepared with 0.5, 1.0, and 2.0 g of NIPAM dosages at this temperature are 303, 375, and 419 nm, respectively. Considering the $D_h$ of the P(St-*co*-NIPAM) core at 25 °C, which is 241 nm by DLS, the thickness of the PNIPAM shell are about 31, 67, and 89 nm, respectively.

Hollow PNIPAM microgels were obtained by removing P(St-*co*-NIPAM) cores using THF. THF is a good solvent for both PSt and PNIPAM. The P(St-*co*-NIPAM) core can be dissolved by THF while the PNIPAM shell can not be dissolved owing to the cross-linked structure. The cross-linked PNIPAM shell can only be swelled by THF rather than be dissolved. The interstice of the swelled PNIPAM shell also provided channels for the segments of P(St-*co*-NIPAM) to disperse from the interior. With the removal of the P(St-*co*-NIPAM) core, hollow microgels were obtained. The removal of the P(St-*co*-NIPAM) core was demonstrated by FTIR spectra. Figure 6 shows the FTIR spectra of the core–shell microspheres before and after treatment by THF. Evidently, after the core–shell microspheres were treated by THF, the characteristic absorption bands of PSt at 3,030 and 3,060 $cm^{-1}$ for C–H stretching vibration of phenyl, and at 700 and 758 $cm^{-1}$ for C–H out-of-plane wagging vibration of single-substituted aromatic ring, completely disappeared while the characteristic peaks associated with cross-linked PNIPAM remained. This indicates that the P(St-*co*-NIPAM) cores were completely removed.

Figure 7 shows the TEM images of the hollow PNIPAM microgels. By negative staining, the morphology of the hollow microgels were observed. That means the cross-linked PNIPAM shell was not destroyed after treated by THF. Unlike formerly reported TEM images [30, 33] of hollow PNIPAM microspheres, the shape is not perfectly spherical. The TEM image at larger magnification (Fig. 7b) provided more detailed information. The hollow microgels collapsed and many drapes formed at the surface. Relative to the size of the whole microgels, the thickness of the PNIPAM shell is very thin at dried state. So, under high vacuum for TEM observation, the shell collapsed.

Compared with condensed homospheres, hollow microspheres have an outstanding advantage that the cavities inside favor to encapsulate large-sized molecules and a large quantity of guest materials. Besides, PNIPAM is sensitive to temperature. Combining the two characteristics, hollow PNIPAM microgel is a promising candidate for controlled release system. The size dependence on temperature of the core–shell microspheres and the hollow microgels is shown in Fig. 8. After the removal of PSt cores, the particles display a larger swelling/deswelling ratio increasing from 11.3 to 17.6. That means the hollow PNIPAM microgels can shrink and swell over a wider range of volume. By removing the core, the PNIPAM shell was released from the constraint of the core.

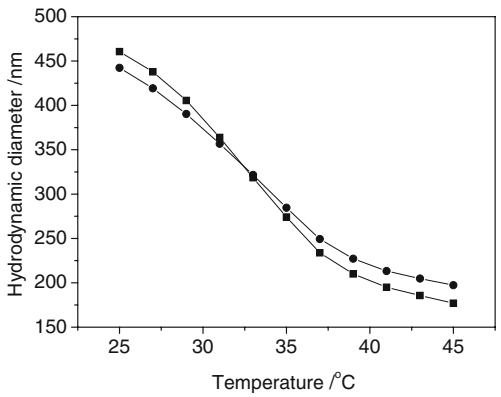



**Fig. 8** Hydrodynamic diameters of the core–shell particles before (*filled circles*) and after (*filled squares*) treated by THF. For the shell preparation, the dosage of NIPAM is 2.0 g and the molar percentage of BIS is 10%

## Conclusions

Monodisperse core–shell microspheres with thermosensitivity were prepared by fabricating a cross-linked PNIPAM shell on P(St-*co*-NIPAM) core. The size of the P(St-*co*-NIPAM) core could be conveniently tuned by only varying the dosages of SDS. Below the CMC of SDS, monodisperse core particles with size from 268 to 43 nm were obtained. The thickness and sensitivity to temperature of the shell could also be tuned by changing the dosage of NIPAM and the molar ratio of BIS to NIPAM in the preparation of the cross-linked PNIPAM shell. Further, the core was removed by physically dissolving using THF as solvent. Then, hollow microgels with temperature sensitivity were obtained. A new route for preparing hollow PNIPAM microgels has been successfully developed.

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