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SHORT COMMUNICATION

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Monodisperse thermosensitive particles prepared by emulsifier-free emulsion polymerization with microwave irradiation

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Abstract The emulsifier-free emulsion polymerization of styrene (St) and *N*-isopropylacrylamide (NIPAAm) was successfully carried out with microwave irradiation, and the monodisperse thermoresponsive poly(styrene-*co*-*N*-isopropylacrylamide) (poly(St-*co*-NIPAAm)) particles with diameters in the range 100–130 nm were prepared. The morphology, size and size distribution of the poly(St-*co*-NIPAAm) particles were characterized by transmission electron microscopy, scanning electron microscopy (SEM) and photon correlation spectroscopy (PCS), respectively. The results showed that poly(St-*co*-NIPAAm) particles had spherical morphology, and the poly(St-*co*-NIPAAm) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation were smaller, more uniform than those obtained with conventional heating. The hydrodynamic diameters of poly(St-*co*-NIPAAm) particles were decreased as the temperature increased from 25 °C to 40 °C, and poly(St-*co*-NIPAAm) particles collapsed remarkably at 32 °C, which is the lower critical solution temperature of the poly(*N*-isopropylacrylamide). The morphology of the assembled poly(St-*co*–NIPAAm) particles was observed by SEM, it was found that monodisperse poly(St-*co*-NIPAAm) particles could assemble to form the two-dimensional order structures.

Keywords Microwave irradiation · Particle · Emulsifier-free emulsion polymerization · *N*-isopropylacrylamide

Introduction

Much attention has been paid towards stimuli-sensitive polymers. Particularly, poly(*N*-isopropylacrylamide) (PNIPAAm) and cross-linked copolymers containing PNIPAAm moieties were reported that exhibit thermally reversible soluble–insoluble change in response to temperature changes across the lower critical solution temperature (LCST) of the PNIPAAm in aqueous solution [1]. The features of the phase transition in aqueous solution made it possible for the PNIPAAm polymers to be studied and applied in many fields, including immunoassay technique [2], controlled drug delivery [3, 4], enzyme and protein immobilization [5, 6], biosensors [7].

The preparation of thermosensitive particles was pioneered both by Pelton in the case of PNIPAAm either alone [8] or with styrene [9]. The pioneering works of styrene with various *N*-substituted-acrylamide derivatives in the case of the emulsifier-free emulsion copolymerization were reported by Kawaguchi et al. [10, 11].

Since Hoshino et al. [12, 13] firstly reported that thermosensitive core-shell *N*-substituted acrylamide-styrene copolymer latexes were prepared by the emulsifier-free emulsion copolymerization methods and many core-shell thermosensitive latexes have been synthesized through the emulsifier-free emulsion copolymerization in the past ten years [14]. Thermosensitive PNIPAAm chains could also be introduced onto the polystyrene seed particles to obtain the final microspheres with sensitivity towards temperature by a two-step process [15]. Chen et al. [16] studied the dispersion polymerization of styrene with PNIPAAm macromonomers to prepare thermosensitive microspheres, and the thermosensitive properties of the obtained microspheres were evaluated by the turbidity of their dispersion solution and the hydrodynamic size of the mirospheres. Xiao et al. [17] prepared the monodisperse thermoresponsive core-shell hydrogel microspheres with poly(St-*co*-NIPAAm) cores and PNIPAAm shells, and systematically investigated the properties of the prepared core-shell hydrogel microspheres. Fang and Kawaguchi [18] reported that thermosensitive PNIPAAm moieties were introduced onto amphoteric styrene/glycidyl methacrylate copolymer seed microspheres, and the obtained microspheres exhibited thermosensitive and amphoteric behavior, which were sensitive to both pH and temperature. Duracher et al. [19, 20] reported that monodisperse cationic amino-containing *N*-isopropylacrylamide-styrene copolymer latexes were prepared by either batch or two-steps emulsifier-free emulsion polymerization of St, NIPAAm, and aminoethylmethacrylate hydrochloride (AEM) using 2,2′-azobis(2-amidinopropane) dihydrochloride as initiator. Moreover, particle size and morphology of the different latexes vs. conversions were examined to further study the polymerization mechanism. Some researchers investigated the physicochemical properties of thermosensitive colloid latexes changed at the LCST of the PNIPAAm. Gao and Wu [21] studied the "coil-to-globule" transition of PNIPAAm on the surface of surfactant-free polystyrene nanoparticles by a combination of static and dynamic laser light scattering. They demonstrated that heating a mixture of polystyrene nanoparticles and PNIPAAm could enhance the adsorption of PNIPAAm chains on the particle surface. Kim and Ballau [22] investigated the volume transition of thermosensitive core-shell particles by dynamic light scattering; the core of the particles consisted of polystyrene, whereas the thermosensitive shell was composed of a network of PNIPAAm containing acrylic acid.

It has been reported in recent years that monodisperse colloidal latex particles assembled to form the order structures, such as two-dimensional films and three-dimensional colloid crystals, which displayed unique optical properties such as Bragg diffraction of light and thus iridescence[23–26]. Asher et al. developed thermally switchable periodic materials using a thermosensitive PNIPAAm polymer, and the diffraction switching behavior was observed by changing the temperature through the LCST of PNIPAM [27–29]. Though the order structures could be formed by different self-assembled methods using monodisperse colloid particles, usually the diameters of colloid particles were large [30–33]. Moreover, as the diameter of the monodisperse colloidal latex particles decreased, the strong Brownian motion might create a state of disorder in the system, so the regular array of the particles became difficult on the substrates [34]. Therefore, it is interesting to develop methods to prepare small and monodisperse thermoresponsive poly(St-*co*-NIPAAm) colloidal latex particles, and to study the assembly of the colloidal latex particles.

Emulsifier-free emulsion polymerization offered strong potential advantages for the preparation of monodisperse microspheres, but monodisperse particles prepared by emulsifier-free emulsion polymerization in water medium with conventional heating were generally bigger than 200 nm. As is well known, microwave irradiation was a special heating energy, which had significant advantages over the conventional thermal methods. Many researchers have focused on studying the polymerization effects with microwave irradiation. Murray et al. [35] firstly reported that monodisperse colloidal microgel particles of PNIPAAm were prepared by emulsion polymerization in the obturator under higher atmospheric pressure with microwave irradiation at 2,450 MHz frequency and 1,000 W power. Zhang et al. [36] reported that stable polystyrene nanoparticles were prepared by emulsifier-free emulsion polymerization with microwave irradiation, and the hydrodynamic radius distribution of polystyrene nanoparticles was narrower than those prepared by conventional heating methods.

The preparation of monodisperse particles smaller than 150 nm through emulsifier-free emulsion polymerization is particularly challenging. The purpose of this study is to prepare the monodisperse particles smaller than 150 nm. We combined the characteristics of microwave irradiation and emulsifier-free emulsion polymerization and successfully prepared monodisperse thermoresponsive poly(St-*co*-NIPAAm) particles with diameters in the range 100–130 nm, which was smaller and narrower than those prepared by emulsifier-free emulsion polymerization with conventional heating. The morphology, size and size distribution of the obtained poly(St-*co*-NIPAAm) particles were mostly studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and photon correlation spectroscopy (PCS). After monodisperse poly(St-*co*-NIPAAm) particles assembled to form the two-dimensional order structures, the morphologies of the two-dimensional order structures were observed with SEM.

Materials and methods

General

Styrene (St) was distilled to remove the inhibitors in vacuum and stored at 4 °C until use. *N*-isopropylacrylamide (NIPAAm) was reagent grade and obtained commercially from Sigma-Aldrich, which was purified by recrystallization from a mixture of toluene-hexane (v/v: 1/1). The water was deionized before use. $K_2S_2O_8$ (KPS) was purified by recrystallization in the deionized water, and then dried in a vacuum.

Apparatus

The SANLE-MP650D microwave oven was purchased from Nanjing Lingjiang Development Co. Ltd. The microwave frequency was 2,450 MHz and the output power was all continuously adjustable within the range of 65–650 W. A 250-mL three-neck round-bottom flask equipped with a reflux condenser, a Teflon paddle stirrer and a nitrogen gas inlet was in the microwave oven.

Table 1 Composition of emulsifier-free emulsion polymerization with microwave irradiation

Sample	St (mol/L)	NIPAAm (mol/L)	KPS (mol/L)	H_2O (mL)
1	0.65	0.029	0.0082	90
2	0.65	0.039	0.0082	90
3	0.65	0.048	0.0082	90
4	0.65	0.058	0.0082	90
5	0.65	0.067	0.0082	90
5*[a]	0.65	0.067	0.0082	90
6	0.65	0.076	0.0082	90
7	0.65	0.086	0.0082	90
8	0.32	0.067	0.0082	90
9	0.48	0.067	0.0082	90
10	0.75	0.067	0.0082	90
11	0.80	0.067	0.0082	90
12	0.96	0.067	0.0082	90
13	0.65	0.067	0.0031	90
14	0.65	0.067	0.0041	90
15	0.65	0.067	0.0052	90
16	0.65	0.067	0.0062	90
17	0.65	0.067	0.0104	90
18	0.65	0.067	0.0146	90

[a] The sample 5* of emulsifier-free emulsion polymerization was carried out with conventional heating

Preparation of poly(St-*co*-NIPAAm) dispersion

Microwave emulsifier-free emulsion polymerization

The composition of emulsifier-free emulsion polymerization with microwave irradiation is given in Table 1. The St, NIPAAm and KPS were dissolved in the H_2O medium (90 mL) with stirring at the rate of 550 rpm. The air in the flask was replaced by a stream of nitrogen and the mixture was kept under nitrogen until polymerization was finished. Under 650 W power, on irradiating the system for 90 s, the reaction system could be initiated at 70 °C. The temperature of the reaction mixture was kept at 70 °C by 130 W. Stable poly(St-*co*-NIPAAm) dispersion was obtained after the reaction stood for 1 h.

Normal emulsifier-free emulsion polymerization

The sample 5* in Table 1 was carried out with conventional heating. All materials including St, NIPAAm, KPS, and water were added into a 250-mL three-neck round-bottom flask equipped with a reflux condenser, a Teflon paddle stirrer and a nitrogen gas inlet. The air in the flask was replaced by a stream of nitrogen, and the mixture was kept under nitrogen until polymerization was finished. The normal emulsifier-free emulsion polymerization was carried out at 70 °C for 24 h.

Transmission electron microscope

The morphology, size and size distribution of poly(St-*co*-NIPAAm) particles were characterized by transmission electron microscopy (TEM-100SX, Tokyo, Japan). The obtained dispersion was diluted with deionized water. A drop of the diluted dispersion was placed on a Formvar-coated copper grid, and the grid was dried in air. The TEM images were obtained at 25 °C with TEM-100SX instrument. Diameters of more than 100 particles were measured from the TEM images. The number average diameter D_n, weight average diameter D_w, and the polydispersity index PDI were calculated with Eqs. 1, 2 and 3, where N_i is the number of particles having diameter D_i

$$D_n = \frac{\sum_{i-1}^{k} N_i D_i}{\sum_{i-1}^{k} N_i} \tag{1}$$

$$D_w = \frac{\sum_{i-1}^{k} N_i D_i^4}{\sum_{i-1}^{k} N_i D_i^3} \tag{2}$$

$$\mathrm{PDI} = \frac{D_w}{D_n} \tag{3}$$

The photon correlation spectroscopy

The average hydrodynamic diameter D_h of poly(St-*co*-NIPAAm) particles was measured by the PCS (Malvern

Instruments Ltd). The poly(St-*co*-NIPAAm) dispersions were diluted with deionized water to get an appropriate concentration, and then poured into a cuvette. The cuvette was set inside a sample holder. The temperature of the holder was maintained at a desired temperature between 25–40 °C and the diluted dispersions were measured with 670 nm wavelength of the laser light and at 90° scattering angle.

Scanning electron microscopy

The poly(St-*co*-NIPAAm) dispersions were placed on an aluminum sample stub to dry, and poly(St-*co*-NIPAAm) particles assembled during the water evaporating progress, then the assembled poly(St-*co*-NIPAAm) particles were sputter coated with gold. The samples were characterized by scanning electron microscope (HITACHI X-650, Scanning Electron Microanalyzer) to observe the morphology of the assembled poly(St-*co*-NIPAAm) particles.

Results and discussion

Morphology of poly(St-*co*-NIPAAm) particles

The morphology, size and size distribution of poly(St-*co*-NIPAAm) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation or with conventional heating were characterized by TEM, respectively. The poly(St-*co*-NIPAAm) dispersions were not dyed with RuO_4 solution.

The TEM images of poly(St-*co*-NIPAAm) particles prepared with microwave irradiation are shown in Fig. 1a–d; the Fig. 1e is the TEM image of the sample 5^* prepared with conventional heating.

As shown in Fig. 1a–d, poly(St-*co*-NIPAAm) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation are spherical morphologies with narrow distribution, the D_n, D_w, *PDI*, of poly(St-*co*-NIPAAm) particles prepared with different NIPAAm concentrations are calculated and listed in the Table 2.

The TEM image of the sample 5^* prepared by emulsifier-free emulsion polymerization with conventional heating at 70 °C is shown in Fig. 1(e), the D_n, D_w, and *PDI* of the poly(St-*co*-NIPAAm) particles are 492.9 nm, 505.4 nm and 1.0254 nm, respectively. From the TEM images and the values of D_n, D_w, *PDI* of poly(St-*co*-NIPAAm) particles, it can be found that the poly(St-*co*-NIPAAm) particles prepared by microwave irradiation are much smaller than those prepared by conventional heating, and the size distribution of particles prepared by microwave irradiation is narrower than those prepared by conventional heating.

The monodisperse poly(St-*co*-NIPAAm) particles could be prepared with microwave irradiation, which was related with the emulsifier-free emulsion copolymerization mechanism. In the emulsifier-free emulsion copolymerization of St and NIPAAm, the KPS initiators decomposed to form hydrophilic SO_4^- groups in the aqueous phase, then the persulfate radicals that initiated the NIPAAm in the aqueous phase to polymerize for the NIPAAm is a hydrophilic monomer and is more reactive than styrene [37], and to produce oligomer radicals. As the oligomer radicals reached a "critical length", they precipitated and agglomerated to form primary particles. The styrene reacted due to the diffusion of the monomer from the droplets and the subsequent swelling in the hydrophobic poly[NIPAAm]-rich primary particles. The particle maintained its stability with the hydrophilic SO_4^- group in polymer chains and the hydrophilic chains provided by the PNIPAAm, and these hydrophilic chains mostly concentrated at the particle/water interface. Consequently, the steady particles could continue to grow until the St monomer droplets disappeared.

In the emulsifier-free emulsion polymerization, the k_d of KPS was $3.35\times10^{-5}\ s^{-1}$ (70 °C) with conventional heating [38], while the k_d of KPS was $8.05\times10^{-5}\ s^{-1}$ (68.5 ± 1 °C) in the microwave irradiation, so microwave irradiation played the main role in enhancing the initiator activity, raising its decomposition rate and accelerating the polymerization process [39]. As the decomposition rate of KPS was accelerated, the initiator efficiency of KPS could be enhanced, and the formation rates of hydrophilic SO_4^- group in polymer chains increased with accelerated decomposition rate of KPS. This resulted in much more stable primary particles being formed under microwave irradiation than under conventional heating, and the chance of second nucleation was less than that under conventional heating. Therefore, the poly(St-*co*-NIPAAm) particles prepared by microwave irradiation are much smaller than those prepared by conventional heating, and the size distribution of microspheres prepared by microwave irradiation is narrower than those prepared by conventional heating.

Effect of the ratio of NIPAAm/styrene on the size of particle

The average hydrodynamic diameter D_h of poly(St-*co*-NIPAAm) particles was measured by PCS, and the effect of the ratio of NIPAAm/styrene on the size of poly(St-*co*-NIPAAm) particles is shown in Fig. 2.

As shown in Fig. 2, the sizes of poly(St-*co*-NIPAAm) particles decreased as the ratio of the NIPAAm/Styrene increased from 0.045 to 0.132. In the emulsifier-free emulsion polymerization with microwave irradiation,

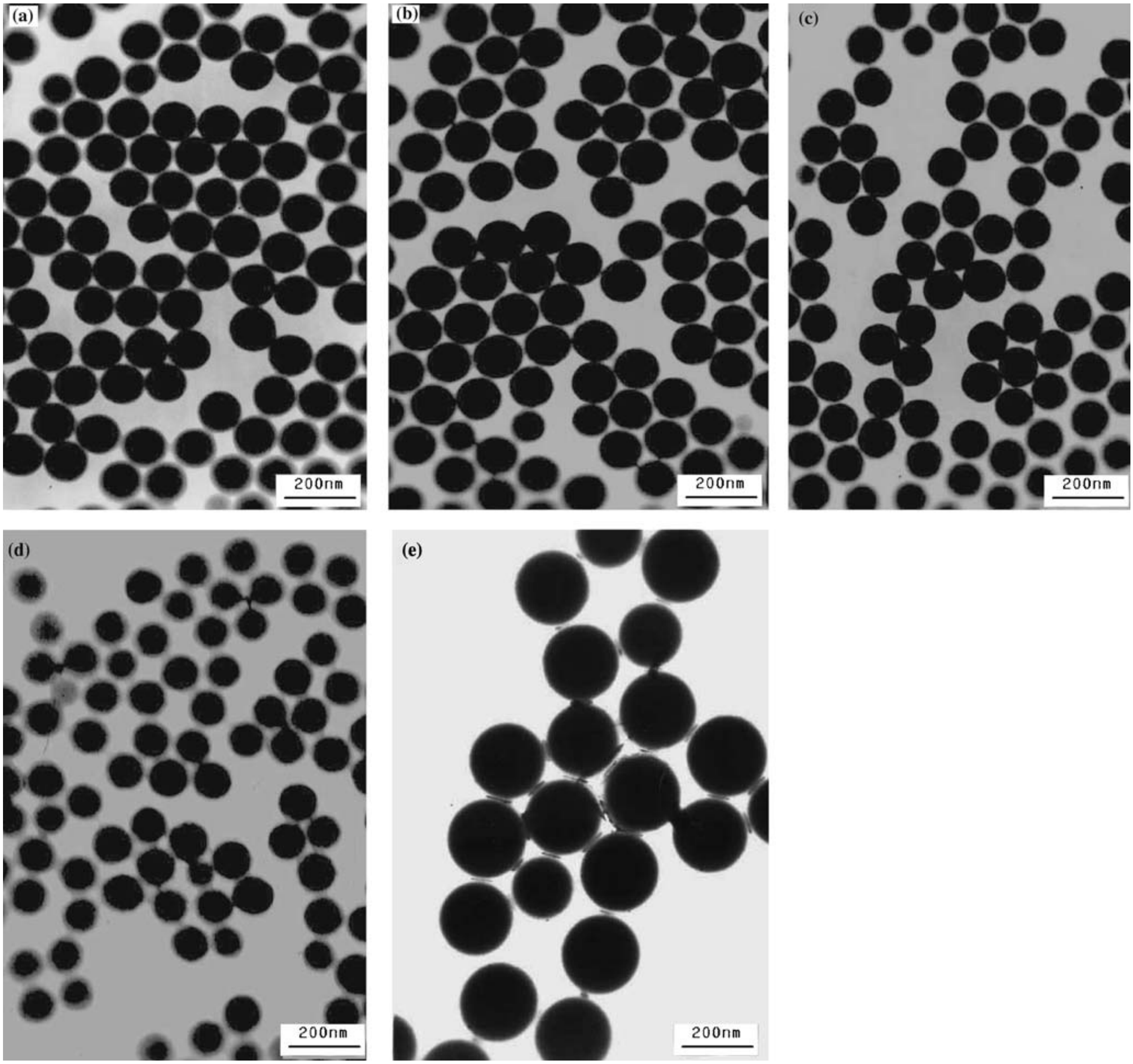

Fig. 1 TEM images of poly(St-*co*-NIPAAm) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation. St: 0.65 mol/L; KPS: 0.0082 mol/L; H_2O: 90 ml; NIPAAm: (a) 0.029 mol/L (b) 0.039 mol/L (c) 0.048 mol/L (d) 0.067 mol/L (e) The Sample 5*, which was carried out with conventional heating. St: 0.65 mol/L; KPS: 0.0082 mol/L; NIPAAm: 0.067 mol/L

the formed hydrophilic SO_4^- group that firstly initiated the NIPAAm in the aqueous phase to polymerize for the NIPAAm is a hydrophilic monomer and is more reactive than styrene [37]. When the hydrophobic poly[NIPAAm]-rich primary particles formed, styrene subsequently was awollen in these primary particles to polymerize. As the ratio of the NIPAAm/Styrene was increased, the more hydrophobic poly[NIPAAm]-rich primary particles could be formed, which indicated the amount of styrene distributing in the primary particles would be decreased, so the sizes of the formed poly(St-*co*-NIPAAm) particles decreased.

Effect of KPS concentration on the size of particle

Figure 3 shows the effect of KPS concentration on the size of poly(St-*co*-NIPAAm) particles. With the KPS concentration increased from 3.14×10^{-3} mol/L to 14.6×10^{-3} mol/L, the average hydrodynamic diameter

Table 2 Diameters of particles prepared with different NIPAAm concentration

Sample	NIPAAm (mol/L)	TEM		
		D_n (nm)	D_w (nm)	PDI
1	0.029	130.0	131.3	1.0100
2	0.039	123.5	124.0	1.0040
3	0.048	121.8	121.9	1.0008
5	0.067	109.2	109.4	1.0018
5*	0.067	492.9	505.4	1.0254
6	0.076	109.1	109.3	1.0018
7	0.086	109.0	109.1	1.0009

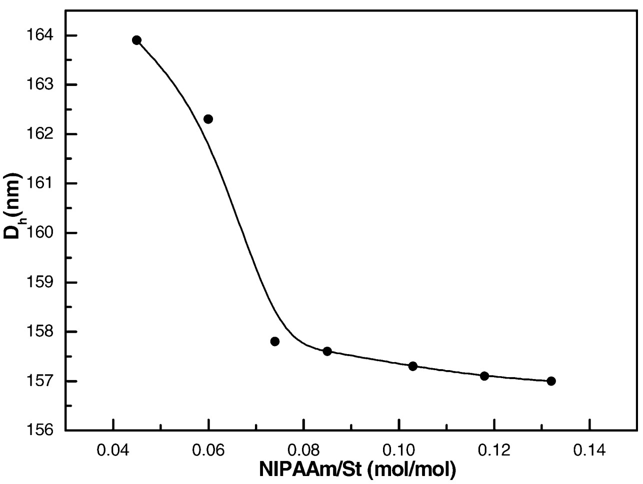

Fig. 2 Effects of the ratio of NIPAAm/Styrene on the size of poly(St-*co*-NIPAAm) particles

D_h of poly(St-*co*-NIPAAm) particles decreased from 220.7 nm to 142.3 nm.

In the emulsifier-free emulsion polymerization with the microwave irradiation, the microwave irradiation played the main role in enhancing the initiator activity, raising its decomposition rate and accelerating the polymerization process. The initiator efficiency of KPS could be enhanced, and the formation rates of hydrophilic SO_4^- group in polymer chains increased with an accelerated decomposition rate of KPS. On the other hand, the amounts of the chain radical might be increased with the KPS concentration increasing. So many stable primary particles could form in a short time, and the number of the stable primary particles increased with an increase in the KPS concentration. For these reasons, the size of poly(St-*co*-NIPAAm) particles decreased with increased KPS concentration.

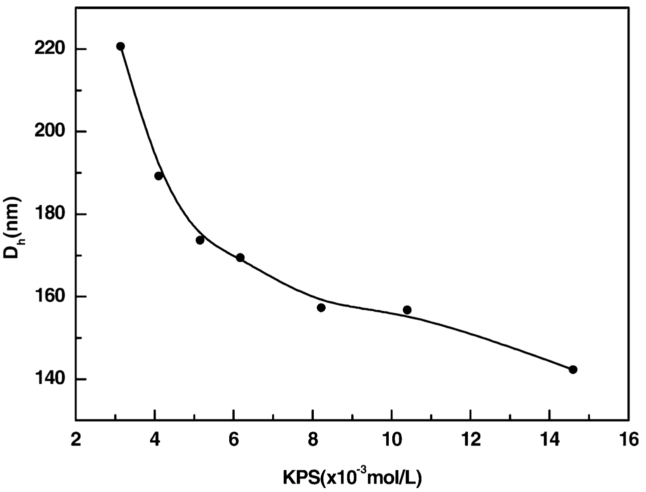

Fig. 3 Effects of KPS concentration on the size of poly(St-*co*-NIPAAm) particles

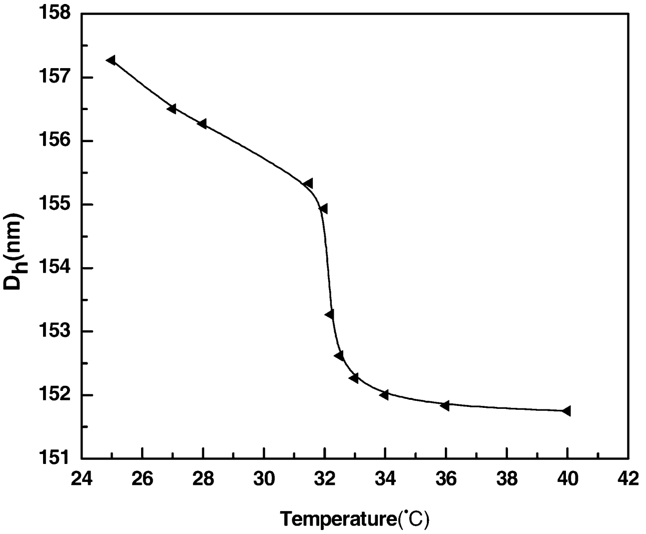

Fig. 4 Effects of temperature on the size of poly(St-*co*-NIPAAm) particles

Thermosensitive property

The hydrodynamic sizes of poly(St-*co*-NIPAAm) particles were measured by PCS at different temperatures, and the results are shown in Fig. 4. The hydrodynamic sizes of poly(St-*co*-NIPAAm) particles decreased as the temperature increased from 25 °C to 40 °C, and the poly(St-*co*-NIPAAm) particles collapsed remarkably at 32 °C.

It was known that PNIPAAm and polymers containing PNIPAAm moieties in the aqueous solution exhibited the LCST behavior with the change in the temperature. In these systems, hydrophobic interactions and hydrogen bonding were the major contributors to the temperature sensitivity. When the temperature of the aqueous solution was raised, hydrophobic interactions arise between nonpolar molecules in water. Up to a certain temperature, water molecules shielded the hydrophobic groups of the polymer chains, and these

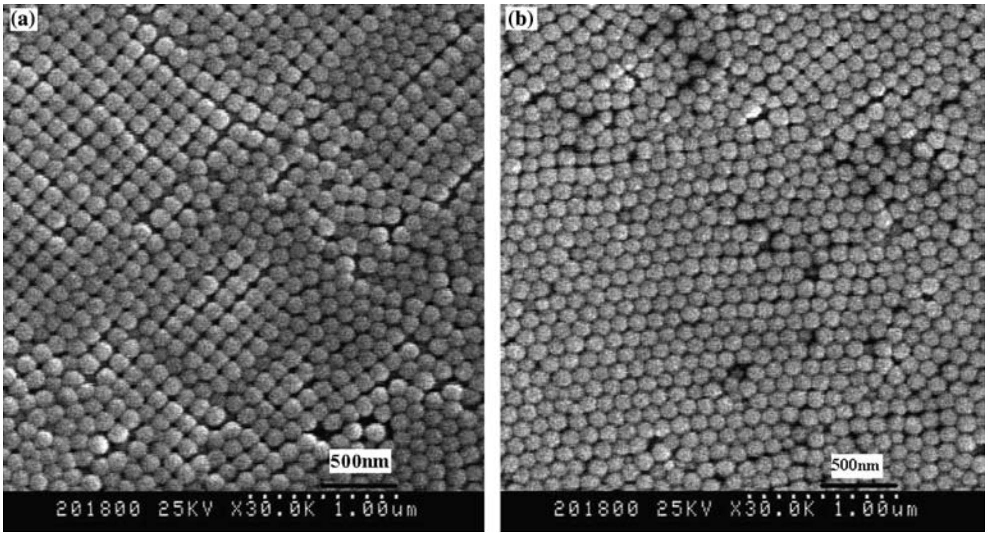

Fig. 5 SEM images of the assembled poly(St-*co*-NIPAAm) particles

water molecules were arranged in a certain pattern to surround the groups. When the temperature was increased above LCST of the PNIPAAm, the immobile water molecules were partially lost, and the protection of the hydrophobic groups was weakened [40]. These reasons resulted in the poly(St-*co*-NIPAAm) particles collapsing remarkably at 32 °C.

Morphology of the assembled poly(St-*co*-NIPAAm) particles

The morphology of the assembled poly(St-*co*-NIPAAm) particles was observed by SEM, the characterized results are shown in Fig. 5. As shown in Fig. 5, monodisperse poly(St-*co*-NIPAAm) particles with diameters in the range 100–130 nm prepared with microwave irradiation could assemble to pack in the two-dimensional order structures on the substrates. Further studies about the properties of the two-dimensional order structures are now in progress.

Conclusion

The monodisperse thermoresponsive poly(St–*co*–NIPAAm) particles with diameters in the range 100–130 nm could be prepared by emulsifier–free emulsion polymerization with microwave irradiation. The TEM results showed that the poly(St–*co*–NIPAAm) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation were smaller and more uniform than those obtained with conventional heating. The effects of the ratio of NIPAAm/St, and the KPS concentrations on the hydrodynamic sizes of poly(St-*co*-NIPAAm) particles were studied, respectively. It was shown that the size of poly(St-*co*-NIPAAm) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation decreased with the increase of the ratio of NIPAAm/Styrene, the size of poly(St-*co*-NIPAAm) particles decreased with the concentration of KPS increased. When the temperature increased from 25 °C to 40 °C, the hydrodynamic sizes of poly(St-*co*-NIPAAm) particles decreased, and the particles shrank remarkably at 32 °C, which is the LCST of the PNIPAAm. The morphology of the assembled poly(St-*co*-NIPAAm) particles was characterized by SEM, and it has been found that the monodisperse thermoresponsive poly(St-*co*-NIPAAm) particles with small diameter prepared by emulsifier-free emulsion polymerization with microwave irradiation could assemble to form the two-dimensional order structures.

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