Preparation of Temperature- and pH-Sensitive, Stimuli-Responsive Poly(*N*-isopropylacrylamide-*co*-methacrylic acid) Nanoparticles

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ABSTRACT: The effects of the monomer ratio, surfactant, and crosslinker contents on the particle size and phase-transition behavior of the copolymer poly(*N*-isopropylacrylamide-*co*-methacrylic acid) (PNIPAAm–MAA) were investigated with Fourier transform infrared, differential scanning calorimetry, and dynamic laser scattering techniques. In addition to the thermoresponsive property of poly(*N*-isopropylacrylamide), ionized methacrylic acid groups brought pH sensitivity to the PNIPAAm–MAA copolymer particles. The polymer particle size varied with the amounts of the monomer ratio, surfactant, and crosslinker. As the monomer ratio and crosslinker content increased and the amount of the surfactants decreased, the particle size increased. The influence of the crosslinker content on the particle size was less significant than the effect of the monomer ratio and surfactants. When the temperature increased, the particles tended to shrink and decreased in size to near or below 100 nm. Particle sizes at 20°C decreased to less than 100 nm with increased surfactant content. The control of the particle size within the 100-nm range makes PNIPAAm–MAA copolymer particles useful for biomedical and heavy-metal-ion adsorption applications. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2226–2232, 2008

Key words: biological applications of polymers; block copolymers; nanotechnology; stimuli-sensitive polymers; surfactants

INTRODUCTION

Stimuli-responsive and thermoresponsive polymer hydrogels are crosslinked polymers that undergo phase transitions in a suitable solvent. In recent years, hydrogels have attracted extensive research interest in various theoretical and applied fields.[1,2] On the basis of their phase-transition property, hydrogels have shown potential applications in drug delivery,[3,4] sensing,[5,6] fabrication of photonic crystals,[7,8] nanoparticle templates,[9,10] and separation and purification technologies.[11,12]

The most important property of hydrogels is their stimulus-responsive behavior, that is, their ability to undergo reversible volume phase transitions in response to environmental stimuli such as the pH, temperature, ionic strength of the surrounding medium, quality of the solvent, and action of the external electromagnetic field.[13,14] The phase-transition behavior of a hydrogel is an imbalance between repulsive and attractive forces acting in the network, such as hydrogen bonding, van der Waals interactions, and hydrophobic interactions. Hydrogels show good colloidal stability, and their particle sizes can be controlled over a wide range of dimensions; this makes them suitable candidates for both fundamental studies and product-oriented research.

Poly(*N*-isopropylacrylamide) (PNIPAAm) is one of the most widely studied thermoresponsive polymers with a low critical solution temperature (LCST) around 32°C.[15] Although some promising results for polymeric self-aggregates as drug carriers have been reported concerning PNIPAAm, stimuli-responsive polymeric nanoparticles are still a new field currently under significant research and development. Limited studies have been conducted that deal with nanoparticles from poly(acrylonitrile-*co*-*N*-isopropylacrylamide), poly(*N*-isopropylacrylamide)-*b*-poly(ε-caprolactone), poly[*N*-isopropylacrylamide-*co*-*N*-(2-hydroxypropyl) methacrylamide-dilactate], poly(ethylene oxide)-*b*-poly(*N*-isopropylacrylamide), and poly(*N*-isopropylacrylamide-*co*-*N*,*N*-dimethylacrylamide-*co*-10-undecenoic acid).[16–20] Among PNIPAAm-

based nanoparticles, the copolymer poly(*N*-isopropy-lacrylamide-*co*-methacrylic acid) (PNIPAAm–MAA) is of special interest because the methacrylic acid (MAA) group introduces additional ionized groups to the copolymer. As a result, the copolymer shows pH-sensitive phase-transition behavior. Furthermore, the PNIPAAm–MAA copolymer can be neutralized by sodium hydroxide to form poly(*N*-isopropylacry-lamide-*co*-sodium-methacrylate) [PNIPAAm–NaMAA], which is useful for the absorbance of heavy-metal ions such as Cu^{2+} for wastewater purification and heavy-metal recovery.

Zhang and Wu[21] studied temperature- and pH-responsive polymeric composite membranes prepared from nanoparticles of PNIPAAm–MAA and their permeability to proteins and peptides in response to environmental stimuli. They showed that the permeability of the solutes across the membranes increased with increasing temperature or particle concentration and decreased with increasing pH and molecular size of the solutes. However, there is a lack of detailed investigations on factors that affect the particle size and phase-transition behavior. Huang and Wu[22] studied the volume phase transition of PNI-PAAm–MAA copolymer nanoparticles in buffer solutions at various pH levels and in aqueous solutions of KCl or ionic surfactants with the dynamic laser scattering (DLS) technique. They showed that the swelling behavior of the nanoparticles had a close relationship with pK_a of the copolymer, and a sharp volume phase transition was obtained. However, the reported diameters of the PNIPAAm–MAA particles were 200–600 nm, and microgels were actually formed. It is well known that many factors affect the size of the particles, including the ratio of the MAA monomer to *N*-isopropylacrylamide (NIPAAm) and the contents of the crosslinkers and surfactant. It is

of significant practical interest to show how these factors influence the size distribution, phase-transition behavior, and ability to absorb heavy-metal ions of the copolymer particles.

The objectives of this work were (1) to synthesize PNIPAAm–MAA particles of various size distributions and (2) to study the effects of the MAA, surfactant, and crosslinker contents on the phase transition and size distribution properties of the particles. Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), and DLS techniques were used in the study.

EXPERIMENTAL

Materials

Research-grade MAA, NIPAAm, *N,N'*-methylenebi-sacrylamide (BIS), sodium dodecyl sulfate (SDS), and potassium persulfate (KPS) were purchased from Sigma–Aldrich, Inc. (St. Louis, MO), and were used without any further purification. Dibasic sodium phosphate and monobasic sodium phosphate for preparing phosphate-buffered saline buffer and Spectrum Spectra/Por 2 RC dialysis membrane tubing with a 12,000–14,000 Da molecular weight cutoff were purchased from Fisher Scientific, Inc. (Pittsburgh, PA).

Preparation of the PNIPAAm–MAA copolymer particles

PNIPAAM–MAA particles were synthesized by precipitation polymerization based on formulations shown in Table I. In the preparation of the particles, the target amount of NIPAAm, MAA, BIS, and SDS was added to 120 mL of deionized water in a 250-mL reactor. NIPAAm and MAA served as the mono-

TABLE I
Summary of the Experimental Design and Selected Results for the Synthesized PNIPAAM–MAA Particles

Experiment	MAA (g)	BIS (g)	SDS (g)	KPS (g)	LCST (°C)	Diameter at 20°C (nm)[a]
1	0	0.033	0.075	0.083	32.06	300.1 (4.482)
2	0.036	0.033	0.075	0.083	32.47	311.3 (2.454)
3	0.072	0.033	0.075	0.083	32.93	358.6 (3.251)
4	0.108	0.033	0.075	0.083	35.45	425.4 (5.347)
5	0.144	0.033	0.075	0.083	32.13	396.7 (5.261)
6	0.576	0.033	0.075	0.083	33.16	444.5 (5.828)
7	1.008	0.033	0.075	0.083	51.31	554.5 (1.671)
8	0.036	0.033	0.100	0.083	35.23	274.4 (1.054)
9	0.036	0.033	0.150	0.083	40.02	140.1 (2.548)
10	0.036	0.033	0.225	0.083	40.02	50.5 (0.228)
11	0.036	0.033	0.300	0.083	45.20	39.9 (2.427)
12	0.036	0.017	0.075	0.083	32.76	341.3 (1.577)
13	0.036	0.500	0.075	0.083	34.35	300.3 (3.003)
14	0.036	0.067	0.075	0.083	37.42	292.0 (4.055)

A reaction time of 4 h, 1.9 g of NIPAAm, 0.083 g of KPS, and 120 mL of the H_2O reaction solution were used for every polymerization process.
[a] The numbers in parentheses are the standard deviations of three measurements.

mers, BIS was the crosslinking agent, and SDS was the surfactant. To control the particle size, different molar ratios of MAA to NIPAAm and various levels of SDS were used (Table I). The solution was stirred for 1 h, was then deoxygenated through bubbling with nitrogen for 40 min, and was finally heated to 70°C in a nitrogen environment. After that, 0.083 g of KPS in a 10-mL water solution was added to the reactor to initiate polymerization. The reaction was kept at 70°C under a nitrogen atmosphere for 4 h with constant stirring. The particle solution that formed was then purified by membrane dialysis against distilled deionized water with a Spectra/ Pros membrane (Fisher Scientific) with a molecular weight cutoff of 12,000–14,000. After polymerization and membrane filtration, the purified copolymer particles were characterized as described.

Copolymer characterization

A Nicolet Nexus 670 FTIR instrument (Thermo Electron Corp., Waltham, MA) was used to characterize the base structure of the copolymer. One drop of PNIPAAm–MAA particles in an aqueous solution after purification was placed on the FTIR crystal, and the spectra were taken. Each sample was measured with 200 scans at a resolution of 4. The collected spectra were analyzed with Omnic software (version 7.2) provided with the FTIR instrument.

LCSTs were measured with a model Q100 DSC (TA Instruments, Inc., New Castle, DE). The test samples were polymerized PNIPAAm–MAA particles in an aqueous solution after purification, without any further processing. For every measurement, a sample of a 10–15-mg particle solution was added to an encapsulated DSC pan. The heating rate was 2°C/min under a nitrogen environment, and each test was run in a temperature range of 15–60°C. DSC allowed the measurement of the heat of the phase transition over a wide range of temperatures and pH values. The onset of the thermogram corresponded to the collapse temperature of the hydrogel particles (i.e., LCST).

The particle size and size distribution of the copolymers were determined with a Zetasizer Nano ZS system (Malvern Instrument, Inc., Worcestershire, United Kingdom). A purified PNIPAAm–MAA particle solution was diluted approximately 100 times with a phosphate-buffered saline buffer in 4.5-mL Spectro cuvettes for measurement. Measurements were performed over a temperature range of 20–60°C in a 0.1M phosphate-buffered saline solution. A HeNe laser beam with a wavelength of 632.8 nm was applied with a detection angle of 90°. The sample temperature was maintained by a built-in thermostat sample holder with an accuracy of 0.01°C. Particle size results were collected with DTS (nano) software (version 5.0) provided with the instrument.

Each sample was measured three times, and the average was used as the sample mean diameter. The Z-average diameter was used as the hydrodynamic size because it was more reproducible than the volume and number weighted mean diameter.

RESULTS AND DISCUSSION

Particle structure

Figure 1 shows a typical FTIR spectrum of the PNIPAAm–MAA copolymer particles with characteristic peaks in the spectrum listed in the caption. For different samples, spectrum peaks were basically at the same positions with no significant intensity change. The amide and carboxylic acid adsorption peaks, which are specific to the NIPAAm and MAA components, respectively, can be identified in the FTIR spectra. The amide peak of the NIPAAm group appeared at 1646 cm^{-1} for amide I and at 1541 cm^{-1} for amide II. Characteristic C=O and C—O stretching bands of the carboxylic acid group of MAA appeared at 1716 and 1290 cm^{-1}, respectively. The FTIR result indicated successful polymerization of NIPAAm and MAA as expected. It has been reported that the reactivity ratio of NIPAAm is $r_1 = 10.2$ and that of MAA is $r_2 = 0.01$ in the NIPAAm/MAA system.[23] Because $r_1 \gg 1 \gg r_2$, it is suggested that in the initial stage of the copolymerization, NIPAAm is incorporated faster, the copolymer is rich in NIPAAm, and MAA monomers are more likely to react at higher NIPAAm conversions. The
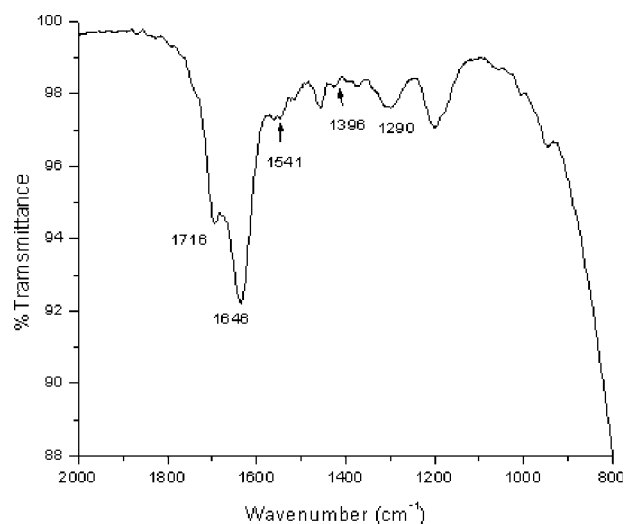
Figure 1 Typical FTIR spectra of manufactured PNIPAAm–MAA (based on samples with MAA/NIPAAm = 0.4 (molar), SDS = 0.075 g, and BIS = 0.033 g). The characteristic peaks are located at 1396 [—CH(CH$_3$)$_2$, C—H bending], 1541 [—CONH, amide II (N—H bending)], 1646 [—CONH, amide I (C=O stretching)], 1716 (—COOH, C=O stretching), 1290 (—COOH, C—O stretching), 2856 (—CH$_2$, C—H stretching), and 2926 cm^{-1} (—CH, C—H stretching).

reaction mechanism indicated an MAA-rich shell with an NIPAAm-rich core morphology. A high conversion of 85–90% could be reached within 1 h of the fast polymerization.[24]

LCST

It is well known that the NIPAAm polymer and copolymers can swell or deswell suddenly upon small temperature changes below or above LCST. This swelling/deswelling is due to specific interactions between the polymers and water, mainly the hydrogen bond between the N or O atoms of the polymers with the water molecules, which depends on both the temperature and the nature of the substituted groups on the N atom. The strength of these hydrogen bonds is believed to decrease when the temperature is increased.

DSC was chosen as the standard experimental method to determine the LCST in this study. It allows the measurement of the heat of the phase transition over a wide range of temperatures with various pH values. The onset of the thermogram corresponds to the temperature of collapse of the polymer and thus was treated as the LCST of PNIPAAm–MAA particles.

Figure 2(A) shows the phase-transition temperatures of PNIPAAm–MAA particles with different MAA/NIPAAm molar ratios. The phase-transition temperatures of PNIPAAm–MAA particles were all higher than that of PNIPAAm without MAA. However, an obvious increase could be detected only for MAA/NIPAAm ratios of 0.075 and 0.7. It is obvious that PNIPAAm–MAA particles inherited the thermo/stimuli-responsive behavior of PNIPAAm. The DSC results for the particles under various pH levels suggested that LCSTs of the particles were also sensitive to pH changes. Poly(methacrylic acid) (PMAA) undergoes a marked pH-induced conformation transition. At low pH levels, PMAA chains are highly compacted to minimize the hydrophobic interaction; at high pH levels, PMAA chains show expanded coils. The swelling and collapsing of PMAA gels are also highly pH-dependent.[25] The polyelectrolyte behavior of the MAA unit introduced various coexistent intramolecular and intermolecular forces, thus complicating the phase-transition process of the hydrogel particles. The MAA group introduced a more hydrophilic group (COO—) to the copolymer, which reduced the hydrophobic interaction that determined the phase transition of the hydrogel. Besides, with highly ionized MAA groups, the electrostatic force also helped to balance the hydrophobic interaction and thus led to an increase of the LCST. This effect was especially obvious at an MAA content level of 0.7, at which an LCST of about 51.31°C was observed. Acrylic acid groups of MAA in the PNIPAAm–MAA copolymer
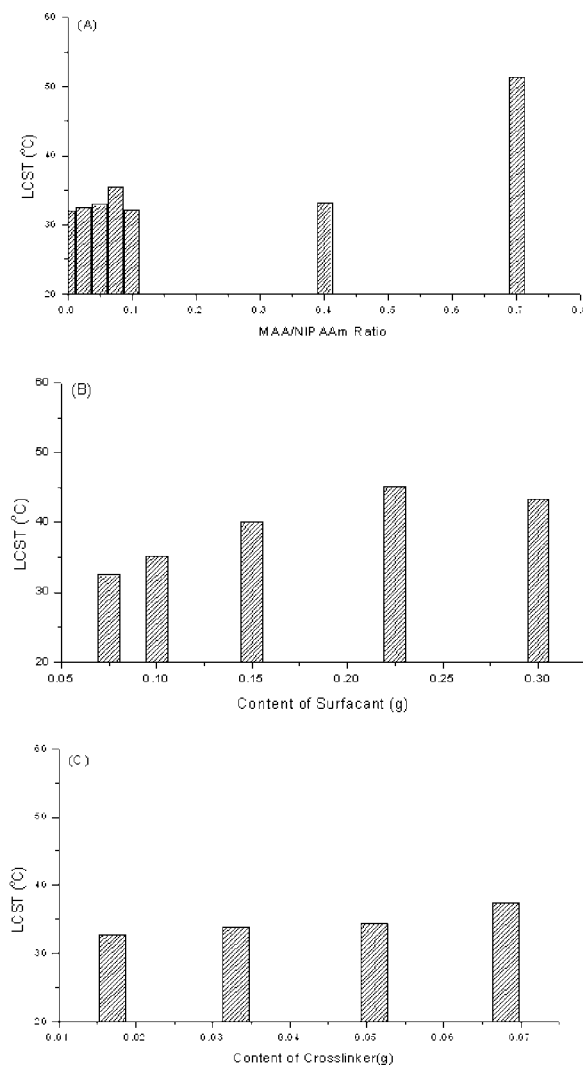
Figure 2 Effects of (A) the monomer ratio, (B) the surfactant content, and (C) the crosslinker content on LCST of PNIPAAm–MAA copolymer particles.

made the particle gel undergo a discontinuous transition, a higher LCST, and a larger volume change, and this is consistent with results reported by other researchers.[26,27] Besides the thermoresponsive property of PNIPAAm, ionized MAA groups brought pH sensitivity to the responsiveness of the PNIPAAm–MAA copolymer particles.

Figure 2(B) shows the surfactant effect on the phase-transition temperature of the PNIPAAm–MAA particles with MAA/NIPAAm = 0.025. It is clear that as the surfactant content increased, there was an apparent increase of the LCST. This was due to the fact that the amphiphilic structure of the surfactant SDS helped to solubilize the polymer in aqueous solutions and thus isolated the hydrophobic polymer segments from the aqueous environment.

The contents of the crosslinker also played an important role in the LCST of the copolymer particles, as depicted in Figure 2(C). Although it was not as

obvious as the effect of the surfactants, LCST of the copolymer particles increased with higher crosslinker contents. This possibly occurred because more crosslinker produced a more compact size of the copolymer particles and thus increased the electrostatic repulsion forces between the polymer chains and prevented the particles from shrinking.
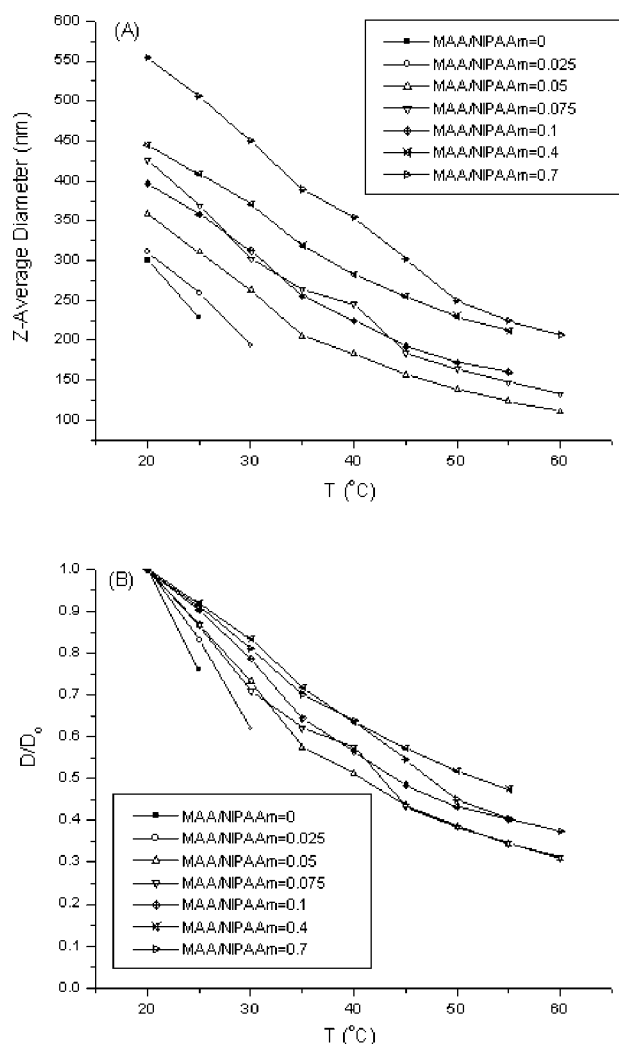
Particle size

Hydrodynamic diameters of PNIPAAm–MAA particles with different MAA/NIPAAm ratios as a function of temperature are shown in Figure 3. It is clear that the Z-average diameter of the particles was composition-dependent. As the MAA ratio increased, the diameter of the copolymer particles increased because more MAA units resulted in longer chains. For each set of samples, the diameter of the particles tended to decrease as the temperature increased because the hydrogel shrank as the temperature increased, especially around its phase-transition temperature.
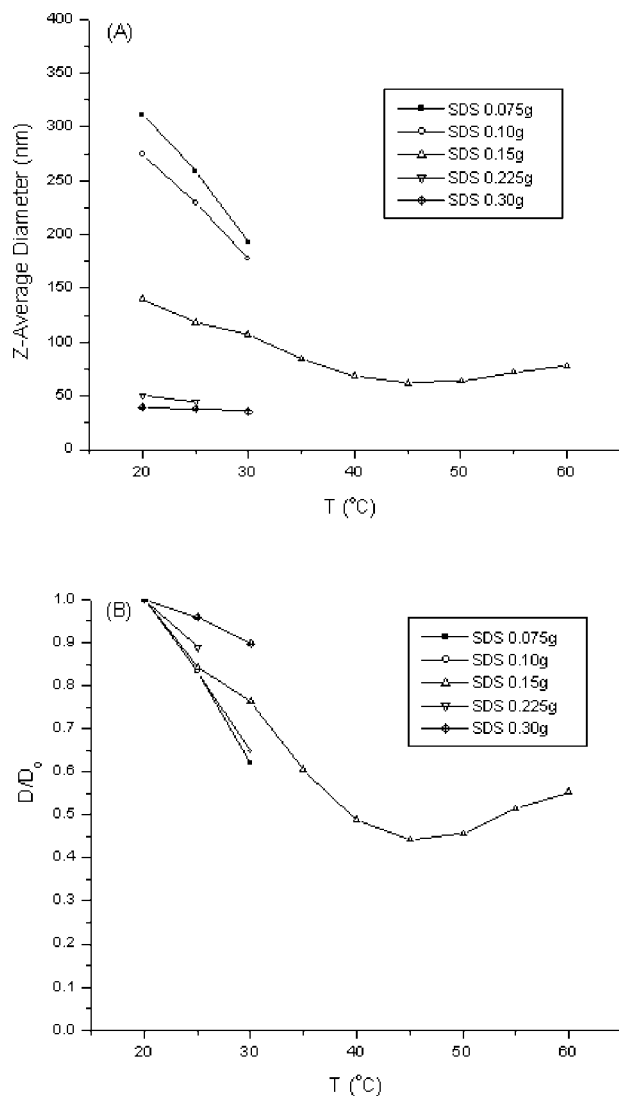
The particles tended to aggregate at a certain temperature level. For example, for PNIPAAm particles without MAA, particles tended to aggregate above 30°C (ca. its LCST). This made it difficult to measure the particle size, leading to incomplete data points over the temperature range of 20–60°C, as shown in Figure 3. Increasing the temperature weakened the hydrogen bonding between the copolymer and water, so polymer chains tended to collapse with one another. As there were more MAAs, the particles were more stable in an aqueous solution as the temperature changed. This should be ascribed to the fact that the MAA groups introduced electrolyte behavior, and the electrostatic repulsion force of the particles helped to stabilize the copolymer particles in solution. The ratio of the particle diameter at a given temperature to the particle diameter at 20°C (D/D_0) was used to indicate the changing tendency of the particles, as shown in Figure 3(B). The ratio was reduced as the MAA ratio increased, and this showed that the hydrophobic interaction was balanced by the effect of electrostatic repulsion from the charged MAA groups. With higher MAA ratios, the electrostatic force in particles became stronger.

The temperature dependence of the copolymer particle diameter with different surfactant contents is shown in Figure 4. Obviously, at the same temperature, the diameter of the copolymer particles decreased as the surfactant content increased. The amphiphilic structure of the SDS surfactant helped to solubilize the polymer particles in aqueous solutions and thus made it possible for polymer chains to form smaller particles. The effect of the surfactant on the diameter of the particles was significant. For example, as SDS changed from 0.10 to 0.3 g, the particle size changed from 274.4 to 39.9 nm at 20°C. Because the PNIPAAm–MAA copolymer was negatively charged on account of ionization of COOH groups and SDS is an anionic surfactant, the contents of SDS helped to disperse the copolymer particles in water. This could be beneficial for controlling the size of the particles for a specific purpose, such as drug delivery. The sharpness of the transition, D/D_0, was reduced as SDS increased. Higher surfactant contents led to stronger repulsion in particles and a smaller volume reduction as the temperature increased. At temperatures higher than 30°C, the particles tended to aggregate because a higher temperature broke the balance of hydrogen bonds between the polymer and water, and the possibility of neighboring polymer chains collapsing with one another increased.

Figure 5 shows the temperature dependence of the diameter of the copolymer particles with different crosslinking agent contents. Although a decrease in the diameter with increasing crosslinker was

Figure 3 Effect of the temperature (T) on the size of PNIPAAm–MAA particles with different MAA/NIPAAm ratios: (A) particle diameter and (B) D/D_0.

the amount of the surfactant and monomer ratio, PNIPAAm–MAA nanoparticles with the desired size for specific applications could be developed.

For the synthesized PNIPAAm–MAA particles, one of the applications is heavy-metal adsorption. Bivalent ions such as Cu, Cd, and Zn can interact with MAA and form metal–polyacid complexes involving two carboxylate groups for each ion in a large domain of pH values.[28,29] For PNIPAAm–MAA particles, it is thought that the chelation efficiency could be much higher than that of their hydrogel counterpart because of their much greater efficient contact area. Furthermore, the stimuli-responsive property of the copolymer provides a potential way to control adsorption and desorption processes, which allows reusing the particles and provides many potential applications such as recovering metal ions in wood treated with metal-based preservatives after its service.
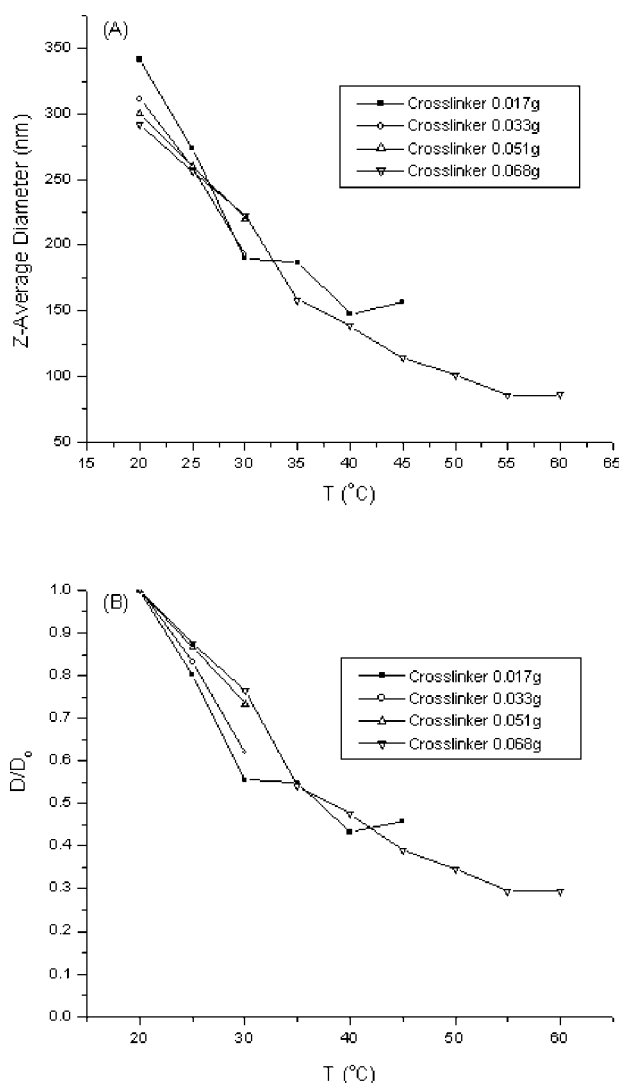
Figure 4 Effect of the temperature (T) on the size of PNIPAAm–MAA particles with different surfactant contents: (A) particle diameter and (B) D/D_0.

observed, the effect of the crosslinker on the particle size was not as obvious as that of the monomer ratio and surfactant. At 20°C, the diameter of the particle decreased from 341.3 to 292.0 nm as the crosslinker content increased from 0.017 to 0.068 g. The sharpness of the transition, D/D_0, was reduced upon the increase of the crosslinker. This was possibly because the increase in the crosslinking of the polymer helped to increase the electrostatic repulsion within particles and thus reduced the volume change.

As shown in Figures 3–5, most of the particle sizes fell in the range of 200–500 nm at 20°C. As the temperature increased, the particle size decreased, and some of the particles came near to or below 100 nm. With particles that were polymerized with higher surfactant contents, the particle size was less than 100 nm at 20°C, and thus nanoparticles were obtained. This result suggested that by the control of

Figure 5 Effect of the temperature (T) on the size of PNIPAAm–MAA particles with different crosslinker contents: (A) particle diameter and (B) D/D_0.

CONCLUSIONS

Copolymer particles of PNIPAAm–MAA were synthesized, and the effects of the monomer ratio, surfactant, and crosslinker contents during the polymerization were investigated in this study. The results showed that PNIPAAm–MAA particles had polyelectrolyte properties and that the electrostatic repulsion of the particles played an important role in the phase transition and particle size of the hydrogel. The monomer ratio and surfactant contents had a more significant effect on the hydrodynamic size of the particle than the crosslinker contents.

The MAA contents in the copolymers had a more complicated influence on controlling the phase-transition behavior. For the particle size, as the MAA contents increased, an apparent increase in the particle size was observed, but the sharpness of the transition was reduced. Also, the stability of the particles increased with an increase in the MAA content as the temperature changed. The increase in the negatively charged SDS surfactant content increased the phase-transition temperature of the copolymers and decreased the particle size dramatically. By control of the surfactant contents in the polymerization, PNIPAAm–MAA nanoparticles were obtained. The particles with increased surface area offer many potential applications, such as heavy-metal adsorption. Future publications in this series will deal with the absorbance properties of the copolymer for heavy-metal ions such as Cu^{+2}.

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