

SYNTHESIS AND PROPERTIES OF ORGANIC-INORGANIC HYBRID P(NIPAM-*co*-AM-*co*-TMSPMA) MICROGELS*

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Abstract Utilizing the hydrolysis and condensation of the methoxysilyl moieties, organic-inorganic hybrid poly(*N*-isopropylacrylamide-*co*-acrylamide-*co*-3-(trimethoxysilyl)propylmethacrylate) P(NIPAM-*co*-AM-*co*-TMSPMA) microgels were prepared *via* two different methods. The first method was that the microgels were post-fabricated from the cross-linkable linear P(NIPAM-*co*-AM-*co*-TMSPMA) terpolymer aqueous solutions above the lower critical solution temperature (LCST) of the terpolymer. For the second method, the microgels were directly synthesized by conventional surfactant free emulsion copolymerization of NIPAM, AM, and TMSPMA. The hydrodynamic diameter and stability of the resultant P(NIPAM-*co*-AM-*co*-TMSPMA) microgels strongly depend on the pH and temperature of the microgel aqueous solution. The hydrodynamic diameters of the microgels decreased with increasing the measuring temperature. The phase transition temperature of the microgels was found to be around 34°C, which was independent of the initial terpolymer concentration and shifted to lower temperature with increasing the preparation temperature. Increasing the initial amount of AM will enhance the instability of the microgels at high pH values. Moreover, the P(NIPAM-*co*-AM-*co*-TMSPMA) microgels obtained from the linear terpolymer had more homogeneous microstructures as compared with the corresponding NIPAM/AM/TMSPMA microgels prepared by one step emulsion copolymerization as revealed by light scattering measurements.

Keywords: Microgel; Thermo-sensitive; Hybrid.

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INTRODUCTION

Stimuli-responsive microgels have attracted extensive investigations due to their potential applications in diverse fields, such as drug-controlled-release system, separation technology, and catalysis, and enzyme immobilization^[1–7]. The most studied stimuli-responsive microgel systems are poly(*N*-isopropylacrylamide) (PNIPAM)-related microgels prepared *via* conventional emulsion copolymerization with the presence of chemical crosslinker, like *N,N'*-methylene-bisacrylamide (BIS) since 1986^[8]. Various colloidal microgel systems with tailored properties were successfully obtained. For instance, thermo- and pH- dual sensitive microgels were synthesized *via* emulsion copolymerization of NIPAM, acrylate-type monomers, and vinylpyridine and so on^[6, 9–20]. However, the microgels prepared *via* conventional emulsion polymerization with the presence of chemical cross-linker usually have non-uniform microstructures. The reaction rate of the chemical cross-linker,

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BIS, was proved to be far faster than that of the monomer, which results in the non-uniform cross-linking density in the microgels and in turn strongly influences the microstructure and properties of the microgels^[21–24]. How to control the microstructure and morphology of the microgels remains an important issue in the research of microgels^[25].

Kuckling and his coauthors first reported a novel method for preparing microgels with more homogeneous microstructure from photo cross-linkable copolymers by utilizing the thermal character of PNIPAM^[6, 26–28]. The colloidal particles formed at elevated temperatures were cross-linked under UV irradiation, leading to the formation of microgels, which had more homogeneous structures than those of microgels prepared *via* conventional emulsion polymerization with the presence of a chemical cross-linker, typically BIS^[27].

We recently developed another route based on similar principle but with hydrolysis induced cross-linking for fabricating microgels with more homogeneous microstructures^[29]. A reactive monomer, 3-(trimethoxysilyl)propylmethacrylate (TMSPMA) with methoxysilyl groups ($-\text{Si}(\text{OCH}_3)_3$) was introduced to form P(NIPAM-*co*-TMSPMA) copolymer. Such copolymer is thermally crosslinkable since the methoxysilyl groups can hydrolyze under moisture at high temperatures into the silanol [$-\text{Si}(\text{OH})_3$] groups and subsequently condense into the cross-linked polysilsesquioxane. Thermo-sensitive P(NIPAM-*co*-TMSPMA) microgels were easily obtained *via* simply heating the copolymer aqueous solution above its LCST. No additional treatment, like UV irradiation, was required. Cross-linked P(NIPAM-*co*-TMSPMA) hydrogel thin films can be also obtained by similar way^[30].

In the present work, a third and hydrophilic monomer, namely acrylamide (AM), was incorporated to afford a P(NIPAM-*co*-AM-*co*-TMSPMA) terpolymer. Linear terpolymer P(NIPAM-*co*-AM-*co*-TMSPMA) was first synthesized here by free-radical copolymerization of NIPAM, AM and TMSPMA. This terpolymer exhibited a LCST of *ca.* 33°C, which is hence very close to the LCST of PNIPAM homopolymer. The corresponding P(NIPAM-*co*-AM-*co*-TMSPMA) microgels were then prepared from the terpolymer aqueous solution without use of any surfactant at a temperature higher than its LCST. The NIPAM/AM/TMSPMA hybrid microgels were also prepared *via* conventional surfactant free emulsion copolymerization (SFEP) of NIPAM, AM, and TMSPMA. Scanning electron microscopy (SEM), dynamic and static light scattering (DLS & SLS) were used to systematically investigate the size, morphology, microstructure and properties of the hybrid microgels.

EXPERIMENTAL

Chemical and Materials

N-isopropylacrylamide (NIPAM: 99%, ACROS ORGANICS) was purified by recrystallization from *n*-hexane. Acrylamide (AM: 99%, Shanghai Lingfeng Chemical Reagent) was recrystallized from acetone. 3-(Trimethoxysilyl)propylmethacrylate (TMSPMA: 98%, ACROS ORGANICS) was dried over CaH_2 overnight and distilled under reduced pressure. 1,4-Dioxane (Shanghai Chemical Reagent) was dried by refluxing in the presence of sodium flake and distilled prior to use. The initiator, α, α' -azodiisobutyronitrile (AIBN) was recrystallized from methanol. Potassium Peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$, Sinopharm Chemical Reagent Co., Ltd) was used as received. All other reagents were of analytical grade and used as received.

*Synthesis of Terpolymer P(NIPAM-*co*-AM-*co*-TMSPMA)*

The linear terpolymer, [P(NIPAM-*co*-AM-*co*-TMSPMA)] was synthesized by free radical copolymerization of NIPAM, AM and TMSPMA in anhydrous dioxane at 80°C. Typically, the preset amounts of NIPAM, AM, TMSPMA and AIBN, 0.70 g, 0.05 g, 0.05 mL, and 5.0 mg respectively, were dissolved in 10 mL anhydrous dioxane in a polymerization tube under magnetic stirring. Oxygen was eliminated by bubbling nitrogen through the solution for 30 min. The polymerization was allowed to proceed for 24 h in an oil bath at 80°C. The reaction mixture was then removed from the bath and slowly cooled down to room temperature. The resultant terpolymer was precipitated with a large amount of dry diethyl ether and collected by filtration, dried in vacuum at 30°C. The terpolymer was stored in desiccators for further uses. The terpolymer P(NIPAM-*co*-AM-*co*-TMSPMA) exhibits a LCST at *ca.* 33°C as revealed by dynamic light scattering (DLS) measurements.

Preparation of P(NIPAM-co-AM-co-TMSPMA) Microgels from Linear Terpolymer

The microgels were prepared from the aqueous solution of linear terpolymer P(NIPAM-co-AM-co-TMSPMA) by utilizing the thermo-sensitive character of the terpolymer with a similar procedure reported in literature^[29]. The terpolymer was first fully dissolved in deionized water to give desired concentrations of 0.40, 0.10, 0.05 g/L at room temperature and filtered through Nylon membrane filters with 0.45 μm pore size. To obtain microgels, the aqueous solutions of terpolymer were heated to the preset temperature above its LCST, *i.e.* 45°C, 50°C, 55°C, and 60°C, respectively, under vigorous stirring (600 r/min) for 24 h. Above the LCST, the terpolymer forms aggregates. The size and shape of the aggregates were then fixed *via* the hydrolysis and condensation of the methoxysilyl moieties ($\text{Si}-\text{O}-\text{CH}_3$), resulting in the formation of microgels^[29]. Afterward, the solutions were cooled down to the room temperature and subjected to further characterization. The microgel samples were named after the terpolymer concentration and the preparation temperature. For example, the sample code “010-50” means that the microgels were prepared at 50°C with the terpolymer concentration of 0.10 g/L.

Preparation of P(NIPAM-co-AM-co-TMSPMA) Microgels via Conventional SFEP

The P(NIPAM-co-AM-co-TMSPMA) microgels were prepared by conventional surfactant-free emulsion polymerization (SFEP)^[8]. The monomers of NIPAM, TMSPMA and AM were dissolved in 38 mL deionized water at 70°C under vigorous stirring (600 r/min). Three series of microgels were prepared where one monomer concentration was systematically varied while keeping the concentrations of the other two monomers fixed. Details about the synthesis conditions are listed in Table 1. Oxygen was eliminated by bubbling nitrogen through the solution. After 15 min, 2 mL of potassium peroxydisulfate solution ($\text{K}_2\text{S}_2\text{O}_8$, 5 mg/mL) was added into the solution to initiate the polymerization. The reaction was continued at 70°C for 6 h. The obtained microgels were then purified by several centrifugation and redispersion cycles.

Table 1. Experimental conditions and relevant properties of the microgels

NIPAM (g)	AM (g)	TMSPMA (g)	Averaged diameter ^a (nm)	Hydrodynamic diameter ^b (nm)	R_g/R_h^c
0.10	0.02	0.01	158 $\pm$ 21	317.2 $\pm$ 1.8	0.52
0.20	0.02	0.01	201 $\pm$ 11	401.8 $\pm$ 1.1	0.58
0.30	0.02	0.01	267 $\pm$ 19	359.3 $\pm$ 3.0	0.74
0.40	0.02	0.01	194 $\pm$ 16	388.1 $\pm$ 4.9	0.62
0.30	0.01	0.01	185 $\pm$ 10	327.9 $\pm$ 2.4	0.73
0.30	0.03	0.01	178 $\pm$ 10	371.1 $\pm$ 2.1	0.69
0.30	0.04	0.01	173 $\pm$ 11	353.3 $\pm$ 5.1	0.72
0.30	0.02	0.02	195 $\pm$ 14	394.3 $\pm$ 3.7	0.63
0.30	0.02	0.03	139 $\pm$ 8	343.8 $\pm$ 4.6	0.58
0.30	0.02	0.04	166 $\pm$ 18	303.1 $\pm$ 2.9	0.61

^a Measured by SEM; ^b Measured by DLS at 25°C; ^c Measured at 25°C

Instruments and Characterization

Number average and weight average molecular weights (M_n and M_w) and polydispersity index of the terpolymer were determined by gel permeation chromatograph (GPC, PL-GPC 220, Polymer Laboratories Ltd.) with tetrahydrofuran as eluent and monodisperse polystyrene as calibration standard. FT-IR spectra were recorded on a Vector 22 Bruker spectrometer. ¹H-NMR of the terpolymer was performed on a 300 MHz Varian Mercury Plus NMR instrument with CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard. The lower critical solution temperature (LCST) of the terpolymer was measured by dynamic light scattering using a 90 Plus Particle Size Analyzer (Brookhaven Instruments Corporation). The terpolymer was dissolved in distilled water to give a concentration of 0.3 wt%. Dust was removed from the solutions of linear polymer by filtering through Nylon membrane filters of 0.45 μm pore size prior to the measurement. For each temperature, the solution was equilibrated for 15–20 min.

The morphologies of the microgels were investigated by scanning electron microscope (HITACHI, S-4800). A droplet of the microgel solution was cast onto the aluminum foils at room temperature. After a few minutes, the excess solution was gently absorbed away by a filter paper. The aluminum foils were then allowed

to dry in air. Before SEM observation, the microgel samples were coated with gold vapors. Several positions of each sample were imaged.

The hydrodynamic diameter (D_h) of the P(NIPAM-*co*-AM-*co*-TMSPMA) microgels was characterized by dynamic light scattering using a 90 Plus Particle Size Analyzer (Brookhaven Instruments Corporation) in the temperature range of 25–60°C. The scattering angle was 90°. Since the size of microgel was far larger than that of linear polymer in solution, Nylon membrane filters of 0.8 μm were used to remove the dust from the microgel solutions by filtration. For each temperature, the solution was kept for 15–20 min to allow equilibrium.

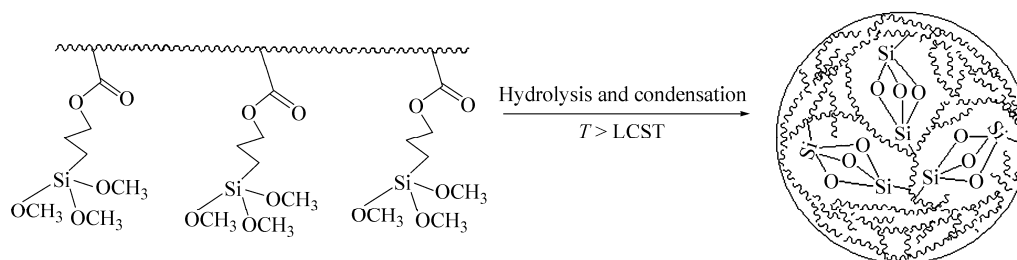
The *z*-average root-mean square radius of gyration $\langle R_g \rangle$ of the microgels was measured by static light scattering (SLS) on a Brookhaven Instrument BI-200SM at 25°C and 60°C, respectively. The range of scattering angle was from 30° to 145° with a step of 5° or 15°. The hydrodynamic radius $\langle R_h \rangle$ of the microgels was also re-measured at scattering angle of 90° by using the same instrument at the corresponding temperatures for calculating the ratio of $\langle R_g \rangle / \langle R_h \rangle$. The microgel solutions were filtered through 0.8 μm Nylon membrane filters before measurements.

RESULTS AND DISCUSSION

The terpolymer, P(NIPAM-*co*-AM-*co*-TMSPMA), was synthesized by free radical copolymerization of NIPAM, AM, TMSPMA with feed ratio of NIPAM:AM:TMSPMA = 14:1:1. The weight average molecular weight M_w and polydispersity index (PDI, M_w/M_n) of the terpolymer were found to be 2.1×10^4 and 2.10, respectively. The FT-IR results confirmed that the copolymerization of NIPAM, AM and TMSPMA had successfully taken place (see Fig. S1 in supplementary material).

P(NIPAM-co-AM-co-TMSPMA) Microgels prepared from Terpolymer Aqueous Solution

The microgels were prepared from the aqueous solutions of terpolymer P(NIPAM-*co*-AM-*co*-TMSPMA) by utilizing the thermo-sensitive character of the terpolymer. Scheme 1 indicates the formation of microgels by the hydrolysis and condensation of TMSPMA units. To obtain microgels, the aqueous solutions of terpolymer were heated to the temperature above its LCST under vigorous stirring (600 r/min) for 24 h. The size and shape of the terpolymer aggregates formed at elevated temperatures were then fixed and preserved *via* the hydrolysis and condensation of the methoxysilyl moieties (Si—O—CH₃), forming the microgels. Figure 1 shows the typical SEM images of the microgels obtained at various terpolymer concentrations and preparation temperatures. The microgel particles were spherical in shape with a broad size distribution. Some microgels were merged together, which might be due to the closed contact of microgels during the drying procedure. The average diameters of the microgels range from several tens nanometer to hundreds nanometer. The introduction of the third comonomer broadens the size distribution of the resultant microgels, which is consistent with those found by Kuckling *et al*.^[6]



Scheme 1 Formation of microgels by the hydrolysis and condensation of TMSPMA units

Figure 2 shows the hydrodynamic diameters (D_h) of the microgels prepared at 50°C from the terpolymer aqueous solution with various concentrations as the function of measuring temperature. Clearly, the hydrodynamic diameters of the microgels decreased with increasing the measuring temperature. The phase transition temperatures of the microgels were observed at around 34°C. The hydrodynamic diameters of the

P(NIPAM-co-AM-co-TMSPMA) microgels also depended on the initial concentration of the copolymer aqueous solution. However, no clear relationship between the microgel size and the initial terpolymer concentration can be found. Furthermore, the normalized swelling ratio of the microgels indicates that the phase transition temperatures of the P(NIPAM-co-AM-co-TMSPMA) microgels were independent of the initial terpolymer concentration as shown in the inset of Fig. 2.

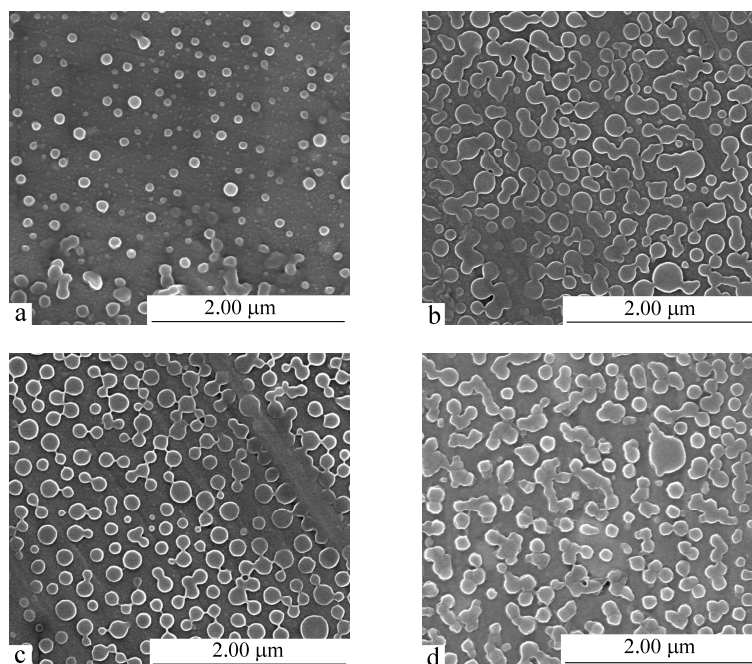


Fig. 1 SEM images of the P(NIPAM-co-AM-co-TMSPMA) microgels at 25°C: (a) 005-50, (b) 010-50, (c) 010-60 and (d) 040-50

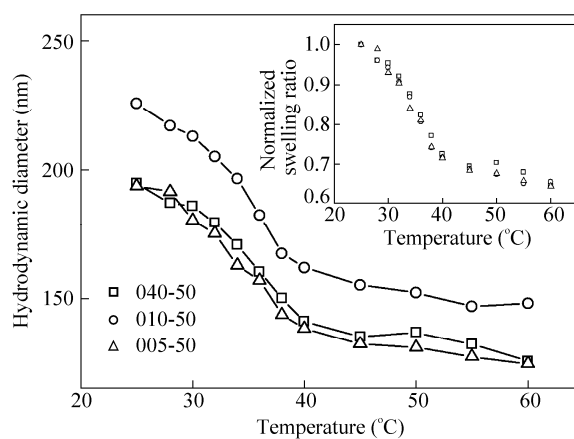


Fig. 2 The hydrodynamic diameters of the P(NIPAM-co-AM-co-TMSPMA) microgels prepared at 50°C from the terpolymer aqueous solution with concentration of 0.40, 0.10, 0.05 g/L as the function of measuring temperature. Inset is the corresponding normalized swelling ratio.

Figure 3 shows that the hydrodynamic diameters and the phase transition temperature of P(NIPAM-*co*-AM-*co*-TMSPMA) microgels depended on their preparation temperature. The sizes of microgels decreased with increasing the preparation temperature, whereas the phase transition temperatures slightly shifted to lower temperatures. These results were in good agreement with those observed for P(NIPAM-*co*-TMSPMA) microgels prepared with similar method^[29]. According to the discussion reported previously, the P(NIPAM-*co*-AM-*co*-TMSPMA) microgels were prepared *via* the inter-chain and intra-chain cross-linking reactions of methoxysilyl groups in the terpolymer aggregations at temperatures higher than its LCST. The terpolymer molecules will form more compact aggregates at higher temperatures, leading to the larger possibility of the inter-chain cross-linking reactions. The cross-linking density of the microgels will be higher for those prepared at higher temperatures. Hence, the hydrodynamic diameters were smaller for the P(NIPAM-*co*-AM-*co*-TMSPMA) microgels prepared at higher temperatures.

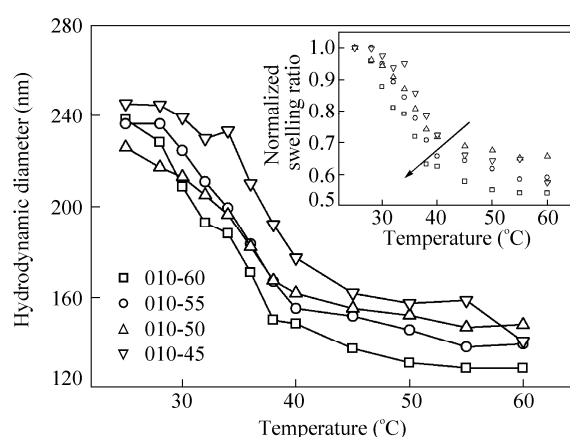


Fig. 3 The hydrodynamic diameters of the P(NIPAM-*co*-AM-*co*-TMSPMA) microgels prepared at various temperatures from the terpolymer aqueous solution of 0.10 g/L as the function of measuring temperature. Inset is the corresponding normalized swelling ratio; The arrow in the inset guides the shift of phase transition temperature of the microgels.

Although AM is a very weak base, the effect of pH on the hydrodynamic diameters and stability of P(NIPAM-*co*-AM-*co*-TMSPMA) microgels were then investigated. Two microgel samples, 040-50 and 010-50 were investigated in the range of pH = 2 to 12. The pH of the microgel aqueous solutions was adjusted by using HCl and KOH aqueous solutions with known concentrations. Three regions can be identified from the experimental data shown in Fig. 4. From pH = 2 to 4, the hydrodynamic diameters of microgels only slightly increased with raising pH value of the solution and reached a local maximum at pH = 4. For pH 4 to 7, the hydrodynamic diameters of the microgels only slightly decreased with increasing pH. In the weak basic condition (pH = 7–9), the hydrodynamic diameters of the microgels were less affected by the pH value. Above pH = 10, the hydrodynamic diameters of the microgels strongly increased again. Precipitation was observed for pH > 11. The results of Fig. 4 indicate that the P(NIPAM-*co*-AM-*co*-TMSPMA) microgels are lack of pH sensitivity because no significant difference in the swelling properties could be observed in the pH range of 2 to 10. However, the higher pH values, *i.e.* pH > 11, lead to the instability and aggregation of the microgels. Precipitation was even observed after several hours for the microgel solutions with pH = 12.

The microstructure of the P(NIPAM-*co*-AM-*co*-TMSPMA) microgels can be characterized by the ratio of $\langle R_g \rangle / \langle R_h \rangle$. $\langle R_h \rangle = \langle D_h \rangle / 2$ can be directly measured by DLS. $\langle R_g \rangle$ can be determined from the very dilute solution of microgels by SLS (see supplementary material). The value of $\langle R_g \rangle / \langle R_h \rangle$ can reflect the conformation and architecture of a polymer chain in solution or the cross-linking density distribution of the microgels^[23, 27, 31, 32]. For instance, for linear and flexible polymer chains, $\langle R_g \rangle / \langle R_h \rangle$ is around 1.5, while for uniform hard spheres, $\langle R_g \rangle / \langle R_h \rangle$ is 0.778. For the PNIPAM microgels prepared *via* conventional emulsion

polymerization with chemical cross-linker BIS, $\langle R_g \rangle / \langle R_h \rangle$ was around 0.55–0.6 at room temperature due to the non-uniform distribution of cross-linking density in the microgels^[23, 31]. Figure 5 shows the ratio of $\langle R_g \rangle / \langle R_h \rangle$ measured at 25°C and 60°C for the P(NIPAM-co-AM-co-TMSPMA) microgels prepared at various temperatures or various terpolymer concentrations. $\langle R_g \rangle / \langle R_h \rangle$ values of the microgels obtained at different preparation temperatures varied in the range 0.73–0.88, whereas $\langle R_g \rangle / \langle R_h \rangle$ values of the microgels obtained at different terpolymer concentrations were in the range 0.73–0.96. All of the $\langle R_g \rangle / \langle R_h \rangle$ values obtained here were close to that of hard sphere, *i.e.* 0.778, for the swollen microgels at 25°C and the collapsed microgels at 60°C, which indicated that the P(NIPAM-co-AM-co-TMSPMA) microgels had more homogeneous microstructures. The cross-linkable comonomers were randomly distributed in the copolymer chains, which may lead to the similar cross-linkable groups in the particle core or the particle shell. Hence, the obtained microgels had more homogeneous cross-linking density.

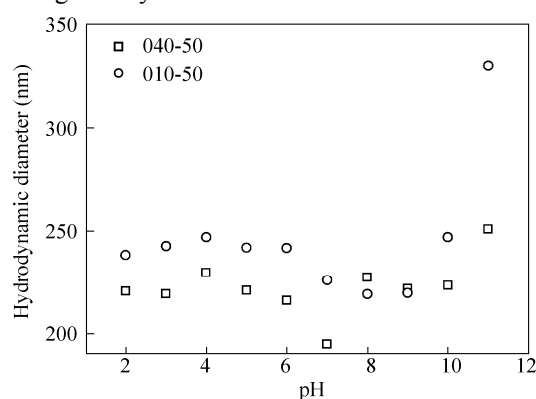


Fig. 4 The hydrodynamic diameters of the P(NIPAM-co-AM-co-TMSPMA) microgels, 040-50 and 010-50, as the function of pH

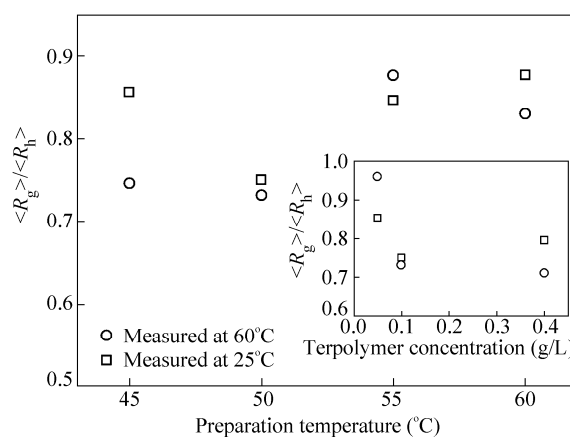


Fig. 5 The ratio of $\langle R_g \rangle / \langle R_h \rangle$ for the P(NIPAM-co-AM-co-TMSPMA) microgels prepared at various temperatures with terpolymer concentration of 0.10 g/L. Inset is $\langle R_g \rangle / \langle R_h \rangle$ for the P(NIPAM-co-AM-co-TMSPMA) microgels prepared at 50°C with various terpolymer concentrations.

The P(NIPAM-co-AM-co-TMSPMA) Microgels Prepared from Conventional SFEP

Figure 6 and Figs. S3–S4 (see supplementary material) show the typical SEM images of the NIPAM/AM/TMSPMA hybrid microgels obtained *via* SFEP with various monomer compositions. It can be seen that increasing the initial concentration of NIPAM from 0.10 g to 0.40 g leads to more spherical microgels (Fig. 6). However, the concentrations of monomers AM and TMSPMA have less effect on morphology of the

resultant microgels (Figs. S3 and S4) in the range of concentration studied. The average diameters of the microgels obtained from SEM images are summarized in Table 1. The results show that the average diameters of the microgels tend to increase with increasing the monomer concentration of NIPAM and to decrease with increasing the monomer concentration of AM or TMSPMA when the other experimental conditions were fixed. Furthermore, the NIPAM/AM/TMSPMA hybrid microgels obtained here have more uniform shape and size distribution than the corresponding microgels prepared from the linear terpolymer, poly(NIPAM-*co*-AM-*co*-TMSPMA), *via* a two-step method. Figure 7 shows that the hydrodynamic diameters of all the obtained hybrid microgels decrease with increasing the measuring temperature. In another word, the hybrid microgels shrink at higher temperatures. The phase transition temperatures of the hybrid microgels were found to be around 35°C. In order to clearly observe the effects of feeding monomer composition on the thermo-sensitivity of the resultant NIPAM/AM/TMSPMA hybrid microgels, the hydrodynamic diameters were also normalized against the hydrodynamic diameter at 25°C and shown in the insets of Fig. 7. The phase transition temperature of the hybrid microgels shifts to the lower temperature with decreasing the initial amount of NIPAM and increasing the initial amount of TMSPMA. These results agree well with those obtained for NIPAM/TMSPMA hybrid microgels^[29]. General speaking, increasing the feeding ratio of monomer to cross-linker tends to decrease the cross-linking density of the resultant microgels, leading to the higher phase transition temperature. Similarly, increasing the cross-linking density of the NIPAM/AM/TMSPMA microgels broadened the phase transition temperature (insets of Fig. 7). Benec *et al.* have attributed the broadening of phase transition to the introduction of hydrophobic comonomer into the microgel^[16]. The hydrophobic comonomer makes the conformational rearrangements of network strands occur over a wider temperature range, resulting in the broad transition of the microgels. Figure 7(B) shows that increasing the initial amount of AM shifts the phase transition temperature of the hybrid microgels to the higher temperature. This is also reasonable because AM is a hydrophilic monomer.

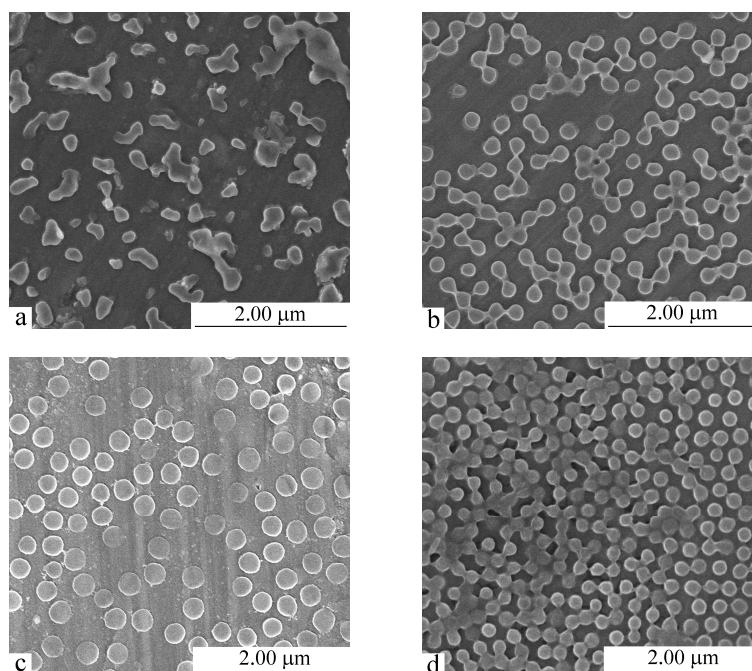


Fig. 6 SEM images of the NIPAM/AM/TMSPMA hybrid microgels prepared with various initial concentrations of NIPAM: (a) 0.10 g, (b) 0.20 g, (c) 0.30 g and (d) 0.40 g. The initial concentrations of AM and TMSPMA were 0.02 g and 0.01 g, respectively.

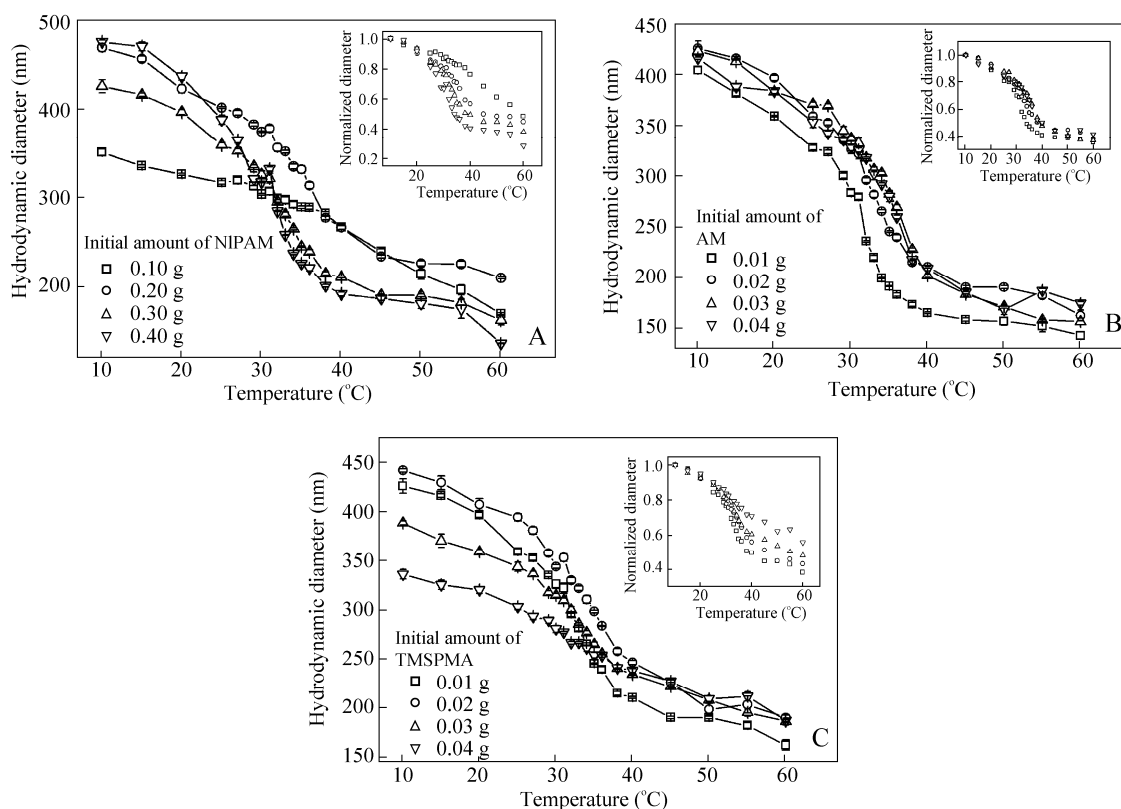


Fig. 7 The hydrodynamic diameters of the NIPAM/AM/TMSPMA hybrid microgels prepared under different experimental conditions as a function of measuring temperature: (A) microgels obtained with various initial amounts of NIPAM, (B) microgels obtained with various initial amounts of AM and (C) microgels obtained with various initial amounts of TMSPMA

Insets are the corresponding normalized hydrodynamic diameters.

The thermo-sensitive properties of the NIPAM/AM/TMSPMA hybrid microgels are also studied at various pH values. For all pH values of the microgel suspensions studied here, the hydrodynamic diameters of microgels decrease with increasing temperature (Fig. S5, see supplementary material). However, the hybrid microgels aggregate and precipitate at 40°C for pH $\approx$ 2.1. The phase transition temperature of the hybrid microgels seems not sensitive to the pH values studied here. Figure S6 (see supplementary material) shows $\langle D_h \rangle$ of the hybrid microgels obtained with various amount of AM as the function of pH value at 25°C. It can be seen that for pH < 9, the hydrodynamic diameters of the microgels only slightly change with pH value, indicating the lack of pH sensitivity of the microgels. However, for pH > 9, the hydrodynamic diameters of the microgels increase drastically with increasing pH value due to the instability. Precipitation was observed for the microgels obtained with 0.01 g AM and 0.02 g AM at pH > 12, whereas the microgels obtained with 0.03 g and 0.04 g AM were already flocculated at pH > 11. In strong alkaline conditions (pH > 11), the increase of KOH in aqueous solution could lead to the increase of free K⁺. The ionized carboxylic groups of microgels were surrounded by a large number of K⁺. The electric shielding of K⁺ had weakened the electrostatic repulsion interactions of microgels so that the microgels became very unstable and the aggregation or precipitation of microgels occurred. These results indicate that increasing the amount of AM enhances the instability of NIPAM/AM/TMSPMA microgels at higher pH values.

The microstructures of the NIPAM/AM/TMSPMA hybrid microgels obtained *via* SFEP were characterized by the ratio of $\langle R_g \rangle / \langle R_h \rangle$ at 25°C as listed in Table 1. For example, the hydrodynamic diameter $\langle D_h \rangle$ of the microgel with the feed ratio of NIPAM/AM/TMSPMA = 0.30 g/0.02 g/0.01 g in the deionized water was

ca. 359.3 nm obtained from Fig. S7 (see supplementary material). The hydrodynamic radius $\langle R_h \rangle$ ($\langle D_h \rangle / 2$) from DLS and the z-average root-mean square radius of gyration $\langle R_g \rangle$ (134.4 nm) of the hybrid microgels from SLS at 25°C could be used to calculate the ratio of $\langle R_g \rangle / \langle R_h \rangle$ (0.74). It can be seen that increasing the amount of cross-linkable monomer TMSPMA leads to the increase of network density and enhances the heterogeneous distribution of cross-linking density, which result in the decrease of $\langle R_g \rangle / \langle R_h \rangle$. $\langle R_g \rangle / \langle R_h \rangle$ is around 0.58–0.74, which is close to those obtained for the PNIPAM microgels prepared *via* conventional emulsion polymerization with chemical cross-linker *N,N'*-methylene-bisacrylamide (BIS) at room temperature^[23, 24]. As is expected, increasing the amount of main monomer NIPAM shows the opposite effects on $\langle R_g \rangle / \langle R_h \rangle$. The values of $\langle R_g \rangle / \langle R_h \rangle$ are quite close to those of the hybrid microgels prepared with various amount of AM from 0.01 g to 0.04 g. It may be attributed to the small amount of AM used. However, for similar amounts of AM and TMSPMA, the effects of the cross-linkable monomer TMSPMA on $\langle R_g \rangle / \langle R_h \rangle$ ratio of the resultant microgels are pronounced. It means that the cross-linkable monomer mainly determines the microstructure of the resultant microgels. Furthermore, the $\langle R_g \rangle / \langle R_h \rangle$ ratios of NIPAM/AM/TMSPMA microgels prepared *via* SFEP are less than those fabricated from the linear terpolymer poly(NIPAM-*co*-AM-*co*-TMSPMA) *via* a two-step method, indicating that the hybrid microgels obtained from the linear terpolymer have more homogeneous microstructure than the corresponding microgels *via* SFEP.

CONCLUSIONS

P(NIPAM-*co*-AM-*co*-TMSPMA) microgels were successfully prepared from the corresponding thermal cross-linkable linear terpolymer poly[*N*-isopropylacrylamide-*co*-acrylamide-*co*-3-(trimethoxysilyl)propyl-methacrylate] or from conventional surfactant free emulsion polymerization (SFEP) *via* the hydrolysis and condensation of the methoxysilyl moieties. The morphology, size, and stability of the obtained hybrid microgels strongly depend on the preparation conditions, environmental temperature and pH value. The hydrodynamic diameters of microgels decrease with increasing temperature for various pH values. The phase transition temperature of the microgels was found to be around 34°C, which was independent of the initial terpolymer concentration and shifted to lower temperatures with increasing the preparation temperature. Increasing the initial amount of AM enhances the instability of hybrid microgels at higher pH value. The microgels prepared by SFEP have more heterogeneous microstructures as compared with the corresponding microgels fabricated from the linear terpolymer poly(NIPAM-*co*-AM-*co*-TMSPMA) *via* a two-step method, of which the $\langle R_g \rangle / \langle R_h \rangle$ ratio was close to that of hard sphere.

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