Sulfur Containing Poly(*N*-isopropylacrylamide) Copolymer Hydrogels for Thermosensitive Extraction of Gold(III) Ions

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ABSTRACT: Poly[*N*-isopropylacrylamide-*co*-[2-(methylthio)ethyl methacrylate]], poly(NIPA-*co*-MTEMA) gels were prepared by free radical polymerization in aqueous solution. The homogeneous and heterogeneous gels were prepared by using 10 mM MTEMA in 5.0%(v/v) ethanol at 10°C and 30 mM MTEMA in 20%(v/v) ethanol at 50°C, in 1.0 and 1.5M NIPA solution, respectively. Homogeneous and heterogeneous gels had swelling ratios at 540 ± 28% and 551 ± 37%, respectively. The extraction of Au(III) ion was studied in batch method. The optimum pHs for the extraction of Au(III) by homogeneous and heterogeneous gels were 1–3 and 1–5, respectively. The suitable extraction time was 3 h at 50°C when using a rod-shaped copolymer (0.7 cm diameter and 1 cm length). The adsorption behavior obeyed the Langmuir and Freundlich isotherms. The maximum sorption capacities of Au(III) onto homogeneous and heterogeneous gels were 62.8 and 322 μmol/g, respectively. The desorption equilibrium was reached within 2–3 h at 10°C by 0.1M thiourea in 5%(v/v) HCl. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3098–3108, 2011

Key words: copolymer; hydrogel; *N*-isopropylacrylamide; 2-(methylthio)ethyl methacrylate; gold(III); extraction

INTRODUCTION

Hydrogels are hydrophilic network-structural polymers possessing high water absorption capacity. Temperature-sensitive hydrogels have been attracting great interest in diverse technological applications due to their unique properties that are changed in response to temperature.[1–4] Many temperature-sensitive polymers such as poly(*N*-substituted acrylamide), poly(vinyl methyl ether), poly(diethylacrylamide), and poly(*N*-vinylcaprolactam) have been reported so far and they have been utilized in the gel form for applications in chemical separation processes[5,6] and metal ion extraction.[7–13] Among temperature-sensitive hydrogels, poly(*N*-isopropylacrylamide) or poly(NIPA) was widely studied since it exhibits remarkable hydration–dehydration changes in aqueous solutions in response to relatively small temperature changes around 32°C,[14] owing to a phase transition that occurs at the lower critical-solution temperature (LCST). Hence, the modification of its physical and chemical properties by copolymerization was of interest.

A number of reports were devoted to the use of poly(NIPA) and its derivative copolymers as solid-phase extraction adsorbents for heavy metal ions in aqueous solution.[7–13] In particular, poly(NIPA) and its derivative copolymers performed a temperature-swing adsorption (TSA) toward metal ions.[10,11] Poly(NIPA) showed an extractive affinity for Au(III) ions[7] and Cu(II)-surfactant complexes.[13] It was found that the amount of metal ion adsorbed was low at 10°C and high at 50°C. Through these studies, the NIPA gel had the potential ability for adsorption of metal ions, especially Au(III) ions. In addition, the adsorption of Au(III) ions on NIPA gel was a promising method for the recovery of gold from gold ores and electronic scraps. However, poly(NIPA) has quite low sorption capacity toward Au(III). In this context, the specificity and extraction property of poly(NIPA) copolymerized with chelating agents toward some heavy metal ions were higher than poly(NIPA).[9]

Since temperature-sensitive copolymers are attractive to improve the selectivity toward Au(III) ion, in this research, a chelating comonomer namely 2-(methylthio)ethyl methacrylate (MTEMA) containing sulfur atom was expected to be an appropriate donor atom for gold ions.[15,16] The novel copolymer hydrogel composed of poly(NIPA) and MTEMA crosslinked

with bis(acrylamide) was synthesized by two different routes of free-radical polymerization (at low and high temperatures). The effect of synthesized conditions on the structure and morphology of the copolymers and their extraction efficiency toward Au(III) ions in aqueous solution were investigated.

EXPERIMENTAL

Materials and reagents

All chemicals were used without further purification. *N*-isopropylacrylamide (NIPA, 97%), 2-(methylthio)ethyl methacrylate (MTEMA, 96%), *N*,*N*'-methylenebisacrylamide (MBAA, 98%), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TEMED, 99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Working Au(III) solutions were freshly prepared by stepwise dilution of 1000 mg/L stock standard solution (Merck, Darmstadt, Germany). All solutions were prepared by using deionized (DI) water with the resistivity higher than $18 M\Omega$.cm. All reagents were of analytical grade.

Synthesis of gels

The preparation conditions were adapted from the Refs. 13, 17. Two different polymers called homogeneous and heterogeneous gels were synthesized. The homogeneous gel is a polymer prepared at a preparation temperature lower than the LCST, whereas the heterogeneous gel is prepared at a temperature higher than the LCST.

Homogeneous gels

The appropriate amounts of NIPA (monomer), MBAA (crosslinker), and TEMED (accelerator) were dissolved in DI water in a test tube (0.7 cm i.d.). Then, MTEMA (comonomer) in ethanol (500 μL) was added and the volume was adjusted to 10 mL. The final concentrations of NIPA, MBAA, TEMED, and MTEMA were 1000 m*M*, 50 m*M*, 10 m*M*, and 10 m*M*, respectively. The mixture solution was sonicated for 15 min and placed in a cold water bath at 10°C under nitrogen purging for 1 h. After that, the polymerization was performed by adding 1 m*M* ammonium peroxodisulfate (APS) in the mixture solution. The cylinder-shaped transparent copolymer was obtained and taken out from the test tube and afterward cut into small pieces ∼ 1.0 cm length and washed with DI water several times to remove unreacted monomers and undesired by products.

Heterogeneous gels

The reaction proceeded using the same methodology but MTEMA in 2 mL ethanol (its final concentration

in the mixture was 30 m*M*) was used, and the mixture was placed in a water bath at 50°C under nitrogen atmosphere for 30 min. The copolymer hydrogel obtained was white and opaque. Poly(NIPA) was also prepared by the same manner without MTEMA comonomer.

Characterization of gels

The synthesized copolymers were characterized by Fourier Transforms Infrared Spectrometry (FTIR, Nicolet Impact 410), Raman Spectrometry (FT-Raman, Perkin–Elmer Spectrum GX), Scanning Electron Microscopy (SEM, Jeol JSM 5410LV), Thermal Gravimetric Analysis (TGA, Netzsch 409), and Differential Scanning Calorimetry (DSC, Netzsch 200).

Swelling behavior study

The degree of swelling was determined gravimetrically by using the procedure previously used in the Ref. 7. A piece of synthesized polymer was immersed in water until saturation. The swollen gel was periodically weighed after removing the excess water at the surface by filter paper. The experiment was repeated until the wet weight of the gel was constant. Later, it was dried in an oven at 110°C until the weight of dried polymer was constant.

#### Measurement of phase transition

Homogeneous polymers were synthesized in a plastic cuvette. The preparation conditions were similar to those presented in "Synthesis of gels." The phase transition of the polymers were studied by determining the optical transmittance using UV–Vis spectrophotometer (Hewlett–Packard HP 8453) at the wavelength of 600 nm over the temperature range of 24–40°C controlled by a thermostatic water bath (Lauda Brinkmann RCS 6-D). From the point of inflection of the turbidity curve, the LCST of homogeneous polymers can be determined.

Gold extraction and desorption experiments

The Au(III) solution was in chloroaurate form $[AuCl_4]^-$. All extraction experiments were performed in triplicate. Various parameters influencing the extraction and desorption of Au(III) were studied as follows.

Extraction studies

Effect of pH, extraction time, and temperature. A rod of gel sorbent (0.7 cm diameter × 1.0 cm length) was weighed and placed in a 14-mL test tube containing an aqueous solution of $HAuCl_4$ (10 mg/L, 3 mL). The temperature was controlled at 50°C. The initial pH of the gold solution was adjusted by 1 and
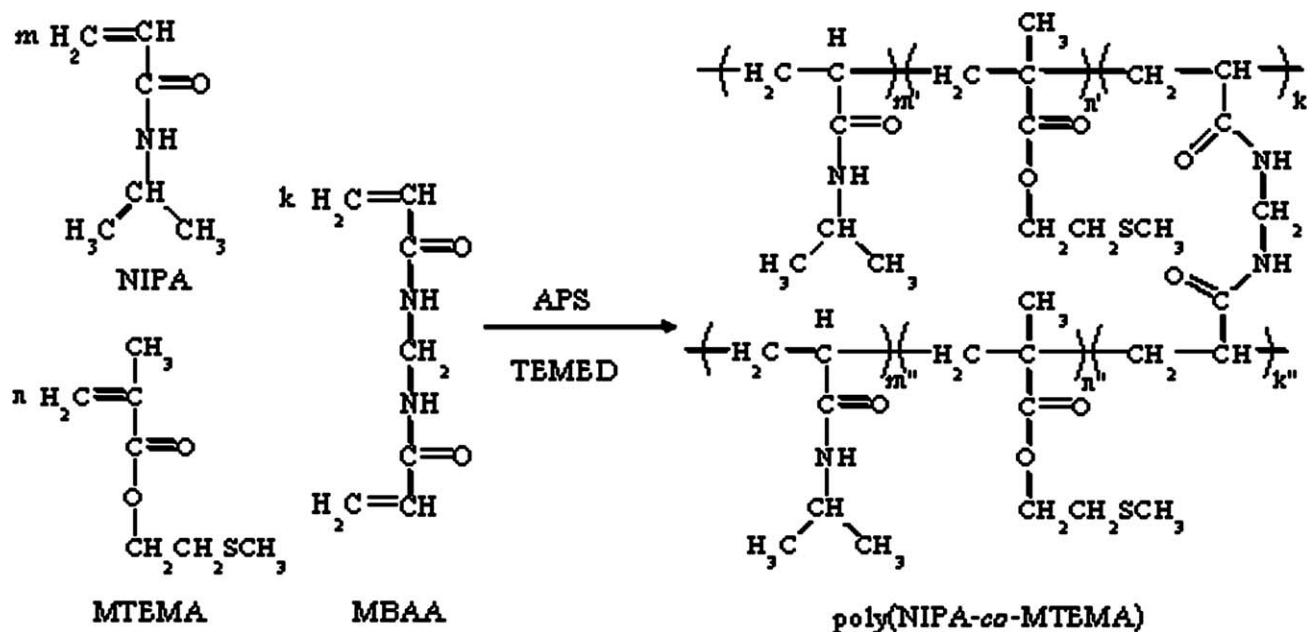
Scheme 1 Synthesis pathway of copolymer.

5%(v/v) HCl and 1 and 5%(w/v) KOH in the range of pH 1.0–7.0. The extraction time was varied in the range of 0.5–8 h for homogeneous polymers and 0.5–5 h for heterogeneous polymers. The effect of temperature was investigated in the range of 10–50°C at the optimum pH and the extraction time for each polymer. The initial and residual concentrations of Au(III) in the solution were determined by a flame atomic absorption spectrometer (FAAS, Perkin–Elmer AAnalyst 100). The extraction efficiency was reported in terms of extraction percentage or % extraction calculated from the difference between the starting amount of Au(III) (N_s, mg) and the amount of Au(III) left in the solution (N_f, mg) according to Eq. (1).

$$\% \text{ Extraction} = \frac{N_s - N_f}{N_s} \times 100 \quad (1)$$

Adsorption isotherm. The adsorption isotherm was studied using various concentrations of Au(III) ion solution in the range of 10–500 mg/L. The temperature of the solutions was thermostatically controlled at $50 \pm 1°C$ and the adsorption time was fixed at 3 h. The residual concentration of Au(III) in the solutions was determined by FAAS.

Desorption studies

Various parameters such as types of desorbing solution, desorption time, and temperature were studied. All desorption experiments were performed in triplicate. Au(III)-adsorbed gels were contacted for 2 h with 3 mL of various types and concentrations of stripping solutions, e.g., DI water, HCl, and thiourea. The optimal desorption time was studied under suita-

ble desorbing solution at different times in the range of 0.5–4 h. The effect of temperature was investigated from 10 to 50°C. The Au(III) ion concentration in the desorbing solutions was determined by FAAS.

RESULTS AND DISCUSSION

Synthesis and characterization of gels

Generally, poly(NIPA) was synthesized by free radical copolymerization in an aqueous solution.[1,18] Since the MTEMA comonomer used is slightly soluble in water, organic solvents should be added to dissolve the comonomer. Some commonly used organic solvents were tested. When an appropriate solvent was selected, synthesis conditions were optimized by varying the ratio of the comonomer and the amount of organic solvent added. The synthesis pathway is displayed in Scheme 1.

Effect of solvent

To study the effect of solvent for facilitating the dissolution of MTEMA comonomer, the extraction efficiency of the obtained gels toward Au(III) ion was considered. The copolymers were synthesized in different solvents including ethanol, 1,4-dioxane, acetone, and *N,N*-dimethylformamide (DMF). The extraction efficiency was considered to select the appropriate solvent in gel preparation. The % extractions were in the range of 70% and 80% for homogeneous and heterogeneous gels, respectively. It was found that all solvents used in the copolymer synthesis showed nearly the same % extraction of Au(III) ion. Consequently, ethanol was selected due to its miscibility with water, low volatility and toxicity.
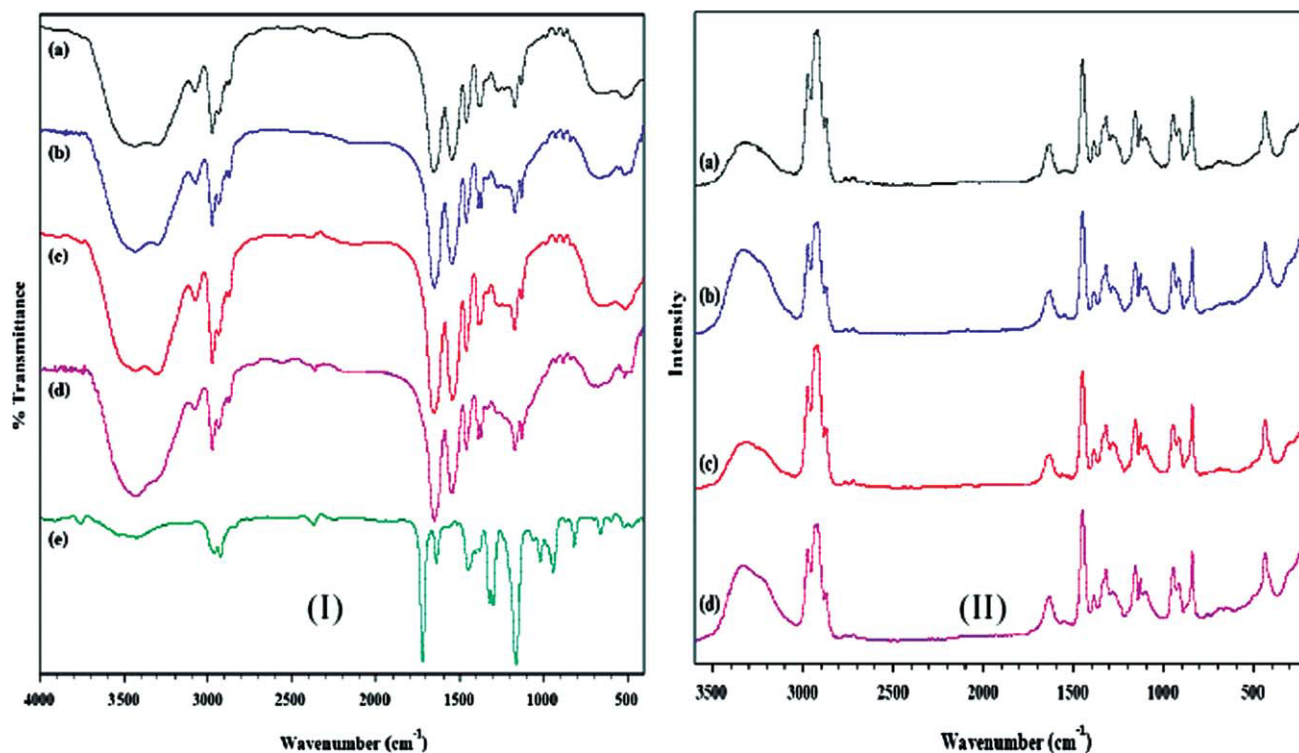
Figure 1 I: FTIR spectra of (a) poly(NIPA) (Homo), (b) poly(NIPA) (Hetero), (c) poly(NIPA-*co*-MTEMA) (Homo), (d) poly(NIPA-*co*-MTEMA) (Hetero), and (e) MTEMA comonomer and II: Raman spectra of (a) poly(NIPA) (Homo), (b) poly (NIPA) (Hetero), (c) poly(NIPA-*co*-MTEMA) (Homo), and (d) poly(NIPA-*co*-MTEMA) (Hetero). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of mole fraction of comonomer and ethanol

Homogeneous gels. The MTEMA solutions were first prepared by dissolving an appropriate amount of the comonomer in 50, 75, 100, and 150 μL of ethanol to obtain the final concentrations of 10, 15, 20, and 30 m*M*, respectively. When the amount of MTEMA added in the solution increased, the % extraction increased slightly with no significant difference in the magnitude of 68–72%. Thus, the optimal final concentration of MTEMA (10 m*M*) was chosen for subsequent experiments. The effect of the amount of ethanol added on gold extraction was also investigated. By fixing the final concentration of MTEMA at 10 m*M*, the % extractions were 58, 66, 68, and 74 when the concentrations of ethanol were 0.5, 1.0, 5.0, and 10.0%(v/v), respectively. These results indicate that ethanol could facilitate the dissolution of MTEMA and, consequently, it could more incorporate in the copolymer network. The extraction efficiency reached the maximum at ∼ 74% when 10.0%(v/v) ethanol was used; however, the poly (NIPA-*co*-MTEMA) gel turned undesirably opaque. Therefore, the optimal conditions for the synthesis of homogeneous poly(NIPA-*co*-MTEMA) could be achieved with 10 m*M* MTEMA in 5.0%(v/v) ethanol. *Heterogeneous gels.* The % extractions were 71, 73, and 84 when the final concentrations of MTEMA

were 15, 30, 45 m*M*, respectively. The extraction efficiency of the copolymer gels increased slightly when increasing the amount of MTEMA. During the polymerization using 45 m*M* MTEMA, two immiscible phases (upper yellow oily phase and lower clear aqueous phase) were observed. The polymerized gel was obtained only from the lower phase. This observation indicated that 45 m*M* MTEMA was too high. Therefore, 30 m*M* MTEMA was chosen for subsequent experiments. The effect of the amount of ethanol added on gold extraction was also investigated. The % extractions were 78, 79, 85, 84, and 85 when the concentrations of ethanol were 1.5, 10, 20, 30, and 50%(v/v), respectively. The % extraction of the gels increased when increasing the amount of ethanol. In conclusion, the optimal conditions of the synthesis of heterogeneous poly(NIPA-*co*-MTEMA) can be achieved with the concentration of MTEMA at 30 m*M* in 20%(v/v) ethanol.

FTIR and FT-Raman

The FTIR spectra of the synthetic polymers (Fig. 1) were recorded using KBr technique. All FTIR spectra exhibit the following absorption bands (cm^{-1}); 2970 and 2870—ν(C—H) of the methyl groups of *N*-isopropyl groups, 2923—ν(C—H) of the methylene
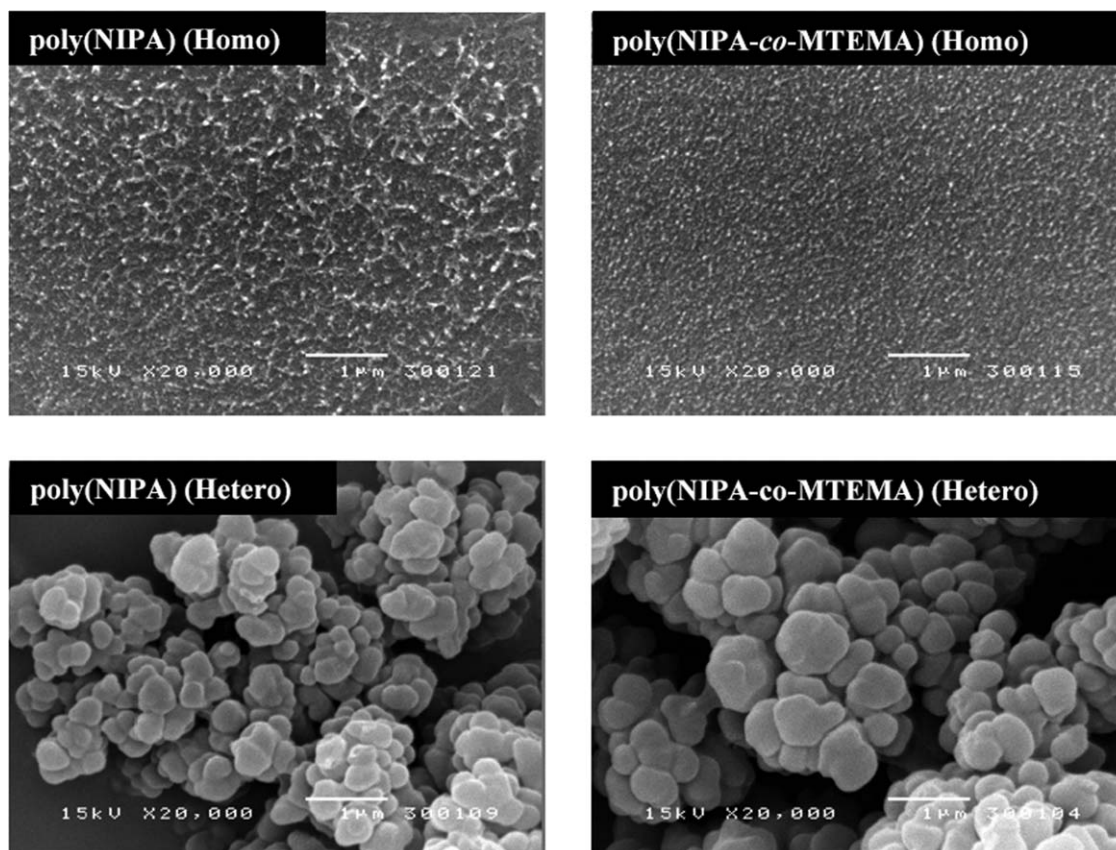
Figure 2 SEM photographs of poly(NIPA) and poly(NIPA-*co*-MTEMA) surface.

groups of the polymer backbone, 1100–1230 and 1648—amide I mainly ν(C= O), 1540—amide II mainly δ(N—H), 3200–3500—ν(N—H) and 1360–1380—ν(C—H) of —CH(CH$_3$)$_2$ in the NIPA repeating units. The FTIR spectrum of MTEMA comonomer is shown in Figure 1 I(e). The characteristic peaks of MTEMA are ν(C—H) of —CH$_2$— and C—O—C, which appear in the range of 2800–3000 cm^{-1} and 1150–1280 cm^{-1}, respectively. The spectra of poly(NIPA) and poly(NIPA-*co*-MTEMA) show only a small difference which is a peak of C—O—C in poly(NIPA-*co*-MTEMA) at 1170 cm^{-1} and appears at slightly higher frequency than poly(NIPA).

The Raman spectra are illustrated in Figure 1 II. The Raman spectra gave many sharper peaks for all polymers than FTIR spectra as follows (cm^{-1}); 2800–3000—ν(C—H) and 3300–3500—ν(N—H) amide. In heterogeneous polymers [Fig. 1 II(d)], the appearance of small peak is ascribed to ν(C—S) of poly(NIPA-*co*-MTEMA) in the range of 570–790 cm^{-1}, which is not present in poly(NIPA).

Scanning electron microscopy

The SEM micrographs (Fig. 2) exhibit the difference between poly(NIPA) and poly(NIPA-*co*-MTEMA) surface image. For homogeneous polymers, the poly(NIPA) surface is rougher than the poly(NIPA-*co*-MTEMA) surface. For heterogeneous polymers, the phase separation due to the condensed states of the polymer chains at high temperature and the difference in size of condensed polymer chains between poly(NIPA) and poly(NIPA-*co*-MTEMA) were observed.

Thermal analyses

TGA curves of all polymers are displayed in Figure 3. The thermograms show three distinctly different weight losses. The first stage was observed at 10.8–12.8% weight loss in the range of 50–200°C due to the loss of water, physically adsorbed on the polymers, and the decomposition of low molecular weight compounds. The second stage showed maximum weight loss around 66.6–75.7% in the wide range of 200–460°C, which is ascribed to a complex process including dehydration and decomposition of aliphatic moieties on polymers. The third stage showed weight loss at 11.7–16.0% between 460 and 700°C. This change was probably due to the decomposition of organic moieties.

The T_g values obtained from DSC curves are 159.7°C, 157.5°C, 157.5°C, and 155.0°C for poly (NIPA) (Homo), poly(NIPA) (Hetero), poly(NIPA-*co*-MTEMA)
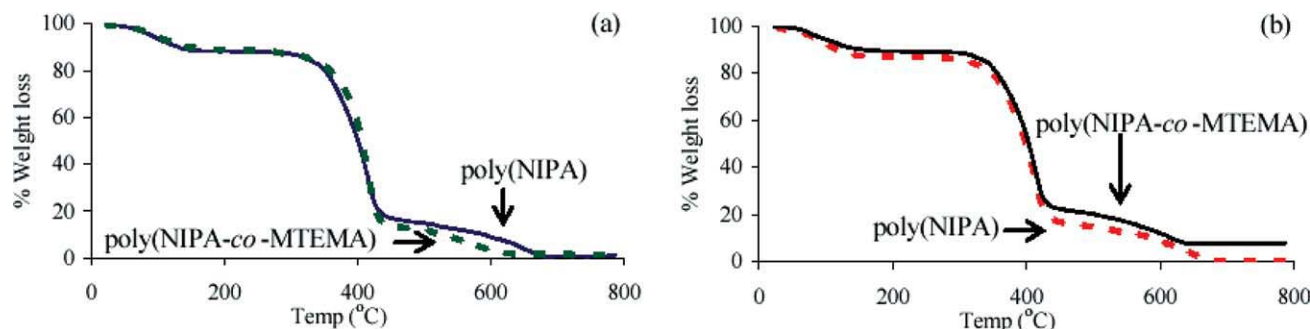
Figure 3 TGA curves of (a) homogeneous gels and (b) heterogeneous gels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Homo), and poly(NIPA-co-MTEMA) (Hetero), respectively. The T_g values of homogeneous and heterogeneous poly(NIPA-co-MTEMA) copolymers agreed with the Ref. 19 that they were slightly lower than that of poly(NIPA).

Swelling behavior

The degree of swelling was calculated from the difference between the weight (g) of dried gel (W_d) and the weight (g) of swollen gel (W_t) according to Eq. (2).

$$\text{Swelling ratio} = \frac{W_t - W_d}{W_d} \times 100 \qquad (2)$$

The swelling ratios of poly(NIPA) (Homo), poly(NIPA) (Hetero), poly(NIPA-co-MTEMA) (Homo), and poly(NIPA-co-MTEMA) (Hetero) were 588 ± 26, 731 ± 63, 540 ± 28, and 551 ± 37, respectively. The synthesized polymers were swollen in water on the account of the hydrophilic pendant (amide and methacrylate groups) in their structure. Both homogeneous poly(NIPA) and poly(NIPA-co-MTEMA) had quite similar swelling ratios because these two gels possess fairly organized structures. By contrast, heterogeneous poly(NIPA) and poly (NIPA-co-MTEMA) showed significantly different swelling ratios. The latter case is most likely due to the unbranched structure of hydrophobic MTEMA moiety.

Phase transition of homogeneous gel

By increasing the temperature, the homogeneous gels underwent phase transition, resulting in turbid gels. In Figure 4, the transmittance of the gels can be seen to decrease steeply with increasing temperature, especially when the temperature was close to the LCST. The LCST is the temperature at half transmittance in the graph.[20] The LCST of poly(NIPA) was 32.2°C in comparison with poly(NIPA-co-MTEMA) which existed slightly lower at 32.0°C. The lower LCST of poly(NIPA-co-MTEMA) attributed to

the incorporation of the comonomer agreed with the Ref. 21 that the LCST of poly(N-isopropylacrylamide-co-N-diacetone acrylamide) or poly(NIPA-co-DAA) decreased as the DAA in the copolymers increased, owing to hydrophobicity of the comonomer.

Gold(III) ion extraction

Effect of pH

The pH of solution is a very important parameter to be studied because of its great influence on the species distribution of Au(III) in aqueous solution.[22,23] The result of Au(III) extraction by the sorbent was displayed as a function of pH, as shown in Figure 5. The extraction efficiency of poly(NIPA-co-MTEMA) was clearly greater than that of poly(NIPA). For homogeneous polymers, it was found that the adsorption behavior of both poly(NIPA) and poly(NIPA-co-MTEMA) was similar in the wide pH range between 1 and 5 due to the fact that the amide group (—CONH—) was possibly protonated and became a positively charge moiety, whereas Au(III) ion is present in chloroaurate form at acidic pH,[24] and the adsorption mechanism occurs probably via ionic interaction. In the case of heterogeneous polymers, both polymers had considerable extraction ability in
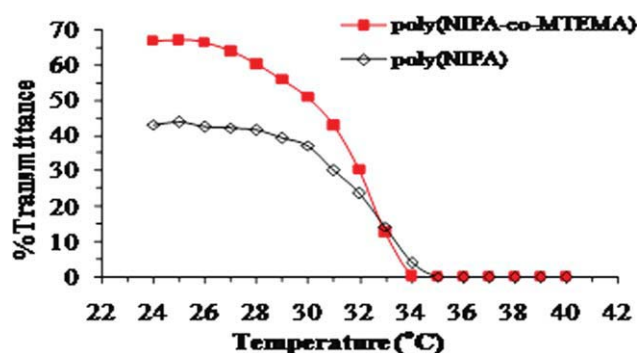

Figure 4 Temperature dependence of light transmittance of the homogeneous polymers ($n = 4$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
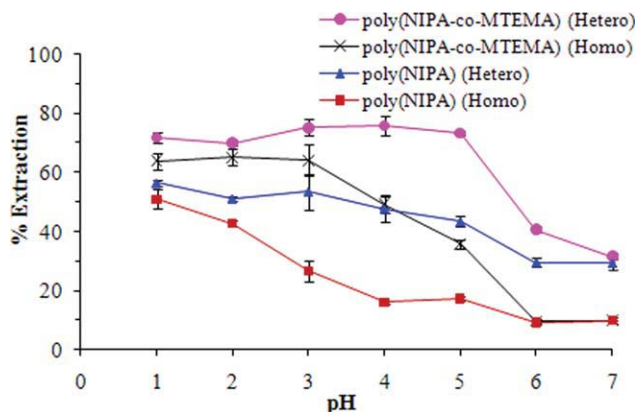
Figure 5 Effect of pH on Au(III) ion extraction ($n = 3$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Effect of extraction time on Au(III) ion extraction ($n = 3$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a wide acidic range (pH 1–5). In addition, the extraction percentage of poly(NIPA-*co*-MTEMA) was noticeably higher than that of poly(NIPA). This observation confirms the success of the incorporation of MTEMA, and that the copolymers could better adsorb Au(III) ion. The higher extraction capacity of the copolymers are strong evidence that the comonomer MTEMA played an important role for Au(III) extraction.

The higher affinity of MTEMA toward the undissociated neutral species (HAuCl$_4$) at pH 1.0 to 4.0 can be explained by the theory of hard–soft-acids–bases (HSAB) after Pearson. Neutral molecules offer a softer character than metal ions. Therefore, the undissociated chloroauric acid, a softer acid than the corresponding ion, can form a coordination bond well with the sulfur donor atom (soft base) of MTEMA. As the main sorption mechanism is considered to be coordination, the extraction efficiency decreased with increasing pH.

In conclusion, the optimum pH range for Au(III) ion extraction was observed at pH 1–3 for the homogeneous copolymer and at pH 1–5 for the heterogeneous copolymer. Hence, the diluted Au(III) solution possessing the pH of 3 would be used in further studies without adjusting pH.

Effect of extraction time

The adsorption phenomena are mainly controlled by the external diffusion and interparticle diffusion in which their kinetics of mass transport are time dependent. In this experiment, the effect of extraction time was investigated to obtain the equilibrium time of the adsorption process. The result shown in Figure 6 indicates that the extraction capacity increased with increasing extraction time and reached equilibrium after 180 min for heterogeneous polymers, whereas the extraction efficiency of homo-
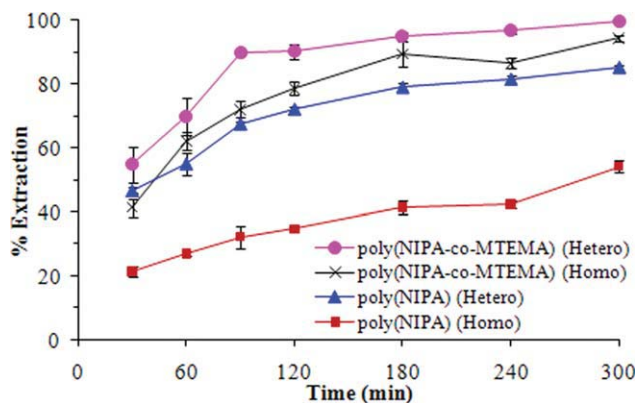
geneous polymers increased slightly when increasing the extraction time up to 180 min. Therefore, the extraction time of 180 min was chosen for extraction in further experiments of both polymers to assure the extraction equilibrium.

Effect of temperature

The extraction capacity of all polymers toward Au(III) ion was investigated as a function of temperature at appropriate pH and contact time. Figure 7 demonstrates the % extraction of each polymer toward Au(III) ion at different temperatures. It was seen that the extraction ability increased with raising temperature due to the fact that the gels could shrink and trap Au(III) ion into the polymer chain. The difference in % extraction of poly(NIPA) gels at low and high temperature was more obvious than that observed for poly(NIPA-*co*-MTEMA) gels, in which there was nearly a 10% difference. Poly (NIPA-*co*-MTEMA) (Hetero) had the highest % extraction. Unless the incorporation of MTEMA
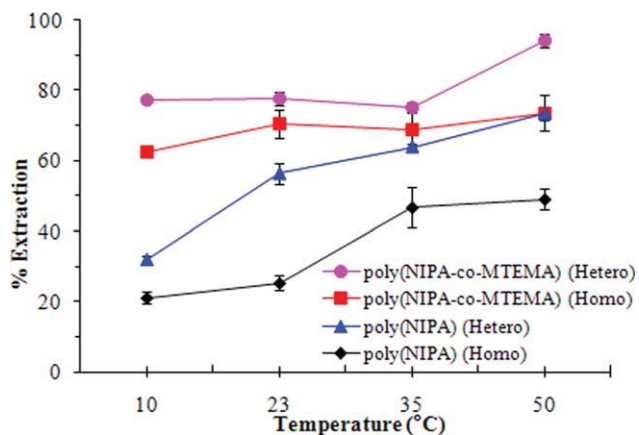

Figure 7 Effect of temperature on Au(III) ion extraction ($n = 3$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Calculated Langmuir and Freundlich Constants for Au(III) Adsorption at 50 ± 1°C

Gel type	Langmuir constants			Freundlich constants		
	N_f^s (µmol/g)	b (L/mol)	r^2	K_f	n	r^2
Poly(NIPA)[a]	58.2	0.11	0.9762	0.39	1.4	0.9809
Poly(NIPA-*co*-MTEMA)[a]	62.8	0.55	0.9890	0.08	2.4	0.9714
Poly(NIPA)[b]	NA	NA	NA	30.4	0.97	0.9882
Poly(NIPA-*co*-MTEMA)[b]	322	0.19	0.7342	2.04	1.5	0.9900

NA, not available.
[a] Homogeneous gels.
[b] Heterogeneous gels.

comonomer in polymer chain reduced the thermosensitive adsorption property compared with poly(NIPA) gels, the synthesized copolymers exhibited a thermosensitive adsorption property for Au(III) ion.

Adsorption isotherms

The adsorption equilibrium between Au(III) ion in aqueous solution and the sorbent through liquid/solid interface can be described by Langmuir and Freundlich isotherms. Both isotherm equations can be transformed to a linear form and, in this way, their two adjustable parameters are easily estimated either by graphical means or by linear regression. The experimental data were treated by both adsorption isotherms. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constant. The model is described by Eq. (3).[25]

$$\frac{C_e}{N_f} = \frac{C_e}{N_f^s} + \frac{1}{bN_f^s} \qquad (3)$$

where C_e is the concentration of metal ion solution at equilibrium (mol/L), N_f is the amount of metal ion per gram of sorbent (mol/g), b is the Langmuir constant related to energy of adsorption (L/mol), and N_f^s is the maximum amount of metal adsorbed per gram of sorbent (mol/g).

The Freundlich isotherm represents multilayer sorption expressed by Eq. (4).[26]

$$\log N_f = \log K_f + \frac{1}{n} \log C_e \qquad (4)$$

where n and K_f are Freundlich constants. The values of n and K_f (Table I) were also obtained from the slope and the intercept of the linear plot of log N_f versus log C_e, respectively.

The experiment was carried out by using a fixed amount of polymer gel in various initial concentrations of Au(III) ion solution at 50 ± 1°C, which is the optimal temperature for adsorption. The equilibrium was attained. The treated experimental data were plotted to illustrate the linear regression line to confirm the applicability of Langmuir and Freund-

lich adsorption isotherms (Fig. 8). The obtained linear equations gained by curve fitting were obtained and the Langmuir and Freundlich parameters were also calculated and are listed in Table I.

In the case of homogeneous gels, the result in Table I with the correlation coefficient (r^2) indicates that the adsorption isotherm of Au(III) onto the gels obeyed both the Langmuir and Freundlich models. The maximum sorption capacities (N_f^s) determined from the Langmuir plots were 58.2, 62.8 µmol/g for poly(NIPA) and poly(NIPA-*co*-MTEMA), respectively. It can be assumed that the surface is homogeneous and all binding sites are equivalent. The solute uptake occurs by a monolayer sorption at definite and localized sites due to a well-organized structure of homogeneous polymers. As a smaller Langmuir constant (b) corresponds to weaker binding affinity, it can be concluded that poly(NIPA) had weaker binding affinity to Au(III) ion than poly(NIPA-*co*-MTEMA).

The adsorption of heterogeneous gels was preceded similarly to homogeneous polymers, but the size of sorbents was reduced by half (0.5 cm length gel was used) owing to high adsorption capacity. The experimental results of Au(III) extraction onto heterogeneous polymers could better fit to the Freundlich model with higher r^2 than to the Langmuir model. This observation indicates that the adsorption occurred on a heterogeneous surface or supporting sites of various affinities and a multilayer sorption is more favorable in a higher concentration range.[26]

Gold(III) ion desorption

The Au(III) ion desorption efficiency is expressed in terms of percentage desorption or elution and calculated according to Eq. (5).

$$\% \text{ Elution } = \frac{N_d}{N_a} \times 100 \qquad (5)$$

where N_d is an amount of Au(III) ion eluted from sorbent (mg) and N_a is an amount of Au(III) ion adsorbed onto gel (mg).

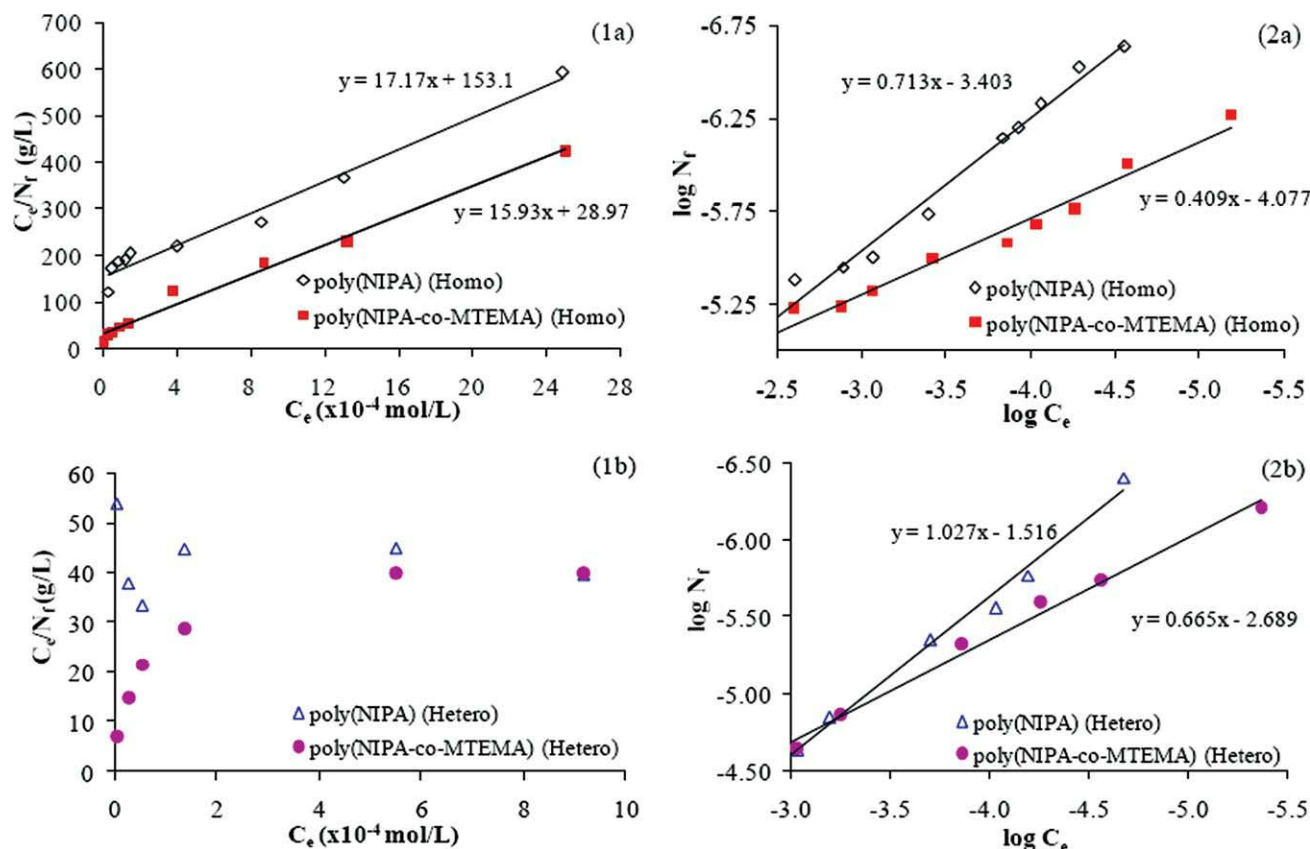**Figure 8** (1) Langmuir and (2) Freundlich adsorption isotherms of Au(III) ion onto (a) homogeneous gels and (b) heterogeneous gels at pH 3, 50 ± 1°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of desorption solution

The selection of eluent depends on the adsorption mechanism and the possibility to perturb interaction between Au(III) ions and active functional groups of the sorbent. As previously mentioned that the equilibrium of chloroaurate anion was driven to neutral chloroauric acid in strong acidic medium, an acidic solution was thus attractive as an eluting solution. An alternative way for desorption is an elution by an eluent containing a ligand that should form a

stronger complex with Au(III) ion than MTEMA. Thiourea (TU), which is a well-known complexing agent and has a high formation constant with gold ions,[27] was also chosen.

The results are shown in Figure 9. The highest elution percentages were achieved with 0.1M TU in 5%(v/v) HCl for poly(NIPA) (Homo), poly(NIPA-co-MTEMA) (Homo), and poly(NIPA-co-MTEMA) (Hetero) with 77%, 90%, and 58% elution,
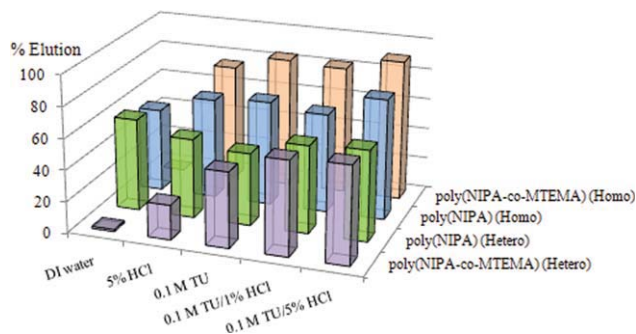

Figure 9 Desorption percentage of Au(III) ion in different types of desorbing solution ($n = 3$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
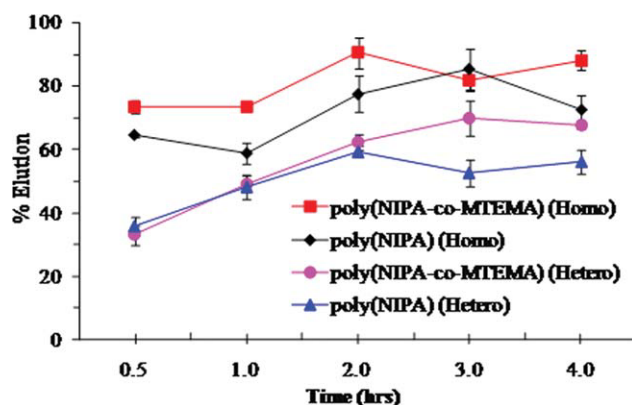

Figure 10 Effect of time on Au(III) ion desorption at 10°C ($n = 3$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
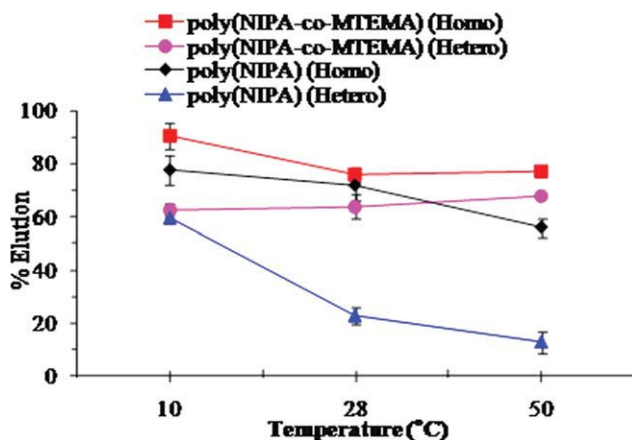
Figure 11 Effect of temperature on Au(III) ion desorption ($n = 3$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

respectively. There was no significant difference in % elution (about 60%) using DI water and 0.1*M* TU in 5%(v/v) HCl for poly(NIPA) (Hetero). Au(III) ion was the most easily desorbed from poly(NIPA-*co*-MTEMA) (Homo). In conclusion, the most suitable eluent was 0.1*M* TU in 5%(v/v) HCl for all polymers except for poly(NIPA) (Hetero) for which DI water was suitable. These eluents would be used in the next experiment.

Effect of desorption time

The rate of desorption was investigated at 10°C. The results in Figure 10 showed the desorption of Au(III) ion as a function of time using 0.1*M* TU in 5%(v/v) HCl for all polymers except poly(NIPA) (Hetero) for which DI water was used. Au(III) ion adsorbed onto homogeneous polymers could be more eluted than that adsorbed in heterogeneous polymers because the homogeneous gels has smoother and less surface area according to SEM images. The elution percentages increased gradually until 2 h after the equilibrium was attained. The highest elution percentages occurred after 2–3 h. The homogeneous polymers exhibited higher elution percentages (about 80–90%) than the polymers (about 50–60%).

Effect of temperature

The desorption of Au(III) ion from each polymer was examined in terms of temperature using its appropriate eluent. The results are presented in Figure 11. The desorption of Au(III) ion decreased gradually with increasing temperature. This result agreed with the properties of poly(NIPA) hydrogel, as previously mentioned, that below the LCST (10°C) good desorption occurred due to the swelling behavior. The highest % elution was at ~ 60–90%. Furthermore, temperature had a greater effect on

the elution efficiency from poly(NIPA) gels than that from poly(NIPA-*co*-MTEMA) gels because Au(III) might coordinate more strongly with S than N. Meanwhile, the elution from poly(NIPA-*co*-MTEMA) (Hetero) was not affected by temperature. In conclusion, the temperature was significant only for the desorption of Au(III) ion from poly(NIPA) gels. In other words, poly(NIPA-*co*-MTEMA) gels exhibit less thermosensitive property than poly(NIPA) gels.

CONCLUSIONS

New random copolymers poly(NIPA-*co*-MTEMA) consisting of two monomers, *N*-isopropylacrylamide (NIPA) and 2-(methylthio)ethyl methacrylate (MTEMA) copolymers were synthesized and subjected to Au(III) ion extraction in comparison with poly(*N*-isopropylacrylamide) or poly(NIPA). Two kinds of poly(NIPA-*co*-MTEMA) called homogeneous and heterogeneous copolymer were prepared at 10°C and 50°C, respectively. Various parameters influencing the extraction and physical property of the copolymers were studied. The effect of pH and temperature of Au(III) ion solution and extraction time were investigated. The adsorption isotherms were also studied. Moreover, in the desorption study, the effect of types of desorbing solution, desorption time, and temperature were investigated. The extraction and desorption optimum conditions toward Au(III) ion were achieved. Heterogeneous poly(NIPA-*co*-MTEMA) showed the highest extraction efficiency but less thermosensitive polymers.

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