Surface Activity of Smart Hybrid Polysiloxane-co-N-isopropylacrylamide Microgels

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ABSTRACT: Amphiphilic smart gels of different sizes (macro, micro, and nano) are widely used in advanced medical, industrial, and environmental applications. They are sensitive, responsive to different environments, and possess a high surface activity to adsorb onto different interfaces. In this study, new amphiphilic alkoxysilane-containing microgels, hybrid polysiloxane microgel, and silica nanoparticles were prepared using a cross-linking surfactant-free cross-linking polymerization technique for N-isopropylacrylamide (NIPAm) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomers. Vinyltrimethoxysilane (VTS) was used as a silane precursor in the cross-linking polymerization to hydrolyze with tetraethoxysilane (TEOS) in ammonia using an emulsion technique, to create polysiloxane microgel and silica nanoparticles. The surface activity measurements confirmed that NIPAm/VTS had a higher surface activity than NIPAm/AMPS-VTS microgels and their hybrid polysiloxane microgel owing to the differences of the cross-linking of microgels from the center to the microgel periphery, which alter their morphologies.

INTRODUCTION

Amphiphilic microgels or nanogels are surface active solid particles consisting of micro-sized or nano-sized cross-linked polymeric networks. They combine the beneficial functions of surfactants and gels to produce soft materials with large encapsulation cavities and swelling capabilities. They have a well-defined hydrophobic core surrounded by an outer hydrophilic shell to interact with the surrounding environments and produce advanced materials for different fields, such as medicine, environment, and energy. In addition, the properties of amphiphilic microgels or nanogels at the interface, such as air–water or oil–water, are tailored by designing a special type of smart material that changes their performance by changing the surrounding environments. The smart amphiphilic microgels or nanogels are designed and synthesized using different techniques, such as grafting of natural polymers followed by ionic gelation, two-stage emulsion polymerization, emulsifier-free polymerization, and radical-based living graft polymerization, to control the sizes, shapes, and structural features and establish the properties and structural–functional relationship. However, designing a new, easy, and cost-effective synthesis method to develop smart amphiphilic microgels or nanogels with highly specific shapes, sizes, and properties is a challenge for scientists.

The smart nanogels or microgels can be typically modified with specific functional groups or encapsulated with inorganic nanoparticles. The ionic nanogels or microgels can be functionalized with sulfonic, carboxylic, and quaternary ammonium salts to be sensitive to the pH of the surrounding environments. Nonionic polymers based on alkyl acrylamides are widely used to synthesize pH- and temperature-sensitive amphiphilic microgels and nanogels. Moreover, the presence of inorganic metal oxides such as magnetite, spinel ferrite-encapsulated nanoparticles in the gel networks produces a smart gel response to a magnetic field. Light and photosensitivite nanogels or microgels have been used for various applications, such as photonics, sensors, drug delivery, and surfactants. Among the different types of inorganic nanomaterials, silica nanoparticles are used to prepare amphiphilic silica-responsive microgels, in which the silica is used as a shell to protect the core from degradation under different environmental conditions. Thus, these microgels could be used under different conditions. N-isopropylacrylamide (NIPAm) microgels combined with silica have various potential applications, such as catalysis, separation, and sensing technologies. In this work, NIPAm is selected as a thermosensitive monomer owing to the presence of the hydrophilic amide group and hydrophobic isopropyl group to control the size of the cross-linked microgel using a surfactant-free technique. Vinyltrimethoxysilane (VTS) monomer is a silicone precursor copolymerized and cross-linked with NIPAm to produce NIPAm microsilane (NIPAm/VTS) microgels. The NIPAm/VTS microgels were hydrolyzed and condensed with tetraethoxysilane (TEOS) to obtain hybrid NIPAm-(polysiloxane)3, PNIPAm-(PSO)3, or nanogels. The silica nanoparticles were prepared by incineration of NIPAm-(PSO)3 at a high temperature. An
ionic monomer based on 2-acrylamido-2-methylpropane sulfonic acid (AMPS) was cross-linked with NIPAm and VTS to prepare ionic terpolymer microgels and nanogels based on NIPAm/AMPS-VTS via radical cross-linking polymerization.

The surface activity of the prepared amphiphilic silane and siloxane microgels and nanoparticles was estimated to determine the critical aggregation concentration (CAC), effectiveness to reduce water surface tension, surface concen-
tation excess, and area per molecule at the air/water interface. The synthesis of inorganic silica nanoparticles combined with the pH- or temperature-sensitive cross-linked microgel or nanogel is expected to produce smart mesoporous multifunctional silica nanomaterials.

## RESULTS AND DISCUSSION

The present work used a high mol percentage of NIPAm (0.8–0.95) nanogel to control their sizes and morphologies. In our previous work, the optimum mol ratio of NIPAm to prepare amphiphilic nanogel and microgel ranged from 0.90 to 0.98. In the present study, NIPAm was copolymerized VTS (silicone precursor) and terpolymerized with hydrophobic VTS and hydrophilic AMPS as an ionic monomer to vary the amphiphilicity of the produced microgels and nanogels. They were cross-linked with N,N-methylene-bis-acrylamide (MBA) using a temperature-programmed radical polymerization technique, as shown in Scheme 1 and the Experimental Section. In this respect, the NIPAm oligomers were prepared at 40 °C (above the lower critical solution transition temperature, LCST, of NIPAm at 32 °C) to break the hydrogen bonds formed between the amide groups and water solvent with hydrophobic interactions induced among the isopropyl groups. The NIPAm oligomers act as a core to control the size of the cross-linked NIPAm/VTS or NIPAm/AMPS-VTS polymers as the shell according to the proposed temperature synthetic diagram presented in Experimental Section. The VTS is used as the silane precursor to hydrolyze with TEOS in basic media to form polysiloxane nanoparticles inside the NIPAm/VTS or NIPAm/AMPS-VTS networks to increase the hydrophilicity of the microgels by replacing the methoxy and ethoxy groups with the hydroxyl groups. The mol fractions of VTS ranged from 0.05 to 0.2 in the NIPAm/VTS microgel and varied from 0.05 to 1 with the incorporation of AMPS into NIPAm/AMPS-VTS networks. It is expected that the variation in the NIPAm, VTS, and AMPS contents affected the morphology of the polysiloxane in the NIPAm-PSO or NIPAm/PAMPS-PSO gel networks. It is very important also to study the effect of the hydrolysis conditions on the stability of amide groups of NIPAm and AMPS toward hydrolysis of TEOS with VTS. Moreover, it is also expected that the presence of AMPS or NIPAm could produce thermosensitive and pH microgels owing to the solubility discrepancy between the microgel components. Because of the higher solubility of NIPAm and AMPS than VTS, more VTS could exist inside the microgel networks, which is favorable to hydrolyze with TEOS to affect the morphology of the microgels. The formation of the core–shell structure of the hybrid silica composite could increase with increasing TEOS hydrolysis inside the microgel networks. Moreover, the sizes of the polysiloxane inside the NIPAm-PSO or NIPAm/AMPS-PSO microgels depend on the total sizes of the microgels. The silica nanoparticles can be obtained by incineration of the NIPAm-PSO or NIPAm/AMPS-PSO microgels at 700 °C, as reported in Experimental Section.

**Characterization of the Microgels and Silica Composites.** The chemical structures of the cross-linked NIPAm/VTS and NIPAm/AMPS-VTS microgels before and after hydrolysis NIPAm-PSO or NIPAm/AMPS-PSO via the formation of polysiloxane microgels were investigated using Fourier transform infrared (FTIR) spectroscopy. The NIPAm (0.8)/VTS (0.2) and NIPAm (0.8)/AMPS (0.1)-VTS (0.1) spectra are selected and represented in Figures 1 and 2a–c, respectively.

The cross-linking polymerization of NIPAm with VTS or AMPS in the presence of MBA was confirmed by the disappearance of the vinyl protons from 3100 to 3000 cm⁻¹ assigned to the ==CH stretching vibration (Figures 1 and 2a–c). The intensity of the broad band at 3452–3437 cm⁻¹ attributed to the −NH or −OH stretching vibration (Figures 1 and 2a–c) was used to confirm the hydrophilicity of the hydrolyzed polysiloxane composites (NIPAm-PSO or NIPAm/AMPS-PSO) or calcined silica NPs. The formation of the −OH group on the PSO surfaces increased more for NIPAm (0.8)/VTS (0.2) (Figure 1b,c) than for NIPAm (0.8)/AMPS (0.1)-VTS (0.1) (Figure 2b,c), as shown by the decreasing −OH band intensity at 3452–3437 cm⁻¹ from the incorporation of AMPS. This can be referred to the consumption of the ammonia due to the presence of a sulfonic group in the chemical structure of AMPS, which affects the hydrolysis of TEOS with the methoxy groups of VTS. The presence of AMPS during the formation of PSO of NIPAm (0.8)/AMPS (0.1)-VTS (0.1) and NIPAm (0.9)/AMPS (0.05)-VTS (0.05) after hydrolysis with TEOS increases ammonia consumption owing to the formation of the sulfonate ammonium salt, which reduced Si−OH on the surface of the PSO composites or NPs. It can also alter the reactivity ratios of VTS with the vinyl amide monomers from the block to alternate or random polymers. The incorporation of NIPAm or AMPS into the chemical structure of the produced VTS cross-linked polymers was observed from the two bands at 1655 and 1565 cm⁻¹ attributed to the primary and secondary amide −CONH− stretching vibrational bands, respectively. The disappearance of
the bands at 2850–2975 cm$^{-1}$, which represent the aliphatic CH stretching from the spectra of the silica NPs (Figures 1 and 2c), demonstrated the complete conversion of the organic PSO derivatives to inorganic SiO$_2$ NP. The appearance of silica NPs bands at 472 cm$^{-1}$ (Si–O rocking vibration), 1076 cm$^{-1}$ (Si–O–H···H$_2$O bending vibration), 1076 cm$^{-1}$ (Si–O–Si stretching vibration), 1635 cm$^{-1}$ (OH bending vibration of the adsorbed water), and 3450 cm$^{-1}$ (OH stretching vibration, hydrogen-bonded) demonstrated the formation of silica in the silica composites or silica NPs.\textsuperscript{35,36} The particle sizes of the silica NP decreased with increasing intensity of the band at 3450 cm$^{-1}$.\textsuperscript{35,35} Moreover, the appearance of Si–OH bending at 910–970 cm$^{-1}$ confirmed a higher concentration of the silanol group at smaller particle sizes. Figures 1 and 2c show that the hydrophilicity and particle sizes of the PSO microgels and silica NPs were altered by the incorporation of AMPS into the microgel networks.

It is very important to study the effect of the hydrolysis conditions on the stability of the amide groups of NIPAm and AMPS from the determination of the chemical compositions of microgels, PSO microgels, and silica NPs. In this respect, energy-dispersive X-ray spectroscopy (EDS) images and data of some selected microgels, PSO microgels, and silica NPs are represented in Figure 3a–d and Table 1. The data confirmed the presence of N in the chemical compositions of the PSO microgels to elucidate the stability of amide groups toward the hydrolysis conditions. It was also noticed that the Si and O weight percentages increased and the C contents decreased with the hydrolysis of microgels to confirm the conversion of ethoxy groups of TEOS and methoxy groups of VTS to Si–OH and Si–O–Si groups. It is also observed that the weight percentages of Si and O (Table 1) agree with the expected theoretical data of silica NPs (theoretical weight percentages of Si and O are 46.66 and 53.33, respectively). The data in Table 1 also confirm the presence of low carbon contents contaminated on the silica NP surfaces although the incineration obtained at 700 °C for 24 h.

The particle sizes, polydispersity index (PDI), and surface charges of the prepared microgels, PSO microgels, and silica NPs were measured by dynamic light scattering (DLS) at different pH values in water and are represented in Figures 4 and 5a–c as representative samples. The effect of pH on the ζ-potentials (mV) and particle sizes (nm) of the prepared microgels, PSO microgels, and silica NPs is illustrated in Figures 6 and 7a–d, respectively. Figure 6a–d is used to determine the isoelectric points of the prepared microgels, PSO microgels, and silica NPs (confirm the pH values of the aqueous solution having zero charges). The measured isoelectric points and PDI data of the prepared microgels, PSO microgels, and silica NPs are listed in Table 2. It is well established that the materials possessing PDI values more than 0.7 are nonuniform and polydisperse, while the materials having PDI values below 0.7 tend to form a uniform and monodisperse distribution that increases with lowering PDI to reach the nearest 0.01 value. The PDI data (Table 2) elucidate that increasing the VTS content from 0.05 to 0.2 mol % produces a more uniform and narrow size distribution (low PDI values, Table 2) and smaller-sized microgels, PSO microgels, and silica NPs (Figure 4a–c). Moreover, the incorporation of AMPS increases the surface charges and reduces the PDI and particle sizes of the microgels and PSO microgels (Table 2, Figures 6 and 7a–d). The particle sizes and PDI reduced with the incorporation of AMPS owing to the repulsive forces between the sulfonate groups at the surface of the microgels, increasing the surface negative charges (Table 2, Figure 7a–d). This can be attributed to the repulsion forces among the sulfonate group of AMPS that occurred during the cross-linking polymerization with NIPAm to produce NIPAm/AMPS nanogels.\textsuperscript{10} The positive surface charges of the prepared microgels, PSO microgels, and silica NPs in acidic or slightly acidic aqueous solution (Figure 6a–d) can be attributed to the protonation of amide groups of NIPAm or AMPS amide and sulfonic groups. The negative surface charges of the prepared microgels, PSO microgels, and silica NPs in basic or slightly basic aqueous solution (Figure 6a–d) can be attributed the deprotonation of the sulfonic group of AMPS or to the formation of some carboxyl groups due to the hydrolysis of amide groups of NIPAm to $-\text{COOH}$ groups. The data of isoelectric points (Table 2) elucidate that all prepared microgels, PSO microgels, and silica NPs have values in acidic pH except NIPAm (0.90)/AMPS (0.05)-VTS (0.05) having isoelectric points at slightly acidic pHs (ranging from 6.1 to 6.5). The effect of pH on the particle sizes of the prepared microgels, PSO microgels, and silica NPs (Figure 7a–d) reduced to lower particle sizes at neutral or slightly basic pHs for the prepared microgels, PSO microgels, and silica NPs that contain AMPS that referred to the dissociation of sulfonic acid groups to sulfonate groups that prevents the agglomeration of the microgels and particles.
The thermosensitivity of the prepared microgels, PSO microgels, and silica NPs can be estimated from the DSC thermograms represented in Figure 8a–c. The lower critical solution transition temperatures (LCST) of the microgels and PSO microgels using DSC thermograms (Figure 8a–c) were determined and are listed in Table 3. The data elucidate that when AMPS was used as a hydrophilic monomer during cross-linking polymerization, the LCST values increased (Table 3) due to the increase in the hydrophilicity of microgels and PSO microgels. The variation of the LCST values (Table 3) confirms...
that the microgels and PSO microgels have amphiphilic character with different hydrophilic and hydrophobic characteristics.

The morphologies of the NIPAm/VTS and NIPAm/AMPS-VTS microgels, PSO microgels, and silica NPs were evaluated by TEM, as shown in Figures 9 and 10a–d. The microgels contained a nearly spherical morphology with the formation of interconnected nanoparticles (Figure 9a). The NIPAm-PSO microgels demonstrated nonuniform spherical dispersed particles (Figure 9b). The silica NPs produced after the incineration of NIPAm (0.95)-PSO (0.05) formed aggregated silica NPs (Figure 9c). The morphology of the silica NPs changed to a well-dispersed completely transparent (fades for a large distance) periphery and dark core (higher cross-linking and interlaced) structure with increasing VTS from 0.05 to 0.2 mol % (Figure 9d, high-resolution image at 10 nm added at the top on the left-hand side). The silica particle size produced from the calcination of NIPAm (0.8)-PSO (0.2) was 55 nm (Figure 9d), with core and shell thicknesses of 39 and 16 nm as a dark core and bright shell, respectively. The reason for the formation of dark core and transparent shell can be referred to the formation of low cross-linked PSO on the periphery of NIPAm (0.8)-PSO (0.2) polymer networks after hydrolysis with TEOS. The presence of transparent periphery is probably that the fast rate of hydrolysis of NIPAm (0.8)-PSO (0.2) with TEOS is fast enough to retain the dispersion stability of the PSO to decrease their contents in the NIPAm-MBA network that acts as shell. Therefore, increasing VTS increased the hydrophobic interaction of NIPAm and oriented the isopropyl groups on the exterior surfaces of NIPAm-VTS. The hydrolyzed PSO was oriented to the surface of the NIPAm-VTS to hydrolyze with TEOS and form a bright shell functionalized on the silica surfaces with the Si–OH group. By comparing the particle sizes evaluated by DLS (Figures 4, 5, and 7a–d) and TEM (Figures 9 and 10a–d), the particle size data of the silica NPs were in agreement. There were differences in the particle sizes of the NIPAm-VTS and NIPAm-PSO microgels evaluated by DLS and TEM, which was attributed to the swelling of the microgel in water confirmed by the DLS measurements to increase the particle size more than that of the dry particles estimated by the TEM techniques. More uniform, spherical NIPAm-VTS and NIPAm-PSO microgels and silica NPs were obtained with the appearance of interconnected spherical morphology (Figure 10a–d). The repulsion force of the negatively charged ionic sulfonate groups during the hydrolysis of VTS with TEOS controlled the uniform size and spherical morphology of NIPAm/AMPS-PSO microgel (Figure 10b). In addition, an increasing AMPS content from 0.05 to 0.10 mol % produced more uniform and porous silica NPs, as shown in Figure 10c,d, respectively. The PDI and particle sizes of silica
NPs produced after calcination of NIPAm (0.80)/AMPS (0.10)-PSO (0.10), NIPAm (0.90)/AMPS (0.05)-PSO (0.05), NIPAm (0.90)-PSO (0.10), and NIPAm (0.8)-PSO (0.20) in 0.001 M of KCl aqueous solution were determined and are summarized in Figure 11a−d. The data agree in harmony with the TEM images (Figures 9 and 10a−d) and confirm the formation of uniform-sized silica NPs after calcination of NIPAm (0.80)/AMPS (0.10)-PSO (0.10) (Figure 11a) and NIPAm (0.8)-PSO (0.20) (Figure 11d).

Surface Activity and Dispersion of the Microgels and Silica Composites. The dispersion and stability of NIPAm-VTS, NIPAm-PSO, NIPAm/AMPS-VTS, and NIPAm/AMPS-PSO microgels are two important features of amphiphilic systems in an aqueous system for drug-delivery and environmental applications.38 The present system based on NIPAm-VTS and NIPAm/AMPS-VTS microgels before and after hydrolysis (NIPAm-PSO and NIPAm/AMPS-PSO) has intriguing characteristics, such as porosity, adjustable morphology, and dimensions that are altered by the composition of the hydrophilic (AMPS), hydrophobic (VTS), and amphiphilic (NIPAm) contents. The prepared NIPAm-VTS, NIPAm-PSO, NIPAm/AMPS-VTS, and NIPAm/AMPS-PSO microgels could behave as surfactants in water. Hence, the surface tensions (γ; mN m−1) of water in the presence of different concentrations (ln C; mmol L−1) of the prepared NIPAm-VTS, NIPAm-PSO, NIPAm/AMPS-VTS, and NIPAm/AMPS-PSO microgels were measured to investigate their dispersion, aggregation diameters, and adsorption characteristics at the air/water interface. The hydrogen bond among the water molecules was reduced (and the free energy of the solution was reduced) by aggregation of the amphiphiles into clusters (micelles), while their hydrophilic or hydrophobic groups were directed externally toward the polar interaction or internally toward the hydrophobic interaction, respectively. Micellization and aggregation were therefore an alternative mechanism for the adsorption of the amphiphiles at the interfaces. The surface balance method was used to determine the CAC from the intersection in the water surface tension (γ) versus ln C plot of the NIPAm-VTS, NIPAm-PSO, NIPAm/AMPS-VTS, and NIPAm/AMPS-PSO microgels, as shown in Figure 12a,b. The surface tension values at the CAC determined by extrapolation as γ cac and the effectiveness to reduce the water surface tension (Δγ = γ water − γ cac, where γ water is the surface tension of pure water, which is 72.2 mN m−1 at 298 K) are listed in Table 4. The CAC value of the NIPAm-VTS microgels increased with increasing VTS from 0.05 to 0.2 mol %. The data confirm that the microgels with a high VTS content aggregated at a higher concentration. Thus, the high VTS content reduced the hydrophobic interactions of the isopropyl groups of NIPAm and enhanced the bonding of the NIPAm amide group with water in the bulk aqueous solution.39−41 The presence of AMPS during the polymerization of NIPAm, VTS, and MBA produced...
more microgels aggregated at a lower concentration than those produced in the absence of AMPS, such as NIPAm (0.8)/AMPS (0.1)-VTS (0.1) and NIPAm (0.8)-VTS (0.2), respectively, although AMPS is more hydrophilic than NIPAm and VTS. The aggregation of the NIPAm/AMPS microgels created core–shell morphologies at a higher concentration and temperature. From the TEM images (Figures 9 and 10a–d), core–shell morphologies of NIPAm (0.8)/AMPS (0.1)-VTS (0.1) were not apparent compared to NIPAm (0.8)-VTS (0.2) and their hydrolyzed PSO and silica NPs. The intramolecular and intermolecular interactions among the microgel particles were owing to hydrogen bonding. In addition, the entanglements were owing to particles in contact within the aggregates. This concept has been proposed for microgels of NIPAm with styrene. The CAC silica composite data of NIPAm (0.95)-PSO (0.05) demonstrated that the composites aggregated at a higher concentration than that of the microgel, confirming the hydrophilicity of the PSO owing to the formation of Si–OH groups. Moreover, the silica composites of NIPAm (0.95)/HVTS (0.05) demonstrated a higher surface tension reduction than that of other microgels and silica composites. These data agree with the concept that excessive solubility increases concentration to provide minimum surface tension. The data listed in Table 4 indicate that NIPAm (0.80)-PSO (0.20) and hydrolyzed NIPAm/AMPS-PSO cannot reduce the water surface tension and cannot act as a surface active material; however, they can exhibit polyelectrolyte composites. The formation of the core–shell spherical morphology for NIPAm (0.95)-PSO (0.05) and NIPAm (0.90)-PSO (0.10) created amphiphilicity of the microgels and their silica composites. The effect of pH on the ζ-potential (surface charges; mV) and particle sizes (Figures 6 and 7a–d)
combined with the surface activity data (Table 4) of NIPAm/AMPS-PSO demonstrated that they behaved as polyelectrolytes and could not interact as amphiphiles. In this system, the modification of NIPAm-VTS with AMPS followed by hydrolysis with TEOS modified the hydrophobicity, hydrophilicity, chain flexibility, and dispersion of the silica composites owing to the difference between the intermolecular and intramolecular interactions with water.

The effect of the aging time on the steady-state surface tension was evaluated, as shown in Figure 13. The aging times of the prepared microgels and surface composites are listed in Table 4. NIPAm-VTS had decreasing aging times with
increasing NIPAm. The nonuniform morphology (Figure 10a−d) of NIPAm-VTS obtained for the microgels with a high NIPAm content and high core thickness lowered the surface tension in a short time. Moreover, the water surface tension was reduced more in the presence of NIPAm (0.9)-PSO (0.1) compared to that of the NIPAm (0.9)-VTS (0.1) microgels at the same concentration, although the aging time to reach the surface tension increased from 90 to 450 s. Thus, the rate of surface tension lowering increased with the formation of the nonuniform morphology, also the particle sizes of the microgels and silica composites increased. The absence of the core−shell morphology for NIPAm (0.9)/AMPS (0.05)-PSO (0.05) decreased the rate of surface tension lowering (increased aging time) compared to that of NIPAm (0.9)-PSO (0.1).

Adsorption at the Interface of the Microgels and Silica Composites. The assembling of silica composites and microgels at the interfaces during the formation of Langmuir monolayers at the air/water interface was investigated by their adsorption at the interfaces. The amount of silica composites and microgels at the air/water interface could be determined from the excess surface concentration
\[
\Gamma_{\text{max}} = \frac{-\partial \gamma}{\partial \ln c} \frac{T}{RT},
\]
where \((-\partial \gamma/\partial \ln c)_T\) is the slope of the plot of \(\gamma\) versus \(\ln c\) at constant temperature \(T\) and \(R\) is the gas constant (in J mol\(^{-1}\) K\(^{-1}\)). The calculated \(\Gamma_{\text{max}}\) and slope of the curves for the prepared NIPAm-VTS, NIPAm-PSO, NIPAm/AMPS-VTS, and NIPAm/AMPS-PSO microgels are listed in Table 4. The \(\Gamma_{\text{max}}\) values at surface saturation measured the effectiveness of adsorption of the amphiphiles at the interfaces. The \(\Gamma_{\text{max}}\) values were used to calculate the minimum area \(A_{\text{min}} = 1016/\Gamma_{\text{max}}\) where \(N\) is Avogadro’s number of amphiphiles at the air/water interface. The \(A_{\text{min}}\) values of the microgels and silica composites are listed in Table 4. Here, \(A_{\text{min}}\) of NIPAm (0.95)-PSO (0.05) was reduced by replacing the methoxy and ethoxy groups of the

### Table 3. LCST Temperature of the Prepared NIPAm-VTS and NIPAm/AMPS-VTS Microgels and Silica Composites Measured by DSC Analysis

| sample                      | status    | LCST (°C) |
|-----------------------------|-----------|-----------|
| NIPAm (0.95)-VTS (0.05)     | microgel  | 33.59     |
| NIPAm (0.9)-VTS (0.1)       | microgel  | 31.55     |
| NIPAm (0.90)/AMPS (0.05)-VTS (0.05) | microgel  | 38.25     |
| NIPAm (0.8)-VTS (0.2)       | microgel  | 43.72     |
| NIPAm (0.8)/AMPS (0.1)-VTS (0.1) | microgel  | 45.17     |
silanes (VTS and TEOS) with hydroxyl groups. The stability of the Langmuir layers of the NIPAm (0.95)-PSO (0.05) composites was more than that of the NIPAm (0.95)-VTS (0.05) microgels, as confirmed by the reduction of the surface tension from 40 to 31 mN m\(^{-1}\). These data differed from the prepared nanogels based on block polymers of ethylene glycol.\(^{46}\) NIPAm (0.90)-PSO (0.10) contained a lower stability than NIPAm (0.90)-VTS (0.10), as demonstrated by the increase of the \(A_{\min}\) value from 0.037 to 0.039 nm\(^2\) molecule\(^{-1}\), which suggested adsorption of the microgels with the hydrophobic NIPAm chain oriented away from the liquid in a tilted position, approaching the cross-sectional area of the NIPAm chain (0.54–0.67 nm\(^2\)).\(^{10,47}\) The proposed mechanism for the adsorption of the NIPAm-VTS and NIPAm/AMPS-VTS microgels at the air/water interface is shown in Scheme 2. Based on \(\Gamma_{\max}\) and \(A_{\min}\) (Table 4), the lower cross-linked core and higher cross-linked shell morphology of NIPAm-VTS and the silica composites NIPAm-PSO facilitated the adsorption of the soft microgel particles more than that of NIPAm/AMPS-VTS and the silica composites NIPAm/AMPS-PSO. The hydrophilic shell and hydrophobic core of NIPAm-VTS and NIPAm-PSO microgels increased the hydrophilic and hydrophobic interactions at the water and air phases, respectively. Consequently, the \(\Gamma_{\max}\) values of NIPAm-VTS and NIPAm-PSO microgels increased owing to the lower \(A_{\min}\) values (Table 4). The dangling-chain sulfonic group of AMPS with the formation of a porous morphology for NIPAm/AMPS-VTS and the silica composites NIPAm/AMPS-PSO increased the sizes and \(A_{\min}\) values. Consequently, the \(\Gamma_{\max}\) values were reduced, and their adsorption at the interfaces decreased. This same observation has been shown with microgels and (oxyethylene) surfactant molecules coexisting at the organic solvent or water/air interfaces.\(^{48–50}\) Finally, the lower \(A_{\min}\) data of NIPAm-VTS and NIPAm-PSO microgels suggested compact adsorption at the interface or complete surface coverage. When AMPS was inserted into the chemical interfaces. The NIPAm (0.90)/AMPS (0.05)-VTS (0.05) microgels had higher \(A_{\min}\) values than those of NIPAm (0.90)-VTS (0.10). The sulfonate groups on the surfaces of the microgels without the core–shell morphology increased the surface area of the microgels and reduced their adsorption at the interfaces. As listed in Table 4, the \(\Gamma_{\max}\) values for NIPAm-VTS were higher than those for the NIPAm/AMPS-VTS microgels; therefore, the replacement of AMPS instead of VTS reduced the adsorption of the microgels at the interfaces, providing a lower surface tension. The lowest value of \(A_{\min}\) obtained for the NIPAm (0.80)/VTS (0.20) system was 0.025 nm\(^2\) molecule\(^{-1}\), which suggested adsorption of the microgels with the hydrophobic NIPAm chain oriented away from the liquid in a tilted position, approaching the cross-sectional area of the NIPAm-VTS and the silica composites NIPAm/AMPS-VTS microgels at the air/water interface is shown in Scheme 2. Based on \(\Gamma_{\max}\) and \(A_{\min}\) (Table 4), the lower cross-linked core and higher cross-linked shell morphology of NIPAm-VTS and the silica composites NIPAm-PSO facilitated the adsorption of the soft microgel particles more than that of NIPAm/AMPS-VTS and the silica composites NIPAm/AMPS-PSO. The hydrophilic shell and hydrophobic core of NIPAm-VTS and NIPAm-PSO microgels increased the hydrophilic and hydrophobic interactions at the water and air phases, respectively. Consequently, the \(\Gamma_{\max}\) values of NIPAm-VTS and NIPAm-PSO microgels increased owing to the lower \(A_{\min}\) values (Table 4). The dangling-chain sulfonic group of AMPS with the formation of a porous morphology for NIPAm/AMPS-VTS and the silica composites NIPAm/AMPS-PSO increased the sizes and \(A_{\min}\) values. Consequently, the \(\Gamma_{\max}\) values were reduced, and their adsorption at the interfaces decreased. This same observation has been shown with microgels and (oxyethylene) surfactant molecules coexisting at the organic solvent or water/air interfaces.\(^{48–50}\) Finally, the lower \(A_{\min}\) data of NIPAm-VTS and NIPAm-PSO microgels suggested compact adsorption at the interface or complete surface coverage. When AMPS was inserted into the chemical interfaces. The NIPAm (0.90)/AMPS (0.05)-VTS (0.05) microgels had higher \(A_{\min}\) values than those of NIPAm (0.90)-VTS (0.10). The sulfonate groups on the surfaces of the microgels without the core–shell morphology increased the surface area of the microgels and reduced their adsorption at the interfaces. As listed in Table 4, the \(\Gamma_{\max}\) values for NIPAm-VTS were higher than those for the NIPAm/AMPS-VTS microgels; therefore, the replacement of AMPS instead of VTS reduced the adsorption of the microgels at the interfaces, providing a lower surface tension. The lowest value of \(A_{\min}\) obtained for the NIPAm (0.80)/VTS (0.20) system was 0.025 nm\(^2\) molecule\(^{-1}\), which suggested adsorption of the microgels with the hydrophobic NIPAm chain oriented away from the liquid in a tilted position, approaching the cross-sectional area of the NIPAm-VTS and the silica composites NIPAm/AMPS-VTS microgels at the air/water interface is shown in Scheme 2. Based on \(\Gamma_{\max}\) and \(A_{\min}\) (Table 4), the lower cross-linked core and higher cross-linked shell morphology of NIPAm-VTS and the silica composites NIPAm-PSO facilitated the adsorption of the soft microgel particles more than that of NIPAm/AMPS-VTS and the silica composites NIPAm/AMPS-PSO. The hydrophilic shell and hydrophobic core of NIPAm-VTS and NIPAm-PSO microgels increased the hydrophilic and hydrophobic interactions at the water and air phases, respectively. Consequently, the \(\Gamma_{\max}\) values of NIPAm-VTS and NIPAm-PSO microgels increased owing to the lower \(A_{\min}\) values (Table 4). The dangling-chain sulfonic group of AMPS with the formation of a porous morphology for NIPAm/AMPS-VTS and the silica composites NIPAm/AMPS-PSO increased the sizes and \(A_{\min}\) values. Consequently, the \(\Gamma_{\max}\) values were reduced, and their adsorption at the interfaces decreased. This same observation has been shown with microgels and (oxyethylene) surfactant molecules coexisting at the organic solvent or water/air interfaces.\(^{48–50}\) Finally, the lower \(A_{\min}\) data of NIPAm-VTS and NIPAm-PSO microgels suggested compact adsorption at the interface or complete surface coverage. When AMPS was inserted into the chemical
structure of NIPAm-VTS (for NIPAm/AMPS-VTS and the NIPAm/AMPS-PSO microgels), minimum $\Gamma_{\text{max}}$ values and maximum CAC and $A_{\text{min}}$ values were observed. These results prevented the close packing of NIPAm/AMPS-VTS and the NIPAm/AMPS-PSO microgels chains adsorbed at the interface. Therefore, the adsorbed NIPAm/AMPS-VTS and their NIPAm/AMPS-PSO microgel did not form a close-packed condensed monolayer at the CAC.

### CONCLUSIONS

Uniform and amphiphilic NIPAm-VTS and NIPAm/AMPS-VTS microgels and silica composites were prepared using a surfactant-free emulsion polymerization technique. The morphology of the silica NP changed to a more uniform well-dispersed core–shell structure with increasing VTS content from 0.05 to 0.2 mol % into NIPAm/VTS. More uniform spherical NIPAm/AMPS-VTS and NIPAm/AMPS-PSO microgels and silica NPs were obtained without the appearance of the bright core and dark shell morphology. The increasing AMPS content from 0.05 to 0.10 mol % produced more uniform and porous silica NP. The CAC silica composite data of NIPAm (0.95)-VTS (for NIPAm/VTS and the NIPAm-PSO microgels, and silica NPs at room temperature. Figure 13. Relation between surface tension and aging times of NIPAm-VTS and NIPAm/AMPS-VTS, NIPAm-PSO and NIPAm/AMPS-PSO microgels, and silica NPs at room temperature.

### EXPERIMENTAL SECTION

**Materials.** The pure-grade chemicals used in this study were purchased from Sigma-Aldrich Co. and used as received. NIPAm, VTS, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), N,N-methylenebis-acrylamide (MBA), and ammonium persulfate (APS) were used to prepare the microgels. Tetraethoxysilane (TEOS), ammonium hydroxide solution (25 wt %), n-hexane, and deionized water were used to prepare the silica composites.

**Preparation Techniques. Preparation of NIPAm Microgels.** Cross-linked NIPAm ($x$)-VTS ($y$) and NIPAm ($x$)-AMPS ($z$)-VTS ($y$) microgels were prepared by a surfactant-free emulsion technique using a modified temperature program, where $x$, $y$, and $z$ are the mol % of NIPAm, VTS, and AMPS, respectively. Half the weight of the NIPAm monomer (0.9 mol % 1.2 g) was dissolovd in 100 mL of deionized water and preheated in a nitrogen atmosphere at 40 °C for 30 min. APS (0.08 g) was dissolved in deionized water (2 mL) and injected into the NIPAm solution to initiate the prepolymerization of NIPAm. The reaction temperature was gradually increased from 40 to 55 °C at a heating rate of 0.33 °C min⁻¹ to obtain a slightly turbid solution. The solution of NIPAm (remaining weight of 0.9 mol %, 1.2 g), VTS (0.1 mol %, 0.337 mL), and MBA (6 mol %, 0.06 g) was dissolved in 100 mL of deionized water and bubbled in nitrogen. The copolymer solution was fed into a NIPAm oligomer at a feeding rate of 0.4 mL min⁻¹ using a syringe pump. The reaction temperature was increased to 65 °C, and the reaction was allowed to proceed for 1 h to complete the cross-linking polymerization time of 4 h. The NIPAm (0.9)/VTS (0.1) microgel was isolated and purified using an ultracentrifuge at 8000 rpm, and the resultant particles were washed with ethanol. The NIPAm (0.95)-VTS (0.05), NIPAm (0.90)-VTS (0.10), and NIPAm (0.80)-VTS (0.20) microgels were prepared by changing the NIPAm and VTS mole ratios, and their yields (%) were 98.3, 95.2, and 93.5%, respectively.

AMPS (0.05 and 0.1 mol %) was added into the NIPAm and MBA mixture to prepare NIPAm (0.9)/AMPS (0.05)-VTS (0.05) and NIPAm (0.8)/AMPS (0.1)-VTS (0.1) with yields of 97.5 and 94.8%, respectively.

**Preparation of NIPAm-PSO Microgels and Silica NPs.** NIPAm-VTS and NIPAm/AMPS-VTS microgels were hydrolyzed in ammonia using an emulsion technique. An NIPAm/VTS or NIPAm/AMPS-VTS microgel (2 g) was dispersed into 100 mL of deionized water using ultrasound for 10 min to obtain a dispersion. A concentrated ammonia solution (28 wt %, 7 mL) was injected into the solution to obtain a clear dispersion. A mixture of n-hexane (20 mL) and TEOS (8 mL) microgels suggested compact adsorption at the interface or complete surface coverage.

### Table 4. Surface Activity Data of the Prepared NIPAm-VTS and NIPAm/AMPS-VTS Microgels and Silica Composites at Room Temperature

| Sample                        | Status     | $\text{cac} \times 10^2$ (mol L⁻¹) | $\gamma_{\text{min}}$ (mN m⁻¹) | $\Gamma_{\text{max}} \times 10^6$ (mol cm⁻²) | $A_{\text{max}}$ (nm² molecule⁻¹) |
|-------------------------------|------------|-----------------------------------|---------------------------------|-----------------------------------------|----------------------------------|
| NIPAm (0.95)-VTS (0.05)       | microgel   | 1.07                              | 40                              | 10.62                                   | 4.3                              | 0.038                           |
| NIPAm-PSO                     |            | 2.20                              | 31                              | 13.67                                   | 5.5                              | 0.030                           |
| NIPAm (0.9)-VTS (0.1)         | microgel   | 3.30                              | 40                              | 11.00                                   | 4.4                              | 0.037                           |
| NIPAm-PSO                     |            | 1.50                              | 42                              | 10.50                                   | 4.2                              | 0.039                           |
| NIPAm (0.90)/AMPS (0.05)-VTS (0.05) | microgel | 3.40                              | 35                              | 8.32                                    | 3.3                              | 0.053                           |
| NIPAm (0.8)-VTS (0.2)         | microgel   | 4.00                              | 41                              | 15.80                                   | 6.4                              | 0.025                           |
| NIPAm (0.8)/AMPS (0.1)-VTS (0.1) | microgel | 2.20                              | 40                              | 11.86                                   | 4.8                              | 0.034                           |

**Figure 13.** Relation between surface tension and aging times of NIPAm-VTS and NIPAm/AMPS-VTS, NIPAm-PSO and NIPAm/AMPS-PSO microgels, and silica NPs at room temperature.
was added into the dispersions dropwise for 40 min under continuous stirring to obtain an emulsion. The reaction proceeded at 35–40 °C for 24 h under continuous stirring (200 rpm). The hydrolyzed NIPAm-PSO or NIPAm/AMPS-PSO microgels were separated using an ultracentrifuge at 12 000 rpm and washing with acetone and ethanol.

The silica nanoparticles were obtained from the incineration of NIPAm-PSO or NIPAm/AMPS-PSO at 700 °C for 24 h.

Characterization. Fourier transform infrared (FTIR) spectra of the silica NPs and microgels were obtained using a Nicolet FTIR (EXUS-670) spectrophotometer. High-resolution transmission electron microscopy (HR-TEM) images for the Si NP, silica composites, and microgels were recorded (JEM-2100F, JEOL, at an acceleration voltage of 200–120 kV) to investigate their morphologies. The surface charges and particle size diameter of microgels and silica NPs were measured at different pH values of aqueous solutions using a
Laser Zeta meter, Malvern Instruments (Model Zetasizer 2000). Differential scanning calorimetry (DSC; Mettler-Toledo model 822) was used to determine the lower critical solution temperature (LCST) of the swelled microgels and silica NPs. The superabundant water evaporated from the swelled gel and the swelled samples were reheated from 10 to 60 °C at a heating rate of 5 °C min−1 under a nitrogen atmosphere. Surface tension measurements of the prepared Si NP, silica composites, and microgels in water were carried out using a drop shape analyzer (DSA-100) with a pendant drop method.

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**Notes**
The authors declare no competing financial interest.

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