Synthesis and Properties of Copolymer Microemulsions of Siloxane and Acrylate with a High Solid Content

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ABSTRACT: Copolymer microemulsions of methyl methacrylate, butyl acrylate, and vinyltriisopropoxysilane with high monomer/surfactant ratios were prepared through a seeded semicontinuous polymerization in the presence of a redox initiator, ammonium persulfate/sodium hydrosulfate. The mean diameter of the particles decreased with an increase in the amount of the surfactant, the monomer concentration, and the vinyltriisopropoxysilane/monomer ratio, but it increased with an increase in the concentration of the initiator. When the initiator concentration was 0.23% (ammonium persulfate/sodium hydrosulfate = 1.5 : 1), the concentration of the composite surfactant was 0.9 wt %, and the reaction temperature was 50°C; the solid content of the microemulsion could be up to 43% with a small particle size (mean diameter) of 39.8 nm. The chemical, freeze–thaw, and mechanical stability of the latexes was tested as well as the thermal stability of the films. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 851–857, 2007

Key words: coatings; copolymerization; emulsion polymerization; latices

INTRODUCTION

In contrast to opaque and milky conventional emulsions and miniemulsions, microemulsions are isotropic, optically transparent or translucent, and thermodynamically stable. The dispersed phase consists of small droplets of 10–100 nm, which result in the characteristic transparency or translucency and unique sizes and shapes.[1–4] The smaller size of the emulsion is very helpful in forming high-quality films as good as solvent coatings.[5] However, in previous research, microemulsions have usually acquired large amounts of a surfactant and yielded low polymer/surfactant ratios. These drawbacks have seriously hindered the industrialization and commercialization of microemulsion polymerization. In recent years, these shortcomings have been overcome with different methods used to increase the amount of the polymer produced with limited surfactant.[6–10]

Silicone-modified acrylates appear to possess the advantages of both siloxane and acrylic resins in overcoming the high cost of siloxane and the poor performance of acrylate resins in thermal stability and water resistance. Since Richard[11] investigated the compatibility of blending an acrylic polymer latex and a silicone emulsion, much research about silicone–acrylic copolymers has appeared. Yasuyuke et al.[12] synthesized and grafted silicone and acrylic emulsions. Park et al.[13] studied the synthesis of four-component silicone–acrylic resins by the free-radical copolymerization of acrylic monomers and 3-methacryloxypropyltrimethoxysilane as a siloxane monomer. The kinetics and fundamental aspects of alkoxysilane hydrolysis and condensation and some advances in using silanes in high-solid emulsions used in waterborne coatings were reviewed by Osterholtz et al.[14] and Ming et al.[15] Our research group has studied conventional siloxane-modified acrylate emulsions.[16,17] However, very few systematic studies of microemulsion polymerizations of siloxane-modified acrylates have appeared.

In this study, high-solid-content siloxane–acrylate microemulsions with a low concentration of a surfactant were obtained by a common polymerization method, seeded semicontinuous microemulsion polymerization, with methyl methacrylate (MMA), butyl acrylate (BA), vinyltriisopropoxysilane (VTIS), and a combined surfactant of a T-type surfmer (VPS) and sodium dodecyl sulfate (SDS). The —Si—OR group, which retains high reaction activity with many other functional groups, was introduced into the polymer chains in microlatexes. The influence of the amount of the combined surfactant, initiator concentration, monomer content, temperature, and siloxane/monomer ratio on the polymerization stability and mean

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TABLE I
Recipes Used in the Series of Experiments

	Monomer (%)		Water (%)	Composite surfactant (%)[b]	Redox Initiator (%)	Conversion (%)	Solid (%)	Coagulum (%)
	Acrylate[a]	Siloxane						
Variation of the surfactant concentration								
SI	28.50	1.50	69.55	0.30	0.15	96.26	28.37	3.1
SII	28.50	1.50	69.25	0.60	0.15	96.70	29.45	1.0
SIII	28.50	1.50	68.95	0.90	0.15	98.14	30.33	0.5
SIV	28.50	1.50	68.65	1.20	0.15	96.05	30.13	—
SV	28.50	1.50	68.35	1.50	0.15	96.90	30.68	—
Variation of the monomer concentration[c]								
MI	19.00	1.00	29.30	0.60	0.10	95.92	19.07	—
MII	28.50	1.50	68.95	0.90	0.15	98.14	30.33	0.5
MIII	38.00	2.00	58.60	1.20	0.20	100.00	41.10	0.7
MIV	42.75	2.25	53.42	1.35	0.23	99.37	43.08	6.9
Variation of the initiator concentration								
II	28.50	1.50	69.07	0.90	0.03	20.15	6.17	—
III	28.50	1.50	69.01	0.90	0.09	95.61	29.65	—
IIII	28.50	1.50	68.95	0.90	0.15	98.14	30.33	0.5
IIV	28.50	1.50	68.89	0.90	0.21	100.00	31.10	—
IV	28.50	1.50	68.83	0.90	0.27	100.00	31.17	—
Variation of the temperature								
T-35	28.50	1.50	68.95	0.90	0.15	29.56	9.35	—
T-40	28.50	1.50	68.95	0.90	0.15	95.27	29.60	—
T-45	28.50	1.50	68.95	0.90	0.15	97.96	30.28	—
T-50	28.50	1.50	68.95	0.90	0.15	98.14	30.33	0.5
T-60	28.50	1.50	68.95	0.90	0.15	100.00	30.90	0.5
Variation of the siloxane concentration								
SiI	30.00	0	68.95	0.90	0.15	99.16	30.73	—
SiII	28.50	1.50	68.95	0.90	0.15	98.14	30.33	0.5
SiIII	27.00	3.00	68.95	0.90	0.15	95.60	28.96	0.9
SiIV	25.50	4.50	68.95	0.90	0.15	98.99	30.34	1.3
SiV	24.00	6.0	68.95	0.90	0.15	99.42	30.41	1.5

[a] $m_{MMA}/m_{BA} = 5 : 4$.
[b] VPS/SDS = 2 : 1.
[c] The monomer/composite surfactant ratio was kept constant.

diameter of the microlatexes was investigated. These microlatexes may be potentially used in drug delivery systems, catalyst carriers, and functional waterborne coatings.

EXPERIMENTAL

Materials

MMA (ICI Acrylics, London, UK) and BA (ICI Acrylics, London, UK) were distilled under reduced pressure before use. VTIS (Cromptom Corp., Middle bury, CT) and VPS (98% pure; Guangzhou Double Bond Trade, LH., Guangzhou, China) were used as received. VPS was a reactive surfactant and had an alkyl group, a hydrophilic alkyl group composed of 6–10 carbons, and other groups. Ammonium persulfate (APS), purchased from the Institute of Chemical Reagents (Tianjing, China), was recrystallized and then dried at room temperature *in vacuo*. Sodium hydrosulfate (SHS) and SDS were analytical reagents

from Shanghai Experiment Reagent Co. (Shanghai, China). Both were used as received.

Synthesis

The polymerization was carried out in a 250-mL, four-necked flask equipped with a reflux condenser, a thermometer, an addition funnel, a small stirring bar driven by an electric stirrer, an N_2 inlet, and a feed inlet. The seeded semicontinuous copolymerization was carried out with the recipe given in Table I. MMA (1.0 g), two-thirds of the total surfactant, and most of the water were stirred into a transparent microemulsion with nitrogen bubbling through it and then heated to the reaction temperature. Solutions of APS in 5.0 g of water and SHS in 5.0 g of water were added to initiate the polymerization, which lasted 0.5 h. The remaining monomers and surfactant were mixed uniformly and were added to the polymerization microemulsion within 4 h continuously and slowly. When the addition was complete,

the reaction continued for another hour at the reaction temperature.

Characterization

Dynamic light scattering (DLS)

The latex particle size and size distribution were determined by DLS with a Brookhaven Instruments Corp. (New York, NY) BI-200SM goniometer with a BI-9000AT digital autocorrelator. A 40-mW helium–neon laser of a 632.8-nm wavelength was used at an angle of 90° at 25°C. The polymer microlatexes were diluted with deionized water to a polymer concentration of about 0.1 wt % before the test.

Transmission electron microscopy (TEM)

The particle size was measured with a JEOL-JEM (Kyoto, Japan) 100CXII transmission electron microscope with phophotungstic acid (PTA) as the staining reagent. A drop of the polymerized latex was diluted in 1 mL of a 0.1% PTA solution. One drop of this diluted latex was put on a copper grid that had been coated with a thin layer of formvar. The average particle size was calculated by the consideration of 100 particles per 25 cm^2.

Appearance viscosity

The appearance viscosity of the microlatexes was measured with a Brookfield DV-1+ viscometer (Middleburo, MA) with an LV 1 spindle at 10 rpm at 25°C.

Thermogravimetric analysis (TGA)

The thermal analysis was carried out in a static air atmosphere at a heating rate of 10°C/min from 25 to 600°C with a PerkinElmer (Wellesley, MA) TGA-7. The samples came from a film of the copolymer.

Mechanical stability

The mechanical stability was determined at room temperature with a Beckman Avanti J-25 high-speed (15,000 rpm) ultracentrifuge (Los Angeles, CA). The microlatex, taken from the reactor at the end of the polymerization, was subjected to high-speed centrifugation for 15 min. The transmittance of the latex was measured with a 756MC ultraviolet–visible (UV–vis) spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) before and after centrifugation.

Electrolytic stability

The electrolytic stability was determined by the titration of 100 g of the latex with 5% $Al_2(SO_4)_3$. The volume of $Al_2(SO_4)_3$ required to coagulate the latex was used as an index of the electrolytic stability.

Freeze–thaw stability

To determine the freeze–thaw stability, the microlatexes were subjected to a number of cycles in which the sample was frozen at −5°C for 10 h and then allowed to thaw at room temperature for 10 h. Both the amount of the formed coagulum and the increase in the particle size were used to evaluate the freeze–thaw stability.

RESULTS AND DISCUSSION

The recipes used in the semicontinuous polymerization of MMA, BA, and VTIS are given in Table I. The conversion percentages were all higher than 96% when the surfactant content was varied between 0.3 and 1.5 wt % in the S series of reactions. The dependence of the formed coagulum on the surfactant content is illustrated in Table I. The formed coagulum obviously decreased from 3.1 to 0.5% as the surfactant concentration was changed from 0.3 to 0.9%. There was no coagulum when the surfactant content was more than 1.2%. This resulted in monomer/composite surfactant ratios of 20 : 1 to 100 : 1. At a low concentration of the composite surfactant, coagulum formation took place as a result of the promotion of the electrostatic instability of the latex particles. A decrease in the double-layer thickness with decreased stability of the latex particles led to decreasing stability of the latex particles. However, a higher
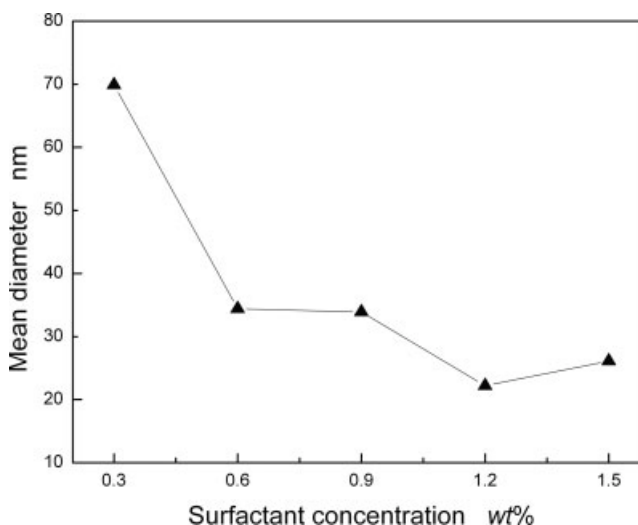

Figure 1 Effect of the composite surfactant concentration on the particle size of silane–acrylate microemulsions.
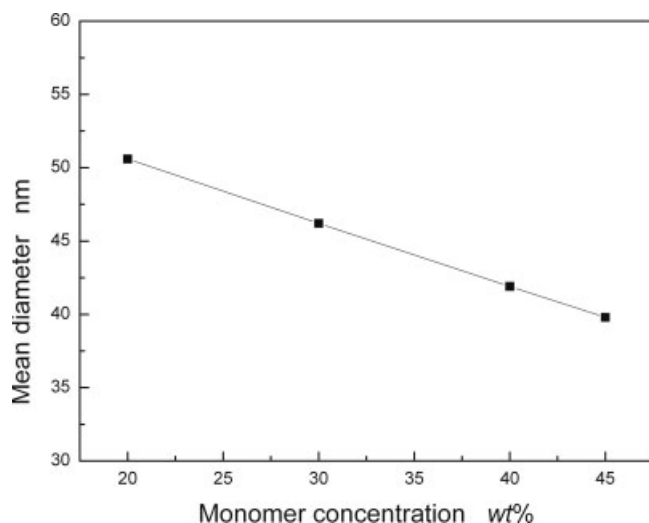
Figure 2 Effect of the added monomer amount on the particle size of silane–acrylate microemulsions.

Figure 3 Effect of the concentration of the redox initiator in the initial microemulsion on the particle size of silane–acrylate microemulsions.

surfactant concentration harmed the water resistance of the films of the copolymer. Then, a 0.9–1.2% concentration of the composite surfactant for a 30% concentration of the monomer was recommended.

Figure 1 shows that the mean diameter changed slightly and tended to increase gradually with the concentration of the surfactant decreasing. If the concentration of the surfactant was too low (e.g., 0.3 wt %), large particles increased, and then the mean diameter got bigger; this suggested that a 0.3 wt % concentration of the composite surfactant was insufficient to protect the siloxane–acrylate microlatexes from aggregating to form large particles under these experimental conditions.

To raise the percentage of the solid in the latex, we varied the monomer concentration from 20 to 45%, keeping the mass ratio of MMA/BA at 5 : 4, the siloxane concentration at 5% with respect to the total monomer, and the monomer/composite surfactant ratio at about 33 : 1. At a high monomer concentration (>40%), the increase in the ionic concentration of the continuous phase reduced the stability of the latex, and more coagulum formed. When the monomer concentration was 45%, up to 6.9% coagulum formed, and this even influenced the solid content. However, the mean diameter (Fig. 2) did not become bigger but became smaller with the increase in the monomer concentration. The result was due to the smaller particle size of the seeds. The seeds became smaller when more surfactant emulsified the constant MMA (1.0 g) in the initial microemulsion, and in the polymerization procedure, the particle size leveled off after the formation of the seed.[8]

To study the effect of the initiator concentration, the polymerization recipes were the same as those shown in the Experimental section, except that the redox initiator concentration in the initial micro-
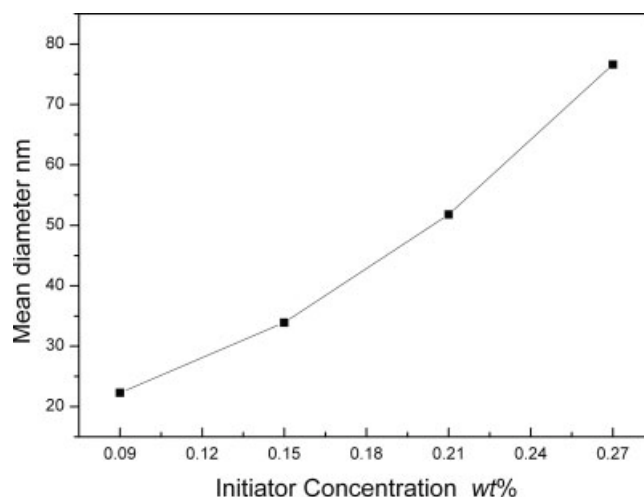
emulsion was varied from 0.03 to 0.27 wt %. At a low concentration of the initiator (0.03 wt %), the conversion was only 20.15%, and the emulsion was milky. This indicated that a low concentration of the initiator reduced the reaction rate. The conversion became higher than 95% when the concentration of the initiator was more than 0.09%, and the appearance of the microemulsions was bluish and translucent. As shown in Figure 3, the particle size of the silicone–acrylate microlatexes increased gradually as the concentration of the initiator increased. The result was perhaps due to the occurrence of inter-particle aggregation; that is, at a high initiator concentration, the nucleation was very fast, so the number of small polymer-containing particles was also very large, and increasing the surface area above the level that
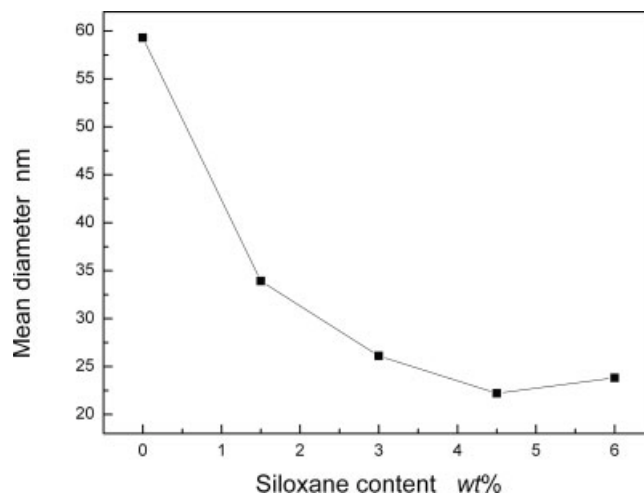

Figure 4 Effect of the siloxane content in the total monomer on the particle size of silane–acrylate microemulsions.

TABLE II
Effect of the Reaction Temperature on the Particle Size of Silane–Acrylate Microemulsions

Sample	Reaction temperature (°C)	Appearance	Mean diameter (nm)
T-35	35	Milky	—
T-40	40	Bluish and transparent	46.2
T-45	45	Bluish and transparent	42.4
T-50	50	Bluish and transparent	33.9
T-60	60	Bluish and transparent	39.9

could be stabilized by only 0.9 wt % composite surfactant resulted in aggregation.

In our synthesis process, the siloxane content could be up to 20% because VTIS was not easily hydrolyzed on account of its hindered group of isopropyl.[15] Figure 4 shows that the mean diameter of the latex decreased rapidly with the addition of the siloxane (VTIS) to the acrylate monomer and decreased continually with an increase in the VTIS/monomer ratio. With an increase in the amount of siloxane, the monomer became more hydrophobic, and this changed the mechanism of nucleation greatly. MMA and BA were more soluble than VTIS, so the nucleation for the MMA and BA system happened mostly in a continuous phase (water) as the APS/SHS initiator had good solubility in water. After VTIS was added, more free radicals entered the monomer-containing micelles to initiate the polymerization. The changed polymerization process led to the decrease in the microlatex particle size. This phenomenon agreed with Capek's[18] conclusion that the surface activity of a monomer plays a decisive role in the polymerization procedure.

The reaction temperature was changed from 35 to 60°C, whereas other experimental conditions were kept unchanged. At a low temperature (<40°C), the initial rate was too low to initiate the copolymerization with the same monomer addition rate, and the seeded microemulsion changed from transparent to milky. Table II shows that the mean diameter of the microlatex synthesized at 50°C was the smallest. The rate of monomer addition was faster than the polymerization rate at 40°C, so the excess monomer that existed in the system acted as a reservoir to supply the polymerizing micelles, leading to the formation of many larger particles. When they were polymerized at 60°C, the microlatexes were larger than those polymerized at 50°C. This phenomenon can be explained as follows: the concentration of small particles being initiated at 60°C was too large for the available surfactant to stabilize the particles individually; this is analogous to the situation with high initiator levels. The mild reaction temperature of 50°C guaranteed a high reaction rate and a small particle size.

TABLE III
Appearance Viscosity (η) and Freeze-thaw Stability of the Synthesized Microemulsions

Sample	$\eta \times 10^3$ (Pa S)	Freeze–thaw cycle
SI	17.6	No pass
SII	18.0	No pass
SIII	18.8	Pass
SIV	23.6	Pass
SV	17.9	Pass
MI	16.3	Pass
MII	21.7	Pass
MIII	37.5	Pass
MIV	47.4	Pass
SiI	22.5	Pass
SiII	18.8	Pass
SiIII	19.5	Pass
SiIV	17.7	Pass
SiV	17.3	Pass

Appearance viscosity

The microemulsion synthesized by the seed semicontinuous polymerization had a low appearance viscosity, as shown in Table III. In series S and Si, the viscosity of the microlatexes did not change greatly with an increase in the surfactant or siloxane content. In the M series, however, the viscosity gradually increased with increasing monomer content within a certain range.

Particle size distribution

A bimodal distribution of the particle sizes was obviously shown by a TEM micrograph of recipe SiIV: the bigger kind had a particle size of about 45 nm, and the smaller kind had a particle size of less than 25 nm. The value was comparable to the value of 22.2 nm measured by DLS. This is shown in Figure 5.

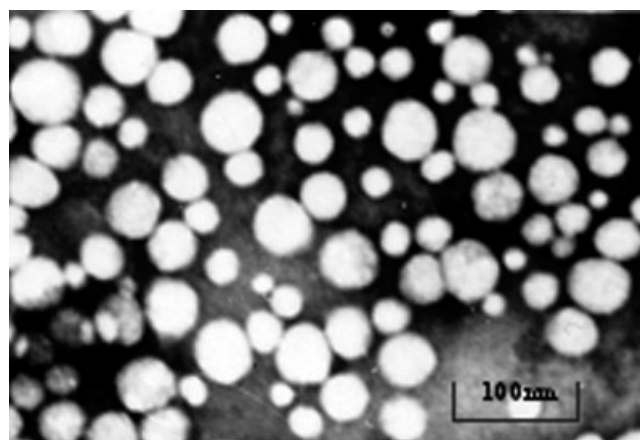Figures 6 and 7 show the particle size distribution of the microlatexes obtained from MIII and SII. The

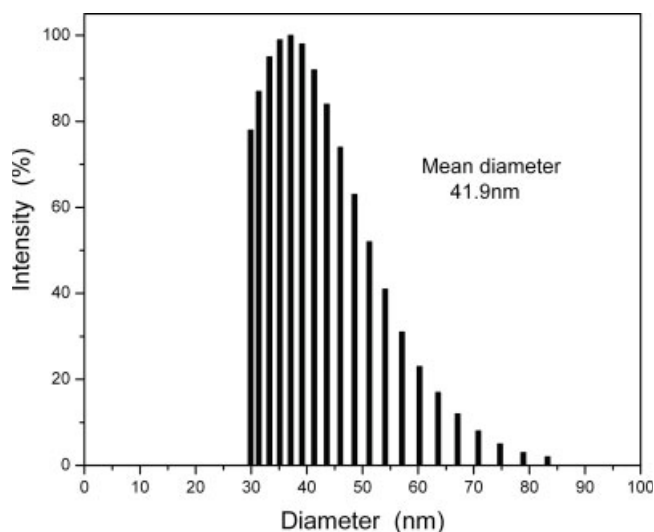**Figure 5** TEM micrograph of the microlatex from recipe SiIV (70,000×).

Figure 6 Particle size distribution of the microlatex from recipe MIII.

mean diameter of the microlatex obtained from MIII was 41.9 nm, with 24% of the particles below 33.82 nm and 52% below 39.12 nm. For the latex from SIII, a bimodal distribution was observed with the first peak at 28.77 nm and the second at 52.63 nm. The mean diameter was 34.4 nm, with 53% of the particles below 30.76 nm. In the oil-in-water microemulsion system of acrylic octadecyl ester and styrene, Tieke and Dreja[19] found that the most possible nucleation locations were solubilization micelles and monomer microdrops without excluding homogeneous nucleation in the aqueous phase. In our oil-in-water system, the better solubility of MMA was useful for the homogeneous nucleation mechanism occurring in the water phase. The two-peak distribu-
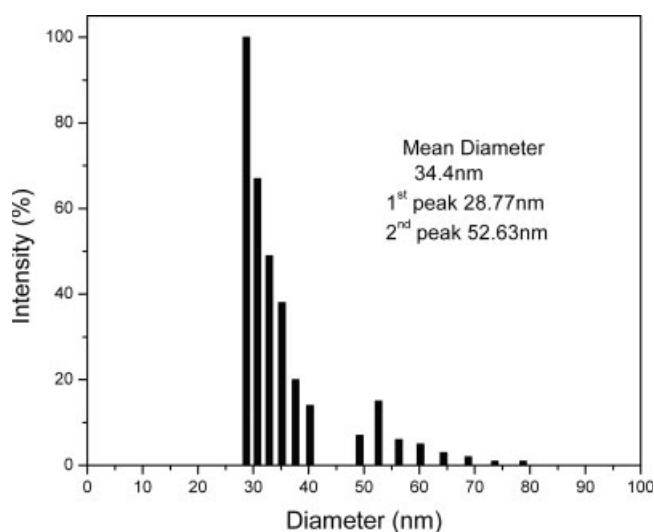

Figure 7 Particle size distribution of the microlatex from recipe SII.

TABLE IV
Transmittance of the Microemulsions from MIII and SiIII

Sample	Transmittance before centrifugation (%)	Transmittance after centrifugation (%)
MIII	30.3	30.4
SiIII	40.8	40.7

tion also indicated that the nucleation of the copolymerization occurred via more than one route.

Mechanical stability

The microemulsion latexes from recipes MIII and SiIII were tested for mechanical stability at 15,000 rpm for 15 min. No coagulum was found at the bottom of the test tube for either latex, and the transmittance of light (Table IV), checked by the 756MC UV–vis spectrophotometer, almost did not change after centrifugation at a high speed; this showed that no increase in the particle size was observed, demonstrating the excellent mechanical stability of the siloxane–acrylate microemulsion.

Electrolytic stability

The microemulsion latexes from recipe MIII and SiIII were tested for electrolytic stability with 5% aluminum sulfate. The added electrolyte, $Al_2(SO_4)_3$, could reduce the double-layer thickness greatly, and this resulted in decreased stability of the latex particles; then, coagulation took place.[9] The MIII microemulsion latex (100g) required 21 mL of $Al_2(SO_4)_3$, whereas SiIII required 23.5 mL of the same for complete coagulation. VPS, the polymerizable surfactant, was anchored onto the latex particles, and this promoted electrostatic stabilization of the latex particles. However, the latexes could not demonstrate very excellent electrostatic stabilization because both kinds of surfactants in the composite surfactant were ionic surfactants.

TGA

Table V shows the thermal analysis results for representative samples with different siloxane ratios with respect to the total monomer. T_5, T_{50}, and T_{95} are the decomposition temperatures for 5, 50, and 95% weight losses, respectively; the remainder included those that could not be decomposed at 600°C. Samples SiI and SiIII showed single degradation. The remainder of sample SiIII (5.255%) was higher than that of sample SiI (0.196%), and the onset temperature of sample SiIII (294.2°C) was higher than that of SiI (289.28°C). This indicated that sample SiIII had better thermal stability. In recipe SiIII, 10% siloxane was added to the monomer, and this changed the in-

TABLE V
Data from Thermal Analysis

Sample	Siloxane ratio (%)	TGA			Remainder (%)	DTG	
		T_5 (°C)	T_{50} (°C)	T_{95} (°C)		Rate (%/min)	Onset temperature (°C)
SiI	0	266.86	299.81	312.08	0.196	52.58	289.28
SiII	5	267.62	302.22	329.44	1.398	58.84	292.29
SiIII	10	269.53	304.37	432.49	2.405	61.01	294.28

DTG, different thermal gravimetry.

ternal structure of the products and improved the thermal character.

Freeze–thaw stability

When freezing occurs, ice crystals separate from the unfrozen latex, reducing the volume of the continuous phase and increasing the ionic concentration of the phase. Therefore, the stability of the latex is reduced, and the latex, which is subjected to high pressure, coagulates. A nonionic surfactant with long ethoxy chains can resist coagulation during the freeze–thaw process.[18]

Resistance to freeze–thaw cycles is very important for the application of a microemulsion because the latex may be frozen during storage or transportation. As shown in Table III, all samples from the M and Si series showed good stability to the three cycles described in the Experimental section. The ethoxy chains in VPS may reduce coagulation during the freeze–thaw process and increase the stability.

CONCLUSIONS

A siloxane–acrylate copolymer microlatex was achieved with the method of seeded semicontinuous copolymerization, and it had a high polymer content as well as nanosize particles with a monomer/surfactant weight ratio of 33 : 1. Polymerization at 50°C produced a microlatex with good properties. The mean diameter of the latex decreased with increasing siloxane feed content. The VTIS monomer

existing in the copolymerization effectively improved the thermal character of the polyacrylate films. Microemulsion latexes have potential applications as coatings in industry.

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