

Study on the Preparation and Properties of Styrene–Butyl Acrylate–Silicone Copolymer Latices

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ABSTRACT: Copolymer latices of styrene–butyl acrylate–silicone were prepared using a semicontinuous addition process and batch and monomer emulsion addition processes. The results showed that a stable latex with narrow particle size dispersion and a high monomer conversion can be obtained only by the semicontinuous addition process. The simultaneous free-radical and ionic copolymerization mechanisms were discussed. 3-Methacryloyloxypropyl trimethoxysilane in this work was used as a coupling agent to form a chemical bond between vinyl polymer and polysiloxane. It was found that the copolymerization reaction and the properties of latex and latex film were obviously influenced by silicone content. When the silicone content was less than 25 wt %, copolymerization proceeded readily and a stable latex could be prepared. With increasing silicone content, monomer conversion, latex stability, film hardness, and tensile strength decreased, whereas the water resistance and impact strength increased. Results of Soxhlet extraction, silicon analysis, and dynamic mechanical properties of latex polymer confirmed the occurrence of copolymerization. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3194–3200, 2001

Key words: styrene–butyl acrylate–silicone copolymer; emulsion copolymerization; polymerization process; latex film property; 3-methacryloyloxypropyl trimethoxysilane

INTRODUCTION

It is well known that polyacrylics and poly(acrylic-styrene) latices have many specific properties such as good film-forming, gloss and transparency, and mechanical properties, and so the latices and their corresponding latex products have been widely used as coatings, paints, adhesives, and the like. On the other hand, polyacryl-

ics and poly(acrylic-styrene) latices have poor water and weather resistance because of their chemical structures, and their mechanical properties are often temperature dependent. These weaknesses bring about a series of disadvantages in application, especially when they are used as coatings for exterior walls in building. In contrast, polysiloxane has many excellent properties as a result of its low glass-transition temperature and surface tension, good water repellency, weather resistance, and thermal stability. Thus the incorporation of polysiloxane into polyacrylics and poly(acrylic-styrene) latices is effective for improving a variety of physical or chemical properties.

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In past few decades, three main aspects of work concerning emulsions of silicone-containing polyacrylics or poly(acrylic-styrene) latices have been carried out by many researchers. Because the core/shell latex particles comprising a soft core and a hard shell can be widely used as impact and toughness or thermal modifiers for thermoplastics and other synthetic resins, most investigations focused on multistage emulsion polymerization, typically involving, first, forming the polysiloxane seed particle and, second, polymerizing the acrylics (or styrene) onto the polysiloxane seed.¹⁻⁸ To improve some properties of common polyacrylic latices, several studies were performed on the emulsion copolymerization of acrylates with silicones,⁹⁻¹⁴ and stable poly(butyl acrylate-methyl methacrylate-silicone) latices were prepared in our previous work.¹⁵⁻¹⁷ In recent years, novel core/shell latex particles with polyacrylate as a core and with polysiloxane as a shell were successfully synthesized through a special seeded emulsion polymerization, and properties of the latices and latex films were also studied.¹⁸⁻²⁰ To date, no results on styrene (St)-butyl acrylate (BA)-silicone (Si) copolymer latices prepared using the one-stage method have been reported.

In this work, the novel stable latices of P(St-BA-Si) were first synthesized by simultaneous free-radical and cationic copolymerization in the presence of 3-methylacryloyloxypropyl trimethoxysilane (MATS) as coupling agent, and the colloidal properties of the latices and corresponding latex film properties were then characterized.

EXPERIMENTAL

Materials

Vinyl monomers used included BA, St, methyl methacrylate (MMA), and methacrylic acid (MAA) (all analytical reagents were from Shanghai Chemical Reagent Plant), distilled under vacuum before use. Silicone monomers used included MATS and octamethyl cyclotetrasiloxane (D_4). MATS was from Aldrich Company (Milwaukee, WI) and D_4 was purchased from the 4th Petrochemical Plant of Jinan and fractionated under reduced pressure before use. Analytical reagents of ammonium persulfate (APS), dodecylbenzene sulfonic acid (DBSA, D_4 polymerization catalyst and surfactant), and sodium dodecylbenzene sulfonate (SDBS, surfactant) were used as received.

Water was deionized and distilled, and its conductivity was below $1 \mu\text{S}/\text{cm}$.

Emulsion Polymerization

In all polymerizations (except indicated), the amount of monomers was controlled in such a way that the solid content of the final latex was 31.7 wt % at complete monomer conversion. Polymerizations were conducted in nitrogen atmosphere, and the latices were finally neutralized with aqueous ammonia after polymerization. A typical recipe is: BA, 24.6 g; St, 22.1 g; MMA, 1.5 g; MAA, 0.6 g; D_4 , 4.86 g; MATS, 0.54 g; APS, 0.24 g; SDBS, 0.34 g; DBSA, 0.79 g; water, 120 g; weight ratio of D_4 : MATS, 9 : 1. In certain recipes, the vinyl monomer : silicone ratio was changed without changing the proportions between vinyl monomers.

Emulsion copolymerization was carried out using three different processes:

1. Batch process (Method A): Water, surfactant, and monomers were charged successively into a reactor and emulsified by stirring for 30 min at 85°C . The aqueous solution of APS and DBSA was then added into the reactor and polymerization was continued for 3 h.
2. Monomer emulsion addition process (Method B): Water (50 g), surfactant, and monomers were mixed at room temperature and emulsified for 30 min by stirring. The obtained monomer emulsion was then continuously introduced for 1.5 h into the reactor containing a solution of APS and DBSA in 70 g of water at 85°C , and polymerization continued for 1.5 h after the end of addition.
3. Semicontinuous addition process (Method C): Monomers, surfactant, and water (90 g) were sufficiently mixed at room temperature and emulsified for 30 min by stirring, after which two-thirds of the obtained emulsion was placed into a dropping funnel; the residual in the reactor was used as substrate. Two-thirds of a solution of APS-DBSA dissolved in 30 g of water was placed into another dropping funnel, and the remainder was poured into the reactor. Then the monomer emulsion and the APS-DBSA solution were simultaneously added dropwise into the reactor at 85°C ; the dropping time for the former and for the latter

was controlled in 1 and 1.2 h, respectively. The polymerization time was limited to 3 h.

Characterization of Latex Properties

Monomer conversion was measured by the gravimetric method. Polymerization stability was characterized using weight percentage of coagulum formed in the polymerization process to the total amount of monomers. Particle diameter (D_p) and morphology were investigated using a transmission electron microscope (TEM) with phosphotungstic acid as staining agent. Surface tension, ζ potential, and viscosity of latices were determined, respectively, on an auto surface tension instrument (JYW-200), electrophoresis apparatus (DXD-2), and a rotating viscometer (NDJ-1). A rheological curve was drawn based on the corresponding shearing stress/shearing strain values obtained on a six-speed rotating viscometer (ZNN-D6).

Characterization of Latex Film Properties

Adhesiveness, flexibility, and impact strength of the latex films covered over tin plate substrate were measured, respectively, using an adhesive test instrument (QFZ-II), a flexibility test instrument (QTX-I), and an impact test instrument (QCJ).

Latex films (~ 1 mm thickness) were cast from a polytetrafluoroethylene mold at ambient temperature. The film hardness was measured using a pendulous hardnessmeter (QBY). Tensile strength, rupture elongation, and permanent set of the films were obtained with a mechanical analyzer (XL-250A). Saturated water absorption (A_w) of the films was characterized by immersing about 2 g of film in deionized water at 80°C for 24 h, comparing the weight of the film before (W_1) and after (W_2) immersion; A_w was defined as $(W_2 - W_1)/W_1 \times 100\%$.

Copolymerization was confirmed by Soxhlet extraction of latex film with toluene as solvent for 12 h, by elemental analysis of silicon (on element analyzer, type 240-B), and by relaxation temperature obtained on torsion braid analysis (TBA) of type GDP-3.

RESULTS AND DISCUSSION

Selectivity of Emulsion Polymerization Processes

Emulsion polymerization is a very important process to produce copolymers with varied composi-

Table I Results of Different Polymerization Processes^a

Process	Conversion (wt %)	Coagulum (wt %)
Method A	88.3	9.8
Method B	57.3	0.6
Method C	93.0	0.2

^aSilicone content was 10 wt %.

tions for a wide range of applications, and the behavior of polymerization and properties of latex and copolymer are strongly dependent on the type of polymerization process.²¹ Differences in polarity and chemical structure of polyacrylics [including P(St-BA)] and polysiloxane are substantial. Polyacrylics are hydrophilic and are often synthesized by free-radical polymerization, whereas polysiloxane is hydrophobic and is usually prepared by a ring-opening polymerization of cyclosiloxane. It was previously reported that free-radical and ring-opening copolymerization could be carried out simultaneously in the system of acrylics and cyclosiloxane when APS-DBSA was used as a composite initiator-catalyst.^{15,16} To obtain a stable and narrow particle dispersed latex with a high monomer conversion, three different copolymerization processes were tested in the presence of APS-DBSA and MATS. The results of monomer conversion and coagulum in copolymerization with 10 wt % silicones are given in Table I.

Observed behaviors during the three polymerization processes were very different. In method A, the coagulated polymer on the wall of the reactor and stirrer was observed when polymerization went above 30 min, and the total coagulum reached 9.8% at the end of polymerization, although 88.3% of equilibrium conversion was obtained. This coagulated polymer cannot be dissolved in butanone or toluene, which means that the polymer is crosslinked. Because the concentration of silicones in the reactor for this method is much higher than that for other methods, this may facilitate the self-condensation of SiOCH₃ groups between MATS molecules, as well as polycondensation of MATS with terminal SiOH groups originating from the ring opening of D₄ and from the hydrolysis of SiOCH₃ groups. This polymerization process is therefore unstable, and precipitates in the latex were observed after 2 days of standing at ambient temperature.

In method B, although stable latex with a little of coagulum was gained, the equilibrium conver-

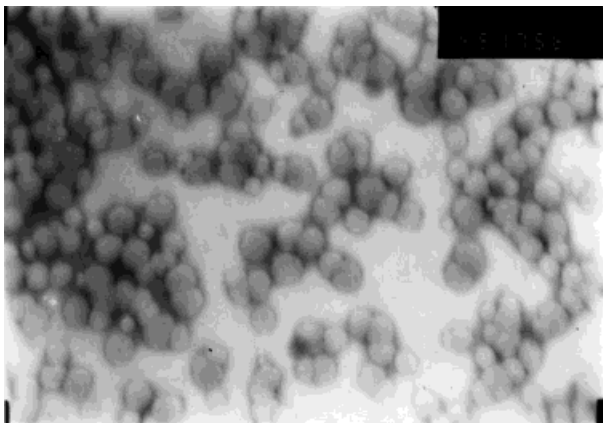


Figure 1 Micrograph of copolymer latex particles produced by method C (magnification $\times 48,000$).

sion was only 57.3%. Because the reactivity ratio of St is higher than that of BA, special attention must be required for the emulsion polymerization of St and BA.²² As polymerization proceeded, the concentration of BA gradually increased, whereas the concentration of APS decreased rapidly because all of the initiator was charged into the reactor at 85°C at the beginning of copolymerization. These phenomena led to a lack of initiator at one time or another, and so a low monomer conversion and stable latex particles swelled with monomers were finally obtained.

In method C, most of the monomers and APS-DBSA initiator-catalyst, respectively, were introduced dropwise, which increased the possibility of copolymerization between vinyl monomer and silicone. Furthermore, because the addition time of the APS-DBSA solution was longer than that of the monomer emulsion, a certain concentration of APS was maintained in the reaction medium and a high monomer conversion was gained. Thus only method C produced slightly blue-colored, stable latex with relatively narrow dispersed latex particles of an average diameter of 88 nm (Fig. 1),

Table III Silicone Contents and Colloidal Properties of Latices

Sample	Surface Tension (mN/m)	Viscosity (mPa/s, 25°C)	ζ potential (-mV)
SA	70.1	3.0	55.2
SAS1	59.8	3.6	—
SAS2	58.0	4.1	60.2
SAS3	54.6	4.7	91.4
SAS4	45.5	5.3	104.9
SAS5	45.1	5.5	79.7

and equilibrium conversion was reached at 93% accompanied by little coagulum.

The following copolymerizations are all affected by method C.

Influence of Silicone Contents on Polymerization and Latex Properties

To study the influence of silicone contents on polymerization and latex properties, experiments were carried out with varying silicone content. The results are given in Table II and Table III. It was found that monomer conversions slightly decreased with increasing silicone content, polymerization proceeded readily, and monomer conversions were higher than 86% in all runs with silicone contents below 25 wt %. Once this content attained 30 wt %, the monomer conversion decreased to 60.8% and a large amount of coagulum was formed during polymerization; the final latex separated into two phases after 1 day standing at room temperature. This may be attributed to the self- and polycondensation of silicones. Because their concentration in the reactor was increased at high silicone contents, the probabilities of self- and polycondensation of silicones were increased and copolymerization with vinyl monomers was therefore reduced.

Table II Influence of Silicone Contents on Polymerization and Latex Properties

Sample	Silicones (wt %)	Conversion (%)	Coagulum (wt %)	D_p (nm)	$N_p \times 10^{-17}$ (1/L)
SA	0	96.3	0	194	0.69
SAS1	2	97.5	0	104	4.51
SAS2	5	96.8	0	102	4.75
SAS3	10	93.0	0.2	88	7.42
SAS4	20	89.0	1.2	82	9.02
SAS5	25	86.0	4.5	105	4.25
SAS6	30	60.8	11.2	—	—

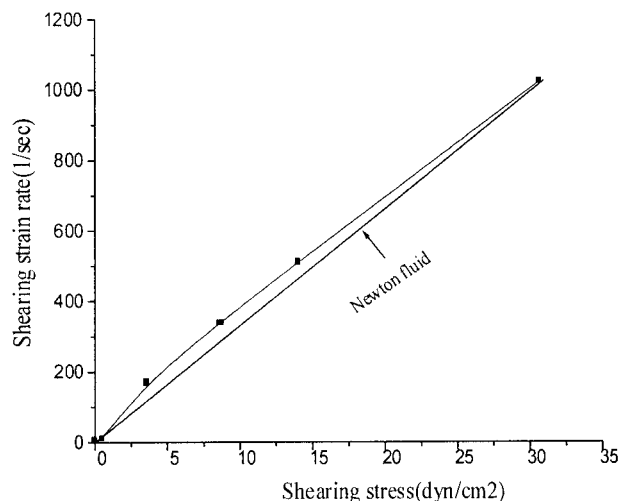


Figure 2 Rheological curve of the latex SAS3 with 10 wt % silicone content.

For copolymer latices (SAS series), it was found that their particle diameter (D_p) and surface tension were smaller than those of P(St-BA) latex (sample SA), and their viscosity and ζ potential were larger than those of SA. Moreover, with the increase of silicone contents from 2 to 20 wt %, D_p and surface tension of latices decreased gradually, whereas viscosity and ζ potential increased. When silicone content further increased to 25 wt %, instead of a decrease of D_p and an increase of ζ potential, D_p became large and ζ potential was obviously decreased. These results imply that good stable latices can be prepared when silicone content was less than 25 wt %, and these agreed well with the above-noted results of conversion and coagulum.

Rheological behavior is one of important properties for latex. As an example, a shearing stress/shearing strain curve of copolymer latex with 10 wt % of silicone content (SA3) was drawn (Fig. 2), thus showing that this kind of latex is very simi-

lar to a Newtonian fluid, although with slight deviation.

Confirmation of Copolymerization

MATS is the key agent in the emulsion copolymerization of vinyl monomers with D_4 . Because MATS possesses one carbon-carbon double bond and three SiOCH_3 groups, it can undergo not only radical polymerization with vinyl monomers but also condensation with terminal Si-OH groups originating from the ring opening of D_4 . St, BA, and silicone units can thus be combined through chemical bonds and P(St-BA-Si) can be synthesized.

For copolymerization of St (M_1) with MATS (M_2), the reactivity ratios are $r_1 = 0.45$ and $r_2 = 0.9^{23}$; for BA (M_1) with MATS (M_2), they are $r_1 = 0.29$ and $r_2 = 2.53^{24}$. Thus in theory the free radical copolymerization of St, BA, and MATS can easily occur. To verify the occurrence of copolymerization of vinyl monomers with silicones, Soxhlet extraction and silicon analysis were carried out for different polymers (Table IV). Results showed that P(St-BA) (sample SA) was completely extracted; in contrast, only 10.1% was extracted for P(St-BA-Si) copolymer (sample SAS5). Moreover, 7.26 wt % of silicon content was determined for the remainder after extracting, the value of which agreed with its theoretical silicon content (8.19 wt %). Results of the investigation showed that the crosslinked P(St-BA-Si) was formed in the latex film because of the self-condensation of silicones, and that the copolymerization did take place as expected.

Another evidence for copolymerization is the relaxation temperature (RT, see Table IV) of latex polymers obtained from TBA measurement. P(St-BA) presented only one RT at 25°C. Two RTs were observed for sample SAS5: one relaxation peak, representing copolymer of St and BA at high temperature, was obviously broadened into the range

Table IV Results of Soxhlet Extraction and Silicon Element Analysis and Relaxation Temperature from Torsion Braid Analysis

Sample	Weight Loss (wt %)	Silicon Content ^a (wt %)		Relaxation Temperature (°C)
		Theoretical	Experimental	
SA	100	0	0	25
SAS5	10.1	8.19	7.26	-112, -3-47

^aFor residual copolymer after Soxhlet extraction.

Table V Silicone Contents and Properties of Films Covered over Tin Plate

Sample	Adhesive ^a (grade)	Flexibility ^a (grade)	Impact Strength (kg/cm)
SA	1	1	40
SAS1	1	1	45
SAS2	1	1	48
SAS3	1	1	>50
SAS4	1	1	>50
SAS5	2	1	>50

^aThe less the data, the better the corresponding properties.

from -30 to 47°C ; another relaxation peak at -112°C represented polysiloxane, which is higher than that of pure polysiloxane ($RT = -123^{\circ}\text{C}$).¹⁷ These changes of RT clearly showed that chemical bonds were formed between vinyl polymer and polysiloxane.

Silicone Contents and Latex Film Properties

The properties of latex films covered over tin plate substrate with different silicone contents were measured, the results of which are shown in Table V. When silicone content was less than 20 wt %, excellent adhesiveness and flexibility were obtained; when this value attained 25 wt % (SAS5), the adhesiveness decreased in spite of the good flexibility because of the low polarity of P(St-BA-Si) at high silicone content. It was found that the impact strength can be obviously improved by incorporating soft polysiloxane into P(St-BA); the impact strength increased from 40 to 48 kg/cm with the increase of silicone content from 0 to 5 wt %, and the value was more than 50 kg/cm when the silicone content was ≥ 10 wt %.

It is known that silicone-containing polymers have low surface energy and low polarity. The

presence of silicone in latex film would increase its water resistance, which is important in coating, paint, and paper industries. From Table VI it can be seen that pure P(St-BA) (sample SA) manifested the largest saturated water-absorption ratio (A_w) of 20.6%; A_w decreased from 20 to 11.2% with increasing silicone content from 2 to 10 wt %; by further increasing the silicon content from 10 to 25 wt %, A_w decreased by only 1.1% (from 11.2 to 10.1%).

The mechanical properties of latex films with different silicone contents are given in Table VI. Because the polysiloxane chain is very flexible at room temperature, the hardness of P(St-BA-Si) decreased with the increase of silicone content. The decrease in tensile strength with an increase of silicone content might be attributed to the eventual microheterogeneous structure in copolymer latex films resulting from different polymer polarities, and further investigation is needed. The permanent set of copolymer was much smaller than that of pure P(St-BA) because of the existence of crosslinked bonds in copolymers.

CONCLUSIONS

1. Copolymer latices of styrene-butyl acrylate-silicone were successfully prepared using a semicontinuous addition process when silicone content was less than 25 wt %. With the increase of silicone content, monomer conversion and stabilities of polymerization and latex decreased.
2. MATS is the key agent in the emulsion copolymerization. Free-radical polymerization of vinyl monomers and ionic ring opening of D_4 can take place simultaneously in the presence of ammonium persulfate and dodecylbenzene sulfonic acid. Results of

Table VI Silicone Contents and Latex Film Properties

Sample	A_w ^a (wt %)	Hardness ($\times 10^2$)	Tensile Strength (MPa)	Elongation at Rupture (%)	Permanent Set (%)
SA	20.6	6.72	69.0	683	16.7
SAS1	20.0	4.55	55.4	693	5.3
SAS2	18.4	3.60	34.0	667	5.9
SAS3	11.2	2.20	16.5	683	6.4
SAS4	10.3	1.85	12.5	767	6.6
SAS5	10.1	1.75	12.0	533	6.9

^aSaturated water absorption ratio of the films at 80°C for 24 h.

Soxhlet extraction, silicon content, and dynamic mechanical analysis of latex films confirmed the occurrence of copolymerization.

- Properties of latex film were significantly influenced by silicone content. With increasing silicone content, the water resistance and impact strength of latex films increased, whereas the hardness and tensile strength decreased.

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