

Preparation of Soap-Free Cationic Emulsion Using Polymerizable Surfactant

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ABSTRACT: A kind of polymerizable surfactant, methacryloyloxyethylhexadecyldimethylammonium bromide (DMHB) was used to synthesize soap-free cationic emulsion with styrene (St), methyl methacrylate (MMA), and methacryloyloxyethyltrimethylammonium chloride (MATMAC) by emulsion polymerization using 2,2'-azobis(isobutylamide hydrochloride) (AIBA) as a cationic initiator. The effects of polymerizable surfactant concentration, initiator concentration, and reaction temperature on the conversion of monomer were investigated. The results indicated that the rate of polymerization could be expressed as $R_p = k_p[AIBA]^{0.42}[DMHB]^{0.45}$ and the apparent

activation energy (E_a) was 83.42 kJ/mol. The particle size, ζ potential, and apparent charge density of cationic latices were also measured. The average diameter of copolymer particles decreased with increasing DMHB, MATMAC, and AIBA content; the charge properties of the particles were decided by the DMHB, MATMAC, and AIBA content. The polymerization mechanism is discussed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1111–1116, 2006

Key words: polymerizable surfactant; emulsion polymerization; cationic soap-free emulsion; kinetics

INTRODUCTION

Cationic soap-free latices prepared by emulsion polymerization have received increasing attention during the past decades. Cationic soap-free latices are widely used in numerous industrial and biomedical field such as chemical additives for papermaking, adhesives, mining and tertiary oil recovery, flocculation aids in wastewater treatment, diagnostic assays cell separation, and drug delivery systems.^{1–3}

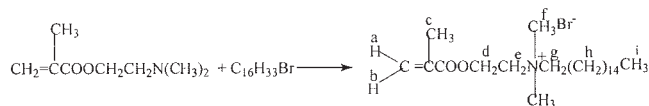
In conventional emulsion polymerization, latices are stabilized by surfactants. Removal of the stabilizer after polymerization is very difficult and coagulation may result, so it is difficult to gain functional polymer latices with a clean surface. Recently, a lot of work has been done regarding the preparation of cationic polymer latices by soap-free emulsion polymerization. Pierre et al.⁴ synthesized a cationic polymer of *n*-butyl methacrylate in an emulsifier-free system initiated by 2,2'-azobis(isobutylamide hydrochloride) (AIBA). Tang et al.⁵ prepared emulsifier-free cationic poly(styrene-methyl methacrylate) copolymer nanoparticles in acetone–water medium under microwave irradiation. To tailor particle characteristics, soap-free emulsion polymerizations are normally performed in the pres-

ence of a small amount of ionic comonomer. The incorporation of ionic monomer units in the copolymer chains can significantly decrease particle size and increase particle surface charge density. For example, Xu et al.⁶ described the soap-free emulsion copolymerization of hydrophobic styrene or acrylate and hydrophilic cationic comonomer *n*-butyl methacrylate ammonium bromide initiated by cationic radical initiator. Liu et al.⁷ reported that soap-free emulsion copolymerization of styrene with 2-(methacryloyloxy) ethyl trimethyl ammonium chloride (MATMAC) was performed in a mixture of water and ethanol. Several research groups^{8,9} also synthesized cationic functional latex via emulsion polymerization using water-soluble amphiphilic block copolymer composed of hydrophilic and hydrophobic segments in place of conventional small-molecule surfactants. But reports on preparing cationic soap-free emulsion using polymerizable surfactant are limited. The use of polymerizable surfactants in emulsion polymerization where the surfactant can copolymerize with monomers may improve the emulsion-stabilizing effects over that of conventional surfactants and inhibit subsequent surfactant migration. The polymerizable surfactants usually have no negative effects on polymerization rate or molecular weight of polymer obtained.

In the present work, we report on the preparation of cationic soap-free emulsion using a cationic polymerizable surfactant. This polymerizable surfactant can be imparted on the surface of latices by covalent attachment. First, we synthesized a cationic polymerizable

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Scheme 1

surfactant, methacryloyloxyethylhexadecyldimethylammonium bromide (DMHB), through a nucleophilic substitution reaction with dimethylaminoethyl methacrylate and *n*-hexadecane bromide. The DMHB was characterized with ^1H NMR, FTIR, and elemental analysis. The critical micelle concentration (CMC) of DMHB was measured. Batch emulsion polymerization was performed with styrene (St), methyl methacrylate (MMA), and comonomer MATMAC in the presence of polymerizable surfactant DMHB using AIBA as initiator. Effects of comonomer, initiator, and polymerizable surfactant concentration on polymerization rate and colloid properties of latex particles have been studied. Finally, the polymerization mechanism was discussed.

EXPERIMENTAL

Materials

Monomers such as St and MMA were distilled under reduced pressure and stored in a refrigerator prior to polymerization. The initiator was AIBA, supplied by Fluka Co., and it was kept at 4°C and used without further purification. MATMAC (75 wt % aqueous solution) and dimethylaminoethyl methacrylate, kindly provided by Qilu Petrochemical Co., were used as received. *n*-Hexadecane bromide was purchased from Fluka Co. Double-distilled deionized water was used throughout, and all polymerizations were conducted in a nitrogen atmosphere.

Preparation of DMHB

DMHB was prepared according to Scheme 1.¹⁰ In a flask equipped with a stirrer, thermometer, and reflux condenser, 1 mol freshly distilled dimethylaminoethyl methacrylate containing a little hydroquinone was re-

TABLE I
Recipe for Preparation of Cationic Soap-Free Latex by Batch Emulsion Polymerization

Ingredients	Amount (g)
Styrene	18
Methyl methacrylate	18
DMHB	X
AIBA	Y
MATMAC	0–6
Water	160

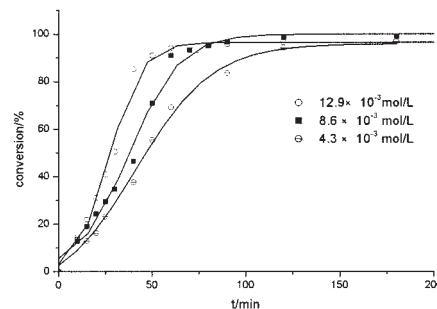


Figure 1 Effect of emulsifier concentration on R_p (St: 0.962 mol/L; MMA: 1 mol/L; MATMAC: 0.05 mol/L; AIBA: 9.2×10^{-3} mol/L, T 65°C).

acted with 1 mol *n*-hexadecane bromide in acetone (about twofold volumes to total reactants) at 40°C for 20 h. After removal of acetone, anhydrous ether was added, and the precipitated solid was filtered and recrystallized repeatedly in dry ethyl acetate. Yield was 60%. The purified product was characterized by FTIR, ^1H NMR, and elemental analysis. Anal. calcd. for $\text{C}_{24}\text{H}_{48}\text{BrNO}_2$: C 62.27 wt %; N 2.88 wt %; H 10.57 wt %; found: C 62.35 wt %; N 3.03 wt %; H 9.95 wt %. FTIR (KBr, cm^{-1}): = C-H 3030; -C-H 2917 and 2849; C = O 1721; C = C 1634; C-O 1172. ^1H NMR (CDCl_3 , ppm): a 5.70(s,1H); b 6.16(s,1H); c 1.97(s,3H); d 4.67(s,2H); e 4.20(s,2H); f 3.53(s,6H); g 3.61, 3.62, 3.63 (t,2H); h 1.26–1.36(m,28H); i 0.88, 0.89, 0.90 (t,3H). The surface activity of DMHB at the air–water interface was measured by K122 full-automatic surface tension measurement instrument at 25°C . The result showed that the CMC of DMHB is 3.68×10^{-4} mol/L.

Preparation of copolymer emulsion

Polymerizations were carried out in a 250-mL flask equipped with stirrer, reflux condenser, and inlet system for nitrogen. Copolymer emulsions were prepared in a batch process using the recipes given in Table I. All reactants and water, except for the initiator, were charged into the reactor. The mixture was

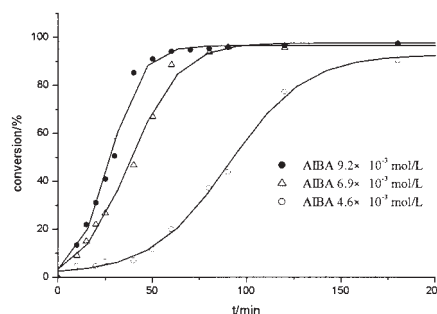


Figure 2 Effect of initiator concentration on R_p (St: 0.962 mol/L; MMA: 1 mol/L; MATMAC: 0.05 mol/L).

TABLE II
Effects of DMHB Concentration on R_p

$E \times 10^3$ (mol/L)	$\text{Ln}E$	dc/dt (min^{-1})	$R_p \times 10^4$ ($\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)	$\text{ln}R_p$
4.3	-5.449	0.01313	4.29	-7.754
8.6	-4.756	0.01789	5.85	-7.444
12.9	-4.351	0.02152	7.04	-7.259

bubbled with nitrogen for about 30 min, and then a very slow surface nitrogen flow was maintained. The polymerizations temperature was controlled at 65°C by partially immersing the reactor in a thermostated water bath. As the temperature of the flask approached 65°C, the initiator in aqueous solution was injected using a glass syringe to start polymerization. The operation conditions were identical for all polymerizations carried out in this work.

Determination of conversion

Monomer conversions were followed by a gravimetric method¹¹. A latex sample withdrawn from the reactor at various time intervals was added with hydroquinone solution to stop the polymerization. The contents were dried in an oven to constant weight. Conversion of this sample can be calculated from the original monomer content and polymer weight obtained. The polymerization rates (R_p in $\text{mol L}^{-1} \text{s}^{-1}$) were deduced from the conversion and time curves. $R_p = dc/dt \times [M_0]$, where dc/dt is the slope of the curve when the conversion is between 20 and 70%, and $[M_0]$ is the concentration of St and MMA.

Latex particle size and morphologies

Latex particle average diameter (D_p) and distribution were determined in water by dynamic light scattering, using Mastersizer2000. Uniformity was used to judge the dispersivity of the latex particles. The distribution of the latex particles was more homogeneous when the number value of uniformity was less. In addition, latex particle morphologies was determined by a JEM-100CXII transmission electron microscopy (TEM). The method was as follows: the emulsion was diluted to about 50 ppm and a drop was placed onto a copper grid and allowed to dry at room temperature. The

TABLE III
Effects of AIBA Concentration on R_p

$I \times 10^3$ (mol/L)	$\text{Ln}I$	dc/dt (min^{-1})	$R_p \times 10^4$ ($\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)	$\text{ln}R_p$
4.6	-5.382	0.00927	3.03	-8.102
6.9	-4.976	0.01596	5.22	-7.558
9.2	-4.689	0.02152	7.04	-7.259

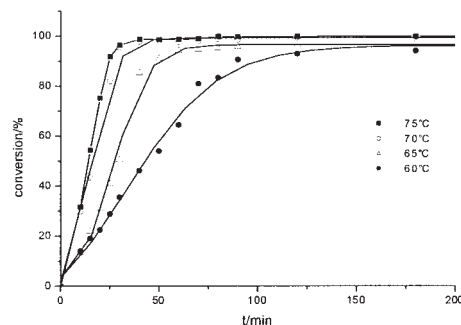


Figure 3 Effect of temperature on R_p (St: 0.962 mol/L; MMA: 1 mol/L; MATMAC: 0.05 mol/L; DMHB: 0.0129 mol/L; AIBA: 9.2×10^{-3} mol/L).

section was stained with a phosphotungstic acid aqueous solution.

ζ potential of latex

The ζ potential of cationic latices was determined from electrophoretic mobility measurements with a JS94F microelectrophoresis instrument. The latex samples were cleaned by dialysis against deionized water until the conductivity of the surrounding water reached a constant level, lyophilized, and redispersed in 0.1 wt % NaCl aqueous solution at 25 °C. Five repeats were conducted.

Colloid titration

The apparent charge density of the cationic latices was determined by colloid titration using a MUTEK PCD03 pH particle charge detector. The latex samples after purification were diluted to 100 mg/L. The mixture was titrated with 0.1 mN potassium polyvinyl sulfate (PVSU). The apparent charge density of these copolymers (E_p) was explained as equivalent mole of charge groups per gram of polymer, calculated according to the following equation: $E_p = V \times C/Wt$, where V is the volume of PVSU solution, C is the concentration of PVSU solution, and Wt is the mass of polymer.

TABLE IV
Effect of Temperature on R_p

T/K	dc/dt (min^{-1})	$R_p \times 10^4$ ($\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)	$\text{ln}R_p$
333	0.01309	4.28	-7.756
338	0.02152	7.04	-7.259
343	0.03148	10.3	-6.878
348	0.04348	14.2	-6.557

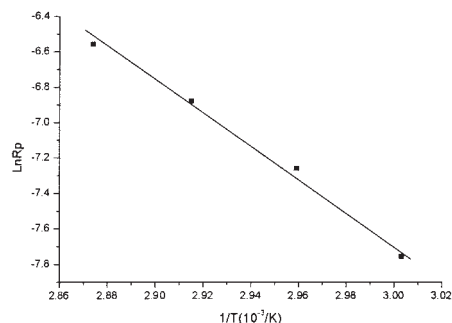


Figure 4 Arrhenius plot for polymerization.

RESULTS AND DISCUSSION

Kinetics study of emulsion polymerization

In the kinetic studies, conversion versus time curves at different DMHB and AIBA contents are shown in Figures 1 and 2, respectively. They indicate that the conversion rate increases with increasing DMHB or AIBA concentrations. This is because the numbers of micelle and free radicals increase when the concentration of polymerizable surfactant DMHB and initiator AIBA increase. From Tables II and III we can deduce that $R_p \propto [\text{DMHB}]^{0.45}[\text{AIBA}]^{0.42}$. Conversion versus time curves for emulsion polymerization in different temperature are reported in Figure 3. As shown in Figure 3, temperature has a dramatic effect on polymerization rate. The polymerization rate and conversion increase with increasing temperature. Obviously, an increase in temperature should lead to an increase in the decomposition rate of the initiator. Studies have shown that the half-life of the initiator (AIBA) is 300 min at 60°C and 38 min at 70°C¹². Furthermore, an increase in temperature can accelerate the diffusion rate of radicals and monomers. As a consequence, the polymerization rate increases. From the data of Table IV, the $\ln R_p$ versus $1/T$ curve is shown in Figure 4; the apparent activation energy is 83.42 kJ/mol according to the Arrhenius equation.

Particle size, distribution and properties

To understand how each of the polymerization conditions such as DMHB, AIBA, and MATMAC content

TABLE V
Effect of DMHB Concentration on the Properties of Latex Particles

Sample	DMHB $\times 10^3$ (mol/L)	D_p (nm)	Uniformity	ζ potential (mV)	E_p ($\mu\text{eq/g}$)
D1	8.6	119	0.2644	24.64	377
D2	12.9	112	0.2596	25.67	426
D3	17.3	107	0.2562	25.98	472

TABLE VI
Effect of AIBA Concentration on the Properties of Latex Particles

Sample	AIBA $\times 10^3$ (mol/L)	D_p (nm)	Uniformity	ζ potential (mV)	E_p ($\mu\text{eq/g}$)
A1	4.6	130	0.2831	23.13	320
A2	6.9	122	0.2634	24.19	359
A3	9.2	119	0.2644	24.64	377

affect the particle average diameter and colloid properties, a series of latex particles was prepared by varying one factor at a time.

Effect of DMHB concentration

The polymerizable surfactant has an important influence on emulsion polymerization. Table V shows the particle size, distribution, ζ potential, and apparent charge density as a function of DMHB concentration at constant AIBA and MATMAC content. The results indicate that with rising surfactant concentration, the particle average diameter decreases, the distribution of latex particles becomes more homogeneous, and ζ potential and apparent charge density of latices also increase.

Effect of AIBA concentration

Table VI shows the particle size, distribution, ζ potential, and apparent charge density as a function of AIBA concentration at constant DMHB and MATMAC content. The particle average diameter decreases as the concentration of AIBA increases. AIBA is a water-soluble cationic initiator decomposing to two positively charged radicals; these positive charges carried on the initiator will provide the stabilization of the latex particles. When the initiator concentration increases, more latex particles are formed; as a result, the particle average diameter decreases. On the contrary, the ζ potential and apparent charge density of latex particles increase.

TABLE VII
Effect of MATMAC Concentration on the Properties of Latex Particles

Sample	MATMAC (mol/L)	D_p (nm)	Uniformity	ζ potential (mV)	E_p ($\mu\text{eq/g}$)
M1	0.1	119	0.2644	24.64	377
M2	0.152	109	0.2576	26.67	604
M3	0.2	106	0.2545	28.89	759
M4	0.253	102	0.2447	31.62	883

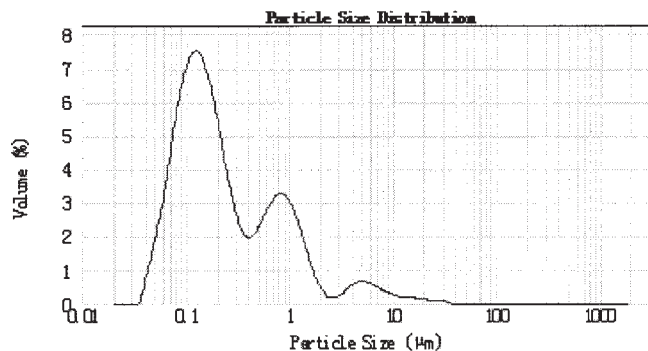


Figure 5 Emulsion polymerization in the absence of MATMAC (St: 0.962 mol/L; MMA: 1 mol/L; DMHB: 0.0129 mol/L; AIBA: 9.2×10^{-3} mol/L, T 65 °C).

Effect of MATMAC concentration

Table VII shows the particle size, distribution, ζ potential, and apparent charge density as a function of MATMAC concentration at constant DMHB and AIBA content. The results indicate that higher MATMAC concentration results in smaller particle size and better dispersivity. When the content of MATMAC increases, the ionic strength in this system also increases, the CMC of DMHB decreases, and more micelles are formed, so the particle average diameter decreases. An increase in MATMAC concentration can lead to more ionic monomer units incorporated in the copolymer chain, which tend to stabilize the particles via electrostatic repulsion. ζ potential and apparent charge density of the latex particles increase with rising MATMAC content.

Polymerization mechanism

Emulsion polymerization is a kind of important industrial technology yielding synthetic elastomers, paint, adhesives, etc. In a classic emulsion polymerization, the polymerization of a scarcely water-soluble mono-

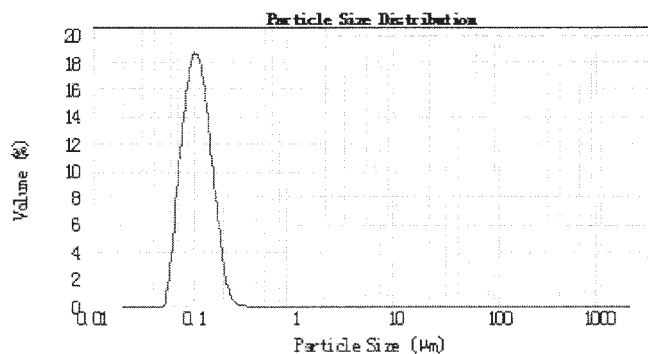


Figure 6 Emulsion polymerization in the presence of MATMAC (St: 0.962 mol/L; MMA: 1 mol/L; DMHB: 0.0129 mol/L; AIBA: 9.2×10^{-3} mol/L; MATMAC: 0.15 mol/L, T 65 °C).

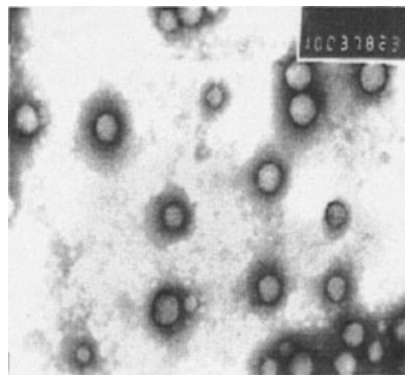


Figure 7 TEM image of emulsion; magnification ratio 100,000.

mer in the presence of a water-soluble initiator and a surfactant, there are mainly two kinds of nucleation theory: one is micelle nucleation mechanism and another is homogeneous nucleation mechanism. As Munro et al.¹³ suggested, none of the mechanisms alone can predict nucleation for all monomers. The solubility of monomer in water has a great influence on the nucleation mechanism.

To avoid the disadvantageous effects caused by small molecular surfactant, we chose the cationic polymerizable surfactant DMHB to carry out emulsion polymerization. DMHB has a molecular structure analogous to cationic surfactants and hence it can form a micelle. DMHB is easy to use for homopolymerization and copolymerization with another vinyl monomer. Unlike an ordinary polymerizable surfactant, the double bond in the DMHB molecular structure is part of the hydrophilic segment; the methacryloyl group is likely distributed over the outer surface of micelle in the water phase when the concentration of DMHB is greater than its CMC value. Therefore, it is possible to form crosslinking polymer particles that could not disperse in water during the polymerization process¹⁴. When the emulsion polymerization of St

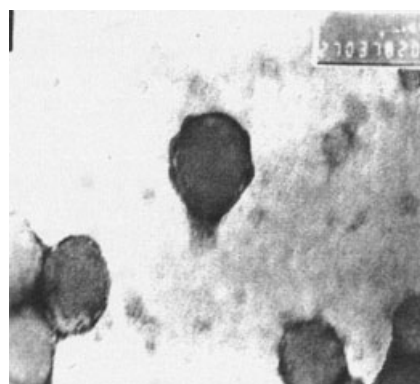


Figure 8 TEM image of emulsion; magnification ratio 270,000.

and MMA was conducted in the presence of DMHB initiated by AIBA, an unstable latex was attained. Its particle size distribution was heterogeneous as shown in Figure 5; the coalescing particles were formed as a result of crosslinking between latex particles and precipitate during the storage process. But when a certain concentration of MATMAC was added to this system mentioned above, obtained stable and monodisperse latex. Its particle size distribution was homogeneous as shown in Figure 6, and its TEM image is shown in Figure 7. This is probably because the incorporation of ionic repeat units in the copolymer chain can effectively enhance the electrostatic stability of particles and retard the coagulation of particles.

The polymerization mechanism could be explained as follows: at the start of polymerization, cationic radicals are formed by dissociation of the water-soluble initiator AIBA; these react with monomer, dissolving in aqueous phase such as St, MMA, DMHB, and MATMAC, to form oligomer-free radicals. These oligomer-free radicals diffuse to the surface or inside of the micelle to initiate the polymerization of monomers. Alternatively, these oligomer-free radicals may react continuously in the water phase to coil up and form primary particles or aggregate to form micelles, which can absorb monomers to continue the polymerization. An important factor must be taken into account: MATMAC is water-soluble monomer and bears a positive charge. The hydrophilic segments mainly composed of MATMAC units in the copolymer are inclined to distribute on the surface of latex and maybe produce short hairs on the particle surface, which can prevent the aggregation between particles by electrostatic interactions and steric hindrance. As shown in Figure 8, the surface of the particles is not smooth. Of course, it is inevitable to generate a small amount of polyelectrolytes. Particle-formation mechanism is depicted in Figure 9.

CONCLUSIONS

We have attempted the synthesis of soap-free cationic emulsion using the polymerizable surfactant methacryloxyethylhexadecyldimethylammonium bromide. The polymerizable surfactant was characterized with ^1H NMR, FTIR, and elemental analysis. The CMC of

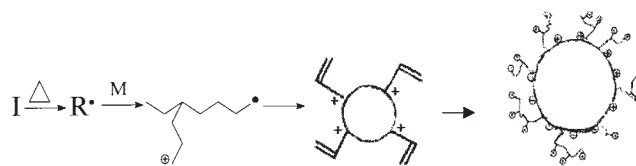


Figure 9 Schematic showing the particle formation mechanism.

the surfactant was 3.68×10^{-4} mol/L. The polymerization kinetics studies indicate the polymerization rate can be expressed as $R_p = k_p[\text{AIBA}]^{0.42}[\text{DMHB}]^{0.45}$, and the apparent activation energy is 83.42 kJ/mol. The average diameter of latex particles decreases with increasing DMHB, MATMAC, and AIBA concentration, and the ζ potential and apparent charge density of latex particles increase with DMHB, MATMAC, and AIBA concentration. During the investigation process, we found that we could not attain stable and monodisperse latex using this surfactant in the absence of MATMAC because the polymerizable group in this surfactant is likely to distribute over the outer surface of the micelle. Instead, a stable and monodisperse latex can be prepared when a suitable amount of MATMAC is added to the polymerization system.

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