

Core-Shell Latex Synthesized by Emulsion Polymerization Using an Alkali-Soluble Resin as Sole Surfactant

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ABSTRACT: A series of alkali-soluble resins were prepared from esterification reaction of styrene-maleic anhydride copolymer (SMA) and four fatty alcohols having different alkyl chains. The critical aggregates concentration of the prepared hemiester was lower than SMA, indicating that modification of SMA resin with long alkyl chains could improve their emulsification efficiency. The detailed experiments of emulsion polymerization of methyl methacrylate and butyl acrylate using these hemiesters as sole surfactants showed that SMA-C12-75, SMA-C14-70, and SMA-C16-65 were good surfactants. In the end, we successfully prepared stable latexes using above three good surfactants with relatively low surfactant concentration and high solid content. Characterization of latexes by Zetasizer and transmission electron microscopy revealed that particles of these latexes have core-shell nanostructure with average particle size below 60 nm. Compared with SMA, the improvement of emulsification efficiency of its hemiesters may come from the better hydrophilic-lipophilic balance and steric stabilization after incorporation of long alkyl chain. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4224–4230, 2013

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INTRODUCTION

Over the past decades, core-shell latexes in size of nanometers have attracted much attention in many applications,^{1–7} such as film fabrication, drug delivery, paper and textile manufacturing and impact modifiers, by taking advantage of the synergically enhanced properties over their single-component counterparts when the core and shell polymers are optimally designed.

Particularly, the amphiphilic core-shell polymer dispersions^{8,9} with relatively robust hydrophilic shell and hydrophobic core can exhibit better pigment dispersion, wetting and rewet properties, and free-thaw stability. These amphiphilic core-shell polymers are usually prepared by emulsion polymerization using alkali-soluble resins (ASRs) as surfactants.^{10–18} ASRs are copolymers of monomers containing carboxylic acid or acid anhydride groups and some hydrophobic monomers. In the two-stage preparation process of amphiphilic core-shell polymers, ASRs are firstly dissolved in alkali aqueous solutions and then formed micelle-like aggregates above the critical aggregates concentration (CAC), which are followed by hydrophobic monomers polymerization to form core polymers within the aggregates. ASRs are commonly used at high levels (≥ 20 wt % based on dry polymer) in emulsion polymerization to provide enough good colloidal stability; therefore, they behave like

hydrophilic shell with enough thickness when absorbed at outer surface of core polymers.

In general, there are two important groups of ASRs. One group contains random copolymers of acrylic acid^{10–14} or methacrylic acid¹⁵ and hydrophobic monomers such as styrene and butyl acrylate. High solid latexes (e.g., 40%) with good colloidal stability can be prepared through using these copolymers as polymeric emulsifiers.¹⁴ The other group is styrene-maleic anhydride (SMA) copolymer resins.^{16–18} SMA resins with different molecular weights¹⁶ and different molar ratios of styrene to maleic anhydride¹⁷ have been studied. However, the solid content of the prepared latexes using SMA as sole surfactant is very low (no more than 25%) and colloidal stability is not good, indicating that SMA resins are not good stabilizers for polymer dispersions.

In this article, we report on facile synthesis of SMA derivatives (i.e., hemiester coming from the reaction of SMA with fatty alcohol having long alkyl chain) and nanosized latexes using hemiesters as sole surfactants. Incorporation of long alkyl chain not only decreases the acid number but also increases hydrophobic parts of the derivatives, thus providing better hydrophilic-lipophilic balance and offering the derivatives better steric stabilization effect from their long side chain structure, so the

Table I. Typical Recipe of Emulsion Polymerization using SMA Hemiester as Sole Surfactant^a

Components	Amount (g)
SMA hemiester	64
Ammonium hydroxide	5
MMA	84
BuA	169
APS	2
Deionized water	476 (350 + 126)

^aTotal solution weight = 800 g; solid content = 40%; SMA hemiester concentration is about 20% based on dry polymer.

SMA hemiesters should perform better as stabilizers for emulsions than SMA itself. Actually, we have successfully prepared styrene-acrylic latexes using SMA derivatives as the only colloid stabilizers. The obtained latexes have following characteristics, which have not been reported in similar works about SMA ASRs: (1) substantially lower stabilizer amount (≤ 15 wt % on a dry polymer base); (2) relatively high solid contents (to ca. 40%); (3) clear core-shell morphology.

EXPERIMENTAL

Materials

SMA 1000P, alternative copolymer of styrene and maleic anhydride (Mn: 2459; Mw: 5562; acid number: 480 mg KOH/g), obtained from Sartomer company, was used as received. From the acid number of SMA 1000P, we could estimate that it had about 10 maleic anhydride groups per chain. Butanol, dodecanol, tetradecyl alcohol, and hexadecanol were obtained from Yonghua Fine Chemicals (Jiangsu China). Ammonium persulfate (APS), ammonium hydroxide (25% wt solution in water) and 4-dimethyl aminopyridine (DMAP) were purchased from Shanghai Sinopharm (Shanghai China). Methyl methacrylate (MMA, Jilin petrochemical), butyl acrylate (BA, Gaoqiao petrochemical), and tetrahydrofuran (THF, Qiangsheng Chemicals) were commercial products and they were all used as supplied. Deionized water was used throughout.

Synthesis of SMA Hemiester

According to Olea et al.,¹⁹ the esterification reactions were carried out in THF solution at 65°C in presence of DMAP as the catalyst. Typically, SMA1000P (50 g) and tetradecyl alcohol (42.8 g) were stirred in THF (200 g) until all the materials dissolved, then DMAP (0.3 g) was added and the reaction solution was kept at about 65°C for 8 h. The products were precipitated in deionized water and the white solid was collected by filtration.

Emulsion Polymerization Using SMA Hemiester

Core-shell latexes were prepared by semicontinuous emulsion polymerization using the recipe shown in Table I. A typical procedure is described as follows: In an 1 L round-bottom glass flask equipped with nitrogen inlet and stirrer, SMA hemiester (64 g), deionized water (350 g), and ammonium hydroxide (5 g) were added and stirred at about 60°C until the hemiester dissolved. When the reaction solution was heated to 85°C, APS

solution (2 g APS dissolved in 126 g deionized water) and the mixture of MMA (84 g) and BA (169 g) were added semicontinuously for 3 h from two dropping funnels.

Surface Tension

SMA and SMA hemiesters were dissolved in deionized water by adding adequate ammonium water to prepare a solution with concentration of 50 g/L, which was then serially diluted. The surface tension of these solutions was then measured by using surface tensiometer (automatic surface tensiometer BZY-1, Hengping Instrument, and Meter Factory, Shanghai, China).

Characterization of SMA Hemiester

Infrared (IR) Spectroscopy characterization of the SMA hemiesters was performed by Nicolet FTIR 6700. Differential scanning calorimeter (DSC) characterization was conducted on TA Q100 instrument with a 20°C/min heating rate. The average molecular weight was measured by gel permeation chromatography (GPC, Waters Breeze). SMA and its hemiesters powder dissolved in THF were injected at a sampling rate of 1.0 μ L/s. SMA hemiesters were further characterized using ¹H-NMR spectroscopic technique performed on a Bruker AVANCE (500 MHz) spectrometer, employing CD₃SOCD₃ solvent.

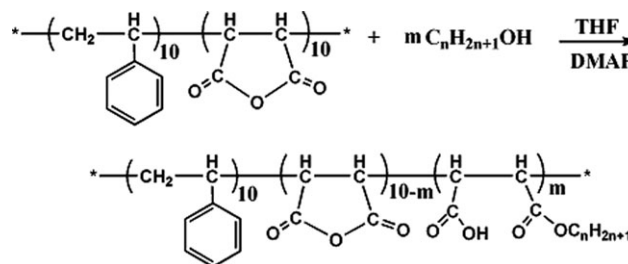
Latex Characterization

The average particle size and size distribution of latex particles were determined using Zetasizer ZEN3600 (Malvern, Britain). Core-shell structure of latexes was observed by Transmission electron microscope (TEM) JEM-2100 (JEOL, Japan) with accelerator voltage of 200 kV. The sample was prepared by adding a drop of diluted dispersions on a carbon-coated copper grid. Upon drying, the particles were stained with a small drop of 0.5 wt % phosphotungstic acid solution for 2 min and then dried at room temperature before TEM analysis. The minimum film forming temperature (MFT) of latexes were determined by Rigaku IV605 MFT tester.

RESULTS AND DISCUSSIONS

Synthesis and Characterization of SMA Hemiester

SMA 1000P is chosen here as the starting material because it has the most maleic anhydride groups which can be easily modified with alcohol by esterification reaction. Four kinds of alcohol, which have different long alkyl chain, that is, butanol, dodecanol, tetradecyl alcohol, and hexadecanol, are used in this article. The preparation process is shown in Scheme 1. For each alcohol, we have performed series of synthesis reactions with different molar ratios of alcohol to maleic anhydride in SMA.



Scheme 1. Synthesis process of SMA hemiesters.

Table II. Parameters and Results of Some Important Esterification Reactions

Sample name	Alcohol	[−OH]/[MA] ^a	AV ^b (mg KOH/g)	T _g ^c (°C)	Result of emulsion polymerization ^d
SMA 1000P	–	–	480	152	N
SMA-C4-20	Butanol	0.2	443	137	N
SMA-C4-60	Butanol	0.6	315	122	N
SMA-C4-100	Butanol	1.0	199	105	N
SMA-C12-20	Dodecanol	0.2	439	126	N
SMA-C12-75	Dodecanol	0.75	265	89	Y
SMA-C12-100	Dodecanol	1.0	139	73	N
SMA-C14-20	Tetradecyl alcohol	0.2	429	119	N
SMA-C14-70	Tetradecyl alcohol	0.7	247	87	Y
SMA-C14-100	Tetradecyl alcohol	1.0	129	65	N
SMA-C16-20	Hexadecanol	0.2	423	112	N
SMA-C16-65	Hexadecanol	0.65	245	81	Y
SMA-C16-100	Hexadecanol	1.0	123	57	N

^a[−OH]/[MA] is the molar ratio of alcohol to maleic anhydride in SMA 1000 P, ^bAV is the measured acid number, ^cT_g is the glass transition temperature of the synthesized sample determined by DSC measurement, ^dThe emulsification efficiency of the synthesized sample was evaluated by emulsion polymerization using the recipe shown in Table I. 'N' denotes the failure and 'Y' denotes the success on preparation of stable latexes with 40 % solid contents.

Parameters and results of some important reactions are listed in Table II.

The success of esterification reaction is first evidenced by IR characterization. Figure 1 shows the IR spectra of SMA 1000P and its typical hemiesters (SMA-C12-75 and SMA-C12-100). The bands at 1856 and 1778 cm^{−1} are attributed to the characteristic absorption of carbonyl group in anhydride. In the spectrum of SMA-C12-75, we can observe the decrease in intensity of characteristic anhydride bands and appearance of bands at 1730, 1707, 2925, and 2854 cm^{−1} that are assigned to absorp-

tion of the ester carbonyl groups, the acid carbonyl groups, and the methylene groups of long alkyl chain, respectively. Those observations are in accordance with the formation of SMA hemiester. For SMA-C12-100, which is the product of SMA and dodecanol with molar ratio of [OH]/[MA] to be 1.0, the almost invisible bands at 1856 and 1778 cm^{−1} in IR spectrum indicate that most anhydride groups of SMA have reacted with dodecanol.

Hemiesters were further characterized by ¹H-NMR spectra (Figure 2). For the SMA 1000P, the resonance peak at 7.0–7.4 ppm is ascribed to the protons of the benzene ring, while the peak at 2.1 ppm is associated with the maleic anhydride backbone. As compared with spectrum of SMA 1000P, some new resonance peaks appear at the spectrum of SMA-C12-100. The weak and broad peak at 12.2 ppm is assigned to proton of

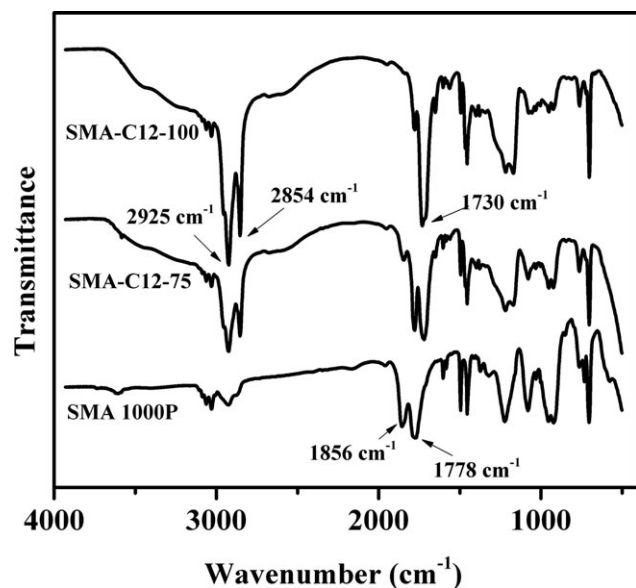


Figure 1. IR spectra of SMA 1000P and its typical hemiesters, SMA-C12-75, and SMA-C12-100.

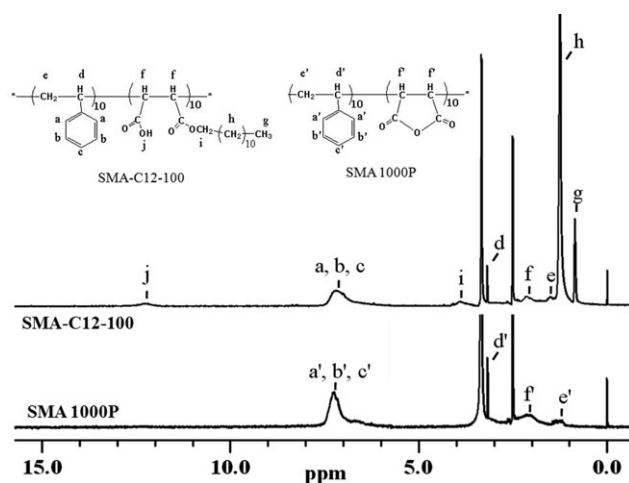


Figure 2. ¹H-NMR spectra of SMA 1000P and SMA-C12-100.

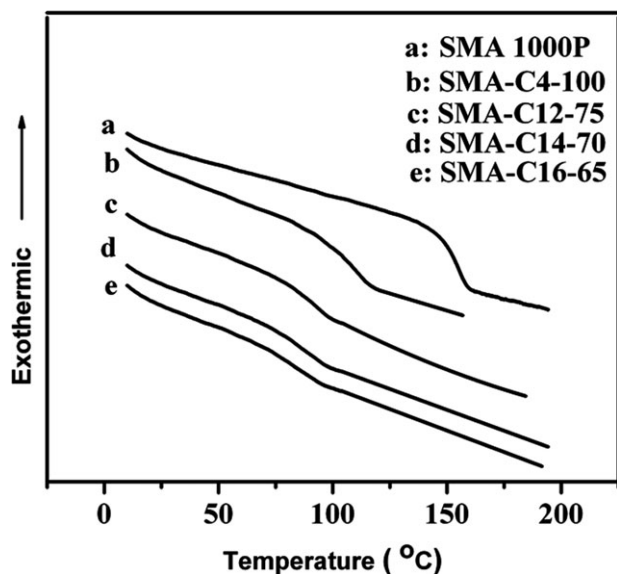
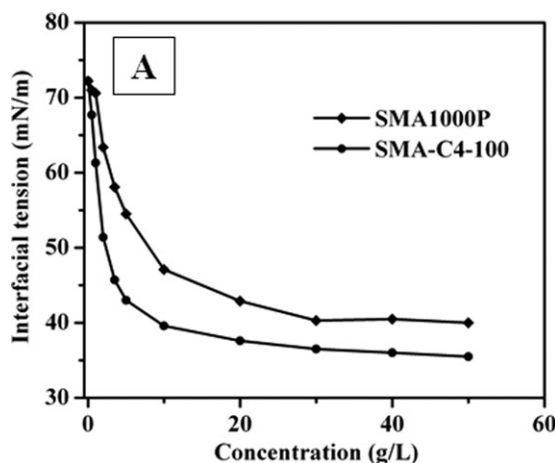


Figure 3. DSC curves of SMA and four typical hemiesters.

carboxylic acid, revealing that the maleic anhydride ring was opened. The peaks at 3.9, 1.2, and 0.8 ppm are assigned to protons of introduced dodecyl chain. Appearance of these new peaks indicate that the esterification of SMA 1000P with dodecanol is successful.

The formation of SMA hemiesters is also supported by the GPC measurement data (now shown herein). The number average molecular weight of the SMA, SMA-C12-75, and SMA-C12-100 are 2459, 3050, and 3459, respectively. It is reasonable that the molecular weight of hemiesters increases because the amount of fatty alcohol introduced into the SMA backbone increases.

DSC curves of SMA and some typical hemiesters are shown in Figure 3, from which we can see that SMA 1000P has the highest glass transition temperature (T_g). After incorporation of fatty alcohol, the T_g of hemiesters gradually decreased as the amount of alcohols or the length of alkyl chains increased. T_g data of all hemiesters are listed in Table II.



Interfacial Tension of SMA Hemiester Solution

We have examined the emulsification efficiency of SMA hemiesters through emulsion polymerization using them as sole surfactants and found that SMA-C12-75, SMA-C14-70, and SMA-C16-65 can be good surfactants for emulsion polymerization with the recipe shown in Table I. The critical micelle concentration (CMC) is another important parameter to evaluate the emulsification efficiency of a surfactant. Polymeric surfactants can form micelle-like aggregates in solution above CAC. By using the interfacial tension measurements, we have determined the CAC of three hemiesters with good emulsification efficiency as well as that of SMA and SMA-C4-100 to make a comparison.

The results of their interfacial tension as a function of surfactant concentration are given in Figure 4. The interfacial tension of SMA 1000P and SMA-C4-100 solution decreased when the concentration increased. The break in the curve is not obvious, which can be attributed to the heterogeneity and complexity of their aggregation behavior. We can just estimate the CAC value of SMA 1000P and SMA-C4-100 to be 30 and 20 g/L, respectively. Compared with CMC of conventional surfactants (<1 g/L), the obviously high CAC of SMA 1000P and SMA-C4-100 indicate that both of them are not good surfactants, which is also evidenced by the fact of failure on preparation of stable latexes with 40% solid contents.

However, the break in the curves for three hemiesters, that is, SMA-C12-75, SMA-C14-70, and SMA-C16-65, is more obvious and easier to distinguish [Figure 4(B)]. From the curves, we can get the CAC of three hemiesters as listed in Table III. After incorporation of longer alkyl chains, the CAC of the obtained hemiesters sharply decreased from 20 to smaller than 3 g/L. Therefore, we can expect that these three hemiesters are good surfactants for latexes preparation. Actually, we have successfully prepared stable latexes with high solid content using them as sole surfactants, which will be discussed in detail later in this article.

Emulsion Polymerization Using Hemiester as Sole Surfactant

We have synthesized series of SMA hemiesters with four different fatty alcohol and different molar ratios of alcohol to maleic

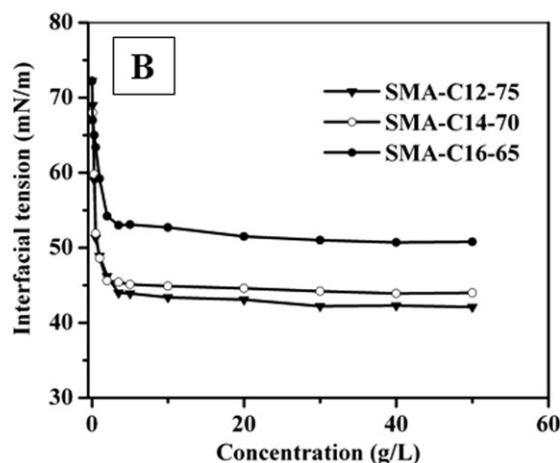


Figure 4. Interfacial tension of ammonium salt of SMA and four typical hemiesters.

Table III. CAC of Typical Surfactants

Surfactant	SMA 1000P	SMA-C4-100	SMA-C12-75	SMA-C14-70	SMA-C16-65
CAC (g/L)	30	20	3.4	2.2	2.4

anhydride for each fatty alcohol, which are listed in Table II. The results of emulsion polymerizations using these hemiesters as sole surfactants show that stable latexes can be prepared only when the surfactant is SMA-C12-75, SMA-C14-70, or SMA-C16-65 and their concentration is as high as 20% (based on dry polymers). Here, we have further studied the emulsion polymerization with varying concentration of these three good surfactants and the corresponding results are listed in Table IV.

For three surfactants, stable latexes could still be prepared without any coagulum when the surfactant concentration decreased to 15% (The images of the synthesized latexes are shown in Figure 5). However, when the surfactant concentration further decreased to 10%, all the latexes were not stable and the amount of coagulum was above 37% of the total polymer. It is worthy to mention that the successful preparation of latexes with relatively high solid content (40%) and relatively low surfactant concentration (15%) have not been reported with SMA derivatives or even other ASRs as surfactants.

SMA has high acid number (480 mg KOH/g), indicating its good hydrophilicity, so it can not form stable micelle-like aggregates below CAC of 30 g/L and the emulsification efficiency of SMA is not good when it is used as sole surfactant. After introduction of appropriate amount of fatty alcohol into SMA backbone, the long alkyl chains, acting as lipophilic parts, increase the hydrophobicity of hemiesters and decrease their CAC. In

Table IV. Characteristics of Latexes Using Hemiesters as Sole Surfactants^a

Sample Name	[Surf] ^b (%)	Stability ^c	Coagulum (%)	Particle size (nm)	
				SA ^d	TEM ^e
L1	10	N	48	-	-
L2	15	Y	0.1	59	55
L3	20	Y	0	51	47
L4	10	N	40	-	-
L5	15	Y	0	43	36
L6	20	Y	0	38	33
L7	10	N	37	-	-
L8	15	Y	0	48	46
L9	20	Y	0	41	38

^aThe recipe is similar to that listed in Table I. The amount of deionized water, APS, and ammonium hydroxide were kept unchanged. The solid content was set to be 40%. The weight ratio of BA to MMA is set to be 2 and the amount of hemiesters is varied according to [Surf] in Table IV, ^b[Surf] is the concentration of used surfactant based on weight of dry polymer. For latex L1, L2, and L3, the surfactant is SMA-C12-75. For latex L4, L5, and L6, the surfactant is SMA-C14-70. For latex L7, L8, and L9, the surfactant is SMA-C16-65, ^cN, unstable; latex with great amount of coagulum during or immediately after the preparation. Y, stable; latex with almost no coagulum after the preparation, ^dParticle size determined using Malvern Zetasizer ^eAverage size determined from TEM images.

addition, the steric stabilization effect of hemiesters is also improved from relatively long side chain, which can protect the latex from coagulating. Therefore, we think that the good emulsification efficiency of obtained hemiesters may come from two improvements: (1) better hydrophilic-lipophilic balance after incorporation of hydrophobic alkyl chain; (2) better steric stabilization effect from long alkyl chain.

Particle Size of Latexes

We have determined the particle size of obtained stable latexes by using Malvern Zetasizer. The results of typical latexes with surfactant concentration of 15% are shown in Figure 6, from which we can find that all particles of latexes are below 100 nm in size with narrow size distribution and the average particle sizes of L2, L5, and L8 are 59, 43, and 48 nm, respectively. Small particle sizes of latexes are also in accordance with their translucent appearance as shown in Figure 5. The particle sizes of other three



Figure 5. Photograph of three stable latexes: left, L2; middle, L5; right, L8. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

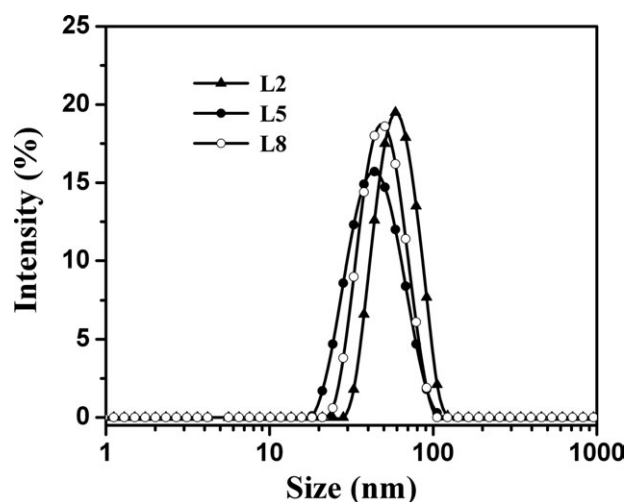


Figure 6. Particle size and size distribution of three latexes.

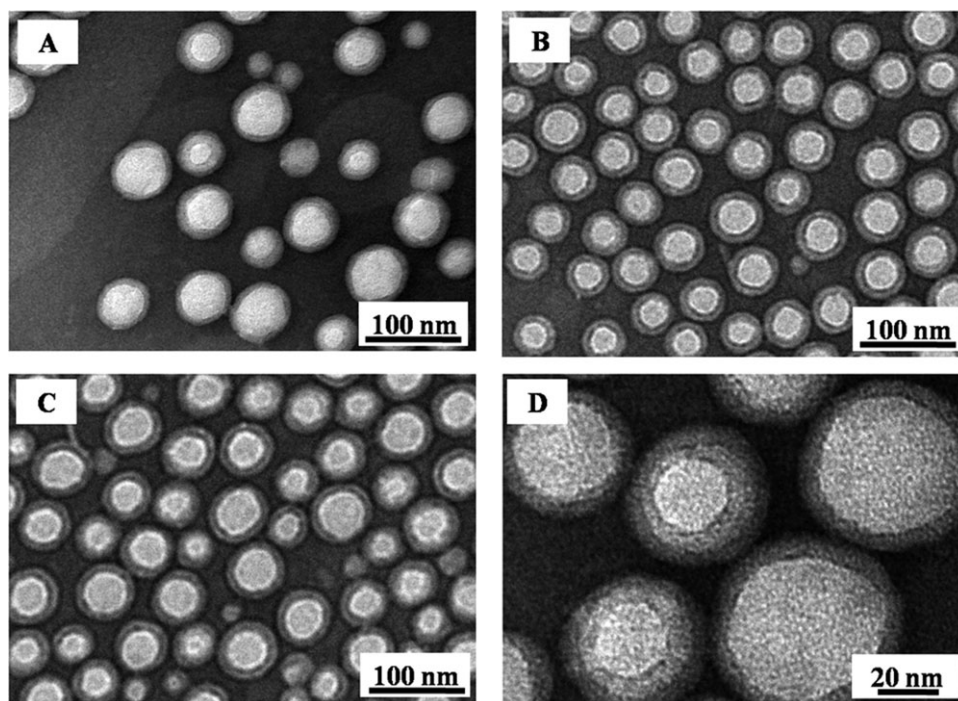


Figure 7. TEM images of three stable latex: (A) L2; (B) L5; (C) and (D) L8.

stable latexes, that is, L3, L6, and L9, have also been determined and the value was listed in Table IV. A similar fact for three surfactants is that the particle sizes of latexes slightly decreased when the surfactant concentration increased from 15 to 20%.

Core-Shell Structure of Latexes

The morphology of stable latexes was observed using TEM measurements. Their images are shown in Figure 7. The darker shells indicate the presence of SMA hemiester due to stronger

electron scattering from benzene ring after phosphotungstic acid staining, while the lighter cores are the copolymer of MMA and BA. All images clearly reveal the core-shell nanostructure, where the copolymer of MMA and BA cores are coated with SMA hemiester shells. From the TEM images shown in Figure 7 and lots of other images not shown, we can obtain a statistical analysis of particle size for the latexes and the results are listed in Table IV. The average particle size from TEM analysis is consistent with that from Malvern Zetasizer measurement.

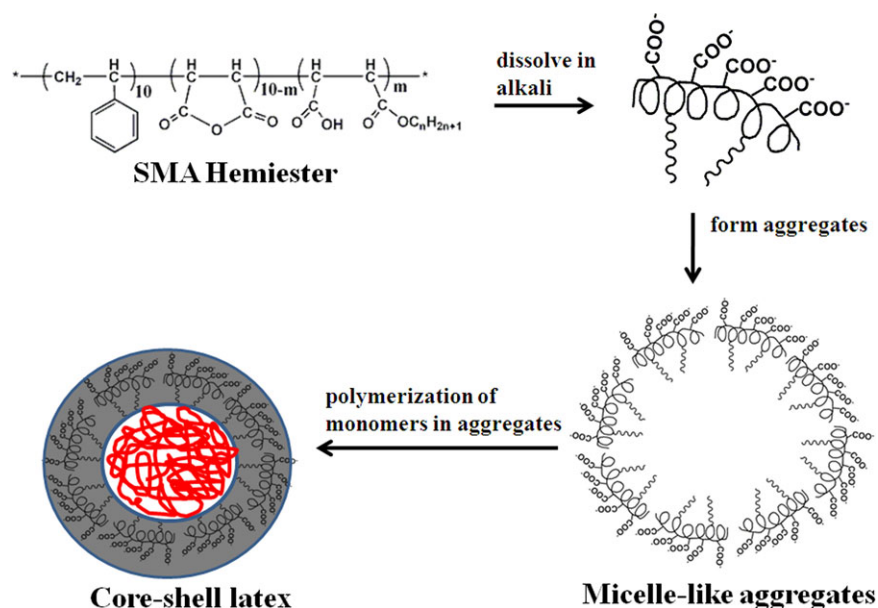


Figure 8. Schematic illustration of formation of core-shell latex. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

T_g of latex L2, L5, and L8 determined from DSC curves (not shown herein) are -5.5 , -6.3 , and -5.9°C , respectively. However, the MFT of latexes are all about 5°C , which are higher than the determined T_g . The reason for MFT obviously higher than T_g may be the fact that the latexes have relatively hard shell with T_g above 80°C , which impede the film formation. Therefore, we should carefully adjust the ratio of core monomers to obtain the core-shell latex with appropriate MFT.

A formation process of core-shell latex is schematically represented by Figure 8. The SMA hemiesters were first dissolved in alkali solution to form micelle-like aggregates, then MMA and BA were added and polymerized in the aggregates. Finally, the core-shell latexes formed with the surfactant absorbed at outer shell and copolymer of MMA and BA as the core.

CONCLUSIONS

This work has shown that modification of SMA ASRs with fatty alcohols having long alkyl chains can improve their emulsification efficiency due to better hydrophilic-lipophilic balance and steric stability. The stable acrylic latexes have been successfully prepared using hemiesters, that is, SMA-C12-75, SMA-C14-70, and SMA-C16-65, as sole surfactants. Those obtained latexes have four characteristics: (1) relatively low surfactant concentration (≤ 15 wt % on a dry polymer base); (2) relatively high solid contents (to ca. 40%); (3) smaller particle size (with average size no more than 60 nm); (4) clear core-shell morphology.

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REFERENCES

1. Guo, T. Y.; Tang, G. L.; Hao, G. J.; Song, M. D.; Zhang, B. H. *J. Appl. Polym. Sci.* **2002**, *86*, 3078.
2. Sparnacci, K.; Laus, M.; Tondelli, L.; Magnani, L.; Bernardi, C. *Macromol. Chem. Phys.* **2002**, *203*, 1364.
3. Khan, A. K.; Ray, B. C.; Dolui, S. K. *Prog. Organ. Coat.* **2008**, *62*, 65.
4. He, C.; Liu, J.; Ye, X.; Xie, L.; Zhang, Q.; Ren, X.; Zhang, G.; Wu, C. *Langmuir* **2008**, *24*, 10717.
5. Lee, J. M.; Lee, D. G.; Lee, S. J.; Kim, J. H. *Macromolecules* **2009**, *42*, 4511.
6. Koskinen, M.; Wilén, C. *J. Appl. Polym. Sci.* **2009**, *112*, 1265.
7. Jiang, S.; Fang, X. H.; Yu, Q.; Deng, J. P.; Yang, W. T. *J. Appl. Polym. Sci.* **2012**, *124*, 4121.
8. Ho, K. M.; Li, W. Y.; Lee, C. H.; Yam, C. H.; Gilbert, R. G.; Li, P. *Polymer* **2010**, *51*, 3512.
9. Li, P.; Zhu, J.; Sunintaboon, P.; Harris, F. W. *Langmuir* **2002**, *18*, 8641.
10. Lee, D. Y.; Kim, J. H. *J. Appl. Polym. Sci.* **1998**, *69*, 543.
11. Lee, D. Y.; Kim, J. H.; Min, T. I. *J. Appl. Polym. Sci.* **1999**, *153*, 89.
12. Wu, Z.; Zhang, Z. *J. Appl. Polym. Sci.* **2007**, *105*, 3492.
13. Peck, A. N. F.; AUSA, J. M. *Macromolecules* **2008**, *41*, 7928.
14. Amaral, M. D.; AUSA, J. M. *Macromol. Rapid. Commun.* **2004**, *25*, 1883.
15. Kato, S.; Sato, K.; Maeda, D.; Nomura, M. *Colloids Surf A* **1999**, *153*, 127.
16. Martínez, A.; González, C.; Porras, M.; Gutiérrez, J. M. *Colloids Surf A* **2005**, *270–271*, 67.
17. Nzudie, D. T.; Dimonie, V. L.; Sudol, E. D.; El-aasser, M. S. *J. Appl. Polym. Sci.* **1998**, *70*, 2729.
18. Yao, Z.; Zhan, J. S.; Chen, M. L.; Li, B. J.; Lu, Y. Y.; Cao, K. *J. Appl. Polym. Sci.* **2011**, *121*, 1740.
19. Olea, A. F.; Acevedo, B.; Martinez, F. *J. Phys. Chem. B* **1999**, *103*, 9306.