

Synthesis of a Novel Polymerizable Surfactant and Its Application in the Emulsion Polymerization of Vinyl Acetate, Butyl Acrylate, Veova 10, and Hexafluorobutyl Methacrylate

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Received 5 February 2007; accepted 26 June 2007

DOI 10.1002/app.27123

Published online 24 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel anionic, polymerizable fumaric surfmer (surfmer) was synthesized. The chemical structure of the surfmer was confirmed with ¹H-NMR, IR, and mass spectrometry. The surfmer was then used with constant addition profiles in the semicontinuous polymerization of vinyl acetate, butyl acrylate, Veova 10, and hexafluorobutyl methacrylate. The particle size, amount of coagulum, and stability against electrolytes and freezing/thawing were evaluated. Films were cast from latices; then, photographs were taken of the films after

immersion in water for days, and the water adsorption was assessed. As a reference, an unreactive surfactant (sodium dodecyl sulfate) was also used for the polymerization. Compared with sodium dodecyl sulfate, the surfmer behaved much better with respect to the stability of the latices and the water sensitivity of the films. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 624–628, 2008

Key words: emulsion polymerization; films; surfactants

INTRODUCTION

Polymerizable surfactants are of interest in emulsion polymerization.^{1–3} Through the use of polymerizable surfactants that can be covalently anchored onto the surface of latex particles, many of the problems encountered with conventional surfactants can be avoided or at least minimized. Polymerizable surfactants can improve the stability of latices versus electrolytes,^{4,5} high shear,⁶ and freezing/thawing⁷ as well as the water sensitivity of the films formed.^{2,5,8,9} Some surfmers have been synthesized and used in emulsion polymerizations of different monomers; no surfmer suits all polymer systems.¹⁰ Therefore, the synthesis and application of new surfmers are needed. For not homopolymerizing and for moderate reactivity,^{5,11,12} maleic surfactants are considered good surfmers. The *trans*-isomers of maleic surfactants, that is, fumaric surfactants, have different properties,¹³ such as easier homopolymerization and different reactivity. No study on fumaric surfmers

has been reported up to now. In this work, a novel fumaric surfmer was synthesized and used in the emulsion polymerization of vinyl acetate, butyl acrylate, Veova 10, and hexafluorobutyl methacrylate. As a reference, an unreactive surfactant, sodium dodecyl sulfate (SDS), was also used for the polymerization. In comparison with SDS, the surfmer behaved better with respect to the stability of the latices and the water sensitivity of the films.

EXPERIMENTAL

Materials

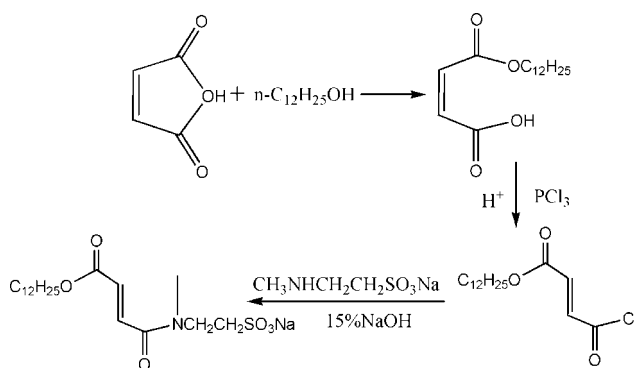
Vinyl acetate, butyl acrylate, Veova 10 (a vinyl ester of a highly branched decanoic acid), and hexafluorobutyl methacrylate were supplied by Dalian Zebon Fluorocarbon Paint Stock Co., Ltd. (Dalian, China), as polymeric grades and were used as received. Sodium *N*-methyl taurine was a solution with a concentration of 25.2%. All other reagents (analytical-grade) were obtained on sale and used as supplied.

Synthesis of the surfmer

The surfmer was synthesized in three steps according to Scheme 1.

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Contract grant sponsor: Dalian Science and Technology Program; contract grant number: 2005A10GX103.



Scheme 1 Synthesis of the fumaric surfactant.

Synthesis of monododecyl maleate according to Hamaide et al.¹⁴

Maleic anhydride (49.03 g, 0.50 mol) and 1-dodecanol (93.17 g, 0.50 mol) were stirred in a melted state at 80°C for 1 h. Heptane (150 mL) was added to the reaction mixture, which was stirred for 15 min at 80°C. The solution was left at room temperature for 3 h and then at 15°C for 2 h and was stirred from time to time.

The precipitate that formed was collected and recrystallized from heptane (150 mL). White, bright crystals of monododecyl maleate (120.30 g, 84.6%) were obtained. The product was analyzed by melting-point measurements (X-6 microscopic melting-point apparatus, Beijing Taik Instrument Co., Ltd., Beijing, China; 57.6–58.0°C) and ¹H-NMR (Inova, Varian, USA; Fig. 1).

¹H-NMR (CDCl₃, 400 MHz, δ, ppm): 0.88 (t, 3H, CH₂—CH₃), 1.27 [m, 18H, —(CH₂)₉—], 1.72 (m, 2H, C—O—CH₂—CH₂), 4.28 (t, 2H, C—O—CH₂), 6.36–6.48 (q, 2H, —CH=CH—, *J* = 12.8 Hz).

Synthesis of monododecyl fumarate chloride

PCl₃ (3.44 g, 0.025 mol) was added dropwise to monododecyl maleate (14.22 g, 0.05 mol) at 45–60°C

in a dry reactor with stirring. As PCl₃ was added, the solid of monododecyl maleate turned into a liquid slowly. After the addition of PCl₃ was finished, 1–4 h was needed for the reaction. A liquid product was obtained.

Synthesis of sodium *N*-methyl-*N*-monododecylfumaroyl taurine

Monododecyl fumarate chloride (15.15 g, 0.05 mol) was added to a solution of sodium *N*-methyl taurine (31.94 g, 0.05 mol) at 70°C. To control the pH to approximately 8–10, a 15% NaOH solution was added. After the addition, the reaction was carried out for 1 h. Then, the solution of the product was dried and recrystallized from 95% ethanol. The product (9.20 g, 40%) was obtained as a white powder with a purity of 92.9%, as determined by two-phase titration. The product was analyzed by ¹H-NMR (Inova, Varian, USA; Fig. 2), IR; Nicolet-20DXB, USA, and mass spectrometry (MS; HP1100 mass spectrometer, USA).

¹H-NMR (D₂O, 400 MHz, δ, ppm): 0.73 (t, 3H, CH₂—CH₃), 1.13 [m, 18H, —(CH₂)₉—], 1.55 (m, 2H, C—O—CH₂—CH₂), 2.92, 3.10 (s, 3H, N—CH₃), 2.99 (t, 2H, CH₂—SO₃), 3.64, 3.72 (t, 2H, N—CH₂), 4.03 (m, 2H, C—O—CH₂), 6.53 [d, 1H, O—C(O)—CH=, *J* = 15.2 Hz], 7.26–7.46 [d, 1H, N—C(O)—CH=, *J* = 15.2 Hz]. IR (KBr, λ, cm⁻¹): 2955 (ν_{as} CH₃), 2918 (ν_{as} CH₂), 2850 (ν_s CH₂), 1719 (ν_{C=O}), 1655 (ν_{C=O}), 1612 (ν_{C=C}), 1474, 1441, 1412, 1364 (δ_{CH₂}, δ_{CH₃}), 1302, 1181 (ν_{C—O—C}), 1272 (ν_{C—N}), 1206 (ν_{as} SO₃⁻), 1056 (ν_s SO₃⁻), 964 (γ_{C—H}), 721 (γ_{CH₂}). MS: *m/z* = 404.2 [M - Na]⁻.

Emulsion polymerization

Pre-emulsification of the monomers

The surfactant (2.87 g) was dissolved in deionized water (28.98 g). Then, vinyl acetate (30.00 g), butyl acrylate (10.00 g), Veova 10 (10.00 g), and hexafluoro-

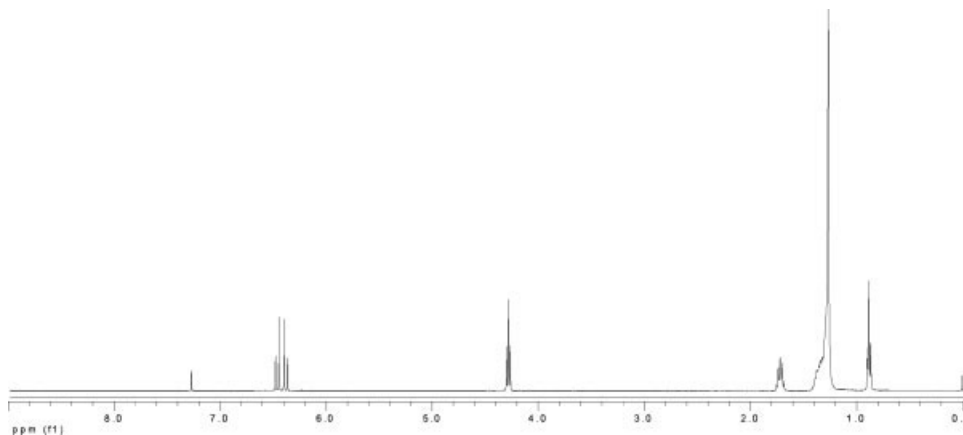


Figure 1 ¹H-NMR spectrum of monododecyl maleate.

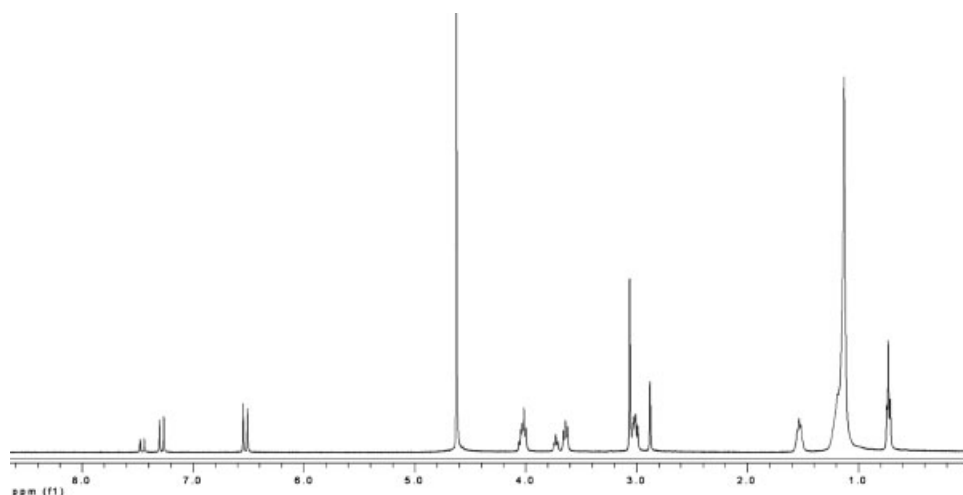


Figure 2 $^1\text{H-NMR}$ spectrum of sodium *N*-methyl-*N*-monododecylfumaroyl taurine.

butyl methacrylate (15.00 g) were added to the surfactant solution with mechanical stirring at 500 rpm and stirred for 30 min, and then 96.85 g of the emulsion of the monomer was prepared.

Semicontinuous polymerization

The emulsion of the monomer (6.00 g), 0.07 g of potassium persulfate (KPS or $\text{K}_2\text{S}_2\text{O}_8$), 0.19 g of NaHCO_3 , and 35.94 g of deionized water were introduced into a 250-mL reactor. Then, the other emulsion of the monomer (90.85 g) was mixed with 0.21 g of KPS and 11.59 g of deionized water. With a rate of stirring of 250 rpm, the temperature in the reactor was raised to 80°C , and the mixture reacted for 15 min; after that, the emulsion of the monomer mixed with KPS was added dropwise at a constant rate for 3 h. Fifteen minutes after the addition of all the emulsion of the monomer, 0.07 g of KPS dissolved in 3.53 g of deionized water was added to the reactor. Then, the polymerization conditions were maintained for an additional 3.75 h. The amounts of the components used in the experiment are presented in detail in Table I.

Characterization of the latices

The amount of coagulum was measured by the collection of coagulum on the reactor wall and stirrer by the filtration of the latex (mesh 300). It is pre-

sented as the weight of coagulum per the total weight of monomer added.

The particle diameter was measured by dynamic light scattering with an LO-C autosizer (Malvern Instruments, UK). The polydispersity index of the particle diameter was calculated automatically. It was considered that the emulsion was monodisperse when the polydispersity index was lower than 0.1.

The conversion was determined and calculated from the mass differences of samples taken before and after evaporation of the liquid phase. The samples were dried, and the residual polymer was weighed.

Stability tests

To 3.0 g of latex, 0.6 g of an electrolyte solution was added; 0.1M NaCl, 0.5M NaCl, 1.0M NaCl, 0.1M CaCl_2 , 0.5M CaCl_2 , and 1.0M CaCl_2 were tested. Immediate flocculation or flocculations after some time were observed visually.

For the freeze/thaw test, some latex (20–30 mL) was kept at -18°C for 18 h. After another 6 h at room temperature, the flocculation of the latex sample was observed.

Water absorption

Latex films were prepared by the placement of the required amount of latex on a glass substrate and

TABLE I
Recipes for Emulsion Polymerization

	Vinyl acetate	Butyl acrylate	Veova 10	Hexafluorobutyl methacrylate	SF	KPS	NaHCO_3	H_2O
Charge (g)	1.86	0.62	0.62	0.93	0.18	0.07	0.19	37.74
Feed (g)	28.14	9.38	9.38	14.07	2.69	0.28	0	42.30
Total (g)	30	10	10	15	2.87	0.35	0.19	80.04

SF, surfmer.

TABLE II
Results of the Polymerization

Surfactant	Coagulum (%)	Solid content (%)	Conversion (%)	Particle diameter (nm)	Polydispersity index
SDS	0.13	43.66	98.07	124	0.00
Surfmer	0.03	43.48	97.66	129	0.04

air-drying at room temperature for 24 h. Films were removed carefully, and square samples ($3 \times 3 \text{ cm}^2$) were prepared and dried at 40°C *in vacuo* for 24 h. The preweighed dry films were immersed in water for days. At various times (ca. once every 3 days), after careful blotting of the surface liquid with paper, the samples were weighed as quickly as possible. The water absorption of the films was calculated as a percentage of the initial weight.

RESULTS AND DISCUSSION

Synthesis and characterization of the surfmer

The surfmer was synthesized in three steps. First, monododecyl maleate was synthesized by the acylation of 1-dodecanol with maleic anhydride. Then, monododecyl maleate was chloridized by PCl_3 , and H_3PO_3 was produced as a byproduct. During the chloridization, as an acid, H_3PO_3 catalyzed the isomerization of *cis*-isomers to *trans*-isomers. In this way, monododecyl fumarate chloride was obtained. In the last step, the surfmer was obtained by the reaction of monododecyl fumarate chloride with *N*-methyl taurine, and an equal molar amount of HCl gas was produced. Fifteen percent NaOH was needed to control the pH to approximately 8–10; at a lower pH, *N*-methyl taurine would be protonized by HCl and lose reactivity, and a high pH would cause breaking of the ester bond of the reactant or product. The *trans* structure of the product was proved by two facts: the peak of 964 cm^{-1} in the IR spectrum is a result of $\gamma_{\text{C-H}}$ of the *trans*-alkene, and the peak of $\gamma_{\text{C-H}}$ of the *cis*-alkene at $800\text{--}650 \text{ cm}^{-1}$ is absent in the spectrum. Other evidence is that *J* of the H on the unsaturated carbon of the surfmer is 15.2 Hz (Fig. 2), which is higher than that of the *cis*-isomer monododecyl maleate (12.8 Hz; Fig. 1). *J* of the H on the unsaturated carbon of the *trans*-alkene is higher than that of the *cis*-isomer.

Emulsion polymerization

Pre-emulsification of the monomers was performed before the semicontinuous polymerization. The traditional surfactant SDS and the surfmer were used for the polymerization, and the data are reported in Table II. With both, monodispersity latices were obtained as the polydispersity indices were lower than 0.1. The conversions of the monomers were high enough, and the amounts of coagulum were very low. A small amount of coagulum was obtained from the polymerization with the surfmer, and this shows that the fumaric surfmer can be used in an emulsion polymerization rightly.

Stability tests

The two latices were studied for electrolyte addition and freeze/thaw testing. The latex stabilized with the surfmer had better stability against electrolytes than that stabilized with SDS (Table III). The latex stabilized with SDS did not resist a high concentration of monovalent salt (0.5–1.0M NaCl) or a low concentration of bivalent salt (0.1–1.0M CaCl_2), whereas the latex stabilized with the surfmer just did not resist a high concentration of bivalent salt (0.5–1.0M CaCl_2). This demonstrates that the surfmer can improve the latex stability against electrolytes.

After one freeze/thaw cycle, the latex stabilized with SDS totally flocculated, whereas the latex stabilized with the surfmer could resist five freeze/thaw cycles; a good result was still obtained even when only an ionic surfactant was used.

Water adsorption and deformation

The films were prepared from the latices and were immersed into water. The weights of the films before and after immersion were weighed from time to time, and the difference between the initial weights

TABLE III
Stability Against the Electrolytes

SF	0.1M NaCl	0.5M NaCl	1.0M NaCl	0.1M CaCl_2	0.5M CaCl_2	1.0M CaCl_2
SDS	+	++	++	+++	+++	+++
Surfmer	+	+	+	+	+++	+++

SF, surfmer.

+, stable after one month; ++, flocculation in time (10–30 days); +++, immediate flocculation.

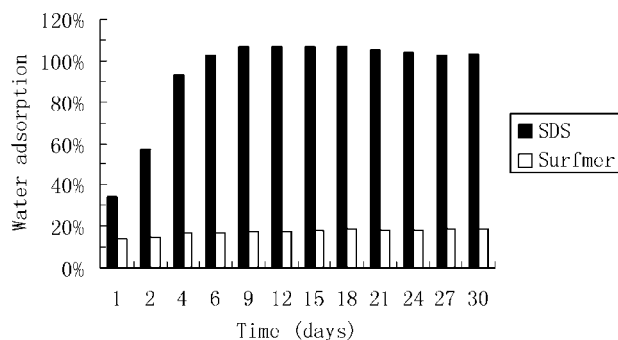


Figure 3 Water adsorption of the films during 30 days.

was calculated (see Fig. 3). To compare the deformations of the films for immersion into water, photographs of the films after immersion were taken (see Fig. 4).

As shown in Figure 1, water adsorption of the film made with SDS increased from 34 to 106% during the first 9 days and then did not apparently change, and water adsorption of the film made with the surfmer was almost steady. After 30 days, water adsorption (104%) of the film made with SDS was much higher than that (18%) of the film made with the surfmer. In Figure 4, the photographs show that the films made with SDS deformed strongly and became crimped and white after being immersed in water for 30 days, whereas the films made with the surfmer did not deform at all and still were transparent. According to the water adsorption and deformation, we could consider that the surfmer had been actually copolymerized into the polymer.

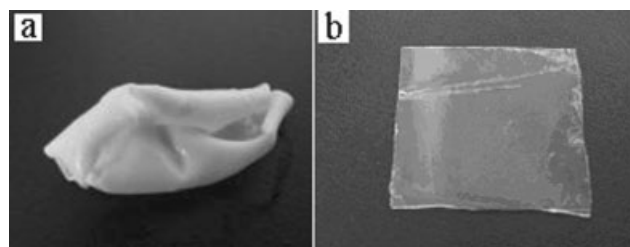


Figure 4 Photographs of films after immersion in water for 30 days: (a) a film made from SDS and (b) a film made from the surfmer.

CONCLUSIONS

A novel fumaric surfmer was synthesized and characterized. It was used in the semicontinuous emulsion polymerization of vinyl acetate, butyl acrylate, Veova 10, and hexafluorobutyl methacrylate. As a reference, an unreactive surfactant, SDS, was also used for the polymerization. With both surfactants, a monodispersity latex was obtained with very little coagulum.

The results of the stability tests show that the fumaric surfmer can improve the stability of latices against electrolytes and freezing/thawing. In particular, the surfmer can largely reduce the water adsorption of films and resist the deformation of films when exposed to water. All this indicates that the surfmer is very effective when used in emulsion polymerization.

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