Soy-Based Surface Active Copolymers As a Safer Replacement for Low Molecular Weight Surfactants

Samim Alam,[†] Harjyoti Kalita,[†] Olena Kudina,[‡] Andriy Popadyuk,[‡] Bret J. Chisholm,[†,‡] and Andriy Voronov*,[‡]

[†]Center for Nanoscale Science and Engineering, [‡]Coatings and Polymeric Materials Department, North Dakota State University, Fargo, North Dakota 58108, United States

S Supporting Information

ABSTRACT: Environmentally friendly soybean-based polymeric surfactants (SBPS) were synthesized using cationic polymerization of a vinyl ether monomer derived from soybean and tri(ethylene glycol) ethyl vinyl ether. The ability of SBPS to form micelles that solubilize hydrophobic molecules has been shown. Micellar "capacity" (size of micellar interior) increased with increasing polymeric surfactant concentration and temperature. The obtained results provide evidence for potential use of SBPS as a safer replacement for low molecular weight surfactants in the solubilization of poorly soluble ingredients in cosmetics. The macromolecules developed can be used as both a surface active agent and an additive that enhances the surface activity of low molecular weight surfactants (for example, anionic sodium lauryl sulfate) in personal-care products.

KEYWORDS: soybean-based polymeric surfactants, cationic polymerization, soybean-based monomer
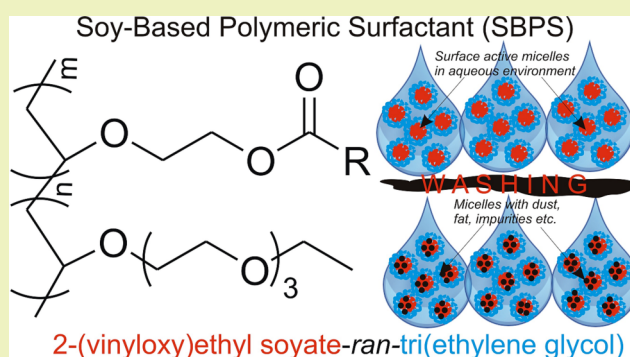
■ INTRODUCTION

The amount of surfactants used in personal-care products in the United States is close to 800 million pounds and is valued at over $70 billion.[1] The personal-care market includes bubble baths, body washes, hand soaps and cleaners, shaving products, hair shampoos, and oral-care products. In 90% of personal-care products that foam, sodium lauryl sulfate (SLS) and ammonium lauryl sulfate (ALS) surfactants are used.[2] SLS and ALS are highly soluble in water at a wide range of pH and temperature, are insensitive to water hardness, and can generate copious amounts of foam.[3] However, being anionic surfactants that contain sulfate groups, they can pose serious health threats. Global consumer products companies now seek new alternative surfactant compositions to substitute for SLS and ALS across their product portfolio.[1] Having the same functional properties as SLS and ALS, the replacement composition should not contain sulfate, sulfonate, or amine oxide groups and should be unaffected by water hardness.

Additional desirable features include production of the novel surfactants from a renewable resource and the use of "green chemistry" for surfactant production.[4] To this end, natural product ingredients are an important trend in global cosmetics, making the development of new environmentally friendly natural product ingredients more prevalent in the personal-care area than in other segments of the surfactant market.[5] To this end, oleo-based surfactants have been commonly derived from plant oils (coconut and palm) or from animal fats.[6−8] In recent years, animal fat feedstocks have been targeted for replacement

by vegetable oils, including growing utilization of soybean oil, which is about 30% of the 2007 world seed oil production.[1] In addition to food uses, the industrial oleochemicals business is investigating the use of high oleic soybean oils as a feedstock for the production of numerous products. These products not only have the ecological benefit of being biodegradable and derived from a renewable resource but also lend different and increased functionality. Independent testing has shown that new oils actually may perform better than petroleum-based products in some uses.[9] High oleic soybean oil is being tested and utilized in cosmetics and has become the predominant feedstock used in the production of surfactants where soybeans are used (another starting material to produce surfactants can be soy protein).[1]

Very commonly used in formulating personal-care products, polymeric surfactants form micelles by self-association of one or several macromolecules containing hydrophilic and hydrophobic sequences distributed along the macromolecular backbone.[10,11] Increasing environmental awareness and the utilization of renewable materials provide opportunities to use soybeans for the production of new polymeric materials, in particular for the synthesis of soybean-based polymeric surfactants.[12,13] To our knowledge, no soybean-based nonionic

polymeric surfactants have been reported for personal-care products.

In this study, we focus on developing novel, environmentally friendly, and efficient soybean-based polymeric surfactants (SBPS) for personal-care applications. The reported synthetic approach combines benefits from using a natural ingredient, soybean oil, as a starting material with an ability of amphiphilic polymeric macromolecules to self-assemble into micelles at a specific concentration (critical micelle concentration, CMC) and solubilize hydrophobic molecules in the micellar interior.

■ EXPERIMENTAL SECTION

Monomer Synthesis. The synthesis of 2-(vinyloxy)ethyl soyate (2-VOES) has been described elsewhere.[15] Tri(ethylene glycol) ethyl vinyl ether (TEGEVE) was synthesized as follows: 16.5 g of di(ethylene glycol) monoethyl ether (99% purity from Aldrich), 8 g of sodium hydroxide, 60 mL of tetrahydrofuran, and 40 mL of deionized water were combined in a 500 mL, 3-neck, round-bottom flask using constant stirring to produce a homogeneous solution. The mixture was cooled to 0 °C, and then 25.7 g of p-toluenesulfonyl chloride (Aldrich, 99% purity) in 50 mL of tetrahydrofuran (THF) was added to the reaction mixture dropwise using an addition funnel and the reaction was continued for 2 h at 0 °C. The reaction mixture was then poured into 100 mL of ice cold water, and the product was extracted with methylene chloride. The organic layer was washed with water and dried with anhydrous magnesium sulfate. The product, i.e., the tosylate of di(ethylene glycol) monoethyl ether (Ts-DEGMEE), was recovered after rotary evaporation of all the volatiles and dried under vacuum overnight. In the second step, 1.5 g of sodium hydride (Aldrich 95% purity) and 75 mL of THF were dissolved in a 500 mL, 3-neck, round-bottom flask equipped with a nitrogen blanket. The solution was cooled at 0 °C, and a solution of 4.77 g of ethylene glycol monovinyl ether (TCI America, 95% purity) in 30 mL THF was added dropwise. Next, a solution of 15 g of Ts-DEGMEE in 45 mL THF was added to the reaction mixture, and the temperature was raised to 60 °C. After 24 h, the reaction mixture was cooled to room temperature and diluted with 150 mL of diethyl ether. The organic layer was washed three times with 75 mL of water and dried with anhydrous magnesium sulfate. The product monomer, TEGEVE, was collected after rotary evaporation of all volatiles and dried under vacuum overnight. Successful synthesis of TEGEVE was confirmed by proton NMR: 6.4 ppm (q, 1H, OCH=C), 4.0−4.2 ppm (m, 2H, C=CH$_2$), 3.4−3.8 ppm (m, 14H, OCH$_2$CH$_2$O, OCH$_2$C), 1.2 ppm (t, 3H, CH$_3$C).

Typical Synthesis of SBPS. All glassware used for the polymerization was dried at 200 °C for 2 h. In addition, 2-VOES and TEGEVE were dried over MgSO$_4$ just prior to polymerization. Polymerizations were carried out in a glovebox equipped with a cold-well. For copolymer 2-VOES-ran-TEG-2, 5.56 g of 2-VOES, 15.0 g of TEGEVE, and 0.007 g of 1-isobutoxyethyl acetate initiator (synthesized as described by Aoshima and Higashimura[15]) were dissolved in 120 mL of toluene and the reaction mixture was cooled to 0 °C. Next, 2.40 mL of a 25 wt % solution of ethylaluminum sesquichloride in toluene was rapidly added to the reaction mixture to initiate polymerization. After 18 h, the polymerization was terminated by the addition of 120 mL of methanol. To purify the copolymer, the terminated reaction mixture was transferred to a 1 L separating funnel and 250 mL of dichloromethane was added. The mixture was washed thrice with 100 mL of water, and the polymer was isolated by vacuum stripping dichloromethane. To remove any unreacted 2-VOES, column chromatography was used with silica gel as the stationary phase and hexane as the mobile phase. Once the unreacted 2-VOES eluted from the column, the purified polymer was flushed from the column with methylene chloride and the polymer was isolated by vacuum stripping the volatiles. For copolymer 2-VOES-ran-TEG-1, the same procedure was used with the exception that the amount of 2-VOES utilized was 3.17 g.

Study of SBPS Critical Micelle Concentration. Critical micelle concentration of SBPS was measured using a pyrene fluorescent probe (concentration of pyrene 5×10^{-7} mol/L) using a previously reported method to measure solubilization.[16] The spectra were taken using a Fluoromax-3 Fluorescence Spectrometer (Jobin Yvon Horiba) with 90° geometry and a slit opening of 0.5 nm. For fluorescence excitation spectra, λ_{em} = 390 nm was chosen. Spectra were accumulated with an integration time of 0.5 nm/s. Critical micelle concentration values were determined with an inaccuracy of ±2% after fitting the semilogarithmic plots of intensity ratio $I_{336.5}/I_{332.5}$ versus log concentration to the sigmoidal curve.

Solubilization of Nile Red by SBPS Micelles. Micellar dyes were prepared by thin film method.[17] According to this method, 0.1 g of polymer and 0.5 mL of acetone solution of Nile red (1 mg/mL) were dissolved in 10 mL of acetone. The solvent was removed by rotary evaporation at 60 °C for 1 h to obtain a solid dye/SBPS matrix. Residual acetone remaining in the dye/SBPS matrix was evaporated overnight under vacuum. The resultant thin film was hydrated with 10 mL of Millipore water; the unincorporated dye aggregates were removed by filtration through 0.45 μm filters.

■ RESULTS AND DISCUSSION

The chemical structure of the SBPSs produced is shown in Figure 1 and Figure S1 in Supporting Information. The

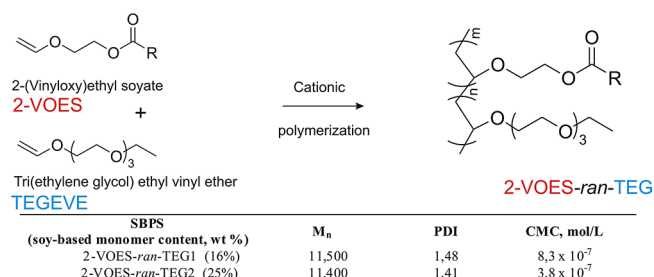| SBPS (soy-based monomer content, wt %)	M_n	PDI	CMC, mol/L
2-VOES-ran-TEG1 (16%)	11,500	1,48	$8,3 \times 10^{-7}$
2-VOES-ran-TEG2 (25%)	11,400	1,41	$3,8 \times 10^{-7}$

Figure 1. Synthesis and characteristics of SBPS (R = soybean oil fatty acid components).

repeating unit possessing the ester group is derived from soybean oil by conducting a base-catalyzed transesterification of soybean oil with ethylene glycol vinyl ether to produce a vinyl ether possessing pendent groups containing the fatty acid esters of soybean oil. The process for producing this vinyl ether monomer, 2-(vinyloxy)ethyl soyate (2-VOES), was developed recently in our group.[14] In addition, a carbocationic polymerization process was developed for 2-VOES, which allowed for high molecular weight polymers to be produced without consuming any of the vinyl groups present in the fatty acid portion of the monomers.[14]

In this work, cationic polymerization was used to synthesize two different SBPSs that differed with respect to the relative ratio of the two repeat units. For these random copolymers, the 2-VOES repeating units serve as hydrophobes while the other repeating unit, which possesses a triethylene glycol (TEG) pendent group, acts as a hydrophilic sequence in the amphiphilic SBPS macromolecules.

It is expected that addition at a concentration above the critical micelle concentration (small quantities) to various formulations, SBPS macromolecules immediately form micelles consisting of a hydrophobic interior and hydrophilic exterior (Figure.2, **top**).

The hydrophilic exterior of SBPS micelles facilitates stability in water, and the hydrophobic interior solubilizes hydrophobic dirt, oils, and other molecular debris. The size of the micellar interior and, thus, its "capacity" for extracting the impurities can
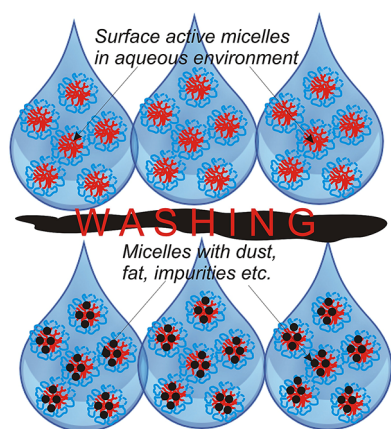
Figure 2. Schematic of SBPS aqueous solution cleaning the surface.

be tuned by the length and number of 2-VOES fragments in SBPS macromolecules. Upon SBPS solution contact with a surface, the "dirt" will be extracted and accumulated into the interior of the micelles and removed from the surface (Figure 2, bottom) when the solution is rinsed.

Figure 1 shows the chemical structures of the two poly(2-VOES-*ran*-TEG) copolymers used in this study. Molecular weight, polydispersity index, and critical micelle concentration of the SBPSs are shown in the table on Figure 1. The chemical structures of the copolymers were confirmed by ^{1}H NMR and FT-IR spectroscopy (Figures S2 and S3 in Supporting Information).

Different surface activities for the synthesized SBPSs were targeted to achieve varying capacities of SBPS micelles in the solubilization of hydrophobic molecules ("dirt") in water. To confirm formation of SBPS micelles in aqueous solution, CMC values were measured using solubilization of pyrene, a well-known fluorescent probe for studying the association behavior of amphiphilic polymers.[18,19] Depending on the environment of the pyrene, a red shift of the absorption band with enhanced excitation intensity was observed due to the migration of the probe from the hydrophilic to the hydrophobic region of the polymer micelles). In our experiments, pyrene excitation spectra were monitored in the wavelength range of 300−360 nm. From the pyrene excitation spectra, the intensity ratios $I_{336.5}/I_{332.5}$ were plotted as a function of SBPS concentration (Figure 3).

A red shift of the fluorescence excitation spectra from 332.5 to 336.5 nm with an increasing SBPS concentration indicates the solubiliz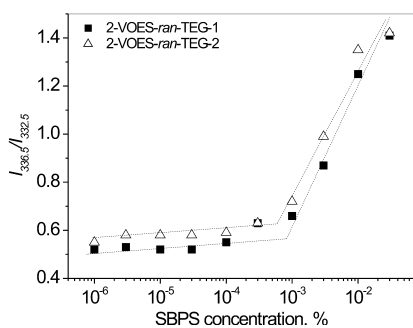ation of pyrene within the micellar hydrophobic environment and the transfer of pyrene molecules from water to the polymer micelles. The sharp increase in the intensity ratio corresponds to the critical micelle concentration for each SBPS. The data indicate that both SBPSs are surface-active and form micelles. The CMC values correlate with the chemical structure of the SBPS.

Changing the ratio of hydrophilic to hydrophobic fragments in SBPS macromolecules results in a difference in recorded CMC values. The CMC increases with an increasing TEG repeat unit content in the reactive mixture from 3.8×10^{-7} mol/L (4.4 mg/L) for slightly more hydrophobic 2-VOES-*ran*-TEG-2 to 8.3×10^{-7} mol/L (9.5 mg/L) for 2-VOES-*ran*-TEG-1. In addition, the low CMCs for both SBPSs indicate that the micelles would provide good stability in solution even after strong dilution, if required for preparation of special formulations.

In the next step, an ability of SBPS micelles to solubilize poorly water-soluble hydrophobic materials in aqueous solutions was shown. Nile red (7-diethylamino-3,4-benzophe-noxazine-2-one) is a lipophilic dye that is insoluble in water[20] and shows no absorption in optical spectroscopy measurements.[21] However, in the presence of a micellar solution of 2-VOES-*ran*-TEG-2 (1% w/v), the dye was immediately solubilized by SBPS micelles in water (Figure 4A). The absorption intensity corresponding to the selected wavelength of 547 nm increases with an increasing SBPS concentration in water. This fact confirms that polymer micelles provide a microenvironment that is capable of sequestering hydrophobic molecules in water. In addition, the increasing absorption intensity recorded for solubilization carried at 37 °C demonstrates that more lipophilic material has been polymer-sequestered from water at higher temperature.

To study the possible synergy of two surfactants, the low molecular weight anionic, SLS, and the polymeric SBPS, the surface activity of SLS/SBPS mixtures was determined using surface tension measurements. The surface tension data showed that, when a small concentration of SBPS (below CMC) is added to the SLS micellar solution (above CMC), the critical micelle concentration of the mixture shifts toward lower (in comparison to pure SLS) values (Figure 4B). Two general conclusions can be drawn from Figure 4B. First, there is an interaction between SLS and SBPS in aqueous solutions which indicates that surface activity of SLS can be changed by adding the SBPS already at low polymer concentration. Second, the critical micelle concentration of an SLS/SBPS mixture is lower than the CMC of SLS itself, showing that surface activity of SLS can be enhanced by adding the SBPS.

In summary, we report on novel, environmentally friendly soybean-based polymeric surfactants synthesized using cationic copolymerization of a monomer derived from soybean oil fatty acids and tri(ethylene glycol) ethyl vinyl ether. The ability of SBPSs to form micelles that further solubilize hydrophobic molecules has been demonstrated. Micellar "capacity" (size of micellar interior) increases with increasing polymeric surfactant concentration and temperature. The obtained results provide evidence for potential use of SBPSs as a safer replacement for low molecular weight surfactants in the solubilization of poorly soluble ingredients in cosmetics. The macromolecules can be used as both surface-active agents and additives that enhance the surface activity of low molecular weight surfactants (for example, anionic sodium lauryl sulfate) in personal-care products.
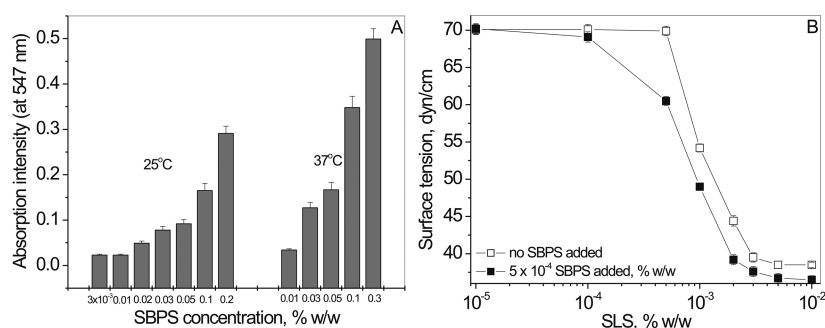

Figure 3. Intensity ratio $I_{336.5}/I_{332.5}$ of the excitation spectra of pyrene in SBPS solutions versus copolymer concentration.

Figure 4. Solubilization of insoluble dye by SBPS macromolecules at 25 and 37 °C in aqueous solutions (A). Surface tension measurements of SLS and SBPS/SLS mixture in aqueous solutions (B).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Chemical structure of 2-VOES-*ran*-TEG copolymers and ^{1}H NMR and FT-IR spectra of SBPS. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Department of Coatings and Polymeric Materials, North Dakota State University, P.O. Box 6050, Dept. 2760, Fargo, ND 58108-6050, United States. Tel.: +1 701 231 9563. Fax: +1 701 231 8439. E-mail address: andriy.voronov@ndsu.edu.

Notes

The authors declare no competing financial interest.

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