Gemini Surfactant Electrospun Membranes

Matthew P. Cashion,† Xiaolin Li,‡ Yan Geng,† Matthew T. Hunley,‡ and Timothy E. Long*†

†Department of Chemistry, Macromolecules and Interfaces Institute, Virginia Tech (0212), Blacksburg, Virginia 24061, and ‡Department of Chemistry, University of Georgia, 1001 Cedar Street, Athens, Georgia 30602

Received June 25, 2009

Our research demonstrates electrospun nonwoven fibrous scaffolds from a low molar mass gemini ammonium surfactant, \(\text{N,N\text{-}didecyl-N,N,N,N\text{-}tetramethyl-N,N\text{-}ethanediylidiammonium dibromide (12-2-12)}\). Cryogenic transmission electron microscopy (cryo-TEM) and solution rheological experiments revealed micellar morphological transitions of 12-2-12 in water and water:methanol (1:1 vol) at high density. The microstructure of 12-2-12 in water transitioned from entangled, cylindrical, threadlike micelles to branched threadlike micelles, and a viscoelastic, entangled, highly branched network of threadlike micelles with increasing concentration finally formed. In sharp contrast, the solution behavior of 12-2-12 in water:methanol produced a drastically different micellar microstructure compared to that in water, and the morphology transitioned from lamellar, globular micelles to overlapped micelles at an overlap concentration \((C_o)\) of 11 wt %. Electrospinning 12-2-12 from water did not produce fibers at any concentration; however, electrospinning 12-2-12 in water:methanol at concentrations greater than \(2C_o\) produced hydrophilic continuous fibers with diameters ranging from 0.9 to 7 \(\mu\)m. High surface area scaffolds with hydrophilic surfaces offer potential as charged controlled-release membranes, tissue engineering scaffolds, and coatings for biologically compatible devices.

Introduction

Electrospinning biologically derived, low molar mass amphiphiles represents an innovative strategy for biocompatible, high surface area fibers for tissue engineering, drug delivery, and biomedical membrane technologies.† Traditionally, the formation of electrospun fibers requires viscous, entangled high molecular weight polymers in solution or in the melt, since sufficient viscosities are necessary to withstand electrostatic forces and whipping instabilities of the charged electrified jet.2–5 Our laboratories were the first to electrospin low molar mass phospholipids based on solutions of asolectin in organic solvents,6 and high surface area membranes with fiber diameters less than 2.8 \(\mu\)m were obtained. However, this initial discovery was limited to phospholipids in organic solvents, and our challenge remained to demonstrate the versatility of electrospinning low molar mass amphiphiles in aqueous solutions.

Asolectin is a soy-derived natural surfactant mixture composed of charged and neutral lipids, and the morphology of asolectin transitions from reverse, spherical micelles into elongated, wormlike micelles (WLMs) with increasing concentration in nonpolar solvents. Asolectin WLMs form entanglements above the entanglement concentration \((C_e)\). In chloroform/\(\text{N,N-dimethylformamide (70/30 by weight)}\), the critical micelle concentration \((C_m)\) was 35 wt % for asolectin, and the scaling relationship of specific viscosity \((\eta_s)\) with concentration \((C)\) was \(\eta_s = C^{2/3}\) at \(C < C_m\), and \(\eta_s \approx C^{0.84}\) at \(C > C_m\). Asolectin WLMs are known to entangle above \(C_m\), similar to polymer coils in solution, and exhibit contour and persistence lengths of approximately 1 \(\mu\)m and 10 nm, respectively.7 The mass-action law controls the uniaxial growth of WLMs, and as the lipid volume fraction increases, the persistence length becomes sufficiently large for WLMs to behave as flexible dynamic analogues to polymers in solution.8,9 Droplets were formed when asolectin was electrospun at \(C < C_e\) due to the absence of WLM entanglements, and beaded fibers were collected when electrospun at \(C = C_e\). Electrospinning continuous fibers from asolectin solutions required a sufficient solution viscosity in order to suppress the Rayleigh instabilities and prevent breakup of the electrified jet.3,10 The three-dimensional, entangled asolectin physical networks at \(C > C_e\) provided the viscosity and physical associations necessary to form continuous electrospun fibers from low molar mass lipids. Electrospinning asolectin scaffolds proved that entangled high molecular weight polymers were not essential to the formation of electrospun fibers; however, some degree of supramolecular association was needed to form continuous fibers from low molar mass precursors.

In this study, we report the aqueous solution behavior and electrospinning of an ammonium gemini surfactant, \(\text{N,N\text{-}didecyl-N,N,N,N\text{-}tetramethyl-N,N\text{-}ethanediylidiammonium dibromide (12-2-12)}\), as shown in Figure 1. Gemini surfactants, which are also known as dimeric surfactants, are an interesting class of amphiphiles due to their low critical micelle concentration (cmc) and intriguing supramolecular assemblies in solution.11–15
Gemini surfactants contain two hydrophobic tails and two hydrophilic headgroups covalently connected with a spacer. Synthetic gemini surfactants include cationic, anionic, zwitterionic, and nonionic functionalities, depending on the incorporated spacer. Consequently, gemini surfactants have received significant industrial attention as emulsifiers and dispersants in detergents, cosmetics, personal hygiene products, coatings, and paint formulations.10–18 Gemini surfactants have also received more recent interest as templates for the synthesis of metal nanoparticles19–21 and as novel gene transfection agents due to their superior surface-active properties and DNA binding capabilities.22–24

The propensity for supramolecular assembly and WLM growth of gemini surfactants strongly depends on surfactant composition, solution temperature, concentration, and solvent.25,26 Zana, Talmon, and Danino explored the influence of spacer group on the structure of ammonium gemini surfactants in water.13,26,29 While others have examined the solution behavior and microstructure of ammonium gemini surfactants in water,13,26,29–31 our investigation correlates solution rheology with cryo-TEM for 12-2-12 in water and water:methanol in order to understand the electrospinning performance of low molar mass surfactants for functional amphiphilic membranes.

Materials and Methods

Materials. 1-Bromododecane (97%), 1,2-bis(dimethylamino)ethane (99%), ethanol (ACS grade anhydrous), ethyl acetate (HPLC grade), ethyl ether (anhydrous), methanol (HPLC grade), and cetlytrimethylammonium bromide (CTAB) (>98%) were purchased from Sigma-Aldrich (St. Louis, MO). 1-Di(dodecylamino)ethane dibromide (12-2-12) gemini surfactant.

Cationic, anionic, zwitterionic, and nonionic functionalities, depending on the incorporated spacer. Consequently, gemini surfactants have received significant industrial attention as emulsifiers and dispersants in detergents, cosmetics, personal hygiene products, coatings, and paint formulations.10–18 Gemini surfactants have also received more recent interest as templates for the synthesis of metal nanoparticles19–21 and as novel gene transfection agents due to their superior surface-active properties and DNA binding capabilities.22–24

The propensity for supramolecular assembly and WLM growth of gemini surfactants strongly depends on surfactant composition, solution temperature, concentration, and solvent.25,26 Zana, Talmon, and Danino explored the influence of spacer group on the structure of ammonium gemini surfactants in water.13,26,29 While others have examined the solution behavior and microstructure of ammonium gemini surfactants in water,13,26,29–31 our investigation correlates solution rheology with cryo-TEM for 12-2-12 in water and water:methanol in order to understand the electrospinning performance of low molar mass surfactants for functional amphiphilic membranes.

Materials. 1-Bromododecane (97%), 1,2-bis(dimethylamino)ethane (99%), ethanol (ACS grade anhydrous), ethyl acetate (HPLC grade), ethyl ether (anhydrous), methanol (HPLC grade), and cetlytrimethylammonium bromide (CTAB) (>98%) were purchased from Sigma-Aldrich (St. Louis, MO). 1-Di(dodecylamino)ethane dibromide (12-2-12) gemini surfactant.

Cationic, anionic, zwitterionic, and nonionic functionalities, depending on the incorporated spacer. Consequently, gemini surfactants have received significant industrial attention as emulsifiers and dispersants in detergents, cosmetics, personal hygiene products, coatings, and paint formulations.10–18 Gemini surfactants have also received more recent interest as templates for the synthesis of metal nanoparticles19–21 and as novel gene transfection agents due to their superior surface-active properties and DNA binding capabilities.22–24

The propensity for supramolecular assembly and WLM growth of gemini surfactants strongly depends on surfactant composition, solution temperature, concentration, and solvent.25,26 Zana, Talmon, and Danino explored the influence of spacer group on the structure of ammonium gemini surfactants in water.13,26,29 While others have examined the solution behavior and microstructure of ammonium gemini surfactants in water,13,26,29–31 our investigation correlates solution rheology with cryo-TEM for 12-2-12 in water and water:methanol in order to understand the electrospinning performance of low molar mass surfactants for functional amphiphilic membranes.

Materials. 1-Bromododecane (97%), 1,2-bis(dimethylamino)ethane (99%), ethanol (ACS grade anhydrous), ethyl acetate (HPLC grade), ethyl ether (anhydrous), methanol (HPLC grade), and cetlytrimethylammonium bromide (CTAB) (>98%) were purchased from Sigma-Aldrich (St. Louis, MO). 1-Di(dodecylamino)ethane dibromide (12-2-12) gemini surfactant.

Cationic, anionic, zwitterionic, and nonionic functionalities, depending on the incorporated spacer. Consequently, gemini surfactants have received significant industrial attention as emulsifiers and dispersants in detergents, cosmetics, personal hygiene products, coatings, and paint formulations.10–18 Gemini surfactants have also received more recent interest as templates for the synthesis of metal nanoparticles19–21 and as novel gene transfection agents due to their superior surface-active properties and DNA binding capabilities.22–24

The propensity for supramolecular assembly and WLM growth of gemini surfactants strongly depends on surfactant composition, solution temperature, concentration, and solvent.25,26 Zana, Talmon, and Danino explored the influence of spacer group on the structure of ammonium gemini surfactants in water.13,26,29 While others have examined the solution behavior and microstructure of ammonium gemini surfactants in water,13,26,29–31 our investigation correlates solution rheology with cryo-TEM for 12-2-12 in water and water:methanol in order to understand the electrospinning performance of low molar mass surfactants for functional amphiphilic membranes.

Materials. 1-Bromododecane (97%), 1,2-bis(dimethylamino)ethane (99%), ethanol (ACS grade anhydrous), ethyl acetate (HPLC grade), ethyl ether (anhydrous), methanol (HPLC grade), and cetlytrimethylammonium bromide (CTAB) (>98%) were purchased from Sigma-Aldrich (St. Louis, MO). 1-Di(dodecylamino)ethane dibromide (12-2-12) gemini surfactant.

Cationic, anionic, zwitterionic, and nonionic functionalities, depending on the incorporated spacer. Consequently, gemini surfactants have received significant industrial attention as emulsifiers and dispersants in detergents, cosmetics, personal hygiene products, coatings, and paint formulations.10–18 Gemini surfactants have also received more recent interest as templates for the synthesis of metal nanoparticles19–21 and as novel gene transfection agents due to their superior surface-active properties and DNA binding capabilities.22–24

The propensity for supramolecular assembly and WLM growth of gemini surfactants strongly depends on surfactant composition, solution temperature, concentration, and solvent.25,26 Zana, Talmon, and Danino explored the influence of spacer group on the structure of ammonium gemini surfactants in water.13,26,29 While others have examined the solution behavior and microstructure of ammonium gemini surfactants in water,13,26,29–31 our investigation correlates solution rheology with cryo-TEM for 12-2-12 in water and water:methanol in order to understand the electrospinning performance of low molar mass surfactants for functional amphiphilic membranes.

Materials. 1-Bromododecane (97%), 1,2-bis(dimethylamino)ethane (99%), ethanol (ACS grade anhydrous), ethyl acetate (HPLC grade), ethyl ether (anhydrous), methanol (HPLC grade), and cetlytrimethylammonium bromide (CTAB) (>98%) were purchased from Sigma-Aldrich (St. Louis, MO). 1-Di(dodecylamino)ethane dibromide (12-2-12) gemini surfactant.

Cationic, anionic, zwitterionic, and nonionic functionalities, depending on the incorporated spacer. Consequently, gemini surfactants have received significant industrial attention as emulsifiers and dispersants in detergents, cosmetics, personal hygiene products, coatings, and paint formulations.10–18 Gemini surfactants have also received more recent interest as templates for the synthesis of metal nanoparticles19–21 and as novel gene transfection agents due to their superior surface-active properties and DNA binding capabilities.22–24

The propensity for supramolecular assembly and WLM growth of gemini surfactants strongly depends on surfactant composition, solution temperature, concentration, and solvent.25,26 Zana, Talmon, and Danino explored the influence of spacer group on the structure of ammonium gemini surfactants in water.13,26,29 While others have examined the solution behavior and microstructure of ammonium gemini surfactants in water,13,26,29–31 our investigation correlates solution rheology with cryo-TEM for 12-2-12 in water and water:methanol in order to understand the electrospinning performance of low molar mass surfactants for functional amphiphilic membranes.
copper grid. Following the plunge-freezing technique for sample preparation, the suspension on the TEM grid was blotted and immersed into a liquid ethane reservoir cooled with liquid nitrogen.\textsuperscript{32} The vitrified solutions were transferred to a Gatan 626 cryo-holder and cryo-transfer stage cooled with liquid nitrogen. During observation of the vitrified samples, the cryo-holder temperature was maintained below $-175^\circ$C to prevent sublimation of vitreous water. The images were recorded digitally using a Gatan low-dose charge-coupled-device (CCD) camera with software package.

**Electrospinning Process.** Electrospinning of 12-2-12 from water did not produce fibers at any surfactant concentration. Electrospun fibers of 12-2-12 were collected from water:methanol (1:1 vol) solutions following our earlier electrospinning procedure.\textsuperscript{2,6,33–38} 12-2-12 was dissolved in water:methanol at various concentrations. The solutions were transferred into a 20 mL syringe with an 18-gauge needle, and the syringe was mounted in a KD Scientific Inc. syringe pump. The positive lead of a Spellman High Voltage Electronics Corp. CZE1000R high-voltage power supply was connected to the syringe needle, and the stainless steel collection target was grounded and placed 12 cm from the needle tip. The fluid was pumped at a constant flow of 5 mL/h, and 25 kV of voltage was applied.

**Results and Discussion**

**12-2-12 Solution Microstructure in Water.** The cmc, surface tension, and interfacial properties of quaternary ammonium gemini surfactants were previously reported.\textsuperscript{26} In polar solvents, the hydrophilic regions of gemini surfactants orient toward the polar environment, with the headgroups located at the interface of the hydrophobic tails and polar solvent. Surfactant spherical micelles transition one-dimensionally into threadlike micelles with increasing concentration, and entanglements form, as shown in the cartoon in Figure 2.\textsuperscript{28,39,40} On the basis of a theoretical model of micellar growth, Kern and co-workers\textsuperscript{31} reported the possibility for three surfactant concentration regimes: (1) a dilute regime of slow increase in micellar size with increasing concentration, (2) a semidilute regime of rapid micellar growth, and (3) a concentrated regime where the aggregation number depends on the net charge of the end-caps. The transition from the dilute regime to the semidilute regime occurs at the overlap concentration, $C^\ast$.\textsuperscript{5} The rate of micellar growth at $C^\ast$ increases due to higher concentrations of bound ions screening the electrostatic interactions between headgroups, and the value of $C^\ast$ decreases as the end-cap energy, $E_c$, increases, $C^\ast \sim 1/E_c^{2.20,41}$ Kern and co-workers observed a $C^\ast$ of 1.55 wt % for 12-2-12 in water at 25°C; however, the concentrated regime was not easily distinguished in their plot of zero shear viscosity vs volume fraction. Bernheim-Grosswasser and co-workers\textsuperscript{39} used cryo-TEM to explore the sphere-to-cylinder transition of 12-2-12 in water at concentrations up to 1.5 wt %. The researchers observed elongated threadlike micelles with a low concentration of branch points, rings, and end-caps at 1.0 wt %, and a branched threadlike micellar network at 1.5 wt %.

Strain controlled solution rheology provided the zero shear viscosity for 12-2-12 in water at a range of concentrations. Figure 3 summarizes the relationship between $\eta_{sp}$ and concentration for 12-2-12 in water, where $\eta_{sp}$ was calculated from the apparent viscosity in the Newtonian zero shear region.\textsuperscript{33} The solution rheological scaling behavior was correlated to cryo-TEM micrographs as shown in Figure 4, and the microstructural changes were consistent with the observed solution rheological scaling behavior. Although rheology is a dynamic experiment and cryo-TEM is static, the visualization of surfactant solutions using cryo-TEM provides an acceptable method to correlate micellar microstructure to rheology. Gonzalez and Kaler\textsuperscript{42} published a review describing the complementary characterisation method of cryo-TEM and solution rheology.

The first transition at 1.5 wt % in Figure 3 represents $C^\ast$, and this value agreed with the transition that others reported for 12-2-12 in water at 25°C.\textsuperscript{31,43} The scaling relationship above $C^\ast$ increased from $\eta_{sp} \sim C_1^{1.7}$ at $C < C^\ast$ to $\eta_{sp} \sim C_2^{1.8}$ at $C > C^\ast$, indicating a much higher rate of micellar growth. Figure 4a depicts the cryo-TEM image of 12-2-12 in water at 1.0 wt % and indicates the presence of entangled, linear, threadlike micelles with long contour lengths and a low concentration of end-caps. The classical definition of $C^\ast$ for polymers, which is the concentration when polymeric coils begin to overlap, is ambiguous for the discussion of noncovalent supramolecular assembly of 12-2-12. Clearly, entanglements are present between the threadlike micelles below 1.5 wt %, as shown in Figure 4a, and the size of the elongated

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Table 1} & \textbf{Description} & \textbf{Value} \\
\hline
\text{C1} & Micron & 1.7 \\
\text{C2} & Micron & 1.8 \\
\hline
\end{tabular}
\caption{Micron Description}
\end{table}

\textsuperscript{36} Hunley, M. T.; McKee, M. G.; Long, T. E. J. Mater. Chem. 2007, 17(7), 605-609.
\textsuperscript{37} McKee, M. G.; Elkins, C. L.; Long, T. E. Polymer 2004, 45(26), 8705–8715.
\textsuperscript{42} Gonzalez, Y. I.; Kaler, E. W.Curr. Opin. Colloid Interface Sci. 2005, 10(5-6), 256–260.
micelles are concentration dependent. The abrupt change in scaling behavior at \( C^* \) is indicative of the transition from the dilute to the semidilute concentration regime, which corresponds to the regime of increased micellar growth.

Figure 4b displays the cryo-TEM micrograph of 12-2-12 in water at 2.4 wt %, \( C > C^* \), and the presence of “Y”-shaped branch points are distinguished between the threadlike micelles. If the junctions in Figure 4b were entanglements, then the contrast would darken from the increased electron density of the overlapping threadlike micelles; however, the contrast does not darken, and the junctions are considered branch points.\(^{42}\) The second transition in Figure 3 at 2.7 wt % represents the transition into the concentrated regime, \( C^{**} \), and the scaling relationship increased from \( \eta_{sp} \sim C^{2.8} \) at \( C^* < C < C^{**} \) to \( \eta_{sp} \sim C^{1.44} \) at \( C > C^{**} \). The cryo-TEM in Figure 4c displays the formation of a highly branched network of entangled, threadlike micelles at 4.1 wt % of 12-2-12 in water. The microstructure in Figure 4c is more difficult to distinguish due to the higher concentration and entangled threadlike micelles. The concentration of cross-links at \( C^{**} \) increased, and the microstructure transitioned from a branched structure to an entangled highly branched network with a higher concentration of threadlike micelles.

This article reports the concentrated regime of 12-2-12 in water and depicts the highly branched network of threadlike micelles with cryo-TEM. Drye and Cates\(^{44}\) theoretically explored the network formation of “living” cross-linked surfactant solutions. As expected, the degree of branching was dependent upon the free energy relationship between forming a cross-link and forming an end-cap. The cross-linking energy was considerably higher for conventional surfactants than the energy required to form a hemispherical end-cap. However, the researchers theorized that lowering the micelle curvature with the addition of salt\(^{45}\) provided a strategy to increase the \( E_c \) and decrease the cross-link energy. The 12-2-12 gemini surfactant did not require additional electrolyte to decrease the mean curvature of the growing threadlike micelles. The covalent linkage between the ammonium groups maintained the headgroups at a closer proximity than electrostatic repulsive forces allow for conventional ammonium surfactants. The gemini microstructure grew uniaxially into elongated, threadlike micelles that formed entanglements as the 12-2-12 concentration increased. The short covalent linkage between the ammonium sites decreased the area of the gemini headgroup, thereby lowering the micellar spontaneous curvature and allowing the surfactants to efficiently pack into a cylindrical geometry. As the number of linear, threadlike micelles increased, the concentration of cylindrical end-caps increased and branch points formed between the threadlike micelles to minimize \( E_c \).\(^{46}\)

---


---

12-2-12 Solution Microstructure in Water:Methanol. The solution behavior of 12-2-12 in water:methanol was explored to compare the influence of a solvent mixture to water on the microstructure and electrospinning behavior of 12-2-12. Methanol has a lower surface tension than water and higher volatility, which is beneficial for electrospinning fibers.\(^{47}\) The solution behavior of 12-2-12 in water:methanol demonstrated drastically different microstructures compared to that in water. The \( \eta_{sp} \) dependence on concentration for 12-2-12 in water:methanol is depicted in Figure 5, and only two concentration regimes were observed. The micellar morphology transitioned from partitioned globular micelles into overlapped micelles at \( C^* = 11 \) wt %. Figure 6a is a cryo-TEM micrograph of 12-2-12 in water:methanol at 10 wt %, \( C < C^* \). Individual irregular globular micelles are distinguished below \( C^* \) with an average diameter of 100 nm. The micelles fused together from the overlapping of individual micelles as \( C > C^* \), as shown for 12 wt % in Figure 6b. Cryo-TEM micrographs at concentrations \( 2C^* \) and \( 4C^* \) were indistinct due to the high concentration of surfactant microstructures; nonetheless,
low-resolution threadlike micelles were distinguished at $2C^*$. Low resolution was expected for highly concentrated samples because cryo-TEM is more suitable for low concentration solutions where individual microstructures are more clearly observed.\(^{(32)}\)

The solution rheology of CTAB in water:methanol was also explored for comparative purposes, and the $C^*$ was measured at 19 wt %. The lower $C^*$ concentration for 12-2-12 ($C^* = 11$ wt %) in water:methanol compared to CTAB resulted from the increased surface activity of gemini surfactants. The micellization of surfactants in a polar environment involves two competing forces: (1) the interaction of the hydrophobic chains with the polar solvent, which drives the formation of micelles, and (2) the electrostatic repulsive forces between the charged headgroups, which opposes micellization.\(^{(36)}\) The dual hydrocarbon tails of gemini surfactants provide a larger thermodynamic contribution for micellization compared to single tail monomeric surfactants.\(^{(11)}\) Also, gemini surfactants have a smaller headgroup area contribution because the gemini charged groups are covalently confined at a closer proximity than electrostatic repulsive forces allow for single head conventional surfactants like CTAB.\(^{(28)}\)

The power law scaling relationships in water:methanol were very similar for both 12-2-12 and CTAB and were dramatically lower than observed for the surfactants in water. In water: methanol, the concentration scaling relationships below and above $C^*$ were 1.5 and 2.4 for 12-2-12 and 1.5 and 2.7 for CTAB, respectively. The decreased scaling relationship in water:methanol compared to water (1.7 and 4.8 for 12-2-12) was attributed to the ability of methanol to more efficiently bridge the interface of the surfactant hydrophilic and hydrophobic domains.\(^{(49)}\) This increased the effective headgroup size and decreased the packing parameter, which lead to the formation of globular micelles as shown in Figure 6.\(^{(50)}\) The larger scaling factors observed for 12-2-12 in water resulted from the optimal volume balance of the head and tail areas of the gemini surfactant, which resulted in the formation of flexible threadlike micelles that were sufficiently long to entangle and form branch points, thus increasing the solution viscosity. In contrast, the globular micellar structure in water:methanol did not permit the same degree of intermolecular associations, and lower viscosities and scaling relationships were observed compared to pure water solutions.

**Electrospinning Gemini Surfactants.** High molecular weight polymers are electrospun from viscous solutions at concentrations typically above $C_e$ or from the melt phase, and chain entanglements for nonassociating polymers are necessary to withstand the Raleigh instabilities and stabilize the whipping electrified jet to produce continuous fibers.\(^{(2,3,5,51)}\) The supramolecular microstructure of 12-2-12 in water and water:methanol lead to highly viscous solutions, which prompted us to investigate the possibility for electrospinning. In addition, threadlike micelles were possible for 12-2-12, and our earlier work described the necessity for entanglements of these WLMs for electrospinning.\(^{(6)}\) The electrospinning studies were conducted at the same temperature and solvent conditions as the solution rheology experiments in order to ensure similar surfactant microstructures. Moreover, all 12-2-12 solutions were electrospun at 25 kV, 5 mL/h syringe flow rate, and 12 cm tip-to-screen (TTS) distance. Figure 7 shows the SEM images of 12-2-12 fibers electrospun from water:methanol. Droplets formed at 20 wt % (Figure 7a) as a result of the low solution viscosity destabilizing the electrified jet. When the concentration was increased to $2C^*$, beaded fibers formed as shown in Figure 7b at 22 wt %. Figure 7c displays the formation of continuous fibers with a low concentration of large beads present and fiber diameters ranging from 0.9 to 7 $\mu$m when electrospinning from 28 wt %. Although fibers were continuous without beaded defects at 30 wt %, the fiber morphology was irregular with diameters ranging from 1 to 6 $\mu$m, as shown in Figure 7d. Continuous fibers with average fiber diameters of 4 and 5 $\mu$m, as shown in Figures 7e and 7f, were electrospun from 42 and 44 wt % solutions, respectively. The threadlike micelle entanglements stabilized the electrospinning jet and resulted in the transition from beads to continuous fibers at concentrations greater than $2C^*$. The 12-2-12 electrospun membranes were completely soluble, and $^1$H NMR spectroscopy of the gemini surfactant mats confirmed that the electric field did not alter the chemical structure of the gemini surfactant.

Asolectin was electrospun from CHCl$_3$/DMF (70/30 by weight) where the lipid microstructure formed reverse cylindrical micelles.\(^{(6)}\) Electrospun beads of asolectin were collected at concentrations below $C_e$ and beaded fibers at $C = C_e$. Continuous electrospun fibers of asolectin were collected at $C \geq 1.2C_e$, and the fiber diameter increased with increasing concentration. Electrospun fibers of 12-2-12, as depicted in Figure 7, displayed a higher surface roughness than asolectin electrospun fibers. The 12-2-12 fiber diameters also increased with concentration due to the higher degree of micellar growth and entanglements; however, smooth fibers were not observed at any concentration. The irregularities in the 12-2-12 fibers were presumed to result from the large applied voltage. Asolectin fibers were electrospun from an applied voltage of 15 kV;\(^{(6)}\) however, 12-2-12 required a voltage of 25 kV to produce fibers. Dietzel and co-workers\(^{(52)}\) correlated

\(^{(51)}\) Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* 2003, 63, 2223–2253.
electrospun fiber morphology to applied voltage and found that increasing voltage changed the electrospinning droplet and resulted in a higher concentration of fiber defects. Electrospinning efforts of 12-2-12 in water did not produce surfactant fibers at any concentration. Greiner and Wendorff \(^{53}\) published an electrospinning review and discussed recent electrospinning efforts from aqueous solutions. The electrospinning droplet forms a Taylor cone in the presence of an applied voltage and a jet is ejected from the Taylor cone if the applied voltage is strong enough to overcome the surface tension of the droplet. \(^{54}\) The solution viscosity, surface tension, and conductivity are key solution parameters in forming electrospun fibers. \(^{51,53,54}\) Electrospinning from aqueous solutions requires a reduction in the surface tension of water, which is typically accomplished with the addition of surfactants \(^{47}\) or cosolvents. \(^{10,51}\) In an effort to understand why 12-2-12 did not produce electrospun fibers from water, the solution conductivity and surface tension for 12-2-12 in water and water:methanol were explored for solutions with comparable zero shear viscosities at \(25^\circ\)C and are shown in Table 1. Electrospun fibers were collected from 42 wt % 12-2-12 water:methanol solutions, which had a surface tension of 26 mN/m and conductivity of 43 mS/cm. Solutions of 2.8 wt % 12-2-12 in water did not produce electrospun fibers, and the solution had a surface tension of 28 mN/m and lower conductivity of 8 mS/cm. The surface tensions and solution conductivities of 12-2-12 in water and water:methanol were within an acceptable electrospinning range; \(^{47}\) however, the 42 wt % water:methanol solution had a higher conductivity due to the much higher concentration of surfactant. Electrospinning from water was not successful potentially due to the low concentration of 12-2-12 in water. In water, 12-2-12 formed very viscous solutions at very low concentrations. Electrospinning requires a jet to eject a continuous fiber from the spinneret droplet and the low surfactant concentration in water may not have facilitated the formation of continuous fibers.

**Table 1. Surface Tension and Conductivity Comparison for 12-2-12 Solutions in Water:Methanol and Water with Comparable Zero Shear Viscosities at 25 °C**

<table>
<thead>
<tr>
<th>12-2-12 solution concentration</th>
<th>zero shear (\eta_0) (Pa s)</th>
<th>surface tension (mN/m)</th>
<th>conductance (mS/cm)</th>
<th>electrospun fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>42 wt % water:methanol</td>
<td>0.0353</td>
<td>26</td>
<td>43</td>
<td>yes</td>
</tr>
<tr>
<td>2.8 wt % water</td>
<td>0.0348</td>
<td>28</td>
<td>8</td>
<td>no</td>
</tr>
</tbody>
</table>


**Conclusions**

The micellar morphological transitions of 12-2-12 in water and water:methanol were characterized with cryo-TEM and solution rheology. The 12-2-12 microstructure in water transitioned from linear, entangled, threadlike micelles to branched threadlike micelles at 1.5 wt %, and at 2.7 wt % the microstructure evolved into a viscoelastic, entangled, highly branched threadlike network. In water:methanol, 12-2-12 produced a considerably different micellar microstructure compared to water, and the micellar morphology transitioned from partitioned globular micelles into overlapped micelles at \(C^*\), 11 wt %.

The supramolecular microstructures of 12-2-12 in water and water:methanol lead to highly viscous solutions, and their electrospinning was explored. Electrospinning 12-2-12 in water did not produce surfactant fibers at any concentration. However, for the first time nonwoven fibrous scaffolds were electrospun from gemini surfactants, with fiber diameters between 0.9 and 7 \(\mu\)m from water:methanol. The 12-2-12 fiber morphology transitioned from beaded fibers into continuous fibers at concentrations greater than 2\(C^*\) in water:methanol. The entangled supramolecular structure of the low molar mass surfactant stabilized the electrospinning jet and resulted in continuous fibers. Electrospinning gemini surfactant fibers from polar solvents represents an innovative strategy to develop high surface area scaffolds or membranes with charged hydrophilic surfaces for the development of charged controlled-release membranes, tissue engineering scaffolds, or for biologically compatible coatings.

**Acknowledgment.** We acknowledge Dr. Eugene G. Joseph of the Department of Chemical Engineering at Virginia Tech for the surface tension measurements and helpful discussions. This material is based upon work supported in part by the U.S. Army Research Office under Grant W911NF-07-1-0452 Ionic Liquids in Electro-Active Devices (ILEAD) MURI.