# Macromolecules

# Polyelectrolyte—Surfactant Complexes as Thermoreversible Organogelators

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Supporting Information

**ABSTRACT:** Poly(*N*,*N*-dimethyl-*n*-octadecylammonium *p*-styrenesulfonate) (PSS-DMODA) polymers were prepared and investigated as organogelators for low-polarity aromatic solvents. Gels were prepared by heating polymer solutions (2.5-20% w/vpolymer) at elevated temperature and then cooling in an ice bath. Gelation was confirmed by the formation of self-supporting samples that did not flow when inverted 180°. Measurement of the gel transition temperature by inversion testing showed a dependence on the concentration of the polymer, the molecular weight of the polymer, and the gelled solvent. Cavitation rheology measurements on a subset of the gels demonstrated that they were viscoelastic solids. Scanning electron microscopy measurements of freeze-dried xerogels and polarized optical microscopy measurements showed



the formation of network structures and birefringent samples, respectively. Aging studies showed syneresis of the gels especially at low concentration and temperature. Gelation was interpreted using a model for reversibly associating polymers. The gelation was attributed to the clustering of the ionic groups to form a physically cross-linked network that restricts the motion of the chains. These polyelectrolyte—surfactant complexes should be a useful class of organogelators as a number of characteristics of the polymer (molecular weight, ionic groups, side-chain length) can be independently varied to tune the properties of the resultant organogels.

# INTRODUCTION

Gels are a complex state of soft matter that are phenomenologically defined as systems containing large quantities of fluid that display solid-like viscoelastic properties over a broad range of time-scales.<sup>1</sup> Organogels are formed when a nonaqueous fluid is gelled, such as an organic solvent. A number of different compounds have been found to act as organogelators including semicrystalline polymers, block copolymers, and low molecular mass organogelators.<sup>2-4</sup> Physical gelation occurs when the organogelator is able to form a stable, three-dimensional percolating network that traps the surrounding fluid. Organogelators have found application in a number of areas from viscosity modification in foodstuffs and organic photovoltaics to templating nanostructured materials. $^{5-7}$  In this paper it is demonstrated that stoichiometric polyelectrolyte-surfactant complexes (PE-SURFs) of poly(*N*,*N*-dimethyl-*n*-octadecyl ammonium *p*-styrenesulfonate) act as organogelators for low-polarity aromatic solvents.

Stoichiometric polyelectrolyte—surfactant complexes (PE-SURFs) are formed by neutralizing each backbone ionic group of a polyelectrolyte with an oppositely charged surfactant. They have attracted interest for their ability to self-assemble into periodic ordered structures.<sup>8–12</sup> The neat polymers have been observed to form cylindrical, lamellar and frustrated lamellar morphologies

driven by the microphase separation between the ionic polymer and the surfactant side-chains.<sup>13</sup> The details of the morphological behavior are dependent on various factors including the electrostatic and hydrophobic interactions and the spontaneous curvature between the ionic and nonionic domains similar to the organization of surfactants and block copolymers.<sup>14,15</sup>

In addition to the neat phase behavior, a number of interesting properties are obtained in solutions of PE-SURFs in organic solvents.<sup>12,16–20</sup> For poly(*N*-ethyl-4-vinylpyridinium dodecyl sulfate) and poly(sodium styrenesulfonate) complexed with different quaternary ammonium surfactants in sufficiently nonpolar solvents the dissociation of the surfactant from the polyelectrolyte is not observed.<sup>16,18</sup> This can lead to a reduction in the intrinsic viscosity due to a contraction of the chain driven by attractive electrostatic interactions. Interchain aggregation has also been inferred from a reduction in the diffusion coefficient as observed by dynamic light scattering measurements.<sup>18</sup> Comparison of water swollen sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles in hexane with the PE-SURF of poly(*N*-ethyl-4-vinylpyridinium AOT)

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in hexane found that this PE-SURF formed a similar structure to the reverse micelles where a comb-like conformation is obtained with the alkyl tails of the AOT solubilized by the solvent.<sup>20</sup> Similarly, lyotropic behavior was found for poly(2-vinylpyridine) (P2VP) or poly(4-vinylpyridine) (P4VP) complexed with p-dodecylbenzesulfonic acid (DBSA) in xylene.<sup>19</sup> Here the xylene was found to selectively swell the hydrophobic surfactant sidechains. However, large polymer concentrations (>50% P4VP or >70% P2VP) were required to observe birefringent morphologies in these systems.

Interchain ionic aggregation and/or micelle formation of PE-SURFs in solution can potentially lead to macroscopic gelation if three-dimensional network structures are formed. For example, stoichiometric hydrogen-bonded complexes of a 36 kDa poly-(N-vinylpyrrolidone) with p-dodecylphenol have been shown to gel toluene solutions above 10 wt % loading of the polymer.<sup>21</sup> Small angle X-ray scattering measurements of these systems were found to be consistent with the formation of worm-like micelles of the polymer complexes. In addition the sol-gel transition temperature was found to increase with increasing concentration of the polymer in solution. Gelation of ionomers in nonpolar solution was predicted theoretically where the interchain aggregation of ionic dipoles results in the formation of a physically cross-linked ionomer network, which gels the solution.<sup>22</sup> In these systems, the sol-gel transition temperature increases with increasing concentration of polymer in solution. Also, macrophase separation occurs at lower concentration due to the unfavorable interactions between the ionomer and the solvent and the attractive interactions between the ionic groups. Qualitatively similar behavior was observed for the acid form of sulfonated polystyrene solutions in Decalin.<sup>23</sup> For example, gelation was observed on cooling solutions of a high molecular weight polymer (MW = 355 kDa, 0.8 mol % sulfonation) at concentrations above 10 wt % polymer where the sol-gel transition temperature increased with increasing polymer concentration. Macrophase separation of the polymer and solvent was observed at lower temperatures in the gels and at lower concentrations.

This paper will demonstrate that organogelation is possible using ionically complexed PE-SURFs. Here well-defined PE-SURFs have been synthesized by reversible addition—fragmentation chain transfer (RAFT) polymerization of a surfactant neutralized monomer. The gelation behavior has been examined as a function of the molecular weight of the polymer, its concentration in solution, and the choice of solvent. It will be shown that in the room temperature gels the PE-SURFs form aggregated network morphologies. Given that the gelation behavior of PE-SURFs is dependent on the molecular structure and the wide number of polyelectrolytes and surfactants that can be purchased or prepared, PE-SURFs are potentially a useful system to molecularly engineer organogels with tunable properties, such as the gel transition temperature.

#### EXPERIMENTAL METHODS

**Materials.** 2,2'-Azobis(2-methylpropionitrile) (AIBN) was purified by recrystallization in methanol. All other reagents were used as received.

*N*,*N*-Dimethyl-*n*-octadecylammonium *p*-Styrenesulfonate (SS-DMODA) Monomer Synthesis. Synthesis of SS-DMODA was based on a previously reported method.<sup>24</sup> First, *N*,*N*-dimethyl-*n*-octadecylammonium hydrochloride (DMODA-HCl) was synthesized. 20 g *N*,*N*-dimethyl-*n*- octadecylamine was dissolved in 100 mL

chloroform, and 5.55 mL (12.1M, 1:1 molar ratio) concentrated aqueous hydrochloric acid was added dropwise to the solution. The chloroform layer was collected, and concentrated on a rotary evaporator. DMODA-HCl was recovered after drying in a vacuum oven (22.1 g, white powder). Yield: 98.4%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 7.27, ppm): 2.92 (2H, t, NCH<sub>2</sub>CH<sub>2</sub>-), 2.74 (6H, s, N-(CH<sub>3</sub>)<sub>2</sub>), 1.73 (2H, m,  $NCH_2CH_2CH_2-$ ), 1.14 (30H, m,  $NCH_2CH_2(CH_2)_{15}CH_3$ ), 0.80  $(3H, t, NCH_2CH_2(CH_2)_{15}CH_3)$ . This salt was then used to synthesize the SS-DMODA monomer. 200 mL of a 0.1 g/mL chloroform solution of the DMODA-HCl was combined with 100 mL of a 0.17 g/mL aqueous solution of sodium *p*-styrenesulfonate and stirred for 30 min. The mixture was poured into a separation funnel and allowed to phase separate for 1 day. The chloroform layer was collected, and dried with anhydrous sodium sulfate and filtered to obtain a clear solution. The solution was concentrated by a rotary evaporator, and the SS-DMODA monomer was recovered by drying in a vacuum oven at room temperature. (31.3 g, white powder). Yield: 97.5%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 7.27, ppm): 7.86 and 7.43 (4H, d, C<sub>6</sub>H<sub>4</sub>), 6.72 (1H, q, C<sub>6</sub>H<sub>4</sub>-CHCH<sub>2</sub>), 5.81 and 5.31 (2H, d, C<sub>6</sub>H<sub>4</sub>-CHCH<sub>2</sub>), 3.03 (2H, t, NCH<sub>2</sub>CH<sub>2</sub>-), 2.87 (6H, s, N(CH<sub>3</sub>)<sub>2</sub>), 1.78 (2H, m, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.26 (30H, m, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 0.88 (3H, t, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 77.00, ppm): 144.22, 138.95, 135.75, and 125.93 (6C, s, C<sub>6</sub>H<sub>4</sub>), 57.82 (1C, s, NCH<sub>2</sub>CH<sub>2</sub>-), 42.83 (2C, s, N(CH<sub>3</sub>)<sub>2</sub>), 31.73 (1C, s, NCH<sub>2</sub>CH<sub>2</sub>-), 29.52-22.49 (15C, m, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 14.07 (1C, s, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>).

Didodecyl-1,2-phenylene Bis(methylene)bistrithiocarbonate RAFT Agent Synthesis. 1-Dodecanthiol (9.05 g, 45 mmol), Aliquat 336 (0.72 g, 1.8 mmol), and 60 mL of toluene were added into a three neck round-bottom flask. The solution was stirred under nitrogen gas in an ice bath for 15 min. Then 50% sodium hydroxide aqueous solution (3.63 g, 46 mmol) was added to the flask and stirred for 15 min. Carbon disulfide (3.44 g 45 mmol) dissolved in 20 mL of toluene was added to the solution, and the color of the solution quickly changed to yellow. After stirring for 15 min, a solution of 1,2-bis(bromomethyl)benzene (5.94 g, 23 mmol) dissolved in 30 mL of toluene was added to the flask. The solution was stirred at room temperature under nitrogen for 12 h. The reaction was terminated by adding 100 mL of deionized water and stirring for 30 min. The mixture was poured into a separation funnel, and a yellow toluene layer was collected and washed with deionized water 3 times. The product was recovered by rotary evaporation (14 g, yellow solid), and further purified by recrystallization in hexane (9.5 g, yellow powder). Yield: 64%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 7.27, ppm): 7.38 and 7.28 (4H, m, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>), 4.70 (4H, s, SCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>S); 3.39 (4H, t, SCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.72 (4H, m, SCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.28 (36H, s, SCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 0.90 (6H, t, SCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 77.00, ppm): 223.10 (2C, s, 2CS<sub>3</sub>), 133.90, 130.99, and 128.41 (6C, s, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>), 38.89 (2C, S, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>), 37.13 (2C, s, 2CS<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 29.62–27.98 (18C, m, 2CS<sub>3</sub>-CH<sub>2</sub> (CH<sub>2</sub>)<sub>9</sub> CH<sub>2</sub>CH<sub>3</sub>), 22.66 (2C, s, 2CS<sub>3</sub>CH<sub>2</sub> (CH<sub>2</sub>)<sub>9</sub> CH<sub>2</sub>CH<sub>3</sub>), 14.09 (2C, s, 2CS<sub>3</sub>CH<sub>2</sub> (CH<sub>2</sub>)<sub>9</sub> CH<sub>2</sub>CH<sub>3</sub>).

**RAFT Polymerization of PSS-DMODA.** RAFT polymerizations to synthesize poly(N,N-dimethyl-n-octadecylammonium p-styrenesulfonate) (PSS-DMODA) polyelectrolyte—surfactant complexes were conducted using conditions developed previously for the polymerization of tri-n-octylammonium p-styrenesulfonate.<sup>24</sup> For each polymerization 10 g of SS-DMODA, RAFT agent, AIBN (1:5 molar ratio to RAFT agent) and 21 mL chlorobenzene were added to make a 1 M monomer solution. The solution was sparged with nitrogen gas for 20 min and then heated to 80 °C for 8 h. The reaction was terminated by quenching in a water bath, and an aliquot was collected to characterize the conversion. The polymer was precipitated from hexane. To remove unreacted monomer from the polymer, the polymer was redissolved in 50 mL of tetrahydrofuran, and 100 mL of deionized water was slowly added to the solution to precipitate the polymer. Three polymerizations were run with RAFT agent concentrations of 1 mmol/mL, 0.5 mmol/mL, and 0.2 mmol/mL (mmol of RAFT agent/mL of chlorobenzene) to target PSS-DMODA molecular weight of 10 kDa, 20 kDa and 50 kDa. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 7.27, ppm): 7.62 and 6.43 (4H, m,  $C_6H_4$ ), 2.99 (2H, t, NCH<sub>2</sub>CH<sub>2</sub>-), 2.67 (6H, s, N-(CH<sub>3</sub>)<sub>2</sub>), 2.09 (1H, s,  $C_6H_4$ -CHCH<sub>2</sub>), 1.69 (4H, m,  $C_6H_4$ -CHCH<sub>2</sub> and NCH<sub>2</sub>CH<sub>2</sub>-(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 1.26 (30H, m, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 0.90 (3H, t, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 1.26 (6C, s,  $C_6H_4$ ), 57.87 (1C, s, NCH<sub>2</sub>CH<sub>2</sub>-), 42.81 (2C, s, N(CH<sub>3</sub>)<sub>2</sub>), 31.84 (1C, s, NCH<sub>2</sub>CH<sub>2</sub>-), 29.66-22.48 (15C, m, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), 14.01 (1C, s, NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>).

**Polymer Characterization.** <sup>1</sup>H NMR spectra were measured on a Varian Mercury-300 MHz spectrometer. Samples were dissolved in deuterated chloroform (99.8%D, Cambridge Isotope laboratories) at concentrations of 10 mg/mL and relaxation time of 5s was used. <sup>13</sup>C NMR spectra were measured on a Varian Mercury-300 MHz spectrometer. Samples were dissolved in deuterated chloroform (99.8%D, Cambridge Isotope laboratories) at concentrations of 150 mg/mL and relaxation time of 5s was used. Polymer molecular weights were determined based on the conversion determined from <sup>1</sup>H NMR and the expected molecular weight of the polymer at 100% conversion.

The molecular weight distribution of the polymers was characterized by size exclusion chromatography (SEC) using a Waters breeze system with three Styragel columns at 35 °C and a refractive index detector with a mixture of THF and 0.02 g/mL tri-*n*-octylamine. The molecular weight vs elution time was calculated using narrow polydispersity polystyrene standards.

**Organogel Preparation and Characterization.** First 0.025–0.2 g of PSS-DMODA polymer was dissolved in 1 mL of organic solvent at elevated temperature in a 4 mL screw cap vial followed by placing the vial in an ice bath for 5 min. Gelation was confirmed if the solution did not flow when the vial was inverted 180°. Benzene and styrene solutions were heated at 80 °C, but toluene and *o*-xylene solutions were heated to 110 and 140 °C, respectively.

After placing the vial in the ice bath, the bath was allowed to warm to room temperature under ambient conditions from 0 °C. The vials were periodically removed and inverted. If any flow of the gel was observed this temperature was recorded as the gel transition temperature,  $T_{\rm gel}$ . For the gels that were stable at room temperature  $T_{\rm gel}$  was first determined by slowly heating the vials in a thermostated reaction block with stepwise temperature changes of 2  $^{\circ}C/15$  min.  $T_{gel}$  was measured as the temperature at which the gels first broke-up when inverted after annealing for 15 min. Two sets of gels were prepared and the  $T_{\rm cel}$ measurements were made four times on the first set and three times on the second set. Four additional measurements were made with the lowest molecular weight polymers in o-xylene (PSS-DMODA-20). Heating rates of 2, 1, 0.5, and 0.33 °C/m were used for these gels. Aging studies of the gels were conducted by leaving the gels on the lab bench at room temperature or on a hot plate (IKA Works RCT basic) in an aluminum heating block (Chemglass Pie-Block) at 60 °C.

Cavitation rheology was used to measure the modulus of the 5 and 10% w/v concentration solutions of the lowest molecular weight polymer (PSS-DMODA-20) in *o*-xylene. The experiment was conducted as described in previous reports.<sup>25,26</sup> The setup consisted of a syringe pump (Braintree Scientific BS-8000), a differential pressure sensor (Omega PX26), a 5 mL gastight syringe (Hamilton) with a 22 gauge needle (BD) and a hot plate (IKA Works RCT Basic) with an aluminum heating block (Chemglass Pie-Block). The pressure was recorded using a 1/8 DIN Process Meter (Omega DP25B–S-A), a USB Data Acquisition Kit (DATAQ DI-145) and a personal computer. A schematic of the experimental setup is shown in the Supporting Information (Figure S1). Vials were sealed with a rubber septum during the cavitation rheology measurements. For each experiment the syringe was filled with air and the needle was lowered into the gel by raising the

hot-plate using a lab-jack. The pressure was zeroed, data collection was started and the syringe pump was turned on and run at a flow-rate of  $6.7 \,\mu \mathrm{L} \,\mathrm{s}^{-1}$ . The critical pressure,  $P_c$ , was determined from the peak in the pressure vs time curve. A representative pressure vs time curve is shown in the Supporting Information (Figure S2). Each gel was prepared by heating at elevated temperature and quenching for 5-15 min in an ice bath and placed in the heating block. Three measurements of the critical pressure were taken at each temperature. Then, 9-12 measurements could be taken before the gel was reannealed at elevated temperature, quenched and then placed back in the heating block for additional measurements. The temperature was adjusted in 4 °C increments and tests were conducted 2-5 min after the temperature reading had stabilized.

This critical pressure was used to determine the modulus of the gel, *E*, from

$$P_c = \frac{2\gamma}{r} + \frac{5}{6}E \tag{1}$$

where  $\gamma$  is the surface tension of the gel and *r* is the inner radius of the syringe needle. This equation was derived from the pressure-growth relationship of the cavity using a neo-Hookean strain-energy function. The surface tension of the gel was assumed to be the same as *o*-xylene with the following temperature dependence<sup>27</sup>

$$\gamma = 32.513 - 0.1101T (^{\circ}C) \tag{2}$$

The birefringence of the gels was examined using a cross-polarized optical microscope (OLYMPUS BX51) with a digital camera in transmission mode. The optical path consisted of the light source, a polarizer, a condenser, the sample, and an analyzer. A hot solution of the PSS-DMODA/solvent gel was taken up into a glass capillary, which was then flame-sealed and allowed to cool to room temperature. The gels were compared to a capillary filled with pure o-xylene to confirm the birefringence of the gel samples. Annealing experiments were conducted by placing the capillary in a hot state (Linkham) to control the temperature. The temperature was incrementally increased by 2 °C and an image was captured after annealing for 5 min. Cooling ramps were run by allowing the stage to cool under ambient conditions. Images were captured at 5 °C intervals during cooling. The birefringence intensity was measured using ImageJ software by measuring the average intensity of a region of the capillary and subtracting the average background intensity obtained in the middle of the image.<sup>28</sup>

The bulk morphology of xerogels of the PSS-DMODA/benzene gels was characterized by scanning electron microscopy (SEM, JEOL-JSM-7401F). The PSS-DMODA benzene gel was frozen in liquid nitrogen, and freeze-dried to obtain a white powder cake. A portion of the powder was placed on conductive tape and sputter coated with silver.

#### RESULTS AND DISCUSSION

**1. Polymer Synthesis.** A series of poly(*N*,*N*-dimethyl-*n*-octadecylammonium *p*-styrenesulfonate) (PSS-DMODA) polymers were prepared by RAFT polymerization of the corresponding *N*,*N*-dimethyl-*n*-octadecylammonium *p*-styrenesulfonate as shown in Scheme 1. The synthesis of the monomer and polymerization scheme followed a previously reported method for the direct polymerization of ammonium sulfonate monomers.<sup>24</sup>

Three polymers were synthesized with target molecular weights of 10, 20, and 50 kDa at 100% conversion by varying the concentration of RAFT agent in the polymerization. Figure 1 shows size exclusion chromatography traces of these polymers run in tetrahydrofuran +2 wt % tri-*n*-octylamine as the mobile phase. The tri-*n*-octylamine was added to mitigate interactions between the polymer and the columns.<sup>24</sup> Fairly narrow polydispersity (PDI) polymers were obtained where the PDI

#### Scheme 1. RAFT Polymerization of SS-DMODA Monomer to Produce PSS-DMODA





**Figure 1.** SEC traces of (a) 10 kDa, (b) 20 kDa, and (c) 50 kDa target molecular weight PSS-DMODA polymers. The curves have been shifted vertically for clarity.

increased with the target molecular weight. The conversion and molecular weight (M) of the polymers were determined by <sup>1</sup>H NMR. As the SS-DMODA monomer is nonvolatile, for each polymerization an aliquot was removed from the reactor, dried under vacuum to remove the solvent and then directly characterized to determine the conversion by measuring the amount of residual monomer. The molecular weight, the degree of polymerization (N), and PDI for the three polymers are listed in Table 1.

**2. Gelation Behavior.** The PSS-DMODA polymers were soluble in chloroform and tetrahydrofuran, but were all insoluble in benzene, toluene, styrene, and *o*-xylene at room temperature. Upon heating at elevated temperature in these less polar solvents, transparent, homogeneous solutions were formed. Assuming that ion dissociation is negligible in these nonpolar solvents, at elevated temperature, the thermal energy is apparently enough to prevent extensive ionic clustering and allow dissolution. These solutions were found to form optically transparent gels after cooling in an ice bath. Figure 2 shows pictures of self-supporting gels formed using PSS-DMODA-38 in benzene over a range of concentrations (Figure 2a) and in benzene, styrene, toluene, and *o*-xylene at 10% w/v polymer. These gels were thermoreversible as the vial could be reheated to form a homogeneous solution, which would regel upon cooling.

The PSS-DMODA/benzene samples that formed gels at room temperature could be freeze-dried to produce PSS-DMODA xerogels. These were imaged by scanning electron microscopy (SEM) and are shown in Figure 3. These SEM micrographs show primarily sheet-like structures, which are reminiscent of the lamellar morphologies observed in neat PE-SURFs, PE-SURF/organic solvent solutions, and bilayer morphologies in surfactant reverse micelles.<sup>8,19</sup> No clear dependence was observed in these images on

# Table 1. Characteristics of PSS-DMODA Polymers

polymer id	target M (kDa)	$M (\mathrm{kDa})^a$	Ν	$PDI^{b}$
PSS-DMODA-20	10	9.4	20	1.18
PSS-DMODA-38	20	18.3	38	1.20
PSS-DMODA-90	50	43.5	90	1.26

 $^a$  Calculated by  $^1{\rm H}$  NMR.  $^b$  Characterized by GPC with THF+2 wt % trioctylamine as the mobile phase.



Figure 2. PSS-DMODA-38/aromatic solvent organogels. Key: (a) benzene organogels at (1) 2.5, (2) 5, (3) 10, and (4) 20% w/v PSS-DMODA-38; (b) 10% w/v PSS-DMODA-38 in (5) benzene, (6) styrene, (7) toluene, and (8) *o*-xylene.



**Figure 3.** SEM micrographs of PSS-DMODA/benzene gels: (a) N = 90, c = 2.5%, (b) N = 90, c = 5%, (c) N = 90, c = 10%, (d) N = 90, c = 20%, (e) N = 38, c = 10%, (f) N = 38, c = 20%, (g) N = 20, c = 10%, and (h) N = 20, c = 20%. The scale bars are 2  $\mu$ m.



Figure 4. POM micrographs of the PSS-DMODA/o-xylene gels. The concentration of the gels increases from top to bottom, while the degree of polymerization of the polymer increases from left to right. The scale bar is 500  $\mu$ m.

the molecular weight or the concentration of the PE-SURF. However, it is not known to what extent the morphology is perturbed by the formation of the xerogel. For example, capillary forces during drying are known to result in shrinkage and further aggregation in gels.<sup>29</sup> Detailed identification of the morphology of the gels would require other characterization techniques, such as X-ray scattering.

The gels were also examined by polarized optical microscopy (POM). Figure 4 shows POM micrographs of 12 PSS-DMODA/ *o*-xylene gels sealed in glass capillaries. Each gel was birefrigent exhibiting a nonzero intensity when imaged through crossed polarizers. On the basis of the SEM data in Figure 3, the birefringence should arise from a combination of both the intrinsic birefringence of the PE-SURF due to differential polarizability of the stretched chains and form birefringence arising from the index of refraction difference between the solvent and the polymer network.<sup>30</sup> The transmitted intensity will then depend on the orientation of the polymer and network with respect to the polarizers. In general, in the lower concentration samples specific regions of bright intensity were observed and more uniform intensity was observed at higher polymer concentrations.

**3. Temporal Stability of Gels.** While the initial gels formed after cooling were always transparent and homogeneous, syneresis and clouding were observed as the gels were aged. A series of images is shown for the *o*-xylene gels aged at room temperature

for 216 h and at 60  $^{\circ}$ C for 16 h in Figure 5. In general, syneresis was observed at lower concentrations and aging temperatures, while clouding of the samples was observed at higher concentration.

This syneresis implies that a macrophase separated system is the equilibrium state for many of these gels. Therefore, gelation appears to be a competing process with phase separation resulting in kinetically trapped gels. This is similar to the results seen in ionomers where ionic clustering results in gel formation, which can further undergo phase separation.<sup>22,23</sup> This points to the main gelation mechanism being the interchain ionic clustering of the PE-SURF. The larger self-assembled structures of the PE-SURF in the network, as inferred from the SEM and polarized optical microscopy measurements, could still contribute to the bulk gel properties. Macrophase separation after gelation would then occur by breaking and reforming of the ionic clusters allowing the chains to reorganize and expel solvent. In general the amount of solvent expelled decreases with increasing polymer concentration. This is consistent with the restricted mobility with increasing ionic association. However, this result would also be expected thermodynamically as the volume of the solvent-rich phase would decrease as the concentration of polymer is increased. A more detailed analysis and separation of the thermodynamics and kinetics of these systems requires the measurement of both the miscibility gap and the gel transitions of these systems as a function of concentration and temperature.

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**Figure 5.** Images of *o*-xylene/PSS-DMODA organogels aged at (a) room temperature, 216 h, and (b) 60 °C, 16 h. The numbers on the left-hand-side indicate the degree of polymerization of the polymer and the numbers across the top of the images indicate the polymer concentration.

Significantly less solvent expulsion is seen at the shorter annealing time at higher temperature, especially at higher concentration. This allows for the determination of the gel transition temperature, which is the subject of the next section.

4. Thermal Transitions of Gels. The transition temperature from a gel to a solution  $(T_{gel})$  was measured by annealing the organogels with stepwise temperature increments and determining the temperature at which they breakup upon inversion. This temperature was assigned to  $T_{\rm gel}$ . For the 2.5% w/v concentration gels,  $T_{gel}$  was difficult to accurately measure due to the simultaneous expulsion of solvent during heating, making the determination of when the gel broke-up very subjective. For the higher concentration gels, as they were heated the gels would become noticeably more fragile and would fracture at higher temperatures if inverted too quickly or shaken. Above  $T_{\rm gel}$  a heterogeneous solution was obtained that would transition to a homogeneous solution upon further increase of the temperature. Figure 6 displays images of a 5% w/v PSS-DMODA-20 in o-xylene during an inversion test. At lower temperatures the system is a gel. At 87 °C, just below the gel transition, some sliding of the entire gel is observed. The gel transition is observed at 89 °C and pieces of the gel are observed in solution until 97 °C.

 $T_{\rm gel}$  vs composition for the three PSS-DMODA polymers in benzene, toluene, and o-xylene for 5, 10, and 20% w/v



Figure 6. Images of a 5% w/v PSS-DMODA-20/o-xylene solution taken on heating.



**Figure 7.**  $T_{gel}$  vs composition for ( $\blacksquare$ ) PSS-DMODA-N20, ( $\blacklozenge$ ) PSS-DMODA-N38 ( $\blacktriangle$ ) PSS-DMODA-N90 in (a) benzene, (b) toluene, and (c) *o*-xylene.

concentration are shown in Figure 7. The error bars indicate one positive and negative standard deviation from the mean. Each point is the average of seven measurements, except for the PSS-DMODA-20/*o*-xylene gels, where 13 (5%), 11 (10%), and 11 (20%) measurements were run.

As the inversion test for  $T_{gel}$  has some measure of subjectivity, cavitation rheology was used as a second measurement to confirm  $T_{gel}$ . This is a new technique where the modulus of a soft gel is measured by initiating a cavity in the system using a syringe and monitoring the critical pressure for mechanical instability.<sup>25,26</sup> Figure 8 shows the modulus of the PSS-DMO-DA-20/*o*-xylene gels at 5 and 10% w/v concentration as a



**Figure 8.** Modulus vs temperature for PSS-DMODA-20/*o*-xylene at (a) 5% w/v and (b) 10% w/v concentration. The error bars indicate one positive and negative standard deviation from the mean. The solid lines in each plot indicate the lowest and highest  $T_{gel}$  value measure by inversion and the dotted line indicated the average  $T_{gel}$  measured by inversion.

function of temperature. This measurement demonstrates that the gels behave as viscoelastic solids. The modulus shows a sharp drop at a temperature near the highest  $T_{\rm gel}$  measured by inversion testing at both concentrations. This point at the highest temperature was the highest temperature where a nonzero modulus could be measured in the material. Therefore, while inversion testing for  $T_{\rm gel}$  tends to slightly underestimate  $T_{\rm gel}$  it should give the proper scaling.

A third measurement was to monitor the birefringence of a 10% w/v PSS-DMODA/o-xylene gel as a function of temperature. Figure 9 shows the intensity measured by polarized optical microscopy on heating followed by cooling for two capillary samples. The raw images at a subset of temperatures are shown in the Supporting Information (Figure S3). One sample showed little intensity on heating, while the second showed a large increase in intensity at 50 °C, which peaked at 60 °C and rapidly decayed back to zero intensity by 70 °C. This intensity rise is likely some restructuring of the sample as the chain mobility increases at elevated temperature. On cooling, both samples showed an increase in intensity starting at ca. 65 °C. It is important to note that the T<sub>gel</sub> was determined to be 87 °C by inversion and 90 °C by cavitation rheology for this gel. As the birefringence is attributed to the self-assembly of the polymer into larger mesophase structures in solution, this provides evidence that it is not required for gelation. However, smaller, more isotropic interchain ionic clusters must still exist in the system for the solutions to remain gels.

**5. Gelation Mechanism.** The preceding experiments demonstrate that the gelation behavior of PE-SURF solutions has a strong dependence on the polymer concentration, molecular weight and choice of solvent. Furthermore, the aging studies demonstrate that the gels are not always the thermodynamic equilibrium state of the system, especially at lower temperature and solution concentration. This behavior is consistent with gelation driven by the physical association of the polymer



**Figure 9.** Measured intensity of polarized optical microscopy images for 10% w/v PSS-DMODA-20/*o*-xylene samples as a function of temperature: (squares) sample 1, (circles) sample 2, (open symbols) heating, (closed symbols) cooling.

through attractive interactions to form a percolating network. While the example of ionomer solutions has already been discussed, this same qualitative behavior is seen experimentally and theoretically in a range of associating polymer systems.<sup>31–36</sup>

In nonpolar solution the dissociation of the ionic groups is minimal, so the association of the PE-SURF occurs through attractive dipole-dipole interactions.<sup>18</sup> The free energy gain from this association will increase with decreasing temperature driving gelation upon cooling.<sup>22</sup> Further details of the gelation mechanism depend on the strength of the attractive interactions. For strong interactions where the associations are essentially irreversible gelation will occur when the percolation of the physically cross-linked network occurs.<sup>2</sup> For weak interactions the associations are reversible. This results in a different model for gelation and is summarized as follows.<sup>36</sup> At the geometrical percolation limit gelation does not occur because the chains can still relax due to the reversibility of the bonds. As the temperature is decreased the size of the ionic clusters grows resulting in a clustering transition where the ionic groups become localized over long time scales. This results in gelation of the solution due to the immobilization of the chains in between clusters. This dynamic behavior was also found to be similar to the vitrification of glasses. In terms of the phase behavior, this model results in a similar phase diagram to the strongly interacting systems, but with lower gel transition temperatures compared to that predicted by percolation.

For PE-SURFs solutions this weak association model appears applicable. Macrophase separation is seen after gelation indicating that the ionic associations are reversible and the system can equilibrate during the time scale of the measurement. In the PE-SURF solution, ionic aggregation should be similar to micellization of small molecule surfactants in organic media.<sup>14</sup> In this case, low critical micelle concentrations have been observed for reverse micelles. This has led to a description of micellization by a step-growth mechanism

$$2S \leftrightarrow S_2 \leftrightarrow S_3 \leftrightarrow \dots \leftrightarrow S_n \tag{3}$$

where S represents an isolated surfactant molecule,  $S_2$  is a dimer,  $S_3$  is a trimer, and  $S_n$  is an *n*-mer. Decreasing the temperature of the system would favor aggregation and shift the equilibrium to the right in eq 3. When the system is quenched from higher temperatures, this ionic clustering should quickly occur resulting in gelation. At low temperatures, the large extent of clustering could result in the formation of larger mesophase structures as observed by the SEM and polarized optical microscopy

measurements. However, these mesophase structures do not appear necessary for gelation as their birefringent signal disappears at temperatures below the gel transition. This gelation process also occurs faster than macrophase separation. Macrophase separation in these systems should also be driven by the attractive interactions between the ionic groups, therefore the initial clustering of the ionic groups appears to kinetically hinder larger scale macrophase separation. Upon heating, the cluster size should begin to decrease, and the gel transition will occur when the clusters are no longer able to restrict the chain dynamics on the time scale of the measurement.

Two other items to consider are the molecular weight and solvent dependence of the gelation behavior. First, the gels persist to higher temperature with increasing molecular weight of the PE-SURF. In terms of the weak association model this is attributed to the slower dynamics of the higher molecular weight chains. This could arise from the additional number of clusters per chain more effectively restricting chain motion. An analogy is the reduction of the glass transition of polymer with decreasing molecular weight.<sup>37</sup> This could be tested by examining gelation over a larger molecular weight range to see if  $T_{gel}$  asymptotes to a higher molecular weight limit. The gel stability also persists to higher temperature going from benzene to toluene to *o*-xylene. The normalized solvent polarity parameter  $(E_T(30)^N)$  of these solvents decreases from benzene (0.111) to toluene (0.099) to o-xylene (0.074 for p-xylene).  $E_{\rm T}(30)^{\rm N}$  is a dimensionless, empirical parameter, which quantifies the solvent polarity or the solvating power of a solvent.<sup>38</sup> Therefore, as the ionic groups become less soluble in the organic solvent their interactions becomes more favorable and persist to higher temperatures.

### CONCLUSION

It has been shown that a polyelectrolyte-surfactant complex can be used as an organogelator for low-polarity organic solvents. The gelation behavior is consistent with that expected for reversibly associating polymers where gelation occurs by ionic aggregation into large clusters, which immobilize the polymer chains. While many different polymers have been found to act as organogelators PE-SURFs have the potential to be a very useful class of organogelators. First, as homopolymers they are easily synthesized by controlled free radical polymerization. Many polyelectrolytes and surfactants are also commercially available and PE-SURFs could also be prepared by mixing in aqueous solutions. Second, large variations in the gel properties could be obtained by modifying the PE-SURF. For example, it was shown that the gel transition temperature could be varied from 20 to 40 °C by varying the molecular weight of the polymer. This transition temperature is also sensitive to magnitude of the ionic interactions in solution. These could also be tuned by varying the choice of surfactant in the system. Combined together, this ease of synthesis and tunable structure offers advantages over other homopolymers where different chemistries would need to be developed to gel a wider range of solvents.

# ASSOCIATED CONTENT

**Supporting Information.** Additional figures showing a schematic of the cavitation rheology experiment, pressure vs time for 10% w/v PSS-DMODA-20/o-xylene gel, and polarized optical microscopy images. This material is available free of charge via the Internet at http://pubs.acs.org.

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