# Redox Active Functionally Polymerized Surfactant Vesicles. Syntheses and Characterization

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**Abstract:** *N*-(11-Methacryloyloxyundecyl)-*N'*-methyl-4,4'-bipyridinium bromide (**2**), *N*-allyl-*N'*-(11-methacryloyloxyundecyl)-4,4'-bipyridinium dibromide (**3**), *N,N'*-bis(11-methacryloyloxyundecyl)-4,4'-bipyridinium dibromide (**4**), *N*-allyl-*N'*-(*n*-hexadecyl)-4,4'-bipyridinium dibromide (**6**), *N*-methyl-*N'*-{3-propylamido-*N'',N''*-bis[2-(10-undecenoyloxycarbonyl)-ethyl]}-4,4'-bipyridinium bromide iodide (**10**), *N*-allyl-*N'*-{3-propylamido-*N'',N''*-bis[2-(*n*-hexadecanoyloxycarbonyl)-ethyl]}-4,4'-bipyridinium dibromide (**11**), *N*-allyl-*N'*-(3-propylamido-*N'',N''*-di-*n*-octadecyl)-4,4'-bipyridinium dibromide (**12**), *N*-{2-(*N',N''*-bis[2-(*n*-hexadecanoyloxycarbonyl)ethyl]maleamoyl)ethyl}-*N'*-methyl-4,4'-bipyridinium bromide iodide (**16**), and *N*-methyl-*N'*-[2-(*N'',N''*-di-*n*-octadecylmaleamoyl)ethyl]-4,4'-bipyridinium bromide iodide (**17**) have been synthesized. **2**, **3**, and **6** formed micelle-type aggregates while sonication of **10**, **11**, **12**, **16**, and **17** led to the formation of predominantly single-compartment bilayers. Exposure of micellar **2** and **3** to ultraviolet irradiation or use of azobis(isobutyronitrile) as an initiator led to the loss of double bond. Vesicles formed from **10**, **16**, and **17** could only be copolymerized by using acrylonitrile and crotyl alcohol. Surfactant vesicles containing double bonds in their head groups (**10–12**) failed to polymerize or copolymerize under the conditions used. The presence of vesicles (unpolymerized and polymerized) has been demonstrated by electron microscopy, $^1$H NMR spectroscopy, substrate entrapment, gel filtration, and light scattering. Polymerized vesicles are appreciably more stable than their unpolymerized counterparts.

## Introduction

The preparation of polymerized vesicles has been reported recently in a number of different laboratories.[2-13] Polymerized vesicles are considerably more stable than their unpolymerized analogs and can therefore be advantageously utilized in photochemical solar energy conversion,[14,15] reactivity control,[16] and drug delivery.[17,18] We have polymerized functional surfactant vesicles either across their bilayers or head groups.[11,12] Importantly these polymerized vesicles showed greatly enhanced stabilities, while remaining fluid.[11] Encouraged by a recent report on vesicle formation from single chain surfactants containing viologen moieties[19] we prepared nine redox active surfactants containing strategically placed vinyl groups and describe here the formation of stable vesicles, their polymerizations, and characterizations.

## Experimental Section

All the compounds and solvents were reagent grade and were used without purification. Water was purified by deionization and subsequent distillation in an all-glass apparatus. Water for light scattering measurements was additionally purified by filtration through appropriate Millipore filters.

4,4'-Bipyridine was obtained from the corresponding dihydrochloride (Aldrich) by extraction with methylene chloride from 1.0 N aqueous sodium hydroxide and subsequent drying and crystallization from benzene–petroleum ether, mp ~114 °C (lit.[20] mp 114 °C). 11-Bromoundecyl methacryloate was prepared, according to the usual procedures, from 11-bromoundecanol and methacryloyl chloride in benzene and pyridine as a base.[3] Starting from 50 mmol of alcohol, 13.1 g (82% yield) of ester was obtained after distillation, bp 145 °C (0.3 torr).

Schemes I and II outline the syntheses of surfactants **2**, **3**, **4**, **6**, **10**, **11**, **12**, **16**, and **17**.

***N*-(11-Methacryloyloxyundecyl)-4-(4'-pyridyl)pyridinium Bromide (1).** 11-Bromoundecyl methacryloate (3.2 g (10 mmol)) and 3.1 g (20 mmol) of 4,4'-bipyridine in 20 mL of *N,N*-dimethylformamide (DMF) were heated for 15 h at 85 °C. After cooling, the reaction mixture was filtered from the bis-derivative **4** and ethyl ether was added. **1** formed as a precipitate which was separated by filtration and washed with ethyl ether and recrystallized from acetonitrile–ethyl ether: 3.8 g (80% yield), mp 104–6 °C. Anal. Calcd for $C_{25}H_{35}BrN_2O_2$: C, 63.15; H, 7.42; N, 5.89. Found: C, 62.2; H, 7.4; N, 5.7.

***N*-(11-Methacryloyloxyundecyl)-*N'*-methyl-4,4'-bipyridinium Bromide Iodide (2).** **1** (2.38 g (5 mmol)) and 3.55 g (25 mol) of methyl iodide in 20 mL of DMF were left standing at room temperature for 2 h. After addition of ethyl ether **2** was filtered from the reaction mixture. Subsequent crystallization from ethanol–ethyl ether afforded 2.84 g (92% yield) of **2**, mp >200 °C. Anal. Calcd for $C_{26}H_{38}BrIN_2O_2$: C, 50.58; H, 6.20; N, 4.58. Found: C, 46.68; H, 5.77; N, 4.26.

***N*-Allyl-*N'*-(11-methacryloyloxyundecyl)-4,4'-bipyridinium Dibromide (3).** **1** (2.38 g (5 mmol)) and a large excess (10 mL) of allyl bromide were refluxed for 1 h. Ethyl ether was added and the product collected

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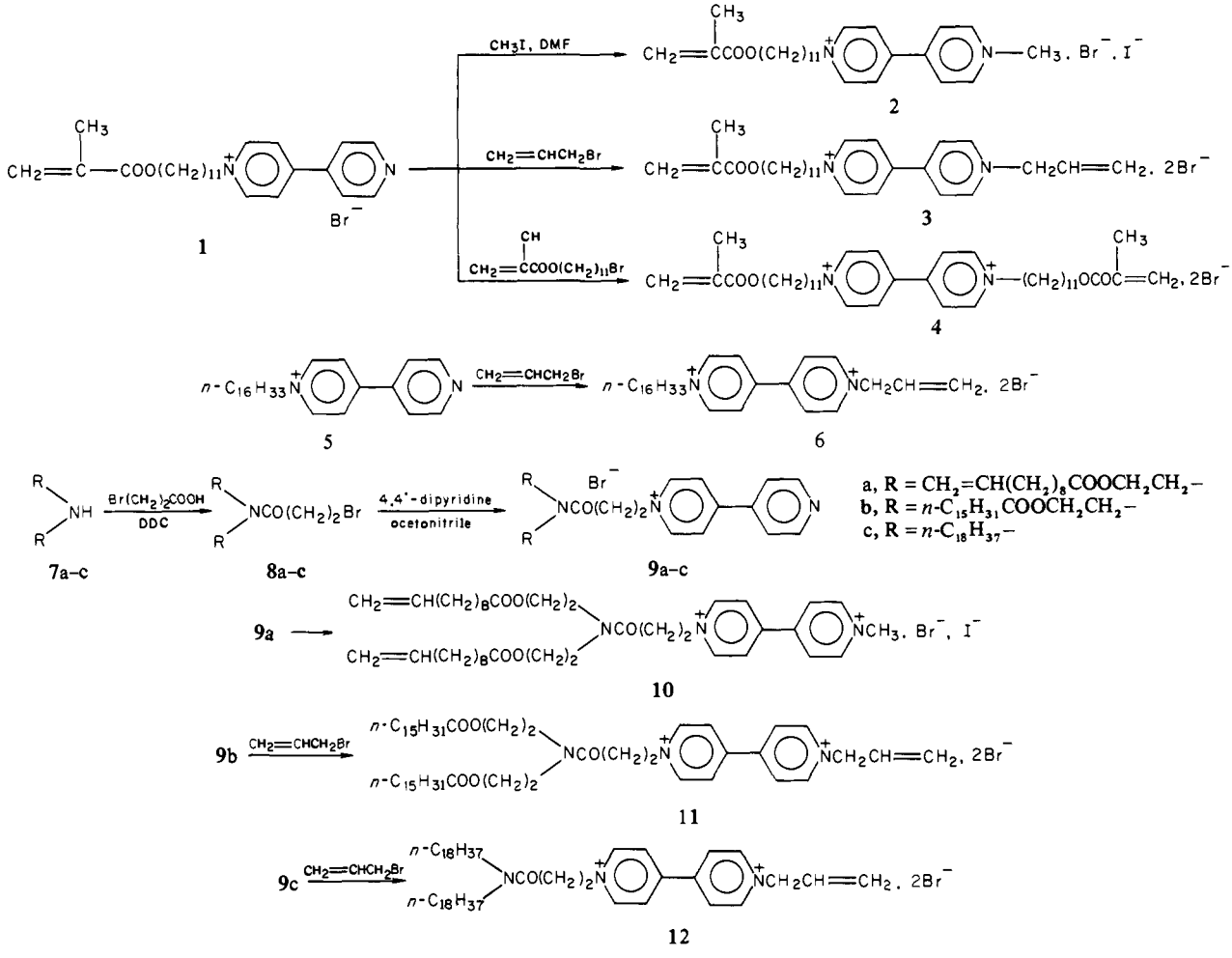
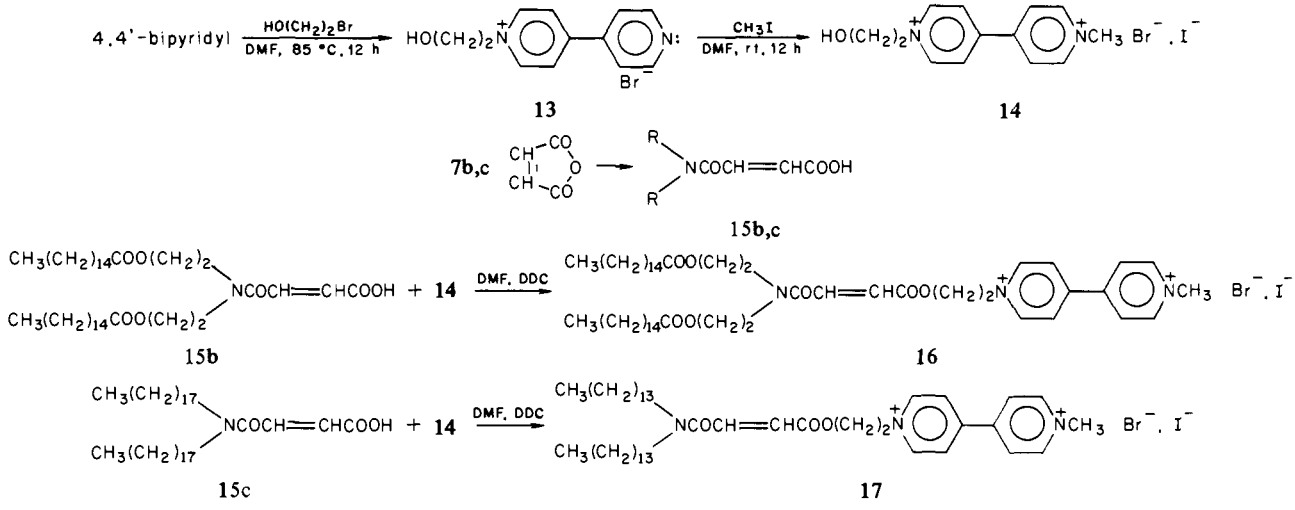
Scheme I



Scheme II



by filtration. Subsequent recrystallization from DMF–ethyl ether gave 2.48 g (95% yield) of **3**, mp >200 °C. Anal. Calcd for $C_{28}H_{40}Br_2N_2O_2$: C, 56.38; H, 6.76; N, 4.70. Found: C, 54.92; H, 6.97; N, 4.83.

***N,N'*-Bis(11-methacryloyloxyundecyl)-4,4'-bipyridinium Dibromide (4).** 4,4'-Bipyridine (1.56 g (10 mmol)) and 7.98 g (25 mol) of 11-bromoundecyl methacryloate were dissolved in 20 mL of DMF and heated at 85 °C for 20 h. After cooling, dioxane was added and **4** was filtered and washed with ethyl ether. Subsequent recrystallization from water gave 5.0 g (63% yield) of **4**, mp >200 °C. Anal. Calcd for $C_{38}H_{62}Br_2N_2O_4$: C, 60.45; H, 7.86; N, 3.52. Found: C, 59.6; H, 7.9; N, 3.5.

***N*-(*n*-Hexadecyl)-4-(4'-pyridyl)pyridinium Bromide (5).** 11-Bromohexadecane (3.05 g (10 mmol)) and 3.1 g (20 mmol) of 4,4'-bipyridine were dissolved in 20 mL of DMF and heated for 15 h at 85 °C. After cooling, the bis derivative was recovered by filtration and ethyl ether was added. Subsequent filtration and recrystallization from acetonitrile gave 2.54 g (55% yield) of **5**, mp 118–120 °C: $^1$H NMR ($CDCl_3$) $\delta$ 9.05 (d, 4 H), 8.25 (d, 4 H), 4.95 (t, 2 H), 1.8–2.5 (m, 2 H), 1.0–2.1 (br s, 26 H), 0.86 (c, 3 H). Anal. Calcd for $C_{26}H_{39}BrN_2$: C, 67.66; H, 8.95; N, 6.07. Found: C, 66.8; H, 8.9; N, 6.1.

***N*-Allyl-*N'*-(*n*-hexadecyl)-4,4'-bipyridinium Dibromide (6).** **5** (2.32 g (5 mmol)) and a large excess (10 mL) of allyl bromide were refluxed for 1 h. Then ethyl ether was added and the product collected by filtration; recrystallization from methanol–ethyl ether gave 2.85 g (98% yield) of **6**, mp >200 °C. Anal. Calcd for $C_{29}H_{44}Br_2N_2$: C, 59.80; H, 7.96; N, 4.81. Found: C, 59.6; H, 7.8; N, 4.8.

**Bis[2-(10-undecenoyloxycarbonyl)ethyl]amine (7a).** Starting from 10.0 g of the corresponding hydrochloride, **7a** was obtained by extraction in ethyl ether from 1 N aqueous sodium hydroxide; drying and removal of the solvent gave **7a** (8.7 g, 94% yield) as a colorless oil: $^1$H NMR ($CCl_4$) $\delta$ 5.3–6.2 (m, 2 H), 4.7–5.2 (m, 4 H), 4.08 (t, 4 H), 2.82 (t, 4 H), 1.8–2.5 (m, 8 H), 1.0–1.8 (br s, 24 H).

**Bis[2-(*n*-hexadecanoyloxycarbonyl)ethyl]amine (7b).** Palmitoyl chloride (60.5 g (0.22 mol)) was added to a solution of 14.2 g (0.10 mol) of iminodiethanol hydrochloride in 200 mL of DMF. After standing for 1.5 h the product spontaneously crystallized. **7b**·HCl was recrystallized from this reaction mixture by addition of 600 mL of methanol: 50.1 g (81% yield), mp 114–115 °C.

**7b·HCl** (10.0 g) was treated with 1 N sodium hydroxide in methylene chloride. After drying and solvent removal recrystallization from pentane gave 18.2 g (97% yield) of **7b**, mp 54–55 °C: $^1$H NMR ($CDCl_3$) $\delta$ 4.13 (t, 4 H), 2.88 (t, 4 H), 2.32 (t, 4 H), 1.0–2.1 (br s, 52 H), 0.87 (t, 6 H). Anal. Calcd for $C_{36}H_{71}NO_4$: C, 74.30; H, 12.30; N, 2.41. Found: C, 70.55; H, 12.37; N, 2.30.

**3-Bromopropionylbis[2-(10-undecenoyloxycarbonyl)ethyl]amine (8a).** **7a** (8.75 g (20 mmol)), 3.67 g (24 mmol) of 3-bromopropanoic acid, and 4.95 g (24 mmol) of *N,N*-dicyclohexylcarbodiimide (DDC) dissolved in 50 mL of anhydrous chloroform were stirred at room temperature for 1 h. After filtration of the urea derivative, the reaction mixture was washed with dilute HCl and then with aqueous sodium bicarbonate. Drying and removal of the solvent gave **8a** (8.13 g, 71% yield) as a colorless oil: $^1$H NMR ($CDCl_3$) $\delta$ 5.5–6.1 (m, 2 H), 4.7–5.1 (m, 4 H), 4.17 (5, 4 H), 3.4–3.8 (m, 6 H), 2.95 (t, 2 H), 1.8–2.5 (m, 8 H), 1.0–1.8 (br s, 24 H).

**3-Bromopropionylbis[2-(*n*-hexadecanoyloxycarbonyl)ethyl]amine (8b).** **7b** (11.64 g (20 mmol)), 3.67 g (24 mmol) of 3-bromopropanoic acid, and 4.95 g (24 mmol) of DDC in 50 mL of anhydrous chloroform were stirred at room temperature for 1 h. After filtration of the urea derivative the solvent was removed under vacuum and the crude **8b** was crystallized from methanol, giving 14.05 g (98% yield), mp 55–56 °C: $^1$H NMR ($CDCl_3$) $\delta$ 4.25 (t, 4 H), 3.5–3.8 (m, 6 H), 2.95 (t, 2 H), 2.30 (t, 4 H), 1.1–2.1 (br s, 52 H), 0.90 (t, 6 H).

**3-Bromopropionyldi(*n*-octadecylamine (8c).** **7c** (Fluka) (10.44 g (20 mmol)), 3.67 g (24 mmol) of 3-bromopropanoic acid, and 4.95 g (24 mmol) of DDC in 50 mL of anhydrous benzene were stirred at room temperature for 3 h. After filtration of the dicyclohexylurea, the crude **8c** was crystallized from ethanol (95%); 8.67 g (66% yield) was obtained, mp 50–54 °C: $^1$H NMR ($CDCl_3$) $\delta$ 3.63 (t, 2 H), 2.05–3.50 (m, 6 H), 2.87 (t, 2 H), 1.0–2.1 (br s, 64 H), 0.88 (t, 6 H).

***N*-{3-Propylamido-*N',N''*-bis[2-(10-undecenoyloxycarbonyl)ethyl]}-4-(4''-pyridyl)pyridinium Bromide (9a).** **8a** (2.86 g (5 mmol)) and 1.56 g (10 mmol) of 4,4'-bipyridine were dissolved in 40 mL of acetonitrile and refluxed for 20 h. The solvent was removed and the resulting oil was recrystallized from ethyl ether–pentane, 2.11 g of **9a** (58% yield), mp 62–65 °C.

***N*-Methyl-*N'*-{3-propylamido-*N'',N''*-bis[2-(10-undecenoyloxycarbonyl)ethyl]}-4,4'-bipyridinium Bromide Iodide (10).** **9a** (1.46 g (2 mmol)) and a large excess of methyl iodide (5 mL) were allowed to stand at room temperature for 15 h. The excess methyl iodide was removed under vacuum, ethyl ether was added, and the dication was filtered. It crystallized from methylene chloride–ethyl ether and gave 1.64 g (94% yield) of **10**, mp 190 °C dec. Anal. Calcd for $C_{40}H_{61}BrIN_3O_5$: C, 55.17; N, 7.06; N, 4.83. Found: C, 54.8; H, 7.0; N, 4.7.

***N*-Allyl-*N'*-{3-propylamido-*N'',N''*-bis[2-(*n*-hexadecanoyloxycarbonyl)ethyl]}-4,4'-bipyridinium Dibromide (11).** **9b** (1.75 g (2 mmol)) and a large excess of allyl bromide (10 mL) were refluxed for 1.5 h. The solvent was removed under vacuum, ethyl ether added, and the solid filtered. After crystallization from methanol–ethyl ether, 1.93 g (97% yield) of **11** was collected, mp 195 °C dec. Anal. Calcd for $C_{52}H_{87}Br_2N_3O_5$: C, 62.83; H, 8.82; N, 4.23. Found: C, 62.7; H, 8.7; N, 4.2.

***N*-Allyl-*N'*-[3-propylamido-*N',N''*-di(*n*-octadecyl)]-4,4'-bipyridinium Dibromide (12).** **9c** (1.63 g (2 mmol)) and a large excess of allyl bromide (10 mL) were refluxed for 1.5 h. The solvent was removed under vacuum; ethyl ether and pentane were added. The solid **12** was filtered and recrystallized from methanol–ethyl ether; it gave 1.66 g (89% yield), mp 190 °C dec. Anal. Calcd for $C_{52}H_{91}Br_2N_2O$: C, 66.86; H, 9.82; N, 4.50. Found: C, 66.7; H, 9.7; N, 4.4.

***N*-(2-Hydroxyethyl)-4-(4'-pyridyl)pyridinium Bromide (13).** 2-Bromoethanol (1.42 mL (20 mmol)) and 7.81 g (50 mmol) of 4,4'-bipyridine in 50 mL of DMF were heated for 15 h at 85 °C. After cooling, the dication was filtered, ethyl ether was added, and the solid **13** was collected (4.33 g, 77% yield); it crystallized from ethanol–ethyl ether, mp 195–197 °C: $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 8.92 (d, 4 H), 8.42 (d, 4 H), 4.80 (br t, 3 H), 3.97 (br t, 2 H). Anal. Calcd for $C_{12}H_{13}BrN_2O$: C, 51.27; H, 4.67; N, 9.96. Found: C, 50.8; H, 4.6; N, 9.8.

***N*-(2-Hydroxyethyl)-*N'*-methyl-4,4'-bipyridinium Bromide Iodide (14).** **13** (2.81 g (10 mmol)) and a large excess (10 mL) of methyl iodide in 30 mL of DMF were allowed to stand at room temperature for 15 h. Ethyl ether was added and the orange solid **14** was filtered; 3.89 g (92% yield) was obtained after crystallization from methanol, mp >200 °C: $^1$H NMR ($Me_2SO$-$d_6$) $\delta$ 9.10 (d, 8 H), 4.80 (br t, 2 H), 4.50 (s, 3 H), 3.97 (br t, 2 H).

***N,N*-Bis[2-(*n*-hexadecanoyloxycarbonyl)ethyl]maleamic Acid (15b).** **7b**·HCl (12.36 g (20 mmol)), 2.35 g (24 mmol) of maleic anhydride, and 3.95 g (50 mmol) of pyridine in 150 mL of anhydrous chloroform were stirred at 40 °C for 3 h. The chloroform was removed under vacuum, ethyl ether was added, and the reaction mixture was washed three times with $10^{-3}$ M hydrochloric acid. Drying and removal of the solvent gave a solid which crystallized from petroleum ether; 9.52 g (70% yield) of **15b** was obtained, mp 62–63 °C: $^1$H NMR ($CDCl_3$) $\delta$ 6.73 (d, $J$ = 12.9 Hz, 1 H), 6.39 (d, $J$ = 12.9 Hz, 1 H), 3.75 (m, $J$ = 6.4 Hz, 4 H), 2.30 (t, $J$ = 6.4 Hz, 4 H), 1.60 (m, $J$ = 7.8 Hz, 4 H), 1.25 (b, 52 H), 0.88 (t, $J$ = 6.9 Hz, 6 H). Anal. Calcd for $C_{40}H_{73}NO_7$: C, 70.65; H, 10.82; N, 2.06. Found: C, 70.64; H, 10.99; N, 2.08.

***N,N*-Di(*n*-octadecyl)maleamic Acid (15c).** Di(*n*-octadecyl)amine (10.44 (20 mmol)) and 2.35 g (24 mmol) of maleic anhydride in 150 mL of anhydrous chloroform were stirred at room temperature for 2 h. The chloroform was removed under vacuum and the crude **15c** was crystallized from acetonitrile to give 11.66 g (94% yield), mp 48–49 °C: $^1$H NMR ($CDCl_3$) $\delta$ 6.22 (s, 1 H), 6.59 (d, $J$ = 12.6 Hz, 1 H), 6.26 (d, $J$ = 12.6 Hz, 1 H), 3.34 (t, $J$ = 6.4 Hz, 2 H), 3.30 (t, $J$ = 6.4 Hz, 2 H), 1.20 (b, 60 H), 0.82 (t, $J$ = 6.8 Hz, 6 H). Anal. Calcd for $C_{14}H_{77}NO_3$: C, 77.48; H, 12.52; N, 2.26. Found: C, 77.67; H, 12.36; N, 2.26.

***N*-(2-{*N'',N''*-Bis[2-(*n*-hexadecanoyloxycarbonyl)ethyl]maleamoyl}-ethyl)-*N'*-methyl-4,4'-bipyridinium Bromide Iodide (16).** **14** (1.27 g (3 mmol)), 2.45 g (3.6 mmol) of **15b**, and 0.74 g (3.6 mmol) of DDC in 20 mL of DMF and 5 mL of anhydrous chloroform were stirred for 24 h at 35 °C. The reaction mixture was filtered from the urea derivative and the solvents were almost completely removed under vacuum. Addition of chloroform and subsequent filtration removed the unreacted **14**; the solvent was then removed under vacuum and the red mixture recrystallized from ethyl ether–pentane and methanol giving 1.46 g (45% yield) of **16**, mp 190 °C dec. Anal. Calcd for $C_{53}H_{87}BrIN_3O_7$: C, 58.67; H, 8.08; N, 3.87. Found: C, 58.2; H, 8.0; N, 3.8.

***N*-Methyl-*N'*-{2-[(*N'',N''*-di(*n*-octadecyl)maleamoyl)]ethyl}-4,4'-bipyridinium Bromide Iodide (17).** **14** (1.27 g (3 mmol)), 2.23 g (3.6 mmol) of **15c**, and 0.74 g (3.6 mmol) of DDC in 20 mL of DMF and 5 mL of anhydrous chloroform were stirred 24 h at 35 °C. The reaction mixture was filtered from the urea derivative and the solvents were almost completely removed under vacuum. Addition of chloroform and subsequent filtration removed the unreacted **14**. The solvent was then removed under vacuum and the red mixture was crystallized from ethyl ether and pentane; the red solid **17** was filtered and recrystallized from methanol, giving 1.69 g (55% yield), mp 180 °C dec. Anal. Calcd for $C_{53}H_{91}BrIN_3O_3$: C, 62.10; H, 8.95; N, 4.10. Found: C, 62.0; H, 8.8; N, 4.1.

Typical vesicle formation involved sonicating between 5 and 10 mg of surfactant in 4 mL of water at 70 °C using the microprobe of a Braunsonic 1510 sonifier set at 70 W. An optically clear solution was obtained in about 5–30 min.

Attempts to polymerize vesicles of compounds **9a**, **10**, **11**, **12**, **16**, and **17** by the AIBN procedure or by light[11] failed to show any decrease of proton signals in the vinyl region by $^1$H NMR. Vesicles prepared from **16** and **17** could be copolymerized. In procedure A, 4 cm$^3$ of vesicle solutions of compound **16** or **17** was sonicated (70 W, 70 °C, 30 min) with acrylonitrile and AIBN, while in procedure B vesicles prepared from **10** were cosonicated with crotyl alcohol and AIBN. The resulting solutions were then placed in an oil bath thermostated to 80 °C for 6 h. $^1$H NMR of the resulting solutions showed complete disappearance of the vinyl protons. Pronounced decomposition of the viologen moiety have accompanied, however, polymerizations.

Polymerizations were monitored by $^1$H NMR using a Varian XL-200 spectrometer in $D_2O$ (Aldrich, 99.8% D) performing 50 000 to 100 000 scans. Disappearance of the vinyl protons in the region $\delta$ 4.5–6.5 ppm were followed at ambient temperature using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard. $^1$H and $^{13}$C spectra were obtained for compounds **1–4**, **6**, **9a**, **10**, **12**, **15b**, **15c**, **18**, and **19** in $CDCl_3$ and **11** in $Me_2SO$-$d_6$ using the Varian XL-200 NMR. $^1$H NMR spectra of the intermediates were taken on a Varian EM 390 instrument.

Samples for electron microscopy were prepared by mixing equal volumes of the polymerized vesicle solution with 5% uranyl acetate solution. This solution was then placed on the copper grid for 1–2 min. Leaving solutions longer than 3 min on the grid seemed to cause clumping of the polymerized vesicles. Electron micrography was performed on a Hitachi HU-11E electron microscope.

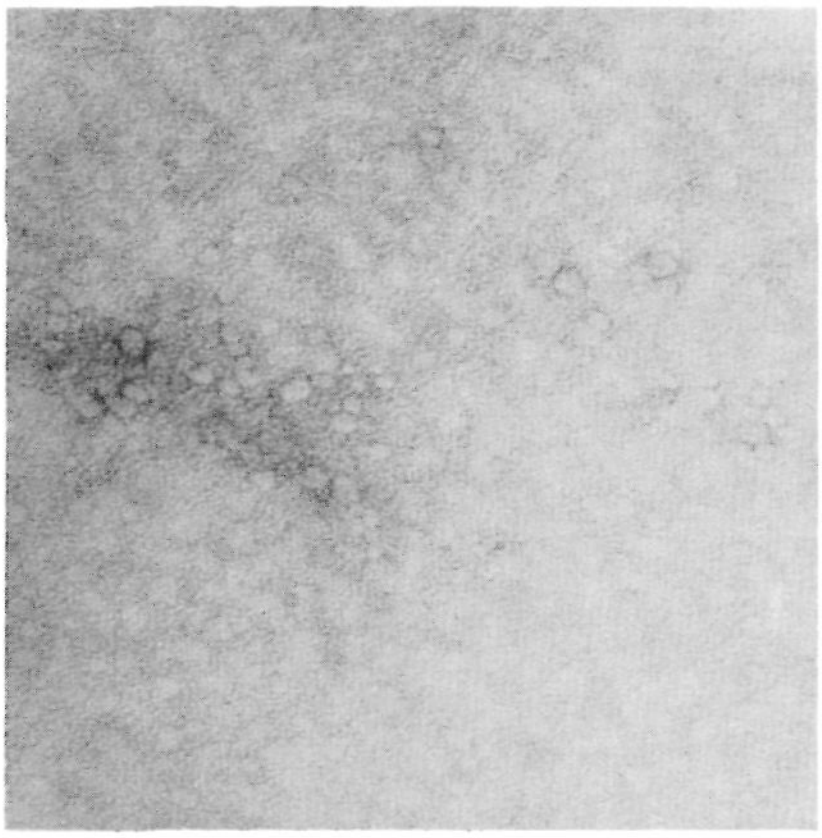


**Figure 1.** Electron micrographs of samples of nonpolymeric vesicles of compound **16**.

Entrapment of 2-aminopyridine hydrochloride (2APHCl) (Aldrich) was performed by sonicating (70 W at 60 °C) equal volumes of 0.57 mM solution of 2APHCl (pH 2.0) with equal volumes of already formed vesicles. The resulting solutions were then divided. Half were polymerized; half were not polymerized. Both solutions (immediately after vesicle formation or polymerization) were passed through a Sephadex column (Sigma G-50-80, 20.80 $\mu$, 16 × 178 mm) using 0.01 N HCl as an eluent to separate bound from free 2APHCl. Once entrapped, the probe remained in the vesicle interior for days.

Fluorescence measurements were made on a SPEX Fluorolog spectrofluorometer in the E/R mode. Generally, 2.5-mm slits with 5-nm band-pass were used. All fluorescence measurements were determined in air-saturated solutions.

Dynamic laser light scattering was determined on a Malvern 2000 spectrometer using the 4880-Å line from a Spectra-Physics 171 argon ion laser as the excitation source.

Stabilities of vesicles to ethanol were investigated by adding 0.1-mL aliquots of ethanol to 2 $cm^3$ of the vesicle or polymerized vesicle solutions (as prepared above), then mixing the resulting solutions and measuring the absorbance change at 400 nm using a Cary 118C spectrophotometer. The equation

$$A_{cor} = A_{obsd} \frac{\text{mL of vesicle + mL of alcohol}}{\text{mL of vesicle}}$$

was used to correct for absorbance change due to dilution.[3]

## Results and Discussion

Dispersion of redox-active surfactants (**10–12**, **16**, and **17**) in water by ultrasonic irradiation at 70 °C resulted in stable optically clear solutions. Increasing the sonication time decreased exponentially the turbidity down to a plateau value. Additional sonication caused no appreciable alteration in the turbidity. As before,[14-16] each surfactant was sonicated as long a time as it took to reach the plateau value in the turbidity vs. sonication time plots. These "well-sonicated" surfactants may be considered to contain predominantly single-compartment surfactant vesicles.[16,21] Surfactants **2**, **3**, and **6** form micelle-like aggregates.

Vesicle formation has been established by the usual criteria: dynamic light scattering, electron micrography, $^1H$ and $^{13}C$ NMR, gel filtration, and substrate entrapments.[21] Figure 1 shows typical electron micrographs. Closed structures are clearly seen. Arguments have been marshalled for the lack of morphological changes of surfactant vesicles on preparing samples for electron micrography either by staining or by freeze etching.[22] Nevertheless, we consider chemical evidence for the presence of bilayer vesicles to be more compelling (vide infra).

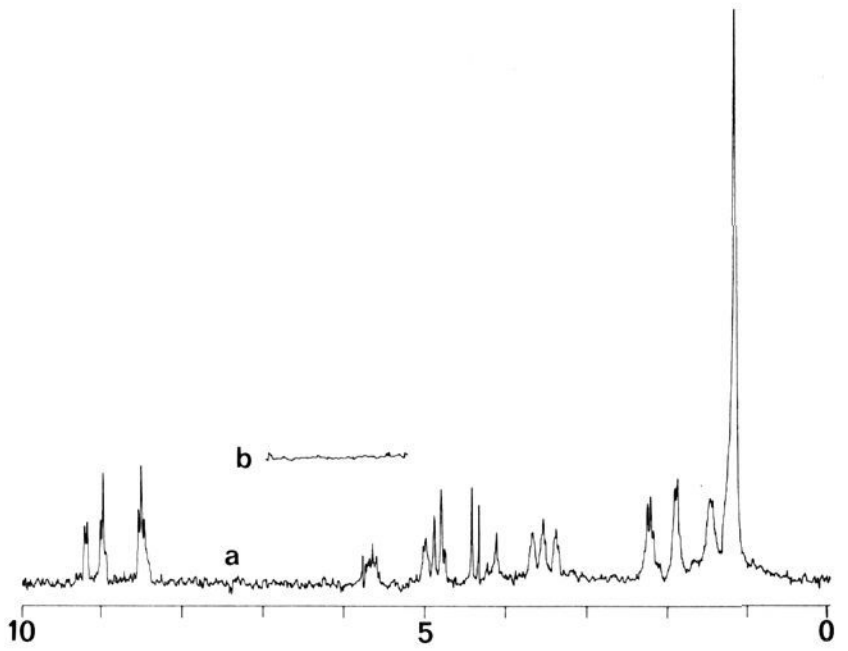



**Figure 2.** $^1H$ NMR of compound **10**: (a) as a vesicle; (b) insert of vinyl region after copolymerization with crotyl alcohol.

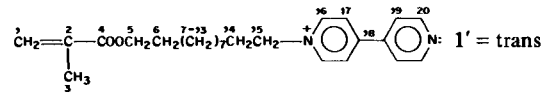
Poorly sonicated surfactants show extremely broad $^1H$ NMR spectra. Conversely, organized surfactant assemblies, like liposomes,[23] show well-resolved sharp NMR signals. The well-resolved $^1H$ NMR absorbances of sonicated redox-active surfactants (Figure 2 and Table I) may, therefore, be taken as evidence for the presence of organized assemblies. They cannot, however, distinguish between micelles and vesicles nor can sharp NMR lines be used as evidence for exclusive vesicle formation. $^1H$ and $^{13}C$ NMR chemical shift assignments of surfactants were made by collecting spectra in $CDCl_3$ or $Me_2SO$-$d_6$ and comparing these data with known chemical shifts of surfactants. The chemical shift assignments were made by comparing data in $D_2O$ with that in organic deuterated solvents. Spin simulations and decoupling experiments were performed on the XL-200 to simulate chemical shifts and coupling and to determine bonding patterns in order to verify the data given in Table I. Typical $^1H$ NMR spectra of the vesicles of compounds **1–4** or **10** show a broad line ($\delta$ 1.2 ppm) due to the $(-CH_2-)_n$ of the long aliphatic chains. Between $\delta$ 2.0 and 4.5, peaks are due to the $(-CH_2-)_n$ bonded as spacer groups between the alkyl chain and the nitrogen of the head group used to separate the nitrogen and the bipyridine rings; $\delta$ 4.5–6.0 is due to the vinyl proton absorptions. The bipyridine rings occur between $\delta$ 8.5 and 9.7 either as two quartets formed by two sets of overlapping doublets (i.e., **6**) or as two doublets and one set of doublets overlapping to form a triplet (i.e., **10**). Compounds **6**, **6a**, **11**, **12**, **16**, and **17** show spectra similar to the above except they also show $CH_3$–R peaks at $\delta$ 0.90 ppm. $^{13}C$ NMR has also been utilized for characterization of the surfactants. These data are also given in Table I.

Gel filtration on Sephadex G-50-80 (21.5 cm × 0.75 cm column) of sonicated **10**, **11**, **12**, **16**, and **17** resulted in the appearance of two peaks: one sharp peak in the void volume (18 mL) and one broad peak at later fractions (40–60 mL). Conversely, sonicated compounds **2**, **3**, and **6** did not appear in the void volume on gel filtration but were eluted as broad peaks in the later fractions (40–60 mL). These results indicate that **10**, **11**, **12**, **16**, and **17** form large aggregates (vesicles) while **2**, **3**, and **6** yield only aggregates that are retained in the cavities of the gel (average molecular weight less than 10 000).

Table II collects data on hydrodynamic radii and polydispersities, determined by dynamic laser light scattering. In agreement with the gel filtration results, vesicles are seen to be formed only from **10**, **11**, **12**, **16**, and **17**. Dilution of these aggregates did not alter their hydrodynamic properties. Increasing sonication times resulted in an exponential decrease of the sizes of the vesicles.

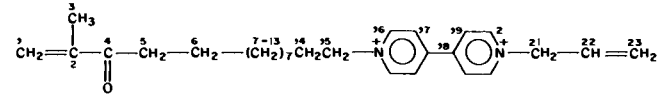
(21) Kunitake, T.; Shinkai, S. *Adv. Phys. Org. Chem.* **1980**, *17*, 435.
(22) Kunitake, T.; Okahata, Y.; Shimomura, M.; Yasunami, S.; Takarabe, K. *J. Am. Chem. Soc.* **1981**, *103*, 5401.
(23) Pope, J. M.; Cornell, B. A. In "Progress in Surface and Membrane Science"; Cadenhead, D. A., Danielli, J. F., Eds.; Academic Press: New York, 1978; Vol. 12, p 183. Nakagawa, T.; Tokiwa, F. In "Surface Colloid Science"; Matijevic, E., Ed.; Wiley: New York, 1976; Vol. 9, p 69.

Table I. $^1$H NMR Data ($\delta$, ppm) for Surfactants, Vesicles, and Polymeric Vesicles[a]



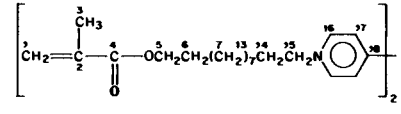

1

| | 1 | 1′ | 2 | 3 | 4 | 5 | 6 | 7–13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1$H NMR, 1 in $CDCl_3$ | 6.09, d $J_{1,1'}=-1.3$ | 5.55, m $J_{1',1}=-1.3$ | | 1.94, s | | 4.13, t $J_{5,6}=6.7$ | 1.68, m $J_{6,5}=6.9$ | 1.25, b | 2.00, b $J_{14,15}=6.6$ | 5.03, t $J_{15,14}=7.4$ | 9.56, d $J_{16,17}=6.9$ | 8.81, d $J_{17,16}=6.9$ | | 8.41, d $J_{19,20}=6.9$ | 7.74, d $J_{20,19}=6.9$ |
| 1, sonicated in $D_2O$ | 5.98 | 5.58 | | 1.91 | | 4.07 | 1.63 | 1.33 | 1.91 | A | 8.8 | 8.62 | | 8.25 | 7.79 |
| 1, sonicated in $D_2O$ + AIBN | disappeared | | | 1.91 | | 4.10 | 1.63 | 1.34 | 1.93 | A | 8.8 | 8.62 | | 8.30 | 7.80 |
| $^{13}$C NMR, 1 in $CDCl_3$ | 125.82 | 125.16 | 136.51 | 18.29 | | 31.87 | 25.87 | 29.31 | 28.53 | 61.88 | 140.86–145.71 | 121.44 | 151.51 | 121.44 | 140.86–145.71 |



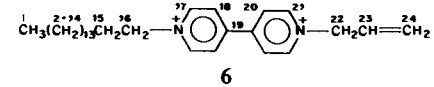

3

| | 1 | 1′ | 2 | 3 | 4 | 5 | 6 | 7–13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 23′ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1$H NMR, 3 in $CDCl_3$ | 6.00, m $J_{1,1'}=-1.0$ | 5.66, m $J_{1',1}=-1.0$ | | 1.86, s | | 4.07, t $J_{5,6}=6.5$ | 1.59, m $J_{6,5}=6.6$ | 1.26, b | 1.97, b | 4.69, t $J_{15,14}=7.5$ | 9.35, d $J_{16,17}=6.7$ | 8.79, d $J_{17,16}=6.7$ | | 8.81, d $J_{19,20}=6.7$ | 9.40, d $J_{20,19}=6.7$ | 5.38, d $J_{21,22}=6.3$ | 6.23, m $J_{22,23'}=16.6$ $J_{22,23}=10.5$ $J_{22,21}=6.4$ | 5.48, m $J_{23,22}=10.5$ $J_{23,23'}=-1.1$ | 5.52, m $J_{23',22}=16.6$ $J_{23',23}=-1.1$ |
| 3, sonicated in $D_2O$ | 5.90 | 5.60 | | 1.81 | | 4.00, t $J_{5,6}=6.5$ | 1.20, b | | | A | 9.00 | 8.45 | | 8.45 | 9.00 | | 5.95 | | 5.55 |
| 3, sonicated in $D_2O$ irradiated by light | 5.90 | 5.60 | | 1.82 | | 4.06, b | 1.20, b | | | A | 9.03 | 8.52 | | 8.52 | 9.03 | 5.25 | A | | A |
| 3, sonicated in $D_2O$ + AIBN | | | | 1.83 | | | 1.20, b | | | | | | | | | | | | |



4

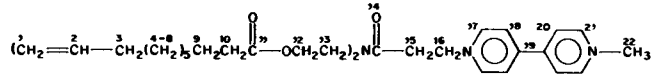
| | 1 | 1′ | 2 | 3 | 4 | 5 | 6 | 7–13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1$H NMR, 1 in $CDCl_3$ | 6.06, m $J_{1,1'}=-1.0$ $J_{1,3}=1.7$ | 5.51, m $J_{1',1}=-1.0$ $J_{1',3}=1.8$ | | 1.70, m $J_{3,1}=1.3$ | | 4.10, t $J_{5,6}=6.6$ | 1.62, m $J_{6,5}=6.6$ | 1.23, b | 2.03, b | 4.03–4.92, t $J_{15,14}=7.6$ | 9.45–9.47, d $J_{16,17}=6.9$ | 9.15, d $J_{17,16}=6.9$ | |



6

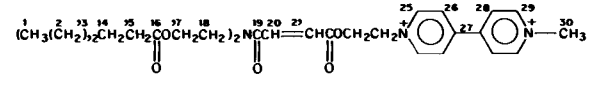
| | 1 | 2-14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 24′ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1$H NMR, 6 in $CDCl_3$ | 0.84, t $J_{1,2}=6.7$ | 1.22, b | 1.96, b | 4.69, t $J_{16,15}=7.4$ | 9.37, d $J_{17,15}=6.6$ | 8.79, d $J_{18,17}=6.6$ | | 8.85, d $J_{20,21}=6.6$ | 9.42, d $J_{21,20}=6.6$ | 5.38, d $J_{22,23}=6.2$ | 6.37, m $J_{23,24'}=16.7$ $J_{23,24}=10.5$ $J_{23,22}=6.1$ | 5.50, m $J_{24,23}=10.6$ $J_{24,24'}=-1.3$ | 5.60, m $J_{24',23}=17.0$ |

| | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **6**, sonicated in $D_2O$ | 0.81, t $J_{1,2}$ = 6.8 | 1.20 | 2.19, b | A | 9.14, d $J_{17,18}$ = 6.7 | 8.64, d $J_{18,17}$ = 6.7 | | 8.67, d $J_{20,21}$ = 6.5 | 9.33, d $J_{21,20}$ = 6.5 | 5.37, d $J_{22,23}$ = 7.0 | 6.19, m $J_{23,24'}$ = 16.8 $J_{23,24}$ = 10.6 $J_{23,22}$ = 7.0 | 5.52, d $J_{24,23}$ = 10.6 | 5.65, d $J_{24',23}$ = 17.0 | | | | | | | |
| | **6**, sonicated in $D_2O$ + AIBN, unpolymerized | 0.81 | 1.20, b | 2.10 | 4.77 | 9.06 | 8.51 | | 8.51 | 9.16 | 5.29 | 6.04 | 5.45 | 5.56 | | | | | | | |



**10**

| | | 1 | 1′ | 2 | 3 | 4–8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1$H NMR, | **10**, in $CDCl_3$ | 4.89, m $J_{1,2}$ = 10.4 $J_{1,1'}$ = −1.1 | 4.95, m $J_{1'2}$ = 17.3 $J_{1'1}$ = −1.0 | 5.77, m $J_{2,1'}$ = 17.9 $J_{2,1}$ = 10.2 $J_{2,3}$ = 6.7 | 2.00, m $J_{3,2}$ = 6.8 | 1.25, b | 1.55, b | 2.26, 2.29, t $J_{10,9}$ = 7.6 | | 4.25, 4.12 | 3.53, b | | 5.19, b | 3.68, b | 9.34, d $J_{17,18}$ = 7.0 | 8.83, d $J_{18,17}$ = 7.0 | | 8.86, d $J_{20,21}$ = 7.0 | 9.60, d $J_{21,20}$ = 7.0 | 4.64, b |
| | **10**, sonicated in $D_2O$ | 4.80, m $J_{1,2}$ = 9.9 | 4.87, m $J_{1'2}$ = 6.8 | 5.70, m $J_{2,1'}$ = 16.9 $J_{2,1}$ = 10.1 | 1.93, m $J_{3,2}$ = 6.9 | 1.20, b | 1.50, b | 2.27, m $J_{10,9}$ = 7.8 | | A | 3.57, b | | 5.02, b | 3.77, b | 9.02, d $J_{17,18}$ = 6.8 | 8.01, d $J_{18,17}$ = 6.8 | | 8.55, d $J_{20,21}$ = 6.8 | 9.21, d $J_{21,20}$ = 6.8 | A |
| | **10**, sonicated in $D_2O$ + AIBN + crotyl alcohol | disappeared | | | 1.94, m | 1.20, b | 1.50, b | 2.27, m | | A | 3.56, b | | 5.01, b | 3.76, b | 9.02, b | 8.55, d | | 8.55, d | 9.21, d | A |
| $^{13}$C NMR, | **10**, in $CDCl_3$ | 127.2 | | 114.2 | 33.7 | 29.3 | 24.8 | 34.2 | 173.7 | 61.7 | 59.1 | 169.6 | 46.5 | 38.0 | 146.8 | 139.1 | 148.8 | 139.1 | 146.9 | 28.6 |



**16**

| | | 1 | 2–13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1$H NMR, | **16**, in $CDCl_3$ | 0.847, t $J_{1,2}$ = 6.4 | 1.22, b | 1.56, b | 2.28, t $J_{15,14}$ = 7.9 | | 4.14, t $J_{17,18}$ = 6.1 | 3.60, b | | 6.27, d $J_{20,21}$ = 11.5 | 6.72, d $J_{21,20}$ = 11.7 | | 4.80, b | 5.36, b | 9.31, d $J_{25,26}$ = 6.1 | 8.81, d $J_{26,25}$ = 6.7 | | 8.81, d $J_{28,29}$ = 6.7 | 9.49, d $J_{29,28}$ = 6.7 | 4.60, s |
| | **16**, sonicated in $D_2O$ | 0.850, t $J_{1,2}$ = 6.4 | 1.27, b | 1.74, b | 2.22, b | | | | | 6.20, d | 6.43, d | | | | 9.08, d | 8.54, d | | 8.54, d | 9.08, d | |
| | **16**, sonicated in $D_2O$ + acrylonitrile, UV irradiated | 0.850, t $J_{1,2}$ = 6.4 | 1.28, b | 1.68, b | | | | | | | | | | 5.22, b | 9.08, d | 8.54, d | | 8.54, d | 9.08, d | |

[a] Symbol A means peak is altered by water irradiation. $J_{xy}$ values in hertz.

Table II. Dynamic Laser Light Scattering of Aggregates Prepared from Surfactants by Sonication

| surfactant | concn, mM | sonication time, min (80 °C, 70 W) | angle, deg | radii,[a] Å | polydispersity index |
|---|---|---|---|---|---|
| 6 | 17.48 | | 90 | 40 ± 20 | 0.55 ± 10% |
| | | | 120 | 55 ± 20 | 0.60 ± 13% |
| | 34.84 | | 90 | 47 ± 10 | 0.60 ± 8% |
| | | | 120 | 50 ± 15 | 0.75 ± 6% |
| | 11.61 | | 90 | 46 ± 15 | 0.60 ± 20% |
| | 5.81 | | 90 | 55 ± 30 | 0.80 ± 25% |
| | 3.48 | | | below CMC (no signal detectable) | |
| 10 | 1.38 | 0 | 90 | 2000 ± 1000 | 1.35 ± 60% |
| | | 15 | 90 | 720 ± 50 | 0.60 ± 3% |
| | | 25 | 90 | 720 ± 50 | 0.60 ± 8% |
| | | 40 | 90 | 730 ± 60 | 0.65 ± 7% |
| | 0.34 | 40 | 90 | 800 ± 70 | 0.70 ± 5% |
| 11 | 1.31 | 0 | 90 | 3000 ± 1000 | 1.40 ± 50% |
| | | 15 | 90 | 1250 ± 200 | 0.40 ± 8% |
| | | 30 | 90 | 735 ± 100 | 0.60 ± 10% |
| 12 | 1.02 | 0 | 90 | 1700 ± 1900 | 1.50 ± 50% |
| | | 15 | 90 | 550 ± 100 | 0.35 ± 7% |
| | | 30 | 90 | 530 ± 50 | 0.20 ± 5% |
| 16 | 1.17 | 0 | 90 | 2500 ± 1000 | 1.10 ± 21% |
| | | 15 | 90 | 720 ± 40 | 0.40 ± 4% |
| | | 30 | 90 | 650 ± 60 | 0.50 ± 6% |
| 17 | 1.02 | 0 | 90 | 3000 ± 1000 | 1.10 ± 30% |
| | | 15 | 90 | 500 ± 30 | 0.60 ± 7% |
| | | 30 | 90 | 500 ± 30 | 0.60 ± 5% |
| | 1.02 | 15 | 90 | 600 ± 30 | 0.35 ± 10% |
| | | | 120 | 530 ± 50 | 0.40 ± 3% |
| | 0.51 | 15 | 90 | 600 ± 40 | 0.35 ± 3% |
| | | | 120 | 550 ± 50 | 0.35 ± 5% |
| | 0.127 | 15 | 90 | 600 ± 30 | 0.30 ± 3% |
| | | | 120 | 550 ± 50 | 0.35 ± 3% |
| | 0.032 | 15 | 90 | 570 ± 30 | 0.35 ± 3% |
| | 0.008 | 15 | 90 | 600 ± 40 | 0.40 ± 5% |
| 2 and 3[b] | | | angle dependent | concn dependent | |

[a] Each value represents the mean of 3–6 measurements determined at 298 K. Errors are obtained by taking deviations from the mean of the separate measurements. [b] Rodlike micelles.[24]

Conversely, the hydrodynamic parameters for **2**, **3**, and **6** were found to be concentration dependent. These data suggest the presence of smaller aggregates for **2**, **3**, and **6**. **6** is likely to form spherical micelles while **2** and **3** are more prone to be present as rodlike structures.[24]

The redox-active surfactants investigated show great degrees of structural variations. They all have flexible tails, rigid segments (the viologen groups) and hydrophilic head groups (once again the viologen groups). With the exception of **4**, only one of the aromatic rings of the rigid viologen dication is substituted by long flexible tail(s). Surfactants **2**, **3**, and **6** contain only single chains and form micelles, while **10**, **11**, **12**, **16**, and **17** contain two alkyl chains and form vesicles.

Vesicles prepared from **10**, **16**, and **17** could only be polymerized in the presence of spacers[22] (acrylonitrile and crotyl alcohol). Polymerization across the head groups could not be accomplished even in the presence of spacers for **11** and **12**. Apparently these double bonds cannot be brought sufficiently close for cross-linking. Conversely, vesicles prepared from surfactants containing head groups on quaternary nitrogens [$(n\text{-}C_{11}H_{23}COOCH_2CH_2)_2N^+(CH_3)CHCH{=}CH_2$, $Br^-$, for example] could be readily polymerized either across both their inner and outer surfaces or, alternatively, exclusively across their outer surfaces.[11]

Polymeric vesicles retain the gross morphologies of their unpolymerized counterparts. Electron micrography (Figure 1) and laser light scattering substantiate this observation. Both unpolymerized and polymeric vesicles entrap and retain 2-aminopyridine (2AP) in their interiors. The appearance of 2AP in the void volume, on gel filtration, is only explicable in terms of its association with the surfactant vesicles.

Exploitation of polymeric redox-active surfactant vesicles in artificial photosynthesis is actively pursued in our laboratories.

**Acknowledgment.** Support of this work by the National Science Foundation (J.H.F.) and by the Consiglio Nazionale delle Ricerche (P.T.) is gratefully acknowledged. We thank NATO for a travel grant. Mario Politi is thankful for a fellowship from CNPq (Brazil).

**Registry No. 1**, 82797-84-0; **2**, 82797-85-1; **3**, 82797-86-2; **4**, 82797-87-3; **5**, 76842-00-7; **6**, 82797-88-4; **7a**, 68052-39-1; **7b**, 13080-33-6; **8a**, 82797-89-5; **8b**, 82797-98-6; **8c**, 82797-99-7; **9a**, 82797-90-8; **10**, 82797-91-9; **11**, 82797-92-0; **12**, 82797-93-1; **13**, 82797-94-2; **14**, 80325-44-6; **15b**, 82797-95-3; **15c**, 82798-00-3; **16**, 82797-96-4; **17**, 82797-95-5; **10** copolymer with crotyl alcohol, 82798-01-4; 11-bromoundecyl methacrylate, 33795-49-2; 4,4′-bipyridine, 553-26-4; methyl iodide, 74-88-4; allyl bromide, 106-95-6; 11-bromohexadecane, 112-82-3; palmitoyl chloride, 112-67-4; iminodiethanol, 111-42-2; 3-bromopropanoic acid, 590-92-1; 2-bromoethanol, 540-51-2; maleic anhydride, 108-31-6; di(*n*-octadecyl)amine, 112-99-2.

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(25) Kippenberger, D. J.; Odberg, L.; Tundo, P.; Fendler, J. H. *J. Am. Chem. Soc.*, to be published.