Although at this point we have very little mechanistic insight into the CO_2-laser-induced heterogeneous chemistry of 2-propanol on CuO, it is apparent that controlled chemistry can be carried out this way. We have made no effort to maximize the yield of one reaction channel and are still in the process of investigating systematic variations in pressure, catalyst composition, and fluence. Nevertheless, even over this fairly limited investigation of the phenomenon, branching ratios ranging from 0.02 to 6 have been observed. At a minimum, our data require both homogeneous and heterogeneous pathways to products. The homogeneous reaction yields largely hydrocarbon, while the heterogeneous pathway gives principally acetone. Much of the tunability in the branching ratio appears to result from changes in the proportions of reaction from these two pathways that can be induced by altering reaction conditions. It would be very difficult to obtain comparable tunability in the branching ratio using normal thermal activation. Pyrolysis of alcohols in the presence of metal oxides usually leads preferentially to dehydrogenation.[13] In the specific system we have employed, 2-propanol with CuO, quantitative data for both reaction channels have apparently not been reported, but it is clear that at relatively low temperatures (~200 °C) acetone is by far the principal product.[7,13] At higher temperatures hydrocarbon products become more prominent, but a range of at least several hundred degrees Centigrade would be required to duplicate the full range of branching ratios observed in the laser chemistry.[14] Pyrolysis of the alcohol in the absence of metal oxides appears to give surface-initiated free-radical chemistry leading mainly to acetone.[15] The estimated barrier for the homogeneous dehydration reaction is 67 kcal/mol, approximately 12 kcal/mol higher than the radical pathway for pyrolysis.[15]

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Registry No. 2-Propanol, 67-63-0; cupric oxide, 1317-38-0.

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Polymeric Surfactant Vesicles. Synthesis and Characterization by Nuclear Magnetic Resonance Spectroscopy and Dynamic Laser Light Scattering

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Abstract: $[CH_3(CH_2)_{15}][CH_2{=}CH(CH_2)_8CONH(CH_2)_6][CH_3]_2N^+Br^-$ (**1**), $[CH_3(CH_2)_{14}CO_2(CH_2)_2]_2[CH_3][CH_2CH{=}CH_2]N^+Br^-$ (**2**), $[CH_3(CH_2)_{14}CO_2(CH_2)_2]_2NCOCH{=}CHCO_2H$ (**3**), and $[CH_3(CH_2)_{17}]NCOCH{=}CHCO_2H$ (**4**) have been synthetized. Sonication of these surfactants led to the formation of vesicles. Vesicles could be polymerized by exposure to ultraviolet radiation or by the use of azoisobutyronitrile (AIBN) as an initiator. Vesicles prepared from **1** polymerized in their bilayers. Vesicles prepared from **2**, **3**, and **4** have double bonds on their headgroups and could, therefore, potentially polymerize both at the inner and outer surfaces or separately at either surface. Polymerization of vesicles prepared from **2**, **3**, and **4** by ultraviolet radiation resulted in the closing of both surfaces. Conversely, addition of AIBN to a solution of these vesicles and subsequent incubation at 80° led to the selective "zipping-up" of the outer surface only. Following the loss of vinyl protons of the surfactant vesicles by ^1H NMR spectroscopy provided evidence for polymerization. Presence of vesicles has been demonstrated by substrate entrapment, gel filtration, and dynamic laser light scattering. Increasing the sonication time led to smaller and less polydisperse vesicles. On polymerization, vesicles maintained the sizes of their nonpolymeric counterparts. Polymeric vesicles were found to be appreciably more stable than their unpolymerized analogues. Polymeric vesicles retained the fluidities of vesicles and underwent thermotropic phase transitions. Addition of KCl led to the growth of both unpolymerized and polymeric surfactant vesicles.

Completely synthetic surfactant vesicles provide useful media for the development of chemistry based on membrane-mediated processes.[5] Areas investigated in membrane mimetic chemistry include reactivity control,[5–7] recognition,[8] solar energy conversion,[9] drug delivery,[10] and analytical applications.[11] These studies have been considerably aided by the large surface potentials and charge

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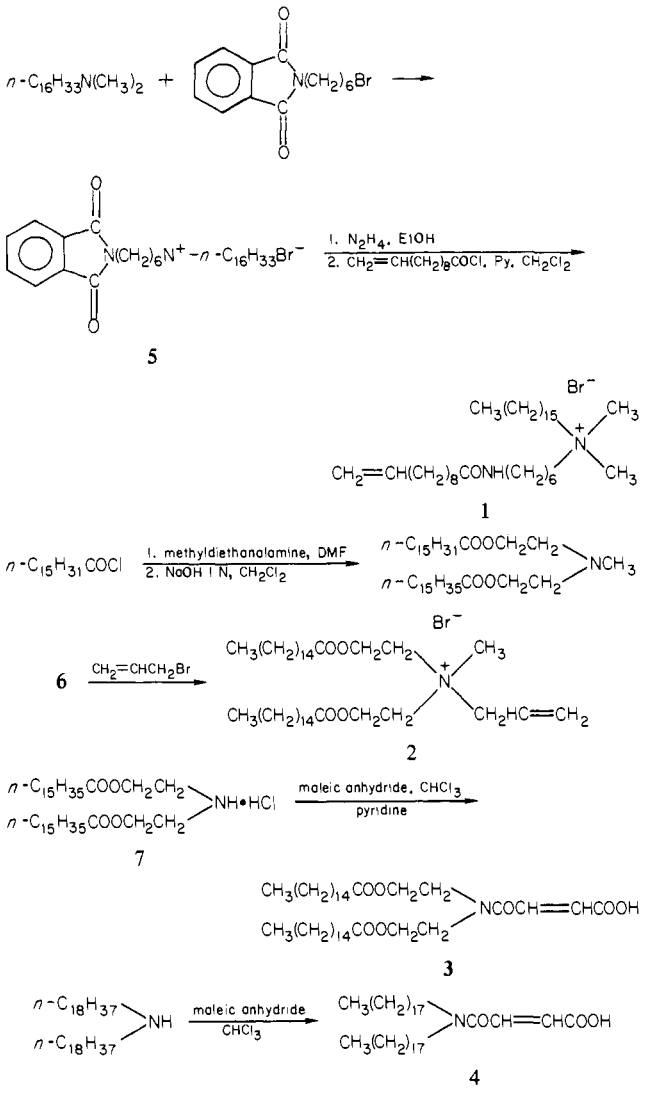
Scheme I



densities on the vesicles[12] and the possibility of chemical functionalizations.[13] Recognizing the need for controlling permeabilities and for obtaining long-term stabilities, polymeric vesicles have recently been prepared in several laboratories.[14-25] Synthesis

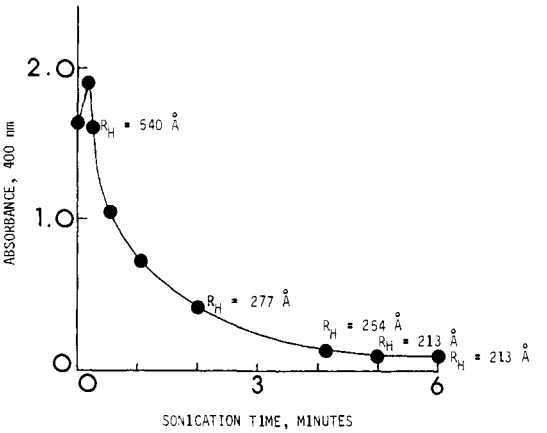
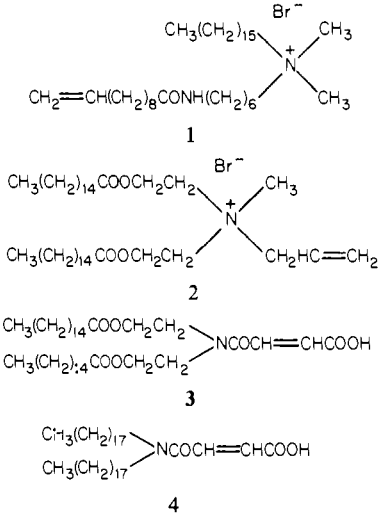


Figure 1. Plot of turbidity (measured at 400 nm) for 0.01 g of **2** per 1.0 mL of water as a function of sonication time at 70 °C using the Branson sonicator microprobe at 70 W. Indicated are the hydrodynamic radii (R_H) at corresponding sonication time, determined by dynamic laser light scattering.

and characterization of vesicles prepared from surfactants **1**, **2**, **3**, and **4** and their polymerization across the bilayers or alternatively at the headgroups are the subject of the present report. Evidence for vesicle polymerization has been obtained by ^{1}H NMR spectroscopy, substrate entrapment, and gel filtration. Dynamic laser light scattering measurements have provided morphological information. In addition to enhanced stabilities and controllable permeabilities, polymeric vesicles, like natural membranes, retain their fluidities and undergo thermotropic phase transitions.



Experimental Section

Scheme I outlines the synthesis of surfactants **1**-**4**. *N*,*N*-Dimethylhexadecylamine (10 mmol) was heated for 10 h at 65 °C with the monophthalimido derivative of 1,6-dibromohexane (9 mmol) to give $[CH_3(CH_2)_{15}][PhthN(CH_2)_6][CH_3][CH_3]N^+Br^-$ (**5**). Recrystallization from benzene–pentene yielded 79% of **5**; mp 74.5 °C. Hydrazonolysis of **5** in EtOH yielded the amine, which condensed in CH_2Cl_2 and pyridine with 10-undecanoyl chloride to give **1**. Recrystallization from CH_3CN and chromatography on silica gel (CH_2Cl_2–MeOH 95:5, v/v) gave an 81% yield; mp 89–90 °C.

Palmitoyl chloride (110 mol) was added to methyldiethanolamine (50 mmol) in 100 mL of DMF. After 2 h at room temperature, crude crystals of $[CH_3(CH_2)_{14}CO_2CH_2CH_2]_2NCH_3$·HCl (**6**·HCl) were obtained. Recrystallization from MeOH gave **6**·HCl in 85% yield; mp 117–118 °C. A 5-mmol sample of **6**·HCl was treated with 1.0 N NaOH

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in CH_2Cl_2 to give 2.74 g of **6** (98% yield); mp 40.1 °C (pentane). **6** (5 mmol) was refluxed with excess allyl bromide for 1 h. After the unreacted bromide was removed the solid **2** was recrystallized from benzene: yield 85%; mp 88–89 °C.

Palmitoyl chloride (110 mmol) was added to diethanolamine hydrochloride (50 mmol) in DMF. After 2 h at room temperature, crude crystals of $[CH_3(CH_2)_{14}CO_2CH_2CH_2]_2NH\cdot HCl$ (**7**) were obtained. recrystallization from MeOH gave an 81% yield; mp 114–115 °C. **7** (10 mmol) in 70 mL of $CHCl_3$ and pyridine (25 mmol) was reacted with maleic anhydride (12 mmol) at room temperature for 1 h. Washing with 5% HCl and recrystallization from petroleum ether gave **3**: yield 70%; mp 62–63 °C.

Dioctadecylamine (10 mmol) and maleic anhydrate (12 mmol) were reacted in 70 mL of $CHCl_3$ at room temperature for 1 h. Removing the solvent and recrystallization from CH_3CN gave **4**: yield 94%; mp 48–49 °C.

All other compounds and solvents were reagent grade and were used without purification. Water was purified by deionization and subsequent distillation in an all-glass apparatus.

Vesicles have been prepared by sonication of **1**, **2**, **3**, or **4** (typically 2–6 mg of surfactant in 6–8 mL of H_2O or D_2O) at 70 °C by using the microtip of a Bransonic 1510 sonifier set at 70 W. Sonication time depended on the surfactant and on the nature of the experiment (see Figure 1).

Vesicles were polymerized either by irradiation with a 450-W xenon lamp for 8–12 h or by heating with an initiator (azoisobutyronitrile, AIBN) at 80 °C for 8–10 h.

^1H and ^{13}C NMR (see Table I) supported the structures and purities of **1**, **2**, **3**, and **4**. ^1H and ^{13}C NMR spectra were taken on a Varian XL 200 spectroemter by using either $CDCl_3$ or Me_2SO-d_6 as a solvent for the surfactants and in D_2O for the vesicles. A total of 50 000–100 000 scans were performed to prove the complete disappearance of vinyl protons. Chemical shifts are given in ppm. All chemical shifts in $CDCl_3$ were assigned with respect to the $CHCl_3$ line (δ = 7.24 ppm vs. Me_4Si). For spectra in D_2O, 2,2-dimethyl-2-silapentane (DDS) (δ = 0) was used as internal standard.

Dynamic light scattering experiments were carried out on a Malvern system with a 15-mW He–Ne laser as excitation source. Autocorrelation was performed on a Ford correlator. The data were treated on a PET Commodore Computer using the cumulant program. Samples were prepared in dust-free distilled water and filtered through appropriate millipore filters just prior to analysis.

Absorption and emission spectra were taken on a Cary 118C spectrophotometer and on a SPEX fluorolog, respectively. Fluorescence measurements were taken in the E/R mode, generally using 2.5-mm slits with 5-nm bandpath.

Results and Discussion

Vesicle Formation. Surfactant **1** is water soluble while **2**, **3**, and **4** are insoluble in water at room temperature. At temperatures higher than 60 °C, they gave, however, opaque solutions (at the concentrations used). Ultrasonic irradiation at 65 °C decreased the turbidity of surfactant solutions. Increasing sonication time resulted in an exponential decrease of turbidity (monitored at 400 nm) down to a plateau value. Decreasing turbidity paralleled the decrease of the size of the surfactant vesicles. At the plateau value in the turbidity vs. sonication plots, surfactant vesicles are seen to reach optimal hydrodynamic radius and uniformity (Figure 1 and vide infra). Further sonication did not appreciably alter the properties of the surfactant vesicles.

^1H NMR spectroscopy provided evidence for vesicle formation. Incompletely sonicated surfactants showed extremely broad unresolved signals. Conversely, well-sonicated surfactants gave well-resolved ^1H NMR spectra with dicrete magnetic resonances corresponding to the chemical shifts of the surfactants in $CDCl_3$ (Table I). Prominent features in the NMR spectra of compounds **1** and **2** are the terminal CH_3 group at $\simeq$0.8 ppm, the CH_{2n} groups in the hydrocarbon chain at $\simeq$1.2 ppm, the CH_3 group on the quaternary nitrogen at $\simeq$4.0 ppm, and the vinyl protons appearing in the 6–7-ppm region. The spectra of **3** and **4** are similar to those of **1** and **2** but lack, of course, the N^+CH_3 absorption. These assignments are based on previous studies on surfactants.[26]

Prominent features in the ^{13}C NMR spectra are the terminal methyl carbon (14.054 ppm), the methylene carbons of the long chain (22.622–33.979 ppm), the carbonyl carbons of the long chain (172.791 ppm), and the two spacer methylene groups between the carbonyl of the long chain and the quaternary ammonium nitrogen (57.485–60.626 ppm). The *N*-methyl carbon absorbs at 49.395 ppm while the other methylene group attached to the quaternary nitrogen absorbs at 65.988 ppm and the vinyl region occurs at 124.018–130.66 ppm (Figure 2 and Table I).

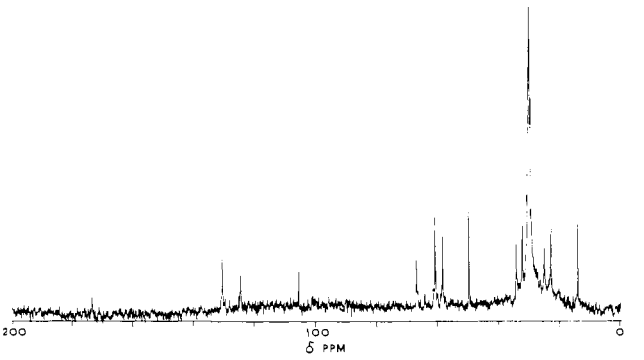

Figure 2. ^{13}C NMR spectrum of sonicated (50 mg/cm^3 of D_2O, sonicated at 70 W) nonpolymerized vesicles prepared from **2**. Chemical shifts were recorded on a Varian XL-200 MHZ instrument at ambient temperature relative to DSS.

Vesicle Polymerization. Polymerized surfactant vesicles were obtained either by heating the vesicles with AIBN or by exposing them to ultraviolet radiation. Polymerization was monitored by following the loss of vinyl protons with ^1H NMR spectroscopy. The complete disappearance of vinyl protons was taken to indicate the completion of polymerization (see Table I).

Polymerization of vesicles prepared from **1** can result in "zipping-up" each half of the bilayer separately or cross-linking them. Polymerization of vesicles prepared from **2**, **3**, and **4** offers the possibility of "closing" separately either the inner or the outer surface. Alternatively, both surfaces can be "zipped up" (Figure 3). Selective polymerization has been achieved for surfactant vesicles prepared from **2**, **3**, and **4** in the present work. Irradiation by ultraviolet light resulted in the complete loss of vinyl protons for vesicles prepared from **2**, **3**, and **4**; conversely, addition of AIBN to already formed vesicles resulted in the loss of 56%, 58%, and 60% of the vinyl protons for vesicles **2**, **3**, and **4**, respectively. Figure 4 illustrates the ^1H NMR spectra for surfactant vesicles prepared from **2** prior and subsequent to exposure to UV light and to AIBN. These results are explicable in terms of the selective polymerization of the outer surface of vesicles **2**, **3**, and **4** by AIBN since due to curvature, there are greater numbers of surfactant molecules located on the outer than in the inner surface of the vesicles. We did not succeed in selectively polymerizing the inner surface of vesicles. Cosonication with AIBN followed by passage through Sephadex G-50-80 and subsequent incubation at 80 °C resulted in the loss of all vinyl protons. These results are quite similar to those obtained for vesicles prepared from $[C_{11}H_{23}CO_2(CH_2CH_2)_2N^+(CH_3)(CH_2CH{=}CH_2)]Br^-$.[24] Ultraviolet irradiation resulted in the complete polymerization of this vesicle, while addition of AIBN to already sonicated vesicles "closed up" only the outer surface.[24]

Characterization of Vesicles and Polymeric Vesicles. Formation of closed bilayer structures were demonstrated by entrapping 2-aminopyridine·HCl in cationic (**1** and **2**) and 1-pyrenesulfonic acid in anionic (ionized **3** and **4**) vesicles. Electrostatic repulsions were considered to ensure the location of the indicators in the middle of the vesicle-entrapped water pools and to facilitate the separation of entrapped indicators from those in bulk water. Entrapment was performed by cosonicating (70 W at 60 °C) equal volumes of 0.57 mM solution of 2-aminopyridine·HCl (pH 2.0) with vesicles prepared from **1** or **2** or of equal volumes of 0.97 mM 1-pyrenesulfonic acid (pH 6.7) with vesicles prepared from **3** or **4**. The resulting solutions were then divided. One part was polymerized by addition of AIBN or by exposure to ultraviolet radiation and the other part was left unpolymerized. Both solutions were passed through a Sephadex G-50-80 (20 μm, 16 × 178 mm) column with 0.01 N HCl for 2-aminopyridine·HCl or water for

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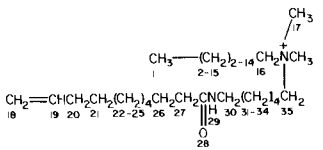
Table I. ^1H and ^{13}C NMR Data for Surfactants, Vesicles, and Polymeric Vesicles

	1	2	3	4	5–14	15	16	17	18	18′	19	20	21	22–25	26	27	28	29	30	31–34	35
																					
^1H NMR, **1** in $CDCl_3$[b] $J_{x,y}$	0.829, t $J_{1,2}=6.8$			1.2			3.22, s $J_{16,15}=6.4$	3.31, s	4.89, m $J_{18,19}=10.267$ $J_{18',19}=17.2$ $J_{18,20}=-1.167$ $J_{18,18'}=2.099$	4.95, m $J_{18',19}=17.113$ $J_{18',20}=-1.719$ $J_{18',18}=2.099$	5.77, m $J_{19,18'}=17.113$ $J_{19,18}=10.267$ $J_{19,20}=6.746$	1.979, q $J_{20,19}=6.746$ $J_{20,18'}=-1.79$		1.20, b		2.227, t $J_{27,26}=7.94$		6.660, t $J_{29,30}=5.93$	3.44, b	1.2, b	3.191, t $J_{33,34}=6.0$
1 sonicated in D_2O[c]	0.80, b			1.2, b			3.20	3.31		4.8, b		5.76, b	2.00, b		1.20, b	2.30, b		6.7, b	3.50, s	1.2, b	3.2, b
1 sonicated in D_2O[c] and polymerized by AIBN	0.80			1.2			3.20, b	3.31		C			2.00, b		1.20, b	2.31, b		6.7, b	3.49, b	1.2, b	3.22, b

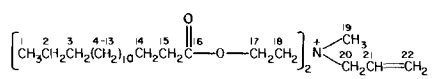
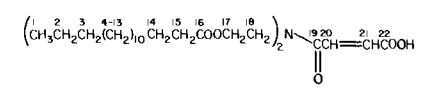
	1	2	3	4–13	14	15	16	17	18	19	20	21	22
													
^1H NMR, **2** in $CDCl_3$[b] $J_{x,y}$	0.848, t $J_{1,2}=6.9$		1.125, b		1.569, m $J_{15,14}=5.9$	2.327, t $J_{16,15}=7.4$		4.624, b	3.99, b	3.41, s	4.431, d $J_{20,21}=6.8$	6.066, m	5.831, d
2 sonicated in D_2O[b]	0.79		1.20		1.50	2.31		A	3.81	3.21	A	6.07	5.77
2 sonicated in D_2O,[b] $h\nu$ radiated	0.80		1.20		1.51	2.31		A	3.81	3.2	A	C	
2 sonicated in D_2O,[b] AIBN added outside	0.80		1.20		B			A	3.81	3.22	A	6.07[d]	5.77[d]
^{13}C NMR, **2** in $CDCl_3$[b]	14.054	22.622	24.608	29.088–29.642	31.855	33.979	172.791	57.485	60.626	49.395	65.988	130.66	124.018
													
^1H NMR, **3** in $CDCl_3$ $J_{x,y}$	0.878, t $J_{1,2}=6.91$		1.253, b		1.597, m $J_{14,13}=7.82$	2.302, t $J_{15,14}=6.4$		3.749, m $J_{17,18}=5.4$	6.389, m $J_{18,17}=5.6$		6.389, d $J_{21,22}=13.3$	6.732, d $J_{22,21}=12.9$	
3, sonicated in D_2O[b] $J_{x,y}$	0.80, t $J_{1,2}=6.9$		1.2		1.47	2.22, b		3.8, m	6.40, b		6.31, b		
3, sonicated in D_2O,[b] AIBN added outside $J_{x,y}$	0.80, t $J_{1,2}=6.9$		1.2		B			3.8, m	6.41, b		6.32, b		
3, sonicated in D_2O,[b] $h\nu$ irradiated	0.80, t $J_{1,2}=6.9$		1.2		1.47	2.25, b		3.8, m	6.41, b		C		
^{13}C NMR, **3** in $CDCl_3$[b]	14.084	22.649	24.760	29.061–29.642	31.882	33.794–33.949	164.808	57.49	60.843	167.363	128.489	134.993	173.333–173.495

Table I (*Continued*)

	1	2	3	4	5	6–16	17	18	18'	19	20	21	22	23
								$(\overset{1}{C}H_3\overset{2-17}{(CH_2)_{16}}\overset{18}{C}H_2)_2N\overset{19}{C}(=O)\overset{20}{C}H{=}\overset{21}{C}H\overset{22}{C}(=O)O\overset{23}{H}$						
^1H NMR, 4 in $CDCl_3$[b]	0.823,					—1.20, b—		3.30, t	3.34, t		6.26, d	6.59, d		6.22, s
$J_{x,y}$	$J_{1,2} = 6.8$							$J_{18,17} = 6.43$	$J_{18',17} = 6.43$		$J_{20,21} = 12.6$	$J_{21,20} = 12.6$		
4 sonicated in D_2O[b]	0.80, t					—1.20, b—		—3.30, b—			6.19, b	6.41, b		
4 sonicated in D_2O,[b] AIBN added to outside	0.79, b					—1.20, b—		—B—			6.20, b	6.42, b[f]		
4 sonicated in D_2O,[b] $h\nu$ irradiated	0.80, t					—1.20, b—		—3.30, b—			—C—			
^{13}C NMR, 4 in $CDCl_3$[b]	14.057	22.637	25.858		—29.065–29.642—		46.515	—48.500—		169.362	128.125	135.700–135.211	166.178–165.980	

[a] Symbols used: A = peak altered by water irradiation, B = obscured by excess AIBN peaks, C = vinyl proton absorptions completely disappeared; chemical shifts in ppm, J values in hertz. [b] Spectra obtained on Varian XL-200 spectrometer. [c] Spectra obtained on a Varian 80 FT spectrometer. [d] Intensity decreased by 56%. [e] Intensity decreased by 58%. [f] Intensity decreased by 60%.

1-pyrenesulfonic acid as eluents to separate the bound from the vesicle entrapped indicator. On gel filtration, a substantial portion of the indicator was retained while a small fraction appeared along with the vesicles or polymeric vesicles (as monitored by turbidity measurements and light scattering).

Surfactant vesicles prepared from **1**, **2**, and **3** were found to be stable for weeks (as determined by the constancy of their turbidity). Those prepared from **4** were stable only for 1 h. The unusual stabilities of these vesicles were also manifested in their resistance to lysis by alcohol. Vesicles prepared from **2**, **3**, and **4** could not be destroyed by the addition of 10%, 33%, and 10% ethanol, respectively. Additional alcohol destroyed the vesicles, of course. Interestingly, dynamic laser light scattering indicated that low concentrations of ethanol initiated fusion of these surfactant vesicles.[27] Polymerization enhanced the stabilities of vesicles prepared from **1**, **2**, **3**, and **4**. The shelf-life of polymeric vesicles is extended several months over their nonpolymeric analogues. They remain stable in ethanol at concentrations well above those that destroy their nonpolymeric counterparts. Addition of 50% Triton X-100 destroyed both unpolymerized and polymerized vesicles by forming mixed micelles. A further demonstration of enhanced stability of polymeric vesicles is their ability to be dried and resuspended without apparent degradation as determined by ^1H NMR and absorption spectroscopic measurements. For example, subsequent to drying polymeric vesicles prepared from **1** in a vacuum desiccator for 4 days, resuspension in D_2O, and heating for 5 min at 60 °C, the ^1H NMR line width and turbidity were practically indentical with those observed prior to water removal.

Fluidity is an important property of synthetic surfactant vesicles. They,[28] just like biological membranes and liposomes,[29] undergo distinct structural changes at a certain temperature, known as the phase-transition temperature, when heated or cooled. Below the phase-transition temperature, lipids in the bilayers are in highly ordered "gel" states, with their alkyl chains in all trans conformations. Above the phase-transition temperature, lipids become "fluid" as the consequence of gauche rotations and kink formation. Phase-transition temperatures have been observed for completely synthetic surfactant vesicles and for their polymeric counterparts.[24,28] Pronounced breaks in the plots of ^1H NMR half-peak line-width broadening in the CH_{2n} protons against temperature both for unpolymerized and polymeric vesicles prepared from **1** (Figure 5) indicate phase changes. Polymerization does not, therefore, lead to complete three-dimensional cross-linking of the surfactant vesicles but presumably to a large number of polymeric units having weight-averaged molecular weights considerably below the moleclar weight of the vesicle. Polymeric vesicles thus combine the advantages of polymers and membranes; they have stabilities like polymers while retaining the beneficial fluidities and organizational abilities of membranes.

Morphological information has been obtained by dynamic laser light scattering.[30] Table II summarizes the data. Several salient features merit discussion. Vesicles prepared from **2** formed easier, are smaller, and are more uniform than those obtained from **3**. These facts prompted our selection of this vesicle for detailed investigations. Even as short a sonication time as 30 sec is sufficient to yield vesicles of **2** with a mean hydrodynamic radius of 538 Å. Increasing the sonication time resulted in decreased turbidity, hydrodynamic radius, and polydispersity (Figure 1 and Table I). There are several indications of decreased polydispersity. Thus, the smaller the difference between R_H values calculated by fitting the data for the first ten channels and those obtained by the cumulants, the more monodisperse the aggregates. Sim-

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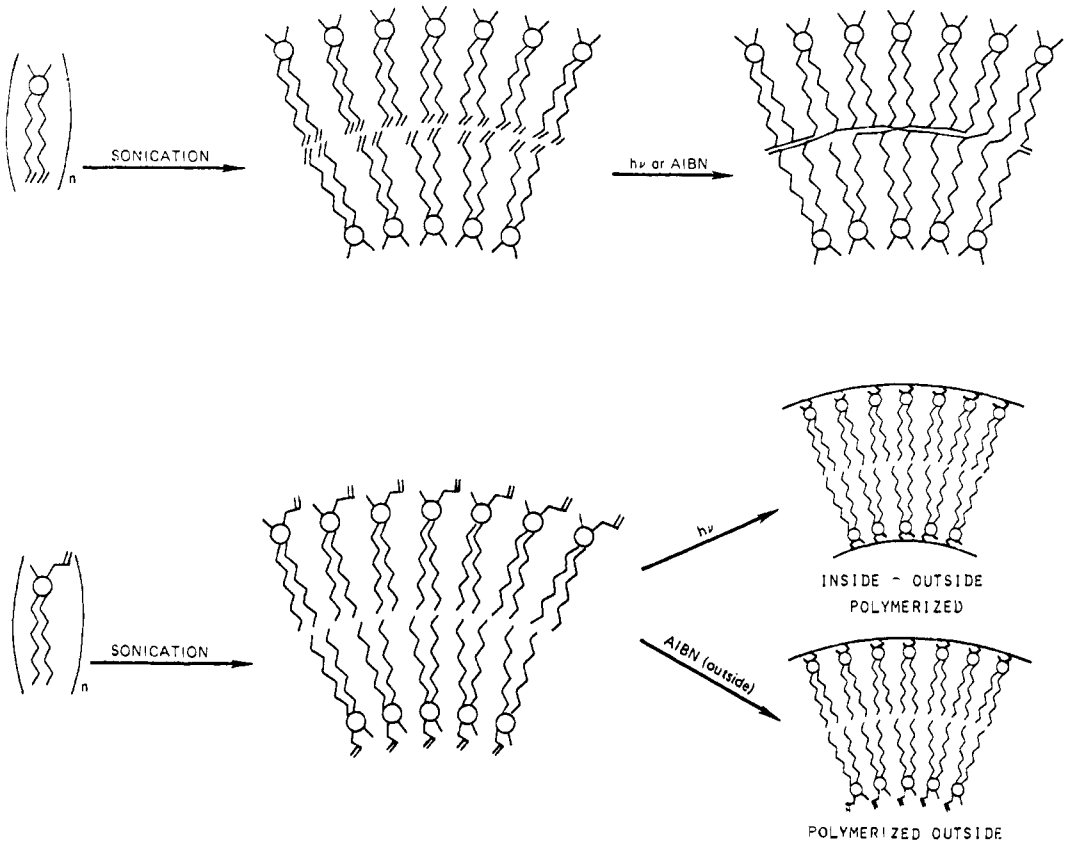

Figure 3. Schematic representation of vesicle polymerization in the bilayer or at the outer and/or inner surfaces.

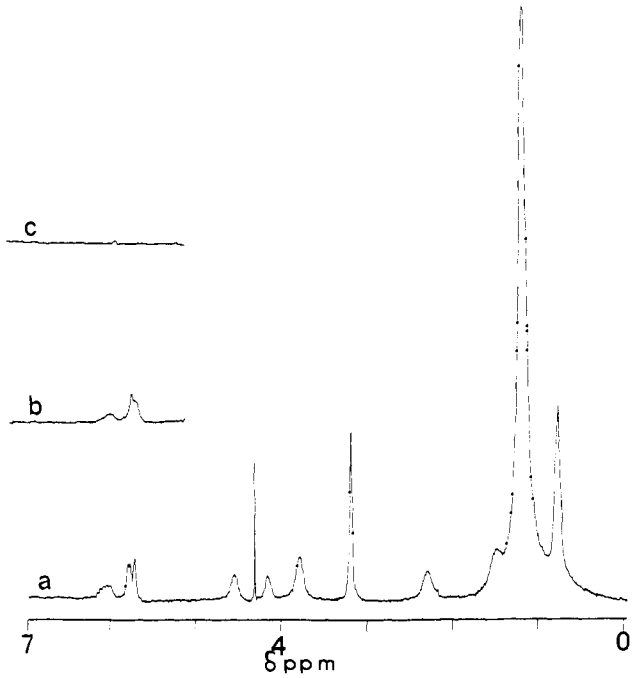

Figure 4. ^{1}H NMR spectra of vesicles prepared from **2** (0.01 mg of **2** per 1.00 cc of D_2O) sonicated for 7 min at 70 °C and 70 W (a). The inserts show the vinyl signals following polymerization by addition of AIBN to the already formed vesicles (b) and by exposure to ultraviolet radiation, 450-W xenon lamp, 10 h (c); 50 000 scans on the 200-MHz instrument of the totally polymerized specimen (by ultraviolet irradiation).

ilarly, smaller variants correspond to more monodisperse vesicles. Also less angular variation of the deduced radii is observed. At smaller observation angles, the larger particles have relatively higher weight. Therefore, if the sample is polydisperse, an angular variation is observed. The size of the vesicles can also be estimated

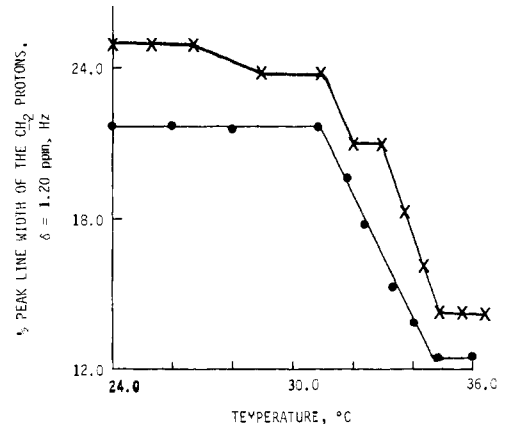

Figure 5. Plots of ^{1}H NMR half-line widths due to CH_{2n} protons at 1.20 ppm against temperature for vesicles prepared from **1** prior (-) and subsequent (x) to polymerization.

from the dissymmetry of the scattered light. The dissymmetry $d(\theta)$ is defined as the ratio of the scattered intensity at $90 - \theta$ and $90 + \theta$. In our case,

$$d(\theta) = I_{45}/I_{135} \quad (1)$$

Determinations at each angle were carried out in triplicate. A knowledge of $d(\theta)$ allows the calculation of the radius of gyration R_G of the vesicles from[31]

$$R_G \simeq \left(\frac{3(d(\theta) - 1)\lambda^2}{16\pi^2 n^2 \cos\theta} \right)^{1/2} \quad (2)$$

where λ is the wavelength of the incident light in vacuo, n is the index of refraction of the scattering medium and θ is the scattering angle. R_G values are given in Table II. The R_G value of a vesicle is only slightly smaller than the actual radius of the vesicle. The

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Table II. Dynamic Laser Light Scattering of Surfactant Vesicles and Polymeric Surfactant Vesicles[a]

compd	sonication time	angle, deg	R_H^{1-10}, Å	R_H^{cum},[c] Å	R_H^{mean},[d] Å	variant[e]	R_G,[f] Å
2	30 sec	90	556	497	538	0.59	1354
		135	573	482		0.60	
		45	657	637		0.79	
	2 min	90	299	287	277	0.51	402
		135	304	285		0.57	
		45	264	260		0.90	
	4 min	90	257	238	254	0.69	586
		135	269	257		0.57	
		45	269	274		0.87	
	5 min	90	236	214	213	0.56	321
		135	240	223		0.49	
		45	219	203		0.63	
	6 min	90	223	249	213	0.59	217
		135	232	209		0.69	
		45	176	182		0.73	
	6 min after standing overnight	90	240	216	208	0.58	
		135	251	216		0.58	
		45	204	192		0.78	
	6 min + KCl to 3×10^{-2} M	90	440	408	511	0.87	1375
		135	498	452		0.86	
		45	657	674		1.10	
	30 sec, polymerized by $h\nu$	90	474	430	410	0.66	677
		135	413	408		0.63	
		45	466	479		0.73	
	2 min, polymerized by $h\nu$	90	304	294	286	0.52	408
		135	308	293		0.54	
		45	277	272		0.63	
	6 min, polymerized by $h\nu$	90	211	201	206	0.34	
		135	210	209			
		45	220	205			
	30 sec, polymerized by $h\nu$ after 3 weeks of standing	90	480	410	421	0.60	
		135	390	402		0.70	
		45	490	450		0.80	
3	20 min	90	950	921	1013	0.13	
		135	1029	968		0.23	
		45	1100	1150		0.60	
	20 min, polymerized by $h\nu$	90	850	830	890	0.42	
		135	960	880		0.50	
		45	1050	960		0.64	

[a] Each value represents mean of three determinations, each differing from the other ±6%. [b] Hydrodynamic radius obtained from fitting data to channels 1-10. [c] Hydrodynamic radius obtained from fitting data to cumulants. [d] Hydrodynamic radius obtained by taking means of R_H^{cum} over all measured angles. [e] Polydispersity index; those with values >1 indicate marked polydispersity. [f] Radius of gyration calculated from data determined at $(90 - \theta)°$ and $(90 + \theta)°$ according to eq 2.

difference between R_G and R_H can be explained by deviations from spherical form. However, we do not attempt to treat this in detail since the relation between R_G and R_H is very complex when there is a size distribution of nonspherical particles, the shapes of which might also fluctuate in time.[31] On the other hand, the remarkedly good agreement between R_H and R_G values for "well-sonicated" vesicles implies appreciable monodispersity and a minimal deviation from spherical symmetry. Vesicles with $R_H \simeq R_G \simeq 210$ Å can only be attributed to fairly uniform single-compartment bilayer aggregates.

Polymerized vesicles retain the sizes of their unpolymerized counterparts. Polymerization of vesicles prepared from **2** by 30-s sonication only alters R_H^{mean} from 538 to 410 Å. Similarly, polymerization of vesicles with $R_H^{mean} = 277$ Å, prepared by 2-min sonication of **2**, leads to polymeric vesicles with $R_H^{mean} = 286$ Å. Polymerized vesicles do not undergo morphological changes even on extended standing (see Table II). It is possible, therefore, to prepare stable polymeric vesicles of controlled dimensions.

Addition of potassium chloride to vesicles prepared from **2** increases the turbidity and the hydrodynamic radius (Table II). Interestingly, both polymeric and unpolymerized vesicles undergo electrolyte-mediated growth. There are subtle differences, however, between vesicles and polymeric vesicles. The KCl-mediated growth of polymeric vesicles prepared from **2** is somewhat slower than that for their unpolymerized counterpart. Aggregated polymeric vesicles appear to be more monodisperse than those formed from unpolymerized ones. The growth could imply either true fusion with mixing in the inner compartments of the aggregated vesicles or just "clumping". Differentiation between these two alternatives and the control of factors effecting them are the subject of our current investigations.

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Registry No. **1**, 84454-86-4; **1** polymer, 84454-88-6; **2**, 84454-87-5; **2** polymer, 84454-89-7; **3**, 80325-45-7; **3** polymer, 84454-90-0; **4**, 60387-06-6; **4** polymer, 84454-91-1; **5**, 84454-83-1; **6**·HCl, 84454-84-2; **7**·HCl, 84454-85-3; *N,N*-dimethylhexadecylamine, 112-69-6; *N*-(6-bromohexyl)phthalimide, 24566-79-8; 10-undecenoyl chloride, 38460-95-6; palmitoyl chloride, 112-67-4; *N*-methyldiethanolamine, 105-59-9; allyl bromide, 106-95-6; diethanolamine, 111-42-2; maleic anhydride, 108-31-6; dioctadecylamine, 112-99-2; potassium chloride, 7447-40-7.