at higher temperatures is noted, as well as the appearance of some conformational transitions occurring at temperatures related to the BuMA content of the copolymers.

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Polymerized Surfactant Vesicles. Determinations of Rates and Degrees of Polymerization in Vesicles Prepared from Styrene-Containing Surfactants

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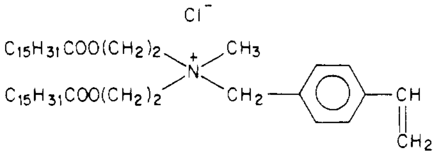
ABSTRACT: Rate constants (η/E values) for laser pulse initiated photopolymerization have been determined for 1200–2700-Å-diameter bilayer surfactant vesicles prepared from dioctadecylmethyl(2-[(4-vinylbenzoyl)oxy]ethyl)ammonium bromide (**3**), from mixtures of dioctadecyldimethylammonium bromide (DODAB) and vinylbenzoic acid, from mixtures of **3** and DODAB, and from mixtures of **3** and vinylbenzoic acid. η/E values were 1.35 J^{-1} for 1650-Å-diameter **3** vesicles, were 0.059 J^{-1} for mixed vesicles prepared from vinylbenzoic acid and DODAB (0.25:1 mole fraction), varied between 0.123 and 1.46 J^{-1} for vesicles prepared from different mixtures of DODAB and **3**, and varied between 0.16 and 0.314 J^{-1} for different mixtures of vinylbenzoic acid and DODAB. Plots of polymerization rate constants against the mole fraction of **3** in vesicles prepared by cosonicating **3** + DODAB were found to increase curvilinearly to a plateau value, indicating domain formation. Subsequent to vesicle polymerizations, cumulants, weight- and number-average molecular weights of the separated poly(vinylbenzoates) and, hence, the average chain lengths were determined by gel exclusion chromatography. The average chain lengths varied from 10 in laser-polymerized **3** vesicles, through 20 in laser-polymerized vesicles prepared from mixtures of DODAB and vinylbenzoic acid, to 40 in laser-polymerized vesicles prepared from mixtures of **3** and vinylbenzoic acid. These relatively small chain lengths were discussed in terms of the restricted geometries prevailing at intravesicular surface polymerizations. Fluorescence measurements and a Monte Carlo based computer simulation of the photopolymerization were used to substantiate the proposed mechanism of vesicle polymerization.

Introduction

Polymerized surfactant vesicles[5–9] have become the most sophisticated systems in the armory of membrane mimetic chemists.[10,11] Vesicles are smectic mesophases of surfactants containing water between their bilayers. Prepared by sonication from such simple surfactants as dioctadecyldimethylammonium bromide (DODAB) or dihexadecylphosphate (DHP), they are single bilayer spherical aggregates with diameters of 500–1000 Å and bilayer thickness of ca. 50 Å.[12] Once formed, vesicles, unlike micelles, do not break down on dilution. Nevertheless, they are dynamic structures. They undergo phase transition, fuse, and are osmotically active. Molecular motions of the individual surfactants in the vesicles involve rotations, kink formation, lateral diffusion on the vesicle plane, and transfer from one interface of the bilayer to the other (flip-flop). Vesicles are capable of organizing a large number of molecules in their compartments. Hydrophobic molecules can be distributed among the hydrocarbon bilayers of vesicles. Polar molecules may move about relatively freely in vesicle-entrapped water pools, particularly if they are electrostatically repelled from the inner surface. Small charged ions can be electrostatically attached to teh oppositely charged vesicle surfaces. Species having charges identical with those of the vesicles can be anchored onto the vesicle surface by a long hydrocarbon tail. These organizational abilities of surfactant vesicles have been exploited in reactivity control, catalysis, transport, drug delivery, and artificial photosynthesis.[10–12]

The need for increased stabilities, controllable sizes, and permeabilities led to the development of polymerized surfactant vesicles.[5–9] Vesicle-forming surfactants have been functionalized by vinyl, methacrylate, diacetylene, isocyano, and styrene groups in their hydrocarbon chains or at their head groups. Accordingly, surfactant vesicles could be polymerized in their bilayers or across their head groups. In the latter case, either the outer or the inner vesicle surfaces could be linked separately. All polymerized vesicles show appreciable stabilities compared with their unpolymerized counterparts. They have extensive shelf lives and remain unaffected by the addition of up to 30% methanol.

Full realization of the potentials of polymerized surfactant vesicles demands a detailed understanding of their structures and the mechanisms of their formation. We have initiated studies on vesicles prepared from surfactants that contained styrene moieties in their head groups (1 and 2).[13-16] The first-order disappearance of styrene absorbances upon photolysis of vesicles prepared from 1 and 2 has been discussed in terms of two-dimensional intravesicular polymerizations.[13] Polymerization substantially stabilized 1 and 2 vesicles but did not appreciably alter their phase transition behavior. These observations are in accord with the formation of relatively short-chain-length polymers. Morphological consequences of photopolymerizations of these vesicles have been discussed in terms of pulling some aryl groups together, thereby creating clefts some 13 Å in diameter.[15,16] Although the kinetic treatment of vesicle photopolymerization allowed the assessment of the average degree of polymerization,[13] direct molecular weight determinations have to date eluded us. No ideal solvent could be found for the polyelectrolytes formed in destroyed polymerized vesicles. To circumvent this problem we have synthesized 3 in which the styrene had been attached to the quaternary nitrogen of the surfactants via a cleavable ester group and report weight-average molecular weight determinations of poly(vinylbenzoic acid), isolated from polymerized 3 vesicles. Vesicles have been also prepared from mixtures of vinylbenzoic acid and DODAB as well as from mixtures of vinylbenzoic acid and 3. Subsequent to polymerizations, weight-average molecular weights of these vesicles have also been determined and compared with those obtained in polymerized 3 vesicles.



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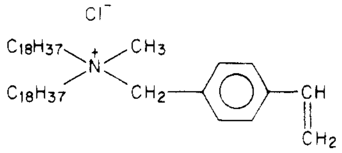

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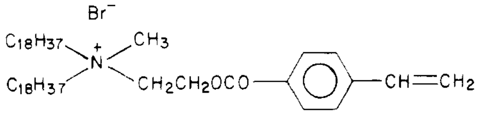

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Experimental Section

Dioctadecylmethyl(2-[(4-vinylbenzoyl)oxy]ethyl)ammonium bromide (3) was prepared from 2-bromoethyl *p*-vinylbenzoate (4). *p*-Vinylbenzoic acid (Aldrich) (3.9 g, 26 mmol), oxalyl chloride (5 mL), and one drop of pyridine were stirred in 30 mL of anhydrous benzene at room temperature for 16 h. The solvent was then removed under vacuum, and 30 mL of benzene was added and removed again. This *p*-vinylbenzoyl chloride was taken up in 50 mL of anhydrous benzene and 6.6 g (53 mmol) of 2-bromomoethanol was added, followed by the slow (0.5 h) addition of 4.2 g (53 mmol) of pyridine in 10 mL of benzene while cooling in an ice bath. The reaction mixture was allowed to warm to room temperature, stirred for an hour, and extracted with ethyl ether in the presence of 1 N HCl. The organic solution was neutralized with aqueous $NaHCO_3$. Drying, solvent removal, and distillation gave **4**: 3.9 g (58% yield); bp 115 °C (1.0 torr); ^1H NMR ($CDCl_3$) δ 7.80 (dd, aromatic protons, 4 H), 5.2–7.0 (m, vinyl protons, 3 H), 4.05 (dt, A_2B_2, 4 H).

Dioctadecylmethylamine[14] (4.2 g, 78 mmol) and 2.0 g (78 mmol) of **4** were heated at 70 °C for 24 h in the absence of solvent and in the presence of 0.1 g of 4-*tert*-butylcatecol. After the mixture cooled, ethyl ether was added and the precipitated **3** was filtered: yield 4.1 g (66%); mp 132–142 °C (after recrystallization from ethyl acetate); ^1H NMR ($CDCl_3$) δ 7.65 (dd, aromatic protons, 4 H), 5.2–7.0 (m, vinyl protons, 3 H), 4.85 (br m, 2 H), 4.20 (br m, 2 H), 3.5 (br m, 7 H), 1.0–2.1 (br, s, 64 H), 0.90 (t, 6 H). Anal. Calcd for $C_{48}H_{88}BrNO_2$: C, 72.87%; H, 11.21; N, 1.77. Found: C, 72.51; H, 10.98; N, 1.84.

Purification and characterization of dioctadecyldimethylammonium bromide ($(C_{18}H_{37})_2N^+(CH_3)_2Br^-$ (DODAB)) have been described.[12]

Deionized water was doubly distilled in an all-glass apparatus. The final stage of distillation included a superheated oxygenated quartz column. Additionally, double-distilled water was filtered through a 0.2-μm Millistak filter system (Millipore Corp.). Usually, it gave a pH of 5.5.

Vesicles were prepared from **3**, DODAB, and different vinylbenzoic acid + DODAB and vinylbenzoic acid + **3** mixtures by dissolving appropriate amounts of the surfactant and vinylbenzoic acid, typically 10 mg, in 0.1 mL of MeOH to which dustless water (typically 10 mL) was added. The sample was then sonicated at 75 °C with the medium tip of the Braunsonic 1510 sonicator set at 70 W for different times. Vesicles used for polymerization and for detailed studies were sonicated until optically transparent solutions were obtained. These solutions were filtered through a 0.2-μm Nucleopore filter and had hydrodynamic radii between 600 and 1400 Å.

A Quanta Ray DCR-1A laser delivering 266-nm, 8-ns, 1–5-mJ pulses was utilized 10 effect vesicle photopolymerizations.[13] Loss of styrene absorbances was monitored as a function of the absorbed light.

Subsequent to polymerizations, weight-average molecular weights of the polymers formed were determined by gel exclusion chromatography with a Zorbax PSM-60 column (Du Pont) on a Waters Associates liquid chromatography system (consisting of a 6000 A chromatography pump, a 440 absorbance detector, and an Omniscribe recorder) at a flow rate of 1 mL/min (5 g of Na_2SO_4 + 1 g of KH_2PO_4/L, pH 7.0). Calibration was performed by means of sulfonated polystyrenes (M_w = 223, 1800, 4400, 8000, 18000, and 35000). Polymerized **3** vesicles (2×10^{-3} M) were destroyed by dilution (5-fold) in 0.01 M ethanolic NaOH and refluxing for 2 h. After the alcohol was evaporated and the long-chain amines were extracted by $CHCl_3$, the pH of the aqueous phase was adjusted to 7.0 prior to injection to the column. Poly(vinylbenzoate), formed in polymerized vesicles prepared from vinylbenzoic acid and DODABC, was separated directly by $CHCl_3$–H_2O (10^{-3} M NaOH) extractions. Analyses were performed on the aqueous samples after adjusting their pH to 7.0.

A Radiometer pHM26 meter was used in conjunction with a combination microelectrode for pH determinations.

Absorption spectrophotometry was carried out either on a Cary 118C or on a Hewlett-Packard 8450 A diode array spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog spectrofluorometer.

Dynamic light scattering was determined on a Brookhaven instrument (goniometer, digital correlator, microcomputer) with a Spectra Physics 171 argon ion laser as the excitation source.[13]

Results

Four different vesicle systems were polymerized in the present work: vesicles prepared from pure **3**, from mix-

Table I
Hydrodynamic Diameters of Surfactant Vesicles and Their Rates of Laser-Initiated Photopolymerizations

vesicle[a]	D_H,[b] Å	η/E,[c] J^{-1}
DODAB	1370	
3	1650	1.35
	2720	0.46
DODAB + 3[d]		
0.081	1350	0.123
0.12	1250	0.247
0.21	1200	1.025
0.44	1640	1.46
0.71	2780	0.643
vinylbenzoic acid + 3[d]		
0.2	2700	0.166
0.4	2700	0.243
0.6	2700	0.314
0.8	2700	0.184
1.0	2700	0.199
vinylbenzoic acid + DODAB[e]		
0.25		0.059

[a] See Experimental Section and Results for preparations. [b] Hydrodynamic diameters of vesicles determined just prior to polymerizations by dynamic scattering at 90°. Each value is accurate to ±50 Å. Polydispersities, Q values, were found to be between 0.3–0.5. [c] Rate constants for laser pulse initiated photopolymerizations at 25 °C in terms of η/E values (being independent of the applied laser energy and surfactant concentration), average of three determinations, each within ±7% of the mean. [d] Expressed in terms of mole fractions of 3. [e] Expressed in terms of the mole fraction of vinylbenzoic acid.

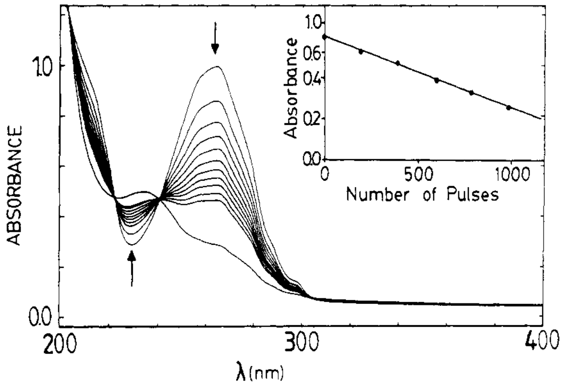


Figure 1. Absorption spectra of 5.8×10^{-5} M, 1650-Å-diameter vesicles prepared from 3 as a function of irradiation by repetitive 0.8-mJ, 266-nm laser pulses. Increasing irradiation results in spectral changes indicated by the arrows. The insert shows the plot of the data according to a first-order decay.

tures of DODAB and 3, from mixtures of DODAB and vinylbenzoic acid, and from mixtures of 3 and vinylbenzoic acid. Hydrodynamic diameters of the vesicles varied between 1200 and 2700 Å (Table I).

Kinetics of Vesicle Polymerizations. Irradiation of vesicles prepared from 3 by 15-ns bursts of 266-nm laser pulses resulted in the loss of absorbances due to the styrene moiety. Figure 1 shows typical absorbance changes as a function of the number of 0.8-mJ pulses. A plot of absorbance against the number of pulses gave good first-order dependencies (insert in Figure 1) as expected from the proposed intravesicular photopolymerizations.[13]

Styryl radicals (M·), formed subsequent to excitation by the laser pulse, underwent polymerization (governed by k_p), formed nonpolymeric photoproducts (governed by k_m), or returned to the ground state (governed by k_s). Kinetic equations for these processes were derived to be[13]

$$dM/dt = \gamma M\cdot \qquad \gamma = k_s - k_p w(t) \tag{1}$$

$$dM\cdot/dt = -\nu M\cdot \qquad \nu = k_m + k_s \tag{2}$$

with the initial condition that

$$M(0) = M_0 - M_0\cdot \tag{3}$$

where $w(t)$ is the average number of nearest monomeric neighbors of M at time t, M_0 is the number of surfactant molecules initially present on the vesicle surfaces, and $M_0\cdot$ is the number of free radicals produced by the laser pulse, given by

$$M_0\cdot = \Phi_r \epsilon E M_0 \tag{4}$$

where Φ_r is the quantum efficiency of free radical formation, ϵ is the molecular cross section at 266 nm, and E is the average energy/cm^2 of the laser pulse, calculated by dividing the measured energy per pulse by the cuvette area. Solving eq 1 and 2 under the condition that $k_p \gg k_m$ leads to

$$M(t) = M_0 - M_0\cdot + \frac{\gamma M_0\cdot}{\nu}(1 - e^{-\nu t}) \tag{5}$$

As before,[13] the cluster of constants equal to the fraction of surfactants consumed after the photochemical events induced by a single laser pulse have subsided is represented by the quantity η

$$\eta = \Phi_r \epsilon E k_p w(t)/(k_m + k_s) \tag{6}$$

so that as $t \rightarrow$ next laser pulse

$$\lim M(t) = M_0(1 - \eta) \tag{7}$$

It is easily induced that the monomer population remaining after η laser pulses is given by

$$M(n) = M_0(1 - \eta)^n \tag{8}$$

which for small η simplifies to

$$M_0(1 - \eta)^n \simeq M_0 e^{-\eta n} \tag{9}$$

The obtained straight-line plots (insert in Figure 1) justify the assumptions used in deriving eq 9.[13] Table I summarizes the kinetic data obtained for laser pulse initiated photopolymerizations of the different vesicles in terms of η/E values (being independent of the applied laser energy and surfactant concentration). Photopolymerizations do not alter the gross hydrodynamic parameters of vesicles. Their hydrodynamic radii, determined by dynamic light scattering, remain unaltered upon polymerization.

Degrees of Polymerizations in Vesicles. Figure 2 shows typical gel exclusion chromatographs of poly(vinylbenzoic acids) formed in polymerized vesicles. Each chromatograph was digitized into i number of data points, with V_i being the retention volume of the ith point expressed in milliliters and h_i being the height from the base line to the curve in absorbance units.[17] The cumulative weight fraction distributions, Cum W_i, were obtained by dividing the partially integrated areas by the total area under the curve. Cum W_i equals the weight fraction of polymer having a retention volume greater than V_i and molecular weight less than M_i. Appropriate values of M_i were obtained by interpolation from the molecular weight calibration curve generated by using the standard sulfonated polystyrenes (insert in Figure 2). The number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights were calculated from the equation[17]

$$\bar{M}_n = \sum_{i=1}^{N} h_i / \sum_{i=1}^{N} (h_i/M_i) \tag{10}$$

$$\bar{M}_w = \sum_{i=1}^{N} (h_i M_i) / \sum_{i=1}^{N} h_i \tag{11}$$

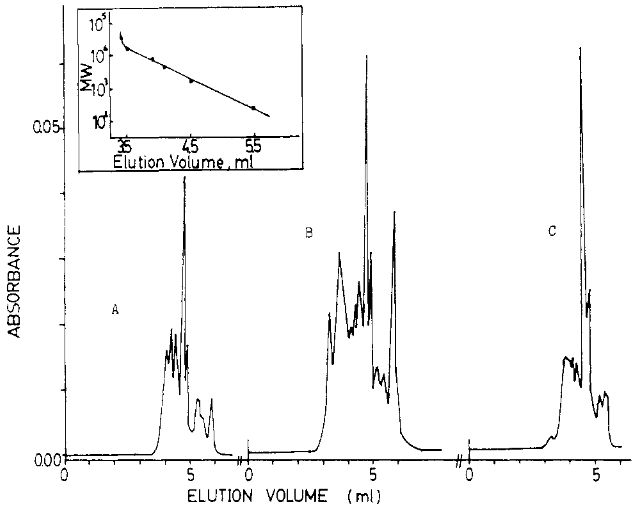


Figure 2. Elution patterns of poly(vinylbenzoic acid) formed in the photopolymerization of vesicles prepared from (A) mixtures of DODAB and vinylbenzoic acid (1:1, mole ratio), (B) mixtures of 3 and vinylbenzoic acid (1:1, mole ratio), and (C) mixtures of DODAB and 3 (1:3, mole ratio). See details in the Experimental Section. The insert shows a calibration plot of polystyrenesulfonates of known molecular weights.

Table II
Weight- and Number-Average Molecular Weights of Poly(vinylbenzoic acid) Formed in the Polymerization of Surfactant Vesicles

vesicle[a]	method of polymerization	$\bar{M}_w$[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$	symbol in Figure 3
3	laser photolysis	1412	885	1.59	C
	AIBN[d]	1167	445	2.62	I
	persulfate[e]	1182	1165	1.01	J
1:1 DODAB–vinylbenzoic acid	laser photolysis	2826	1105	2.56	F
	AIBN	1706	1111	1.53	G
	persulfate	1756	429	4.09	H
1:1 3-vinylbenzoic acid	laser photolysis	5644	1188	4.75	E
1:0.8 3-vinylbenzoic acid	laser photolysis	3723	711	5.23	D
9:1 DODAB-3	laser photolysis	1220	874	1.39	A
1:3 DODAB-3	laser photolysis	2299	1007	2.28	B

[a] Ratios are expressed as mole fractions. [b] Weight-averaged molecular weight, determined by eq 10. [c] Number-average molecular weight, determined by eq 11. [d] Adding 3 mg of AIBN to vesicles prepared from 10 mg of surfactants and heating for 1 h at 80 °C. [e] Adding 5 mg of potassium persulfate to vesicles prepared from 10 mg of surfactants and heating for 1 h at 80 °C.

Table II summarizes $\bar{M}_w$ and $\bar{M}_n$ values. Ratios of $\bar{M}_w/\bar{M}_n$, indicative of the breadth of the molecular weight distribution, are also given in Table II. Figure 3 shows the cumulants. Lack of smoothness, seen in most of the cumulants, is indicative of a multimodal molecular weight distribution. A multimodal molecular weight distribution is clearly discernible in the elution patterns of poly(vinylbenzoates) formed in surfactant vesicle polymerization. A case in point is the behavior of poly(vinylbenzoates) formed in the polymerization of vesicles prepared from 1:1 mixtures of 3 and vinylbenzoic acid (B in Figure 2). Multimodal molecular weight distributions are most pronounced for polymers having large weight-average molecular, weights and high polydispersities, indicated by large $\bar{M}_w/\bar{M}_n$ values (D–F in Figure 3 and Table II). Smooth cumulants were observed for monodisperse low molecular weight poly(vinylbenzoates), formed in the persulfate-initiated polymerization of vesicles prepared from 3 (see J in Figure 3 and Table II). Sharp transitions in the cumulant plots imply high degrees of monodispersities (see A and J in Figure 3). Despite the complex behavior of the cumulants, the largest populations of weight-average molecular weights of poly(vinylbenzoates), formed in vesicles A–J, fall within the ranges 1000–2500 (see the breadth of inflections in the cumulants in Figure 3).

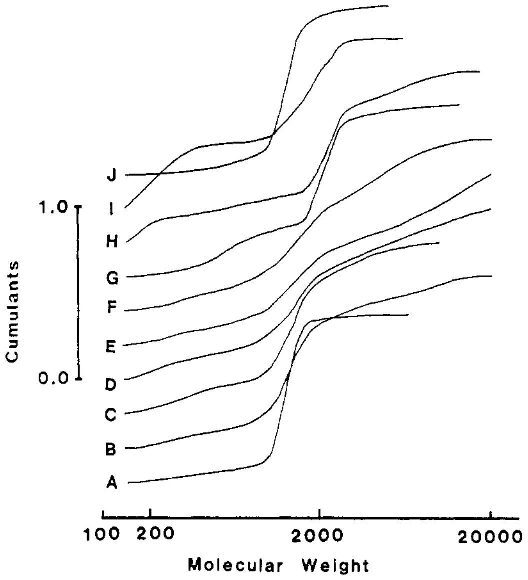


Figure 3. Cumulative weight fraction molecular weight distributions (see Results) for poly(vinylbenzoic acids) formed in the photopolymerization of vesicles prepared from pure surfactants or from mixtures (in mole fraction) of surfactants: (A) DODAB-3 (9:1); (B) DODAB-3 (1:3); (C) pure 3; (D) 3-vinylbenzoic (1:0.8); (E) 3-vinylbenzoic acid (1:1); (F) DODAB–vinylbenzoic acid (1:1); (G) DODAB–vinylbenzoic acid (1:1) polymerized by AIBN; (H) DODAB–vinylbenzoic acid (1:1) polymerized by persulfate; (I) pure 3 polymerized by AIBN; (J) pure 3 polymerized by persulfate. The Y scale for each curve varied from 0 to 1.0; for the sake of clarity, each curve has, however, been arbitrarily displaced.

The average chain length formed at the beginning of the vesicle photopolymerization was also assessed by recording the absorption of stirred vesicle samples prior and ca. 30 s subsequent to exposure to a single 8-mJ laser pulse ($\Delta C_s = \Delta A/\epsilon l$, where ΔA is the absorption change determined in the Hewlett-Packard 8450 A diode array spectrophotometer, ϵ is the extinction coefficient of 3, and l is the path length of the cell) and comparing this absorption change with that observed in flash photolysis on the 0.5-ms time scale ($\Delta C_f = -\Delta I/(2.3d\Delta I_0)$, where Δi_0 is the absorption change determined in the laser flash photolysis after a single laser pulse, d is the width of the laser flash, and I_0 is the base line absorbance). The average ratio of monomers consumed during chain propagation to the initial free radical is given by[13]

$$\frac{\Delta M}{M} = \frac{2.3d\Delta I_0}{l\Delta l}\,\frac{\text{area of cuvette}}{\text{area of laser path}} \tag{12}$$

The average chain length of polymers formed in the photopolymerization of 1700-Å-diameter vesicles prepared from 3 was found to be 19. No detectable transient was observed on the laser flash photolysis of vesicles prepared from mixtures of DODAB and vinylbenzoic acid.

Fluorescence Spectra. The relative fluorescence intensity due to vesicles prepared from 3 (A in Figure 4) was

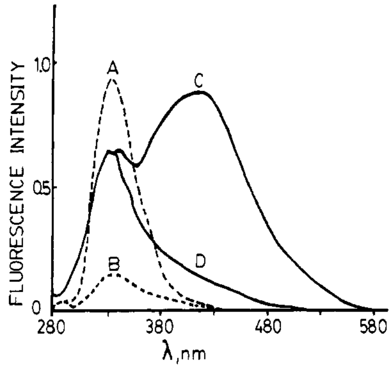


Figure 4. Emission spectra of 3 × 10^{-5} M 3 vesicles (A) and 3 × 10^{-5} M DODAB vesicles containing 3 × 10^{-5} M vinylbenzoic acid (B) prior to polymerization. Spectra C and D are emission spectra of polymerized vesicles prepared from (A) and (B). Excitation wavelength is 265 nm.

found to be appreciably greater than that due to mixed vesicles (having an absorbance identical with that of **3** at the excitation wavelength) prepared from DODAB and vinylbenzoic acid (B in Figure 4). Apparently, the fluorescence quantum efficiency of vesicles prepared from surfactants containing a styrene moiety in the head group (**3**) is some 5.2-fold higher than that prepared from dioctadecyldimethylammonium surfactants containing vinylbenzoates as their counterions. Upon polymerization, the excimer yield in vesicles prepared from **3** (C in Figure 4) is substantially greater than that obtained from cosonicated mixtures of **3** and vinylbenzoic acid. Excimer formation is likely to be hindered by electrostatic repulsions between the charged counterions in the mixed polymerized vesicles.

Discussion

The rate constant for the photopolymerization of 1650-Å-diameter vesicles prepared from **3** (Table I) is appreciably smaller than that reported previously for 900-Å-diameter vesicles prepared from **2** (4.95 J^{-1}).[15] This difference is most likely to originate in the greater effective distance between the styrene head groups in **3** than that in **2**. In **3**, the benzene moiety is separated from the quaternary nitrogen atom by two methyl groups and an ester linkage. This renders the styrene group to be more "floppy" than that in **2**, where it is separated only by one CH_2 group from the quaternary nitrogen. Indeed, it is not inconceivable that the styrene group is able to fold back into the bilayer of **3** vesicles. Support for this geometrical effect is provided by comparing rates of photopolymerizations of differently sized vesicles prepared from **3**. Increasing the size of vesicles to 2720 Å decreased their photopolymerization rates to 0.46 J^{-1} (Table I).[18] It should be noted that in **3** vesicles the bromide ion effectively decreased the triplet lifetime and, hence, the quantum field for radical formation.

The rate constant for the photopolymerization of vinylbenzoic acid coated DODAB vesicles was found to be an order to magnitude smaller than that observed for vesicles prepared from **3** (Table I). The lesser reactivity of the former system can be accounted for in terms of the diminished quantum efficiency of its excited-state formation compared with that of pure **3**. Fluorescence quantum efficiency of vesicles prepared from DODAB and vinylbenzoic acid is seen to be some 5-fold smaller than that prepared from **3** (compare B and C in Figure 4). This reduction in fluorescence quantum yield is not due to enhanced intersystem crossing to the triplet state, a precursor of the free radical, since the flash photolytically determined yields of triplets and radicals are considerably smaller in vinylbenzoic acid coated DODAB than in **3** vesicles. Decreased vinyl fluorescence is due to quenching by the bromide counterions left on the vesicle surface. This fact and the relative hydrophobicity of vinylbenzoate can be taken as evidence for counterion exchange in vesicles prepared from DODAB and vinylbenzoic acid.

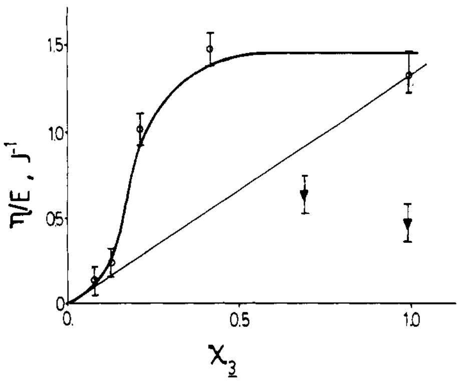


Figure 5. Plot of the kinetic data for the polymerization of vesicles prepared from cosonicated mixtures of DODAB and **3** as a function of the mole fraction of **3**. Diameters of the vesicles were between 1200 and 1650 Å (●) and between 2720 and 2770 Å (▲).

Inclusion of nonpolymerizable DODAB into the matrix of **3** vesicles had a pronounced effect on the rates of photopolymerization. Cosonication of two structurally different surfactants may, a priori, lead to separate populations of vesicles formed from the two surfactants, to a single population of vesicles constituting uniformly mixed surfactants, and finally to a single population of vesicles composed of nonideally mixed surfactants. Vesicles prepared by cosonicating increasing amounts of DODAB with **3** polymerized at decreasingly smaller rates (Table I). Plots of polymerization rate constants against the mole fraction of **3** in vesicles prepared by cosonicating **3** and DODAB were found to be increased curvilinearly to a plateau value (Figure 5). These data are only compatible with the presence of a single population of nonideally mixed vesicles containing polymerized domains. Ideal mixing of polymerizable and nonpolymerizable surfactants would result in a linear increase of the photopolymerization rate with increasing mole fractions of the polymerizable surfactant present in the mixed vesicle (see straight line in Figure 5) since the probability of a radical to find a polymerizable styrene moiety decreases linearly with decreasing **3** in the mixed **3** + DODAB vesicles. Domain formation has been suggested previously to be responsible for the nonideal behavior of vesicles prepared from mixtures of $(C_{18}H_{37})_2N^+(CH_3)CH_2C_6H_4CH{=}CH_2Cl^-$ and $(C_{18}H_{37})_2N^+(CH_3)_2Cl^-$[15] and those from mixtures of dimyristoyl phosphatidylcholine and a polymerizable dialkylammonium surfactant containing one diene group in each chain.[19]

Lateral phase separation in smetic mesophases composed of surfactants having different molecular shapes is well documented.[20-22] Domains are likely to be present as soon as the vesicles are formed. The time scale for domain formation, τ, can be estimated from[22]

$$\frac{1}{\tau} = \frac{1}{2}D_{\text{diff}}\left(\frac{2\pi}{\lambda}\right)^2 \qquad (13)$$

where a periodic (plane wave) variation in concentration, characterized by a wavelength λ, is built up after adjusting external conditions (temperature, sonication) in such a way that the mixed system starts to decompose into two phases. Taking λ to be 100 Å and D_{diff} to be 10^{-7} cm^2/s,[15] a value of 1 μs is obtained for τ. This very fast time scale implies the instantaneous presence of domains in mixed vesicles following cosonication. Even if domains are disturbed by the laser pulse, their reorganization is much faster than the time scale of radical propagation.[13] Interest in domain formation in surfactant vesicles is prompted by their potential to provide an on-command release mechanism to be utilized in target-directed drug deliveries.[7]

The small degree of polymerization of vesicles containing relatively mobile styrene head groups is entirely consistent with the observed fluidities of these polymerized vesicles.[16] Geometrical restrictions preclude the formation of large chains upon intravesicular surface polymerizations. The vesicle curvature has a marked effect on the rates and the degrees of polymerizations. Increasing the size of vesicles results in the formation of larger polymers at a slower rate. Vinylbenzoic acid coated DODAB vesicles polymerize slower and form somewhat larger polymers than those obtained in vesicles prepared from **3**. The average chain length of poly(vinylbenzoates) formed on DODAB vesicle surfaces is 20 (2820:140 = 20, Table II). Apparent surface restrictions and vesicle curvature presumably prevent the formation of larger chains. The largest polymers are formed in vesicles prepared by cosonicating **3** with vinylbenzoic acid. The average degree of polymerization of these vesicles is 40. Acting as spacer between the styrene head groups in **3**, vinylbenzoic acid increases the effective concentration of the monomers undergoing chain propagation and relieves the tension on the polymer due to the surface curvature.

A Monte Carlo based computer simulation of the photopolymerization process has been developed.[23] This program generates maps of photopolymerized surfactant vesicle surface morphology, calculates median cleft diameters and intermonomer separations, and plots chain length vs. irradiation time; hence the final number-average and weight-average chain-length distributions are found. The salient feature of the latter analysis is that the final number- and weight-average chain-length distributions do not follow a normal distribution but show a significant asymmetry due to a large population of short chains formed in the latter stages of photopolymerization because of radical trapping and deactivation in surface regions where no further unpolymerized monomers are available for bonding. The results of the computer-generated weight-average chain-length distribution for parameters pertinent to the vesicles in this study are shown in Figure 6. The close correspondence with the experimentally determined weight-average molecular weight distribution is seen by comparison with Figure 2.

Differences between kinetically and directly determined degrees of photopolymerization of vesicles prepared from **3** can now be readily rationalized. The chain length determined kinetically (19; see Results) at the early stages of photopolymerization is biased to higher degrees of photopolymerization. Conversely, the chain lengths of poly(vinylbenzoate) determined by gel exclusion chromatography (10, Table II) represents weight-average molecular weights obtained after the complete photopolymerization of vesicles prepared from **3**.

Due care should be exercised, however, on extending the results of the present study to other surfactant vesicle polymerizations. Vesicles prepared from different surfactants containing different polymerizable groups at different positions will give rise to different degrees and rates of photopolymerizations. Depending on the method of polymerization, average chain lengths of 677 and 135 were estimated to be present in polymerized vesicles prepared from **4**. Similarly, polymers formed in vesicles prepared from **5** and **6** were estimated to contain about 500 monomer units.[25]

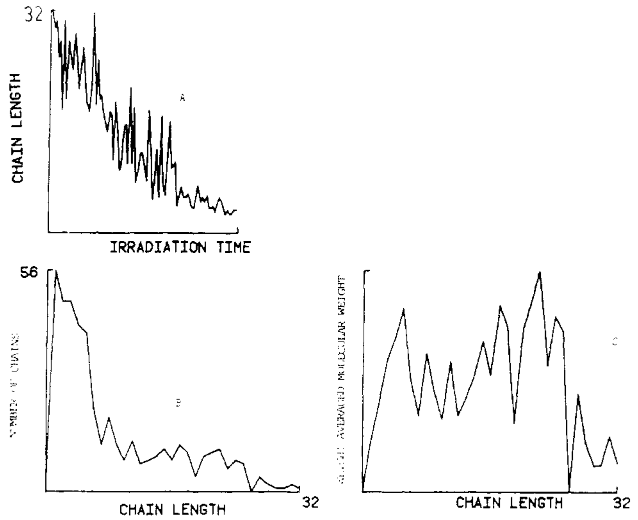
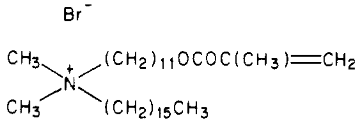


Figure 6. Computer simulation of surfactant vesicle photopolymerization. Monomer equilibrium distance = 10.00 Å, nitrogen–nitrogen separation distance in polymer chain = 7.00 Å, total number of monomers in simulation = 6400, encounters per radical lifetime = 100, total number of free radicals = 450, and average separation of head groups after polymerization = 12.86 Å. (A) Average chain length as a function of irradiation time. (B) Number of chains vs. chain lengths and (C) weight-average molecular weight vs. chain lengths. See Discussion for details.



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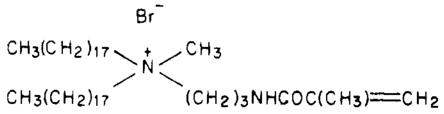

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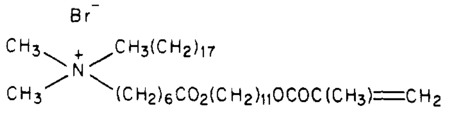

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Registry No. **3**, 98085-14-4; (**3**)·(vinylbenzoic acid) (copolymer), 98193-89-6; **4**, 98170-67-3; DODAB, 3700-67-2; poly(*p*-vinylbenzoic acid) (homopolymer), 28391-39-1; *p*-vinylbenzoic acid, 1075-49-6; *p*-vinylbenzoyl chloride, 1565-41-9; 2-bromoethanol, 540-51-2; dioctadecylmethylamine, 4088-22-6.

References and Notes

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Effects of Photopolymerization on Surfactant Vesicle Surface Morphology

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ABSTRACT: Properties of vesicles and polymerized vesicles prepared from $[C_{15}H_{31}CO_2(CH_2)_2]N^+(CH_3)CH_2C_6H_4CH{=}CH_2,Cl^-$ (1) have been investigated by transient dichroism and electron paramagnetic resonance measurements using erythrosin, 5-doxylstearic acid [FA(12,3)], and 5-doxylphosphatidylcholine [PC(12,3)] as reporters. Erythrosin added to nonpolymerized 1 vesicles showed no rotation anisotropy over the millisecond time domain. Conversely, erythrosin added to polymerized 1 vesicles showed marked temperature-dependent anisotropies. At room temperature, the time dependence of polarization anisotropy, $r(t)$, rose to a plateau value over the 0.5-ms time scale. At higher temperatures the plateau was lost and the anisotropy decay became measurable. Plots of anisotropy decays vs. temperature indicated the occurrence of a phase transition at 33 °C. The rise of $r(t)$ was rationalized by assuming the partitioning of erythrosin among different environments with different lifetimes and anisotropies. The temperature dependence of the hyperfine splitting of FA(12,3) and PC(12,3) added to sonicated 1 vesicles indicated phase transitions at 26.5 and 31.0 °C. Examination of FA(12,3) added to polymerized 1 vesicles indicated a phase transition temperature of 35 °C. Hyperfine splittings of PC(12,3) added to polymerized 1 vesicles decreased almost linearly with increasing temperatures, indicating a considerable broadening of the phase transition reported. At 25 °C, both spin probes appear to be less immobilized in polymerized than in nonpolymerized vesicles. This observation coupled with the transient dichroism of erythrosin substantiated the proposed formation of clefts on the vesicle surfaces upon photopolymerization. Differential scanning calorimetry of multicompartment 1 vesicles (prepared by vortexing 1) indicated a phase transition temperature at 35 °C. Upon polymerization the transition broadened and the gel-to-liquid phase transition temperature increased to 65 °C. These data indicate intrabilayer polymerizations in multicompartment vesicles.

Introduction

Full realization of the potentials of polymerized surfactant vesicles[3–7] demands a detailed understanding of their structures and of the mechanisms of their formation. Recently, we reported the kinetic consequences of the photolysis of vesicles prepared from a surfactant that contained a styrene moiety in its head group: $[C_{15}H_{31}CO_2(CH_2)_2]_2N^+(CH_3)CH_2C_6H_4CH{=}CH_2,Cl^-$ (1).[8] The observed first-order disappearance of the styrene absorbances have been found to be independent of the vesicle concentration and have been discussed, therefore, in terms of two-dimensional intravesicular surface polymerizations.[8] Flash photolysis of argon-bubbled vesicular solutions of 1 by 15-ns, 266-nm, 2-mJ laser pulses has indicated the competition of initiation, propagation, and termination within the 1-ms to 2-s time domain. Vesicle solutions have been found to be restored, therefore, to a new equilibrium of monomers, polymers, and photoproducts prior to the arrival of the next laser pulse at a 2-Hz repetition rate. Applying the energy in successive, essentially equal increments has allowed expressing the data in terms of

$$M(n) = M_0(1 - \eta)^n \qquad (1)$$

where n, $M(n)$, and M_0 are the numbers of equienergy laser pulses, the remaining nonpolymerized surfactant after n pulses, and the initial surfactant, respectively. η, the fraction of the double-bonded monomers consumed after the photochemical events induced by a single laser pulse had subsided, is defined by

$$\eta = \Phi_r \epsilon E k_p/(k_m + k_s) \qquad (2)$$

where Φ_r is the quantum efficiency of styryl radical formation, ϵ is the extinction coefficient at 266 nm, and E is the average energy/cm^2 of the laser pulse; k_p, k_m, and k_s are rate constants for polymerization, monomer re-formation, and formation of nonpolymerized photoproducts. The obtained good linearity of the laser photopolymerization plots has justified the assessments of the average polymer chain length in the vesicles (i.e., the degree

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