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Photopolymerization of Vesicles Prepared from *n*-Hexadecyl 11-(4-Vinylbenzamide)undecyl Hydrogen Phosphate and from Mixtures of Dioctadecyldimethylammonium Bromide and *n*-Hexadecyl 11-(4-Vinylbenzamide)undecyl Hydrogen Phosphate

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ABSTRACT: Surfactant vesicles, prepared from *n*-hexadecyl 11-(4-vinylbenzamide)undecyl hydrogen phosphate (**4**) and from mixtures of **4** and dioctadecyldimethylammonium bromide (**2**), have been photopolymerized by exposure to a 450-W xenon lamp or to repetitive, 265-nm, 20-ns laser pulses. Changes in the temperature, the pH, and the composition of the vesicles, as well as polymerization, profoundly affected the ^{31}P NMR spectra. Thus, a high-resolution signal at −10.95 ppm (relative to 1.0×10^{-2} M methylenediphosphonic acid) was observed at 70 °C for vesicles prepared from **4** at pH 5.8. Decreasing the temperatures decreased the motion of the phosphorus head group due to "liquid-to-solid" phase transition and broadened the ^{31}P NMR line width. Increasing the pH or incorporating **2** into **4** vesicles caused a downfield shift and line narrowing. Polymerization manifested in broadening of the ^{31}P NMR line width. Irradiation of vesicles, prepared from **4** and from mixtures of **4** and **2**, resulted in time, composition, and temperature-dependent changes of the absorption spectra. Absorbances due to the styrene moiety decreased exponentially with increasing photolysis. The pseudo-first-order rate constants, k_ψ values, calculated for steady-state irradiations, remained independent of the amount of **4** in vesicles prepared from mixtures of **4** and **2** at 23 °C, but it increased with increasing amounts of **4** at 70 °C. Breaks in the Arrhenius plots for the photopolymerization of vesicles prepared from 40:60 **4**/**2** showed the presence of two-phase transitions, indicating unequal distribution of surfactants. The first transition, having a phase transition temperature of 48 ± 2 °C, corresponded to the value determined for vesicles prepared from 40:60 **4**/**2** surfactant mixtures. The second transition, having a phase transition temperature of 65 ± 3 °C, was suggested to be due to patches of **4** assembled at higher temperatures. Data obtained in the repetitive 10-Hz laser photolysis allowed the assessment of the degrees of polymerization of **4** to be approximately 2. Number-averaged molecular weights of 3010 and 1500 and corresponding degrees of polymerizations of 5.1 and 2.5 were also determined from vapor phase osmometry measurements in photopolymerized vesicles prepared from **4** and from a 40% **4** and 60% **2** mixture. Irradiation with repetitive laser pulses at different frequencies afforded values for the propagation and termination rate constants for **4** in MeOH and for vesicles prepared from **4** and from a 40% **4** and 60% **2** mixture.

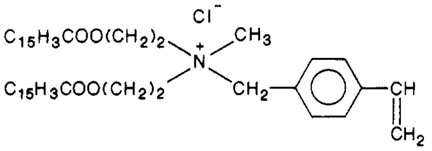
Introduction

Potential industrial applications have prompted the interest in polymerized vesicles.[1–6] The ability of polymerized vesicles to provide stable compartments of different microenvironments has been exploited in controlled release and delivery of drugs and other materials, immunorecognition, catalysis, transport, and artificial photosynthesis.[7–9]

Vesicles are closed-bilayer, single (SUVs), or multilamellar (MLVs) structures prepared from naturally occurring phospholipids or synthetic surfactants.[10] A vesicle-forming surfactant contains, typically, two C12–C20 hydrocarbon chains and a phosphate, sulfate, or quaternary ammonium head group. Introduction of vinyl, methacrylate, diacetylene, isocyano, and styrene moieties in the hydrocarbon chains or in the head groups led to polymerizable surfactants.[1–6,11] Vesicles prepared from polymerizable surfactants could subsequently be polymerized in their bilayers or across their outer or outer and inner head groups. Alternatively, exchanging the vesicle counterions by appropriate monomers and subsequent polymerization introduced the concept of polymer-coated vesicles.[12–15] Polymerized and polymer-coated vesicles showed enhanced stabilities and permitted some degree of permeability and morphology control.[1–5]

Optimization of permeability control requires an understanding of the kinetics and the structural changes which accompany vesicle polymerizations. These mechanistic details are being scrutinized in several laboratories.[15–24] Attention is focused in our laboratories to styrene-containing surfactants. We have found the photopolymerization of vesicles prepared from **1** (dioctadecyldimethylammonium bromide (**2**) functionalized by a styrene moiety in the head group) to result in pulling some 10–20 aryl groups together and thereby creating surface clefts.[20] Subsequently, we showed the degree of polymerization for vesicles prepared from an analogous surfactant (**3**) to vary between 10 and 20.[15] Larger degrees of polymerization were observed for vesicles prepared from mixtures of **2** and vinylbenzoic acid as well as from mixtures of **3** and vinylbenzoic acid.[15]

Polymerizations of vesicles prepared from a negatively charged surfactant (**4**) and from mixtures of **4** and **2** are the subject of the present report. ^{31}P NMR spectroscopy has provided structural information on vesicles prepared from 4 and from mixtures of 4 and 2 prior and subsequent to photopolymerization. Polymerizations were mediated by irradiation either by a 450-W Xenon lamp or by repetitive, 20-ns, 265-nm laser pulses. Following the absorption decrease, due to the styrene moiety in 4, as a function of time in the irradiations by the 450-W Xenon lamp, led to apparent pseudo-first-order rate constants for the polymerization. Variations in the absorption decrease per laser pulse as a function of frequency irradiation allowed the assessment of the rate constants for propagation, k_p, and termination, k_t, for the photopolymerization of vesicles prepared from 4 and from mixtures of 4 and 2.



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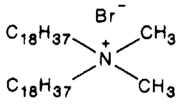

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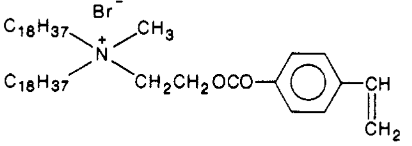

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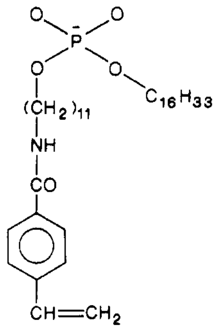


4

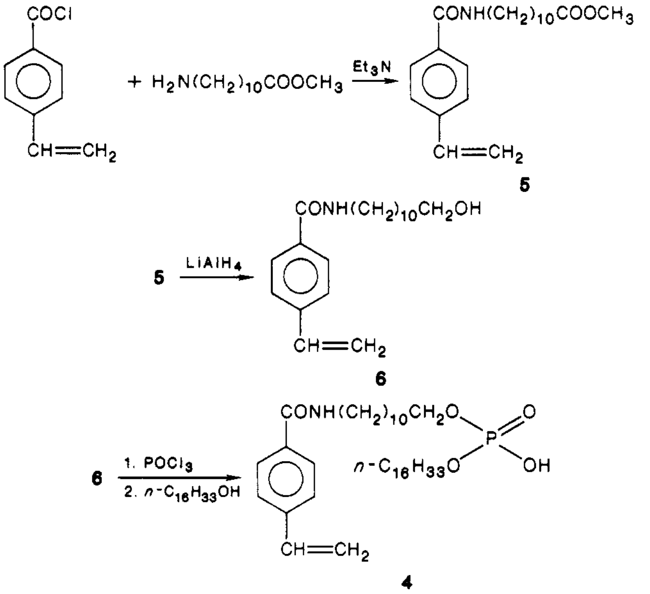
Experimental Section

n-Hexadecyl 11-(4-vinylbenzamide)undecyl hydrogen phosphate (4) was prepared as indicated in Scheme I. 4-Vinylbenzoyl chloride was prepared by the dropwise addition of 4.9 mL (57 mmol) of oxalyl chloride (containing 1 drop of pyridine) to 3.84 g (25.9 mmol) of 4-vinylbenzoic acid, dissolved in 70 mL of anhydrous benzene. Subsequent to allowing the reaction to stand 15 h at room temperature, the solvent was removed under vacuum. Excess oxalyl chloride was removed by anhydrous benzene and subsequent rotary evaporation (repeated twice). The obtained oil was characterized by ^{1}H NMR (^{1}H NMR ($CDCl_3$) δ 7.6 (dd, aromatic protons, 4 H), 5.15–7.0 (m, vinyl protons, 3 H)) and used in the subsequent step of the synthesis.

Methyl 11-(4-vinylbenzamide)undecanoate (5) was prepared by the slow addition (0.5 h) of the previously synthesized 4-vinylbenzoyl chloride, dissolved in a few milliliters of $CHCl_3$, to a suspension of 6.52 g (25.9 mmol) of methoxycarbonylammonium chloride and 10.8 mL (77.7 mmol) of triethylamine, dissolved in 170 mL of $CHCl_3$, at 5 °C. The suspension was allowed to warm to room temperature and then washed with aqueous HCl and with aqueous $NaHCO_3$. Subsequent to drying, the solvent was removed and the resulting solid was crystallized from ethyl acetate: obtained 7.43 g of 5, yield 83%; mp 78–79 °C; ^{1}H NMR ($CDCl_3$) δ 7.5 (dd, aromatic protons, 4 H), 5.15–7.0 (m, vinyl protons, 3 H), 6.3 (br, s, 1 H), 3.6 (s, methyl, 3 H), 3.35 (t, 2 H), 2.3 (t, 2 H), 1.0–2.0 (br s, 18 H). Anal. Calcd for $C_{21}H_{31}NO_3$: C, 73.01; H, 9.04; N, 4.05. Found: C, 73.32; H, 9.17; N, 4.11.

11-(4-Vinylbenzamide)undecanol (6) was prepared by the addition (in 10 min) of 12.1 g (35 mmol) of 5, dissolved in a few milliliters of THF to a suspension of 3.5 g (92.2 mmol) of $LiAlH_4$, in 150 mL of THF at 0 °C, under vigorous stirring. The suspension was stirred for an additional 10 min at 0 °C and then poured into cold water. After acidification (HCl), the compound was twice extracted with warm $CHCl_3$ and dried and the solvent was removed by rotary evaporation. Recrystallization from ethyl acetate yielded 9.46 g of 6: yield 85%; mp 108 °C; ^{1}H NMR ($CDCl_3$) δ 7.50 (dd, aromatic protons, 4 H), 5.15–7.0 (m, vinyl protons, 3 H), 6.2 (br s, 1 H), 3.2–3.8 (m, 4 H), 1.0–2.0 (br s, 18 H). Anal. Calcd for $C_{20}H_{31}NO_2$: C, 75.65; H, 9.86; N, 4.41. Found: C, 75.67; H, 9.90; N, 4.44.

Scheme I



n-Hexadecyl 11-(4-vinylbenzamide)undecyl hydrogen phosphate (4) was prepared by stirring 3.0 g of 6 (9.47 mmol) and 4.32 mL of $POCl_3$ (47.3 mmol) in 100 mL of anhydrous benzene in a 250-mL, round-bottom flask for 1 h at room temperature. The excess $POCl_3$ was rotary evaporated following repeated additions (four times) of 50 mL of anhydrous benzene at temperatures not exceeding 50 °C. The last portion of $POCl_3$ was removed in high vacuum (~0.5 mmHg). Anhydrous benzene (100 mL) and 2.29 g (9.45 mmol) of *n*-hexadecyl alcohol were added to the residue and heated at 60 °C for 21 h. Following the removal of benzene, the oily residue was stirred with 80 mL of *tert*-butyl alcohol and 20 mL of 5 N aqueous NaOH at room temperature for an hour. The solution was acidified with 35% HCl, and the *tert*-butyl alcohol was removed by rotary evaporation. Addition of water and cooling resulted in the formation of 4 as white precipitate. Filtration and crystallization from acetone led to pure 4, mp 93–95 °C; ^{1}H NMR ($CDCl_3$) δ 7.50 (dd, aromatic protons, 4 H), 5.15–7.0 (m, vinyl protons, 3 H), 3.65–4.20 (br q, 4 H), 3.20–3.65 (br t, 2 H), 1.0–1.9 (br s), 46 H), 0.90 (t, 3 H). Thin-layer chromatography (silica gel, chloroform/EtOH, 70:30 v/v) indicated the presence of a single spot. Anal. Calcd for $C_{36}H_{64}NO_6P$: C, 69.3; H, 10.37; N, 2.25; P, 4.98. Found: C, 69.75; H, 10.91; N, 1.60; P, 5.06.

Dioctadecyldimethylammonium bromide (2 (Aldrich)) was used as received. Purities of the surfactants were established by thin-layer chromatography (on Merck aluminum oxide, 60 F_{254}, type E, using $CHCl_3$).

Vesicle solutions were prepared by injecting a methanolic solution of appropriate concentrations of 4 or a mixture of 4 + 2 (0.5 mL at 60 °C) into 25.0 mL of water. The resultant milky solution was sonicated at 75 °C and 70 W by using the microtip of a Braunsonic 1510 sonicator until is cleared (15–60 minutes). Titanium particles were removed by centrifugation for 5 min at 3000 rpm. The total surfactant concentration, i.e., [4] or [4] + [2], was kept at 2.0×10^{-3} M.

Vesicles were polymerized by irradiating argon bubbled samples by a 450-W Xenon lamp or by 265-nm, 20-ns laser pulses (12 ± 7 mJ/pulse) using the fourth harmonic of a Quanta Ray DCR Nd:YAG laser at different frequencies.

Absorption spectra were recorded on a Hewlett-Packard 8450 A diode-array spectrophotometer.

Proton-decoupled ^{31}P NMR spectra were taken on a GN-360 MHz spectrometer at 145.805 MHz, operating in the Fourier transform mode. The spectrometer was interfaced with an Aspect 3000 computer and equipped with a temperature control device. D_2O was used as internal lock and externally added 1.0×10^{-2} M methylenediphosphonic acid, MDP, set the standard at 0 ppm. The number of scans was between 2500 and 10000 was a spectrum width of 10000 Hz. Pulses (45°) were used at 0.2–0.5-s interpulse and 200-ms delay time. Spin–lattice relaxation times (T_1) measurements employed a 180°–τ–90° inversion recovery sequence with at least 10 values and a 2-s delay between acquisitions.

Table I
^{31}P NMR Chemical Shifts and Line Widths of Nonpolymerized and Photopolymerized Vesicles Prepared from Mixtures of 4 and 2[a]

vesicles[b]	^{31}P chem shifts δ[c]			line widths, Hz
100% 4, NP, pH 5.8	−18.77	(−10.95)	(−11.01)[d]	126.61
100% 4, P at 23 °C, pH 5.8	−18.83	(−11.01)		220.22
100% 4, P at 70 °C, pH 5.8	−18.54	(−10.72)		214.35
	−19.94	(−12.12)		102.37
40% 4, NP, pH 3.8	−17.58	(−9.76)	(−9.87)[d]	72.00
40% 4, P at 23 °C, pH 3.8	−17.58	(−9.76)		108.83
15% 4, NP, pH 4.3	−17.43	(−9.61)	(−9.67)[d]	73.34
15% 4, P at 23 °C, pH 4.3	−17.55	(−9.72)		97.80
5% 4, NP, pH 7.3	−17.46	(−9.64)	(−9.91)[d]	51.11
5% 4, P at 23 °C, pH 7.3	−17.64	(−9.82)		92.13

[a] ^{31}P NMR measurements were performed at 80 °C. [b] Percentages of 4 in mixtures of 4 + 2 (w/w): NP, nonpolymerized; P, polymerized; pH determined at room temperature. [c] Chemical shifts are related to externally added 1.0×10^{-2} M MDP. Those in parentheses were converted to trimethyl phosphate standard, taking trimethyl phosphate, −7.82 ppm on the H_3PO_4 scale. [d] Values determined in ref 23.

Table II
^{31}P Spin-Lattice Relaxation Times

sample	T_1, s
vesicles prepared from 4 in $CHCl_3$	2.86
vesicles prepared from 100% 4, NP, pH 5.8	0.337
vesicles prepared from 100% 4, P at 70 °C, pH 5.8	0.140
vesicles prepared from 40% 4 and 60% 2, NP, pH 3.8	0.473
egg lecithin vesicles[b]	2.4 3.0
didecylphosphatidylcholine liposomes[c]	1.0–2.9[d]

[a] ^{31}P spin-lattice relaxation times measured at 80 °C: NP, nonpolymerized; P, polymerized; pH determined at room temperature. [b] At 27 °C, taken from ref 29. [c] Taken from ref 30. [d] Temperature dependent.

Molecular weights were determined by means of vapor phase osmometry using a Hewlett-Packard Macrolab 800 instrument. The instrument was calibrated by standard techniques using 0.8 g/L benzil in $CHCl_3$.[25]

Results and Discussion

^{31}P NMR Spectroscopy. The ^{31}P NMR spectra, taken at 80 °C, of vesicles prepared from 4 and from mixtures of 4 and 2 prior and subsequent to photopolymerization are illustrated in Figure 1. Table I collects data for the observed chemical shifts and line widths of the different vesicle systems investigated.

The appearance of high-resolution signals is indicative of the presence of vesicles. Similar spectra were observed for vesicles prepared from neutral and synthetic phospholipids.[26-29] The observed ^{31}P NMR shifts for unpolymerized vesicles prepared from 4 at 70 °C at pH 5.8, −10.95 ppm, is in accord with that reported previously (−11.01 ppm)[23] under similar conditions. The spin–lattice relaxation times of the ^{31}P nuclei, T_1 values, in vesicles prepared from 4 was determined in the present work to be 0.337 s. In contrast, the T_1 value of 4 in $CHCl_3$ was measured to be 2.86 s (see Table II). ^{31}P NMR relaxation times of phospholipid vesicles are also included in Table II. It is interesting to note that two peaks, ca. 0.13 ppm apart, were observed for egg-lecithin vesicles and that these two resonances relaxed on two distinct time scales.[30] The longer relaxation time (3 s) was assigned to ^{31}P resonances originating at the outer surfaces of the vesicles, while the shorter T_1 value (2.4 s) was attributed to lipids which were distributed at inner surfaces. The dependence of ^{31}P spin–lattice relaxation times on a large number of parameters[26] precludes a meaningful comparison of the values obtained for liposomes with those reported here. In general, information on molecular motion can be inferred from spin–lattice relaxation times. Thus, the data in Table II indicate substantially shorter relaxation times and increased mobilities of 4 in vesicles above the phase transition temperature than in $CHCl_3$. Similarly, T_1 values can be profitably compared among unpolymerized and polymerized vesicles prepared from 4 and from mixtures of 4 + 2.

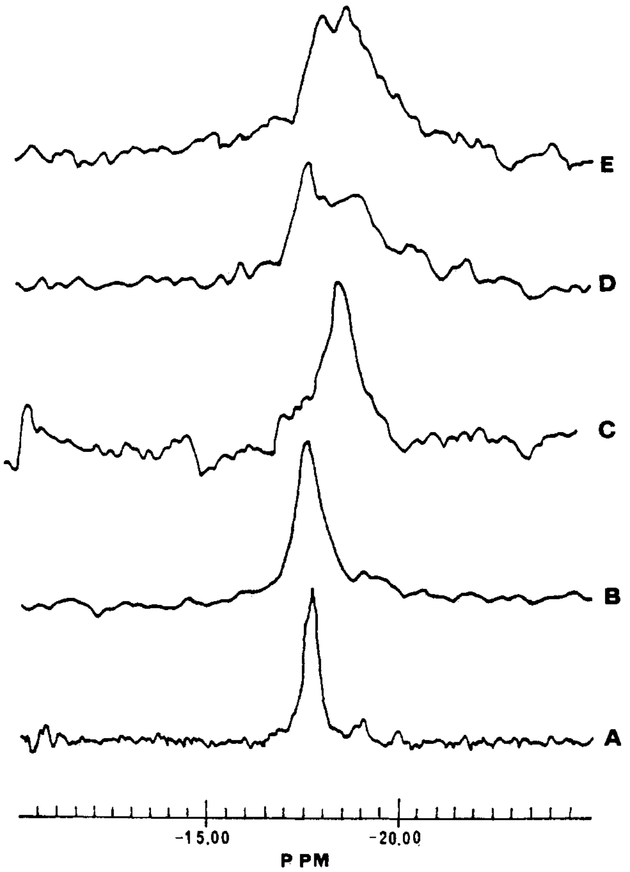


Figure 1. Proton-decoupled 145.8-MHz, ^{31}P NMR spectra of vesicles prepared by sonication of (a) 8×10^{-4} M 4 in 1.2×10^{-4} M 2 [40:60], nonpolymerized; (b) 8×10^{-4} M 4 in 1.2×10^{-4} M 2 [40:60], polymerized; (c) 2×10^{-3} M 4, nonpolymerized; (d) 2×10^{-3} M 4, polymerized at room temperature; and (e) 2×10^{-3} M 4, polymerized at 70 °C. All spectra were recorded at 80 °C. D_2O 15 (w/w %) was added to all preparations prior to recording. Between 2000 and 3000 scans were recorded. Chemical shifts are related to $\delta\{CH_2[PO(OH_2)_2]_2\}$ 0.

Both the temperature and the pH affect the ^{31}P NMR spectra.[31] The phase transition of vesicles prepared from 4 is 60 ± 3 °C.[23] At 70 °C, the surfactant molecules are in their "liquid" state and the motion of the phosphate head group is relatively unhindered. Decreasing the temperature results in a "liquid-to-solid" phase transition which manifests in the broadening of the ^{31}P NMR line width. The ^{31}P NMR signal of vesicles prepared from 4 undergo pronounced downfield shift and concomitant line width narrowing upon increasing the pH. ^{31}P chemical shifts for protonated and unprotonated 4 vesicles were previously measured at 80 °C to be −11.01 and −9.24 ppm, respectively.[23] Barring other factors, the ^{31}P NMR shift provides information on the effective hydrogen ion concentration of the vesicle surfaces.

Behavior of vesicles prepared from mixtures of 4 and 2 were analogous to that observed previously.[23] Formation of surfactant ion pairs in vesicles caused a downfield shift and narrowing of the ^{31}P NMR signal with respect to vesicles containing entirely 4 (Table I). These data in-

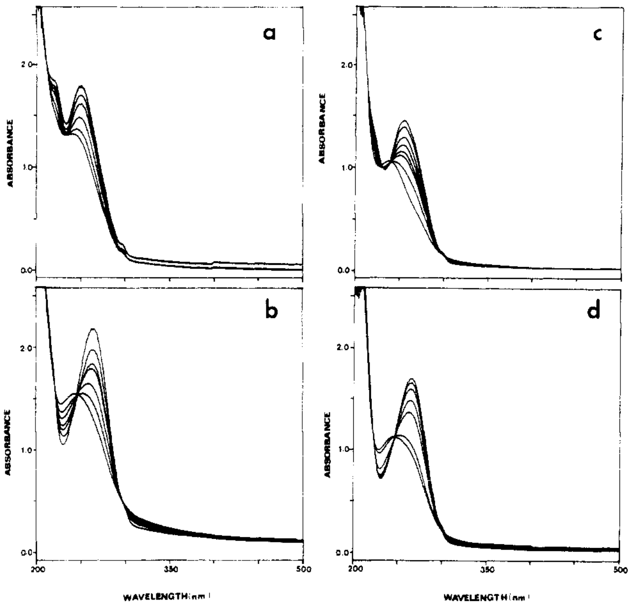


Figure 2. Absorption spectra of vesicles prepared from mixtures of 4 and 2 as a function of irradiation by a 450-W xenon lamp: (a) 1.5×10^{-4} M 4 in 2.2×10^{-4} M 2 [40:60] irradiation at room temperature; (b) 1.5×10^{-4} M 4 in 2.2×10^{-4} M 2 [40:60] irradiation at 70 °C; (c) 1.2×10^{-4} M 4 in 6.5×10^{-4} M 2 [15:85] irradiation at room temperature; and (d) 1.2×10^{-4} M 4 in 6.5×10^{-4} M 2 [15:85] irradiation at 70 °C. Increasing irradiation results in a decrease in the absorbances at 250–254 nm.

dicate strong interactions between the oppositely charged phosphate and ammonium head groups and a resultant decrease of mobility. The increased ^{31}P spin–lattice relaxation time (Table II) in vesicles prepared from mixtures of 4 and 2 is in accord with this interpretation.

Polymerization of vesicles prepared from 4 and from mixtures of 4 and 2 broadens markedly the ^{31}P NMR signal (Figure 1 and Table I). This is, of course, the expected result of the decreased isotropic motion of the surfactants upon linking.

Photopolymerization Initiated by Steady-State Irradiation. Irradiation of argon-bubbled vesicles prepared from 4 and from mixtures of 4 and 2 by a 450-W Xenon lamp resulted in the progressive loss of absorbances due to the styrene moiety. There are subtle differences in the spectra of the vesicles and in the spectral changes due to polymerization (Figure 2). The absorption maximum of vesicles prepared from 4 (247 nm) progressively shifts to longer wavelengths upon decreasing its concentration to 40% (250 nm), 15% (254 nm), and 5% (256 nm) in vesicles prepared from mixtures of 4 and 2 (Figure 2). Good isosbestic points were observed at 70 °C for all polymerizations and at room temperature for vesicles prepared from mixtures containing 5% and 15% of 4. Lack of isosbestic points are apparent in the room-temperature polymerization of vesicles prepared from 4 and from 40:60 mixtures of 4 and 2 (Figure 2).

Styrene absorbances in vesicles prepared from 4 and from mixtures of 4 and 2 decreased exponentially with increasing irradiation. Good first-order plots were obtained up to 40–50% photoconversion (see Figure 3 for typical plots). Pseudo-first-order rate constants for the photopolymerization of vesicles prepared from mixtures of 4 and 2 at different compositions and temperatures are given in Table III. Rate constants for polymerization at 23 °C are seen to be independent of the content of 4 in vesicles prepared from mixtures of 4 and 2. Within experimental error, the observed rate constants, k_ψ values, are the same for vesicles containing 5, 15, 40, and 100% 4. Conversely, above the phase transition temperature, k_ψ linearly increased with increasing amounts of 4 in vesicles prepared from mixtures of 4 and 2 (Table III). These results are explicable in terms of the formation of relatively short

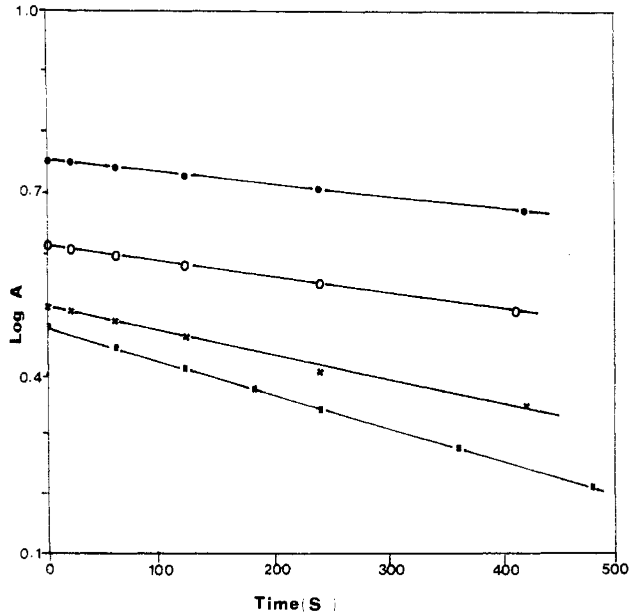


Figure 3. Plots of absorption changes as a function of irradiation time for vesicles prepared from (■) 100% 4; (×) [40:60] 4 and 2 mixture; (○) [15:85] 4 and 2 mixture; and (●) [5:95] 4 and 2 mixture. Total surfactant concentration was kept at 2.0×10^{-4} M.

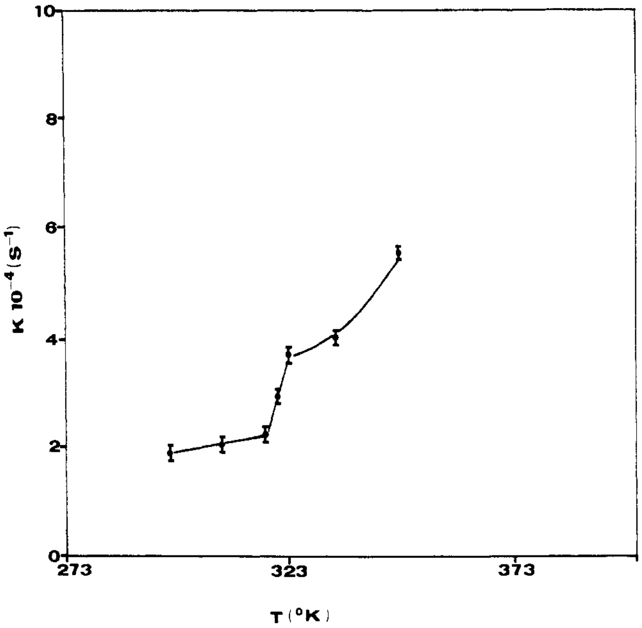


Figure 4. Arrhenius plot of the photopolymerization of vesicles prepared from 1.5×10^{-4} M 4 in 2.2×10^{-4} 2 [40:60].

Table III
Rate Constants for Vesicle Photopolymerizations Initiated by Steady-State Irradiation

% 4 in vesicles prepared from 4 + 2 (w/w)	$10^4 k_\psi$,[a] s^{-1}						
	23.0 °C	35.0 °C	45.0 °C	51.0 °C	60.0 °C	70.0 °C	75.0 °C
5.0	1.90					1.90	
15.0	1.94					3.20	
40.0	1.90	2.0	2.2	3.7	4.0	5.6	5.6
100.0	1.93					7.0	

[a] Calculated from the first-order plots of absorption decreases vs irradiation times, covering up to 40–50% photoconversion.

Table IV
Kinetic Parameters Obtained in Photopolymerizations Initiated by Laser Pulses at 25 °C

sample	$\eta/\bar{E}$,[a] J^{-1}	$\overline{DP}$	k_p/k_t	k_p, $M^{-1}\ s^{-1}$	k_t, $M^{-1}\ s^{-1}$
4 in MeOH[b]			5×10^{-5}	1.4×10^{2}	2.7×10^{6}
vesicles prepared from **4**	1.71	2.5	1.5×10^{-4}	2.5×10^{3}	1.7×10^{7}
vesicles prepared from 40:60 **4**/**2**	1.43	2.1	1.2×10^{-3}	8.9×10^{3}	7.7×10^{6}
vesicles prepared from **3**[c]	1.35	10			
styrene[d]			44		4.75×10^{7}

[a] Fraction of double-bonded monomers consumed after the photochemical events induced by a single laser pulse had subsided, normalized to be independent of the laser energy. Average of four to give determinations each within ±8% of the mean. [b] Concentration of **4** = 1.0×10^{-4} M. [c] Taken from ref 15. [d] Taken from ref 37.

chain oligomers and in terms of higher rates of concentration-dependent propagation in the more fluid vesicles.

Figure 4 shows the Arrhenius plot for the initial rates of photopolymerization of vesicles prepared from mixtures of 40% **4** and 60% **2**. The break in this plot clearly indicates the presence of a phase transition between 45 and 51 °C with a mean phase transition temperature of 48 ± 2 °C. Phase transition temperatures of vesicles prepared from pure **4** and **2** have been determined to be 60 ± 5[23] and 36 ± 2 °C,[32] respectively. The transition observed in Figure 4, having a phase transition temperature of 48 ± 2 °C, clearly cannot correspond to that ascribable to **2**. It agrees well, however, to the value determined previously by different techniques for vesicles prepared from mixtures of 40% **4** and 60% **2** (48 ± 3 °C).[23] Activation energy for the phase transition has been calculated to be 75 ± 10 kJ mol^{-1}. This value is in the range associated with styrene photopolymerizations.[33]

Photopolymerization Initiated by Laser Pulses. Irradiation of vesicles prepared from **1** or **3** by 266-nm, 15-ns repetitive laser pulses, arriving in *equal intervals*, have been shown to result in the exponential decrease of the absorption due to the styrene moiety.[20,21] Importantly, the rates of absorption changes were found to be independent of the concentration of the surfactant but linearly dependent on the energy of the laser pulses. These observations were rationalized in terms of two-dimensional, intravesicular processes which allowed us to model the photopolymerization on a *per vesicle* rather than on a concentration or unit volume, basis. The proposed model assumed that the vesicle surface is hexagonally packed so that each monomer, M, is surrounded by six of its nearest neighbors, that the photoproduction of the styryl radical, $M^\bullet$, is governed by $\Phi_r\bar{\epsilon}\bar{I}$ (where Φ_r is the quantum efficiency for the formation of $M^\bullet$, $\bar{\epsilon}$ is the mean molar extinction coefficient over the absorption range (λ) expressed in cm^2 per monomer, and $\bar{I}$ is the mean intensity over λ, i.e., $\bar{\epsilon}\bar{I} = \int^{290\text{nm}}_{230\text{nm}}\epsilon(\gamma)L(\gamma)\,d\gamma$ where $L(\gamma)$ is the spectral irradiance of the source), and that $M^\bullet$ can undergo three major processes: link with other monomer(s) to propagate a polymer chain (a process governed by k_p), return to the ground state (a process governed by k_s), and react with oxygen, impurity, the wall of the vessel, yielding nonpolymeric photoproducts (a process governed by k_m).[20] These considerations led to eq 1 and 2 which governed the consumption of monomers and radicals, where $M(t)$ and

$$dM/dt = (\Phi_f - 1)\bar{\epsilon}\bar{I}M + k_sM^\bullet - k_pw_tM^\bullet + f[M^\bullet]^2 \tag{1}$$

$$dM^\bullet/dt = \bar{\epsilon}\bar{I}\Phi_rM - (k_m + k_s)M^\bullet - (1 - f)[M^\bullet]^2 \tag{2}$$

$M^\bullet(t)$ are respectively the number, per vesicle, of double-bond-containing monomers remaining and free radicals present at time t, f is the fraction of free radicals involved in combinations and disproportionations which restore double-bonded monomers, w_t indicates the average number of nearest monomeric neighbors M at time t, and Φ_f is the quantum efficiency for non-radical-producing, excited-state depletion ($\Phi_f + \Phi_r = 1$). Linearization of eq 1 and 2 led to

$$dM/dt = k_IM^\bullet \qquad k_I = k_s - k_p \tag{3}$$

$$dM^\bullet/dt = -k_{II}M^\bullet \qquad k_{II} = k_m + k_s \tag{4}$$

with the initial condition that

$$M(0) = M_o - M_o^\bullet \tag{5}$$

where $M_o^\bullet$, the number of styryl radicals produced per laser pulse, is equal to $\Phi_r\bar{\epsilon}\bar{E}M_o$, $\bar{E}$ is the average energy per cubic centimeter of the laser pulse, calculated by dividing the measured energy per pulse by the cuvette area, and M_o is the original number of monomers in the vesicle. Solving eq 3 and 4 resulted in

$$M^\bullet(t) = M_o^\bullet e^{-k_{II}t} \tag{6}$$

$$M(t) = M_o - M_o^\bullet + (k_IM_o^\bullet/k_{II})(1 - e^{-k_{II}t}) \tag{7}$$

Assuming that $k_p \gg k_m$ and defining a quantity, η, as the fraction of the double-bonded monomers consumed after the photochemical events induced by a single laser pulse have subsided, i.e.

$$\eta = \Phi_r\bar{\epsilon}\bar{E}k_p/(k_m + k_s) \tag{8}$$

so that

$$\lim_{t \to \text{next laser pulse}} M(t) = M_o(1 - \eta) \tag{9}$$

resulted in

$$M(n) = M_o(1 - \eta)^n \tag{10}$$

and

$$\frac{dM(n)}{dn} = \ln(1 - \eta)M(n) \tag{11}$$

where n represents the number of laser pulses used to mediate the polymerization. In accord with eq 11, plots of the logarithm of absorbance changes (related to $dM(n)/dn$) against n resulted in straight lines for the laser-induced polymerization of vesicles prepared from **1** and **3**.[20]

Similar methods have been employed here for the laser-induced photopolymerization of vesicles prepared from **4** and from mixtures of **4** and **2**. Figure 5 illustrates typical absorption changes in vesicles prepared from mixtures of **4** and **2** as a function of irradiation by repetitive, 10-Hz laser pulses. The insert shows the plot of the logarithm absorptions at 260 nm vs the number of laser pulses. The obtained η values divided by the applied average laser energy, E (determined to be 2.6×10^{15} photons/monomer), are collected in Table IV.

An important consequence of the two-dimensional surface photopolymerization model[20] is that the average

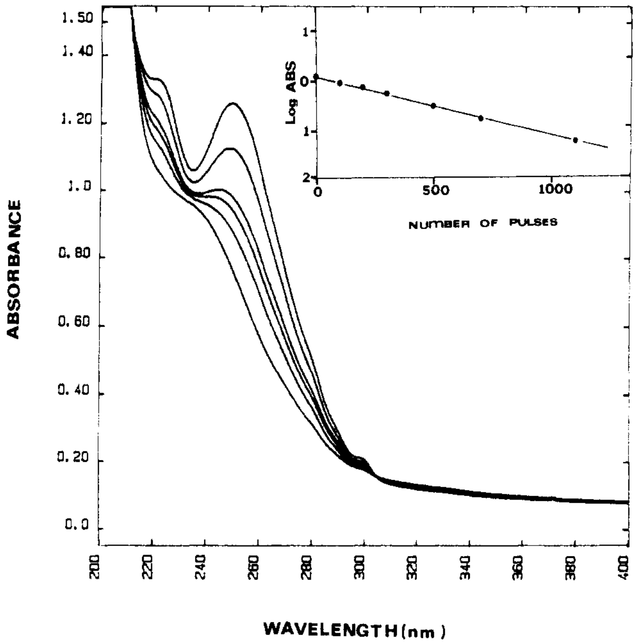


Figure 5. Absorption spectra of vesicles prepared from 1.1 × 10^{-4} M **4** in 1.6 × 10^{-4} **2** [40:60] as a function of irradiation by repetitive, 2.0-mJ, 265-nm laser pulses. The insert shows the plot of the data according to a first-order decay.

chain lengths of the polymers formed in the vesicles (i.e., the degree of polymerization), $\overline{DP}$, can be assessed from

$$DP = \eta/\Phi_r\bar{\epsilon}\bar{E} \qquad (11a)$$

where $\bar{\epsilon}$ was determined to be 1.8 × 10^{-17} cm^2/monomer. Substituting the η values from Table IV into eq 11 led to $\overline{DP}$ values of ca. 2 for the polymerization of vesicles prepared from **4** and from mixtures of **4** and **2**. It should be emphasized that these values, in view of the gross approximations involved, are highly approximate with estimated errors of ±80%. In spite of these uncertainties, the data are clearly not compatible with any appreciable degrees of photopolymerization of these vesicles.

An additional application of laser-initiated polymerizations has been recently described. Exposure of monomers to repetitive laser pulses in *different increments* was shown tantamount to the use of the rotating sector which controlled the frequency of the intervals when the sample was exposed to illumination and darkness.[34-36] Under "pseudo-stationary state" conditions, both the maximum concentration of $M^\bullet$ detectable immediately after the laser pulse, $[M_{max}^\bullet]$, and the minimum concentration of $M^\bullet$ prevailing immediately before the arrival of the next pulse, $[M_{min}^\bullet]$, are invariant of the time interval between the consecutive laser pulses, t_0. The concentration of radicals, $[M^\bullet]$ per pulse, ρ, is given by

$$[R_{max}] - [R_{min}] = \rho \qquad (12)$$

Under the experimental conditions, the duration of the laser pulse (20 ns) is very much shorter than the dark intervals (0.01–10 s) and the formation of $M^\bullet$ is virtually instantaneous. Assuming that

$$\frac{\text{number of radicals generated in a given pulse}}{\text{total number of radicals}} = \text{constant} = \beta \qquad (13)$$

the rate of polymerization, R_p can be expressed by[34-36]

$$y = \frac{R_p}{[M^\bullet]}t_0 = \frac{k_p}{k_t}\ln\left\{1 + \frac{\rho k_t t_0}{2}\left[1 + \left(1 + \frac{4}{\rho k_t t_0}\right)\right]\right\} \qquad (14)$$

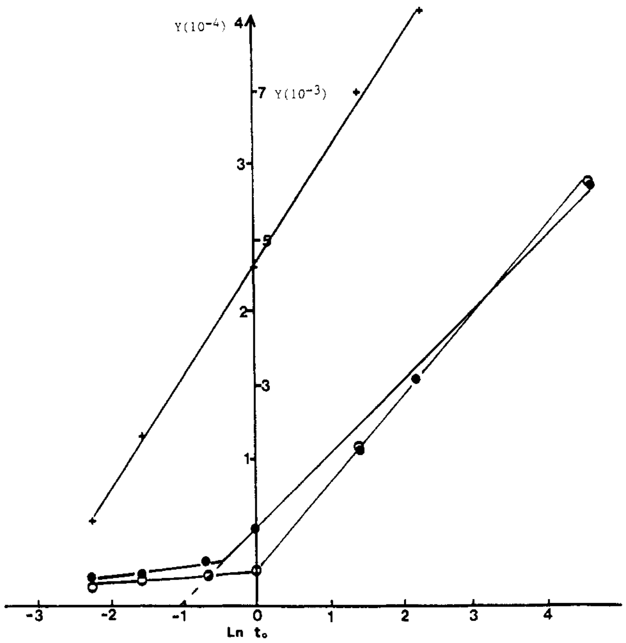


Figure 6. Plot of y vs ln t_0, according to eq 16: (○) 40% **4** + 60% **2** vesicles (y scale on the right-hand side); (●) **4** in methanol (y scale on the left-hand side); and (+) 100% **4** vesicles (y scale on the right-hand side).

where y is the fraction of monomer polymerized per each laser pulse and k_p and k_t are the rate constants for the propagation and termination of the polymerization, respectively. Choosing conditions such that $\rho k_t t_0 \gg 1$ allows the simplification of eq 14 to

$$y = \frac{R_p}{[M_o^\bullet]}t_0 = \frac{k_p}{t_0}\ln(\rho k_t t_0) \qquad (15)$$

which can be arranged to

$$y = \frac{k_p}{k_t}\ln(\rho k_t) + \frac{k_p}{k_t}\ln t_0 \qquad (16)$$

Thus, plotting y against ln t_0 allows the calculation of k_p and k_t.

Figure 6 shows plots of the data for the pulsed-laser-initiated photopolymerization of **4** in methanol and in the form of vesicles prepared from **4** and from a 40:60 mixture of **4** and **2** according to eq 16. It should be remarked that each y value was taken as the mean of several measurements (typically four to five), each of which differed from the mean by no more than 8%. A y value was obtained by exposing the sample to a set of n_1 number laser pulses (typically n_1 = 10) at the appropriate frequency and using the formula

$$y = \frac{A_{I/\epsilon} - A_{II/\epsilon}}{A_{I/\epsilon}n_1} \qquad (17)$$

where A_I and A_{II} are the absorbances prior and subsequent to exposure to the set of laser pulses and ϵ is the extinction coefficient of **4** at 250 nm, taken to be 1.4 × 10^4 M^{-1} cm^{-1}. Good linearity of the plots in Figure 6 validates the assumptions involved in reaching eq 16. The obtained rate constants, k_p, and k_t, are summarized in Table IV. Rate constants for the termination, k_p, are of the same order of magnitude as that determined for styrene photopolymerization (Table IV).[37] The appreciably smaller $k_p k_t$ ratios for the photopolymerization of **4** than that obtained for styrene is the expected consequence of the small degrees of polymerization.

Vapor Phase Osmometry. The number-average molecular weights of the species formed upon polymerization of vesicles prepared from 4 and from mixtures of 40% 4 and 60% 2 were determined to be 3010 and 1500, respectively, by vapor phase osmometry. The corresponding degrees of polymerization, 5.1 and 2.5, indicate the formation, on the average, of small oligomers and dimers. These low degrees of polymerizations are in accord with those assessed from the laser-initiated photopolymerizations (Table IV).

Conclusion

Unequal distribution of neutralized ion pairs and charged species in photopolymerized vesicles prepared from mixtures of negatively (4) and positively (2) charged surfactants is the most significant result of the present study. The observed two-phase transitions were attributed to 4 + 2 ion pairs and to separated patches of 4 in the vesicle matrices. The importance of domains is that they provide a mechanism for releasing the contents of vesicles.[3] Kinetic measurements of photopolymerization, as well as vapor phase osmometry, indicated very small degrees (2-5) of photopolymerizations. With the exception of one report,[19] similar small degrees of polymerizations[15,20,21] were observed for vesicles prepared from styrene-containing surfactants.

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Registry No. 4, 116437-66-2; 4 (homopolymer), 116437-67-3; 4/2, 116466-63-8; 4/2 (homopolymer), 116466-65-0; 5, 116437-64-0; 6, 116437-65-1; $POCl_3$, 10025-87-3; 4-vinylbenzoyl chloride, 1565-41-9; hexadecyl alcohol, 36653-82-4; $H_2N(CH_2)_{10}CO_2CH_3$, 28691-27-2.

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Laser-Initiated Polymerization of Methyl Methacrylate: Repetition Rate Effect on Molecular Weight Distribution

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ABSTRACT: The critical effect of the pulsing frequency on the molecular weight distribution of the laser-initiated polymerization of methyl methacrylate has been characterized. High laser repetition rates (i.e. 40 Hz) result in a significant decrease in polymer yield as well as a marked change in the structure of the molecular weight distribution curves. The individual peaks observed in the GPC of the poly(methyl methacrylate) generated are simulated by a series of successive Poisson distribution functions.

In the past few years there have been a number of reports dealing with the use of pulsed lasers as sources to free radical polymerization.[1-20] Due to the immense industrial and technical interest in lasers as candidates for imaging and photoresist processing,[4] basic studies that describe the kinetics and mechanisms of laser-initiated