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A Novel Two-Dimensional Photopolymerization at an Oriented Bilayer Surface. Effective Molecular Weight Control Using Membrane State and Chain Transfer

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ABSTRACT: Extremely high molecular weight polymers can be produced under mild conditions in a bilayer state by taking advantage of a well-defined bilayer surface and fixation of the photoinitiator (dihexadecyl *N*-[[[ethoxy(thiocarbonyl)]thio]acetyl]-L-glutamate) at the most effective position for initiation. The similar situation was observed for the chain-transfer reaction at the bilayer surface: a chain-transfer agent with double alkyl chains could control acutely the molecular weight of polymers using the present bilayer system whereas a similar compound lacking the long alkyl chains could not act as a molecular weight controller. We also established that the phase separation of bilayers composed of a nonpolymerizable fluorocarbon component and a polymerizable hydrocarbon component was useful in controlling the molecular weight. This study demonstrates that completely regulatable polymerization at a two-dimensional bilayer surface should require not only orientation of the monomer molecule at a membrane surface but also an optimum molecular design of the photoinitiator and the chain-transfer agent.

Polymerization of bilayer membranes has attracted wide attention because of the practical and biological interest in polymerized vesicles showing enhanced stabilities. There is also a closely related fundamental interest in low-dimensional reactions. Many types of polymerizable vesicles have been prepared and studied mainly on increasing mechanical stability.[1] In most of those cases, UV irradiation and/or appropriate initiators were used for initiation of polymerization. However, the position of those initiators resulting from solubilization into bilayer matrix and adsorption on bilayer membrane surface were not readily fixed near the polymerizable groups, and thus the preparation of high molecular weight membranes has not been particularly successful. Synthetic bilayer membranes are two-dimensional arrays of molecules and are useful tools for ordering of molecules. The molecular ordering produces various interesting properties. It was found that *J* aggregates of anionic cyanine dyes were formed at the changed surface of cationic bilayer membranes[2] and that macroscopic orientations of electron spins were achieved by using anionic Cu^{II} chelates embedded in cationic membrane surfaces.[3] One may consider, therefore, that the well-defined charged surface of bilayer membranes is a suitable vehicle for the regulation of the polymerization of a monomer containing an opposite charge. Regen et al.[4] built "polymer-encased vesicles" by the photopolymerization of dioctadecyldimethylammonium with methacrylate as a polymerizable counterion. Extracted polymer material had an IR spectrum identical with that of an authentic sample of poly(methacrylic acid). They also report data on the molecular weight (M_w = 85 000 in 0.002 M HCl) and tacticity of the polymer obtained.

We now report the effective molecular weight control of the polymers formed upon photopolymerization of mixed bilayer membranes composed of xanthate-based compound **1**, which has been reported to serve as an effective photoinitiator,[5] polymerizable amphiphile (**2**), and fluorocarbon amphiphile (**5**) or tribromomethane derivative (**3**) as a molecular weight controller. Since fluorocarbons are not readily miscible with hydrocarbons, this property has been used to control the phase separation of bilayer membrane.[6,7] It is also well-known that tribromomethane derivatives can be an effective chain-transfer agent for radical polymerizations. We have found that ultrahigh molecular weight polymers in a bilayer state can be produced under mild conditions by taking advantage of the well-defined bilayer surface and fixation of the photoinitiator at an effective position as shown in Figure 1.[8,9] This is a novel system for the efficient molecular weight regulation of polymeric membranes.

Experimental Section

Preparation of Dihexadecyl *N*-[[[Ethoxy(thiocarbonyl)]thio]acetyl]-L-glutamate (1). Sodium *O*-ethylxanthate (0.37 g, 2.6 mmol) and 1.1 g (1.7 mmol) of *N*-(α-chloroacetyl)-L-glutamic acid dihexadecyl ester[10] were dissolved in 100 mL of THF and refluxed for 4 h in the dark, and then NaCl formed was separated and THF was removed. The residues were recrystallized from methanol, giving a pale yellow powder: yield 52%; mp 54 °C. The purity was confirmed by the UV spectrum (λ_{max} = 278: $\pi-\pi^*$ transition of SC(=S)O; ϵ_{max} = 1.13×10^4 L mol^{-1} cm^{-1}). The NMR spectrum was consistent with the structure: NMR ($CDCl_3$) δ 0.89 (t, 6, CH_3), 1.45 (s, 2, C(=S)OCH_2). Anal. Calcd for $C_{42}H_{79}O_6NS_2$: C, 66.53; H, 10.50; N, 1.85. Found: C, 66.39; H, 10.58; N, 1.78.

Dihexadecyl *N*-[(Trimethylammonio)acetyl]-L-glutamate *p*-Styrenesulfonate (2). The polymerizable amphiphile **2** was prepared by the anion-exchange reaction of the corresponding double-chain ammonium chloride with sodium styrenesulfonate. The chloroform solution (10 mL) of dihexadecyl *N*-[(trimethylammonio)acetyl]-L-glutamate chloride[10] (1 g, 1.4 mmol) and the methanol solution (30 mL) of sodium styrenesulfonate (0.44 g, 2.1 mmol) were mixed and stirred for 4 h at room temperature. After separation of NaCl formed and removal of solvent, the residues were extracted with chloroform, giving a colorless powder: yield 72%; mp 81–82.5 °C; NMR ($CDCl_3$) δ 0.89 (t, 6, CH_3), 5.28, 5.76, 6.72 (d, 3, vinyl), 7.43, 7.80 (d, 4, phenyl). Anal. Calcd for $C_{50}H_{90}O_8N_2S$: C, 68.30; H, 10.32; N, 3.19. Found: C, 68.22; H, 10.40; N, 3.02.

Dihexadecyl *N*-(Tribromoacetyl)-L-glutamate (3). A THF solution (20 mL) of 9.5 mmol of tribromoacetyl chloride (3.0 g) was added with stirring to a THF solution (50 mL) of 3.0 g (4.7 mmol) of the tosylate salt of dihexadecyl L-glutamate and 3.0 g (23 mmol) of triethylamine in an ice bath. Upon further stirring at room temperature for 24 h, the mixture was washed and dried. The solvent was removed, and the residue was recrystallized from methanol, giving a pale yellow powder: yield 2.5 g (60%); TLC ($CHCl_3$) R_f 0.65 single spot; IR 1660 (C=O, amide), 1750 cm^{-1} (C=O, ester). Anal. Calcd for $C_{39}H_{52}O_5NBr_3$: C, 54.82; H, 6.13; N, 1.64; Br, 28.05. Found: C, 54.59; H, 5.96; N,

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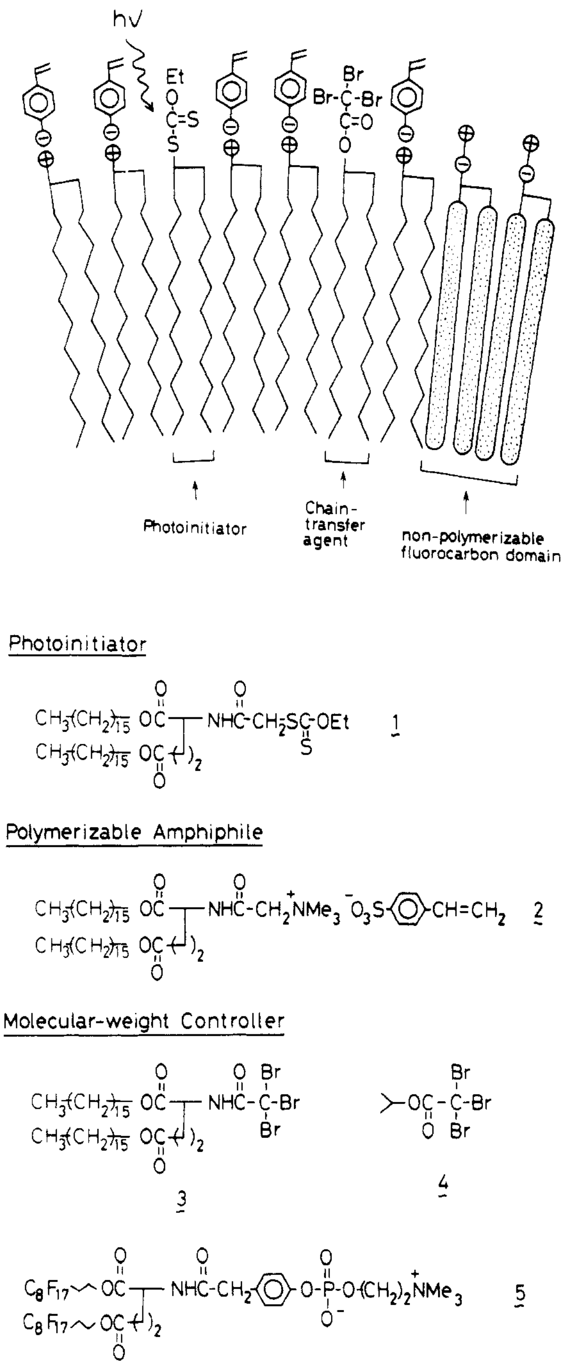

Figure 1. Schematic illustration of the novel photopolymerization bilayer system and structures of the photoinitiator, polymerizable amphiphile, and molecular weight controllers.

1.60; Br, 27.89. Bromine analysis was performed by the micro-Carius method.

Isopropyl Tribromoacetate (4). A chloroform solution (20 mL) of 7.7 mmol of tribromoacetyl chloride (2.4 g) was added dropwise to a chloroform solution (50 mL) of 0.9 g (15 mmol) of isopropyl alcohol and 1 g (7.9 mmol) triethylamine in an ice bath, and the mixture was stirred for 24 h at room temperature. After removal of chloroform, THF was added to the residue and then triethylamine hydrochloride was separated. THF and excess isopropyl alcohol were removed in vacuo, and the residue was dissolved in chloroform and washed with water and dried. The solvent was removed, and the yellow oil was obtained: yield 1.4 g (54%); IR (neat) 1750 cm^{-1} (C═O, ester). Anal. Calcd for $C_5H_7O_2Br_3$: C, 17.73; H, 2.08; Br, 70.75. Found: C, 17.58; H, 2.17; Br, 70.55.

Bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl) *N*-[*p*-[[[Hydroxy[2-(trimethylammonio)ethoxy]phosphoryl]oxy]phenyl]acetyl]-L-glutamate (5). The tosylate salt of bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl) L-glutamate was prepared according to the literature.[11] A THF solution (20 mL) of 7.7 mmol of the tosylate salt (9.4 g) and 5 g (35 mmol) of triethylamine was added dropwise to a THF solution (50 mL) of 1.2 g (7.8 mmol) of (*p*-hydroxyphenyl)acetate and 1.4 g (7.8 mmol) of DEPC (diethyl phosphorocyanidate) as a condensator with ice-cooling. The mixture was stirred for 48 h at room temperature, and triethylamine hydrochloride was separated. After removal of the solvent, the residue was dissolved in a small amount of THF and then washed with hot water. The precipitate was collected by filtration, giving white powder: yield 3.6 g (40%); TLC ($CHCl_3$–MeOH 4:1) R_f 0.67 single spot; IR (KBr) 1670 (C═O, amide), 1750 cm^{-1} (C═O, ester); NMR ($(CD_3)_2CO$) δ 2.65 (t, 4, CF_2CH_2), 6.7, 7.1 (d, 4, phenyl).

2-Chloro-2-oxo-1,3,2-dioxaphosphorane was prepared according to the literature.[12] A THF solution (20 mL) of 6.7 mmol of 2-chloro-2-oxo-1,3,2-dioxaphosphorane (1 g) was added dropwise to a THF solution (50 mL) of 3.0 g (2.6 mmol) of bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl) *N*-[(*p*-hydroxyphenyl)acetyl]-L-glutamate and 1.4 g (10.6 mmol) of triethylamine in an ice bath, and the mixture was stirred for 98 h at room temperature. Triethylamine hydrochloride was separated and then the solvent was removed. The residue was recrystallized from methanol, giving an orange powder: yield 1.3 g (38%); TLC ($CHCl_3$–MeOH 4:1) R_f 0.68 single spot. The product thus obtained (1.3 g, 1 mmol) was dissolved in 50 mL of THF and allowed to react with large excess triethylamine in an ampule for 3 days at 50 °C. The solvent was removed, and the residue was recrystallized from methanol, giving a pale yellow powder: yield 0.4 g (30%); TLC ($CHCl_3$-MeOH 4:1) R_f 0.86 single spot; NMR ($(CD_3)_2CO$) δ 2.65 (t, 4, CF_2CH_2), 3.50 (s, 9, N^+CH_3), 6.8, 7.1 (d, 4, phenyl). Anal. Calcd for $C_{38}H_{33}O_9N_2PF_{34}$: C, 34.10; H, 2.49; N, 2.09. Found: C, 34.26; H, 2.21; N, 1.95.

Measurements. Samples were prepared in distilled, deionized water. Chloroform solutions of amphiphiles were air-dried, and the thin films were then dispersed by sonication with a Branson Sonifier 250 (microtip, sonic power 40 W, 2 min) in water at room temperature. Sample solutions were incubated for at least 30 min before use at $T < T_c$ (20 °C). Electron microscopy (Hitachi H 600 electron microscope) was carried out for negative stained samples with uranyl acetate. The phase-transition behavior of bilayer solutions was obtained from differential scanning calorimetry (DSC). The samples (20–60 mM) were sealed in an Ag sample pan and heated from 5 to 90 °C at a rate of 1 °C/min with an SSC-573 (Seiko Electric Co. Ltd., Tokyo). ^1H NMR (400-MHz) spectra were recorded on a JOEL, JNM-GX400 FTNMR spectrometer from D_2O solutions (3,3,3-trimethyl-1-propanesulfonic acid sodium salt as an internal standard).

Photopolymerization. Photopolymerizations of aqueous bilayers were carried out upon UV irradiation with a low-pressure mercury lamp at 30 °C in a Pyrex tube under N_2 atmosphere after degassing. A Pyrex tube can cut off UV light with $\lambda < 260$ nm. The polymerization processes were monitored by UV spectroscopy (instrument, Shimadzu UV-2100).

The molecular weights of polymerized bilayer membranes were estimated by gel permeation chromatography (GPC) (instrument, Shimadzu LC-5A; eluent, THF; standard, polystyrene ($\leq 10^7$)) as follows. After evaporation of water from the polymerized samples, trace amounts of water were removed as an azeotropic mixture with benzene, and then the residues were dissolved in THF.

Results and Discussion

Aggregation State of Pure and Mixed Polymerizable Amphiphile in Water. Clear solutions were obtainable when the pure polymerizable amphiphile **2** (60 mM) and the binary mixture (**1**–**2**, [**1**]:[**2**] = 1:33) were dispersed in water by sonication. It has been found that amphiphiles derived from dialkyl glutamate give well-developed bilayer structures.[10] Thus, it is expected that **2** and **1**–**2** would also give a bilayer structure even though styrenesulfonate was used in place of chloride as the counterion. Figure 2a shows the electron micrograph of **1**–**2** mixed aqueous dispersion negatively stained by uranyl acetate. The well-developed bilayer structure (multi-

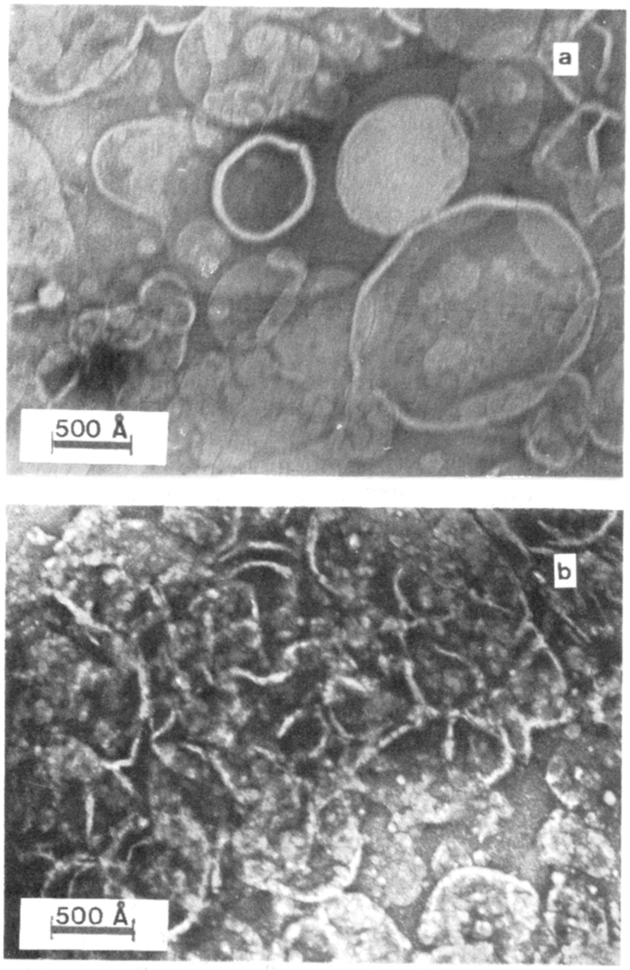

Figure 2. Electron micrograph of 1/2 ([1]/[2] = 1/33) mixed aqueous dispersion negatively stained by uranyl acetate (a) before and (b) after photopolymerization.

Table I
DSC Data of Polymerizable and Polymerized Bilayers

bilayer system	T_c, °C	ΔH, kJ mol^{-1}
2 (chloride form)	41	31.2
2	35	23.2
1/**2** ([**1**]/[**2**] = 1/100)	35	24.7
polymerized **1**/**2**	43	35.3
2/**3** ([**3**]/([**2**] = [**3**]) = 0.08)	35	26.8
2/**4** ([**4**]/([**2**] = [**4**]) = 0.08)	35	27.0
2/**5** ([**5**]/([**5**] = [**2**]) = 0.40)	35	29.2

walled vesicles) is clearly observed.

The phase-transition behavior of those aqueous dispersions was studied by DSC (Table I). The aqueous dispersion of **2** gives an endothermic peak at 35 °C due to the gel-to-liquid crystal phase transition (T_c), which is lower than that (41 °C) of the chloride form. A similar depression of the phase-transition temperature was found by Ringsdorf et al.[13] They studied the effect of counterions (sodium and choline methacrylate) on molecular ordering in the dihexadecyl phosphate bilayer membrane on the basis of spectroscopic and thermal properties and concluded that the penetration of counterions into the bilayer would lead to bilayer disordering and depression of T_c on going from sodium to choline methacrylate. The same explanation applies to the phase-transition behavior of the bilayer formed by **2**. When small amounts of **1** (([**1**]:[**2**] = 1:(33–100) (molar ratio)) were added to **2**, clear solutions were also obtainable by sonication as described above, and the peak temperature (35 °C) in the DSC of a typical mixture ([**1**]:[**2**] = 1:100) was quite close to the T_c of pure **2** (Table I). The transition enthalpy (ΔH) of the mixture (24.7 kJ mol^{-1}) was very close to that of pure **2** (23.2 kJ mol^{-1}). These results imply that incorporation of **1** into a bilayer of **2** does not affect the membrane physical state and that the photoinitiator is dispersed homogeneously in the polymerizable membrane matrix as illustrated in Figure 1.

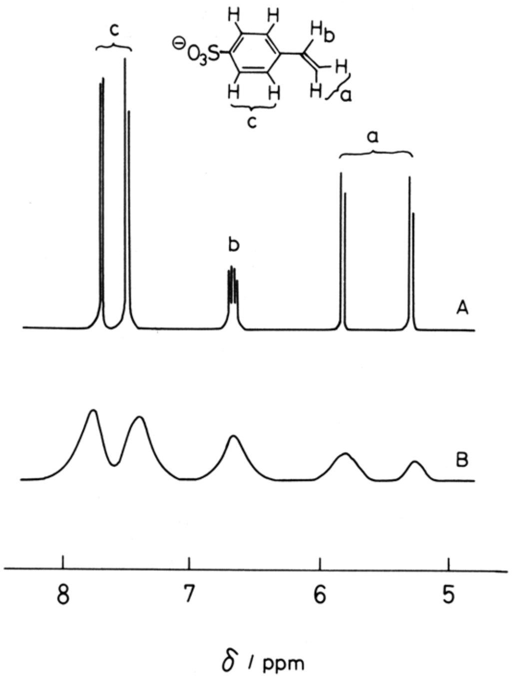

Figure 3. ^{1}H NMR spectra of sodium styrenesulfonate (A) and aqueous dispersion of **2** (B) in D_2O.

To obtain information regarding molecular ordering of the membrane-bound styrenesulfonate, ^{1}H NMR spectra of styrenesulfonate in both water (D_2O) and aqueous bilayer were measured at 20 °C, which is below T_c (Figure 3). It is known that an extreme line broadening for each proton signal of amphiphile is observed when the amphiphile forms an ordered bilayer structure.[14,15] In Figure 3, it is clearly observed that proton signals assigned to phenyl and vinyl groups for the membrane-bound styrenesulfonate give remarkable line broadening, whereas the free styrenesulfonate in D_2O gives only sharp signals. This strongly suggests that styrenesulfonate as the counterion would be bound and ordered at the oriented bilayer surface. Proton signals for the other parts (hydrophobic tail and hydrophilic head group) of **2**, of course, showed considerable line broadening (not shown in Figure 3).

Photopolymerizations of Aqueous Bilayers. Photopolymerizations were carried out upon UV irradiation with a low-pressure mercury lamp at 30 °C in a Pyrex glass tube under N_2 atmosphere after degassing. Aqueous dispersions become slightly turbid with irradiation, but no precipitate was observed during polymerization. Figure 4 shows the absorption spectral change upon UV irradiation for pure **2** and **1**/**2** mixed bilayer assembly. The absorption maximum at 256 nm corresponds to the styrenesulfonate moiety of **2**. In the pure **2** (dashed line in Figure 4), the absorbance showed only a slight decrease even after 4 h of irradiation. In the presence of **1** (solid line in Figure 4), on the other hand, the monomer peak decreased rapidly with irradiation and a new peak, probably due to the formation of polymer, appeared at 225 nm. After 4 h of irradiation the monomer peak totally disappeared. It is important to show the initiator con-

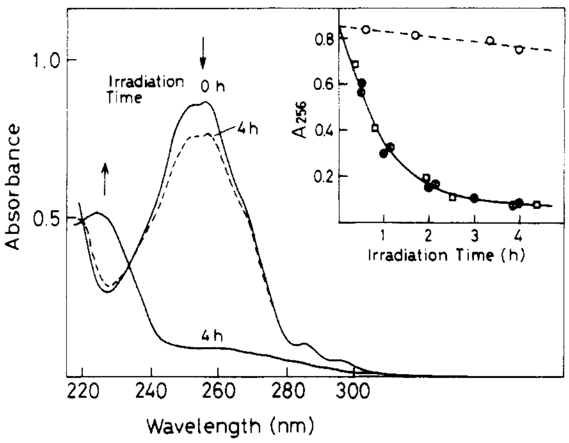

Figure 4. Absorption spectral change of pure **2** bilayer (dashed line) and **1**/**2** mixed bilayer (solid line) upon UV irradiation. [**2**] = 1.5 × 10^{-4} M; 30 °C. The inset shows the time course of the absorbance at 256 nm: (○) [**1**]/[**2**] = 0; (□) [**1**]/[**2**] = 1/1000; (●) [**1**]/[**2**] = 1/100; (◐) [**1**]/[**2**] = 1/33.

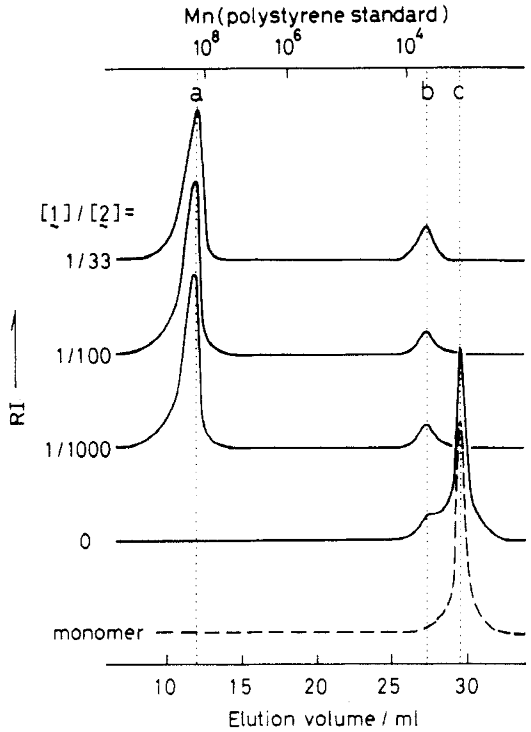

Figure 5. GPC elution patterns of photopolymerized products (solid lines) for **1**/**2** binary bilayer systems from THF solutions. Dashed line shows monomer **2** prior to photopolymerization.

centration dependence of photopolymerization processes. The inset of Figure 4 shows the absorbance change at 256 nm of mixed bilayers with different compositions ([**1**]:[**2**] = 0, 1:1000, and 1:33) as a function of irradiation time. In the absence of **1** ([**1**]/[**2**] = 0), photopolymerization was suppressed almost completely under these experimental conditions. After small amounts of **1** were added into the bilayer matrix, the absorbance decreased smoothly. The extent of decrease was independent of the concentration of **1**. These results suggest that an efficient photopolymerization proceeds preferentially with initiation of radicals generated from **1** in a two-dimensional field of the bilayer surface.

Figure 5 shows GPC patterns from the THF solutions. In the absence of **1**, GPC gives two peaks in the low molecular weight region, which are assigned to the unreacted monomer (c) and oligomer (b), respectively. No peak is observed in the high molecular weight region. In contrast, when small amounts of **1** ([**1**]:[**2**] = 1:1000, 1:100, and 1:33) are incorporated in the bilayer matrix, a large peak in the extremely high molecular weight region (a) is observed, together with a small peak in the oligomer region. The fraction of each peak (wt %, F_a, F_b, and F_c) and the average molecular weight (M_n, M_w) estimated by polystyrene standard are summarized in Table II. The F_b (ca. 10%) in the presence of **1** is probably ascribable to oligomers resulting from photodimerization or other reactions of **2** because its peak maximum in the GPC chromatogram is consistent with the oligomeric products formed in the absence of **1**. Fendler et al.[16] reported that bilayer vesicles prepared from dioctadecylammonium bromide containing a covalently bound styryl group at the hydrophilic portion were polymerized with a 266-nm laser pulse, which corresponds to the absorption maximum of the styrene moiety, to give only oligomeric products (degree of polymerization, DP_n = 3–8). In our system, thus, the oligomers appearing in the c region in Figure 5 would be produced mainly upon direct excitation of the styrenesulfonate moiety of **2**.

F_a (fraction of polymer) values are about 90%, and the molecular weights based on polystyrene, surprisingly, reach $M_n = 3 \times 10^7$ ($M_w/M_n = 1.5$): $DP_n = 7 \times 10^4$ in the presence of **1**, independent of initiator concentrations. When the aqueous bilayer solution of **2** (chloride form) and the aqueous poly(sodium styrenesulfonate) separately prepared were mixed, the instantaneous precipitation due to formation of polyion complex of the polyanion and the cation bilayer component was observed. In contrast, in our bilayer system no precipitate was observed during polymerization in spite of the formation of high molecular weight polymers. In order to define the aggregation state of the polymerized aqueous dispersions, electron microscopy observation and DSC measurements were conducted. In Figure 1b, layer structures are obviously observable even after polymerization, though the aggregation morphology is considerably changed from a well-developed bilayer vesicle to a stringlike aggregate upon photoirradiation. The DSC thermogram for the polymerized solution ([**1**]:[**2**] = 1:100, 30 °C, 4 h of irradiation) gives a single endothermic peak due to a crystal–liquid crystal phase transition with slight broadening at 43 °C, which is higher than that of the unpolymerized counterpart (see Table I). ΔH is also greater for a polymerized sample than for the corresponding unpolymerized sample. Such enhancement of phase-transition temperatures has also been reported for other polymerizable bilayer systems.[13] These morphological and thermal properties suggest that the mixed aqueous solutions of **1** and **2** are in a *bilayer state* even after polymerization.

Molecular Weight Control at Bilayer Surface by Chain-Transfer Reaction. Tribromomethane derivatives have been widely used as chain-transfer agents for conventional radical polymerization. We prepared a new tribromomethane derivative (**3**) containing two long alkyl chains and having a similar molecular structure in the hydrophobic moiety to both the polymerizable amphiphile **2** and the photoinitiator **1**. This chain-transfer agent is expected to locate near the polymerizable groups of **2** when incorporated into bilayer matrices due to the similarity in the molecular structure. The chain-transfer agent **4** was also employed as a model compound for **3** in comparison. When the required amounts of **3** ([**3**]–([**2**] + [**3**]) = 0.03–0.10) were added into **2**, clear solutions were obtained by sonication, and the peak temperature (35 °C) in the DSC of a typical mixture ([**3**]–([**2**] + [**3**]) =

Table II
Effect of Photoinitiator 1 Incorporated into Bilayer Matrix 2 on the Molecular Weight of Polymer Produced upon UV Irradiation at 30 °C for 4 h

	a		b		c			
[1]/[2]	F_a[a]	M_n[b]	F_b[a]	M_n[b]	F_c[a]	M_n[b]	M_w/M_n (a)	DP_n (a)
monomer	0		0		100	410		
0	0		14.0	1.20×10^3	86.0	415		
1/1000	88.5	2.88×10^7	11.5	1.15×10^3	0		1.4	7.02×10^4
1/100	90.6	2.98×10^7	9.4	1.10×10^3	0		1.5	7.27×10^4
1/33	85.3	3.12×10^7	14.7	1.18×10^3	0		1.4	7.61×10^4

[a] Weight fraction (%). [b] Calculated from standard polystyrene calibration.

Table III
Comparison of Kinetic Data with Conventional Chain-Transfer Polymerization

			DP_n	
[3]/([2] + [3])	f_0	$M_n \times 10^{-3}$	obsd	calcd[a]
3	32.3	13000	32000	3.2
6	15.7	170	42	1.6
8	11.5	4	10	1.1
10	9.0	2	4	0.9

[a] Calculated value from eq 1; $1/DP_{n,0} = 0$; $C_f = 3.0$; $x_m = 0.96$; $f_0 = [2]/[3]$.

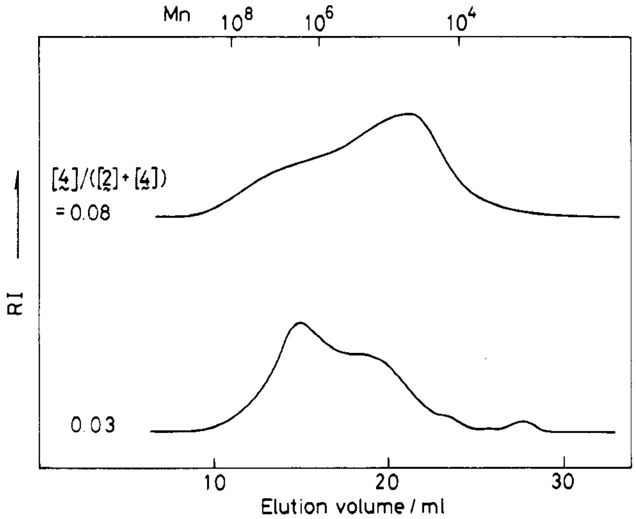

Figure 6. GPC elution patterns of photopolymerized products for 1/2/4 ternary bilayer systems. [1]/[2] = 1/100; [4]/([2] + [4]) = 0.08 (upper curve) and 0.03 (lower curve).

0.10) was consistent with the T_c of pure 2 (see Table I). This means that the addition of 3 to the 2 bilayer did not affect the membrane physical state. A similar situation was observed for the mixture of 4 and 2.

Photopolymerizations for both 3-2 ([3]-([2] + [3]) = 0.03, 0.06, 0.08, and 0.10) and 4-2 ([4]-([2] + [4]) = 0.03 and 0.08) mixed bilayers proceeded smoothly upon UV irradiation in the presence of the photoinitiator 1 ([1]-[2] = 0.01). After 4 h of irradiation, the monomer peak (λ_{max} = 256 nm) in the UV spectra disappeared completely in every case. Figure 6 shows GPC patterns of the 4-2 system from THF solutions prepared in a manner similar to that described above. A remarkable broadening of the GPC chromatogram was observed and the molecular weight of polymers obtained was distributed over a wide range independent of the concentration of 4. In contrast, when one uses 3 as a chain-transfer agent the GPC gave a single peak, as shown in Figure 7, for each concentration of 3 together with a small peak in the low molecular weight region, which might be ascribable to oligomeric products formed by direct excitation of the styrenesulfonate moiety of 2 as discussed previously. Furthermore, the peak maximum for major peaks shifted systematically to the lower molecular weight region with increasing concentration of 3. The molecular weight, M_n, and degree of polymerization, DP_n, calculated on the basis of major peaks in the GPC curves in Figure 7, are listed in Table III. Table III also includes the values of DP_n for the solution polymerization of styrene in the presence of tribromoacetic acid, which is employed as a model system for these two-dimensional bilayer systems. The values of DP_n were simulated by using the conventional chain-transfer equation (integral form; eq 1)[17,18] where

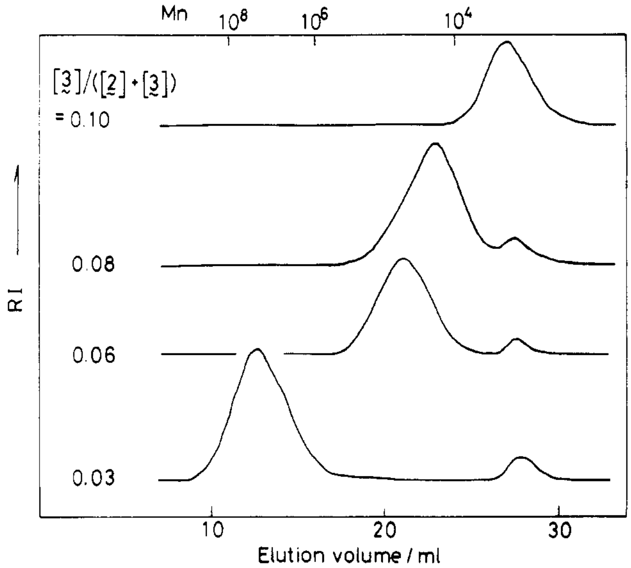

Figure 7. GPC elution patterns of photopolymerized products for 1/2/3 ternary bilayer systems. [1]/[2] = 1/100; [3]/([2] + [3]) = 0.03, 0.06, 0.08, and 0.10.

$$\frac{1}{DP_n} - \frac{1}{DP_{n,0}} = -C_f \frac{\ln(1 - x_m)}{f_0 x_m} \qquad (1)$$

$DP_{n,0}$, C_f, and f_0 are the degree of polymerization of polymers obtained in the absence of chain-transfer agent, the chain-transfer constant (3.0 for styrene and tribromoacetic acid system),[19] and the molar ratio of monomer and chain-transfer agent in feed, respectively. x_m denotes the conversion of monomer (molar fraction), which is assumed to be 0.96 for computation of the DP_n values. The calculated DP_n's change only in a narrow range (3.2–0.9) with the concentration of chain-transfer agent. On the other hand, the observed DP_n's for bilayer systems change dramatically in a wide range (32 000–4), which are always larger than the corresponding calculated values and, of course, do not obey conventional radical chain-transfer kinetics (eq 1).

These results strongly suggest that the tribromomethyl group of 3 may be fixed at the bilayer surface and near the polymerizable groups, thus providing for effective molecular weight control. In contrast, 4 was distributed and located at random in the bilayer matrices.

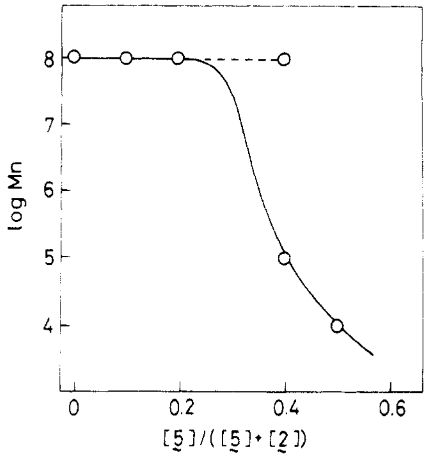

Figure 8. Plots of log M_n vs the molar fraction of 5 in bilayer mixture (5/2). [1]/[2] = 1/100.

Molecular Weight Control at Bilayer Surface Using Phase Separation. Clear solutions were obtained when ternary mixtures of the zwitterionic fluorocarbon amphiphile **5**, **1**, and **2** ([1] + [2] + [5] = 60 mM, [1] = 0.6 mM, [5]-([2] + [5]) = 0.1–0.5) were dispersed in water by sonication. The reason for employing **5** with a zwitterionic head group is to prevent the electrostatic interactions with the anionic styrenesulfonate. The DSC for a typical mixture of [5]-([2] + [5]) = 0.4 gave an endothermic peak, at 35 °C, consistent with the phase-transition temperature of the pure **2** bilayer (see Table I), although the shape of the peak became slightly broader than that of the pure **2** bilayer. This result implies that two bilayers (**2** and **5**) are almost completely immiscible and form a domain over each other. We prepared four types of aqueous bilayer solutions with different compositions ([5]-([2] + [5]) = 0.1, 0.2, 0.4, and 0.5). The monomer peak at 256 nm in the UV spectra for these solutions decreased upon UV irradiation, and then after 4 h of irradiation the monomer peak disappeared completely. This spectral data may suggest that photopolymerizations proceed effectively in the phase-separated polymerizable hydrocarbon domains containing small amounts of photoinitiator (**1**), consistent with the result of DSC.

In Figure 8, log M_n, calculated on the basis of the GPC curves for the resulting polymers (not shown here), is plotted against the fraction of fluorocarbon amphiphile ([5]-([2] + [5])) in the mixed bilayer membranes. When the fraction of fluorocarbon is below 0.2, the molecular weight of the polymers reaches $\sim 10^7$. This implies that the domain size of fluorocarbon components in the bilayer matrices may be too small to affect the molecular weight of polymer formed. When the fraction increases to 0.4, two kinds of polymer are generated: i.e., high molecular weight ($\sim 10^7$) and low molecular weight ($\sim 10^5$) polymers. We do not have any direct evidence for explaining this phenomenon, but one interesting possible explanation, which will require further exploration, is that the formation of high and low molecular weight polymers is due to an intervesicular polymerization and an intravesicular polymerization, respectively. The fact that the aggregation morphology of amphiphile **2** changes from a well-developed vesicle to a stringlike aggregate upon photopolymerization supports such an explanation (see Figure 2). Above 0.5 (the fraction of fluorocarbon), a considerably low molecular weight polymer ($M_n = 10^4$) with 100% conversion is formed.

Conclusion

The present study demonstrates that (i) extremely high molecular weight polymers can be produced under mild conditions in a bilayer state by taking advantage of the well-defined bilayer surface and fixation of the photoinitiator at the most effective position for initiation, (ii) a similar situation is observed for the chain-transfer reaction at the bilayer surface: the chain-transfer agent **3** containing double alkyl chain can control acutely the molecular weight of polymers using the present bilayer system whereas **4** without a long alkyl chain cannot act as a useful molecular weight controller, and (iii) the phase separation of binary bilayers composed of a nonpolymerizable fluorocarbon component and a polymerizable hydrocarbon component is also useful in controlling the molecular weight. These findings strongly suggest that completely regulatable polymerizations at a two-dimensional bilayer surface should require not only the orientation of monomer molecule at the membrane surface but also the optimum molecular design of the photoinitiator for high molecular weight polymer formation and of the chain-transfer agent for precise molecular weight control.

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References and Notes

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