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Extremely High Molecular Weight Polymer Formation Using a Photoinitiation System of Xanthate Fixed at an Oriented Bilayer Surface

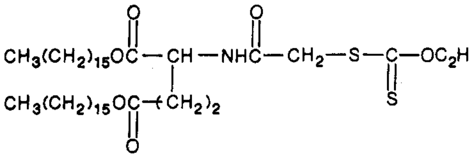
In this paper we present a new polymerizable bilayer system in which a photoinitiator containing two long alkyl chains is fixed at the adjacent polymerizable groups in a bilayer matrix. In such a bilayer system, photopolymerization proceeds smoothly in a bilayer state and the formation of super high polymer is observed under a mild condition.

Polymerizable bilayer membrane is useful for the modification of bilayer physical properties, e.g., increasing mechanical stability and decreasing membrane permeability. Extensive investigations[1] on polymerization behaviors of such polymerizable bilayer membranes have been carried out. In most of such cases, UV irradiation and/or appropriate initiators were employed for initiation of polymerization. However, the position of those initiators resulting from solubilization into bilayer matrix, adsorption on bilayer membrane surface, and so on were not readily fixed near the polymerizable groups and was not always suitable for initiation.

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 charged surface of cationic bilayer membranes[2] and that macroscopic orientations of electron spins were achieved by using anionic Cu^{II} chelates embedded into cationic membrane surfaces.[3] It seems 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 $\bar{M}_w$ (85 000 in 0.002 M HCl) and tacticity of the poly(methacrylic acid) obtained.

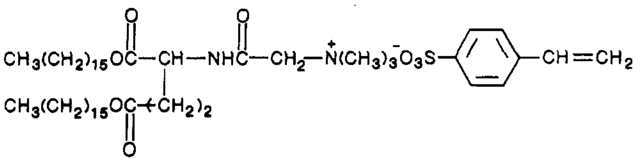
We have reported that bis(isopropylxanthogen) disulfide and xanthate-terminated polymers are useful for a design of well-defined block copolymer because they serve as effective photonitiator and primary radical terminator.[5]

In the present study, we show a new polymerizable bilayer system in which a photoinitiator (1)[6] consisting of two long alkyl chains and a xanthate group which are coupled via a glutamate connector is fixed near polymerizable groups in a bilayer matrix (2).[6]



$$\begin{array}{l}\mathrm{CH_3(CH_2)_{15}O\overset{O}{\overset{\|}{C}}-CH-NH\overset{O}{\overset{\|}{C}}-CH_2-S-\underset{S}{\underset{\|}{C}}-OC_2H_5}\\ \mathrm{CH_3(CH_2)_{15}O\underset{O}{\underset{\|}{C}}\!\!-\!\!(CH_2)_2}\end{array}$$

1



2

Clear solution was obtainable when the polymerizable amphiphile (60 mM) was dispersed in water by sonication (Branson Sonifier 250). Kunitake et al. showed that amphiphiles derived from dialkyl glutamate give well-developed bilayer structures.[8] It is expected that 2 would also give a bilayer structure even though styrene sulfonate were used in place of chloride as the counteranion. The aggregation morphology of this new polymerizable amphiphile will be described elsewhere. Differential scanning calorimetry (DSC) gives an endothermic peak at 35.2 °C due to the gel-to-liquid crystal-phase transition (T_c), which

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

	a		b		c		$\bar{M}_w/\bar{M}_n$	$\overline{DP}_n$
[1]/[2]	$F_a{}^a$	$\bar{M}_n{}^b$	$F_b{}^a$	$\bar{M}_n{}^b$	$F_c{}^a$	$\bar{M}_n{}^b$	(a)	(a)
1/33	85.3	3.12×10^7	14.7	1.18×10^3			1.4	7.61×10^4
1/100	90.6	2.98×10^7	9.4	1.10×10^3			1.5	7.27×10^4
0			14.0	1.23×10^3	86.0	415		
monomer					100	412		

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

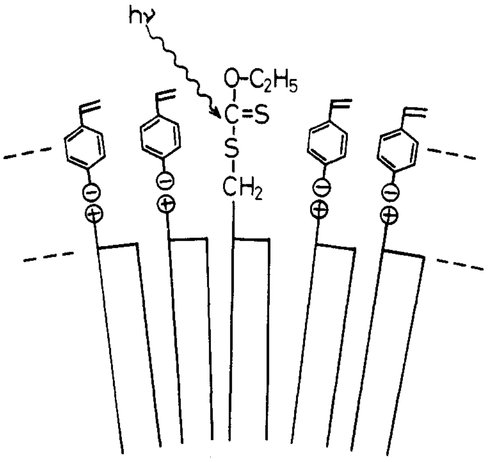

Figure 1. Schematic illustration of the polymerizable bilayer system in which a photoinitiator is fixed near the polymerizable groups.

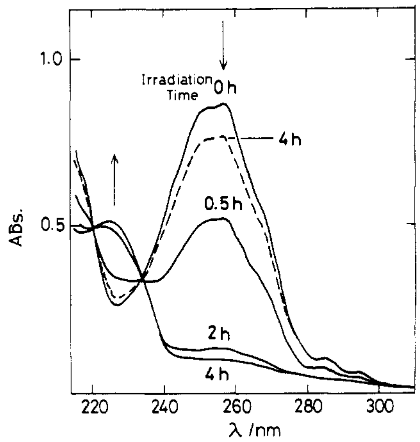

Figure 2. Absorption spectral change of 2 bilayer (dashed line) and 1/2 mixed bilayer (solid line) upon UV irradiation at 30 °C: [2] = 0.15 mM; [1]/[2] = 1/33.

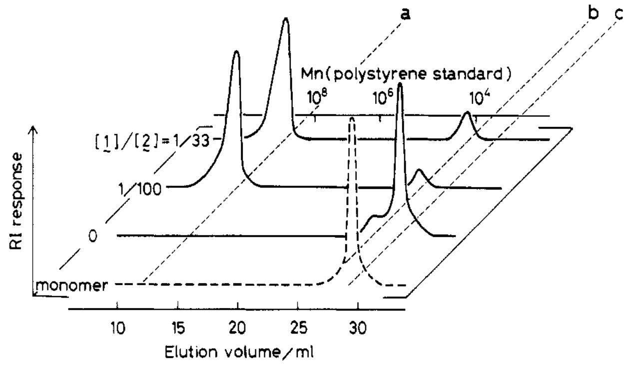

Figure 3. GPC elution patterns for photopolymerized products (solid lines) from THF solutions. Dashed line shows monomer 2.

is lower than that (43 °C) of the chloride form. The same observation was reported by Ringsdorf et al.[9] When small amounts of 1 ([1]/[2] = 1/(20 – 100) (molar ratio)) were added into 2, clear solutions were also obtainable by sonication, and the peak top temperatures (35.0 and 35.3 °C for 1/100 and 1/33, respectively) in DSC of those aqueous solutions were very close to the T_c of 2. This implies that the incorporation of 1 into 2 bilayer matrix did not affect the membrane physical state and that the photoinitiator was dispersed homogeneously in the polymerizable membrane matrix as illustrated schematically in Figure 1.

Photopolymerizations were carried out upon UV irradiation with a low-pressure mercury lamp at 30 °C in Pyrex tube under N_2 atmosphere after degassing. Aqueous dispersions became slightly turbid with irradiation but any precipitant was not observed during polymerization (within at least 4 h). Figure 2 shows the absorption spectral change upon UV irradiation of 2 and mixed bilayer assembly ([1]/[2] = 1/33) as a function of time. The absorption maximum at 256 nm corresponds to the styrene sulfonate moiety of 2. In the absence of 1 (dashed line in Figure 2), the absorbance showed only slight decrease even after 4 h of irradiation. On the other hand, in the case of the mixture (solid line in Figure 2), the monomer peak decreased rapidly upon irradiation and a new peak probably due to the formation of polymer appeared at 225 nm. After 4 h of irradiation the monomer peak disappeared almost completely. These results were consistent with the GPC data as described later. The DSC thermogram for a 4-h-irradiated sample ([1]/[2] = 1/33) gave a new broad peak at 40 °C, which is higher than one before irradiation, suggesting the formation of polymerized bilayer membrane.

In order to confirm the formation of polymer, we measured GPC for the 4-h-irradiated samples as follows. After evaporation of water, trace amounts of water were removed as an azeotropic mixture with benzene and then the residues were dissolved in THF. Figure 3 shows GPC patterns from those 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, and no peak is observed in the high molecular weight region under these experimental conditions. In contrast, when small amounts of 1 ([1]/[2] = 1/100 and 1/33) are incorporated in the bilayer matrix, a main peak in the extremely high molecular weight region (a) is obviously observable, 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 ($\bar{M}_n$, $\bar{M}_w$) estimated by poly(styrene) standard are summarized in Table I. The F_b (ca. 10%) for [1]/[2] = 1/100 and 1/33 is probably ascribable to oligomers (dimer or trimer) resulting from photodimerization or other reactions of 2 because its peak top in the GPC chromatogram is consistent with the peak top for the oligomeric product formed in the absence of 1. F_a (fraction of polymer formed) values are about 90% and the molecular weights, surprisingly, reach $\bar{M}_n = 3 \times 10^7$ ($\bar{M}_w/\bar{M}_n = 1.5$): $\overline{DP}_n = 7 \times 10^4$ for both cases under mild conditions (30 °C, 4-h irradiation).

When the aqueous bilayer solution of **2** (chloride form) and the aqueous poly(sodium styrene sulfonate)[10] separately prepared were mixed, the instantaneous precipitation due to formation of polyion complex of the polyanion and the cationic bilayer component was observed. Since no precipitate was observed during polymerization for the mixed bilayer systems (**1** and **2**) in spite of the formation of high molecular weight polymers, the resulting polymers would have a suitable conformation for maintaining an aqueous bilayer state.

In summary, 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. Attempts to reveal the conformational structure of such polymers and the morphology of polymerized bilayer membranes are now in progress.

Registry No. 1, 114908-01-9; 2 (homopolymer), 114908-03-1.

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(6) The photoinitiator of **1** was prepared as follows.[7] Sodium *O*-ethyl xanthate (0.37 g, 2.6 mmol) and 1.1 g (1.7 mmol) of *N*-(chloroacetyl)-L-glutamic acid dihexadecyl ester[8] 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 UV spectrum (λ_{max} = 278 nm: π–π^* transition of SC(=S)O; $\epsilon_{max} = 1.13 \times 10^4$ L mol^{-1} cm^{-1}). 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. The polymerizable amphiphile of **2** was prepared by anion-exchanging reaction of the corresponding double-chain ammonium chloride[8] with sodium styrene sulfonate. The chloroform solution (10 mL) of double-chain ammonium chloride (1 g, 1.4 mmol) and the methanol solution (30 mL) of sodium styrene sulfonate (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.

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(10) Poly(sodium styrene sulfonate) was prepared by radical polymerization of sodium styrene sulfonate with sodium *O*-ethyl xanthate in aqueous solution upon UV irradiation and purified by reprecipitation from aqueous solution into methanol to remove unreacted monomer.

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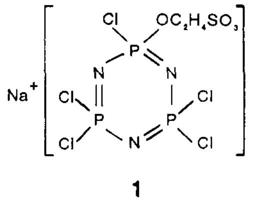
A New Class of Cation Conductors: Polyphosphazene Sulfonates

In recent years there has been considerable interest in the mechanism of charge transport in solvent-free polymer electrolytes and in the potential application of these electrolytes in electrochemical devices.[1-3] Most attention has been paid to polymer electrolytes formed from linear-chain polyethers, poly(ethylene oxide) or poly(propylene oxide) with alkali metal salts. Recently, polymer electrolytes based on phosphazene and siloxane comb polymers have been reported, which exhibit better conductivity at room temperature than for the linear-chain polyether electrolytes.[4-6] The high conductivity of these materials arises from their highly flexible polymer segments. A drawback for most polymer electrolytes is that the transference number for the cation lies in the range 0.3–0.5. In order to increase the fraction of the charge carried by the cation, we have experimented with polymers in which the anion is covalently attached to the polymer (polyelectrolytes). Conventional polyelectrolytes are rigid materials in the absence of solvent; however, we have shown that certain plasticizers greatly improve the conductivity of polymers such as sodium poly(styrenesulfonate), and we suggested that polyelectrolytes that incorporate flexible groups by covalent bonds would be a logical next step.[7,8] This more elegant approach was realized by LeNest and co-workers who synthesized a polyelectrolyte based on cross-linked ether networks containing phosphate charged groups.[9] Conference reports of other flexible polyelectrolytes also have appeared.[10] Also, the electrical properties of a polyether–polyelectrolyte blend have been investigated.[11] In this communication, we report the synthesis and conductivity of a new class of polyelectrolytes having phosphazene backbone and with sulfonate and oligoether side chains.

As a model system for the analogous reaction with linear poly(dichlorophosphazene), $[NPCl_2]_n$, we investigated the equimolar reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with the disodium salt of 2-hydroxyethanesulfonic acid, $NaOC_2H_4SO_3Na$, in THF in the presence of 15-crown-5. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows two sets of an A_2B pattern [set i, 22.2 ppm (d), 0.5 ppm (t), ^2J(PP) = 45 Hz; set ii, 22.8 ppm (d), 3.9 ppm (t), ^2J(PP) = 66 Hz] in the intensity ratio 3:2. The chemical shift and intensity of the signals suggest that the products should be assigned as compounds **1** and **2**: The ^{31}P NMR assignments for **2** were confirmed by the $^{31}P\{^1H\}$ NMR spectrum of the product obtained from the equimolar reaction of $N_3P_3Cl_6$ with sodium ethanesulfonate, $NaC_2H_5SO_3$; A_2B pattern, 21.8 ppm (d), 3.4 ppm (t); ^2J(PP) = 64 Hz consistent with a monosubstituted derivative, $N_3P_3Cl_5(OSO_2C_2H_5)$. Thus, the alkoxysulfonate acts as a difunctional reagent toward $N_3P_3Cl_6$. ^{31}P NMR spectra gave no indication of the presence of spirocyclic or ansa products. Also, intensities in the ^{31}P NMR gave no evidence for intermolecular condensation products. Surprisingly, the sulfonate is sufficiently nucleophilic to displace chlorine atoms from the $\equiv PCl_2$ center.



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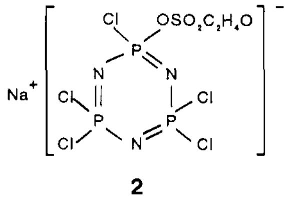

2

In THF the dinegative compound, $NaOC_2H_4SO_3Na$, reacts with an excess of linear $[NPCl_2]_n$ in the presence

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