Macromolecules 1987, 20, 2029-2030

## References and Notes

(1) Kurata, M. *Thermodynamics of Polymer Solutions*; translated from the Japanese by H. Fujita, Harwood Academic: Chur, 1982.

(2) Koningsveld, R.; Chermin, H. A. G.; Gordon, M. *Proc. R. Soc. London, A* **1970**, *319*, 331. In this paper, the interaction function $\Psi$ is defined in the Gibbs free energy by

$$\Psi = \phi_0\phi_1 g_{01}(\phi_1,\phi_2) + \phi_0\phi_2 g_{02}(\phi_1,\phi_2) + \phi_1\phi_2 g_{12}(\phi_1,\phi_2)$$

This expression gives the $\chi$ interaction function as eq 20 with $\chi_{0i}$ and $\chi_{12}$ defined by

$$\chi_{0i} = g_{0i} - \phi_0(\partial g_{0i}/\partial\phi),\ i = 1 \text{ or } 2$$

$$\chi_{12} = g_{12} + \phi(\partial g_{12}/\partial\phi)$$

(3) Kennedy, J. W. *A Specialist Periodical Report, Macromolecular Chemistry*, Bartholomew: Dorking, UK, 1980; Vol. 1, Chapter 14.

(4) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411.

(5) One of the reviewers notified us that eq 21 can be rewritten as

$$\chi = \xi_1^2\chi_{01}^b + \xi_2^2\chi_{02}^b + \xi_1\xi_2(\chi_{01}^b + \chi_{02}^b - \chi_{12}^*)$$

when $\chi_{0i}$ and $\chi_{12}^*$ are composition-independent. Thus, a casual comparison of this equation with eq 19 suggests that

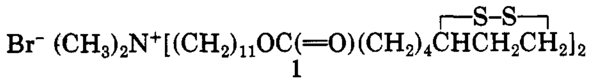
$$\chi_{ii}^b = \chi_{0i}^b,\ \chi_{12}^t = (\chi_{01}^b + \chi_{02}^b - \chi_{12}^*)/2$$

though physical meaning of the relations is an open question.

# Communications to the Editor

## pH-Triggered Vesicle Polymerization†

In this paper we show that surfactant vesicles derived from bis[11-(lipoyloxy)undecyl]dimethylammonium bromide (1) undergo rapid ring-opening polymerization,

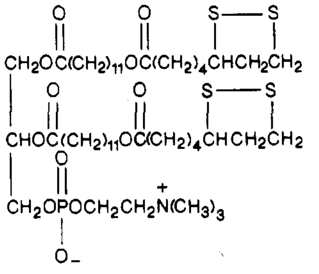


$$\mathrm{Br^-\ (CH_3)_2N^+[(CH_2)_{11}OC({=}O)(CH_2)_4\overbrace{\mathrm{CHCH_2CH_2}}^{S-S}]_2}$$

1

when the pH of the dispersion is raised from 3.0 to 4.0. The pH-sensitivity of this polymerization affords a unique synthetic route to polymerized vesicles which should allow for the successful incorporation of highly sensitive comembrane components.

Phospholipid and surfactant vesicles serve as important models for biological membranes, as carriers of drugs, and as potential devices for solar energy conversion. While considerable progress has been made in the synthesis of polymeric analogues over the past 7 years,[1] new classes of polymerizable surfactants are needed, which will allow for milder polymerization conditions to be employed.[2] Recently, we have shown that vesicles composed of 1,2-bis-[12-(lipoyloxy)dodecanoyl]-*sn*-glycero-3-phosphocholine (2) can be polymerized via a ring-opening process at pH 8.5, using dithiothreitol (DTT) as an initiator.[3] In the course of examining the scope of lipoic acid based surfactants for polymerized vesicle synthesis, we discovered that vesicles made from 1 are rapidly and quantitatively polymerized when the pH is modestly raised from 3.0 to 4.0. This report details our preliminary findings.



2

Addition of 1.00 g (2.15 mmol) of bis(11-hydroxyundecyl)dimethylammonium bromide[4] to 50 mL of a 0.22 M dichloromethane solution of lipoic acid anhydride,[3] containing 0.57 g (4.7 mmol) of 4-(dimethylamino)pyridine, followed by (a) stirring for 24 h at room temperature under nitrogen, (b) filtering and concentrating the product mixture under reduced pressure, and (c) chromatographic purification (silica, $CHCl_3/CH_3OH$), afforded 1.66 g (92%) of 1 as a yellow oil.[5]

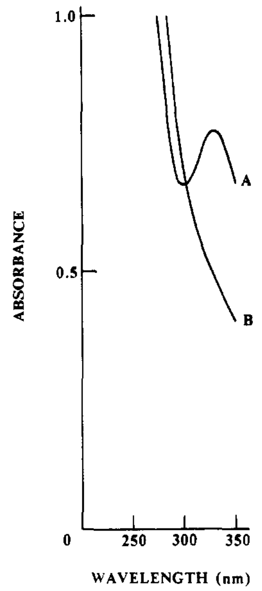


**Figure 1.** UV spectra of nonpolymerized (A) and polymerized (B) vesicles derived from 1.

Dispersal of 30 mg of 1 in 3 mL of $10^{-3}$ M HCl, by vortex mixing at room temperature, followed by 10 repetitive passes through a 0.1-μm Nuclepore membrane,[6] produced a vesicle dispersion ranging in diameter between 300 and 1300 Å (electron microscopy and dynamic light scattering).[3] Thin-layer chromatography (TLC), immediately after extrusion, indicated complete retention of the monomeric state. Upon standing for 7 h at 23 °C, approximately 50% of surfactant was converted into polymer (UV analysis[3]). In contrast, when the pH of the dispersion was raised from to 3.0 to 4.0 (or to pH 7.0), via addition of aqueous NaOH, *complete polymerization was observed within 1 min*, as indicated by the disappearance of the 1,2-dithiolane moiety ($\lambda_{max}$ 330 nm, Figure 1) and by the retention of all of the surfactant at the origin of the TLC plate. Adjustment of the pH to 3.5 resulted in a 50% conversion to polymer after ca. 5 min.

Electron microscopic examination revealed no significant alteration in particle size after polymerization (Figure 2); light scattering also confirmed the retention of the size

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† Supported by a grant from Kurita Water Industries, Ltd., Tokyo Japan.

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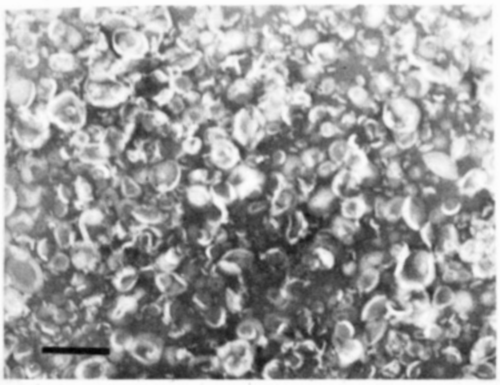

**Figure 2.** Transmission electron micrograph (2% ammonium molybdate stain) of polymerized vesicles of 1; bar represents 2000 Å.

distribution. Gel filtration of polymerized vesicles of **1**, using a Sephadex G-50 column, resulted in a quantitative recovery in the void volume (nitrogen analysis).[7] Similar to polymerized vesicles made from **2**,[3] and in contrast to linear disulfide-based phospholipid polymers,[8] freeze-dried polymerized vesicles of **1** were insoluble in chloroform and chloroform/methanol (1/1, v/v). We attribute this insolubility to extensive cross-linking within the bilayer.

The precise mechanism of initiation has not yet been established. Based on the pH dependence noted above, we hypothesize that polymerization proceeds via initial hydroxide displacement on the disulfide moiety, followed by ring opening via thiolate ion–disulfide interchange.[9] The greater sensitivity of this polymerization toward pH than that observed for vesicles of **2** is believed to be a consequence of the greater penetrability of the hydroxide ion across the ammonium surfactant bilayer.[10]

From a synthetic standpoint, surfactant **1** extends the applicability of polymerized vesicle chemistry to include substrates that are unstable under basic conditions, have limited stability under acidic pH, and decompose under standard thermal-induced or photoinduced polymerization conditions.[1] Efforts aimed at exploiting **1** for the synthesis of functional polymerized vesicles are now in progress.

**Acknowledgment.** We are grateful to James Stefely for valuable technical assistance.

**Registry No.** 1, 109088-38-2; 1 (homopolymer), 109088-39-3.

## References and Notes

(1) Reviews: Bader, H.; Dorn, K.; Hashimoto, K.; Hupfer, B.; Petropoulos, J. H.; Ringsdorf, H.; Sunimoto, H. In *Polymeric Membranes*; Gordon, M., Ed.; Springer Verlag: Berlin, 1985; p 1. Fendler, J. H.; Tundo, P. *Acc. Chem. Res.* **1984**, *17*, 3.

(2) Regen, S. L. *Polymerized Vesicles*, presented at the NATO Workshop on "Frontiers in Polymerization Catalysis and Polymer Synthesis", Feb 1–6, 1987, Bendor Island, France. Regen, S. L. In *Liposomes: From Biophysics to Therapeutics*; Ostro, M. J., Ed.; Marcel Dekker: New York, 1987; p 73.

(3) Sadownik, A.; Stefely, J.; Regen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 7789.

(4) Foltynowicz, Z.; Yamaguchi, K.; Czajka, B.; Regen, S. L. *Macromolecules* **1985**, *18*, 1394.

(5) $R_f$ 0.4 [silica, $CHCl_3/CH_3OH$ (9/1, v/v)]; IR ($CHCl_3$) $\nu_{C=O}$ 1720; $^1H$ NMR ($CDCl_3$) $\delta$ 1.30 (br s, 36 H, $(CH_2)_9$), 1.5–1.8 (m, 12 H, $(CH_2)_3$), 1.8–2.1 and 2.4–2.7 (m, 4 H, $SCHCH_2CH_2S$), 2.25–2.35 (t, 4 H, $CH_2CO_2$), 3.05–3.25 (t, 4 H, $CH_2S$), 3.4 (s, 6 H, $CH_3N^+$), 3.45–3.65 (m, 6 H, $CH_2N^+$ and CHS), 4.0–4.15 (t, 4 H, $CH_2OCO$); UV (EtOH) 330 nm. Anal. Calcd for $C_{40}H_{76}NO_4S_4Br$: C, 56.98; H, 9.08; N, 1.66; S, 15.21. Found: C, 56.68; H, 8.98; N, 1.64; S, 14.64. Surfactant **1** is best stored as a 0.01 M dichloromethane solution in the dark at 5 °C.

(6) Mayer, L. D.; Hope, M. J.; Cullis, P. R. *Biochim. Biophys. Acta* **1986**, *858*, 161.

(7) Fukuda, H.; Diem, T.; Stefely, J.; Kezdy, F. J.; Regen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 2321.

(8) Samuel, N. K. P.; Singh, M.; Yamaguchi, K.; Regen, S. L. *J. Am. Chem. Soc.* **1985**, *107*, 42.

(9) Parker, A. J.; Kharasch, N. *Chem. Rev.* **1959**, *59*, 583.

(10) Previous studies of vesicles derived from synthetic ammonium surfactants have shown that hydroxide ions move rapidly across such bilayers: Moss, R. A.; Schreck, R. P. *Tetrahedron Lett.* **1985**, *26*, 6305.

(11) On leave from Kurita Water Industries, Ltd.

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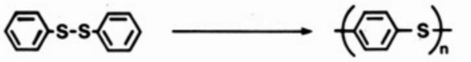
## Poly(*p*-phenylene sulfide)-Yielding Polymerization of Diphenyl Disulfide by S–S Bond Cleavage with a Lewis Acid

Poly(*p*-phenylene sulfide) (PPS) has been commercially produced from *p*-dichlorobenzene and sodium sulfide.[1,2] Condensation of alkali-metal salts of *p*-halothiophenols has been also reported for the PPS preparation.[3–5] However, these polymerizations proceed at high pressure and temperature. PPS–like polymers have been prepared by oxidizing thiophenol with aluminum chloride and thionyl chloride[6,7] or concentrated sulfuric acid,[8] but these preparations result in highly branched and cross-linked polymers with primary chains of low molecular weight. We report in this paper that diphenyl disulfide reacts with a Lewis acid to cleave its S–S bond and is easily polymerized to a linear PPS at room temperature and atmospheric pressure (eq 1).



(1)

Diphenyl disulfide (0.1 mol) is allowed to react with $SbCl_5$ (0.1 mol) in nitrobenzene (100 mL) for 1 day at room temperature. The polymer was isolated in 88% yield as white powder having an empirical formula $C_6H_4S$[9] and was soluble in hot *N*-methylpyrrolidone. The structure including the 1,4-phenylene unit was confirmed by IR (Figure 1). The absorption attributed to 1,4-phenylene at 820 $cm^{-1}$ indicates a linear or 1,4-conjugated phenylene sulfide structure. No typical absorption at ca. 850 $cm^{-1}$, which implies isolated ring hydrogen, excludes a branching and cross-linking structure. This spectrum agrees with that of commercially available PPS. The X-ray diffraction pattern was similar to that of commercial PPS Ryton. The DSC thermogram of the obtained PPS[10] suggested the molecular weight of more than $10^3$ by using the relationship between the molecular weight and the melting point of PPS.[11]

The polymerization also proceeded with other Lewis acids such as $AlCl_3$, $TiCl_4$, and $MoCl_5$ although the polymer yield and molecular weight were influenced by the Lewis acid and solvent species. Similarly bis(2,6-diethylphenyl) disulfide with a Lewis acid yielded poly(2,6-diethyl-1,4-phenylene sulfide) of which structure was confirmed by IR, $^1H$ NMR, $^{13}C$ NMR, and elemental analysis.[12] The polymer was soluble in chloroform and its molecular weight was 4300–6000 (vapor pressure osmometry).

When thiophenol was used as a starting material, the polymerization in the presence of a Lewis acid and an oxidizing agent gave also PPS at room temperature. Thiophenol is considered to be first oxidized to diphenyl disulfide and then polymerized.

This polymerization did not proceed in basic solvents such as acetonitrile. Equimolar amounts of Lewis acid and

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