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NEW SYNTHETIC VESICLES FORMED BY POLYMERIC QUATERNARY AMMONIUM BROMIDE WITH DOUBLE ALKYL CHAINS

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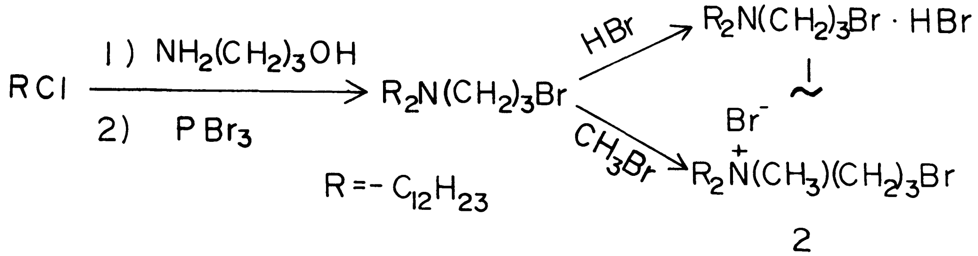
Sonic dispersal of 3-bromopropyldidodecylamine hydrogen bromide resulted in the formation of stable polymeric vesicles by quaternization reaction in aqueous solution. It could be expected that the amphiphilic aggregation and ultrasonic irradiation can facilitate the polymerization through the quaternization.

Formation of biomembrane-like bilayer vesicles from a totally synthetic didodecyldimethylammonium bromide was first reported by Kunitake et al.$^{1)}$ However, synthetic dialkyl amphiphilic vesicles are unstable and undergo fusion on standing. Recognizing the need for enhanced stability, Regen reported the first synthesis of polymerized surfactant vesicles.$^{2)}$

The polymeric vesicles reported up to date have been functionalized with vinyl, methacrylate, isocyano, styrene, and diacetylene groups.$^{3)}$ These vesicles with polymerizable double bonds can be polymerized either by exposing to UV irradiation or by radical polymerization with an initiator soluble in water or organic solvent.

Vesicles formed by polyionenes were first reported by Kunitake et al.$^{4)}$ In the present letter, a different class of synthetic polyionene vesicles were formed by polycondensation reaction. First to be synthesized was 3-bromopropyldidodecylamine hydrogen bromide 1, then which was polymerized by quaternization. 3-Bromopropylmethyldidodecylammonium bromide 2 was prepared as a model compound to compare with 1.

1 and 2 were synthesized by using the sequence of reaction shown in Scheme 1. These compounds were confirmed by ^{1}H NMR, IR spectroscopy and elemental analysis: 1, mp 78 °C. Found: C,58.31; H,10.17; N, 2.44%. Calcd for $C_{27}H_{57}N_1Br_2$: C, 58.80; H, 9.69; N, 2.54%. 2, mp 134 °C. Found: C, 58.89; H, 10.33; N, 2.42%. Calcd for $C_{28}H_{59}N_1Br_2$: C, 59.46; H, 9.80; N, 2.48%.



SCHEME I.

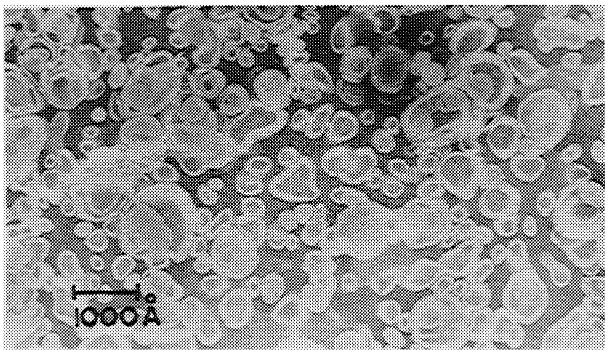


Fig. 1. Electron micrograph derived from **1**. magnification, x 96000.

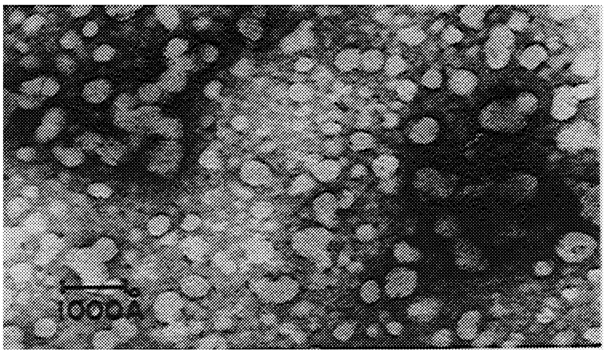


Fig. 2. Electron micrograph derived from **2**. magnification, x 96000.

The amphiphile **1** was dispersed in water by sonication at 80 °C for 30 min(Branson bath type B-52, 240 w). The pH of thus obtained dispersion was then adjusted to 10 with 1.0 M NaOH. And the resulting dispersion was again sonicated for polymerization through quaternization at 80 °C for 30 min. The pH of the resulting polymeric dispersion was 8.2-8.6 indicating the quaternization of amines. Lyophilized polymeric product was quite different in solubility compared with **1**, being insoluble in most of solvents. Monomeric **1** was soluble in many common organic solvents.

Electron micrographs recorded on a JEOL 100-X, using 2% uranyl acetate as a staining agent, confirmed the presence of closed vesicles having diameters ranging between 300 and 1400 Å. The vesicles are mostly multi-lamellae of bilayers of ca. 50 Å width. **1** gave well developed multi-walled vesicles compared with low molecular weight analogue **2**. Further evidence for closed vesicles comes from the entrapment of $[^{14}C]$ sucrose. Sephadex G-50-80 was used for gel permeation chromatography. The amount of $[^{14}C]$ sucrose entrapped into **1** vesicles were about 2%.

In order to evaluate the stability of vesicles, we have examined their response to the addition of ethanol and the observed absorbance was measured. The turbidity (absorbance at 400 nm) of polymeric **1** vesicles solution remained almost constant up to 25% ethanol(v/v). In contrast, similar experiments conducted with vesicles derived from **2** showed precipitation at 5% ethanol. On standing at room temperature, the vesicles of **2** remain stable for ca. 72 h. However, the polymeric vesicles of **1** were stable for at least several months.

Detailed characterization and morphological studies of these and other related vesicles are now in progress and the full accounts will be published elsewhere.

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