SYNTHESIS AND CHARACTERIZATION OF BIOMIMETIC POLYMER VESICLES AND POLYMER MONOLAYER MEMBRANES FOR BIOELECTRONIC APPLICATIONS

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It is a challenge to replace currently used lipid membranes with synthesized polymer for the development of future nanoscale hybrid devices. Self-assembled, amphiphilic ABA triblock copolymer has been suggested as a potential new biomimetic membrane[1]. Therefore, the polymer membrane has attracted attention in recent years for the fabrication of biosensors and nano-containers. In spite of this increasing demand, a systematic study including electrical properties together with protein reconstitution has not yet been performed on polymer vesicles and films. Logically, new materials should be developed and their basic properties fully characterized for applications in an engineered membrane device. To our knowledge, there has been no report on the measurements of basic electrical properties such as capacitance-voltage (C-V) and current-voltage (I-V) characteristics using a self-assembled triblock copolymer. In this study, we report the synthesis of amphiphilic triblock copolymer vesicles and Langmuir Blogett (LB) monolayers. The electrical characteristics and the possible functions of these synthesized polymer structures are presented as well.

Recently, we have synthesized the biomimetic triblock copolymer PEtOz-PDMS-PEtOz, [poly(2-ethyl-2-oxazoline)-poly(dimethylsiloxane)-poly(2-ethyl-2-oxazoline)], by ring-opening-cationic polymerization in the presence of NaI (Fig. 1). The formation of vesicles with this polymer in buffer solution was confirmed by transmission electron microscopy (TEM) (Fig. 2). The thickness of the wall was measured to be about 5nm. The diameter of the vesicles ranged from 150nm to 250nm. The electrochemical properties of PEtOz-PDMS-PEtOz films were investigated by electrochemical impedance spectroscopy (EIS). For free film analysis, a modified two-compartment Teflon cell with platinum electrodes placed on opposite sides of a thin partition was used. The partition supported polymer monolayer spread over a small aperture. Impedance spectroscopy was obtained in 1M KCl buffer solution (Fig. 3). The EIS data were fitted to an equivalent electric circuit model of R(RC) and compared to simulated data.

The Langmuir-Blodgett technique was used to deposit monolayer and multilayer PEtOz-PDMS-PEtOz films on a substrate. A typical pressure area isotherm of PEtOz-PDMS-PEtOz is shown in Figure 4. It has been found that solid phase condensation occurs at a surface pressure of 46.7mN/m around a mean molecular area of 2.1nm^2. This LB film technique has been used for the fabrication of metal-insulator-metal (MIM) devices (Fig. 5). Top electrodes were fabricated through the contact shadow mask. The number of deposited layers was controlled at 1, 5, 10, and 20. From the measured C-V and I-V data, electrical properties of the films were obtained. In order to derive an accurate value for the dielectric constant, TEM was used to measure the film thickness. Reconstitution of membrane proteins into polymer vesicles has been tested with various proteins such as Omp F, Aquaporin, Cytochrome Oxidase (COX), F_0F_1-ATP synthase, and Bacteriorhodopsin (BR). The incorporation of proteins was confirmed by binding modified 10nm gold particles to the His tag region or exposed cysteine residues of incorporated proteins and imaged by TEM. For measurement of BR proton pumping activity, ΔpH was measured using pH sensitive fluorescent pyranine after exciting proteopolymersomes in a fluorometer at a specific wavelength and duration.

References:

[1] Alexandra Graff, Marc Sauer, Patrick Van Gelder, and Wolfgang Meier, PNAS, 99(8) (2002) 5064.

Figures:

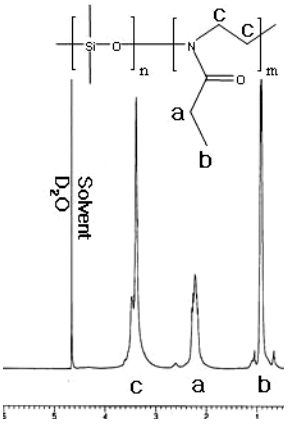


Fig.1 ^{1}H NMR spectrum of PEtOz-PDMS-PEtOz

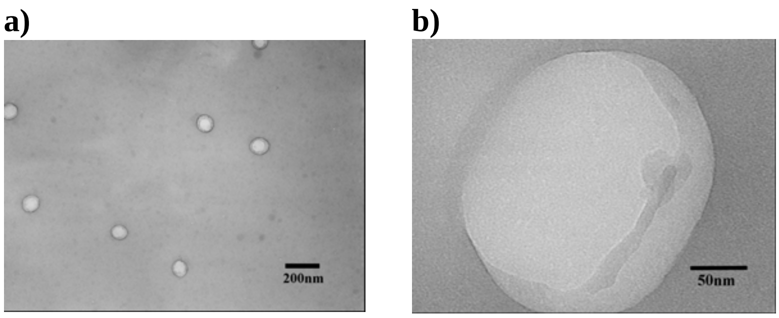


Fig.2 TEM micrographs of polymer vesicles a) low magnification and b) high magnification

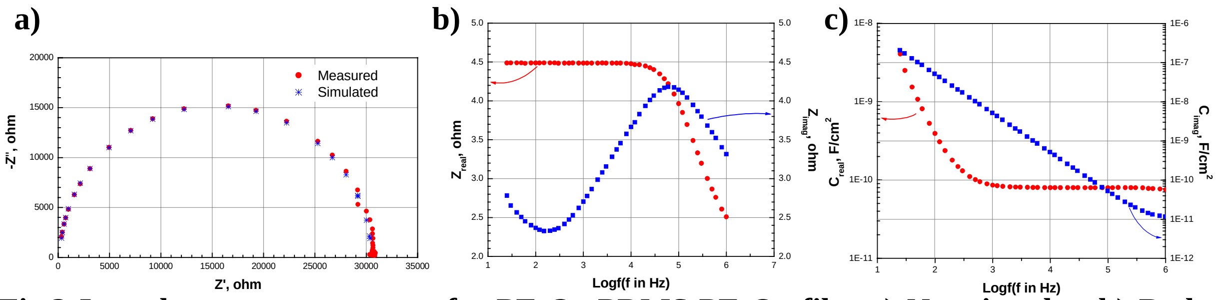
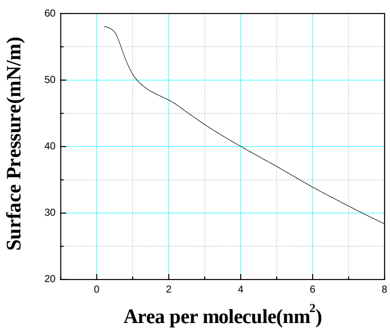


Fig.3 Impedance spectroscopy of a PEtOz-PDMS-PEtOz film a) Nyquist plot, b) Bode plot, and c) capacitance as a function of frequency



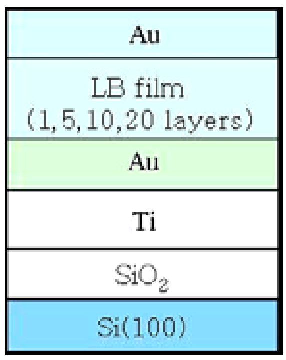


Fig.4 Surface pressure-area isotherm of PEtOz-PDMS-PEtOz on pure water

Fig.5 Schematic of C-V and I-V measurement system