

Elucidating hydration state of poly (propylene oxide) in the glyco polymer vesicle membranes by SANS measurement.

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We have recently developed intrinsically permeable polymer vesicles based on maltopentaose-b-poly(propylene oxide) block-co-polymers (Figure 1a).[1] In aqueous solution, the polymer self-assembles into unilamellar vesicles. In contrast to other vesicles, the vesicles show molecular-weight-dependent molecular permeability. Low-molecular-weight compounds ($< 5 \times 10^3$ g/mol) diffuse into the vesicles. We also proved that the permeability is due to the partition of solute molecules into the polymer membrane. Accordingly, we hypothesized that this permeation should be ascribed to the weakly hydrophilic nature of the PPO block. Specifically, the degree of hydration of the PPO layer in the membrane should contribute to facilitating the partition and, therefore, enhance molecular permeation.

To determine the degree of hydration of the PPO layer in the membrane, we previously used SAXS measurements in a preliminary study to obtain the corresponding electron-density profile using a theoretical fitting equation from a bilayer membrane model. The model fit of the SAXS data was consistent with an electron density of the hydrophobic layer (330 e/nm^3) that is almost identical to that of solvent (H_2O ; 334 e/nm^3). Given that the electron density of PPO is comparable to that of H_2O , the degree of hydration in the PPO layer cannot be quantified using SAXS measurements.

We therefore proposed to subject carbohydrate-b-PPO vesicles to SANS measurements in order to quantify the degree of hydration of the PPO layer in the polymer-bilayer membranes of such polymer vesicles. Figure 1b shows SANS profile from maltopentaose-b-poly(propylene oxide) block polymer vesicles in D_2O . The scattering curve showed a slope of -2 at

low q region, suggesting the presence of thin plate structure. To gain further structural information, the scattering curve was fitted with the bilayer membrane model, which provide information on a bilayer cross-sectional structure. The model fits the SAXS data almost overall q -range and is consistent with a hydrophobic layer thickness of 9.3 nm, hydrophilic layer thickness of 2.0 nm, SLD of a hydrophobic layer (PPO layer) of $1.0 \times 10^{10} \text{ cm}^{-2}$ and SLD of a hydrophilic layer (maltopentaose layer) of $6.4 \times 10^{10} \text{ cm}^{-2}$ (Figure 1c). The size of hydrophobic and hydrophilic segment was identical to the data obtained from the previous SAXS analysis. It should be noted that SLD of the PPO layer was much higher than theoretical SLD value of PPO ($3.43 \times 10^9 \text{ cm}^{-2}$). This difference can be attributed to the hydration of PPO with D_2O . To obtain volume fraction of D_2O in PPO layers, we assumed that all the entire polymers are included in the bilayer region of the vesicles. We also imposed the hydrophobic layer is composed of all the PPO group and of a small amount of D_2O . Based on these assumptions, we are able to calculate the volume fraction of D_2O in the PPO layer by using following equation.

$$y_{\text{core}} = \frac{\rho_{\text{ppo}} + (1 - y_{\text{core}}) \rho_{\text{D}_2\text{O}}}{\rho_{\text{core}}}$$
, where ρ_{core} , ρ_{ppo} , $\rho_{\text{D}_2\text{O}}$, y_{core} is experimental SLD value of PPO layer, theoretical SLD value of PPO, theoretical SLD value of D_2O , and volume fraction of PPO in the hydrophobic layer, respectively. The volume fraction of D_2O in PPO layer was calculated to be ca. 11% by above equation. More interestingly, in the presence of kosmotropic salt such as Na_2SO_4 , the SLD of hydrophobic layer was decreased to $5.5 \times 10^{10} \text{ cm}^{-2}$, indicating that the degree of hydration in the hydrophobic layer reduced. Since the degree of hydra-

tion would affect on the molecular permeability as mentioned above, the rate of molecular permeation would be controlled by changing external environment.

In summary, we conducted SANS measurements of maltopentaose-block-poly(propylene oxide) in D₂O. We successfully obtained a clear evidence for the hydration of the hydrophobic PPO layer in the polymer bilayer membrane and were able to quantify the volume fraction of D₂O in PPO layer. To the best of our knowledge, this is the first observation showing the hydration of hydrophobic layer in polymer bilayer membranes.

[1] T. Nishimura, Y. Sasaki, K. Akiyoshi, *Adv. Mater.*, 2017, 29, 1702406

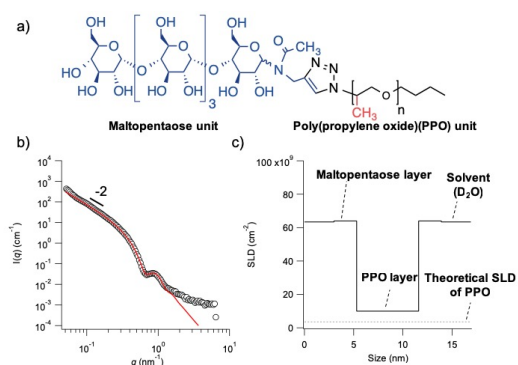


Figure 1 a) Chemical structure of maltopentaose-b-PPO, b) SANS profile of maltopentaose-b-PPO vesicles and a theoretical curve from the bilayer membrane model, c) SLD profile of maltopentaose-b-PPO vesicles

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