Structural analysis of polyion complex vesicles

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Polymer vesicles glab considerable attentions, but their dynamic aspects have been scarcely studied due to the difficulty to observe the dynamics. We plan to conduct neutron spin echo (NSE) measurements to investigate the dynamics and elastic modulus of bilayers of polymer vesicles in the future. In the present experiments, we performed small-angle neutron scattering (SANS) measurements to clarify the static structure and establish the experimental conditions for the future NSE measurements.

Anionic–neutral and cationic–neutral block copolymers (Fig. 1; not deuterated) in D_2O containing NaCl were mixed in a 1:1 molar ratio of anion and cation. These polymers are known to self-assemble in water through electrostatic interactions [1–3]. SANS experiments were conducted for the samples at SANS-U. We used drum-shaped cells with a path length of 2 mm. The sample-to-detector distance were 12 m and 2 m.

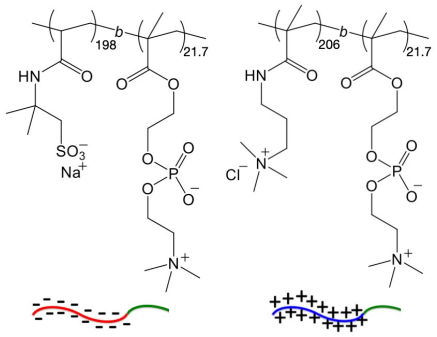

Fig. 1. Anionic–neutral and cationic–neutral block copolymers used in this study.

Figure 2 shows representative SANS profiles, where polymer concentration was 0.5 wt%, and the added NaCl concentrations were 0.1, 0.3, 0.5 M. All profiles followed $I(q) \sim q^{-2}$, indicating vesicle formation. The profiles also exhibited oscillations around q = 0.2–0.4 nm^{-1}. The minimum positions (q*; indicated by allows) are related to the thickness of the bilayer (d) as $\sin(q^*d) = 0$. Notably, the q values can be accessed in the NSE measurements. Further, the data revealed that the bilayer thickness decreased from 24 nm to 21 nm when the NaCl concentration was increased from 0.1 to 0.5 M. It is presumed that electrostatic attraction between anionic and cationic blocks leads to stretching of these blocks in the low NaCl concentration, and the increase in the NaCl concentration decreases the electrostatic attraction, thus relieving the chain stretching. In summary, we confirmed that vesicles were formed from the block copolymers used in this study and clarified that the bilayer thickness can be tuned by adding NaCl.

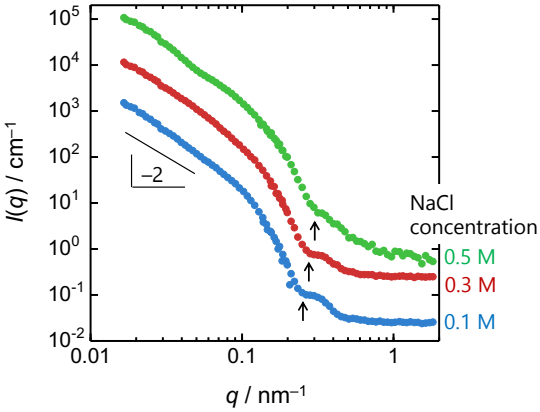

Fig. 2. SANS profiles for the polymer vesicles, where polymer concentration was 0.5 wt%, and added NaCl concentrations were 0.1, 0.3, 0.5 M. $I(q)$ denotes the scattering intensity, q stands for the momentum transfer.

[1] R. Takahashi *et al.*, Macromolecules **48**, 7222 (2015).
[2] R. Takahashi *et al.*, Macromolecules **49**, 3091 (2016).
[3] R. Takahashi *et al.*, Macromolecules **55**, 684 (2022).