Structure of Ionic Bottlebrush Polymers in Water

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Bottlebrush polymers, which consist of a single main chain and densely packed multiple side chains, have recently attracted much attention. These polymers have a semi-rigid cylinder-like structure because the main chain takes on a fully extended conformation as a result of the excluded volume effect between the side chains. The length and diameter can be controlled independently by precise control of the main and side chains through living polymerization. Unlike micelles, bottlebrush polymers are all covalently linked, so there is no aggregation-disaggregation equilibrium depending on temperature and concentration leading to the stable cylindrical structure. Although the structure of bottlebrush polymers has been directly observed by atomic force microscopy in a dried state under air, it is difficult to say that it reflects the original structure in solution.

Recently, we have succeeded in synthesizing the world's longest bottlebrush polymer using two orthogonal living polymerizations, ROMP and ATRP [1]. Based on the synthetic method, we prepared bottlebrush polymers bearing trimethyl ammonium, possessing 300 nm-long and several ten nm-diameter (unknown diameter in solution state). The bottlebrush polymers are well-dissolved in water. Previously, through SAXS measurements, we found that the ionic bottlebrush polymers form hexagonal structure at concentrations of 2-10 wt% in water. The lattice constant of the hexagonal structure increases with decreasing concentration. The ionic bottlebrush polymer used here has precisely controlled lengths of its main and side chains, but the diameter of the bottlebrush polymer varies greatly depending on the morphology of the polymeric side chains in water (e.g., expanded coil state, ideal coil state, globule state). Therefore, it is necessary to obtain the diameter based on the SANS measurement rather than the side chain length estimated by size exclusion chromatography in order to get the structural information of the brush in water and understand the relationship between the diameter and the lattice constant of the hexagonal structure.

Samples for SANS measurements were prepared by dissolving the bottlebrush polymer in D_2O at 0.1 wt%. Figure 1 shows the SANS profiles of the ionic bottlebrush polymers with different diameter. Black and Red lines indicate the ionic bottlebrush polymers with smaller and larger diameters, respectively. Each diameter was estimated to be 18.5 nm and 22.4 nm from the curves in Guinier region (0.004 – 0.02 $Å^{-1}$). The diameter is much smaller than the lattice constant of the hexagonal structure (~80 nm) at 2 wt% aqueous solution. This result show that there is no interpenetration between side chains of neighboring bottlebrush polymers in the hexagonal structure.

[1] Y. Yamauchi *et al*, *Angew. Chem. Int. Ed.* **2021**, *60*,1528-1534.

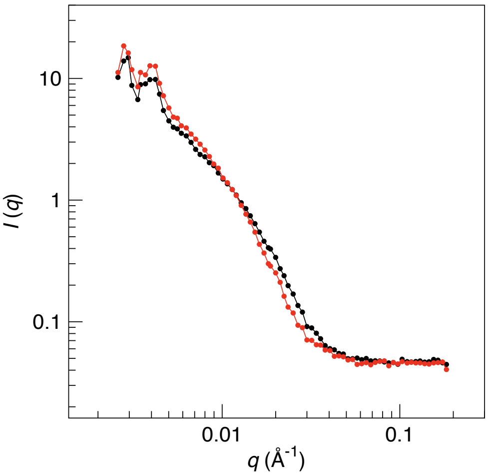

Fig. 1. Neutron scattering intensity for the ionic bottlebrush polymers in D_2O (0.1 wt%). Red and black represent the ionic bottlebrush polymers with larger and smaller.