Structural analysis of physisorbed complexes of gold nanoparticles and cyclic PEG

T. Yamamoto[A], T. Watanabe[A]

[A]*Hokkaido Univ.*

In the field of polymer chemistry, the synthesis of polymers with diverse topologies and their properties originating from their "shape" have long been a subject of interest. Specifically, it is known that cyclic polymers exhibit unique properties in various physical characteristics, such as a decrease in hydrodynamic volume and an increase in diffusion rate. However, reports on their function at surfaces and interfaces have been very limited until now. In contrast, we have succeeded in stabilizing gold and silver nanoparticles by the physical adsorption of cyclic PEG (c-PEG), as opposed to the previously limited method of chemical adsorption via a gold-thiol reaction [1]. This adsorption on surfaces and interfaces, based on the cyclic topology, is a very interesting phenomenon, but its detailed mechanism is not yet understood. To elucidate the mechanism of this adsorption, we are currently conducting comprehensive research, including simulating the adsorption of c-PEG on nanoparticle surfaces using computational chemistry, and quantifying the adsorbed molecules using techniques like NMR and thermal analysis. Among these approaches, the structural analysis of the gold nanoparticle-c-PEG complex (AuNPs/c-PEG) using SANS is a complementary method and holds an important position for obtaining detailed structural information on the adsorbed state.

Recently, our research group has confirmed that the same adsorption phenomenon of c-PEG can be observed even when using our own synthesized AuNPs, in addition to the commercially available AuNPs used previously. Therefore, in this experiment, we determined the R_g of the AuNPs/PEG complexes and investigated the influence of the PEG topology on the adsorption structure and the effect of the AuNPs used on the physical adsorption of c-PEG.

AuNPs/PEG complexes were prepared by mixing an aqueous dispersion of AuNPs, synthesized by our research group via citrate reduction of $HAuCl_4$, with an aqueous solution of HS-PEG-OMe or c-PEG. This mixture was then left overnight to reach adsorption equilibrium. The resulting AuNPs/PEG complexes were then purified by repeating concentration and solvent exchange using ultrafiltration with 0.2 mM citric acid in D_2O to remove any unadsorbed PEG. SANS measurements were performed using a quartz cell (1 mm thick). The scattering intensity curves obtained for the AuNPs/c-PEG and AuNPs/HS-PEG-OMe complexes were then compared.

The SANS measurements of the various AuNPs/PEG complexes were successful, and representative data are shown in Figure 1. The scattering curves for the AuNPs/c-PEG and AuNPs/HS-PEG-OMe complexes showed differences in shape and intensity, which reflected the structural characteristics of the complexes. For example, a significant increase in scattering intensity was observed in the low-q region in the order of AuNPs, AuNPs/c-PEG, and AuNPs/HS-PEG-OMe, clearly demonstrating the formation of complexes due to the adsorption of c-PEG and HS-PEG-OMe, respectively.

[1] T. Yamamoto *et al.*, Nat. Commun. **11**, 6089 (2020), *Nanoscale Adv.* **4**, 532 (2022).

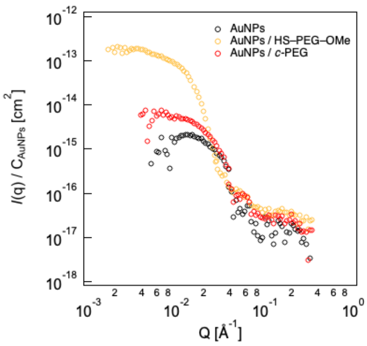

Fig. 1. Scattering intensity curves for AuNPs, AuNPs/c-PEG, and AuNPs/HS-PEG-OMe