Molecular Weight-Dependent Structural Changes of Gold Nanoparticle–Cyclic PEG Complexes

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Polymers with a variety of topologies, and the properties that arise from their "shape," have attracted sustained interest in polymer chemistry. Cyclic polymers in particular are known to display distinctive physical behavior, for instance, a reduced hydrodynamic volume and an accelerated diffusion rate. Their behavior at surfaces and interfaces, however, has scarcely been reported to date. Against this background, we have demonstrated that gold and silver nanoparticles can be stabilized through the physisorption of cyclic PEG (c-PEG), in contrast to the conventional approach that relied on chemisorption via a gold–thiol reaction [1]. Although this topology-driven adsorption at surfaces and interfaces is a highly intriguing phenomenon, its underlying mechanism remains unresolved. To clarify how this adsorption proceeds, we are pursuing a multi-pronged investigation that combines computational-chemistry simulations of c-PEG adsorption onto nanoparticle surfaces with quantification of the adsorbed species by NMR, thermal analysis, and related techniques. Within this framework, structural characterization of the gold nanoparticle–c-PEG complex (AuNPs/c-PEG) by SANS serves as a complementary approach and occupies a key role in extracting detailed structural information on the adsorbed state.

More recently, our group has verified that the same c-PEG adsorption behavior occurs not only with the commercially sourced AuNPs employed earlier but also with AuNPs prepared in-house. Accordingly, in the present study we evaluated the R_g of the AuNPs/PEG complexes and examined both the effect of PEG topology on the adsorbed structure and the influence of the AuNPs themselves on the physisorption of c-PEG.

The AuNPs/PEG complexes were obtained by combining an aqueous dispersion of AuNPs prepared in our laboratory through citrate reduction of $HAuCl_4$ with an aqueous c-PEG solution, and allowing the mixture to stand overnight so that adsorption equilibrium was reached. The complexes were subsequently purified by repeated concentration and solvent exchange via ultrafiltration against 0.2 mM citric acid in D_2O, thereby removing any PEG that had not adsorbed. SANS measurements were carried out in a 1 mm quartz cell, and the resulting scattering-intensity profiles of the AuNPs/c-PEG complexes were compared.

SANS measurements on the AuNPs/PEG complexes across a range of molecular weights were carried out successfully, with representative results presented in Figure 1. The scattering profiles of the AuNPs/c-PEG complexes differed in both shape and intensity, mirroring the structural features of each complex. Notably, the scattering intensity in the low-*q* region increased markedly with increasing c-PEG molecular weight, providing clear evidence that complex formation arises from c-PEG adsorption and is governed by the molecular weight of the polymer.

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

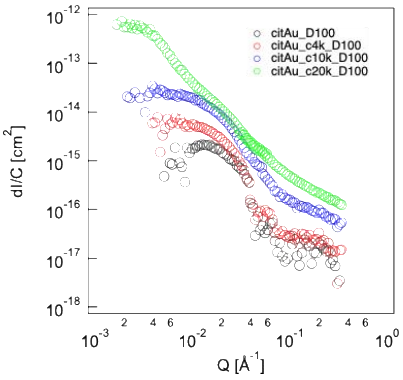

Fig. 1. Scattering intensity profiles for AuNPs, AuNPs/c-PEG with various molecular weights.