Self-Assembly Nanostructures in Biomimetic Polymeric Materials

This report features the works of Shiao-Wei Kuo and his co-workers published in RSC Adv. ***2****, 6295 (2012) and Polym. Chem.* ***3****, 882 (2012).*

Biomimetic polymers, assembled in functional building blocks, are artificial materials inspired by nature, meaning that a biologically active entity is attached to a polymer in a designed chemical reaction. The translation of biological principles to synthetic polymers provides greatly enhanced mechanical properties of the materials for tissue engineering and drug delivery, etc. At a laboratory for supramolecular polymer chemistry and physics led by Prof. Shiao-Wei Kuo from National Sun Yat-sen University, Taiwan, his group specializes in self-assembly supramolecular nanostructures and nanocomposites. They have recently developed nacre-like biomimetic nano-composites and peptide-based polymers, of which their nanostructures were investigated with synchrotron-based small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD) at beamlines **BL23A1/BL17A1**, NSRRC.

Nacre, an inorganic and organic composite material, is typically found on the inside portion of shells, and is referred as mother-of-pearl. The nacreous structure consists of aragonite platelets (a crystallographic form of $CaCO_3$) and an organic matrix (proteins and polysaccharides) arranged in a *brick-and-mortar* structure with the organic matrix serving as a glue. The *brick-and-mortar* arrangement of ordered organic and inorganic layers is generally believed to confer enhanced strength and toughness on materials. Kuo *et al.* utilized clay and water-soluble poly(vinyl alcohol) (PVA) as an inorganic and organic composite, to mimic the nacre-like structure prepared with a simple solution-casting method.[1] As revealed in two-dimensional wide-angle X-ray scattering (WAXD) patterns, and with a scanning electron microscope (SEM) and a transmission electron microscope (TEM), the composite film exhibited highly ordered smectic clay layers (Fig. 1(a)). These authors observed that, on applying a normal stress larger than the yield stress—about 40 MPa, white shear bands developed at strains larger than 10 %, much like the conditions in which crazing of organic PVA is suppressed by inorganic fillers of clay sheets, indicating that the nacre-like structure reinforces the mechanical property of the clay/polymer nano-composite films with a clay content greater than 30 mass per cent.

Polypeptides, composed of amino-acid monomers, have become of recent interest in developing synthetic routes for the designation of polypeptide sequences to make products for applications in biotechnology. Polypeptides are able to assemble hierarchically into ordered conformations, such as α-helices, which can be regarded as a rigid rod stabilized by intramolecular hydrogen-bonding interactions, and β-sheets, a secondary structure also stabilized with intermolecular hydrogen-bonding interactions. Kuo *et al.* synthesized new peptide-based block polymers -- polystyrene-

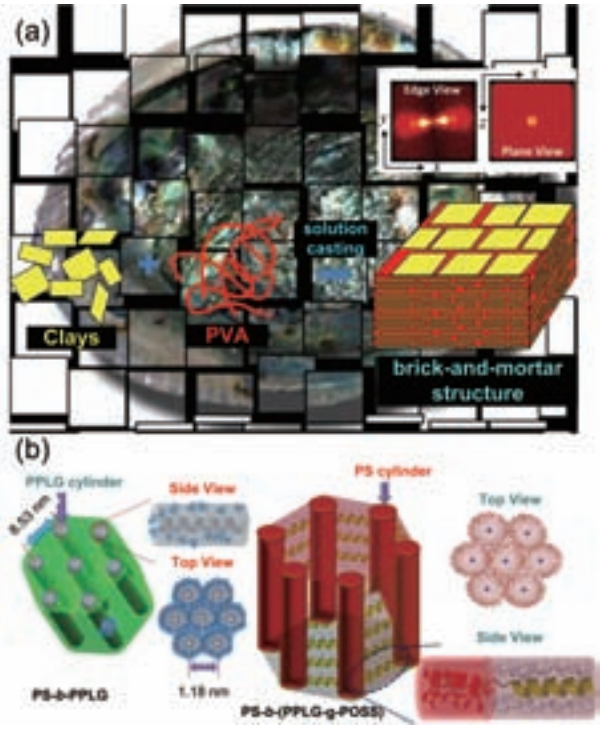

Fig. 1: (a) Preparation of biomimetic self-assembled brick and mortar structures, based on solution casting. (b) Hierarchical cylinder-within-cylinder structures formed from PS-*b*-PPLG (left) and PS-*b*-(PPLG-g-POSS) (right). Figure (b) is adapted from Ref. 2.

block-poly(g-propargyl-L-glutamate), PS-*b*-PPLG, and polystyrene-*block*-poly(g-propargyl-L-glutamate-g-polyhedral oligomeric silsesquioxane), PS-*b*-(PPLG-g-POSS) -- to investigate the self-assembly of POSS-containing rigid-rod polypeptide chains and microphase separation of the peptide-based block polymers.[2] As revealed by WAXD data, the β-sheet conformation of PS-*b*-PPLG transforms into an α-helix rigid rod-like structure after an increased degree of polymerization and an incorporation of the POSS units into the PS-*b*-(PPLG-g-POSS) system. From SAXS and WAXD data, they proposed a hierarchical cylinder-within-cylinder structure with hexagonal packing lattices in PS-*b*-(PPLG-g-POSS) and PS-*b*-PPLG (Fig. 1(b)), in which small cylinders formed with rigid-rod polypeptide segments, and large cylinders consisted of a microphase separation of the peptide-based block polymers.

References

1. W. Zhu, C.-H. Lu, F.-C. Chang, and S.-W. Kuo, RSC Adv. **2**, 6295 (2012).
2. Y.-C. Lin and S.-W. Kuo, Polym. Chem. **3**, 882 (2012).