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Block-copolymer-like supramolecules confined in nanolamellae†

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This paper describes the development of a new concept in supramolecular assembly of existing functional polypeptides to form diblock-like molecular clusters through complementary hydrogen-bonding interactions, providing a potential route toward design and fabrication of block copolymer-like supramolecular materials.

The design of supramolecular polymers utilizing well-defined hydrogen-bonding interactions has received intensive attention and the desire to use functional small-molecule building blocks through non-covalent interactions of functional molecules has led to the advent of supramolecular materials chemistry.¹ This area of science is primarily focused on the design of functional units capable of ordering into multi-leveled structures by the static self-assembly process.² Multiple hydrogen bonding interactions used in supramolecular systems are moderately strong and highly directional. These supramolecules possess desirable properties such as thermo-reversibility and responsiveness to external stimuli including pH, solvent polarity, temperature, and concentration^{3–5} and also improved thermal and mechanical stabilities as compared with single-hydrogen-bonding systems.³

Polyhedral oligomeric silsesquioxane (POSS) with a general structure of $(\text{RSiO}_{3/2})_8$ shows several important features, including the cubic siloxane cage and the distribution of the eight pendant arms from the cube in a three dimensional arrangement. POSS derivatives comprise a family of molecularly precise, near-isotropic molecules that have diameters ranging from 1 to 3 nm, depending on the number of silicon atoms in the central cage and the nature of its peripheral substituent group.^{6–12} Over the past decade, POSS molecules have attracted considerable interest as “self-healing” high-temperature nanocomposites and space-survivable coatings,^{13,14} low- k dielectric materials,¹⁵ and as templates for the preparation of nanostructural materials such as liquid crystalline polymers,¹⁶ catalysts,¹⁷ dendrimers,¹⁸ and multi-arm star polymers.^{19–21}

Polypeptides are biological macromolecules that are composed of amino acids. A typical polypeptide is composed of different amino acids in different proportion and combination. The conformational studies of model polypeptides are important for making steps toward the biological characteristic of more complex proteins.²² Generally, the secondary structure of peptide chains plays a crucial role in the

formation of the well-defined tertiary structure of proteins.²³ The knowledge of the primary structure of the peptide chains is also critical for many biochemical and biophysical studies. The α -helix to coil transition in polypeptides with the thermodynamic driving forces was described by Schellman^{24,25} almost 50 years ago. From a synthetic point of view, the most well-known example is poly(γ -benzyl-L-glutamate) (PBLG) that has been employed as a model rigid-rod polymer^{26,27} in bulk and solution states,²⁸ providing its unique behavior such as thermotropic liquid crystalline ordering,^{29,30} thermo-reversible gelation,^{31,32} *etc.* In addition, the synthesized PBLG has both α -helix and β -sheet secondary structures stabilized by intra- and intermolecular hydrogen bonds,³³ which is the most studied secondary motif due to its high frequency in natural proteins.

In our previous study, we combined the well-defined macromolecular architectures of polyhedral oligomeric silsesquioxane (POSS) and PBLG to generate polymeric building blocks having distinct 3-D shapes for the self-assembly of supramolecular structures.³⁴ Furthermore, we also reported that the hydrogen bonding interactions of POSS-based supramolecular macromers can be used in an orthogonal fashion to expand their application in proton exchange membranes.^{35,36} There remain many aspects of forming block copolymer-like clusters transferred from binding and recognition events in fundamental research into non-covalent systems. In this study, we devised a strategy of synthesizing an aminophenyl functional initiator containing a uracil (U) unit and then converted it through a ring-opening polymerization (ROP) to a well-defined polymer (U-PBLG). We prepared a POSS macromer containing multi-functional diamidopyridine units (MD-POSS) through a click reaction of propargyl-functional POSS with azide modified diamidopyridine compounds. The U-PBLG is expected to interact with its complementary MD-POSS to form self-assembly ordered structures of the complementary uracil-diaminopyridine (U-DAP) pairing. In addition, the periodic spacing of fabricated secondary cholesteric nano-lamellar morphology can also be controlled by varying the mixing ratio of U-PBLG/MD-POSS blends to tailor the surface activity of the nanolamellae for specific requirements and applications. Herein, we investigated these blends including peptide conformations and functional interactions.

Syntheses and molecular recognition properties of MD-POSS and U-PBLG

A new nanoparticle MD-POSS was synthesized through a click reaction between propargyl-functional POSS with azide modified

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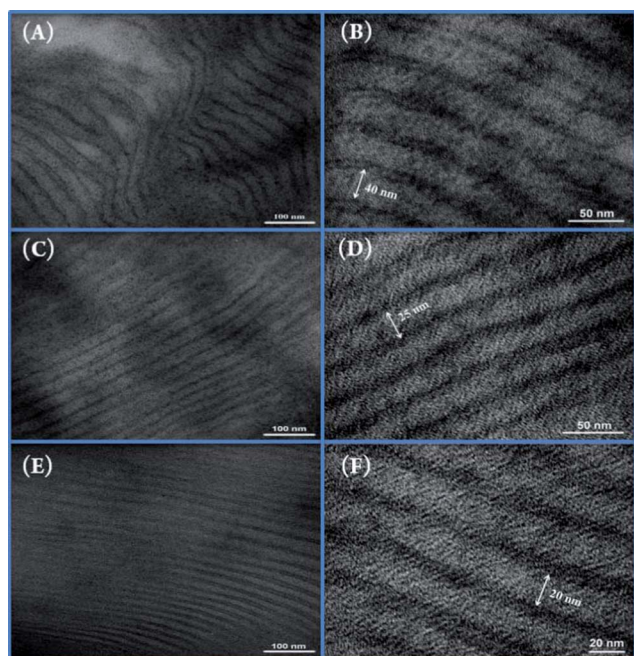
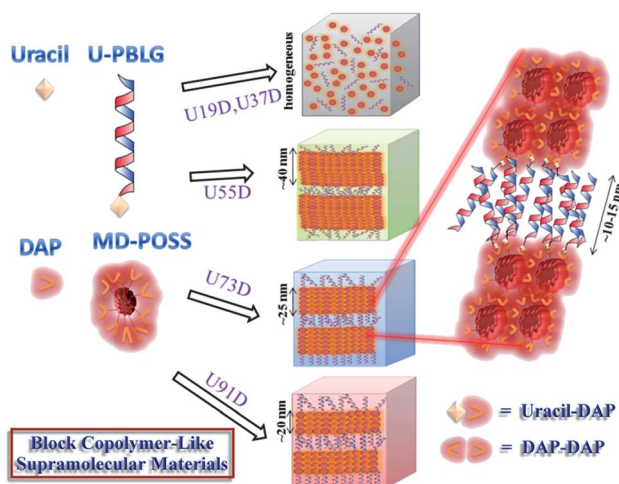


Fig. 2 TEM images of (A) U55D, (C) U73D and (E) U91D and enlargements of (B) U55D, (D) U73D and (F) U91D.

specific structures with a relatively regular structure. In addition, U-PBLG/MD-POSS complexes display strong positions at $1 : 3^{1/2} : 4^{1/2}$, corresponding to the distance between the planes of hexagonally packed PBLG rods. Previous studies indicated that the short-chain PBLG (DP = 30) in solid state cannot assemble to form the cholesteric liquid crystalline and ordered large-scale secondary cholesteric twisting structures.^{41–44} Therefore, the U-DAP interaction must play a critical role in facilitating the formation of the specific twisted microstructures.

To directly observe the microstructure of the U-PBLG/MD-POSS complexes, TEM measurements were carried out (Fig. 2). TEM results showed the random coil structures for U19D and U37D (in Fig. S10†), indicative of amorphous morphologies with a well-dispersed POSS. On the other hand, it also revealed that the highly complementary hydrogen bonding was present within the U-PBLG/



Scheme 2 Morphology of MD-POSS/U-PBLG blends.

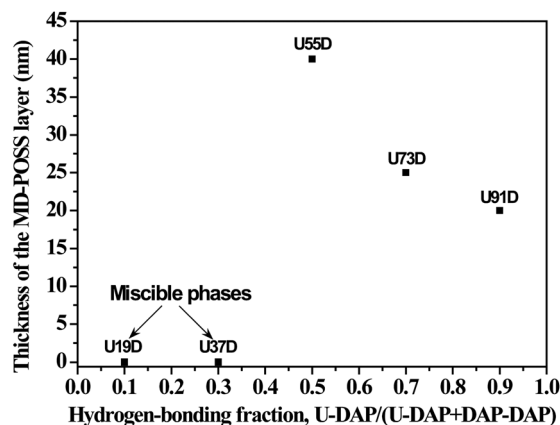


Fig. 3 Thickness of the MD-POSS *versus* hydrogen-bonding fraction as measured by TEM.

MD-POSS complex and resulted in a miscible phase. For the U55D, U73D and U91D blends, well-ordered lamellar structures can be observed as shown in Fig. 2. The dark regions correspond to the U-PBLG phase while the bright regions are attributed to the MD-POSS phase. In addition, all the complexes possess lamellar structures with a U-PBLG phase of 10–15 nm. In the case of the U55D complex, the TEM micrograph shows that the distance between MD-POSS phases is *ca.* 40 nm. On the other hand, the U73D and U91D complexes possess a relatively small distance between MD-POSS phases (*ca.* 20–30 nm). According to the above, the increase in the fraction of the MD-POSS within the blends leads to change in the distance between MD-POSS phases due to the assembled MD-POSS through DAP-DAP interaction (Scheme 2 and Fig. 3). Through appropriate design of compositions of the U-PBLG/MD-POSS complexes, the *d*-spacing of the cholesteric lamella morphology can be controlled, enabling us to tailor the surface activity of the nanolamellae for specific requirements and applications.

Conclusions

In summary, U-PBLG/MD-POSS complexes were prepared exhibiting ordered cholesteric lamellar structures. The *d*-spacing between MD-POSS phases can be controlled by varying the component ratio of the complexes, which has rarely been observed previously. This U-PBLG/MD-POSS supramolecular system is the first organic/inorganic supermolecule possessing diblock copolymer-like morphological properties as a result of complementary interactions and provides a potential route toward design and fabrication of block copolymer-like supramolecular materials.

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