Complex Self-Assembly of T-shaped and Tetra-block Molecules

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Investigation of molecular self-organization is one of the key areas of chemical research and soft matter physics, while also aiding the understanding of biological systems. Complex self-organized superstructures have been realized in block copolymers [1,2] and dendritic molecules [3-5]. However, recently it was shown that different complex superstructures can also be formed by other low molecular weight materials such as T-shaped molecules with three incompatible segments. These T-shaped molecules have a rod-like biphenyl or terphenyl core, to which a polar group is attached at each end and a long aliphatic chain to a lateral position (“bolaamphiphiles”) [6]. Alternatively, an aliphatic chain is attached at each end and a polar chain, with or without an ionic terminal group, is attached laterally (“facial amphiphiles”) [7-11].

The T-shaped molecules are shown to be versatile in forming complex mesophases, as shown for example in Figure 1 for bolaamphiphiles. With increasing length of the attached lateral chain, the observed phases change from smectic (Sm), through a series of honeycomb structures consisting of different polygonal shaped columns, back to lamellar phases (Lam), now with the rigid rods parallel to the layers and with different types of in-plane order. As the size of the lateral chains is increased further, recent studies reveal the existence of a number of previously unknown phases in the region beyond Lam phases, including several cubic phases. The way T-shaped molecules assemble in these cubic phases is rather different from those in the lyotropics, due to a complex combination of nano-phase separation and curvature elasticity.

Our recent research has also been extended to the self-assembly of tetra-block amphiphiles. The general molecular structure of these tetra-block molecules is shown left. The chemical constituents of the two side groups, R₁ and R₂, can either be the same or different. When the two side groups are the same, honeycomb structures similar to those observed in T-shaped molecules are resulted. However, when R₁ ≠ R₂, and the two groups are immiscible, more complex structures are.