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

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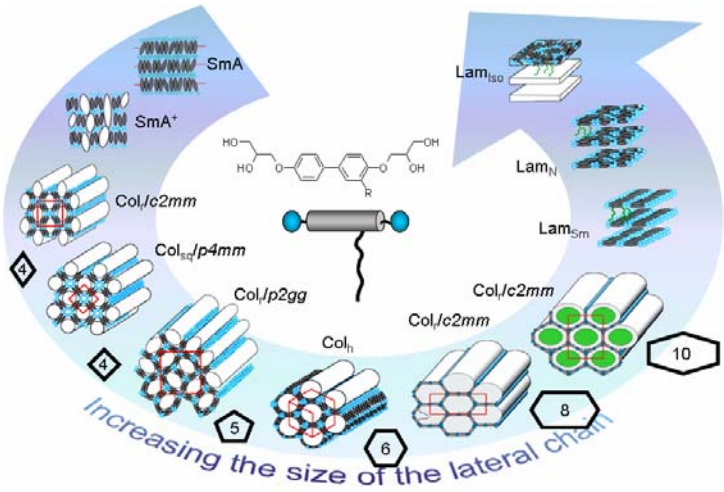
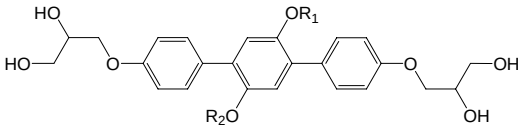
Investigation of molecular self-organization is one of the key areas of chemical research and soft matter physics, while also aiding the understanding of biological systems. Complex self organized superstructures have been realized in block copolymers [1,2] and dendritic molecules [3-5]. However, recently 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, R_1 and R_2, 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 $R_1 \neq R_2$, and the two groups are immiscible, more complex structures are.

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