Taming Liquid Crystal Self-Assembly:
The Multifaceted Response of Nematic and Smectic Shells to Polymerization

JungHyun Noh, Benjamin Henx and Jan P. F. Lagerwall
University of Luxembourg, Physics & Materials Science Research Unit, Luxembourg, Luxembourg

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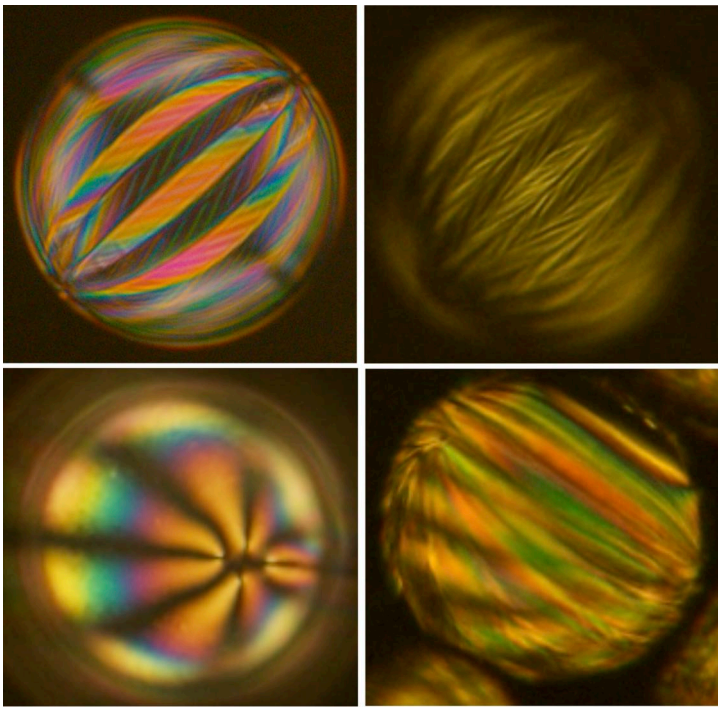
Layman's abstract

High-performing functional materials derive their attractive properties in part from their chemistry—which atoms and molecules are in the material and how do they interact?—and in part from how the atoms and molecules are arranged and the overall structure of the material. In composites, for instance, the distribution and orientations of fillers within the matrix are key to their performance. The most exquisite composites, where chemistry and structure are in perfect harmony, are found in the high-performance materials of Mother Nature, for instance in the shells of beetles and crustaceans. Here regular arrangements of organic polymer chains, with helical or herringbone arrangements, are combined with inorganic fillers in the right places and proportions. The most amazing aspect about these beautiful and impressive composite materials is that they form by themselves: they are self-assembled.



Self-assembly is also a key property of liquid crystals, exhibiting the unique property of being processable as a fluid while at the same time displaying the long-range order that otherwise is seen only in solid crystals. Moreover, by changing temperature, transitions between different liquid crystal phases can take place, each exhibiting a different type of self-assembled order. It may be purely orientational, sometimes with a helical modulation, and it can be with 1D or 2D positional order. Under the right constraints, liquid crystals may also form a herringbone-like ordering.

These non-biological self-assembling materials could be very useful in developing artificial high-performing functional materials that in many respect mimic the biological gold standard. However, while the fluid state is useful in processing, the liquid crystal eventually needs to be turned into a solid so it can be used as a durable material. This can be achieved by polymerizing the liquid crystal, or a fraction of it. We then create a network throughout the liquid crystal by connecting reactive molecules, and the self-assembled liquid crystal order guides the structure of the network as it forms. Liquid crystal polymerization is normally done on a flat sample contained between glass substrates,

and it can then be difficult to remove the produced polymer from the substrates. Moreover, this procedure limits the sample topology to a flat film, yet some of the most interesting self-assembled structures of liquid crystals develop when the liquid crystal is allowed to curve, as in a spherical shell. Such liquid crystal shells, which can be produced in a microfluidic pathway, give rise to spectacular optical textures, reflecting their diverse possibilities of self-assembly into different long-range ordered structures. Unfortunately, these shells are very delicate. The liquid crystal is enclosed between two water phases, and the liquid-liquid interfaces are too weak to render the shell durable. Shells easily rupture and have a typical lifetime from just minutes to hours.

In their new *Advanced Materials* paper, Noh et al. apply the polymerization strategy to liquid crystal shells, freely suspended in a water phase, thus without any substrate from which the polymer needs to be freed. Thereby they extend the lifetime to the order of months, making it realistic to use these unusual structures in advanced materials design. By just changing the temperature at which polymerization is carried out a few degrees up or down, they produce curved polymers with very different structures. It is even possible to tune the degree of polymerization to just give mechanical stability to the shell, without fully locking in the internal structure. This leaves the liquid crystal responsive, of use for instance in sensing. On the other hand, by increasing the degree of polymerization and lowering the temperature, the authors create thin spheres in which the polymer chains are arranged in herringbone patterns, reminiscent of the inspiring materials that Nature provides us with. The polymerization of liquid crystal shells thus opens a rich new toolbox, with which we can expect attractive high-performance functional materials to be developed.