Watching a Liquid-Crystal Helix Unwind

Liquid crystals have many versatile applications but are best known for the liquid-crystal displays that drive the billion-dollar smartphone and flat-screen industries. Chirality, the absence of inversion symmetry, plays an important role in chemistry, biology, and materials science. Introducing molecular chirality into a liquid crystal may lead to a twisting force that can modify the equilibrium state usually observed in liquid crystals, resulting in various helical structures. However, achiral molecules have also been observed to form helical structures—for example, the helical nanofilament (HNF) phase—due to spontaneous chiral symmetry breaking. Now, for the first time, researchers have directly measured the helical pitch of a liquid-crystal HNF at various temperatures using linearly polarized, resonant soft x-ray scattering (R-SoXS) at the ALS. The work opens the door to understanding the relationship between structure and property in important organic materials, including liquid crystals, lipid tubules, and peptoids.

The NOBOW molecular structure and a simplified structural model of an HNF. In a chiral liquid crystal, stacked molecular layers form a twist—a useful property in LCD technology. NOBOW transforms from the B4 (helical) phase to the B2 (flat) phase at 142 °C, and from the B2 phase to the isotropic phase at 170 °C. The colored surfaces indicate individual layers that can slide over one another (“smectic” layers).

To address this challenge, researchers applied linearly polarized, resonant soft x-ray scattering (R-SoXS) at Beamline 11.0.1. In typical R-SoXS experiments, the scattering contrast can be very sensitive to x-ray energy near absorption edges. Here, the researchers have gone a step further by exploiting the coupling between the linear polarization of the x-rays and the molecular bond orientations, so that the scattering contrast depends on the orientation of the molecule with respect to the x-ray polarization. Experiments were performed on drop-cast films of NOBOW in a solvent (either chloroform or chlorobenzene) with horizontally and vertically polarized x-rays at two different x-ray energies. The results show a strong peak at 283.5 eV (near the carbon K-edge), corresponding to a half-pitch of about 90 nm, roughly in agreement with data from indirect TEM measurements. The peak is anisotropic, with stronger...
Beyond the Flat-Panel Display

Everywhere you look these days, you will likely spot at least one person whose eyes are glued to a flat-panel liquid-crystal display. There’s no doubt that liquid-crystal displays have revolutionized the way we experience the world, opening a magic, pocket-sized window to far-away people and places. It’s not really magic, though; it’s science with a history reaching back to the late 1800s, when the first liquid crystal was identified. It then took 75 years for the discovery to become more than an academic curiosity, with the first rudimentary displays appearing in the 1960s.

Today, interest in liquid crystals remains intense in industrial labs, where the ability of helical liquid-crystal layers to twist light has been ingeniously exploited to improve the quality of displays. In the academic sphere, developments in nano- and biotechnology have sparked renewed creativity in liquid-crystal research. The liquid-crystal example studied in this work presents a promising self-assembling, nanosegregated architecture with potential as an efficient charge-transport system for organic photovoltaics. It also forms porous networks that could be used for the synthesis and separation of chiral biomolecules—pharmaceuticals for example—where “handedness” is crucial. These are just a few examples of why the development, by Zhu et al., of a technique allowing direct measurement and control of liquid-crystal properties is important.

(a) R-SoXS data from drop-cast films of NOBOW in a solvent of chlorobenzene. Experiments were performed with horizontally and vertically polarized x-rays (red arrows), at two different x-ray energies (279.5 and 283.5 eV). The scattering contrast increases dramatically near the carbon K-edge (284.2 eV). (b) Temperature dependence of the helical half-pitch scattering profile. Left: Heating from room temperature (RT) to the B4-phase critical temperature ($T_c = 142 °C$). The peak intensity increases and the peak shifts slightly to smaller $Q$. Right: Cooling from the isotropic phase ($T_c = 170 °C$). The peak position does not change after the remnant chloroform is driven out. Note that the peak position is much lower on cooling ($Q \approx 0.0052 \text{ Å}^{-1}$, half-pitch ~120 nm) than on heating ($Q \approx 0.007 \text{ Å}^{-1}$, half pitch ~90 nm).

Scattering perpendicular to the x-ray polarization direction.

As the NOBOW films were heated to the isotropic phase ($170 °C$), the peak intensity slowly increased and sharpened, suggesting that thermal annealing leads to improved ordering. Interestingly, the helical half-pitch increased, from 86 to 97 nm, before the peak intensity started to drop without changes in pitch, suggesting that the B4 helix does not continuously unwind into the flat B2 phase, but rather undergoes melting.

Surprisingly, the half-pitch of HNFs formed upon cooling from the isotropic phase is about 120 nm, much larger than before heat treatment and the same as in pure NOBOW. The observation suggests that HNFs may adopt the preferred curvature of the pure material after temperature cycling, attaining an equilibrium pitch. When a small amount of solvent molecules are mixed in during drop-casting, the HNFs apparently form with a shorter half-pitch (~86 nm), nearly 30% shorter than that obtained after temperature cycling. The researchers proposed that the addition of guest solvent molecules increases the strain in the top and bottom halves of individual layers, increasing the preferred curvature and resulting in a shorter helical pitch.

Immediate use of RSoXS in investigating other helical structures in liquid crystals is possible. Such future studies will shed light on the complex interplay between elastic forces and the orientation and chirality of the constituent molecules.