Our research is in the area of solid-state organic chemistry, which lies at the interface between physical organic chemistry and materials science. We use crystalline solids as models to probe fundamental issues about physical processes, molecular interactions and chemical reactions that are important for fabrication, stabilization and application of technological materials. Much of our most recent work has focused on the phenomena of ferroelastic and ferroelectric domain switching,\textsuperscript{1-2} in which application of an external force or electric field to a crystal causes the molecules inside the crystal to reorient, in tandem, to a new orientational state (Figure 1).

To better understand and control the domain switching process, we have designed and synthesized over twenty closely related, ferroelastic organic crystals. Our approach has been to use crystalline inclusion compounds, in which one molecule (the guest) is trapped within the crystalline framework of a second molecule (the host). By keeping the host constant and varying the proportions and kinds of guests, it has been possible to tailor these materials so that domain switching is rapid and reversible (which is desirable for high technology applications). Inclusion compounds therefore serve as powerful systems for understanding the specific molecular mechanisms that control domain switching.

Figure 1. Schematic representation of irreversible ferroelastic domain switching in a crystal that is distorted from hexagonal symmetry. (For 2,10-undecanediione/urea, the arrows represent one layer of guest carbonyls and the principal component of the strain in this antiferroelectrically ordered material.) Before stress (left), the crystal is in the extinguishing position and appears magenta when viewed between crossed polars and a $\lambda$ plate. After stress (right), a large domain has been reoriented by approximately 60° about the channel axis. Concomitant reorientation of the optical indicatrix allows transmission of light, and for thin crystals, a shift toward yellow interference colors.

Much of our work has focused on a series of urea inclusion compounds containing alkanediones such as 2,10-undecanediione (see Figure 2). These inclusion compounds are channel structures in which the guest is trapped within a honeycomb framework of host molecules. The urea host forms a well-defined helical

**Keywords:** ferroelastic, inclusion compound, birefringence, twinning, epitaxy, new research

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A network of hydrogen bonds that surround the long chain guest molecules, which are packed within van der Waals contact along the channel axis. Although many urea inclusion compounds occur as high-symmetry, incommensurate (nonstoichiometric) structures, certain alkanediones form commensurate structures in which the urea turns into the channel to form hydrogen bonds between its syn N-H group and the carbonyl of the guest. For guests with channel axis repeats that are integer or half-integer multiples of the repeat of the urea helix, guests within a channel are related by either translation or twofold screw axes, and the inclusion compounds form low symmetry structures that can exhibit ferroelastic domain switching. In the case of 2,10-undecanediione/urea, there are two guests for every three turns of the urea helix, and the guests within a channel are related by twofold screw axes. This crystal is orthorhombic with space group C2221.

Figure 2. Chemical structures for the guest (2,10-undecanediione) and host (urea), which form a channel inclusion compound with the stoichiometry of one guest for nine host molecules. On the urea, syn and anti hydrogens are designated Hs and Ha.

Application of external anisotropic stress to a {110} face of 2,10-undecanediione/urea gives rise to a ferroelastic domain reorientation, as depicted in Figure 1. In this helical inclusion compound, several events are required for the domain switching process to occur. When stress is applied to the left side of this crystal (as shown in Figure 3), the guests must rotate in a clockwise fashion about their long axes to relieve the stress. As they rotate, the guests break their hydrogen bonds to the host, and the host molecules, in turn, rotate back into alignment along the vertical channel wall (100). In order to establish the new (daughter) domain, the guests must translate up the channel axis by 1.84 Å and form hydrogen bonds with the next urea in the helix (which rotate into the channel). In the left-handed helical structure shown in Figure 3, clockwise rotation of the guest requires that the guests progress out of the plane of the figure and toward the viewer. In the same manner, stress applied to the lower right {110} face of the same crystal gives rise to a counterclockwise rotation of the guest molecules. To establish the daughter domain, the guests would progress down the channel (away from the viewer) to the next available urea in the helical structure. In an enantiomorphic crystal (containing a right handed helix), the direction of progression would be the opposite.

Crystals of 2,10-undecanediione/urea and related materials ordinarily grow as twinned crystals containing several sectors. In such crystals, which are distorted significantly from hexagonal metric symmetry, twinning can occur across (130)(130) or (110)(110) boundaries (Figure 4). As shown by synchrotron white beam X-ray topography, these are unstrained twin boundaries in which the two adjacent domains are epitaxially matched with each other. In other words, for each boundary, the projection of the strain for a given domain onto the twin boundary is equal to that for the adjacent domain. Local disorder occurs at the twin interface because the network of host-guest hydrogen bonds is disrupted, but only unstrained twin boundaries are allowed in crystals with significant distortion.

These rotational twins can be observed quite readily with a polarizing microscope containing a compensator (λ plate). Because the crystal is distorted significantly along [100], the crystals are biaxial and have significant birefringence when viewed down the channel axis. For thin crystals, it is possible to observe interference colors, which differ for the differently oriented domains (Figure 5). Thicker crystals do not
Figure 3. Channel axis view of 2,10-undecanedione/urea showing orientation of applied stress (a horizontal, b vertical). This structure contains a left-handed urea helix, as defined by the chain of C=O--H\textsubscript{a}-N hydrogen bonds. Guest molecules are related by a twofold screw axis along the channel, and their mean planes lie near the (010) plane.

Figure 4. (a) Schematic diagram of twinning across a (130)(130) boundary. Note that this allowed twin boundary is perpendicular to the \{110\} face of the crystal and that the strain on each side of this domain wall is projected onto the boundary in an equivalent manner. (The guest carbonyls and the [100] axes make approximately 30˚ angles with the boundary.) (b) Twinning across a (110)(110) boundary. Again, there is no strain because within each sector, [100] makes the same angle of approximately 60˚ with the twin boundary.

exhibit interference colors in the visible region of the spectrum, but they do exhibit characteristic extinction orientations. In addition to the observable rotational twinning, urea inclusion compounds are known to exhibit chiral twinning in which right and left handed helical structures are formed within the same crystal.\textsuperscript{4} For strongly birefringent crystals such as 2,10-undecanedione/urea this type of twinning is ordinarily invisible because the linear birefringence is orders of magnitude larger than the optical rotation.

It is now possible to quantitatively map the orientation and magnitude of a crystal’s birefringence using a Metripol microscope.\textsuperscript{5} This device utilizes a rotating polarizer-\(\lambda/4\) plate-analyzer to map the birefringence for each pixel in an image. In the experiment, intensity maps are collected for a series of polarizer orientations, and a Fourier analysis of the intensity variation gives rise to three maps: intensity, indicatrix orientation and retardation. With small retardations, data collected at one wavelength are sufficient to
Figure 5. Photomicrograph of 2,10-undecanediol/urea (crossed polarizers, λ plate) grown in less than a minute by evaporation of methanol. The horizontal dimension of the crystal is 65 µm. Differently oriented domains, which are separated by the twin boundaries shown in Figure 4, are distinguished by their interference colors. For example, the beige and green sectors at the bottom of the crystal are separated by the (130)(130) interface shown in Figure 4a.

establish the direction of the slow axis. For larger retardations, it is possible to establish the absolute retardation (i.e. the order) by collecting intensity data at three wavelengths. In the example shown below the crystal was thin enough for one wavelength to yield the correct indicatrix orientation.

For ferroelastic crystals such as 2,10-undecanediol/urea, the orientation map reveals domain orientations directly since the slow axis corresponds to [100]. The retardation map contains further information about disorder within and between domains and can be used to identify the most highly ordered regions of a sample for crystallographic structure analysis. With in situ stress experiments, domain switching can be imaged directly and hysteresis loops can be generated. This method is therefore an important complement to our in situ stress studies using synchrotron white beam X-ray topography, which can be used to evaluate dislocations and strain in the presence and absence of stress.

For crystals containing an 80:20 mixture of 2,10-undecanediol and 2-undecanone, the ferroelastic domain switching is reversible, and the crystals display remarkable memory effects in which the daughter formed under stress quickly reverts to the original orientation when the stress is released. The memory effects are thought to be related to differences in perfection between the mother and daughter domains, so the retardation map, which provides information about perfection, is useful for evaluating these differences (Figure 6).

The Metripol microscope is especially useful for ferroelastic crystals in which the distortion from hexagonal metric symmetry is small (or zero with optically anomalous crystals). In such crystals, the birefringence is typically so small that ordinary light microscope techniques cannot be used to distinguish different sector orientations. In ferroelastic crystals of 2,19-eicosanediol/urea, for example, birefringence mapping reveals domain orientations quite readily. Because the distortion from hexagonal metric symmetry is so small in this crystal, ordinary rules of epitaxy do not apply, and domains that would ordinarily be mismatched can coexist on either side of a common domain wall.

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Figure 6. Metripol images ($\lambda = 610$ nm) of a portion of a urea inclusion crystal containing an 80:20 mixture of 2,10-undecanediol and 2-undecanone. The top panel (a-c) shows orientation maps for the crystal before stress (a), under 21 centiNewtons of force applied horizontally across the face (b), and after release of stress (c). The bottom panel (d-f) contains the retardation images for the same conditions as a-c. In each image, the color scale shows either the orientation of the slow axis (top panel) or the retardation as $|\sin \delta|$ (bottom panel), and the lines depict the orientation of the slow axis and the magnitude of the retardation. This crystal contains a horizontal (130) twin boundary, as depicted in Figure 4. In figure b, the slow axis of the daughter domain (light blue) is vertical. This corresponds to the [100] axis, as depicted in Figure 1. The changes in retardation shown in e (and which are related to crystal perfection) are not easily discerned with ordinary light microscopy.

Because the birefringence maps generated by the Metripol can take as little as a few seconds to generate, this method should be useful for in situ monitoring of crystal perfection during growth. In our work, it is rapidly becoming an indispensable tool for studying ferroelastic and ferroelectric domain switching and mechanisms of crystal growth.

We gratefully acknowledge NASA (NAG8-1702) and the NSF (DMR-9619191) for funding this research.

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