

Chapter 6

Conclusions

“Structure dictates function” has become a common theme in discussions of chemistry and biology. For urea inclusion compounds, this mantra cannot be ignored. Although the basic structure of most urea inclusion compounds is the same, small differences in guest structure can have an appreciable effect on its interactions with the urea host and ultimately on the crystal structure and its properties. Herein, trends in structure and function have been documented for 2,9-decanedione/urea and 2,10-undecanedione/urea and crystals containing those guests and small amounts of structurally similar impurities. Although the guests are very similar in molecular functionality, appreciable differences in UIC topology are induced by a simple difference in guest length, and therefore in its capacity to interact with the host. What follows are remarkable changes in physical properties such as optical behavior, patterns of guest incorporation and ferroelasticity. By studying crystals containing these guests and varying amounts of the corresponding monoketone (either 2-decanone or 2-undecanone), many important features of these crystals have been elucidated.

Since UICs of either 2,9-decanedione or 2-decanone are optically uniaxial, it is interesting that mixtures of the two form biaxial UICs. Using a growth model developed in this laboratory, it was possible to rationalize patterns observed in the optical behavior of a crystal grown from a solution containing mostly 2,9-decanedione and a small amount of 2-decanone. Since the *origin* of optical anisotropy in these UICs is not understood, some questions remain about the optical behavior exhibited by crystals such as this one. Overall, however, these patterns of incorporation for guest and guest impurity adhere to

the conclusions of Lahav, McBride, and others, who were the first to rationalize symmetry lowering in solid solutions and whose discoveries provided a framework for the investigations described: symmetry lowering arises from the non-random incorporation of guest impurities. More importantly, it is possible to rationalize those patterns of symmetry reduction.

Although they contain only one additional carbon, 2,10-undecanedione and its monoketone analogue (2-undecanone) form radically different UIC structures than their ten-carbon counterparts. These guests are about 0.2 Å too short for the $2c'_g = 3c'_h$ (33 Å) commensurate repeat. In this regard, the mono- and diketone UICs differ: 2,10-undecanedione forms hydrogen bonds with ureas at both ends and can therefore match the 16.5 Å commensurate length, whereas 2-undecanone cannot (since lacks one hydrogen bond acceptor). Nevertheless, UICs of both grow as flat {001} plates.

A more obvious difference between UICs of 2,9-decanedione and 2,10-undecanedione is their physical properties: 2,10-undecanedione/urea exhibits a ferroelastic strain that can be reoriented upon the application of a compressive stress. The ferroelastic nature of this crystal has been studied for many years and depends on the extent of interaction between the host and guest. As discussed in Chapter 4, the replacement of diketone by an adequate amount of 2-undecanone “guest impurity” facilitates pseudoelastic reversion because monoketone guest interrupts the host-guest hydrogen bond network. This phenomenon was investigated by monitoring pseudoelasticity as a function of guest composition and applied strain. These studies indicate a critical threshold for impurity concentration: above 13-14% 2-undecanone, pseudoelastic behavior is observed reliably, even at strains as high as 2.4%.

The threshold phenomenon appears reasonable when one considers that domain switching involves cooperative motions that extend over large distances in a stressed crystal. By studying the kinetics of domain reversion for a variety of mixed-guest crystals, it was postulated that monoketone guests, which disrupt the network of host-guest hydrogen bonds, facilitate the repair of crystal defects. The repair of crystal defects had been observed earlier in a growing crystal of 2,10-undecanedione/urea, and this process appears to be dictated by the preservation (or recovery) of strain epitaxy along boundaries separating domains. Mismatch at domain interfaces can provide a defect structure in a stressed crystal that may favor domain reversion; however, other stress-induced defects might oppose reversion. The combined effect of defects that favor and those that resist domain reversion influences the energetics of mother and daughter domains and ultimately determines whether pseudoelasticity is observed.

For ferroelastic crystals of 2,10-undecanedione/urea, the presence of submicroscopic (nanoscopic) domains has been inferred from synchrotron white-beam X-ray topography experiments. Strain mismatch between nanoscopic domains and their surroundings provides a possible means for the formation of stress-induced defects discussed above and a mechanism for pseudoelasticity and defect annealing. In this mechanism, nanoscopic domains that are epitaxially matched in the unperturbed crystal become mismatched with the daughter domain created during the stress experiment. Thus, the driving force for pseudoelastic reversion is thought to be the recovery of strain epitaxy between nanoscopic domains and their neighbors. In experiments where a stressed crystal was monitored using a combination of optical and diffraction methods, domains possessing the hypothesized unit cell orientation were identified, and their

behavior was monitored as a function of applied stress. These experiments led to the formulation of a more comprehensive model for ferroelastic domain switching and rubber-like behavior in this class of materials. Two additional experiments sought, unsuccessfully, to measure the population of the displacive twin thought to be present in a stressed crystal; these (and others) underscore the difficulty in studying this phenomenon. However, further work that probes the structures of the nanoscopic domains and their role in the domain switching process will undoubtedly be fruitful.

Overall, the study of urea inclusion compounds is a very exciting endeavor and can provide insights into more general questions of crystal growth, structure and properties. Although “structure dictates function”, these studies have inspired an antecedent to that statement that appears to apply to this crystal system, and possibly others: *molecular interactions dictate structure*. By tailoring the interactions between components of ordered systems such as urea inclusion compounds, it should be possible to elucidate how those interactions affect crystal properties; it should also be possible to design crystals with specific, interesting properties.