Summary

Different polymorphic forms of a crystalline compound lead to different properties of the material, in particular the crystal morphology. In this study crystals of organic dyes play the major role because their anisotropic optical properties, as employed in photographic films and ink jet inks, depend strongly on the crystal morphology. Crystal morphology depends on the growth rate of each facet, which, once understood, can be tuned to obtain particles with optimal properties for their use. Therefore, understanding of the polymorphic behavior and the influence on the growth morphology is key to control the properties of the crystalline product. A number of model compounds, most of them dyes, have been used for this study.

In chapter 2 the polymorphic behavior of an isoxazolone model dye is studied. It turns out that the dye has at least three polymorphs, which are monotropically related. The solubility of two of the polymorphic forms has been determined for a wide range of concentrations in three solvents. The solubility curves show regular solution behavior for not too high concentrations. At the highest concentrations, however, a clear deviation is observed. This is interpreted as arising from structural ordering of the dye molecules in solution. The thermodynamically stable form occurs as rhombic shaped crystals. One metastable polymorph grows with a needle-shaped morphology. For both of these forms single crystals could be obtained suitable for determining the crystal structure using X-ray diffraction. These two polymorphs can co-exist in solution, depending on the crystallization conditions, but in time the mixture transforms into the stable polymorph. As a solid, outside the solution, the structure of the needle crystals is stable for months. The metastable third polymorph grows only from the melt and undergoes a solid-solid phase transition to the needle shaped form within hours at any temperature below the melting point. This third form could not be isolated.

In chapter 3 the experimental and predicted growth morphologies of two polymorphs of the isoxazolone dye are compared. The crystal habit of both polymorphs depends on the supersaturation during growth. The Monte Carlo simulations of the growth of the relevant faces correctly predict the shape and the dependence on supersaturation of the crystal morphology for the stable polymorph. For the metastable polymorph, the order of morphological importance is reproduced correctly, as well as the needle-like morphology.

In chapter 4 we study the effect of additives and solvents on the growth morphology of the stable polymorph of the model dye. Using a range of additives with small differences in molecular structure, the growth inhibiting effects of the additives is revealed. The additives act face selectively, either by incorporating into the crystal lattice or owing to their presence at the surface. The solvents are only active at the surface and changes in morphology can be related to the polarity of the solvent. The effects of the additives and solvents are also visible in the surface topology as observed using atomic force microscopy. The surface-active additives even result in a different growth mechanism.

In chapter 5 we continue to study surface structures and crystal morphology of materials used in photographic films, now using silver carboxylates. The crystal morphology of these compounds is determined. Although the crystal structures form a homologous series, the various crystals are not isomorphous. The morphological importance of the fast growing top facets depends on the supersaturation and also on the carbon chain length. The surface topology of the largest faces is studied on a molecular scale, showing a 2D birth and spread mechanism. The experimental surface structure combined with molecular modeling leads to a detailed understanding of the growth and shape of these silver carboxylates.

In chapter 6 we use the anisotropic optical properties of several dyes to determine the internal structure of magnetically aligned crystals in solution. The deposition method in photographic films results in a similar ordering of the crystals as obtained by magnetic alignment. Three cyanine dyes, representing the so-called J- and H-aggregates and a combined class of these, and of which the crystal structures are known, are used for the alignment study. The obtained stacking geometries agree with the single crystal structures found, therefore magnetic alignment can be a valuable tool for structural analysis of such materials.

In the final chapter magnetic alignment in a high magnetic field is applied to isoxazolone, the model dye of the first chapters, to study its effect on nucleation and growth of crystals. Without a magnetic field the thermodynamically stable polymorph nucleates, while in the field the needle-shaped metastable polymorph is formed. This difference in nucleation behavior may be explained by an entropic effect in the formation free energy of clusters during nucleation. However, the anisotropy of the magnetic susceptibility of the unit cells of the two polymorphic forms cannot explain the observed nucleation behavior.