Project B2: Structural models of semiconducting polymers

Principal investigators: M. Brinkmann, P. Samorì (Strasbourg) / M. Sommer (Freiburg)

Current state of the research. Recent developments in the synthesis of semiconducting polymers (SCPs) have considered alternating copolymers based on the association of two or more monomeric units in the chains. Combination of electron-rich and electron-deficient units can lead to interesting new properties of the SCPs. For instance, it is possible to obtain low bandgap or electron-transporting polymers, i.e. to tune the electronic and optical properties of the polymers. These properties are however strongly dependent on the packing of the chains in a crystal. New structural issues, e.g. polymorphism and liquid crystal→crystal transitions, must therefore be addressed. In particular, this implies to be able to establish the packing of the monomeric units in a unit cell of the polymer crystal, especially regarding the p-stacking. In this perspective, Brinkmann group has shown, in collaboration with M. Sommer (IRTG), that alternating copolymers made of naphthalenebisimide (NDI) and bithiophene (p(NDI2OD-T2)) display a peculiar polymorphism with both segregated and mixed stacking modes of NDI and T2 units in two distinct polymorphic forms. This was possible through a well-controlled oriented growth using directional epitaxial crystallization and orientation on alignment layers of poly(tetrafluoroethylene) (PTFE). Accordingly, this approach is strongly based on the combination of *i*) oriented growth of SCPs films and *ii*) in-depth structural characterization using TEM (electron diffraction, low dose High Resolution TEM). In some cases, the possibility to grow single crystals of SCPs can also be of great interest to determine structural models as recently illustrated for the case of the form II of P3HT.

Contributions of the principal investigators. The Brinkmann group has developed and applied the method of electron diffraction to structure determination of key polymers like regioregular poly(3-hexylthiophene) (P3HT) and poly(dialkylfluorenes). In particular, structural models of form I and II of P3HT have been obtained. Here the group combines growth control in highly oriented films and electron diffraction in a TEM using the rotation/tilt approach. This allows to determine experimentally the space group and the unit cell of the polymorphs. In a second step, molecular modelling (Cerius2 program package) is used to propose structural models of the SCPs. This modelling is essential in order to correlate electronic properties e.g. charge transport to the packing of the chains in the crystal. P. Samori has a strong expertise in the use of scanning probe techniques to study electrical and electronic properties of individual supramolecular nanostructures, in the tailoring of interfaces of organic electronic devices, and in the fabrication and characterization of multifunctional supramolecular devices such as field-effect transistors. M. Sommer has a strong expertise in the synthesis and self-assembly of conjugated polymers via a variety of polymerization techniques

Research project and collaborations. This project aims at pursuing our research on structure determination in new emerging p-conjugated semiconducting polymers used in plastic electronics. We plan to advance the structural analysis of SCPs using quantitative electron diffraction approaches, which is a natural and timely evolution from the commonly employed trial-and-error methodology. The development of these approaches represents the core of the proposed PhD project. Applications will involve the structure elucidation of NDI-based alternated copolymers; they will be carried out in collaboration with M. Sommer and G. Reiter in Freiburg, where the doctoral researcher will spend some time. Collaboration with P. Samorì on the characterization of the electronic properties of the SCPs is also planned.