

Let us imagine a situation in which instead of a plastic, yet quite fragile, smartphone in the pocket and a separate charger we have a credit-card-like elastic device charged from photovoltaic cells printed directly on the apparel. Despite in the 21<sup>st</sup> century we got used to frequent innovations in electronics, our minds still associate the electronics with solid and often brittle items rather than flexible, tissue- or leaf-like organic materials. Novel findings in the field of organic, and hence flexible, semiconductors indicate that moving some of the electronics from stiff and brittle silicon to flexible circuits printed on fabrics or foils is only a matter of not-too-distant future. Technological progress in this field is, however, limited by the availability of suitable materials.

In the range of most promising materials for organic electronics one can find conjugated polymers, i.e. long linear molecules (referred to as macromolecules, because of their size) composed of atoms joined together by alternating single and double chemical bonds. Under some circumstances, such an array of chemical bonds enables transferring electric charge carriers: electrons (negative charge carriers) or holes (positive charge carriers). Poly(3-alkylthiophenes), P3ATs in short, are among the most important conjugated polymers. As many others conjugated polymers P3ATs are semiconductors. Because their good solubility, these polymers can be processed by ink printing: gravure, screen, ink-jet or other technologically relevant techniques. The essence of the ink printing is formation of the pattern, which solidifies as a result of ink drying. So, the ink printing can be considered a special case of a solution crystallization of ink components. The studies on crystallization of inks containing P3ATs, their derivatives and some other additives is the main objective of the project.

Electronic properties of P3ATs are inherently related to their crystalline structure and morphology. Despite this is well known, it is still under debate what are the key factors driving the solution crystallization and formation of particular crystalline structures. Unarguably, crystallization and crystal structure in a certain way depend on chemical structure of macromolecules forming the ordered domains. Hence the electronic properties of P3ATs can be primarily modified by changing their molecular structure. Structure modification can be achieved either by changing architecture of all the monomer units or by joining different monomer units within a single macromolecule. The latter, known as copolymerization, allows tuning the polymer properties, such as solubility or the ability to form crystals by variation of different monomer unit ratios. Mixing polymers with non-polymeric additives, often yields in binary blends (or composites), and can also be considered a way to control the crystallization being sensitive to the presence of interfaces. It is worth to mention here that one of the easiest ways to mix of polymers such as P3ATs with other molecules is dissolving all blend components in a common solvent to form a homogeneous solution. Formation of the blends out of the conjugated polymers and conducting additives seems particularly interesting, especially when the blend components reveal different type of conductivity, i.e. one component is electron- while the other one is hole-conducting. Such systems are formed when P3ATs are blended with, for instance, perylene diimide derivatives (PDIs). Recently it was demonstrated the addition of PDI to P3AT may enhance the hole conductivity of P3ATs and may also cause the components to form bicontinuous crystalline paths in the blend, which enables transporting of holes and electrons in a single material. The boundary conditions for forming of such structures are, however, not known.

Our research is aimed at demonstrating that a careful tuning of the chemical architecture of P3ATs and PDIs may enable control over formation of crystals in the blend and hence tailoring the electronic properties of the materials. The change of alkyl chains at PDIs or P3ATs will enable tuning their solubility, solution aggregation behavior and crystallization. In the case of P3ATs the aggregation in solution and crystal structure depend also on the specific interactions between polymer backbones, referred to as  $\pi$ - $\pi$  interactions because they rely on attracting of different molecules by  $\pi$  electrons present in their double chemical bonds. Additionally the crystallization can be modulated by the P3AT:PDI ratio. In our research we want to demonstrate the role of alkyl and aromatic groups on interactions between P3AT and PDI molecules in solution. Further, we want to show that such interactions, together with a variation in solubility can drive the formation of the required crystalline forms in the solid blends. Also, it will be interesting to see if there is any systematic correlation between different molecular (and hence crystal) structures and the electronic properties of the blends. So briefly, the main goal of our studies will be finding the relationships between molecular structure, crystallinity and conductivity of the P3AT:PDI blends.

In order to reach the above goals, we need to study the structure of molecules and materials, with a number of experimental techniques. The most important are nuclear magnetic resonance and infrared spectroscopies (NMR and FTIR respectively), differential scanning calorimetry (DSC) and X-ray diffraction. In order to evaluate the electronic properties, we will test the blends as active materials of real electronic devices: field-effect thin film transistors (OFET). The experimental data will enable us to fully picture the role of crystallinity on the charge transfer in the blends and hence our research should enable to tailor the electronic properties of materials intended for use in printing technologies of organic semiconductors by a rational design and selection of the components.