

Manipulation of Functional Polymers on the Molecular and Mesoscopic Scale

Sabine Ludwigs

IPOC-Functional Polymers, Institute of Polymer Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart; sabine.ludwigs@ipoc.uni-stuttgart.de

This talk will give an overview over current activities of my research team on the manipulation of semiconducting polymers based on thiophene units on the molecular and mesoscopic scale.

On the molecular scale, we have recently managed to synthesize branched thiophene polymers by different chemical routes and by electropolymerization.^[1,2] Relationships between the molecular architecture and functional properties such as absorption behavior and energy levels will be discussed and highlighted.

On the mesoscopic scale our latest results on controlled crystallization of semiconducting polymer thin films will be presented. While our first studies had focused on the work-horse of the solar cell community poly(3-hexylthiophene)^[3], we have recently started to work on two donor-acceptor copolymers: the p-type low bandgap poly{[4,4-bis(2-ethylhexyl)-cyclopenta-(2,1-b:3,4-b')dithiophene]-2,6-diyl-alt-(2,1,3-benzo-thiadiazol)-4,7-diyl} (PCPDTBT)^[4] and the n-type poly{[N,N'-bis(2-octylododecyl)-1,4,5,8-naphthalene-dicarboximide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)} (PNDI2OD-T2)^[5]. While PNDI2OD-T2 is known to be highly crystalline, PCPDTBT has long been regarded as marginally crystalline or even 'amorphous'. We show that methods such as solvent-vapor crystallization or shear alignment allow us to induce and control crystalline order over large areas in thin films of both polymers. We find that changes in morphology are closely related to changes in absorption spectra. Furthermore the impact of differently crystallized films on charge transport and solar cell performance is discussed.

[1] M. Goll, A. Ruff, E. Muks, F. Goerigk, B. Omiecienski, I. Ruff, R.C. González-Cano, J.T. Lopez Navarrete, M.C. Ruiz Delgado, S. Ludwigs, *Functionalized branched EDOT-terthiophene copolymer films by electropolymerization and post-polymerization "click"-reactions*, **Beilstein J. Org. Chem.** 11, 2015, 335.

[2] M. Scheuble, T.V. Richter, M. Goll, S. Link, J.T. López Navarrete, A. Ruff, M. C. Ruiz Delgado, S. Ludwigs, *Branched polythiophenes by Ni-catalyzed Kumada coupling*, **Polymer Chemistry**, 5, 2014, 6824.

[3] K. Tremel and S. Ludwigs, *Morphology of P3HT in thin films in relation to optical and electrical properties*. In S. Ludwigs, ed., *P3HT revisited – From molecular scale to solar cell devices*, **Adv. Polym. Sci.** (Springer, Heidelberg, 2014), Vol. 265.

[4] F.S.U. Fischer, D. Trefz, J. Back, N. Kayunkid, B. Tornow, S. Albrecht, K.G. Yager, G. Singh, A. Karim, D. Neher, M. Brinkmann, S. Ludwigs, *Highly crystalline films of PCPDTBT with branched side chains by solvent vapor crystallization: Influence on Opto-Electronic Properties*, **Adv. Mater.** 27, 2015, 1223.

[5] K. Tremel, F.S.U. Fischer, N. Kayunkid, R. Di Pietro, R. Tkachov, A. Kiri, D. Neher, S. Ludwigs, M. Brinkmann, *Charge transport anisotropy in highly oriented thin films of the acceptor polymer P(NDI2OD-T2)*, **Adv. Energy Mater.** 4, 1301659 (2014).