

WORLD POLYMER CONGRESS



macro
2018

1-5 July 2018
Cairns Convention Centre
Australia
www.macro18.org

Proudly presented by



ABSTRACT BOOK

Modeling solid state transitions in poly(3-alkylthiophenes)

M. Casalegno¹, A. Famulari¹, G. Raos¹, S. V. Meille¹

¹Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Italia

Optoelectronics properties and potential applications of materials are strongly dependent on solid-state organization both at the molecular scale and at the dimensions of typical crystalline entities, for polymers less than one micron. The ways materials respond or age, reorganizing structurally because of thermal or pressure treatments, or irradiation, or electrical stimulation, etc., are also of basic interest. Except in very rare cases, it is however nearly impossible to follow experimentally these transitions, except for slow processes, or more generally, for selected features. On the other hand, complete structural models are normally accessible only for the initial and final structure. The case of organic polymers for optoelectronics applications is possibly an extreme case in the above scenario, as they normally organize poorly in the solid state, and it is hence difficult even to devise sensible initial and final models for structural transitions.² This fact depends on their molecular structure, which, practically for all of them, is characterized by a π -conjugated, often heterocycle containing main chain, essential for charge transport and relatively long alkyl side chains, that make these materials processable. In transitions of such molecules, the new structure evolves by a negotiation involving the different main chain and side chain properties, leading in some instances to microphase-segregated structures.

Here we focus on poly(3-alkylthiophenes) (P3ATs), widely used p-type semiconductors in organic electronics, because they are a relatively simple but also fully representative family of conjugated polymers, and they have been extensively studied for decades.^{3,4} In particular, we describe atomistic molecular dynamics (MD) simulations of experimentally observed structural transitions of poly(3-butylthiophene),⁴ poly(3-hexylthiophene) (P3HT),^{3,5} and other P3ATs, from selected ordered states to more disordered structures which, under appropriate circumstances, can be followed continuously. The study was made possible by the development of a force-field⁶ appropriately adapted to P3ATs and by the identification of selected, reliable starting models.^{3,5} The molecular assemblies resulting from the simulation process (**Fig.1**) display at high temperature extensive deviations of the main chains from planarity, along with substantial reorganization leading to development of dislocations, and of stacking defects of various kinds, in part frozen in upon cooling. The observed, plausibly entropy driven, transitions will be discussed in the context of organic electronics and of polymer phase transitions modeling.

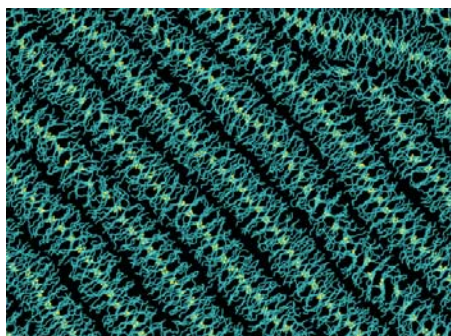


Figure 1. Representative snapshot, viewed along the chain axis, of the P3HT structure obtained from a 40-ns MD simulation, performed on a cell containing about 50000 atoms, at a nominal temperature of 530 K and 1 atm, starting from a relaxed structural model. The main-chain backbones are orthogonal to the viewing plane.

O. Ostroverkhova, *Chem. Rev.* **2016**, *116*, 13279-13412.

² J. Rivnay, S. C. B. Mannsfeld, C. E. Miller, A. Salleo, M. F. Toney, *Chem. Rev.* **112**, 5488–519 (2012).

³ M. Brinkmann, *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49*, 1218.

⁴ A. Buono, H. S. Nguyen, G. Raos, M. Catellani, S. V. Meille, *Macromolecules* **2010**, *43*, 6772-6781.

⁵ F. P. V. Koch, M. Heeney, P. Smith, *J. Am. Chem. Soc.* **2013**, *135*, 13699–13709.

⁶ M. Moreno, M. Casalegno, G. Raos, S. V. Meille, . R. Po., *J. Phys. Chem. B* **2010**, *114*, 1591-1602.

Stefano Valdo Meille

Title: Professor

Affiliation, Country: Politecnico di Milano, Italy

Phone: +39 0223993021 Fax: +39 0223993080 E-mail: valdo.meille@polimi.it

Personal History: Since 2000 full professor at CMIC Dept., Politecnico di Milano (Italy)

Research interests: X-ray and electron crystallography, crystalline polymers modeling and properties, polymers and organic materials for optoelectronics applications

