ORGANIC SEMI-CONDUCTORS FOR ADVANCED ELECTRONICS:

DETAILED ATOMISTIC SIMULATION OF THE STRUCTURAL, PACKING AND MORPHOLOGICAL PROPERTIES OF AMORPHOUS AND CRYSTALLINE POLY-ALKYL-THIOPHENE (PAT) SYSTEMS

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INTRODUCTION - MOTIVATION

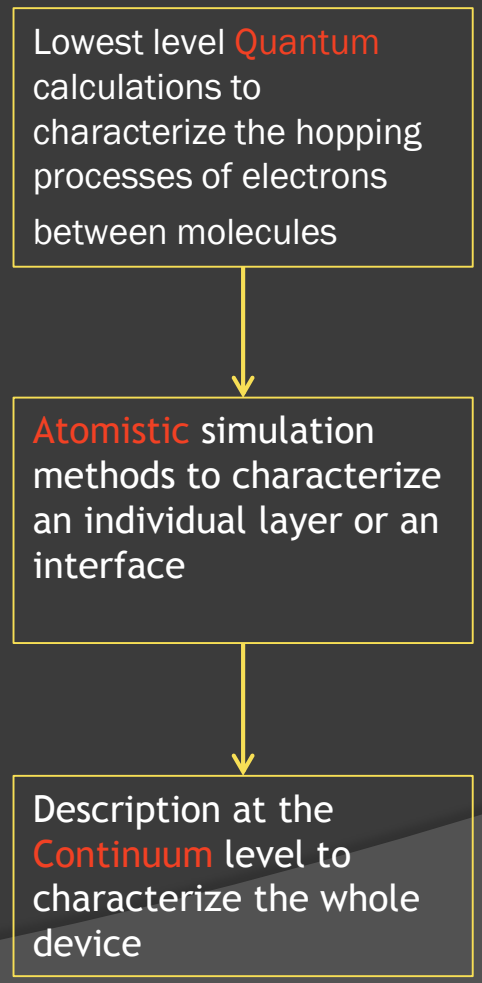
✓ *MMM@HPC Concept*

- Integrate simulation methods of different time/length scale in a unified workflow
- Model devices which are based on different micro- and nanostructured components

An illustrative example:

✓ Modelling of charge transport through OLEDs

Performance of the device is a property of the whole system not of an individual component



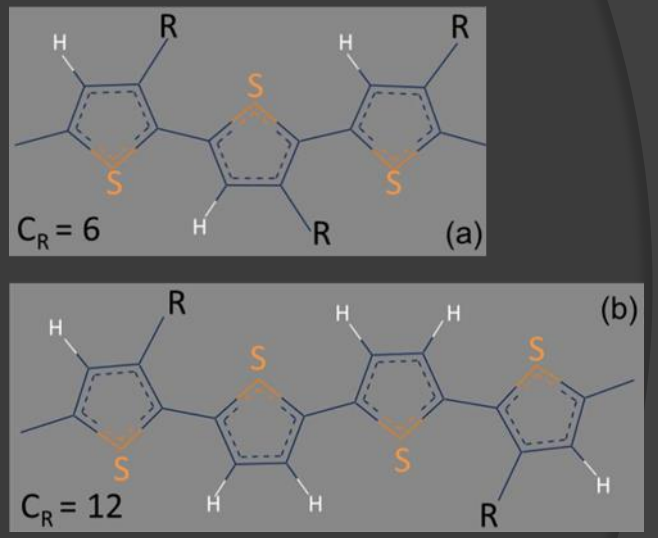
INTRODUCTION - MOTIVATION

✓ *Charge transport in Polymer Based Devices*

✓ Link between morphology protocols and charge transport protocols

1. Generation of fully equilibrated atomistic structures of model materials (Rr-P3HT, PQT)
2. Kinetic Monte Carlo calculations for the computation of charge transfer properties

➢ Outcome: Charge transfer rates inside crystalline domains, inside amorphous domains, In the interfacial area, and of course through the entire material



Schematic representation of (a) Regioregular P3HT (Poly-3Hexyl-Thiophene) and (b) a PQT (poly[5,5'-bis(3-alkyl-2-thienyl) 2,2'bithiophene]) unit

INTRODUCTION - MOTIVATION

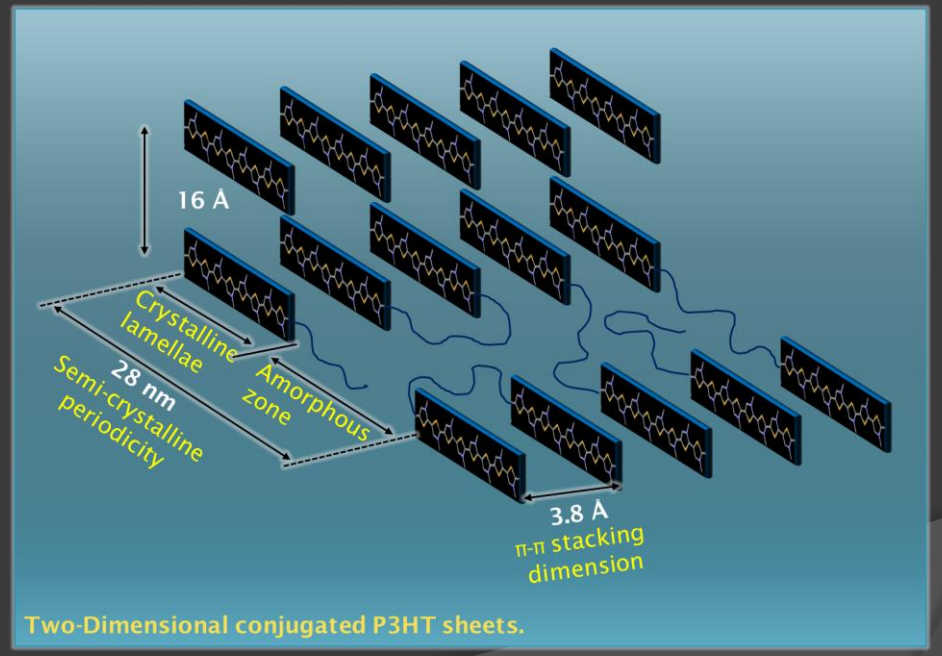
- Polythiophenes represent a broad family of polymeric semiconductors with unique opto-electrical properties; their electrical conductivity coupled with thermal stability can play an important role in the proper functionality of organic based electronic products like organic light-emitting diodes (OLEDs) and organic field effect-transistors (OFETs).

- Regioregular poly-3-hexylthiophene (Rr-P3HT)
  - High carrier mobility (0.1 $cm^2/V\ s$ in the ordered state)
  - High degree of solubility

- Periodic microstructure[1, 2]
  - Alternating crystalline domains separated by amorphous regions
  - Disordered zones with chain ends, chain folds and tie molecules

- Hierarchical ordering

1. *π-π* stacking distance 3.8 Å
2. Interlayer distance 16 Å
3. Semi-crystalline lamellar periodicity 28 nm



Two-Dimensional conjugated P3HT sheets.

1. Brinkmann, M.; Wittmann, J. C. *Adv Mater* **2006**, *18*, 860
2. Brinkmann, M.; Rannou, P. *Macromolecules* **2009**, *42*, 1125

OBJECTIVE

- This work is a first insight into the atomistic structure and chain self-organization of the two extreme phases of Regioregular poly-3-hexylthiophene (Rr-P3HT)
- Detailed atomistic molecular dynamics (MD) simulations with the all-atom Dreiding force-field separately for the pure crystalline and the pure amorphous phases of relatively large Rr-P3HT systems (~30000 atoms)
- Fully relaxed structures, representative of the crystalline and amorphous phases of P3HT with realistic density, atomic packing and low potential energy in a wide range of temperatures

Ultimately:

- Subsequent study of charge transport properties using large-scale kMC calculations of electronic properties, based on pre-computed (from lower level quantum-mechanics calculations) charge hopping rates

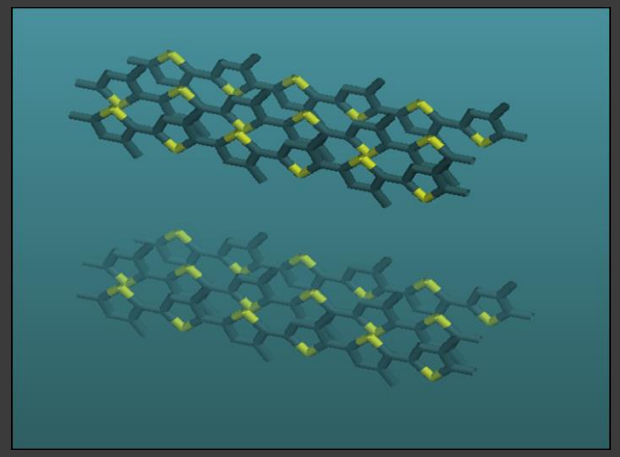
SIMULATION PREDICTIONS (Crystalline phase)

✓ *Systems studied*

- Based on the observation[1] that the size (~8 nm) of the crystalline regions of P3HT is MW-independent, the following systems were considered:

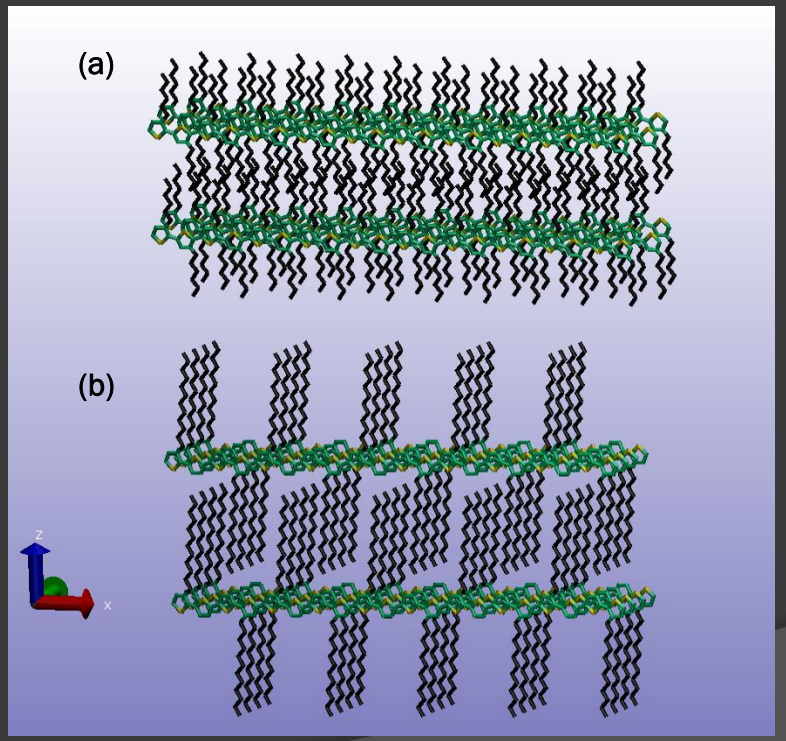
1. 64-chain 20 thiophene rings (20-3HT) long system (size < 8 nm)
2. 48-chain 30 thiophene rings (30-3HT) long system (size ~11 nm)

- Both with initial setup in the "staggered" arrangement[2]



In the "staggered" arrangement molecules are shifted by one thiophene ring along the backbone

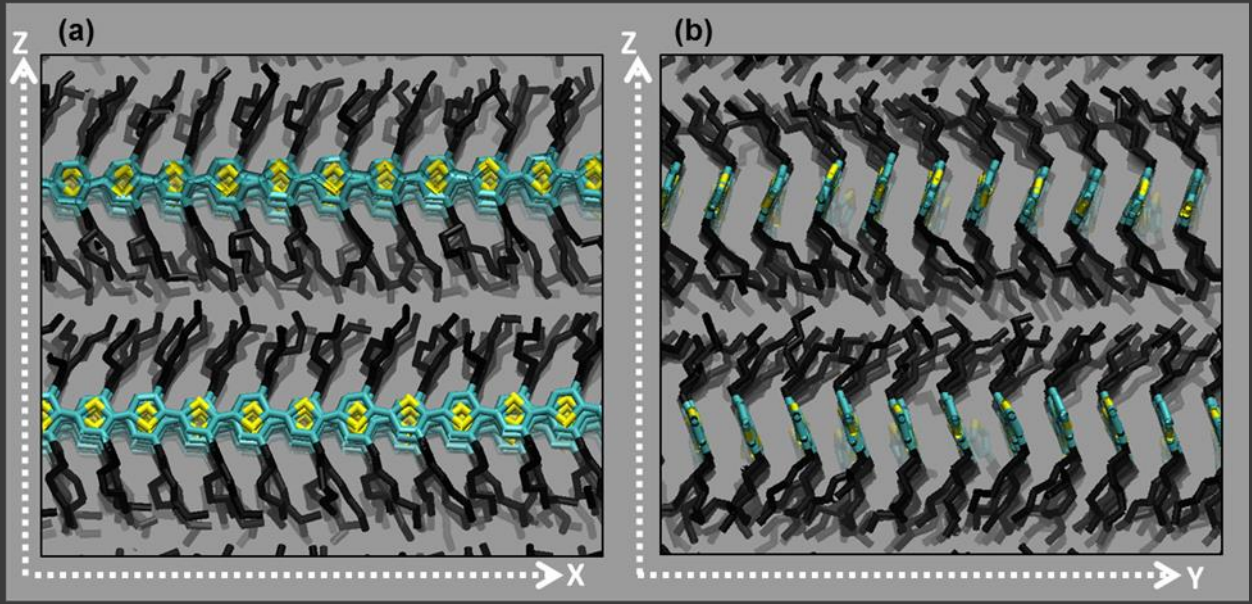
1. Brinkmann, M.; Rannou, P. *Macromolecules* **2009**, *42*, 1125
2. Maillard, A.; Rochefort, A. Phys Rev B **2009**, 79



The initial configurations of the (a) **20-3HT** system and (b) **20-QT** system the used in the MD simulations of the crystalline phase

SIMULATION PREDICTIONS (Crystalline phase)

✓ *Structure*



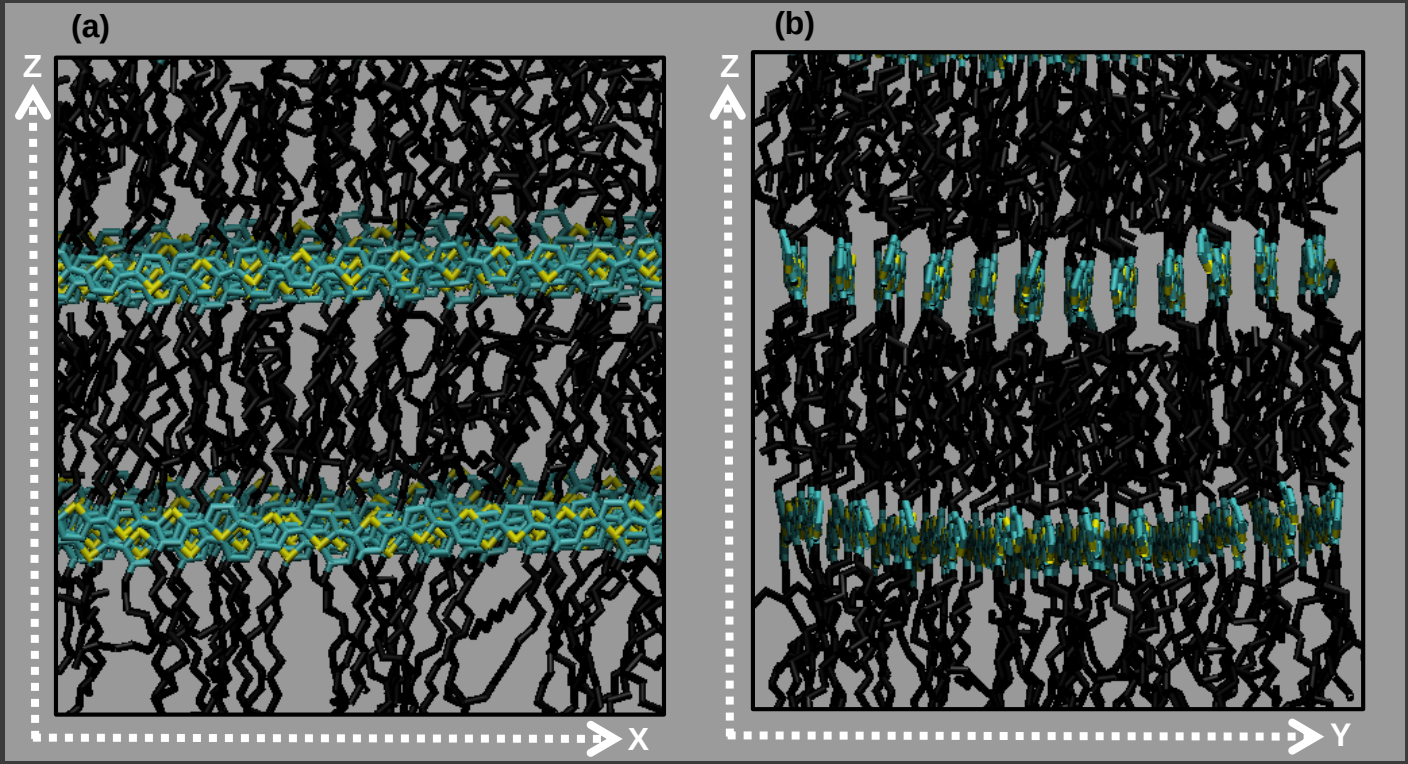
The final configuration of the 3hexyl-20thiophene ring system acquired after the MD simulation at 300K for 27 ns in (a) the XZ projection and (b) the YZ projection

- Poly-3HT chains display a *zigzag*[1,2], non interdigited[2,3,4] and tilted smectic-like structure

1. Brinkmann, M.; Rannou, P. Macromolecules **2009**, 42, 1125
2. Melis, C.; Colombo, L.; Mattoni, A. J Phys Chem C **2011**, 115, 576
3. Kline, R. J.; DeLongchamp, D. M.; Fischer, D. A.; Lin, E. K.; Richter, L. J.; Chabinyc, M. L.; Toney, M. F.; Heeney, M.; McCulloch, I. Macromolecules **2007**, 40, 7960
4. Do, K.; Huang, D. M.; Faller, R.; Moule, A. J. Phys Chem Chem Phys **2010**, 12, 14735

SIMULATION PREDICTIONS (Crystalline phase)

✓ *Structure*



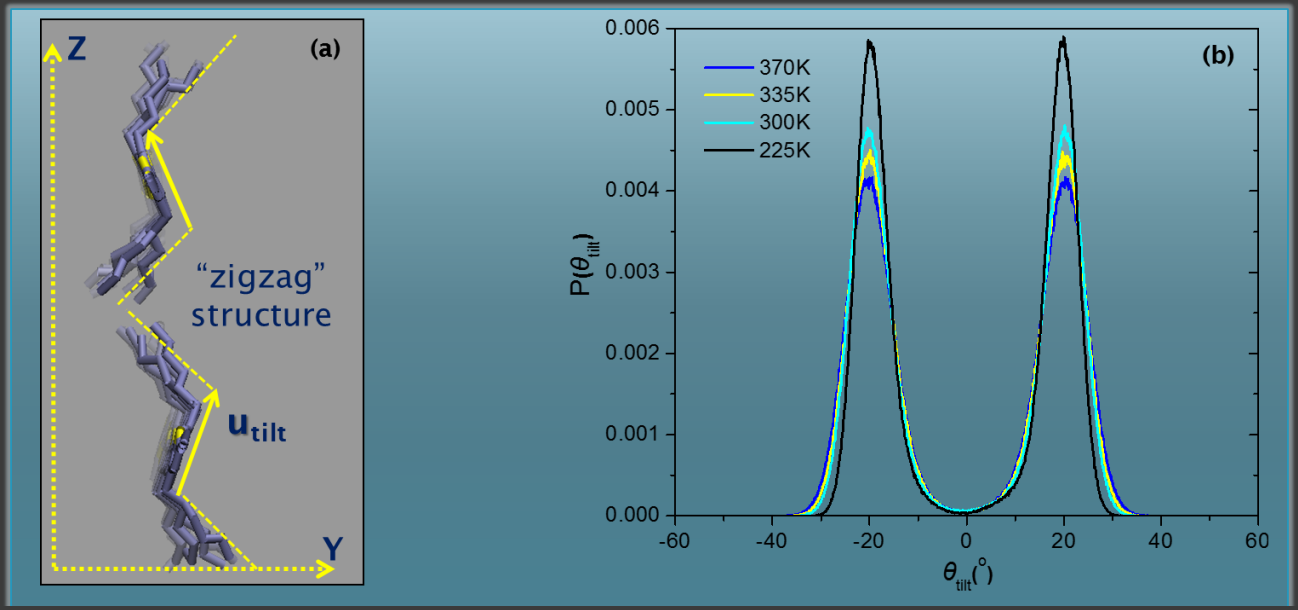
The final configuration of the **20-QT** system acquired after the MD simulation at **300K** for 27 ns in (a) the XZ projection and (b) the YZ projection

- In the 20-QT system side C_{12} chains are fully interdigited with a less ordered and not tilted structure

✓ Contrary to 20-QT system, 20-3HT side-chain attachment density is too large to allow interdigitation

SIMULATION PREDICTIONS (Crystalline phase)

✓ *Structure*



(a) Representation of the "zigzag" structure adopted by the 3hexyl-20thiophene chains inside the crystal; the u_{tilt} vector defines the tilt angle formed between the Z axis and the rings plane. (b) The tilt angle distribution of the 20-3HT ring planes for all simulated temperatures

- 20-3HT chains display a "zigzag" structure observed between the thiophene rings and the alkyl branches as shown in (a)
- There is a preferential value of the tilt angle around 20° consistent with resent first principal density functional calculation findings[1]

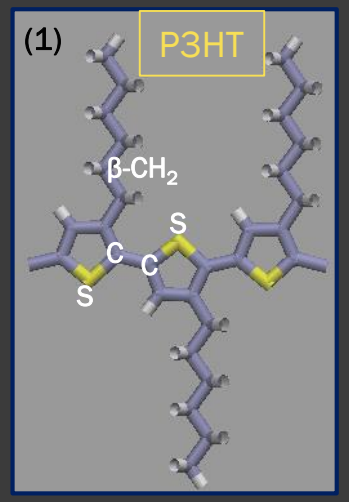
1. Northrup, J. E. Phys Rev B **2007**, 76

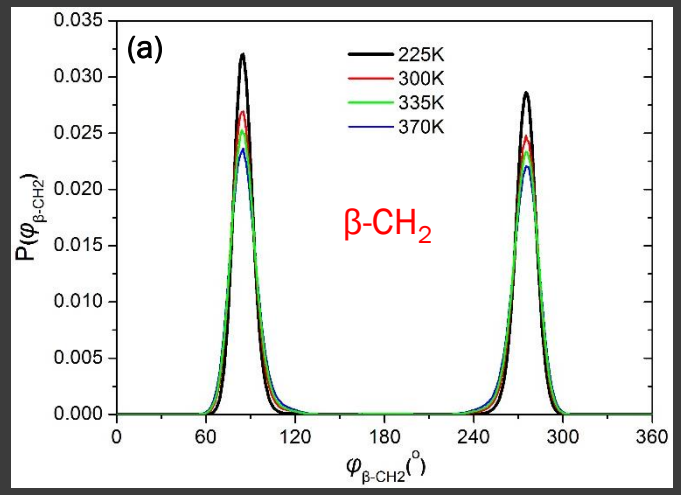
SIMULATION PREDICTIONS (Crystalline phase)

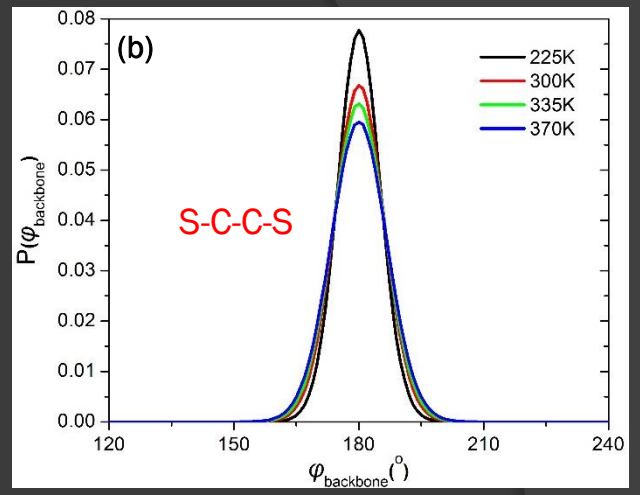
✓ *Structure*

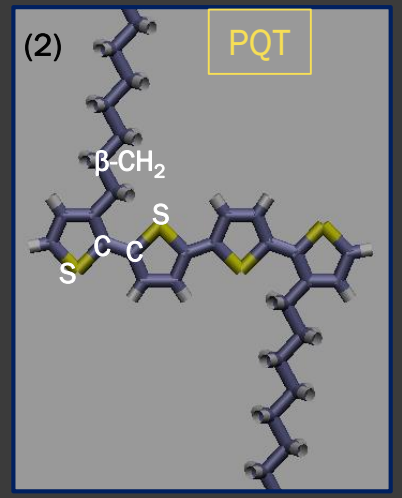
- The rotation of the second bond (a) with respect to the ring's plane (around 90º) reflects the "zigzag" structure
- For the inter-ring dihedral (b) there is a degree of deviation of the rotational angle between the backbone thiophene rings out of coplanarity (180º ± 20º)[1]

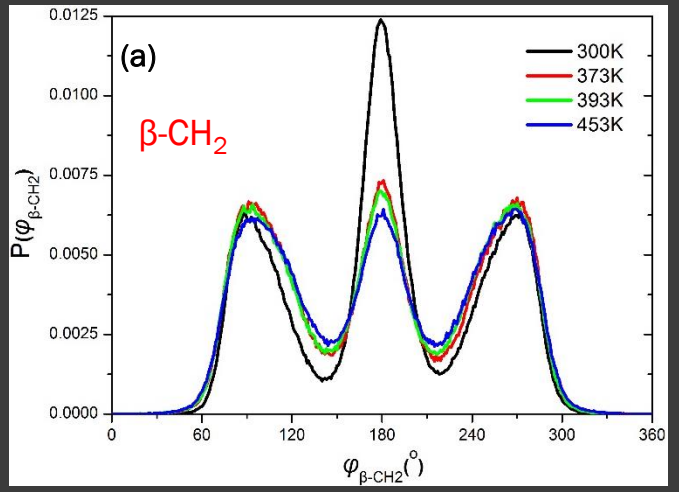
1. Lan, Y. K.; Huang, C. I. J Phys Chem B **2008**, 112, 14857

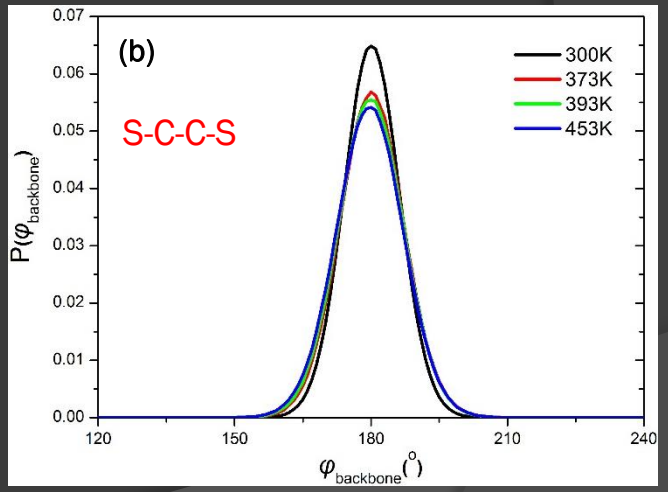












(a) Second (β-CH2) bond dihedral distribution of the Hexyl branches and (b) inter-ring dihedral (SCCS) distribution among consecutive rings in the backbone for (1) **20-3HT** crystal and (2) **20-QT** crystal

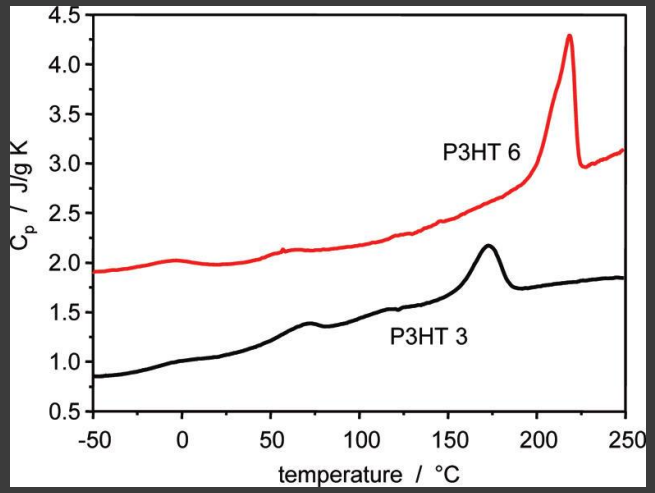
SIMULATION PREDICTIONS (Crystalline phase)

✓ *Rr-P3HT Phase Transition*

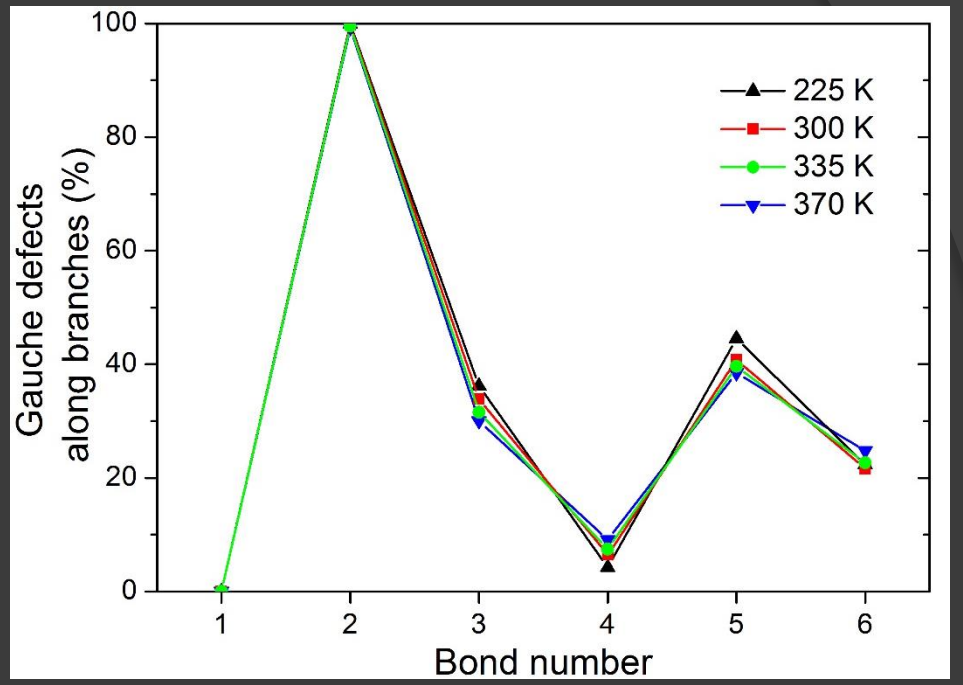
- DSC measurements[1,2,3,4]

1. Side-chain melting/disordering – crystal to liquid crystal state at ~60°C
2. Main-chain melting at 210-250°C

DSC for 2 different Mw P3HT samples



(Pascui et al. (*Macromolecules* **2010**)

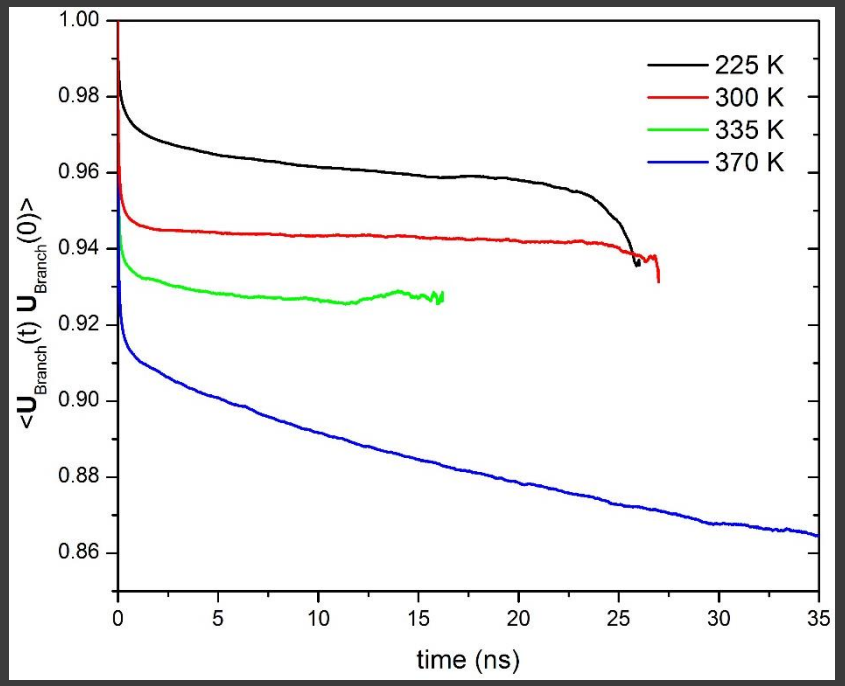


Percentage of bonds in the gauche configuration for the dihedral angles along the hexyl branch, and their temperature dependence

1. Malik, S.; Nandi, A.K. J Poly Sci Part B Polym Phys **2002**, 40, 2073
2. Hugger, S.; Thomann, R.; Heinzel, T.; Thurn-Albrecht, T. Colloid Polym Sci **2004**, 282, 932
3. Pascui, O.F.; Lohwasser, R.; Sommer, M.; Thelakkat, M.; Thurn-Albrecht, T.; Saalwachter, K. Macromolecules **2010**, 43, 9401
4. Wu, Z.; Petzold, A.; Henze, T.; Thurn-Albrecht, T.; Lohwasser, R.H.; Sommer, M.; Thelakkat M. Macromolecules **2010**, 43, 4646

SIMULATION PREDICTIONS (Crystalline phase)

✓ *Dynamics of side chains*



Decay of the time autocorrelation function $\langle U_{Br}(t) \cdot U_{Br}(0) \rangle$ for the unit vector U_{Br} directed from one end of the 20-3HT hexyl branch to the other, as a function of simulation temperature

- No relaxation of the side chains for temperatures equal or below T=335K
- At T=370K, <UBr(t)•UBr(0)> goes slowly to zero

$$\left\langle \mathbf{u}_{Br}(t) \cdot \mathbf{u}_{Br}(0) \right\rangle = A \exp\left(-\frac{t}{\tau_{KWW}} \right)^{\beta}$$

τ_{KWW} : characteristic relaxation time parameter

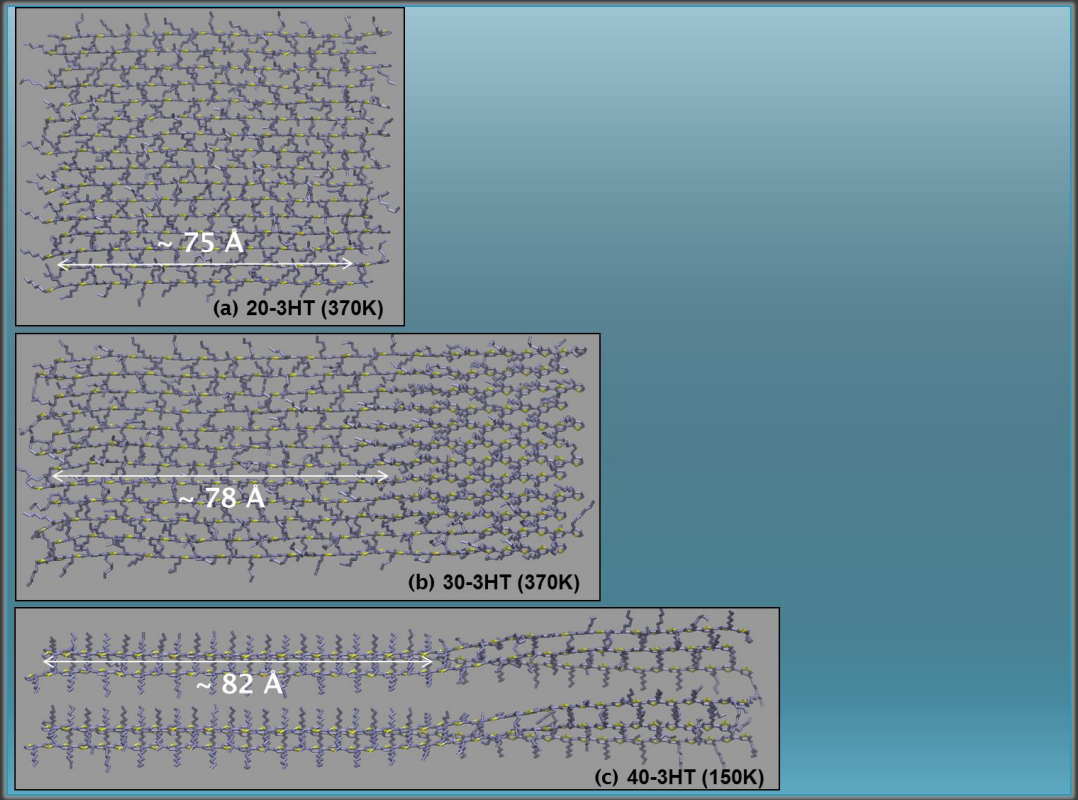
β : stretching exponent parameter

$$\tau_c = A \frac{\Gamma\left(\frac{1}{\beta}\right)}{\beta} \tau_{KWW}$$

τ_c ~10 sec at T = 370K

SIMULATION PREDICTIONS (Crystalline phase)

✓ *MW dependence (20-3HT .vs. 30-3HT)*

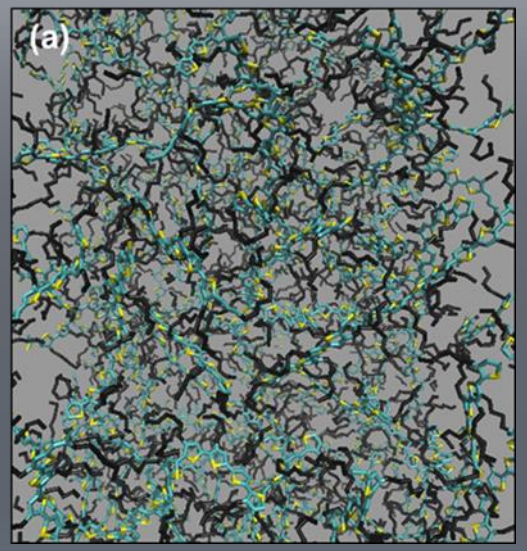


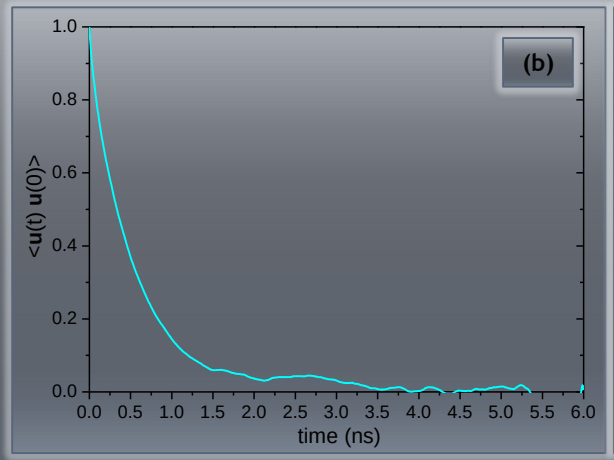
The final configuration of (a) the 3hexyl-20thiophene ring system (64 chains) and (b) the 3hexyl-30thiophene ring system (48 chains) at the end of the MD simulation at 370K (top views). In (c), the final configuration of a 3hexyl-40thiophene ring system acquired at the end of a test simulation at 150K

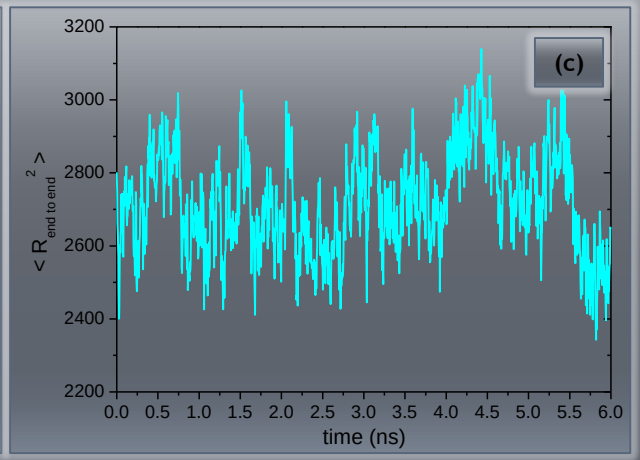
- There is a subsequent chain twisting for the longer crystal systems at distances along the backbone from its one end approximately equal to 8 nm
- This chain twisting is even more pronounced for the 40-thiophene ring system

SIMULATION PREDICTIONS (Amorphous phase)

- 20-3HT crystal is annealed at a high temperature (800K)
- A fully relaxed and uncorrelated final configuration devoid of any signs of crystallization is obtained





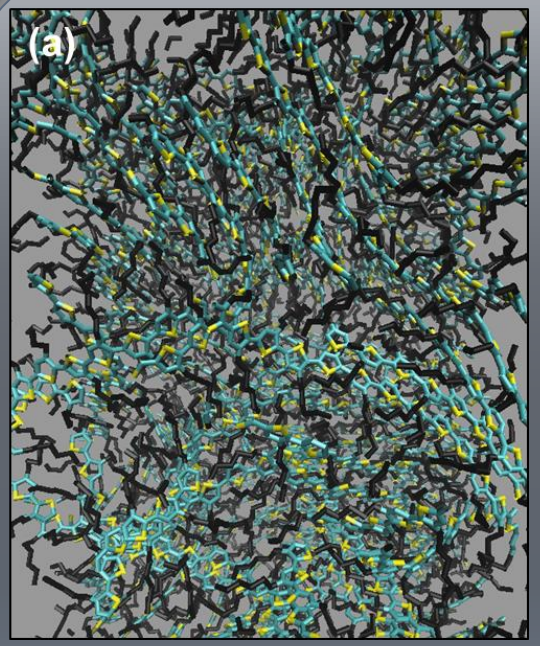


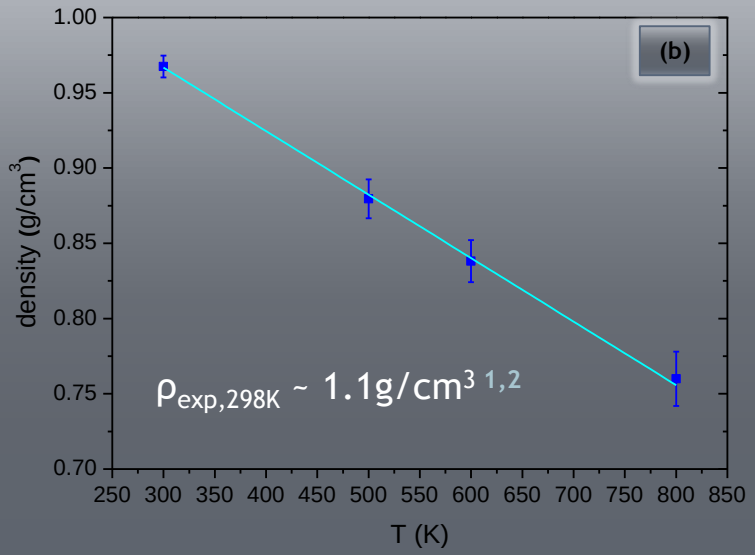
(a) Final configuration of the 3hexyl-20thiophene amorphous system after annealing the crystal at a high temperature (800K). (b) The autocorrelation function of the end-to-end unit vector in the course of the MD annealing process of the 3hexyl-20thiophene amorphous system at 800K and (c) the evolution of the instantaneous value of the mean square end-to-end distance of the 20-3HT backbone at the same temperature

- Several configurations from the equilibrated part of the MD annealing trajectory (Fig. 8b) served as starting points for executing gradual coolings

SIMULATION PREDICTIONS (Amorphous phase)

✓ *Semi-crystalline transition*





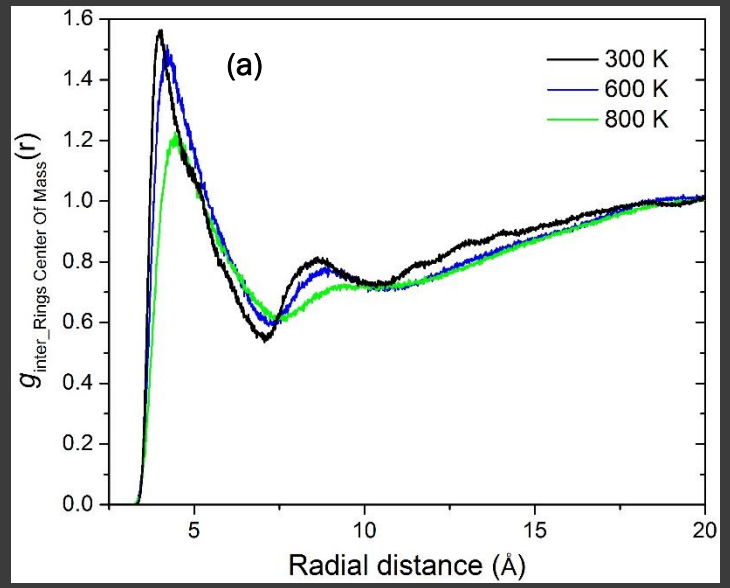
(a) Semi-crystalline structure of the 3hexyl-20thiophene at 300K acquired at the end of the gradual cooling process. (b) The density of the 20-3HT melt (averaged over all sets of coolings) as a function of simulation temperature

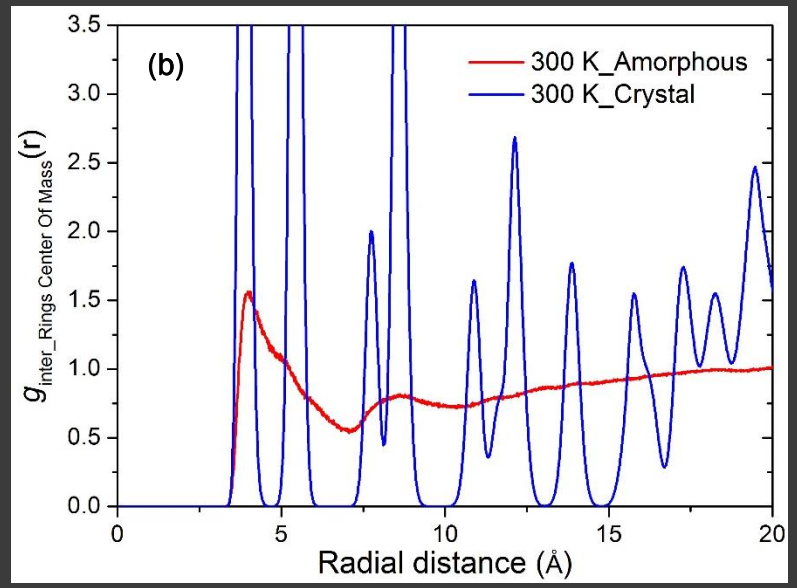
- Cooling at 300K causes the initial, disordered structure of the 20-3HT polymer (a) to start exhibiting signs of crystallization (indicative of the formation of a semi-crystalline system)

1. Mardalen, J.; Samuelsen, E. J.; Gautun, O. R.; Carlsen, P. H. Solid State Communications **1991**, 77, 337.
2. Marchant, S.; Foot, P. J. S. Polymer **1997**, 38, 1749.

SIMULATION PREDICTIONS (Amorphous phase)

✓ *Radial distribution functions*



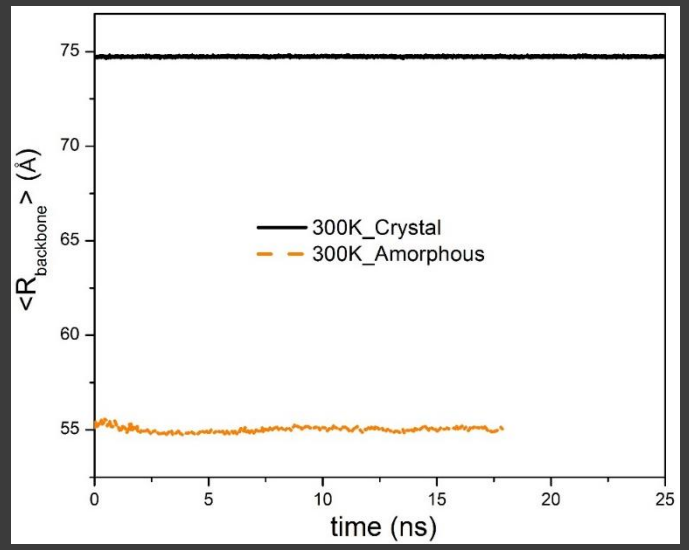


Radial distribution functions of the amorphous 20-3HT system during the MD runs at 300K, 600K and 800K of (a) the center-of-mass of rings belonging to different chains. (b) Comparison of the ring center-of-mass RDF between the pure crystalline and the pure amorphous phases of P3HT at 300K

- Shift to smaller distances of the nearest neighbors with decreasing T
- More pronounced intensity peak at 300K
- Peak forming at higher distance at 300K reflects a transition to a structured glassy state

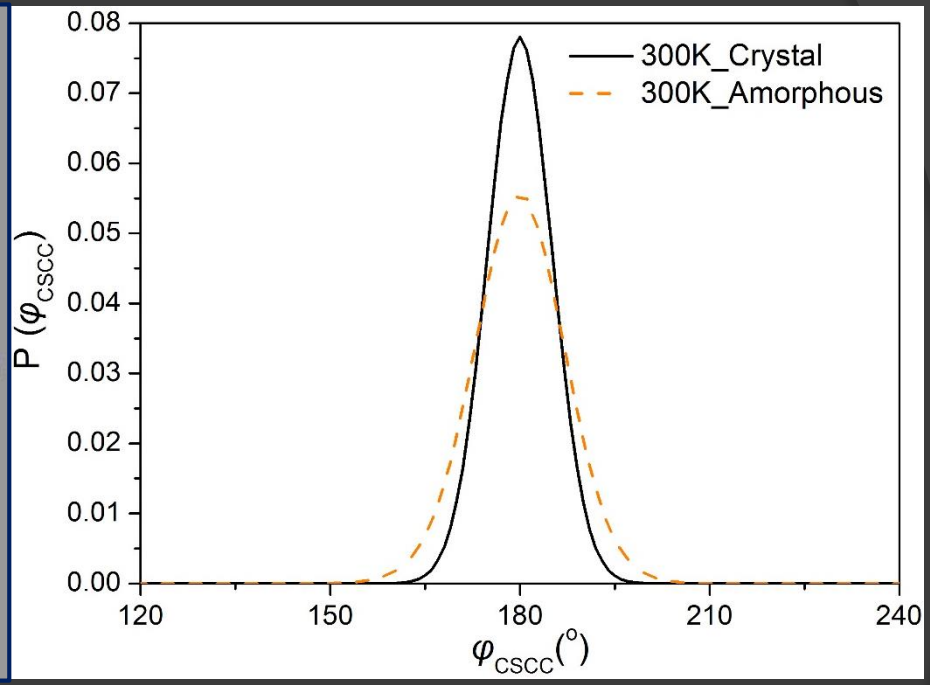
SIMULATION PREDICTIONS (Amorphous .vs. Crystal)

✓ *Chain dimensions in ambient conditions*



Evolution of the instantaneous end-to-end distance of the 20-Ring long backbone for the pure crystalline and amorphous phases of the 20-3HT polymer at 300K

- Chains are appreciably bend in the amorphous phase
- Rod-like chains in the Crystal-state

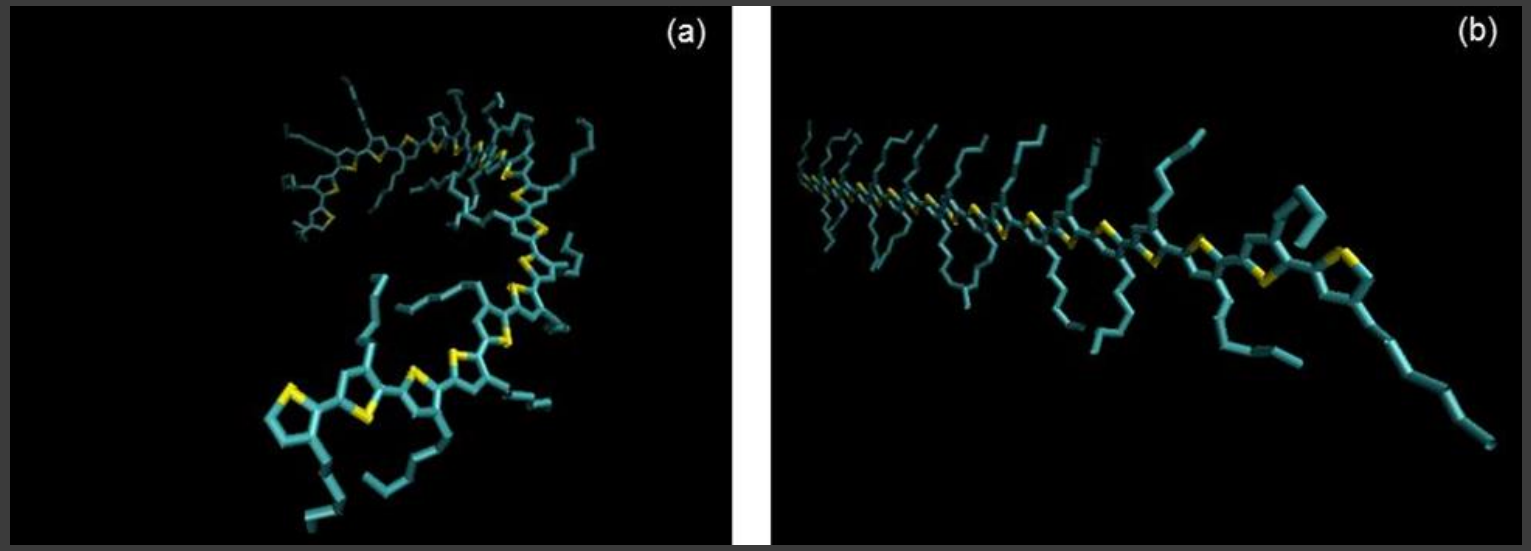


Distribution of the **CSCC** dihedral for P3HT chains in the amorphous and crystalline domains at T=300K

- **CC** bond holds much less all-trans population in the amorphous phase than the crystalline one

SIMULATION PREDICTIONS (Amorphous .vs. Crystal)

✓ *Chain dimensions in ambient conditions*



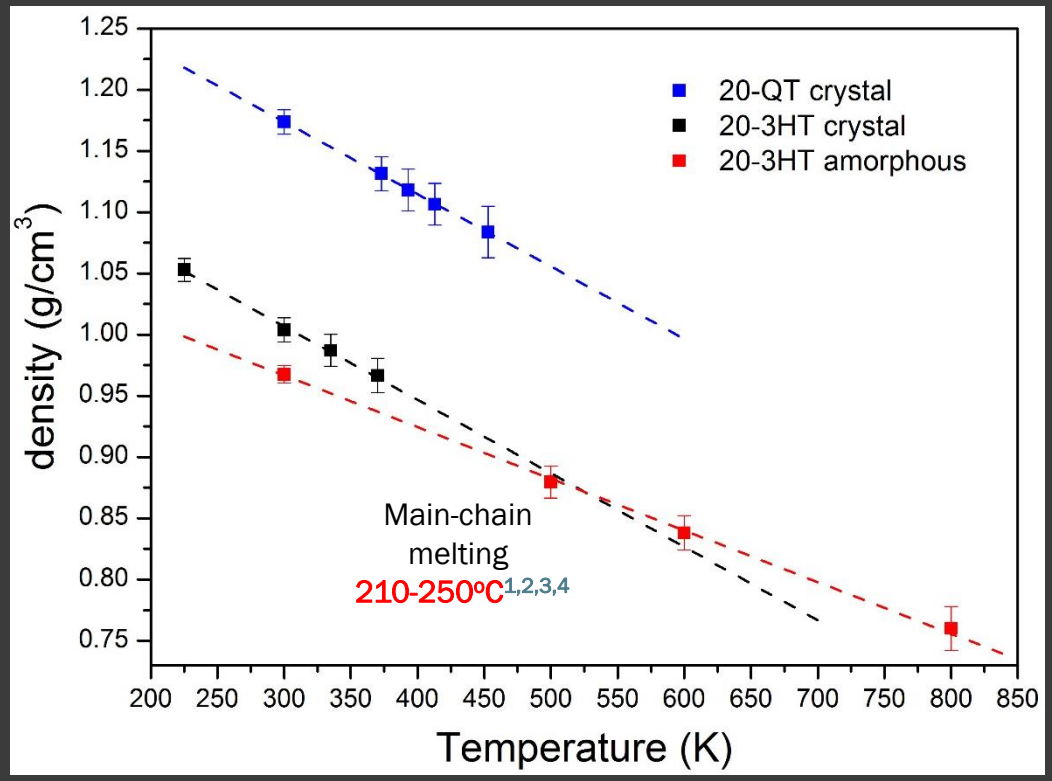
Typical configurations of two randomly selected (a) amorphous and (b) crystalline P3HT chains from our MD simulations with the **20-3HT** polymer at T=300K

- Chains in the amorphous state are quite bent
- The conjugation length is decreased significantly[1]

1. Crossland, E. J. W.; Tremel, K.; Fischer, F.; Rahimi, K.; Reiter, G.; Steiner, U.; Ludwigs, S. Adv Mater 2012, 24, 839

SIMULATION PREDICTIONS (Amorphous .vs. Crystal)

✓ *Temperature dependence of system's density*



The density of 20-QT and 20-3HT crystal and 20-3HT melt as a function of simulation temperature

- 20-QT crystal is denser than 20-3HT due to the interdigitation effect
- The fitting curves of ρ(T) for the pure crystal and pure amorphous phase of P3HT cross in the point which corresponds qualitatively to main-chain melting

1. Malik, S.; Nandi, A.K. J Poly Sci Part B Polym Phys **2002**, 40, 2073
2. Hugger, S.; Thomann, R.; Heinzel, T.; Thurn-Albrecht, T. Colloid Polym Sci **2004**, 282, 932
3. Pascui, O.F.; Lohwasser, R.; Sommer, M.; Thelakkat, M.; Thurn-Albrecht, T.; Saalwachter, K. Macromolecules **2010**, 43, 9401
4. Wu, Z.; Petzold, A.; Henze, T.; Thurn-Albrecht, T.; Lohwasser, R.H.; Sommer, M.; Thelakkat M. Macromolecules **2010**, 43, 4646

PERSPECTIVES

➢ Publication

"All-atom molecular dynamics simulation of temperature effects on the structural, thermodynamic and packing properties of the pure amorphous and pure crystalline phases of regioregular P3HT"

Orestis Alexiadis and Vlasis G. Mavrantzas
Macromolecules, **2013**, 46 (6), pp 2450–2467

➢ In the short term

- Complete MD simulations for PQT system
- In detail comparison of the morphological properties and local structure of P3HT and PQT in both Pure Phases

➢ Simulation of fully semi-crystalline Rr-P3HT samples

- Complete the implementation of an atomistic Monte Carlo algorithm capable of predicting morphology in model P3HT systems with realistically large MWs
- Generation of structures containing both amorphous and crystalline regions (i.e., a semi-crystalline material)
- Configurations borrowed from these MC studies will then be used as input to subsequent all-atom MD studies to fine-tune chain packing

◎ THANKS FOR YOUR ATTENTION