Polymeric Semiconductors: Molecular Ordering, Charge Transport and Macroscale Mobility

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Georgia Institute of Technology

An Introduction to Georgia Tech

One of the **oldest** ChBE programs in the US

Founded in 1901

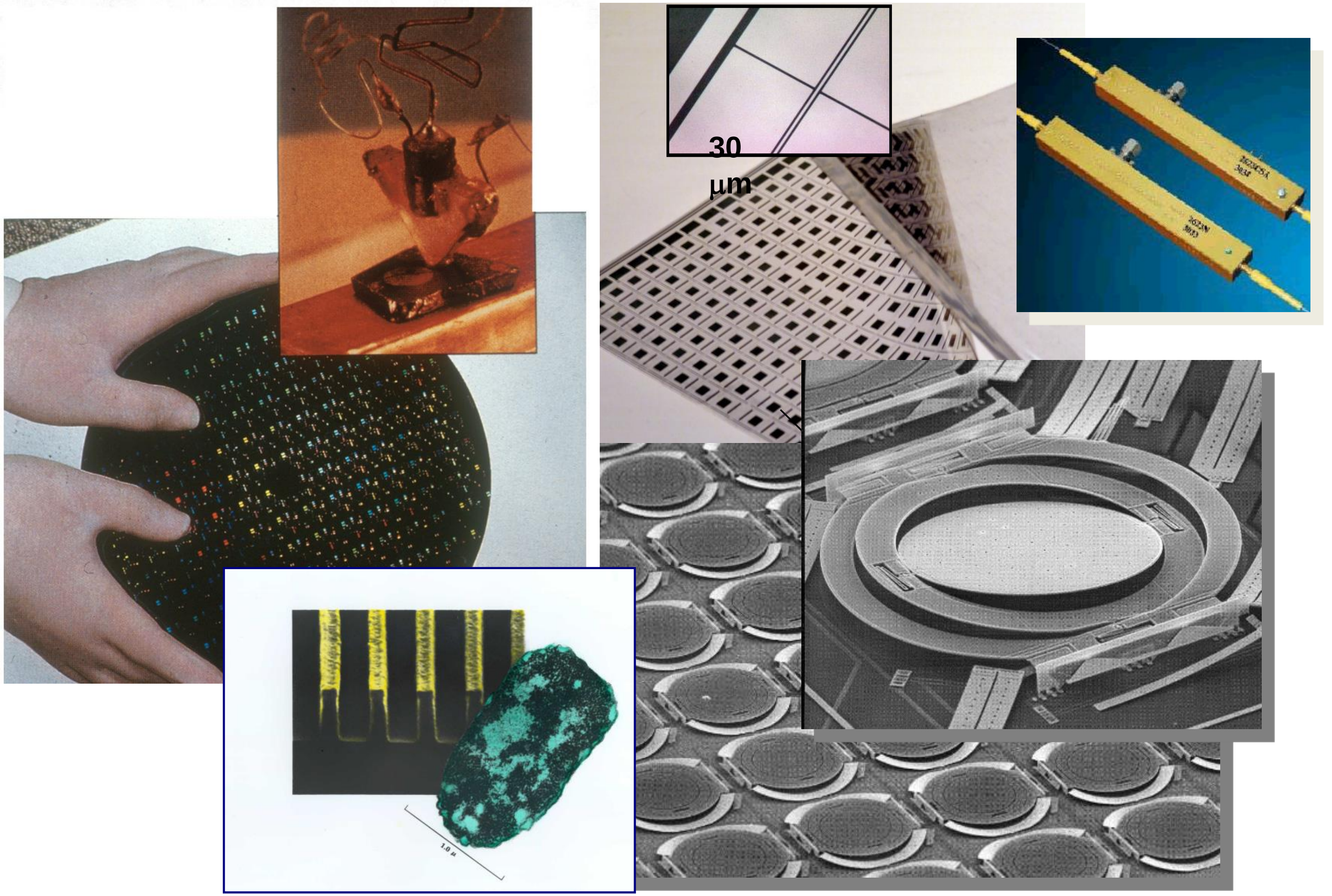
One of the **largest** ChBE programs in the US

215+ Graduate students
900+ Undergraduate students
45 Faculty

One of the **most respected** ChBE programs in the US

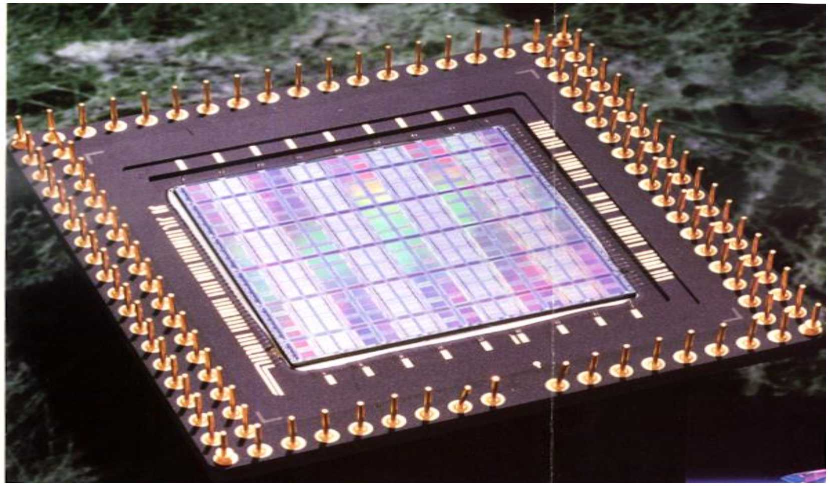
Undergraduate and Graduate Programs ranked in top 10
College of Engineering ranked in top 5 internationally

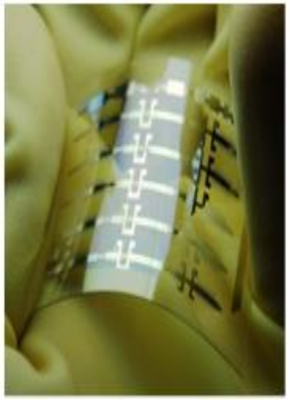
Polymers in Electronics and Photonics



Materials and Processes

- Lithographic materials and processes
  - Silicon device processing
- Dielectric materials (low and high-k)
  - Packaging materials
- Organic semiconductor materials for plastic electronics
  - Active device layers





‘All-Printed’ Plastic Electronics

Silicon based semiconductor technology today:

- Conducted in ***$5B+*** Fabs (clean rooms a must!)
- Features smaller than 30 nm
- Rigid, inflexible 12” diameter substrates
- Subtractive processing

All-printed plastic electronics alternative:

  – Using cost-effective printing presses, or even ink-jet printers
  – Large-area, reel-to-reel processing
  – Flexible, conformable, bendable plastic and paper-like substrates
  – Additive,’ink-like’ processing

Semiconductor Mobility Magnitudes (cm²/Vs)

Semiconductor	Mobility
Silicon single crystal	>1,000
Polysilicon	100
Amorphous silicon	0.1-1
Single nanotube	100-1,000
Organic single crystal	*10*
Pentacene film	*1-10*
Polycrystalline sublimed organic	*0.01-10*
Soluble oligomer/polymer	*0.01->1*

Advantages of Organics

- mobilities can be more uniform, and less limited by surface states and grain boundaries
- covalent integration with molecular receptors for sensors
- moderate temperature processing
- large area coverage, solution deposition possible
- mechanical and thermal compatibility with plastic and other flexible substrates
- rational control of polarity and threshold voltage, for circuit tuning and memory applications

Charge Transport in Organic Semiconductors:

Needs:

Materials Issues

Increased electrode conductivity
Increased semiconductor mobility
Improved gate dielectric

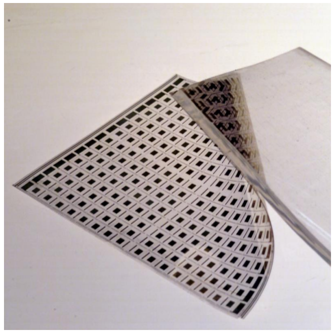
Device Issues

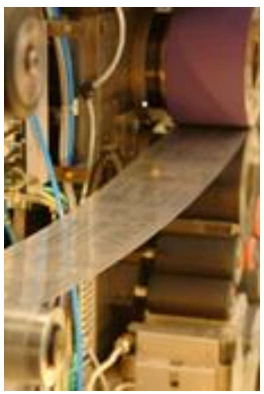
Decreased conductor resistivity:
understand mechanism
Control of carrier transport in organics
Control of FET properties:
effect of impurities, charge traps, etc
Charge injection

Process Issues

Identify critical limiting bulk/surface
Improved semiconductor properties
Control of thin film morphology

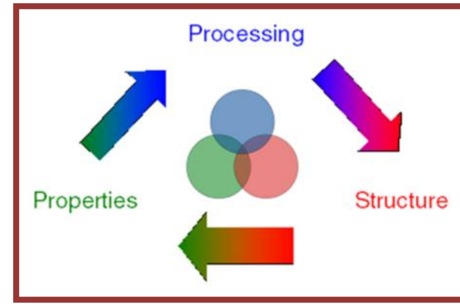
Polymers in Electronics and Photonics

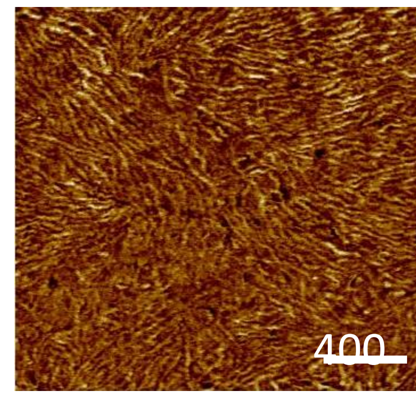


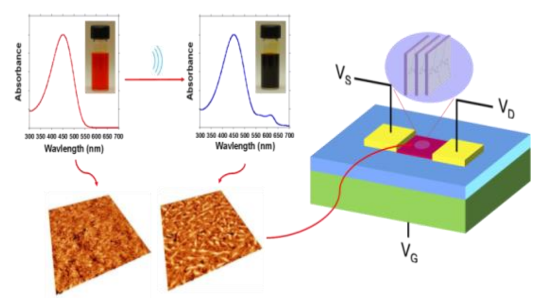


Polymer/hybrid materials and processes for *plastic electronics and photovoltaics:*

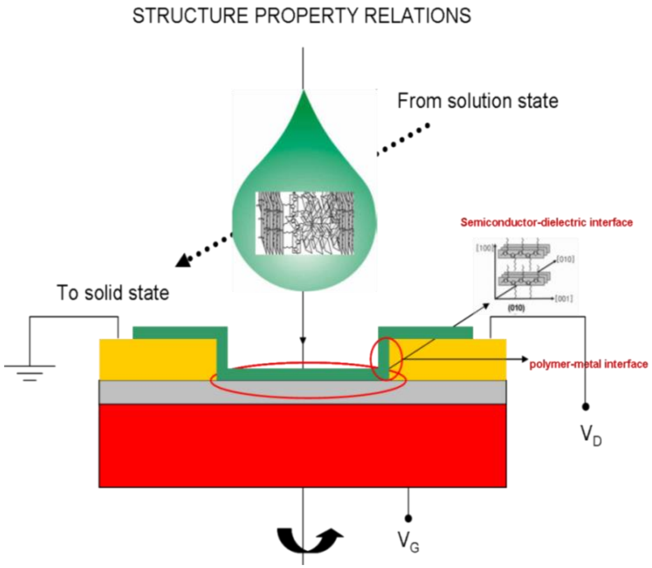
- *Design and development of new materials chemistries*
- *Develop structure-process-property relationships to guide robust materials and process design*
- *Understand and utilize mechanisms associated with thin-film morphology evolution.*

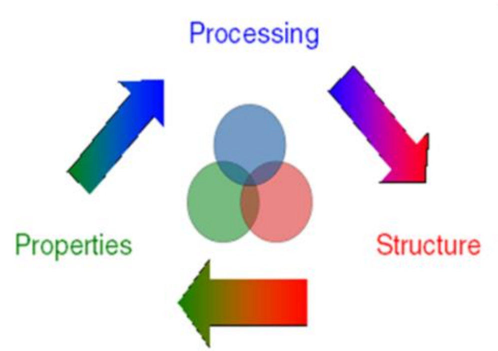


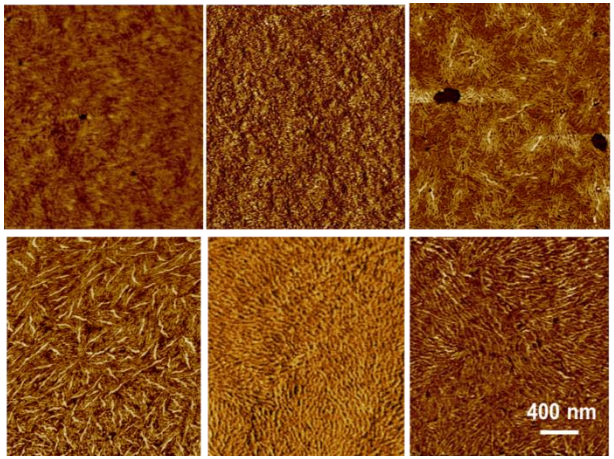




Order and Disorder







MECHANISM OF CONDUCTING CHANNEL FORMATION

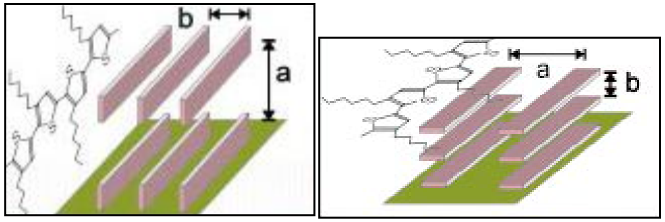
CONTROL OF MICROSTRUCTURE

ROLE OF CRYSTALLINITY

CONJUGATION EFFECTS: INTRA- VS INTER-CHAIN

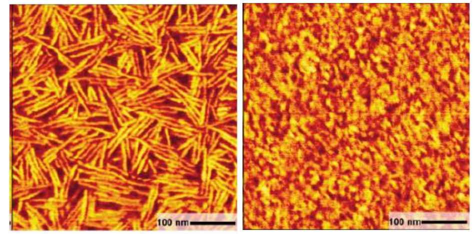
- Semiconducting polymer properties strongly dependent on *final* thin film morphology (microstructure).
  - highly process dependent
- Microstructure development *during film formation* not well understood

Role of Microstructure



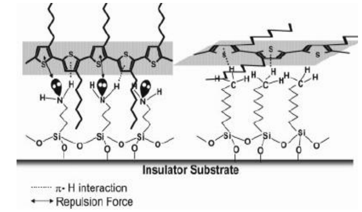
Sirringhaus et.al. Nature 1999, 401, 685.

Regioregularity dependent texture



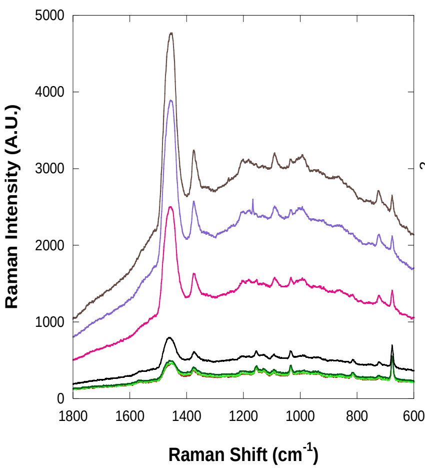
Kline et.al., Adv. Mater. 2003, 15, 1519.

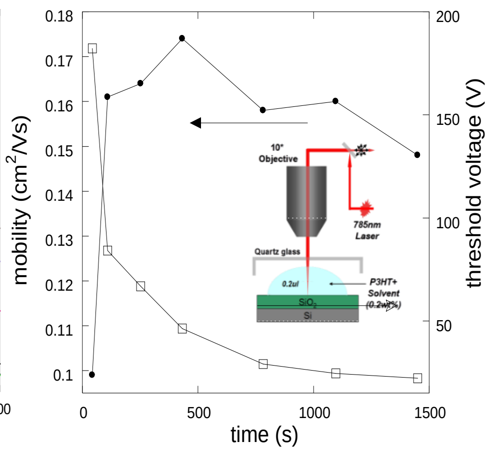
Effect of polymer MW



Kim et.al., Adv. Func. Mater. 2005,15, 77

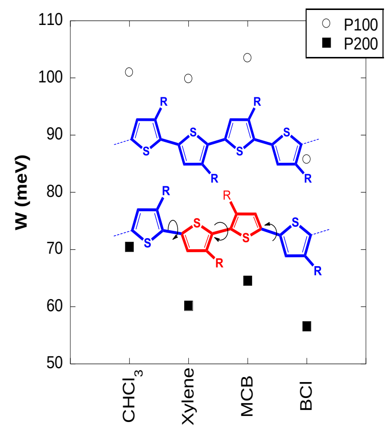
Semiconductor-dielectric interface

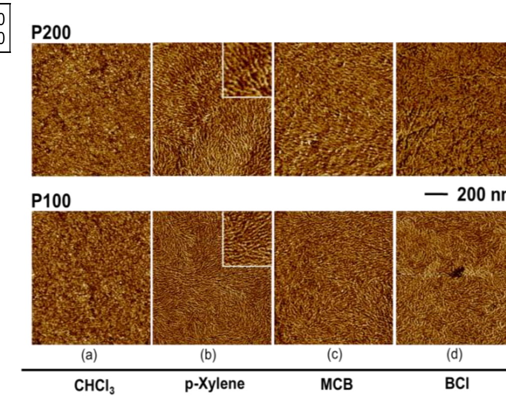




J. Am. Chem. Soc. 2011, 133, 7244.

J. Phys. Chem. C 2011, 115, 11719.

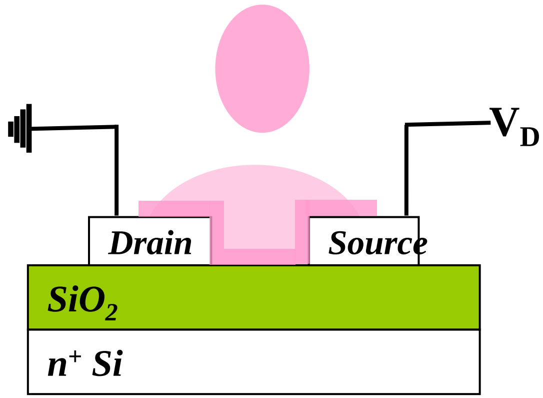


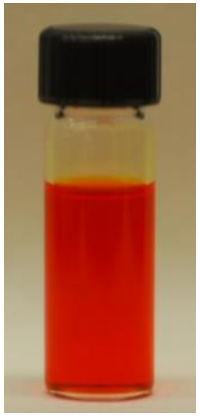


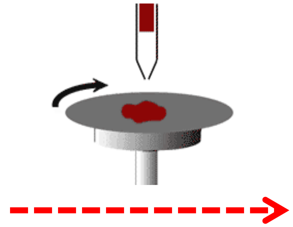
** Aiyar, et al., Chem, Mater. 2012*

- ❑ What is the role of microstructure?
- ❑ How can microstructure be *tuned*?

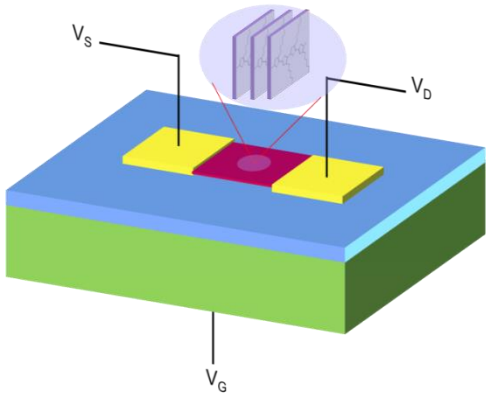
Conducting Channel Formation

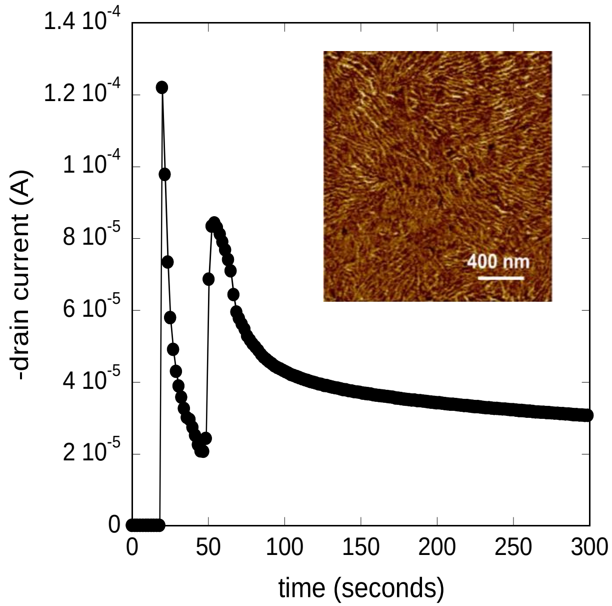






Intermediate phase transitions?

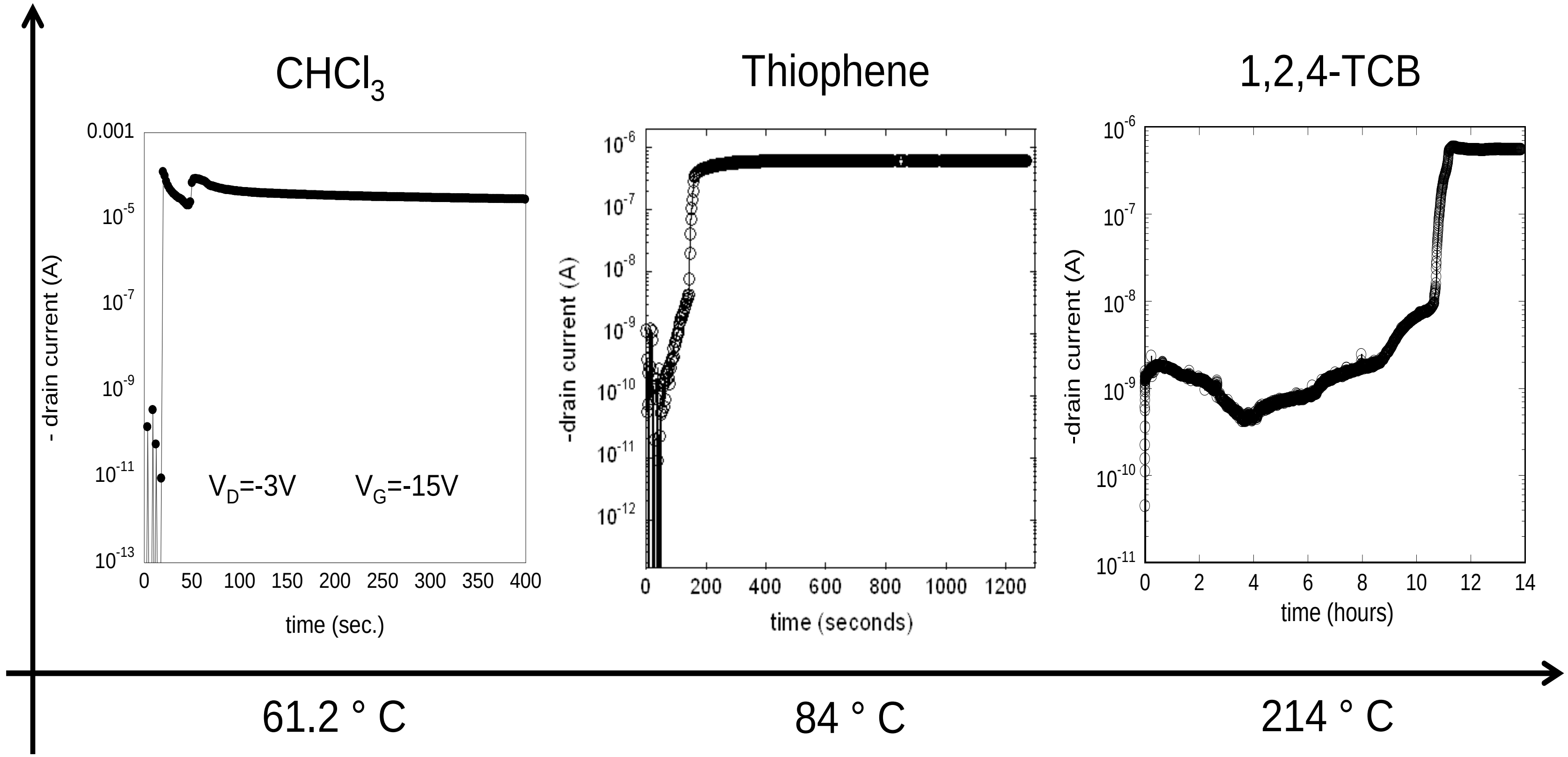




**in chloroform*

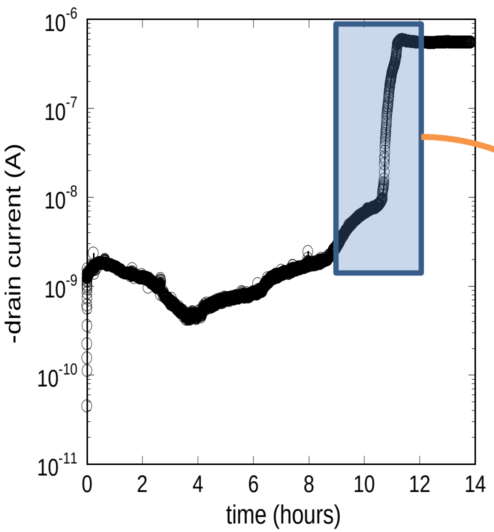
- Drain current fluctuates *during* film formation
- Polymer chains rearrange as a function of time: percolation effects
- Bulk vs interface effects
- Evolution of microstructure?

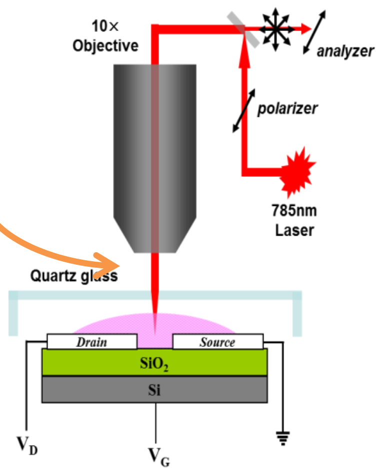
Extending Solvent Evaporation Time

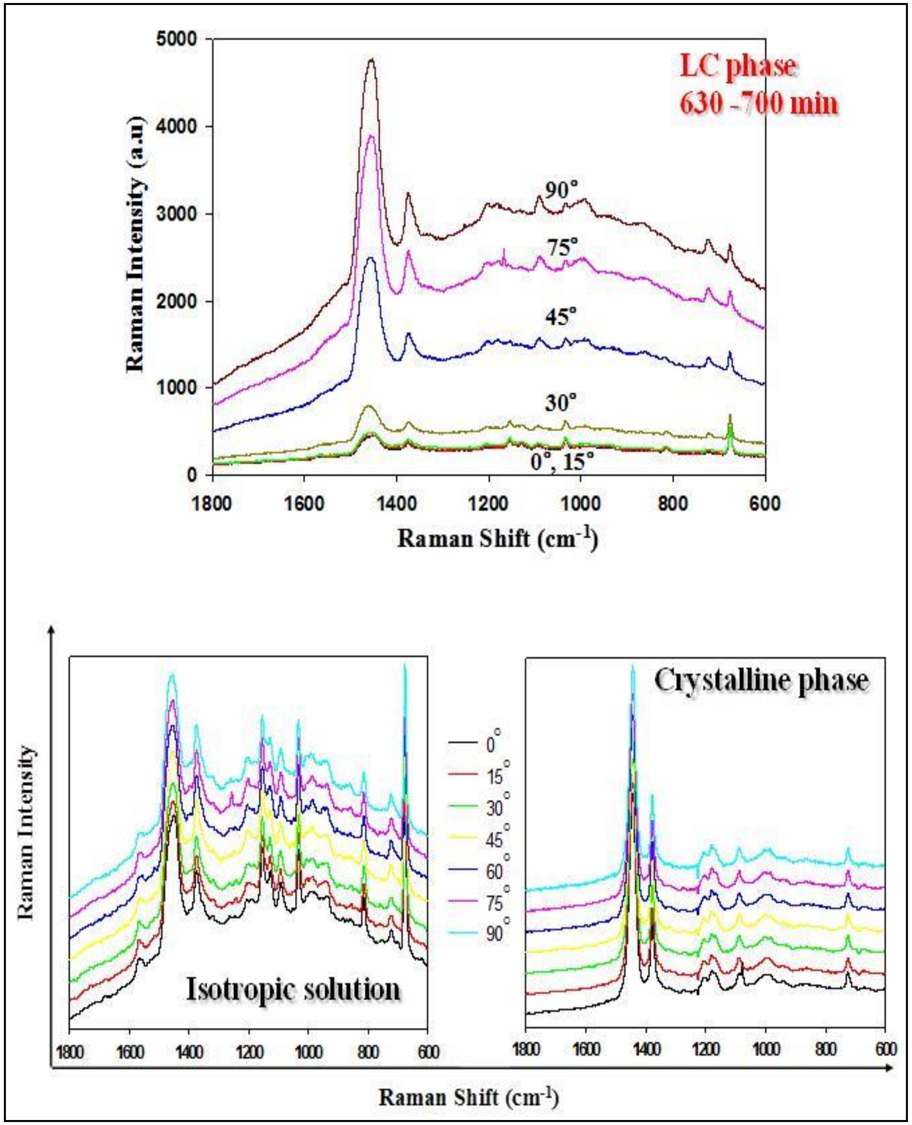


- Time required for conducting channel formation scales with solvent evaporation rate
- As evaporation proceeds, polymer concentration increases - percolation

Correlation with Structure?



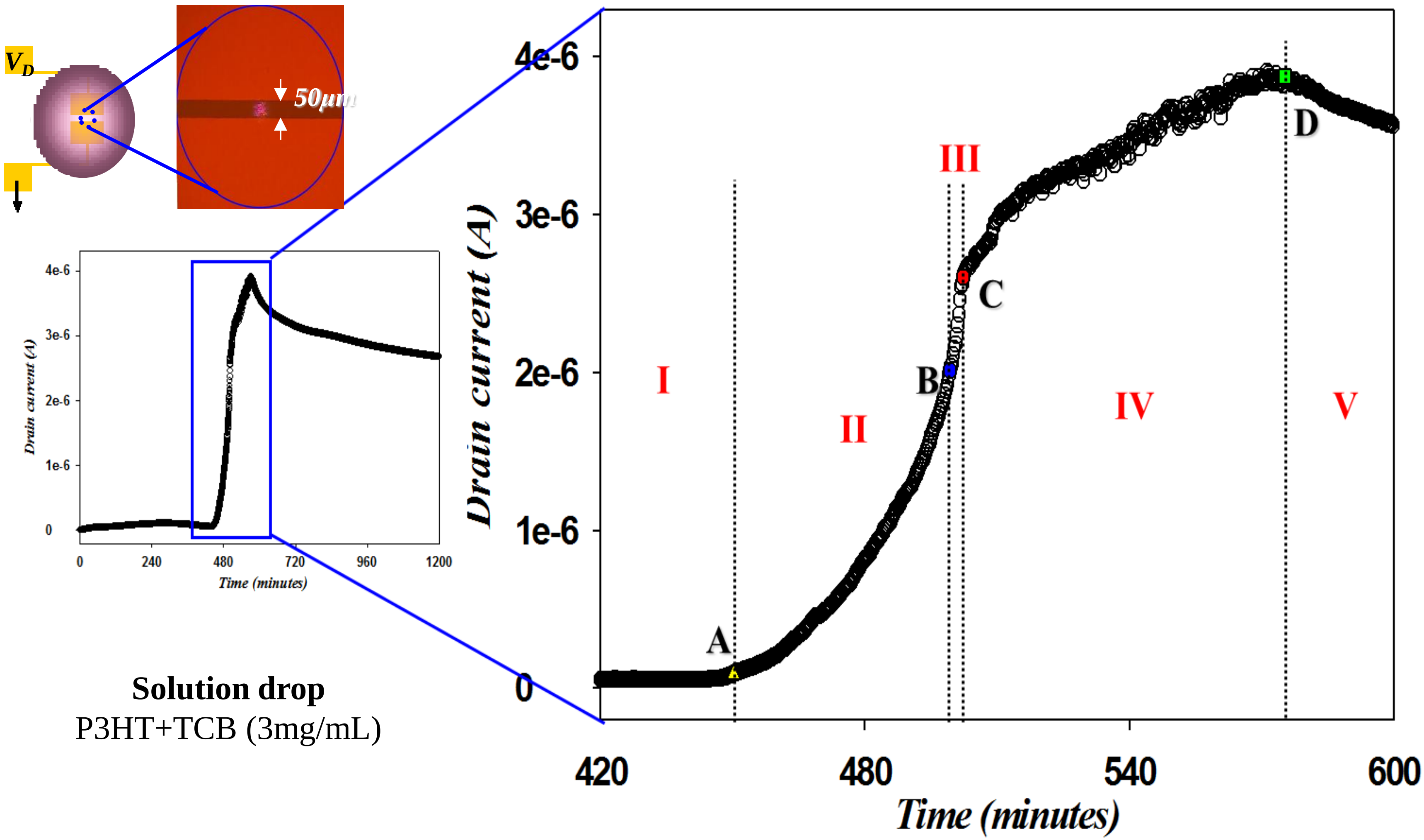




- Lyotropic LC phase coincident with sharp increase in current
- Long range order in LC phase
  - **Potential consequences for macroscopic charge transport**

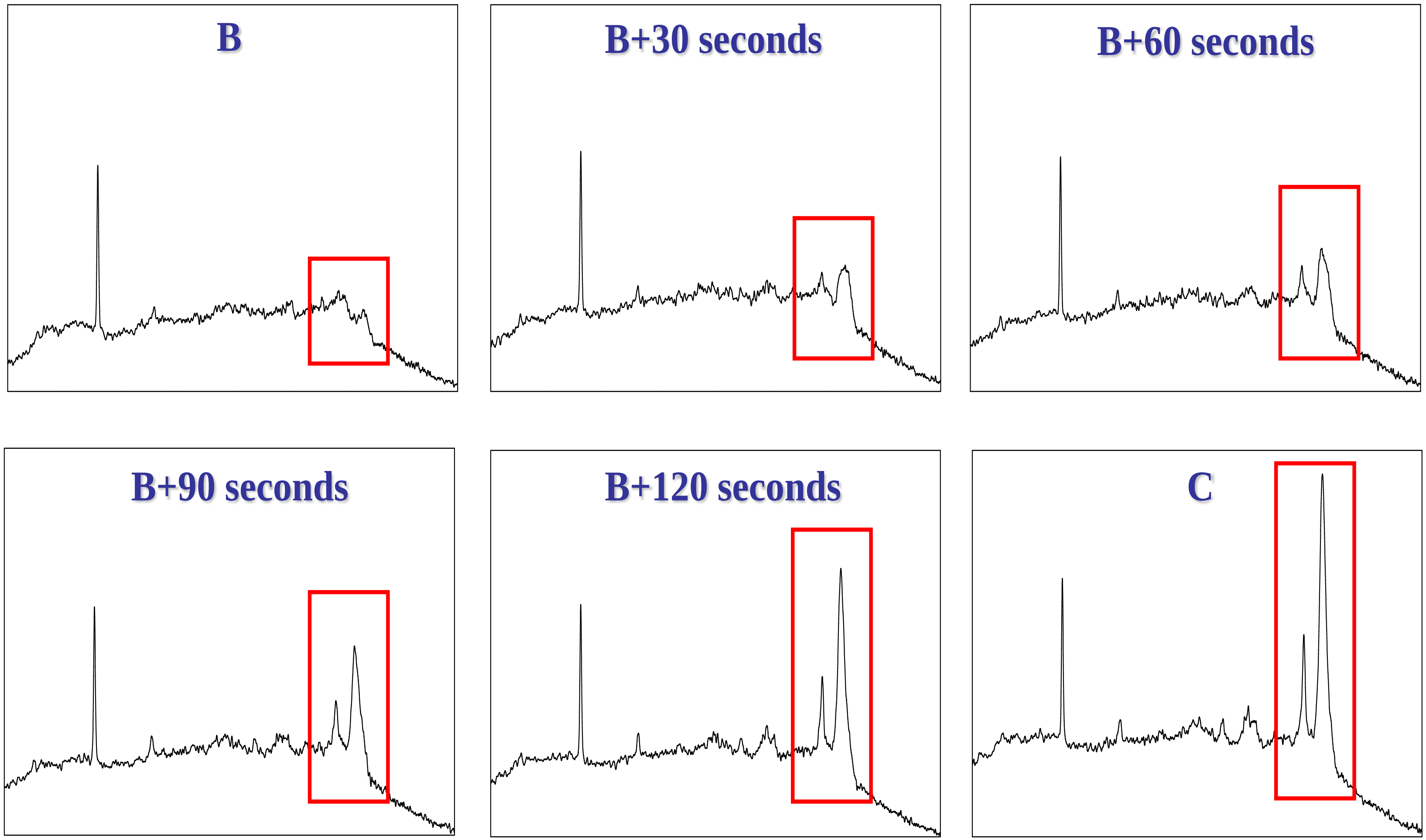
J. Am. Chem. Soc. 2011, 133, 7244.

Sharp Onset of the Drain Current



Solution drop
P3HT+TCB (3mg/mL)

Raman Spectral Changes

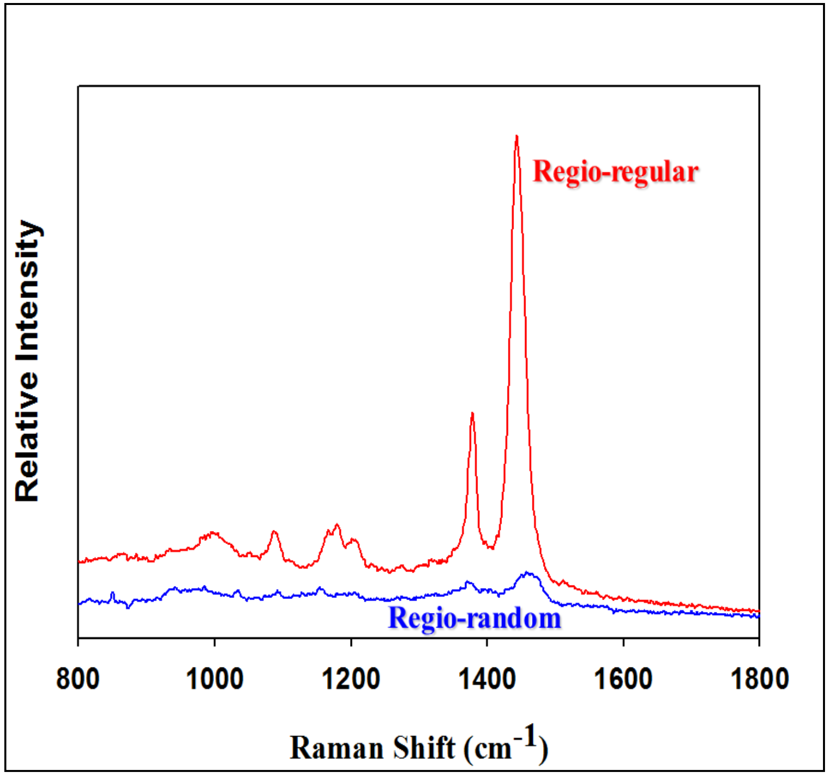


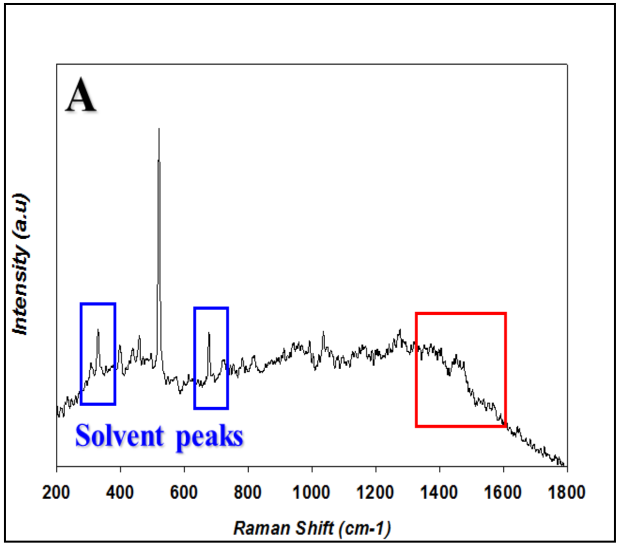
Crystalline vs Amorphous Phases

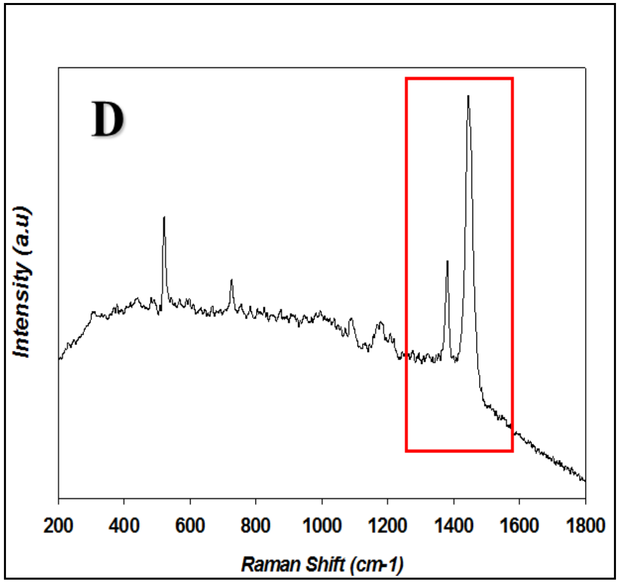
Raman spectroscopy:

regio-regular P3HT (Semi-crystalline) vs.

regio-random P3HT (Amorphous)

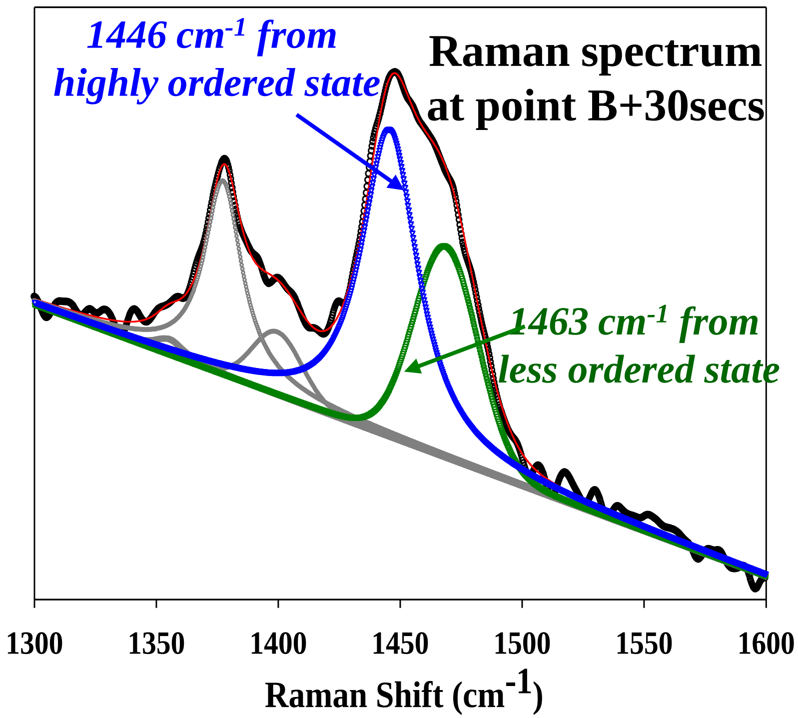


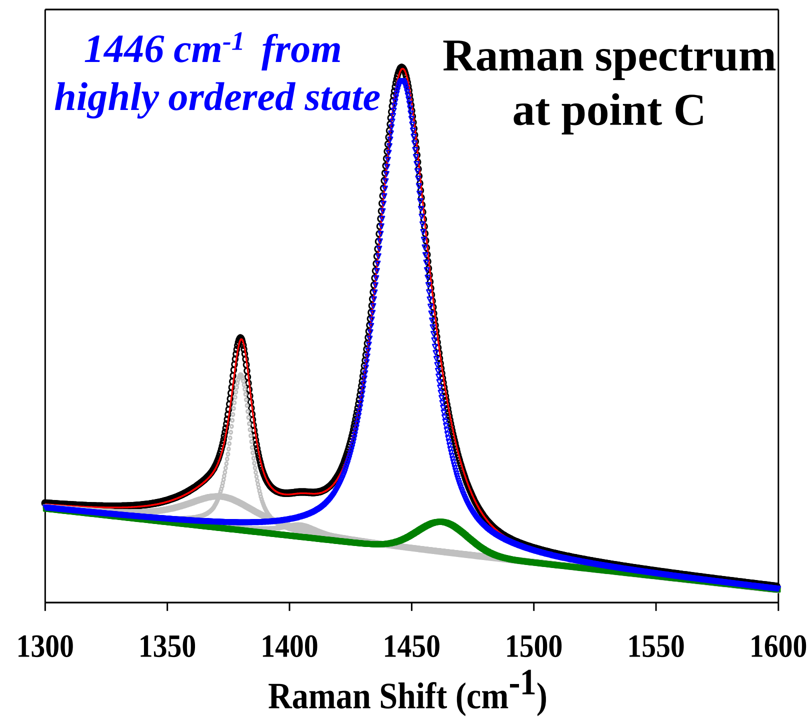




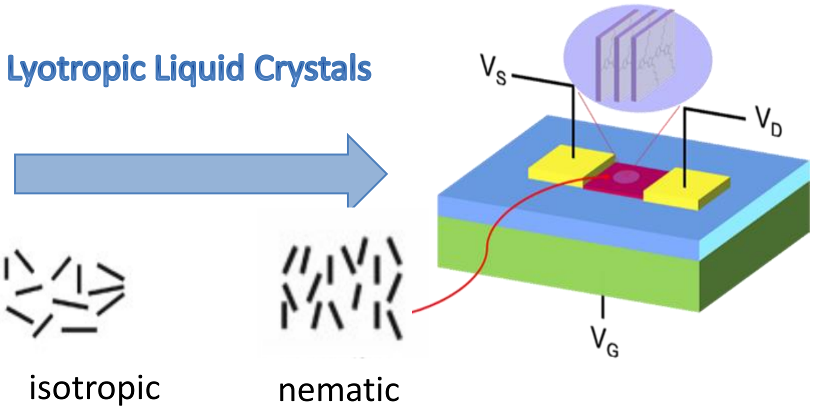
Evolving Microstructure

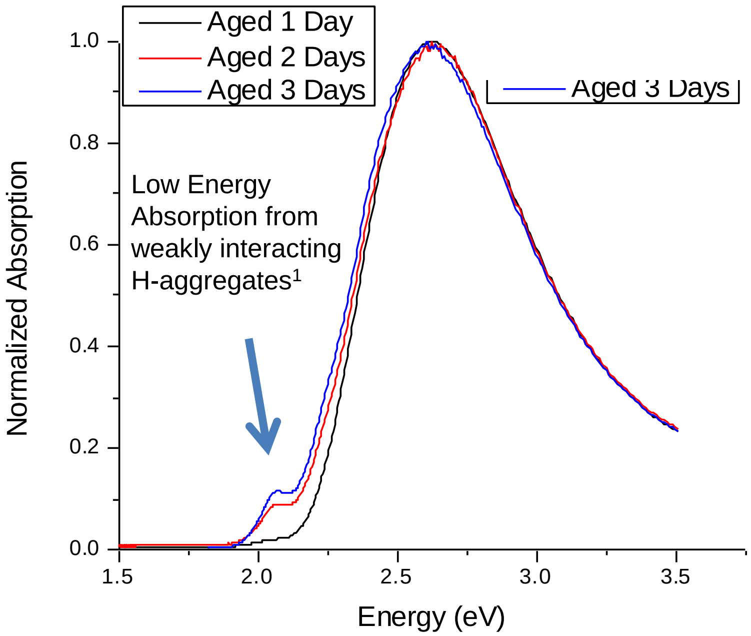
- Asymmetric peak shape evolves rapidly into a symmetric profile
  - Rapid nucleation and crystallization of P3HT chains

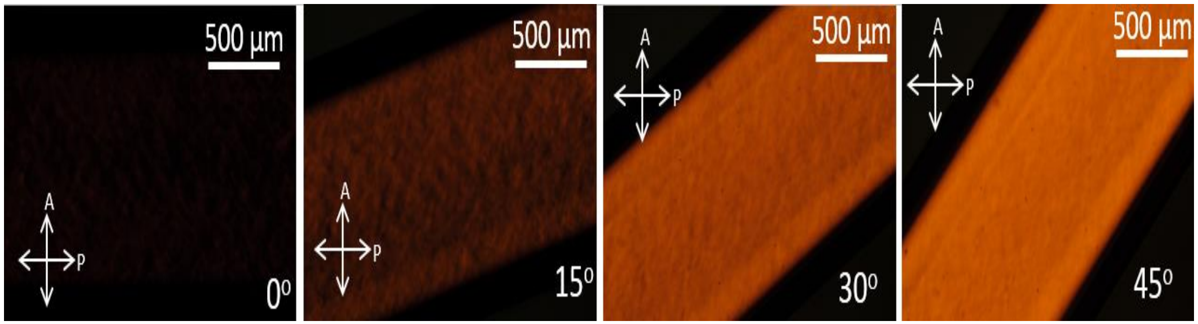




Liquid Crystal Poly(3-hexylthiophene) Solutions

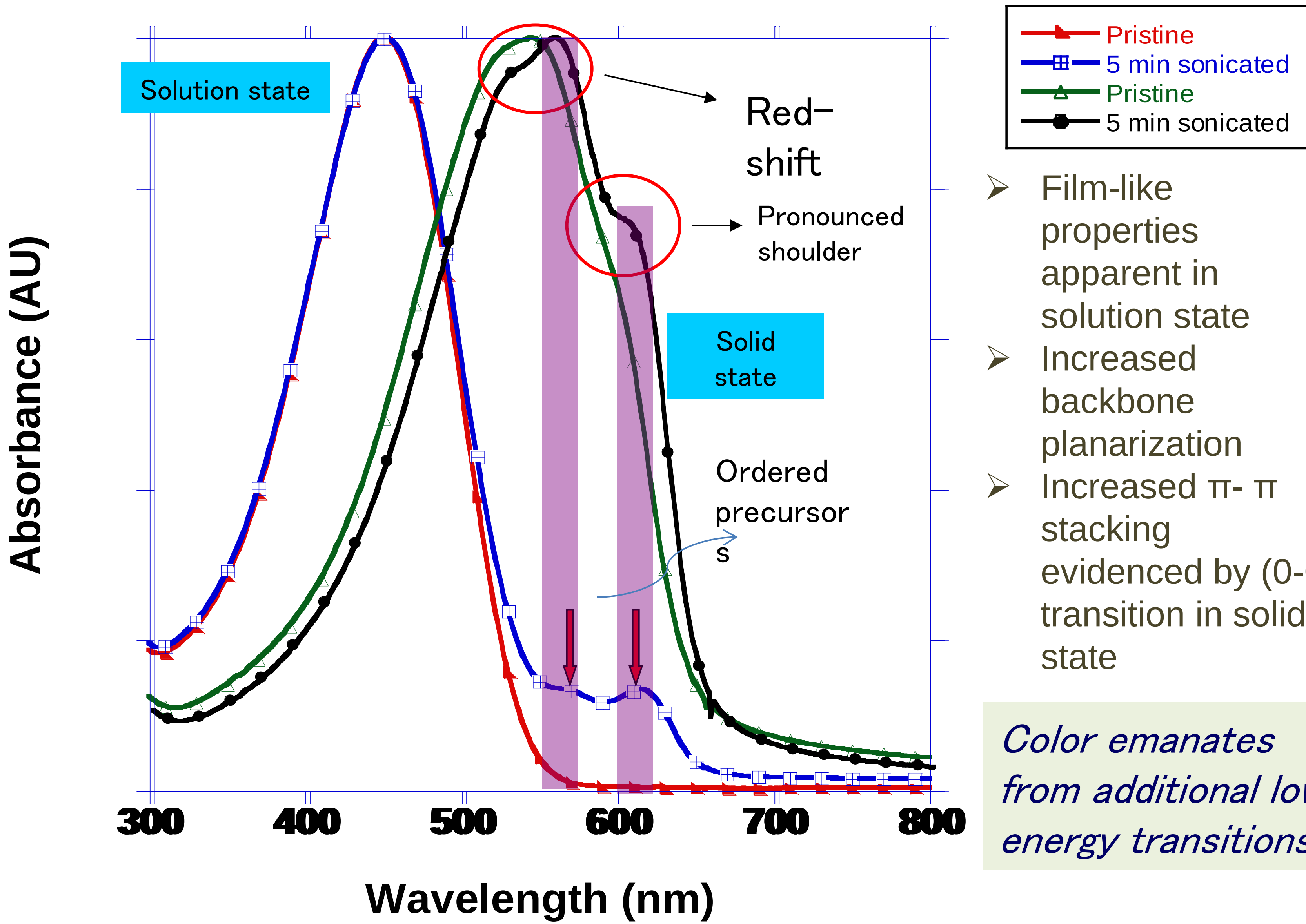






Polarized Optical Microscopy of aged P3HT solutions show long-range order and monodomain character

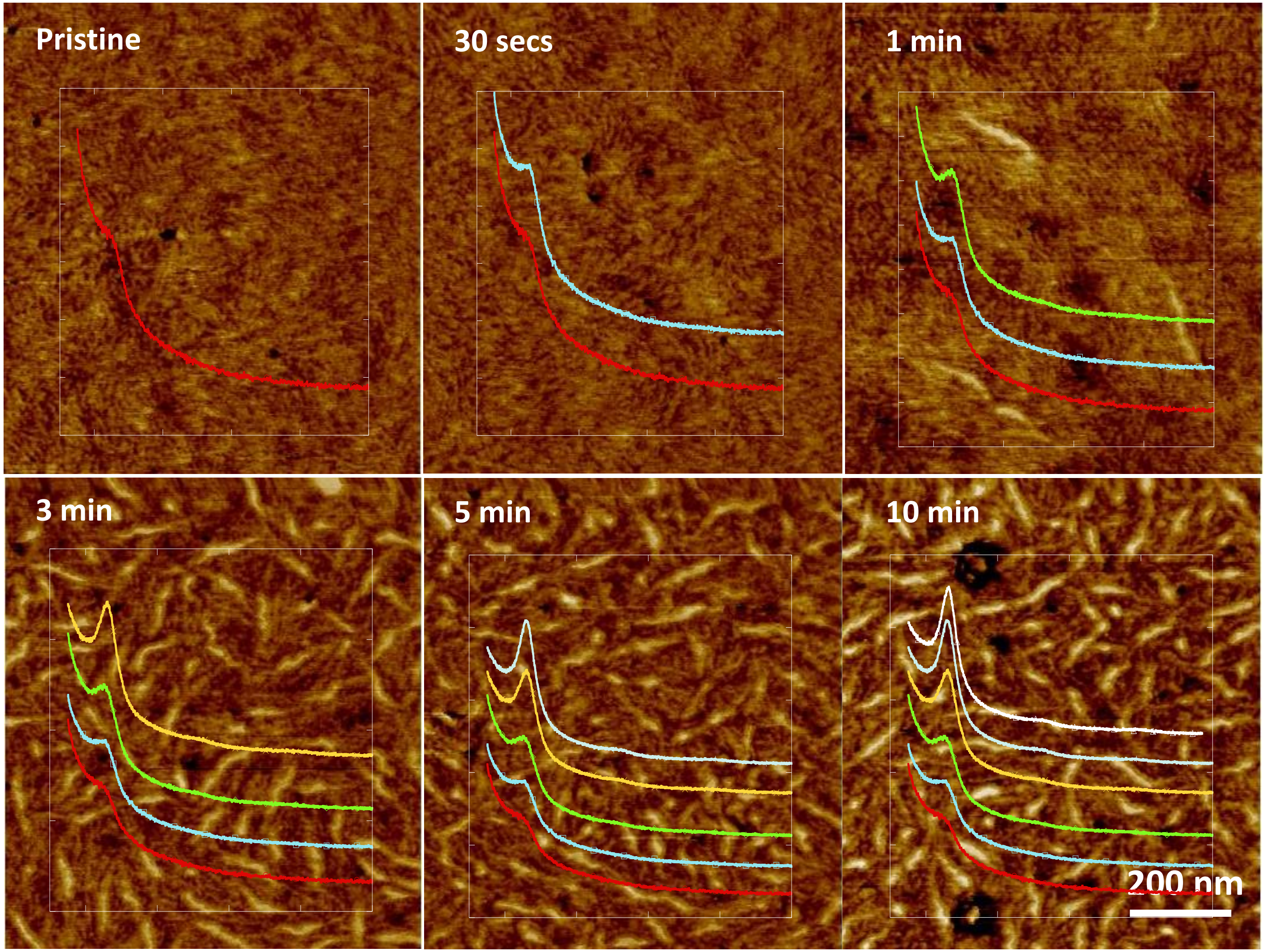
Processing: Ultrasound Induced Effects



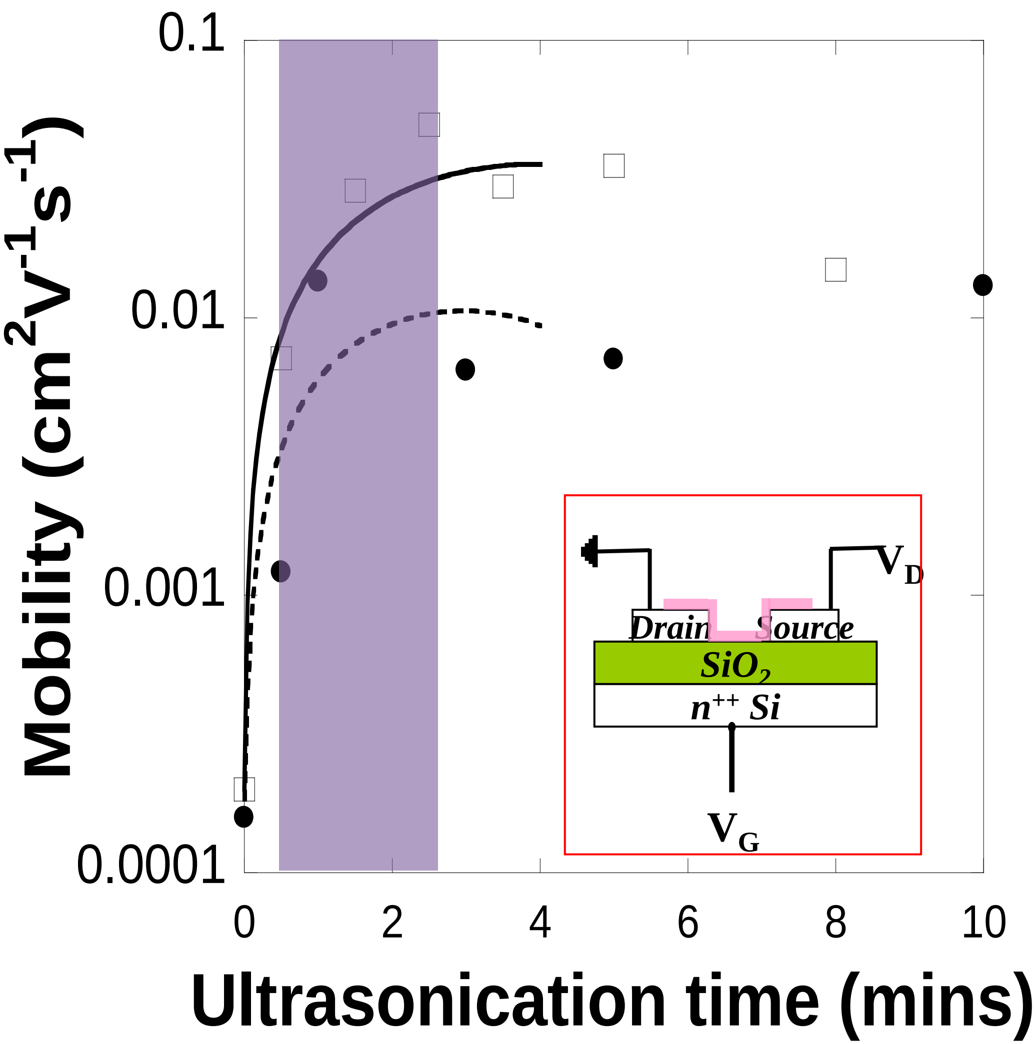
- Film-like properties apparent in solution state
- Increased backbone planarization
- Increased π- π stacking evidenced by (0-0) transition in solid state

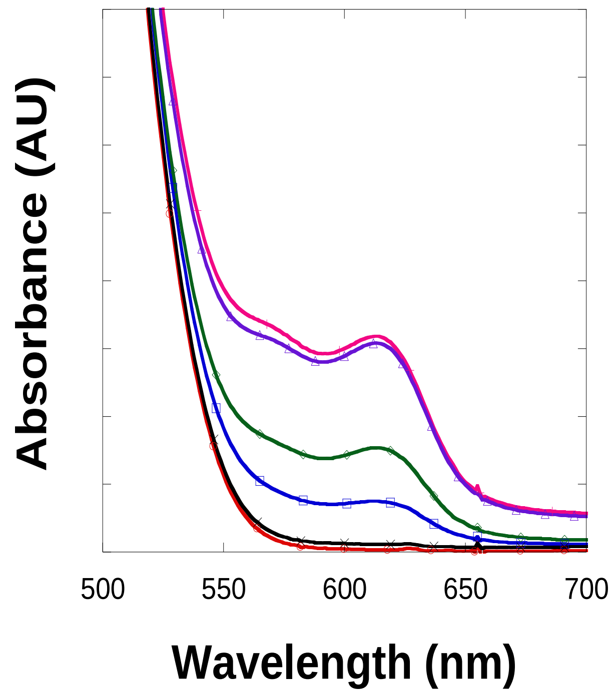
Color emanates from additional low energy transitions

Microstructure and Crystallinity



Impact on Charge Transport

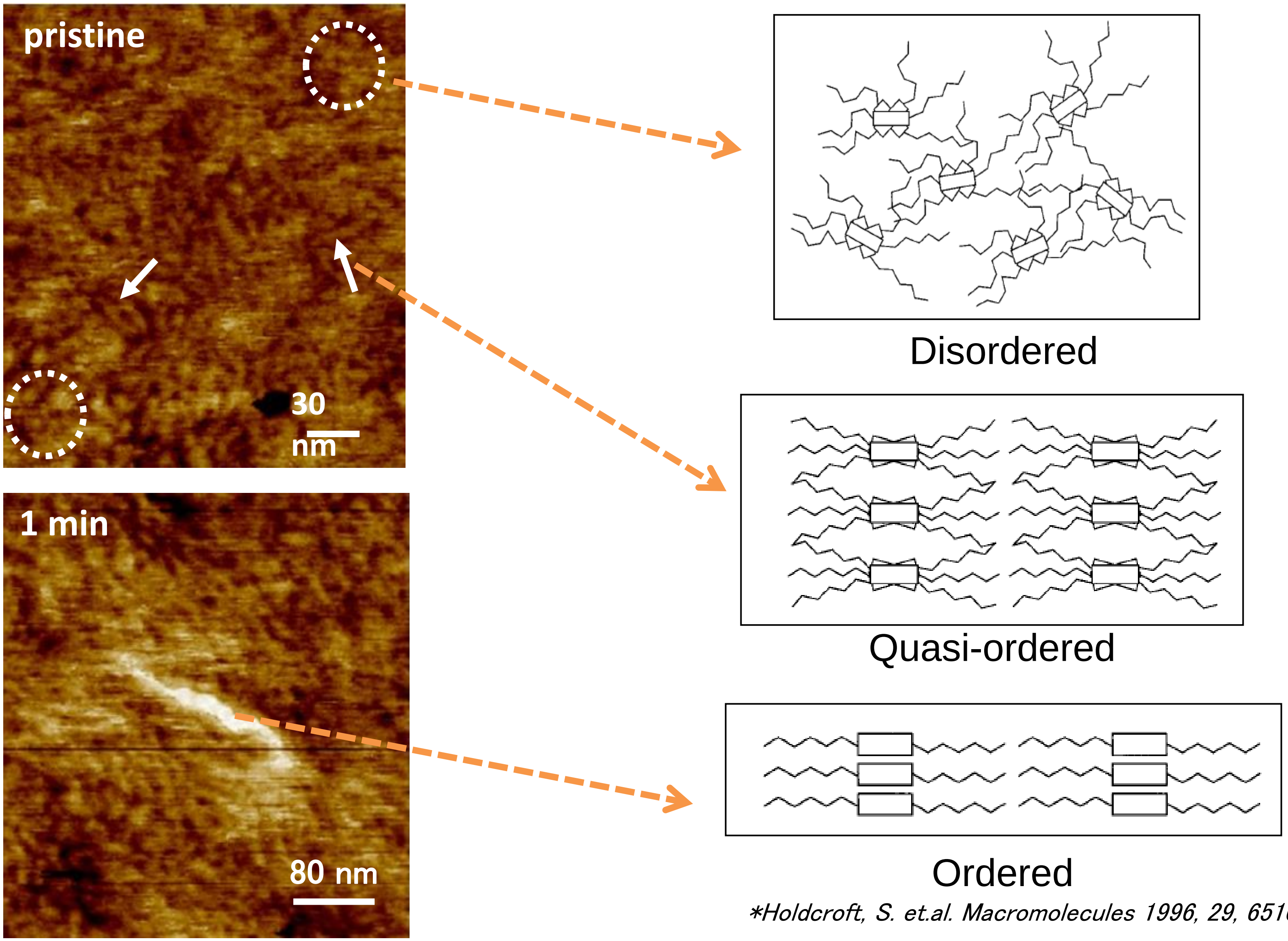




- Almost 2 order of magnitude increase in mobility
- Saturation of mobility beyond 1-3 mins sonication

Percolation type charge transport

Multiphase Morphology

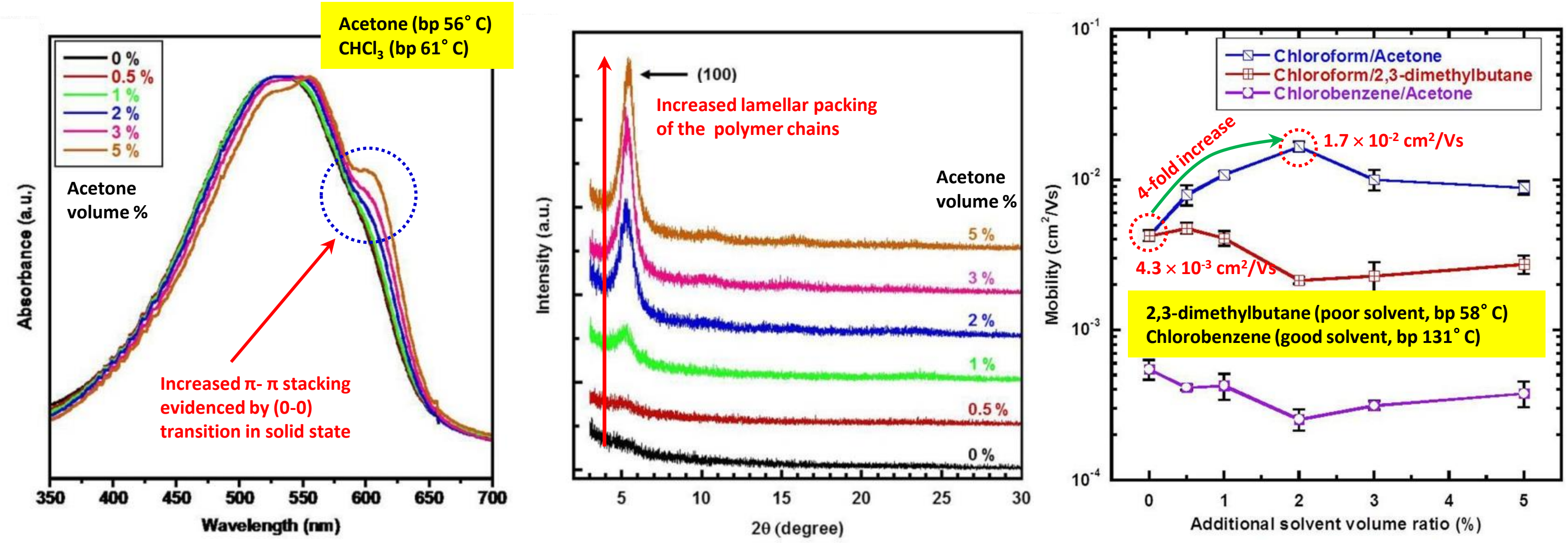


**Holdcroft, S. et.al. Macromolecules 1996, 29, 6510.*

Solvent Characteristics and Molecular Ordering

Impact of binary solvent:

- **high volatility**
- **hydrogen bonds with the majority solvent**



M. Chang, et al, *ACS Nano*, 2013

Hansen Solubility Parameter Analysis

Solvents	P3HT (mg/ml)
Chloroform	> 5
Hexane	< 1
Dimethyl Sulfoxide (DMSO)	< 1
Dimethyl Formamide (DMF)	< 1
N-Methyl-2-Pyrrolidone (NMP)	< 1
Acetonitrile	< 1
Acetone	< 1
Cyclohexanone	< 1
Benzyl Alcohol	< 1
Tetrahydrofuran (THF)	1 – 3
o-Dichlorobenzen	> 5
p-Xylene	1 – 3
Methanol	< 1
Trichloroethylene	> 5
1,2,4-Trichlorobenzene	> 5
Chlorobenzene	> 5
Toluene	2 – 4
Carbon Disulfide	> 5
Diethyl Ether	< 1
Thiophene	> 5
Pyridine	< 1

< 5 mg/ml → Poor solvent assigned a value of "0"
> 5 mg/ml → Good solvent assigned a value of "1"

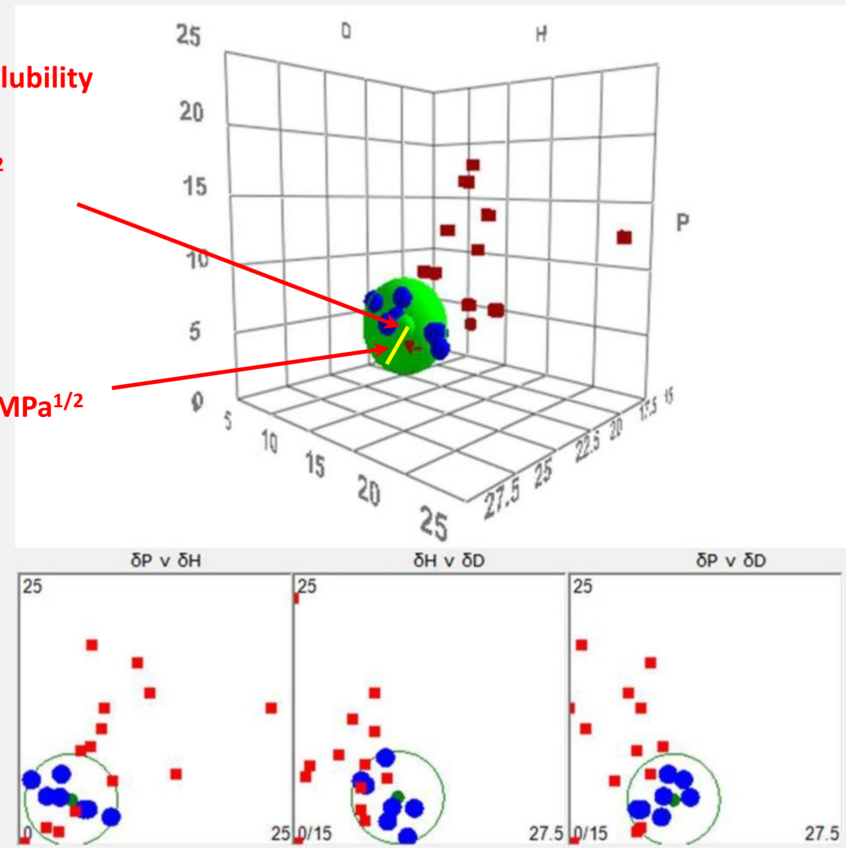
P3HT Hansen solubility parameters:

δ_D: 19.45 MPa$^{1/2}$

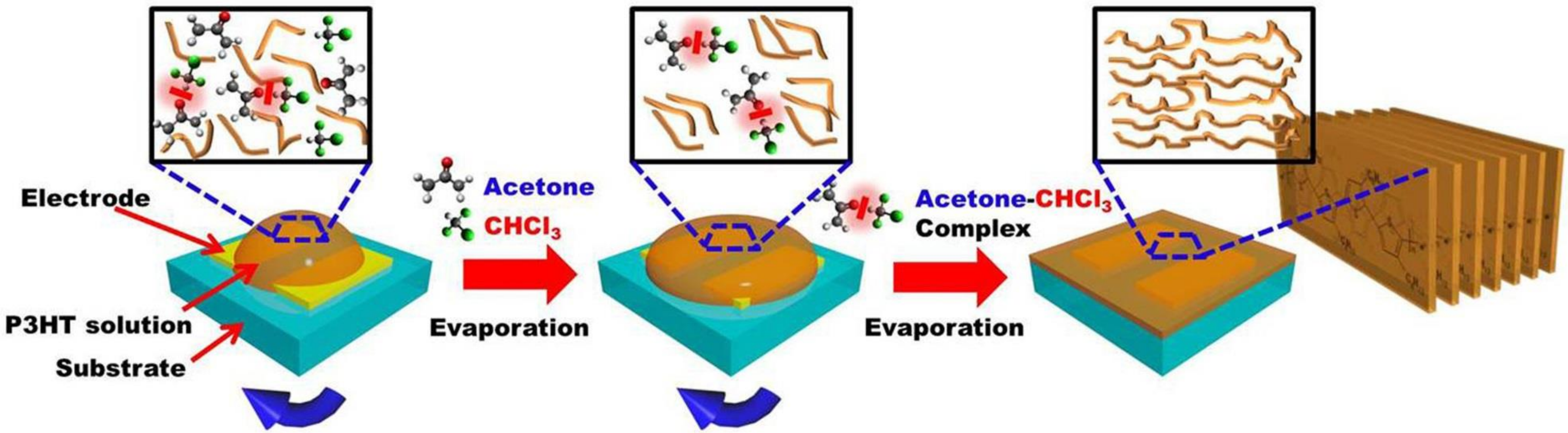
δ_P: 3.97 MPa$^{1/2}$

δ_H: 4.19 MPa$^{1/2}$

R_0: 4.20 MPa$^{1/2}$

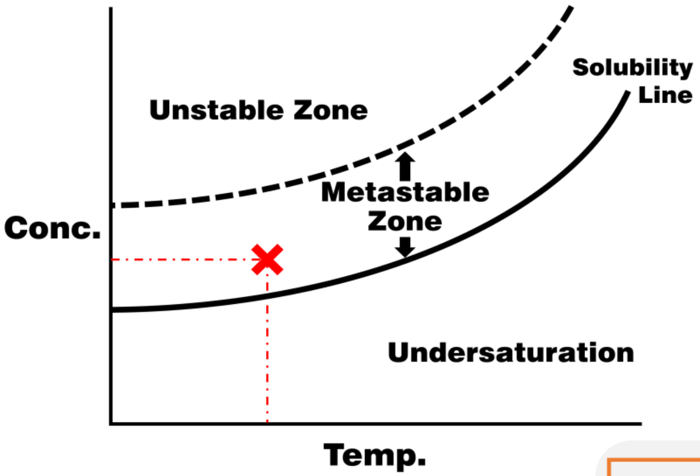


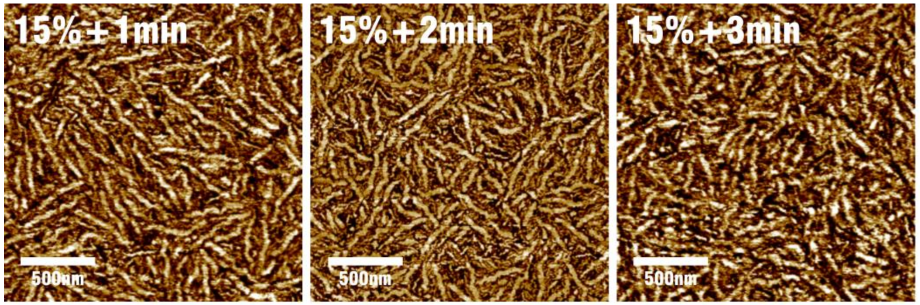
Mechanistic Illustration of Molecular Ordering



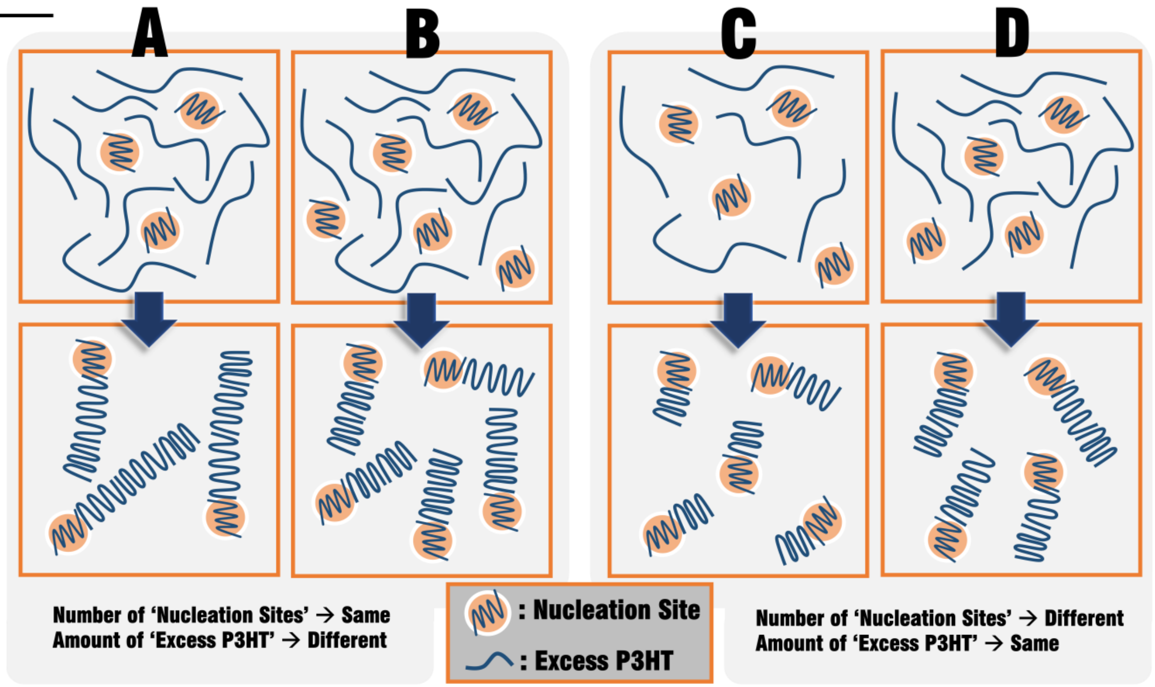
- Molecular ordering of P3HT chains and subsequent charge transport characteristics of resultant thin films can be influenced through solvent characteristics
- Hansen solubility parameters provide valuable insight into the relationships between thin-film morphology, molecular ordering and device performance

P3HT Aggregation Revisited





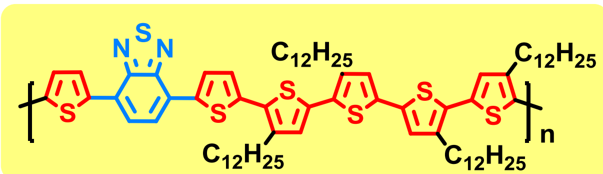
Generic P3HT self-assembly: a case for 2-step crystallization



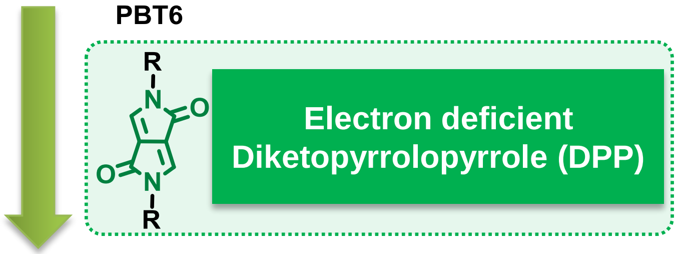
Rational Design of Branched Side Chains for Enhanced Mobility

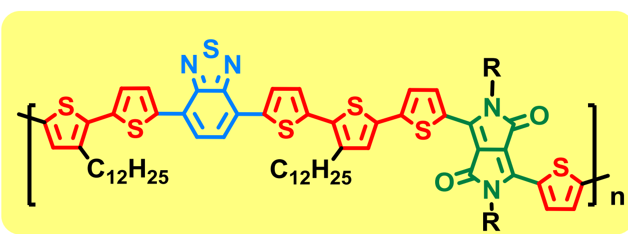
Polymer Design:

- DPP deepens HOMO energy level further enhancing air stability
- ICT (formed by BT-thiophene-DPP coupling) narrows bandgap
- Fused feature of DPP facilitates charge carrier transport

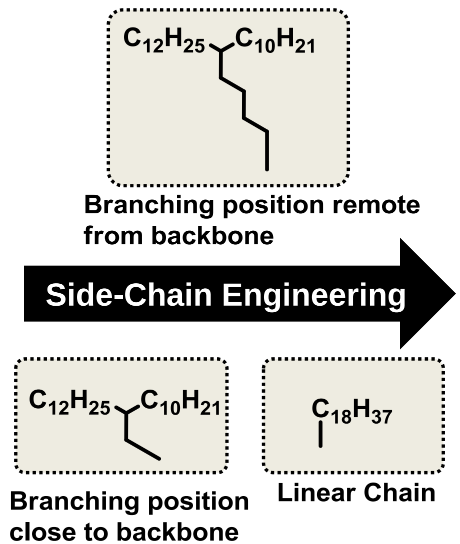


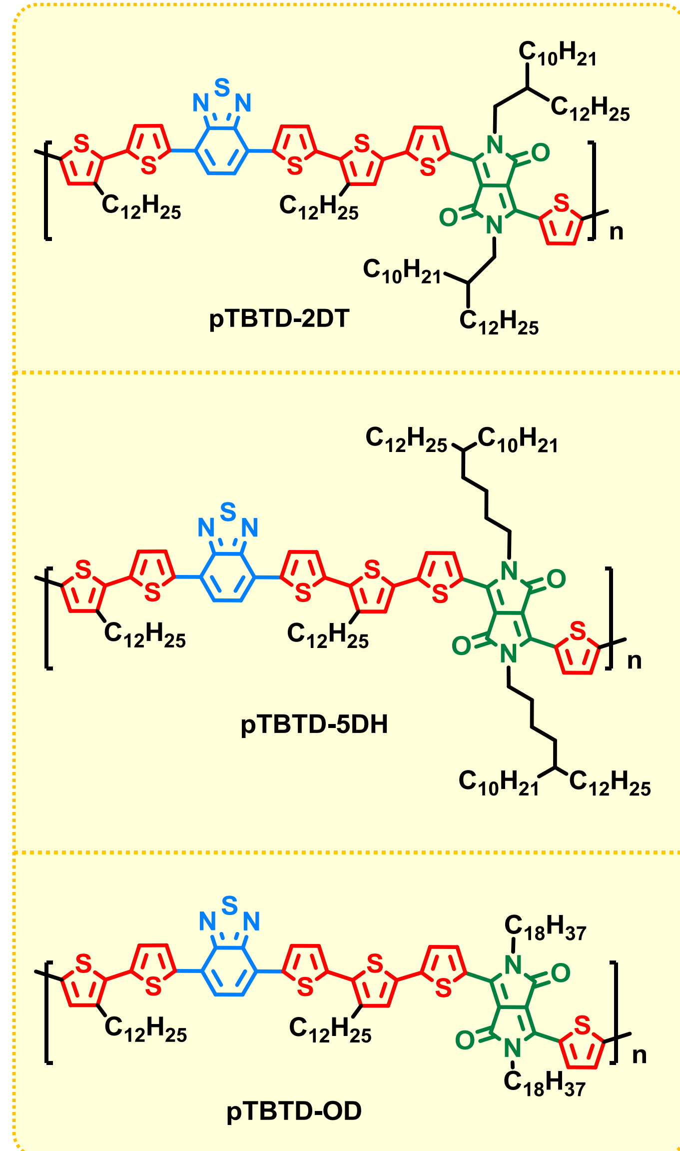
PBT6





pTBTD





Side Chain Design:

- Enhance pTBTD solution processability
- Enhance π-π intermolecular interaction of pTBTD via branch position

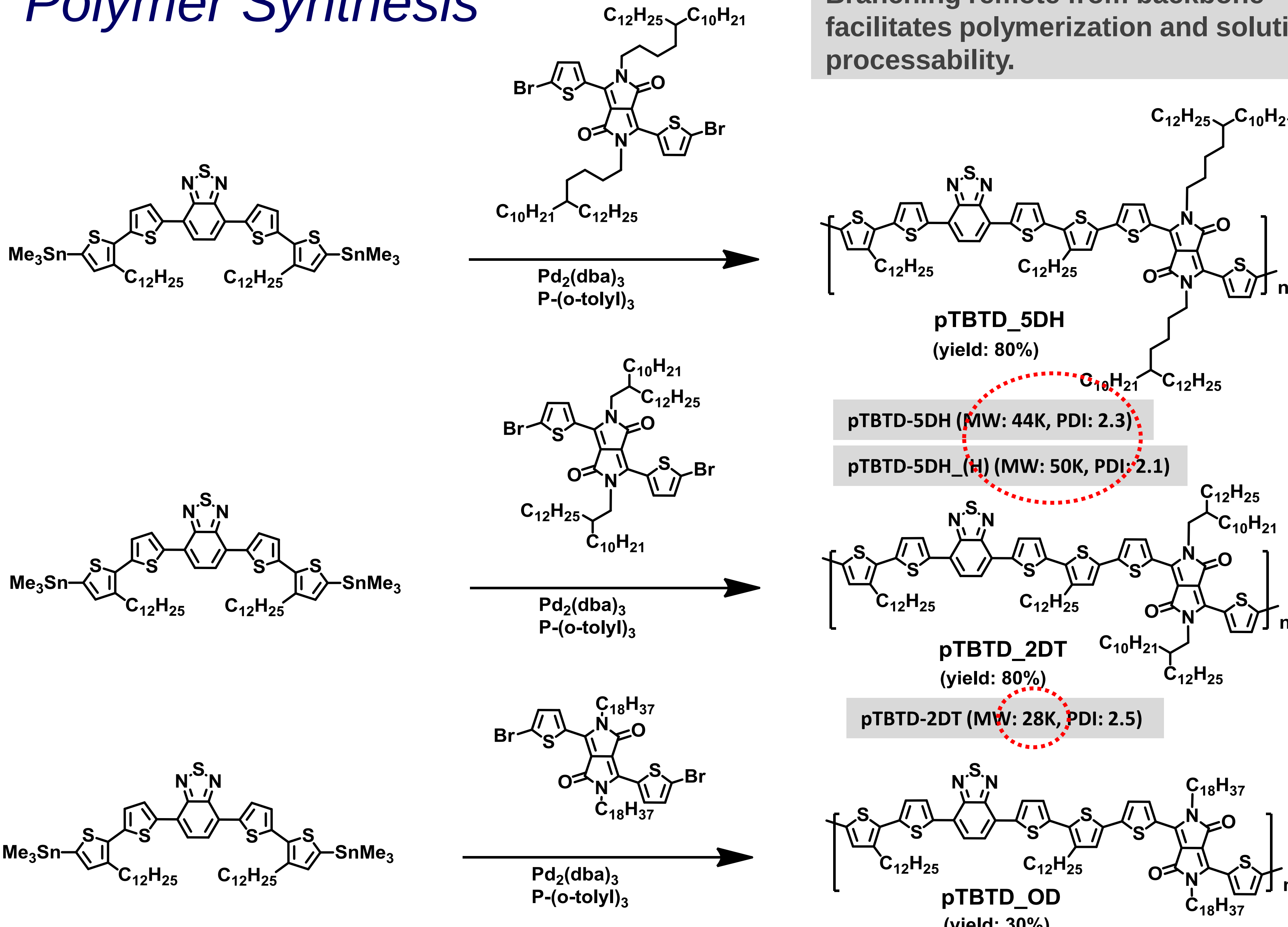
terthiophenes (donor)

benzothiadiazole (acceptor)

diketopyrrolopyrrole (acceptor)

Polymer Synthesis

Branching remote from backbone facilitates polymerization and solution processability.



pTBTD-5DH (MW: 44K, PDI: 2.3)

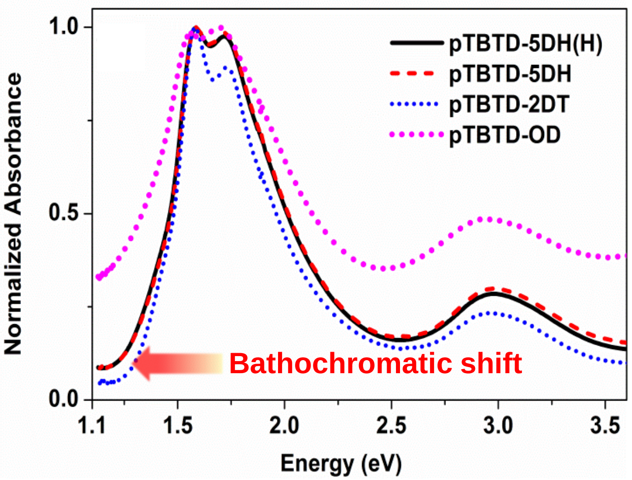
pTBTD-5DH_(H) (MW: 50K, PDI: 2.1)

pTBTD-2DT (MW: 28K, PDI: 2.5)

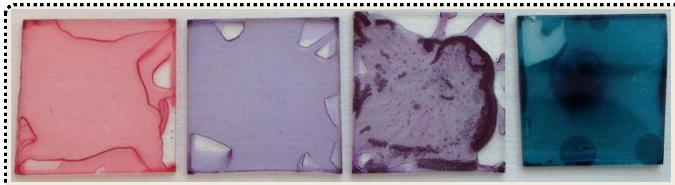
pTBTD-OD (MW: 14K, PDI: 2.5)

Polymer Characterization

UV/vis absorption spectroscopy

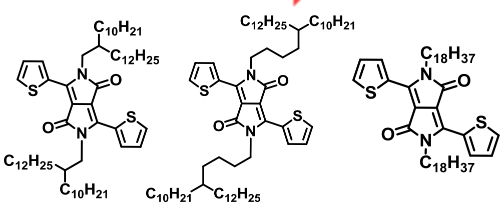


- π-conjugation enhances due to branching position



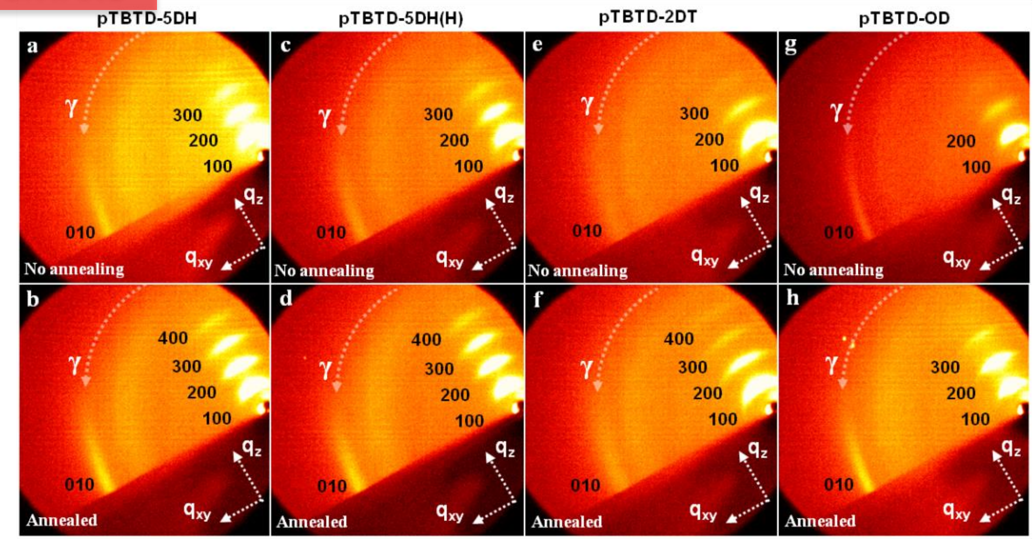
7b 7a 7c pTBTD_5DH

Bathochromatic shift



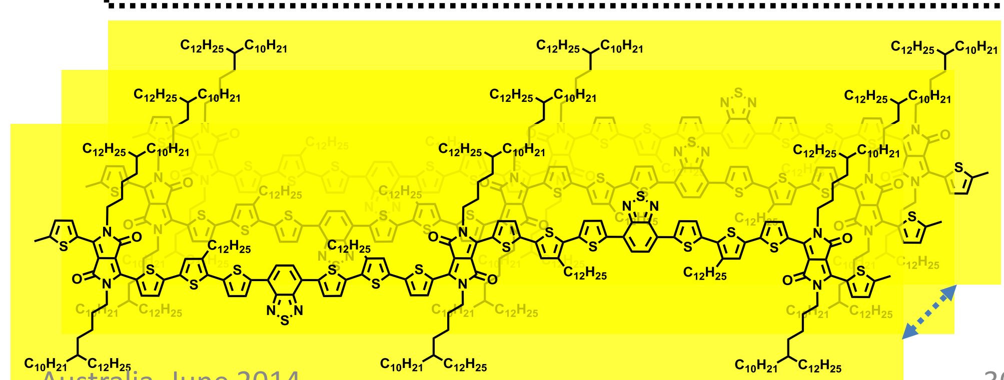
- π-π intermolecular interaction enhances due to branching position (reduced steric hindrance between side chains)

2D-GIWAXS



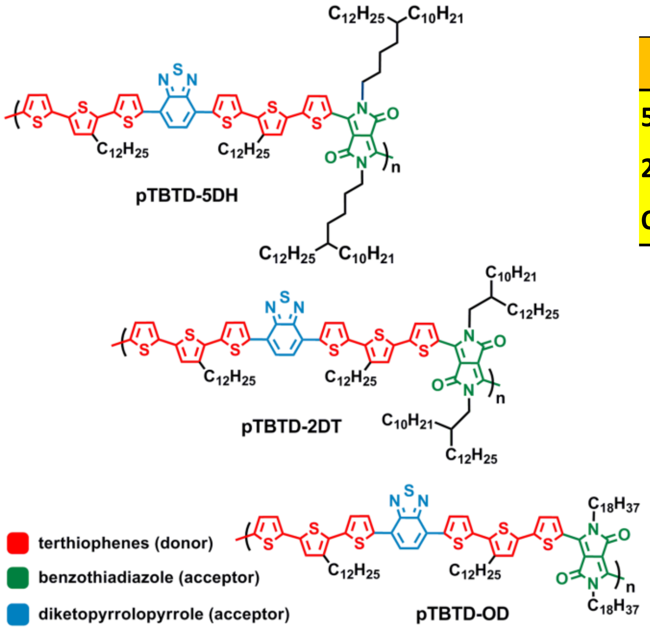
	pTBTD-5DH(H)	pTBTD-5DH	pTBTD-2DT	pTBTD-OD
d-spacing (Å)	24.55	24.88	22.07	22.29
π-π stacking (Å)	3.59	3.61	3.73	3.62

•π-π interchain stacking is narrowed due to branching position away



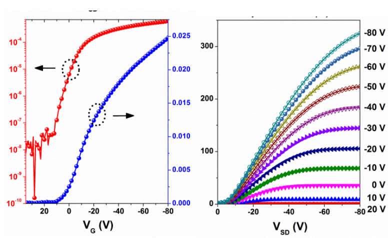
π-π stacking distance

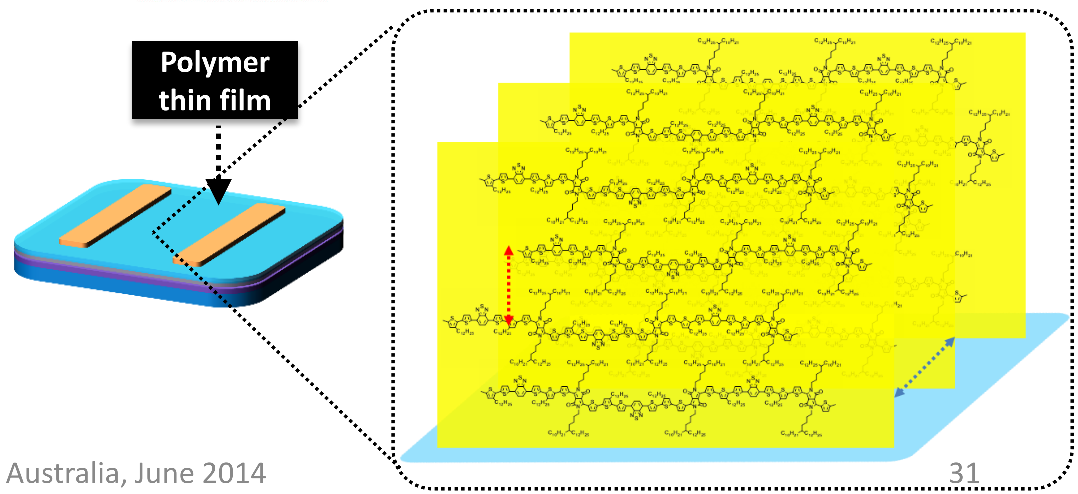
Mobility and Side Chain Design

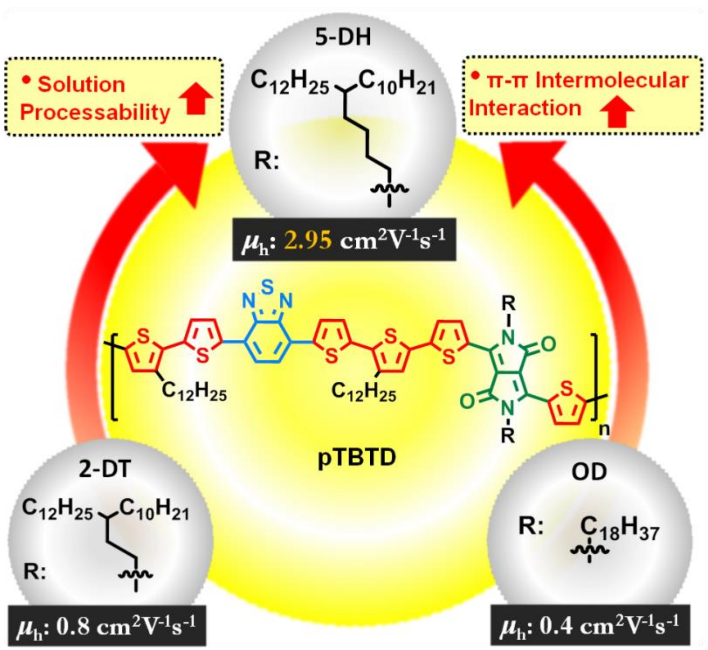


	Solubility	π - π Intermolecular Interaction
5-DH (branching remote to backbone)	Superior	Superior
2-DT (branching close to backbone)	Superior	Reduced
OD (linear chain)	Reduced	Superior

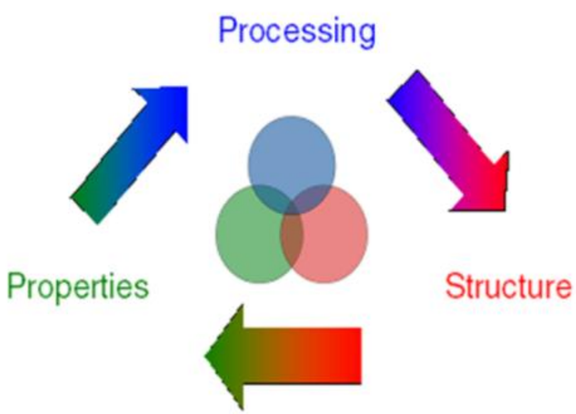
Remote branching merges the advantages of Branched and linear chains





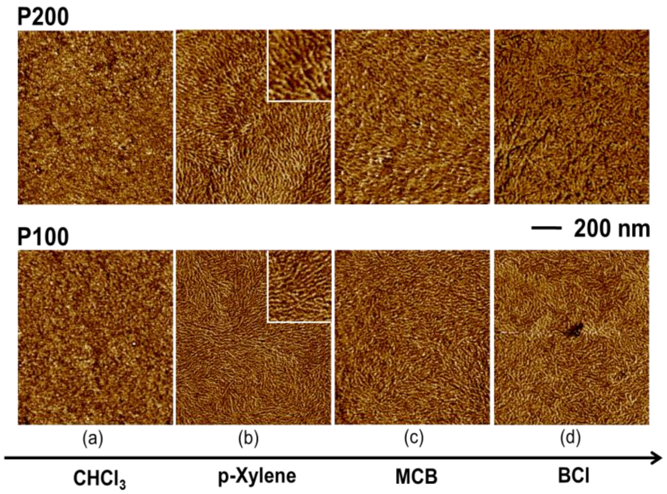


Conclusions



Molecular structure in conjunction with materials processing influences electronic properties/device performance of polymeric semiconducting materials

- All aspects of structure, regioregularity, molecular weight, molecular weight distribution, substitution pattern, etc. have a significant impact on conjugated polymer performance.
- Impact of intermediate phases between the isotropic solution and crystalline states requires investigation.



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