X-ray Scattering of Thin Films of Organic Semiconducting Materials

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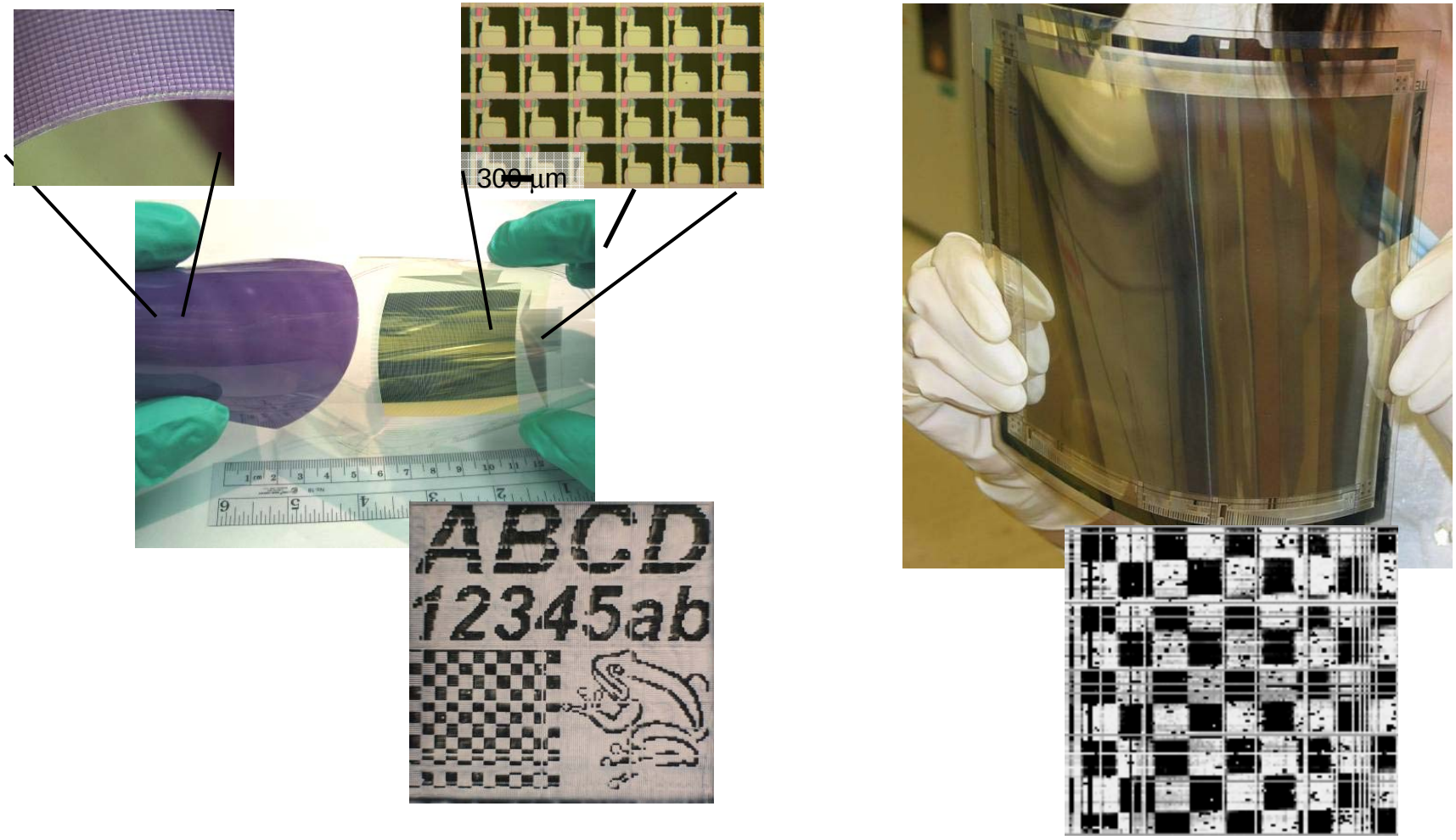
Flexible Displays and Imagers

electrophoretic medium

printed backplane

Photosensor array



Flexible backplanes with a-Si and organic TFTs and photosensors

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Thin Films of Organic Semiconductors

Uses:

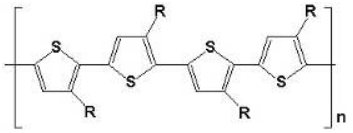
- Electronics: displays (TFTs)
  biosensor devices (TFTs, LEDs)
- Energy: Photovoltaics
  Solid-state lighting (LEDs)

Characteristics:

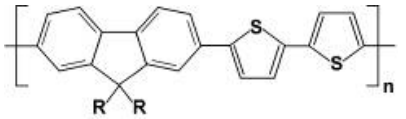
- small molecules or rigid-rod, conjugated polymers
- hole and electron conductors
- amorphous to semicrystalline films
- polymers form gels in solvent

Devices:

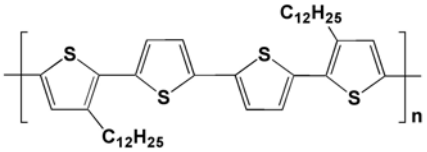
thin films (< 100nm)
single, multi-, or blended layers



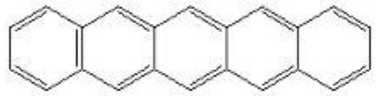
P3HT



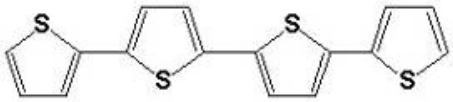
F8T2



PQT-12

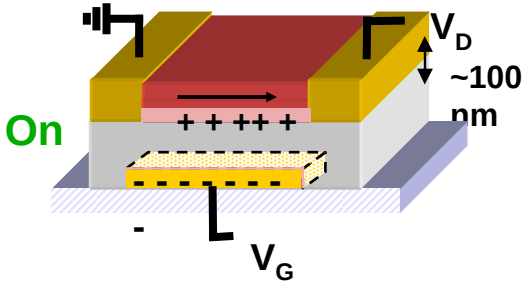


pentacene

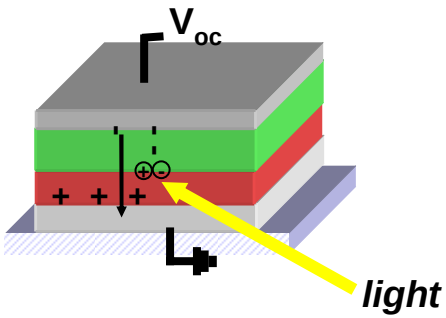


oligothiophenes

Thin-film transistor



Photovoltaic cell



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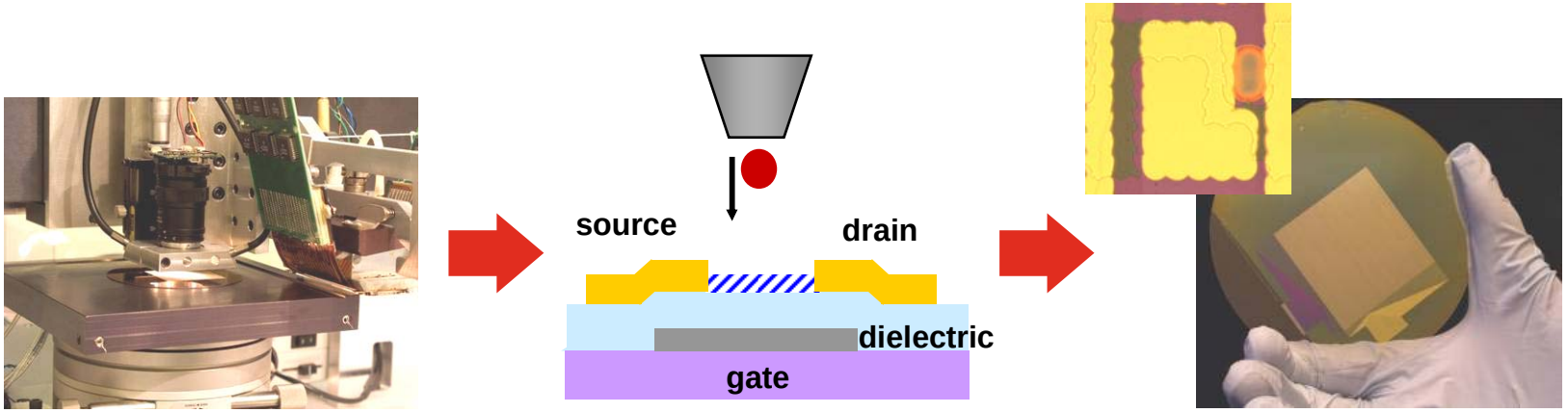
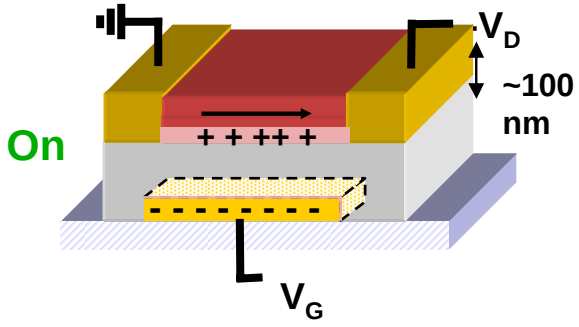
Printable Semiconductors



Conduction in thin-film transistor (TFT) occurs within 1-2 molecular layers of the dielectric



Interfacial interactions between semiconductor and dielectric critical to operation

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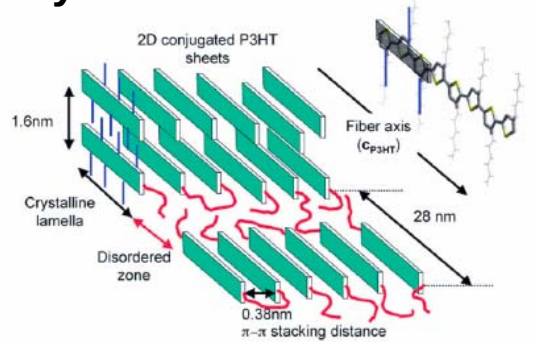
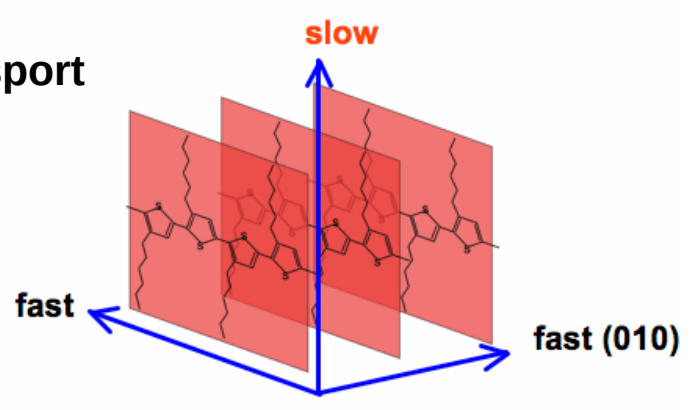
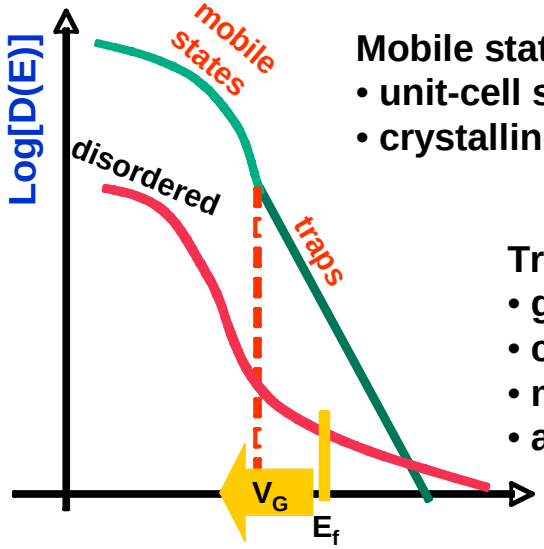
Charge transport linked to the microstructure

Semicrystalline structure



Transport

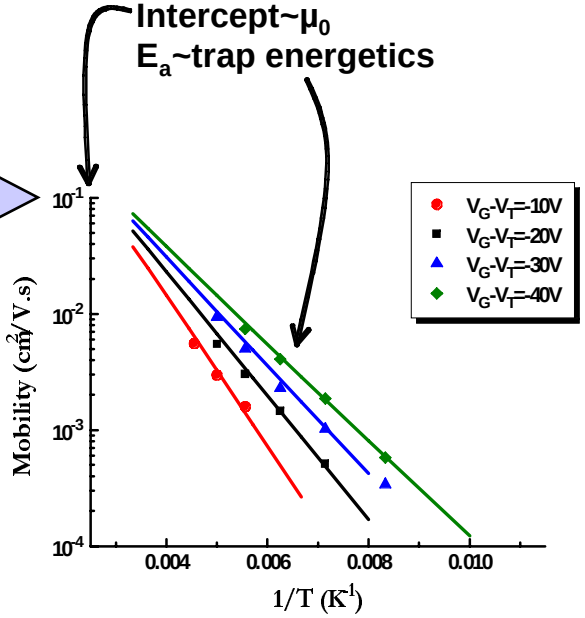




Mobile states depend on:
- **unit-cell structure**
- **crystalline order**

$\mu(V_G, T)$

Trap distribution depends on:
- **grain-boundary structure**
- **crystalline texture**
- **mosaicity**
- **amorphous states**



Factors affecting microstructure in thin films:

- substrate roughness, surface energies, thermal processing, solvent, etc.

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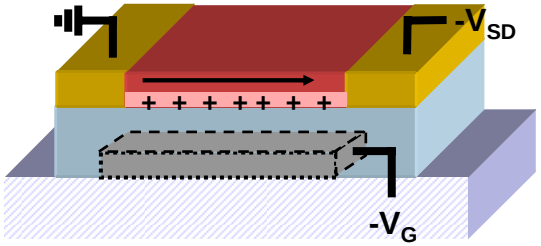
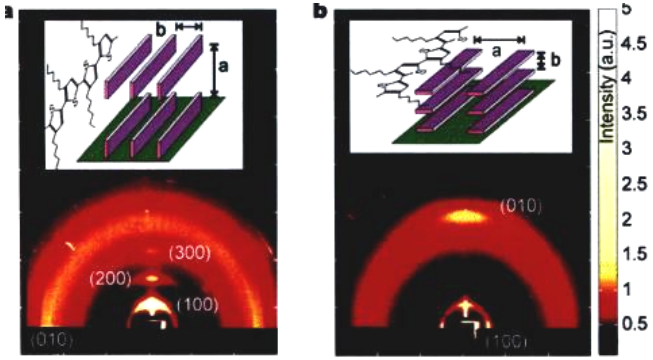
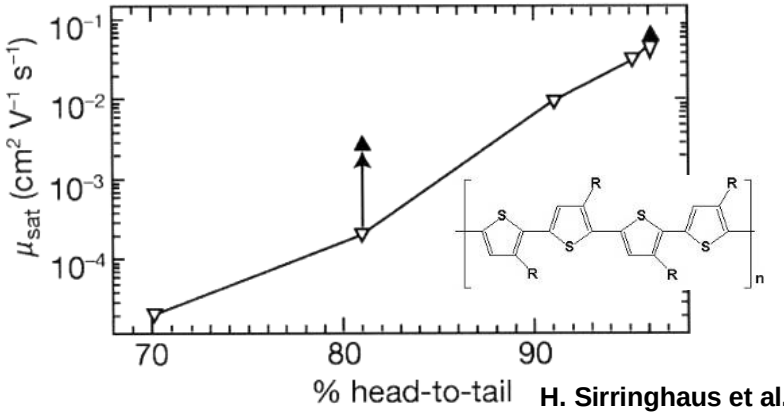
Polymer TFTs: Bulk vs. Interfacial Structure



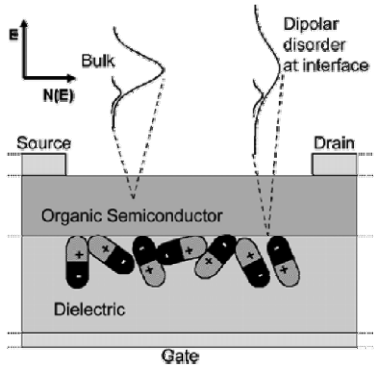
Microstructure of Semiconductor



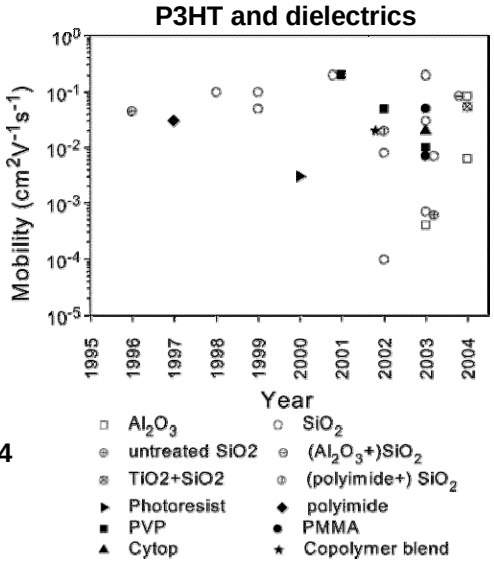


H. Sirringhaus et al., *Nature* 1999

Interfacial Structure



J. Veres et al., *Chem. Mat.* 2004



Difficult to study bulk polymer and interfacial structure separately

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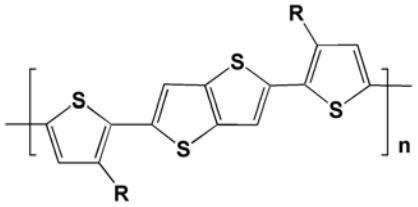
Thermal Transitions in Semiconducting Polymers

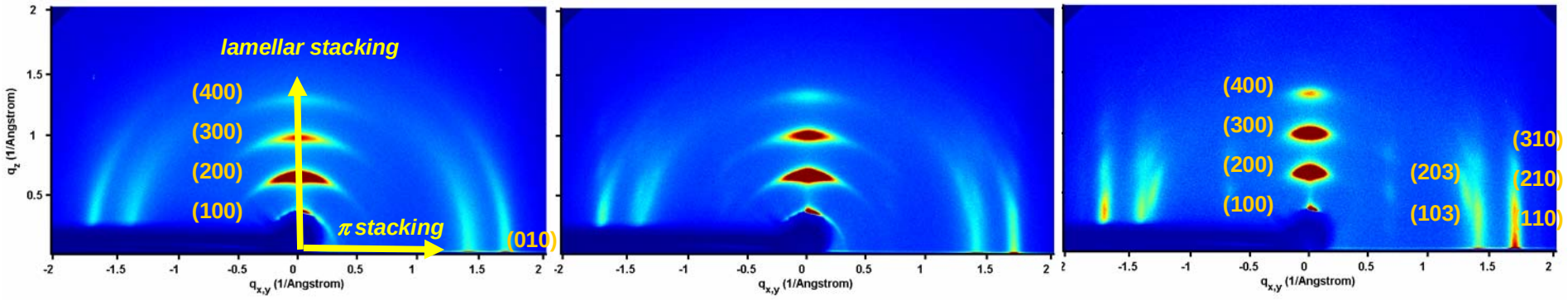
PBTTT

- highest field-effect mobility for polymers
- LC mesophase above ~140° C
- annealing improves mobility and device performance



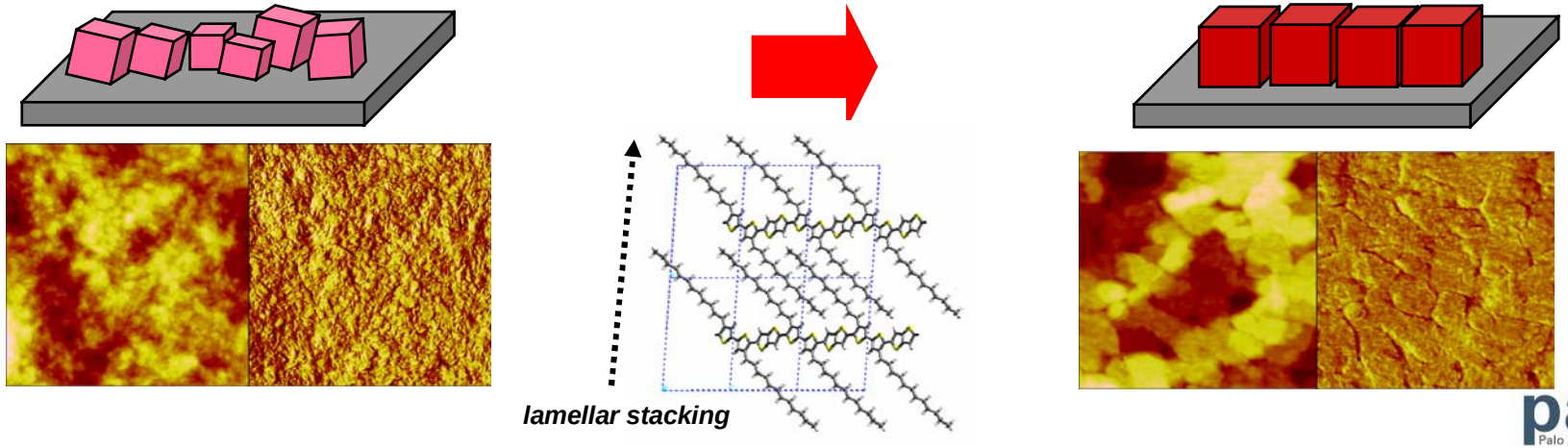
McCulloch, et. al. *Nat. Mater.* 2006

as-spun | **after 140° C** | **after 180 C**



misoriented & disordered crystals

increased lamellar and π order



X-ray data from 11-3 using image plate detector (typically ~300 s exposures)

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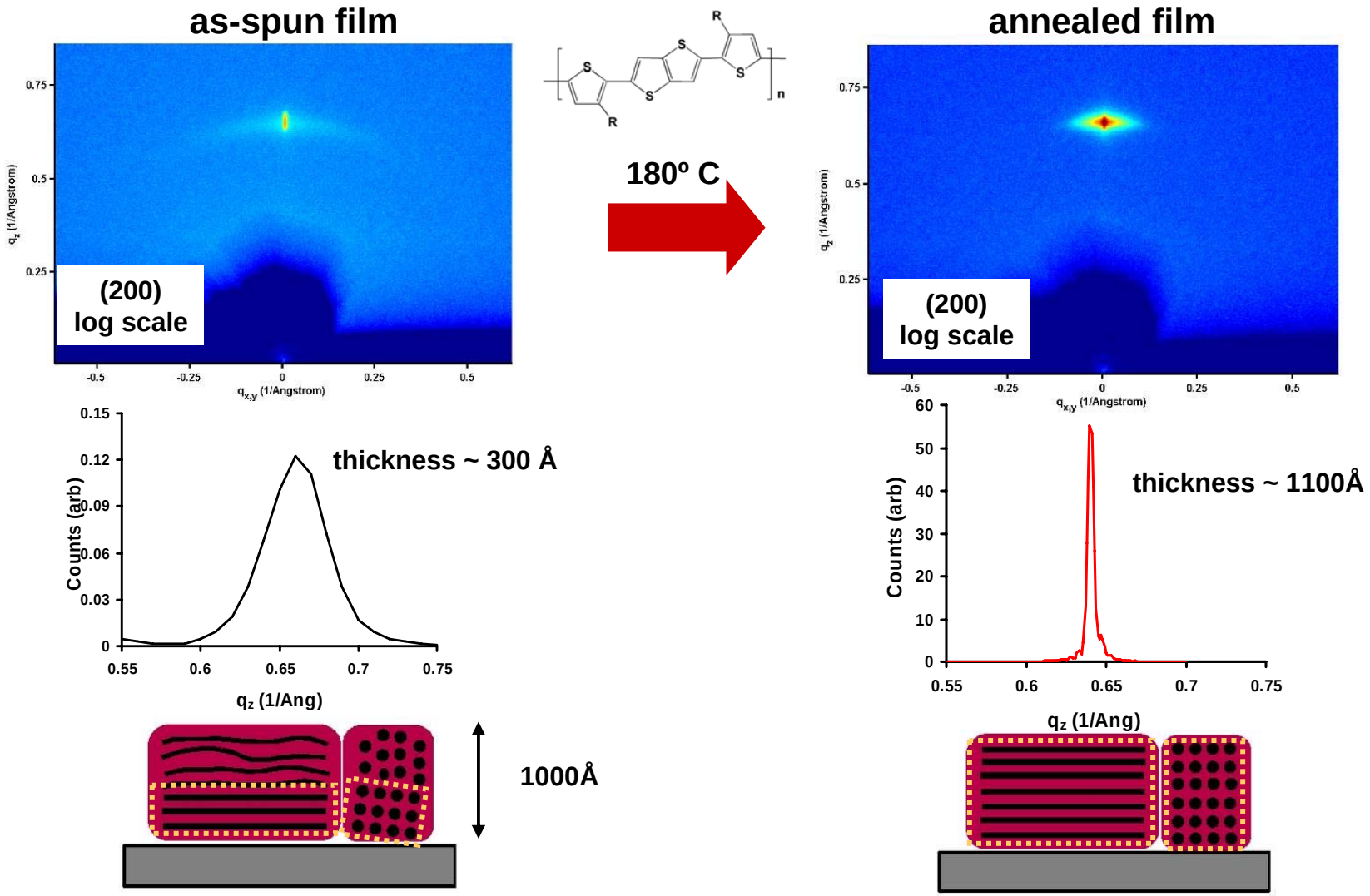
Lamellar Order: Domain Growth



Annealing improves order and orientation of crystalline domains

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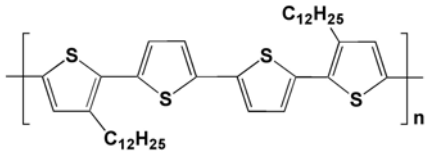
In-situ Studies of Thin Film Crystallization

(100) specular peak

=fast cooling



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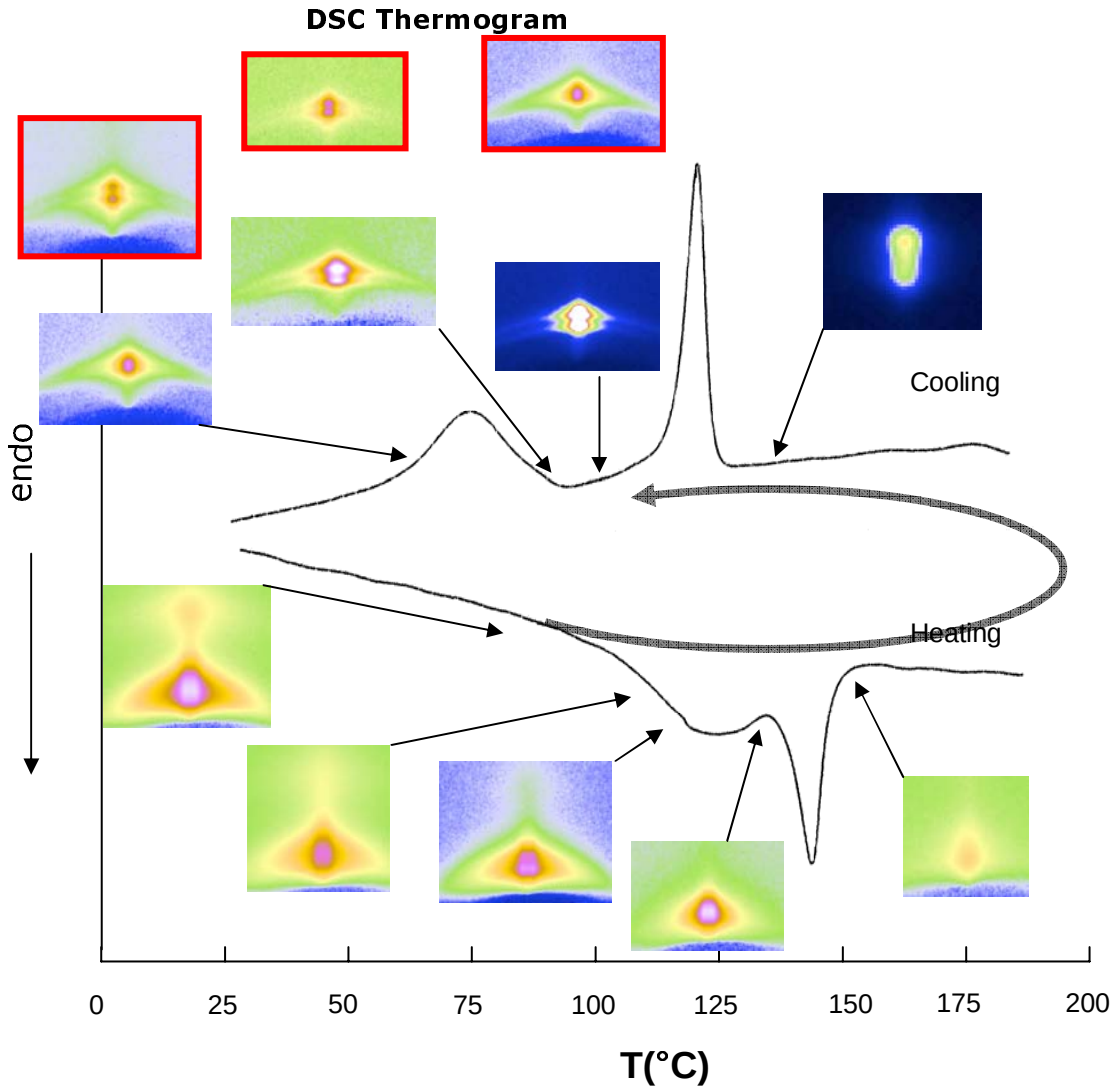

Sidechain rigid-rod polymers have layered microstructure

in-situ studies can examine crystallization and phase behavior of these materials

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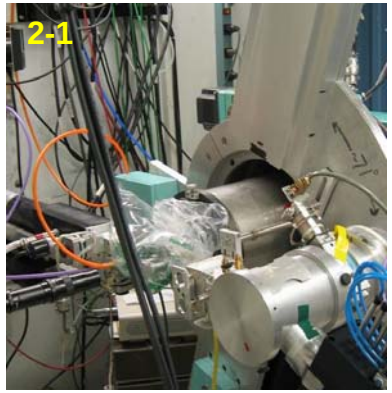
Future Needs

Environmental Control

- most polymers degrade in air & room light & high intensity x-rays appear to ablate material
- inert atmosphere helpful to preserve sample during run
  (currently using a He-filled plastic bag…)
- ability to swell polymer with solvent atmosphere might be interesting,
  e.g. examination of gel form



Hot Stages for Crystallization studies

- melt-recrystallization studies are important
  350° C will cover most materials (typical decomposition temp)
- for many systems, dynamics are fast - e.g. response < 1 minute

- Faster temperature stages would be useful to minimize time required to reach temperature for scans; rapid cooling would be useful for quenching structures

- 2 or 3 T/Cs to ensure that the sample stage and sample surface are at the desired temperature.

- Cooling stage to go below RT

Future Needs

Data Acquisition

- convenient to do survey scans with area detector and then high-res scan on same beamline

- array detector for higher resolution grazing scattering (7-2)

- more rapid detection in area scans: it would be much better to be able to do rocking rapidly at different temperatures rather than the "panoramic shot" of reciprocal space

Data Processing

- image analysis (difficult currently during run)

in-house processing software, e.g. Fit2D replacement

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