

X-ray Scattering of Thin Films of Organic Semiconducting Materials

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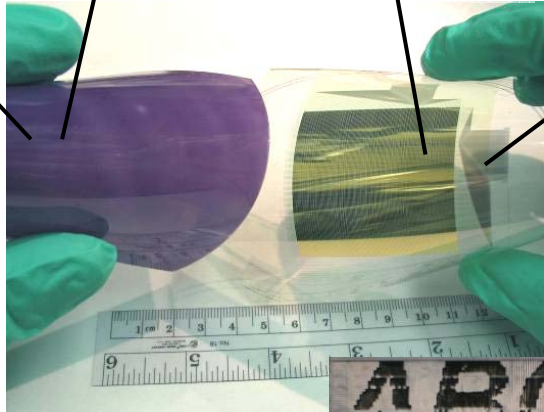
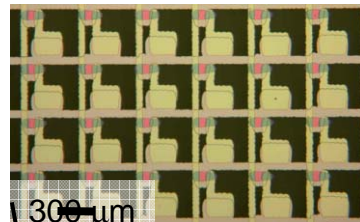
Alberto Salleo
Stanford

Flexible Displays and Imagers

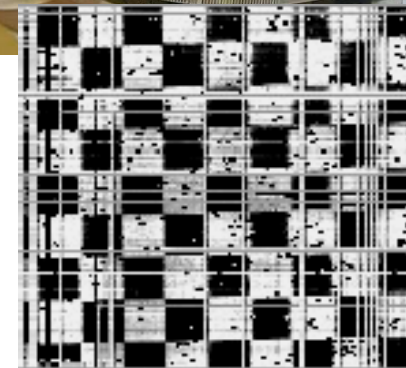
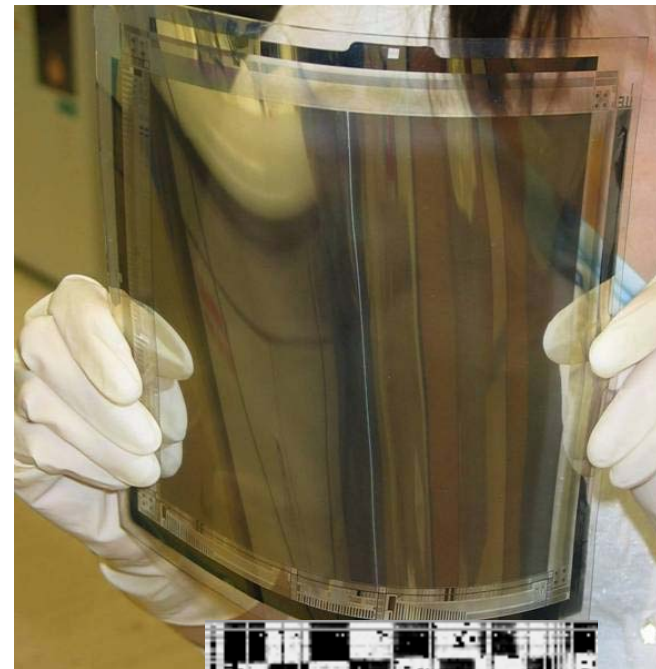
electrophoretic medium



printed backplane



Photosensor array



Flexible backplanes with a-Si and organic TFTs and photosensors

Thin Films of Organic Semiconductors

Uses:

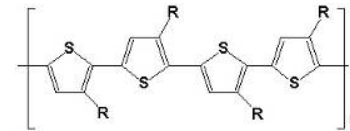
- Electronics: displays (TFTs)
biosensor devices (TFTs, LEDs)
- Energy: Photovoltaics
Solid-state lighting (LEDs)

Characteristics:

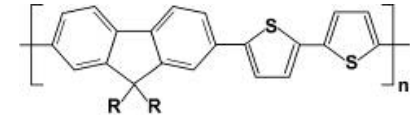
- small molecules or rigid-rod, conjugated polymers
- hole and electron conductors
- amorphous to semicrystalline films
- polymers form gels in solvent

Devices:

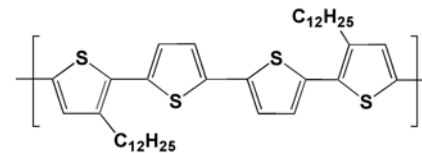
- thin films (< 100nm)
- single, multi-, or blended layers



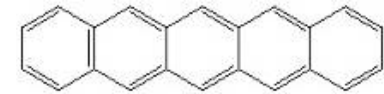
P3HT



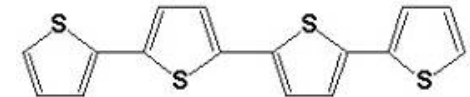
F8T2



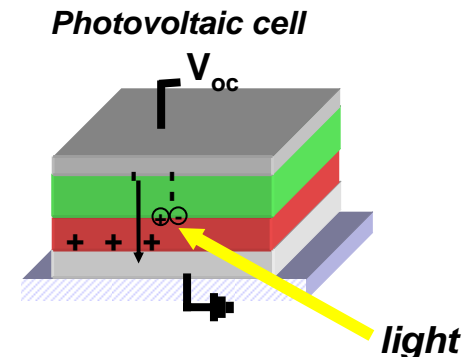
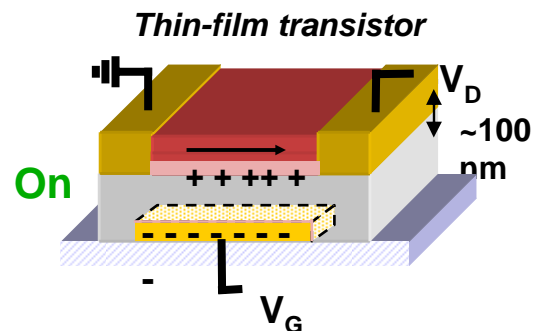
PQT-12



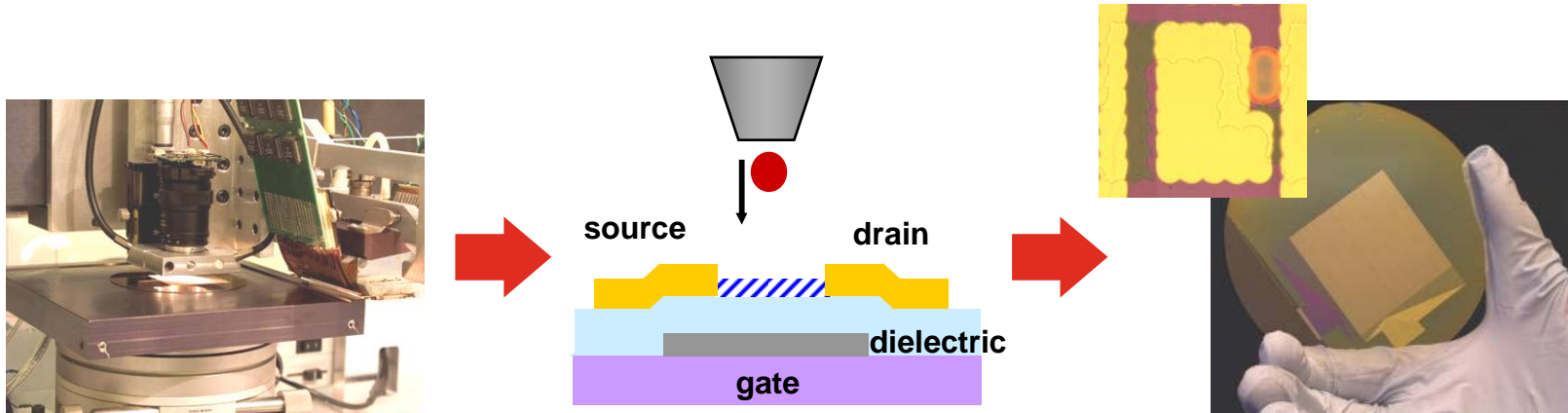
pentacene



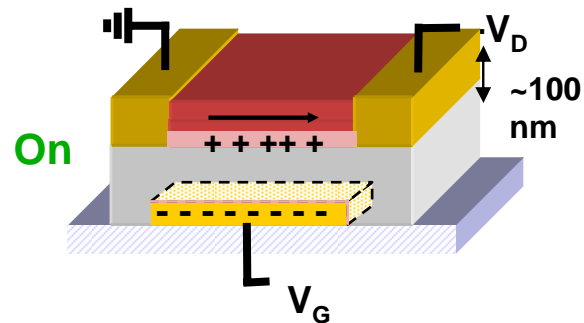
oligothiophenes



Printable Semiconductors



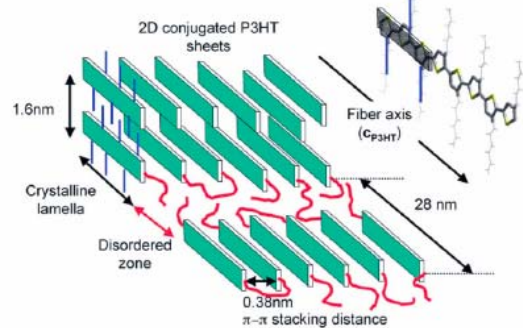
Conduction in thin-film transistor (TFT) occurs within 1-2 molecular layers of the dielectric



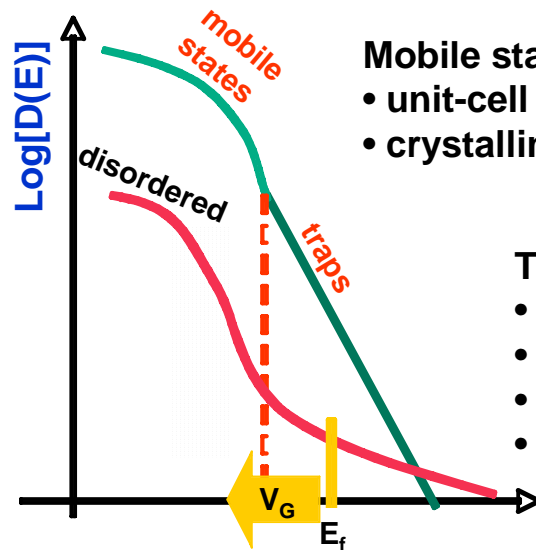
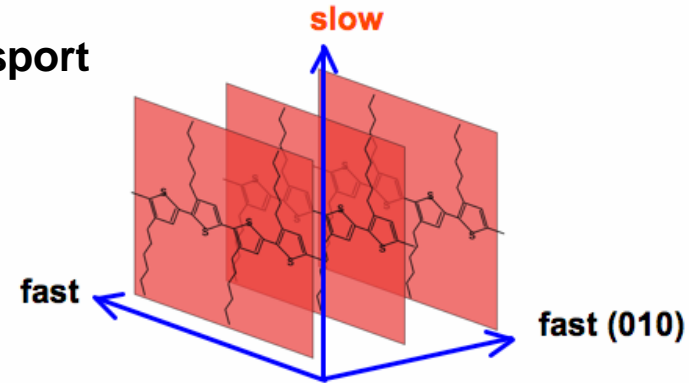
Interfacial interactions between semiconductor and dielectric critical to operation

Charge transport linked to the microstructure

Semicrystalline structure



Transport



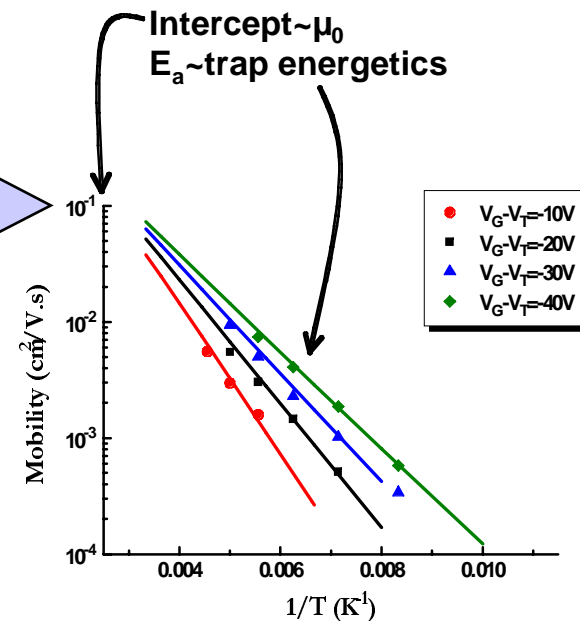
Mobile states depend on:

- unit-cell structure
- crystalline order

$\mu(V_G, T)$

Trap distribution depends on:

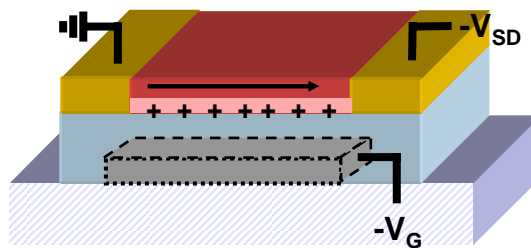
- grain-boundary structure
- crystalline texture
- mosaicity
- amorphous states



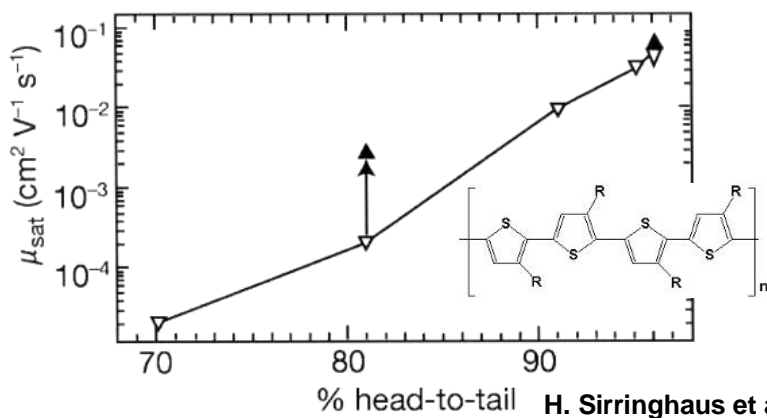
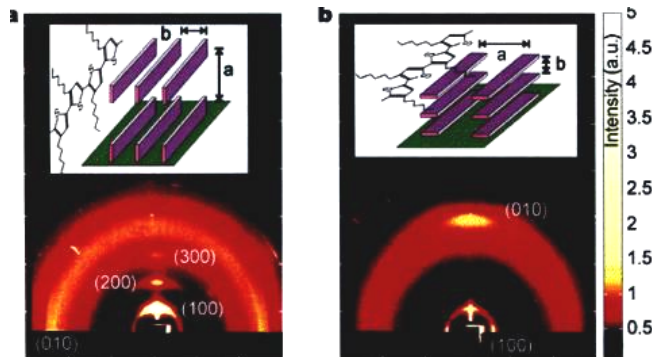
Factors affecting microstructure in thin films:

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

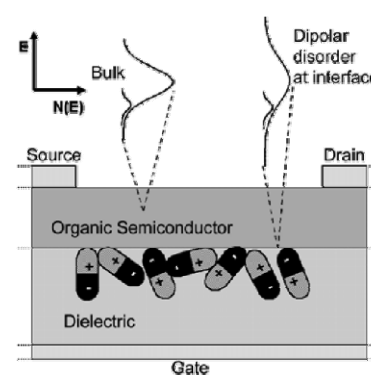
Polymer TFTs: Bulk vs. Interfacial Structure



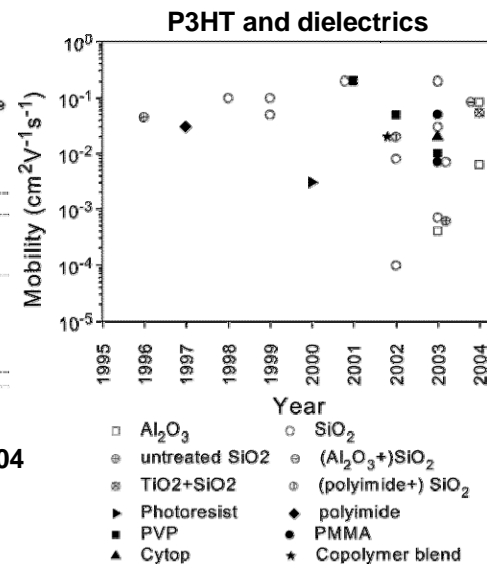
Microstructure of Semiconductor



Interfacial Structure



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

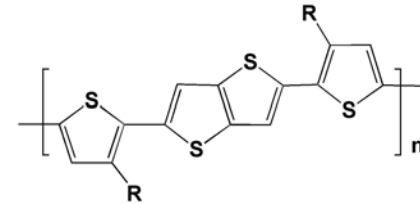


Difficult to study bulk polymer and interfacial structure separately

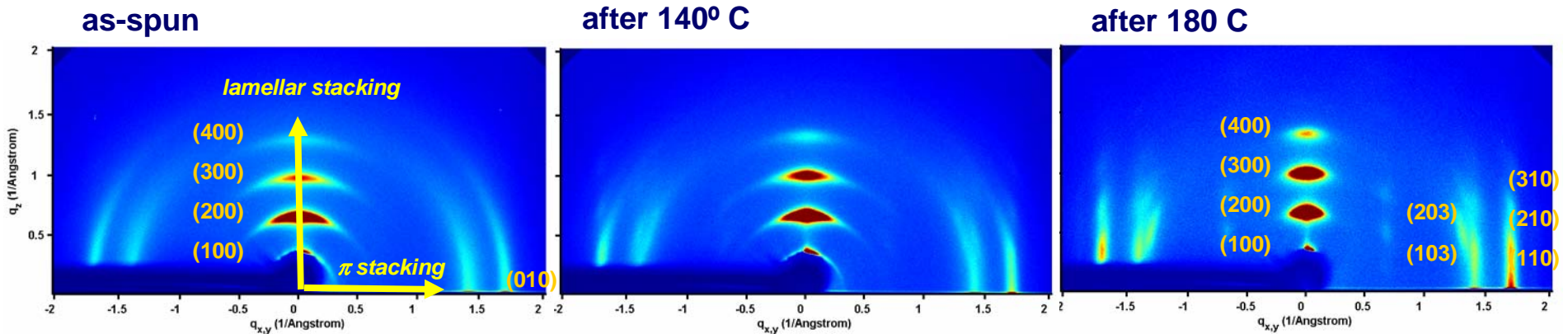
Thermal Transitions in Semiconducting Polymers

PBTTT

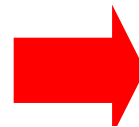
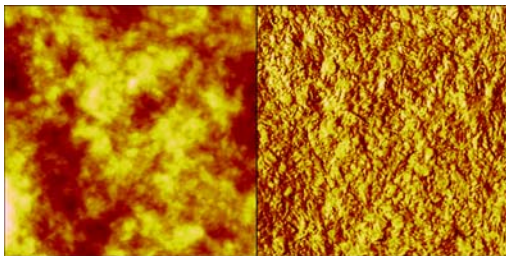
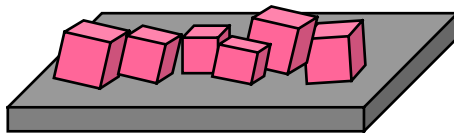
- highest field-effect mobility for polymers
- LC mesophase above $\sim 140^\circ\text{C}$
- annealing improves mobility and device performance



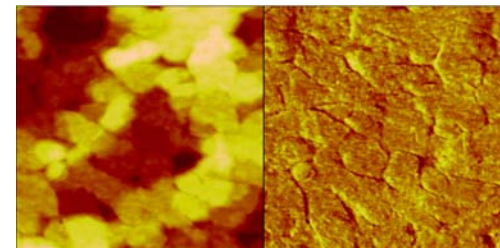
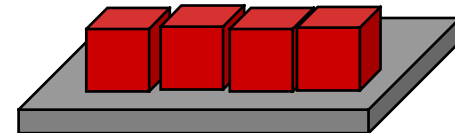
McCulloch, et. al. *Nat. Mater.* 2006



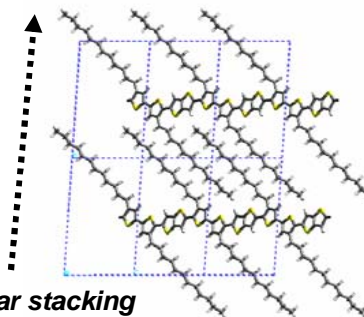
misoriented & disordered crystals



increased lamellar and π order

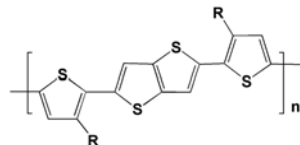
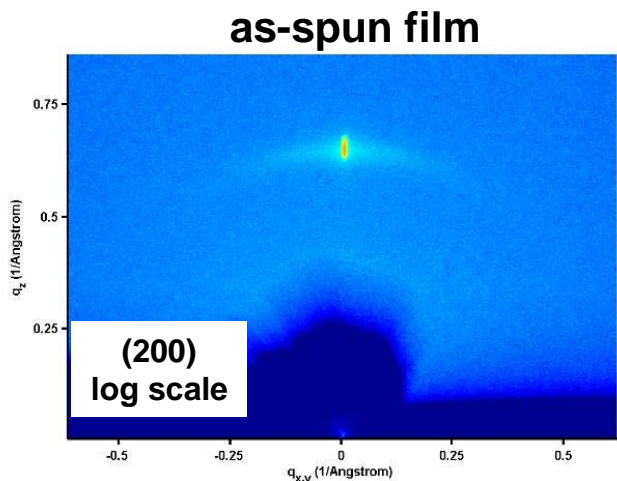


lamellar stacking

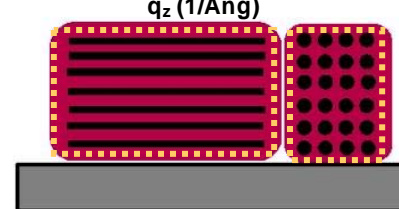
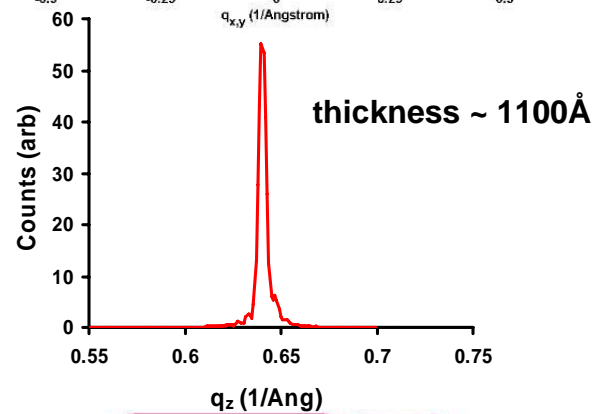
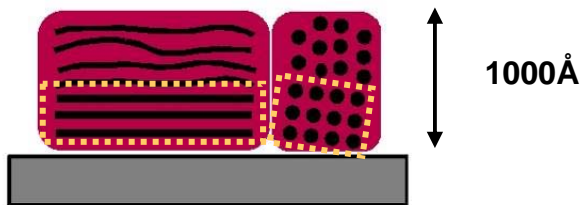
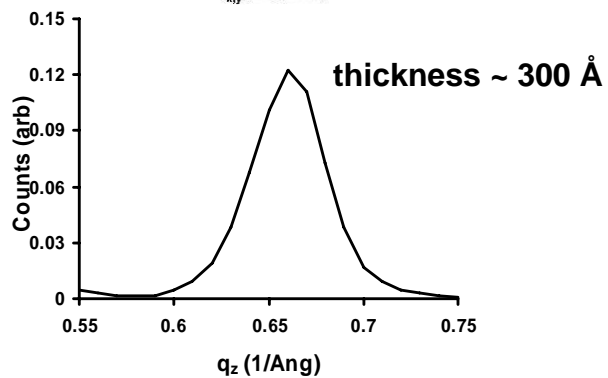
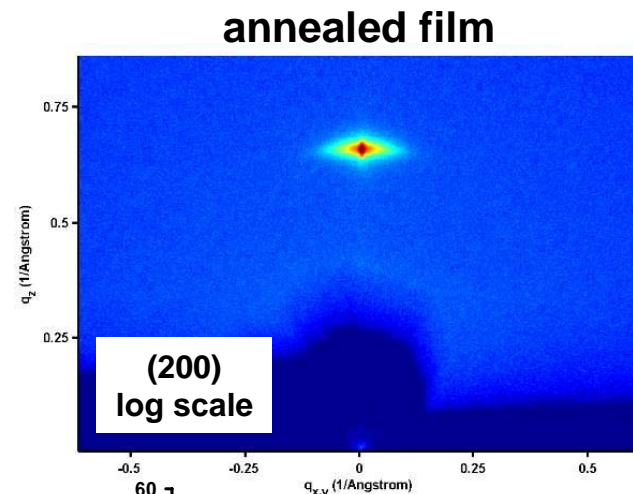


X-ray data from 11-3 using image plate detector (typically ~ 300 s exposures)

Lamellar Order: Domain Growth



180° C



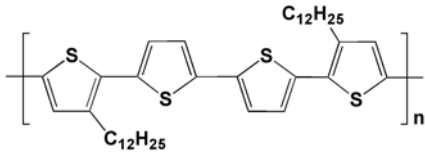
Annealing improves order and orientation of crystalline domains

In-situ Studies of Thin Film Crystallization

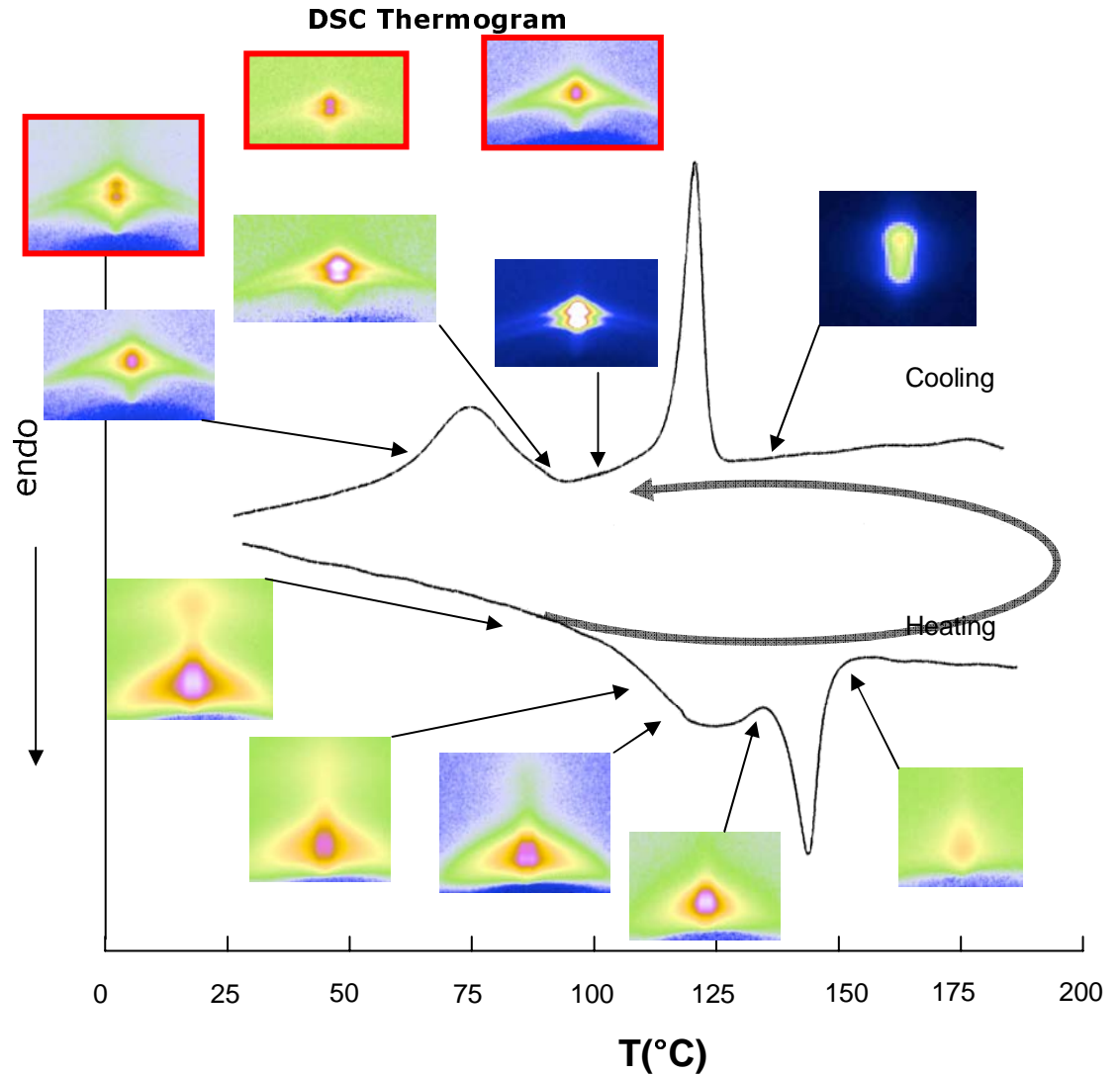
(100) specular peak



=fast cooling



PQT-12



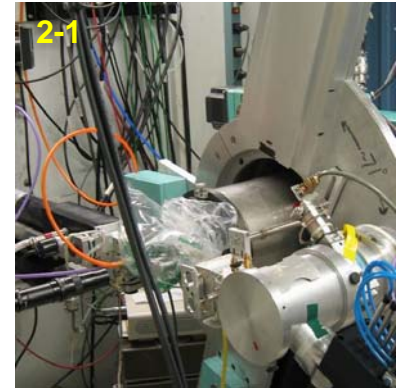
Sidechain rigid-rod polymers have layered microstructure

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

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