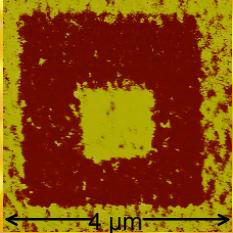


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Structure and Properties of Ferroelectric Polymers at the Nanoscale



Stephen Ducharme, Vladimir Fridkin*

Department of Physics & Astronomy
Nebraska Center for Materials & Nanoscience
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*Institute of Crystallography, RAS, Moscow

Ferroelectric Thin Films

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Structure & Properties of Ferroelectric Polymers at the Nanoscale

1

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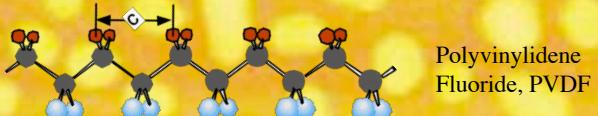
UNIVERSITY OF Nebraska Lincoln

OUTLINE

- 1. PolyVinylidene Fluoride
- 2. Langmuir-Blodgett Films
- 3. PVDF analogs
- 4. Ferroelectric Memories
- 5. Nanoscale Properties
- 6. Switching Dynamics
- 7. Pyroelectric Scanning
Microscopy (PSM)

▶ credits Structure & Properties of Ferroelectric Polymers at the Nanoscale 2

1. Ferroelectric Polymers



Poly(vinylidene fluoride) & Copolymers

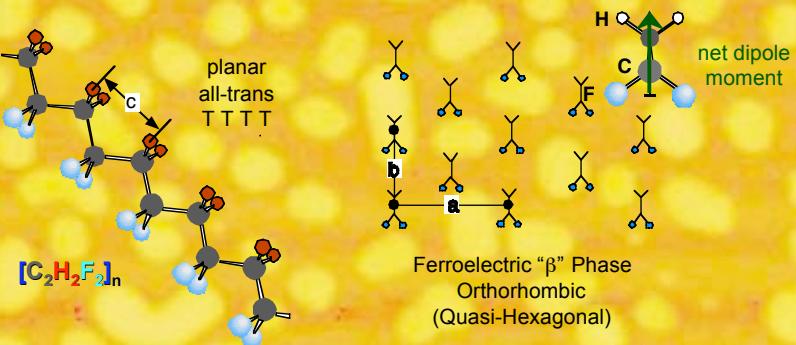
Odd Nylons & Cyanopolymers

VDF Oligomers

Structure & Properties of Ferroelectric Polymers at the Nanoscale

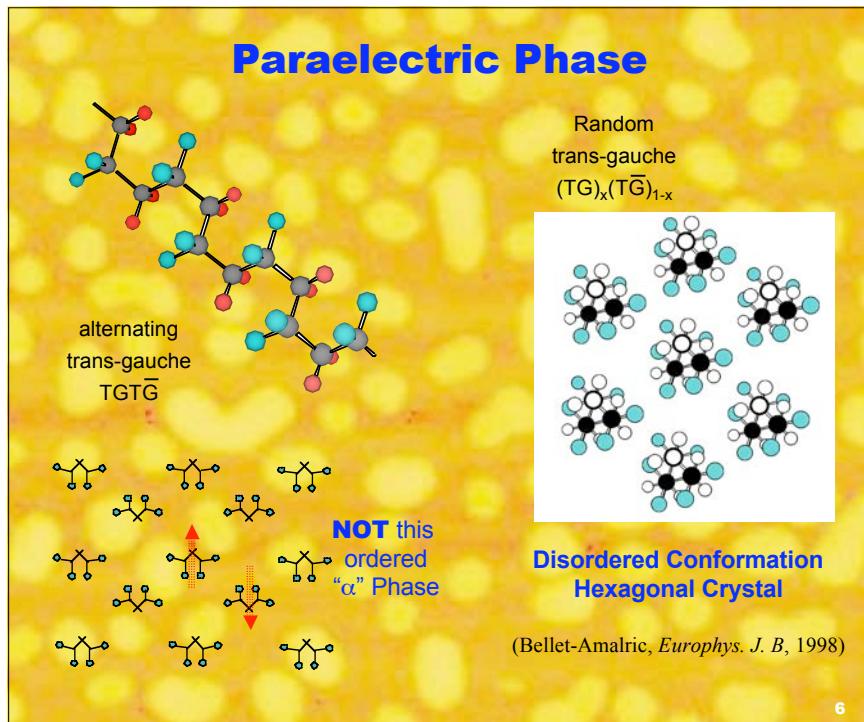
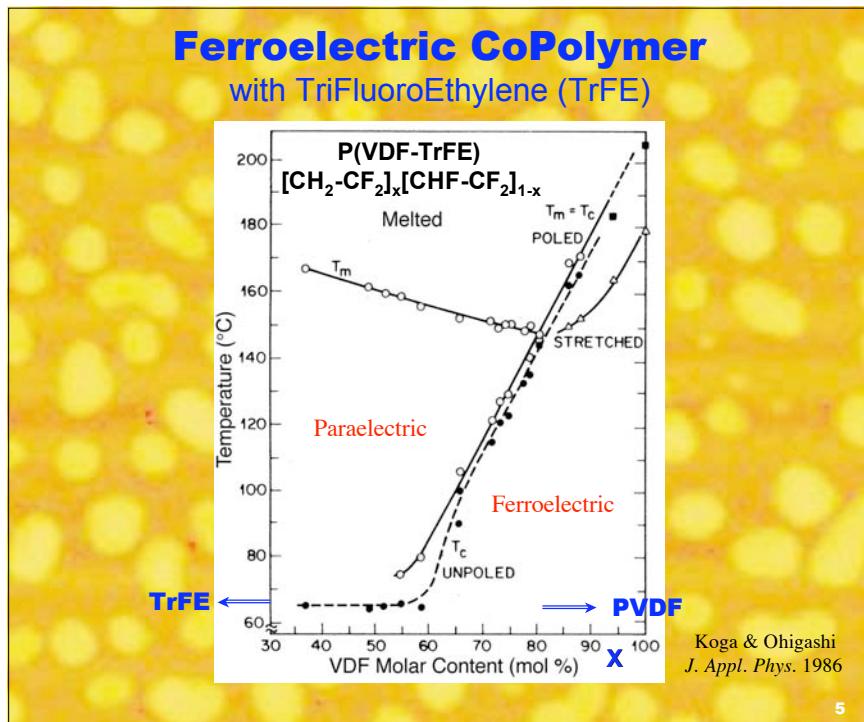
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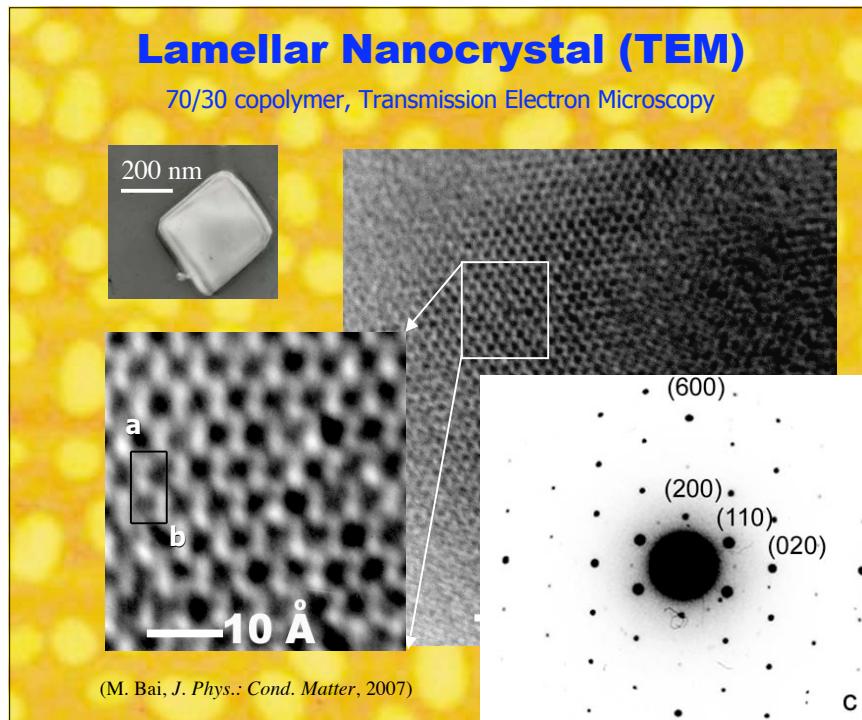
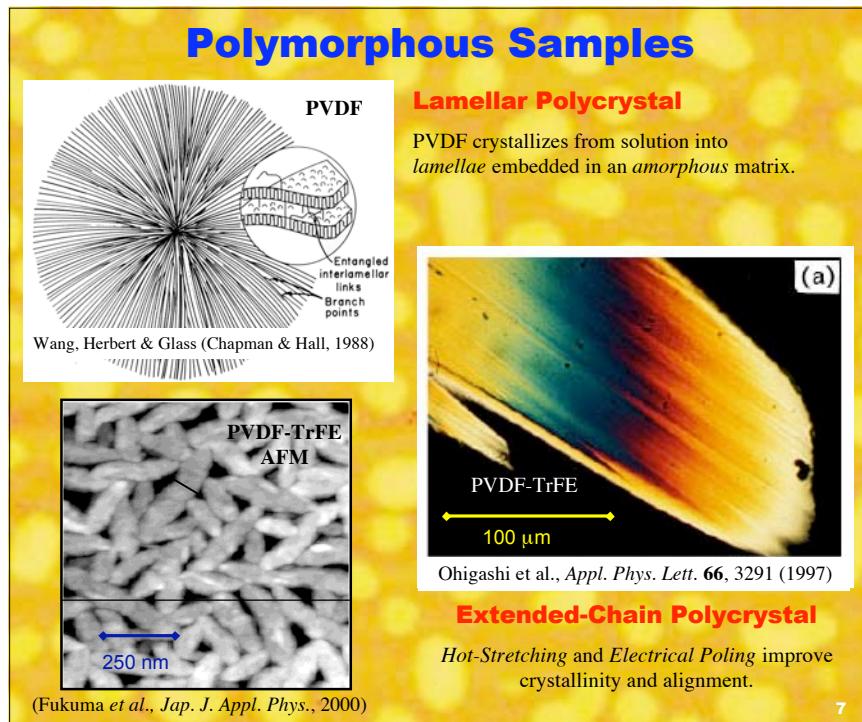
PolyVinylidene Fluoride (PVDF)

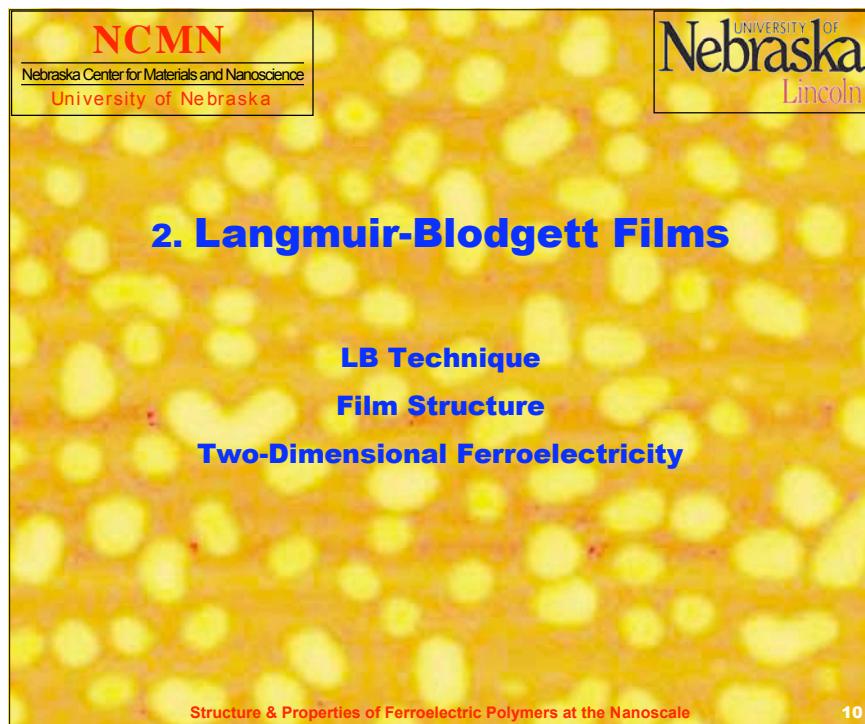
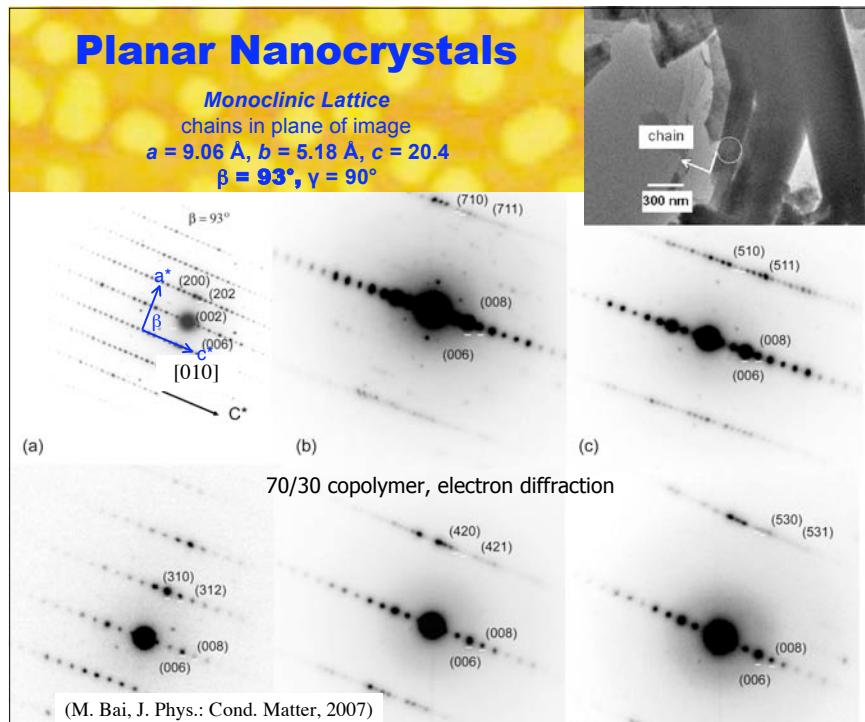


- Piezoelectricity discovered (Kawai, 1969)
- Ferroelectricity established ca. 1980
- $P_s \approx 0.1 \text{ C/m}^2$, $T_C \approx 200^\circ\text{C}$
- Chemically inert and stable
- Kynar®, Solef®, Floraflon® ...
- Piezo transducers, Membranes, Paint

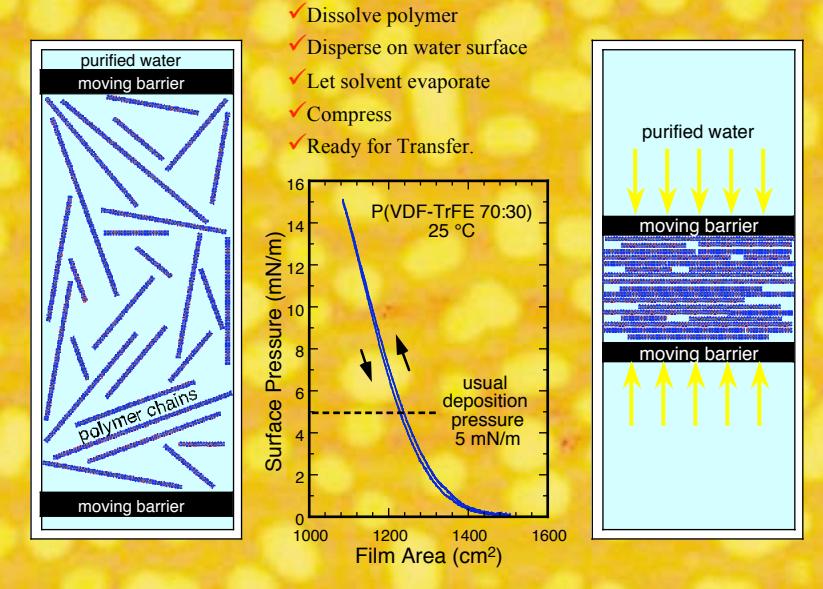
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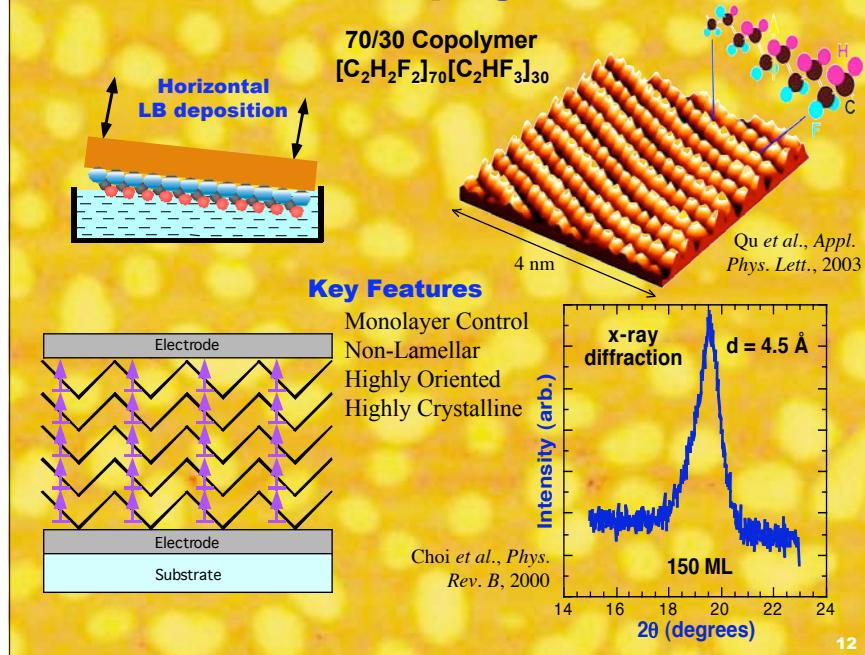


Langmuir-Blodgett Deposition

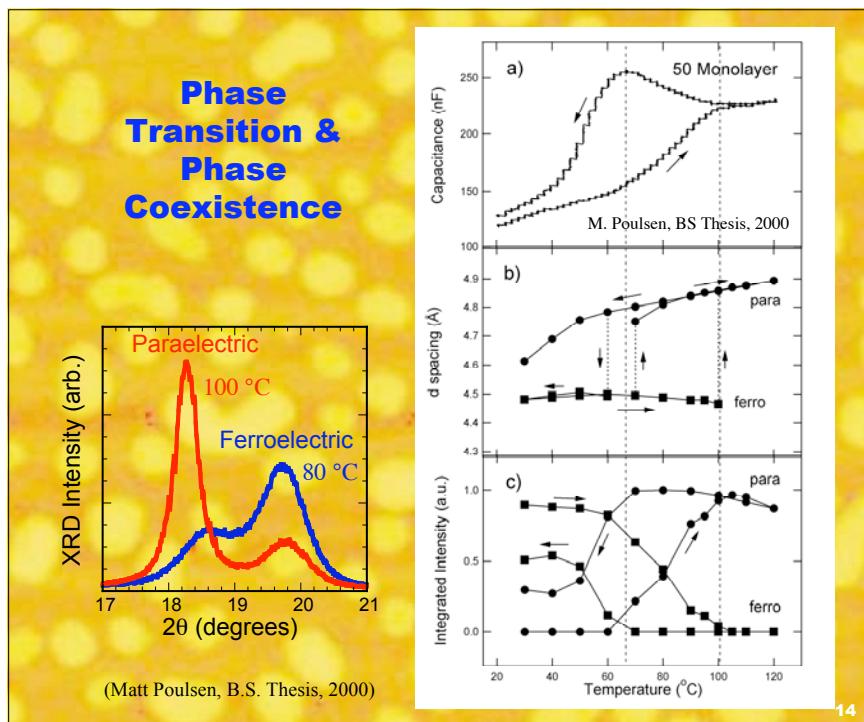
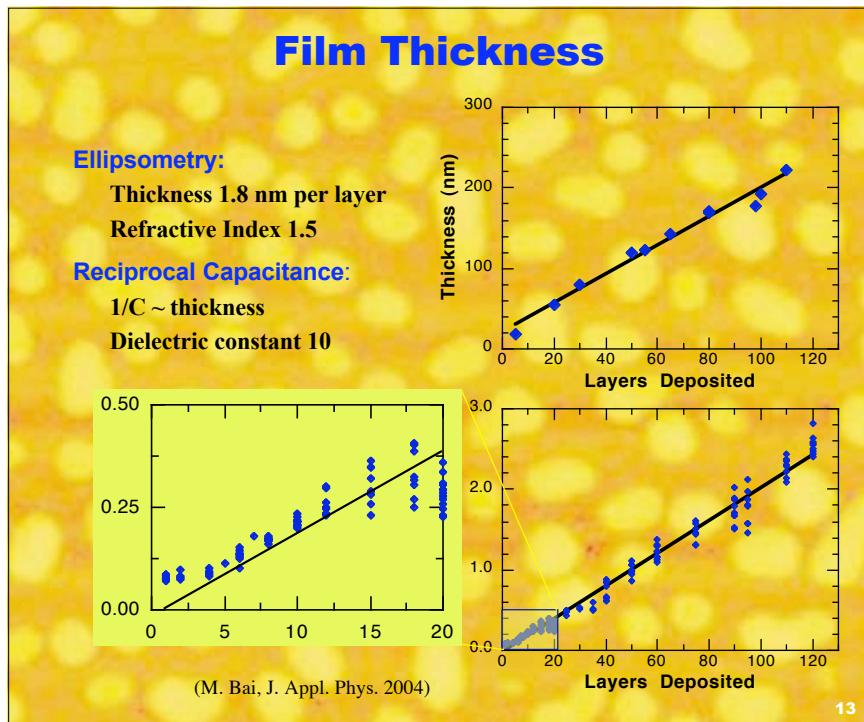


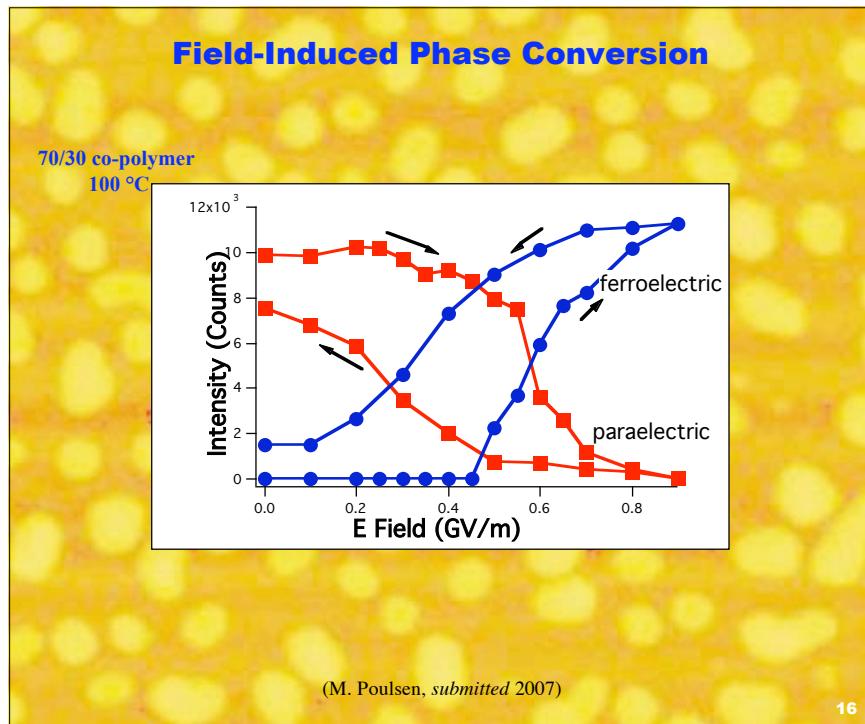
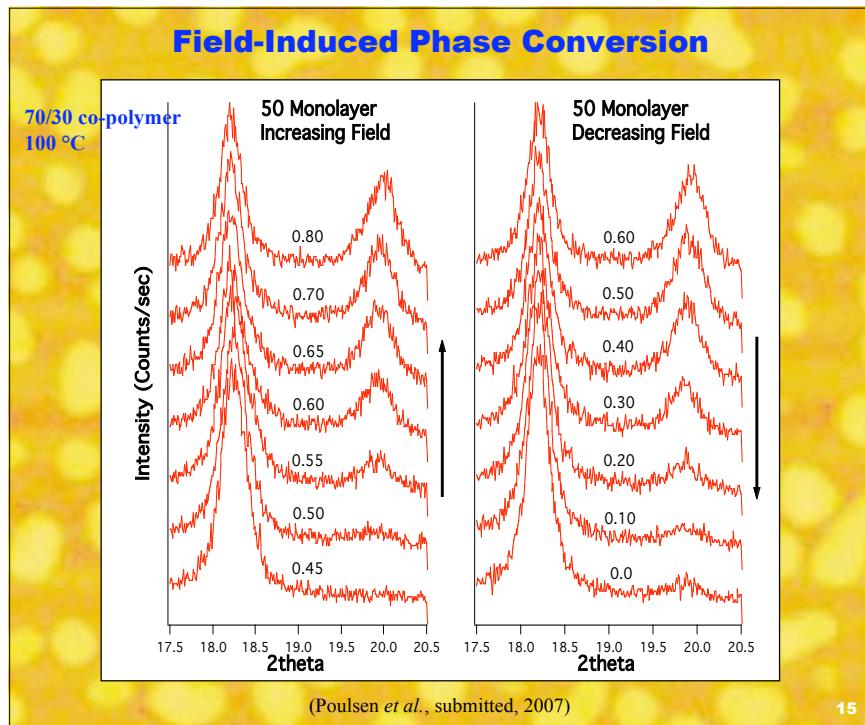
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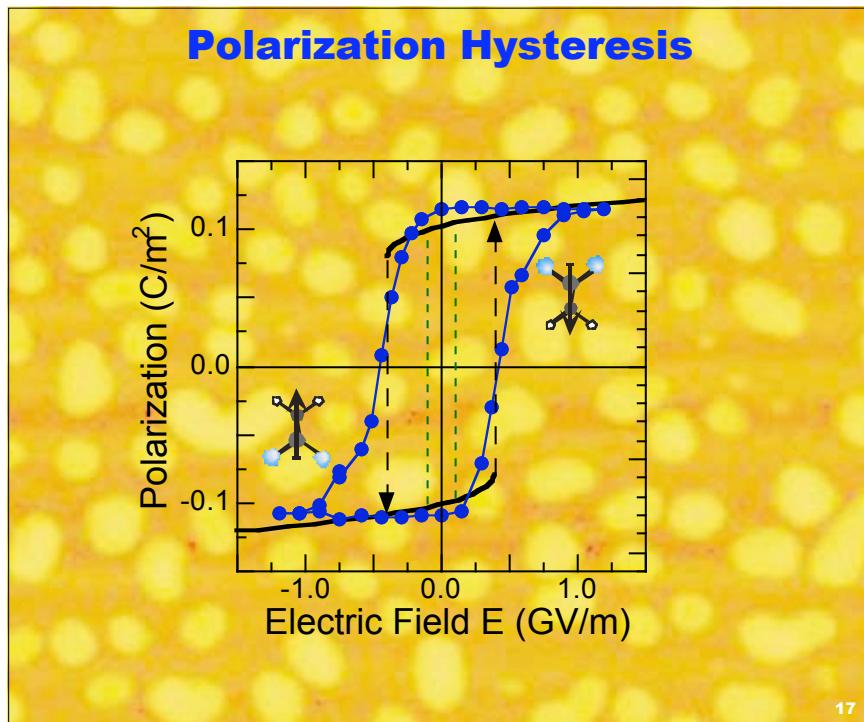
Ferroelectric Copolymer LB Films



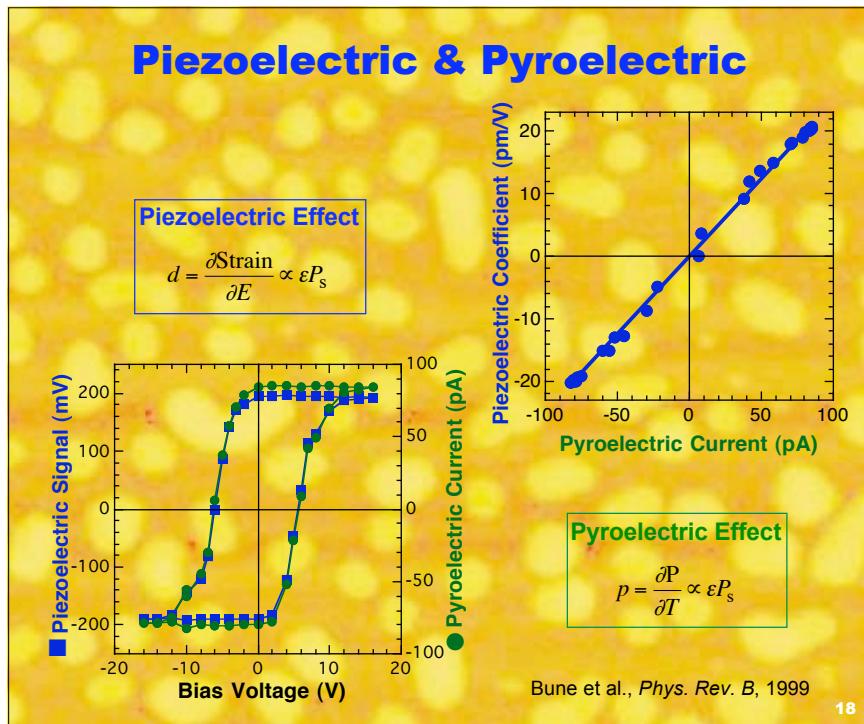
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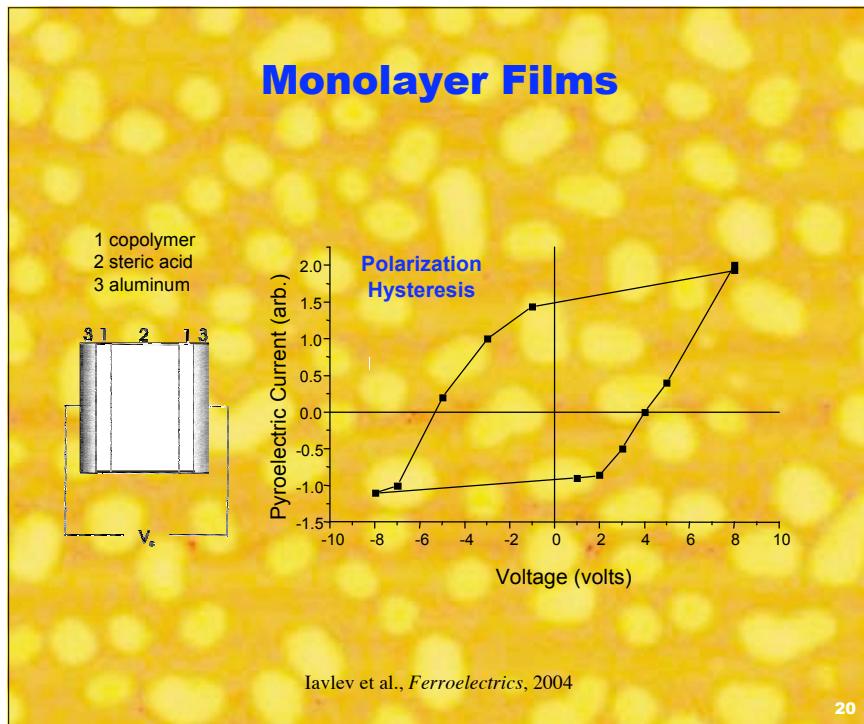
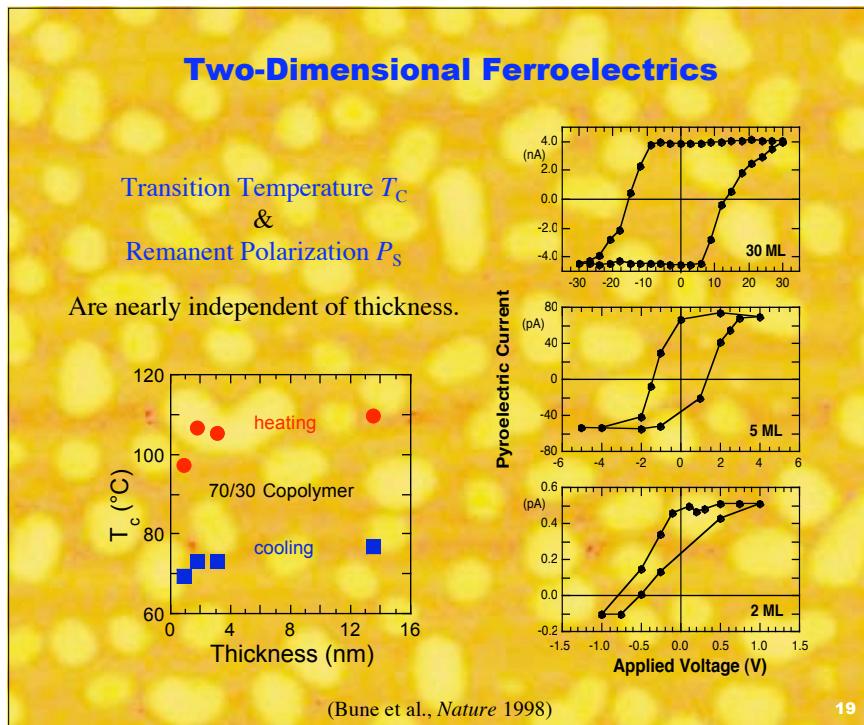


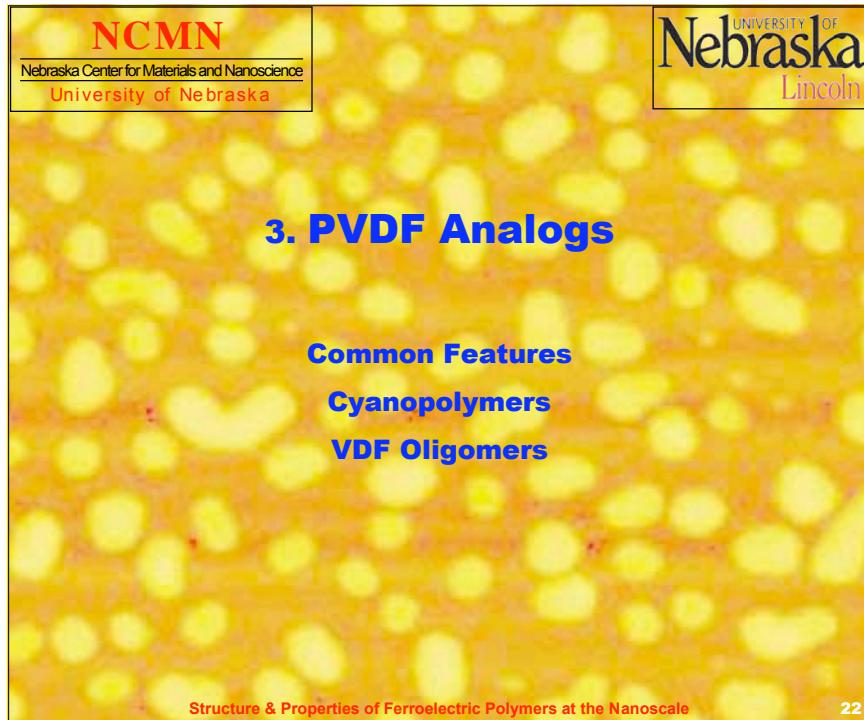
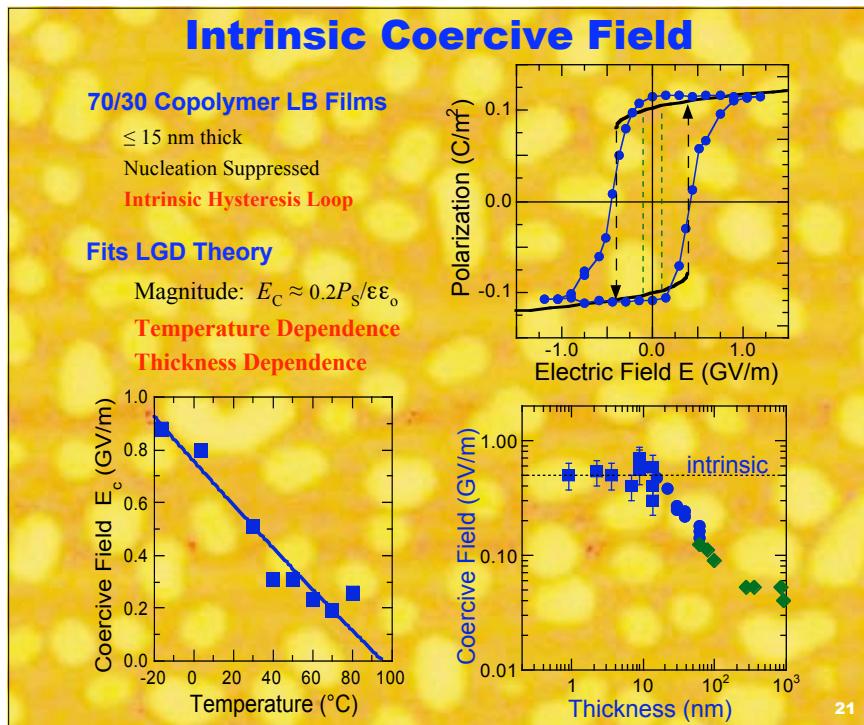


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Other Polar Polymers

Common Features

Narrow Rod-Like Polymers

Fixed Electric Dipole

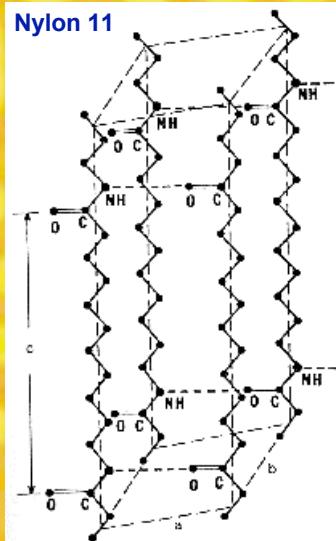
Odd Nylons (m odd)



Fluorine Replacement $[\text{CH}_2-\text{CF}_2]$

Chlorine analogs $[\text{CH}_2-\text{CCl}_2]$

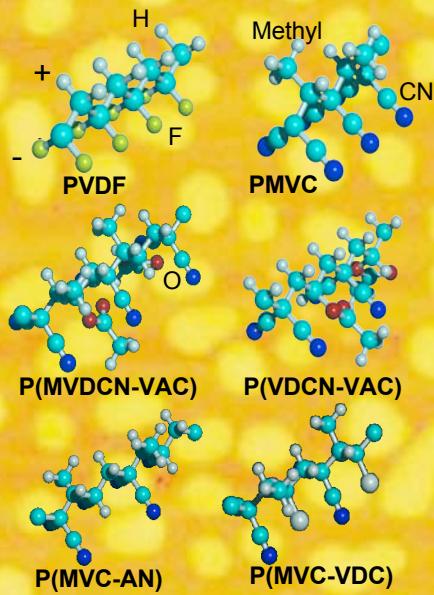
Cyanide analogs $[\text{CH}_2-\text{C}(\text{CN})_2]$



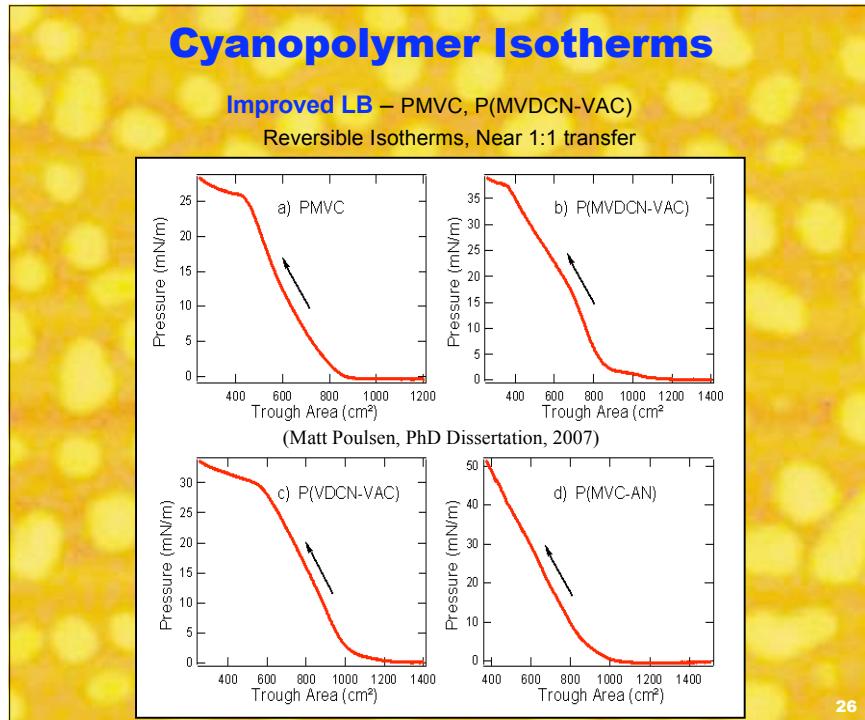
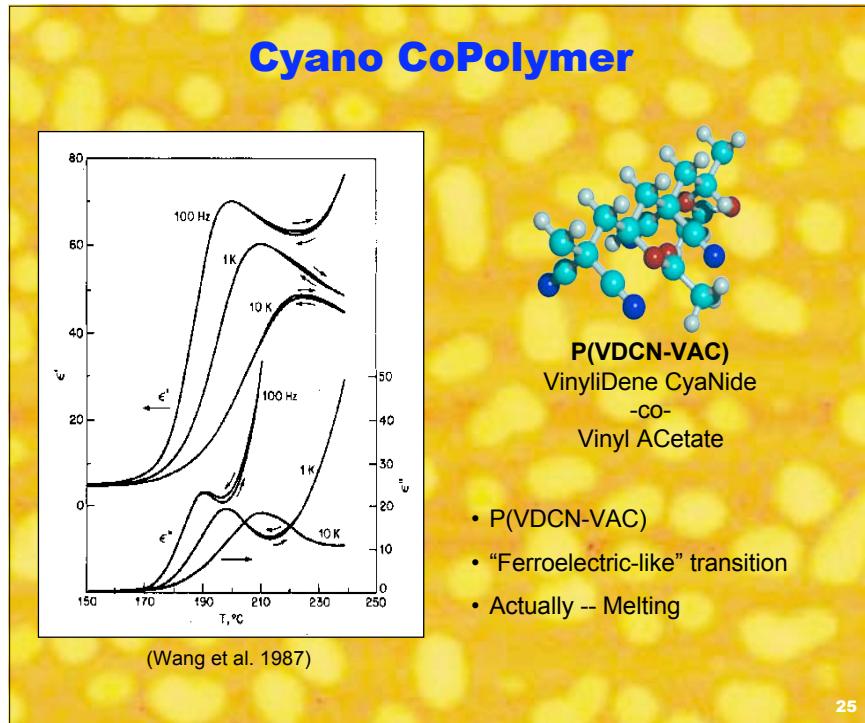
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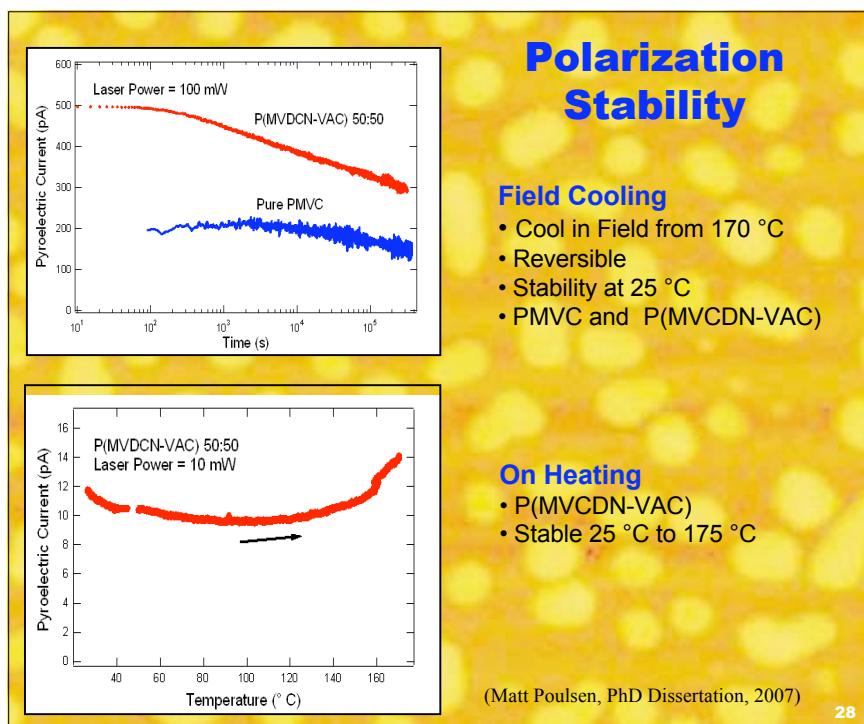
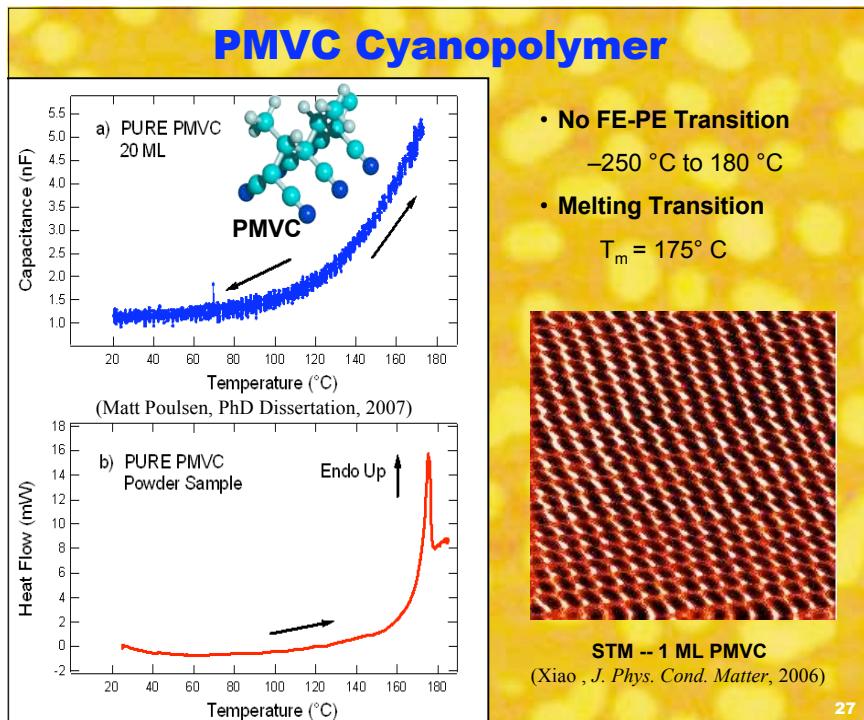
CyanoPolymers

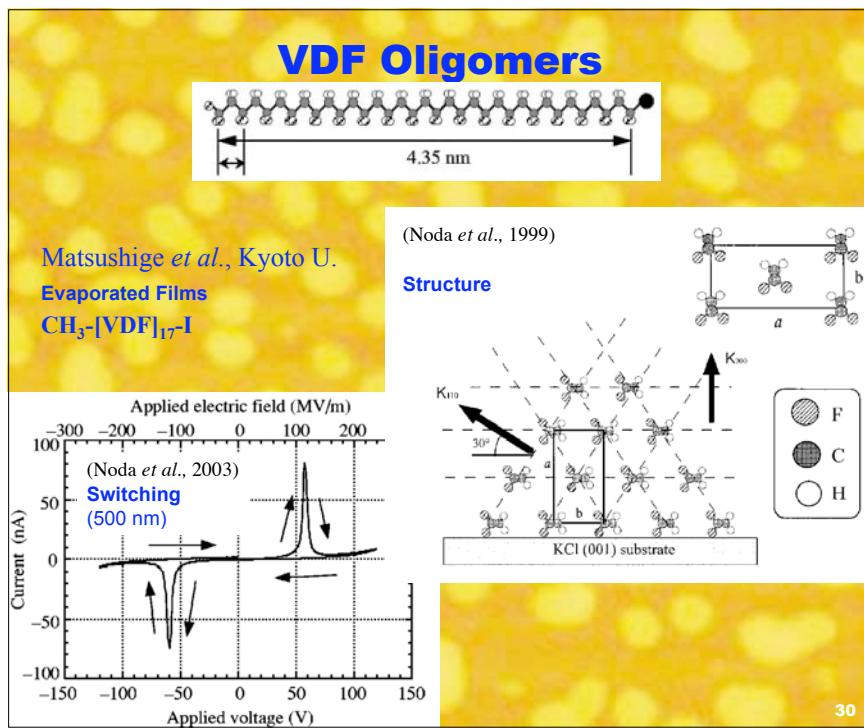
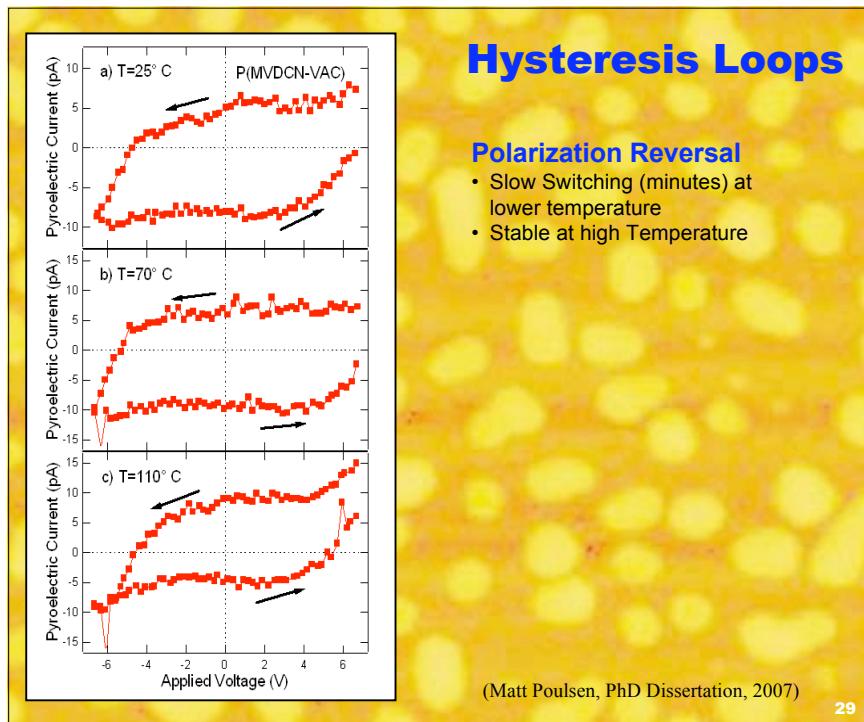
- Chemical analogs PVDF (CH_2-CF_2)
- Replace F with Cl, CN,
- Methyl groups ($-\text{CH}_3$) to increase amphiphilicity (for better LB films)
- Polymers & Copolymers

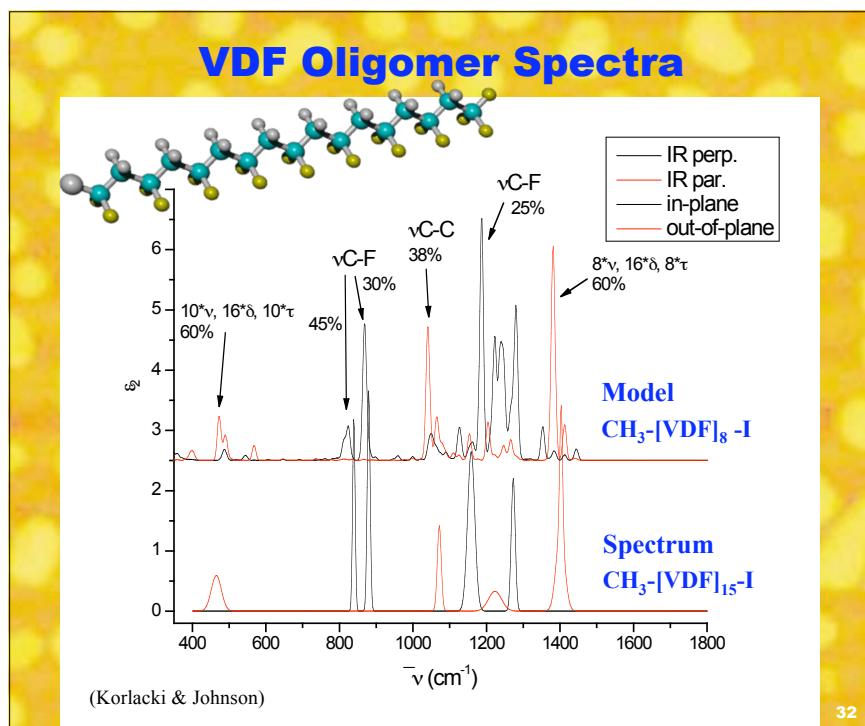
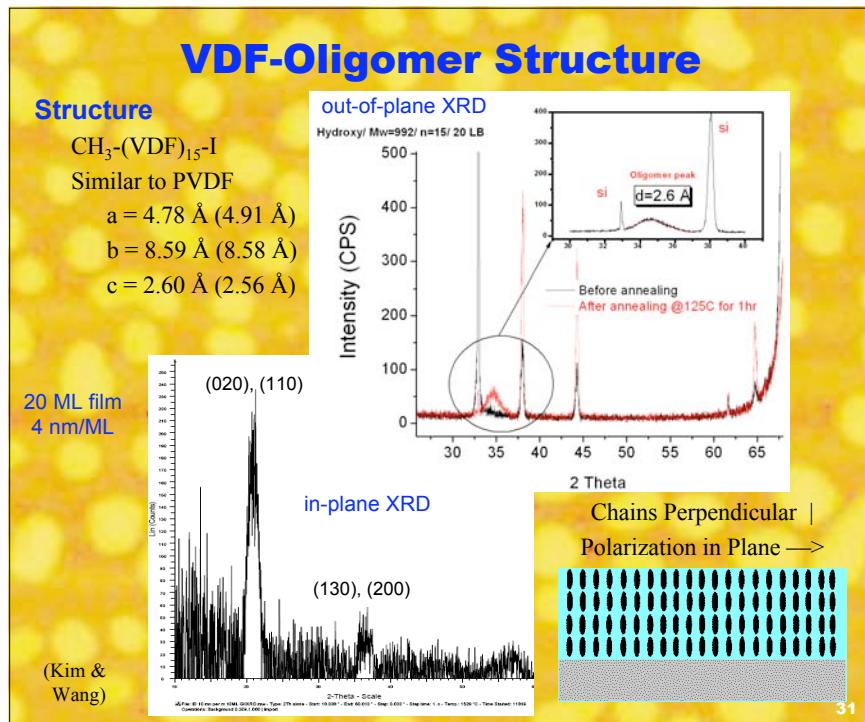


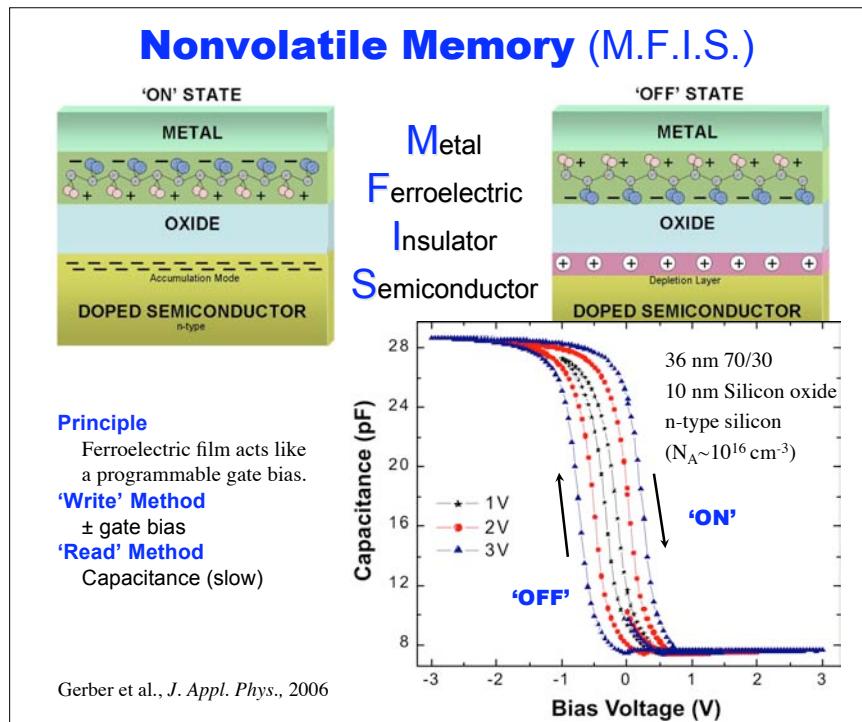
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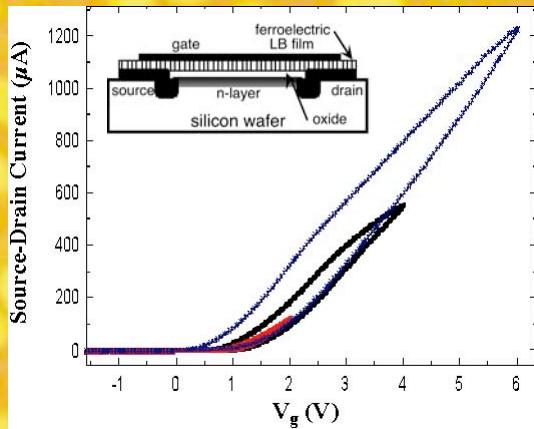






Ferroelectric Field-Effect Transistor

Allows fast, nondestructive, Readout

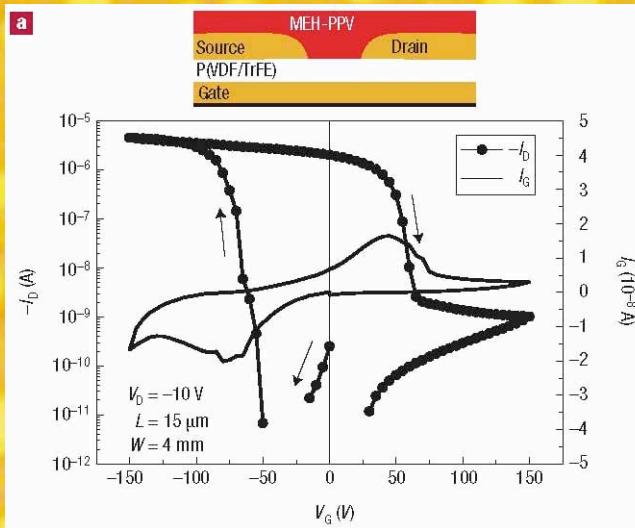


Sample Construction

- 19 nm 70/30 copolymer
- 10 nm Silicon oxide
- n-type silicon ($N_A \sim 10^{16} \text{ cm}^{-3}$)

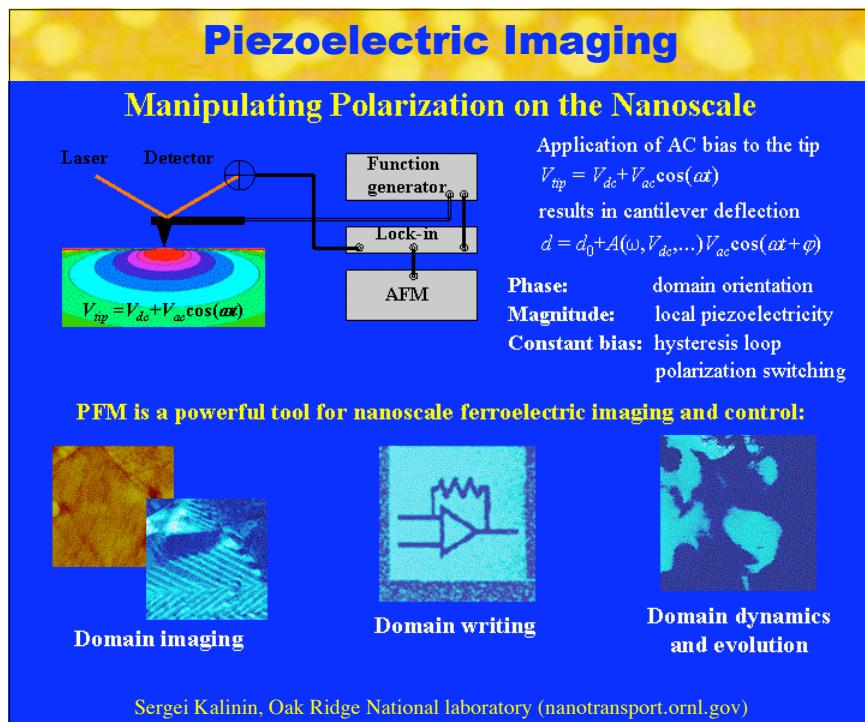
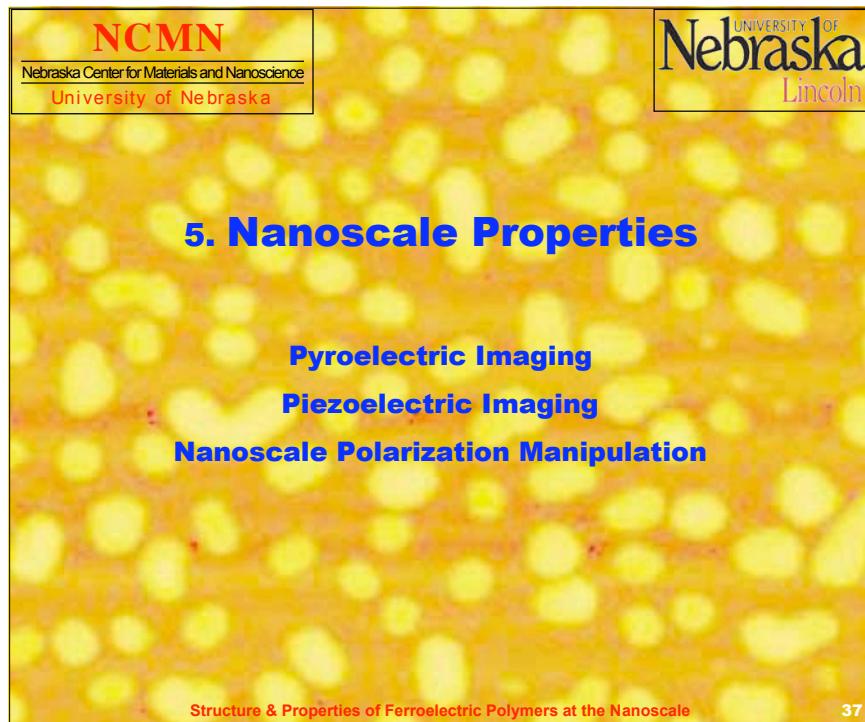
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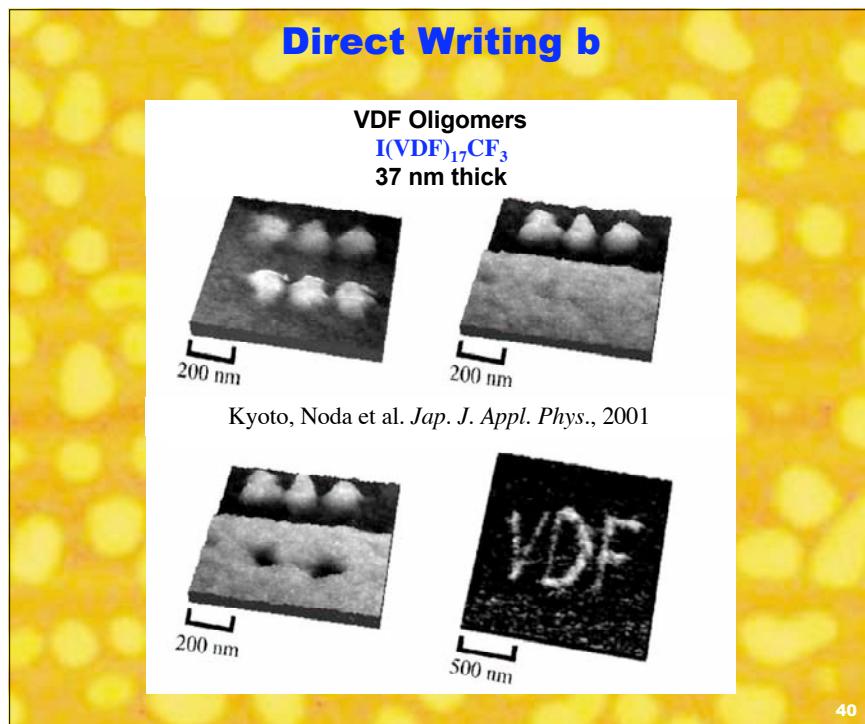
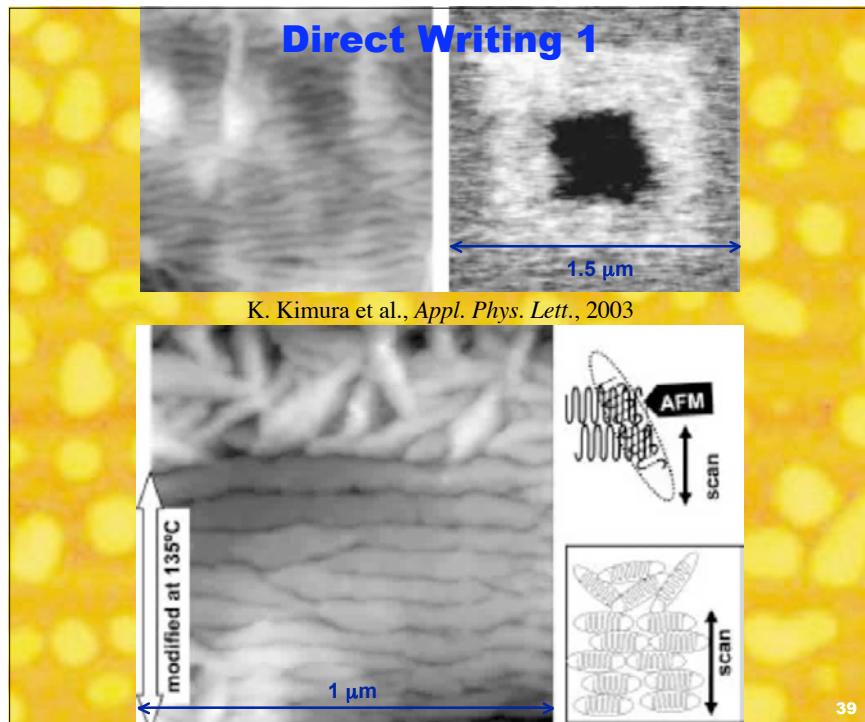
All-Organic Ferroelectric Memory

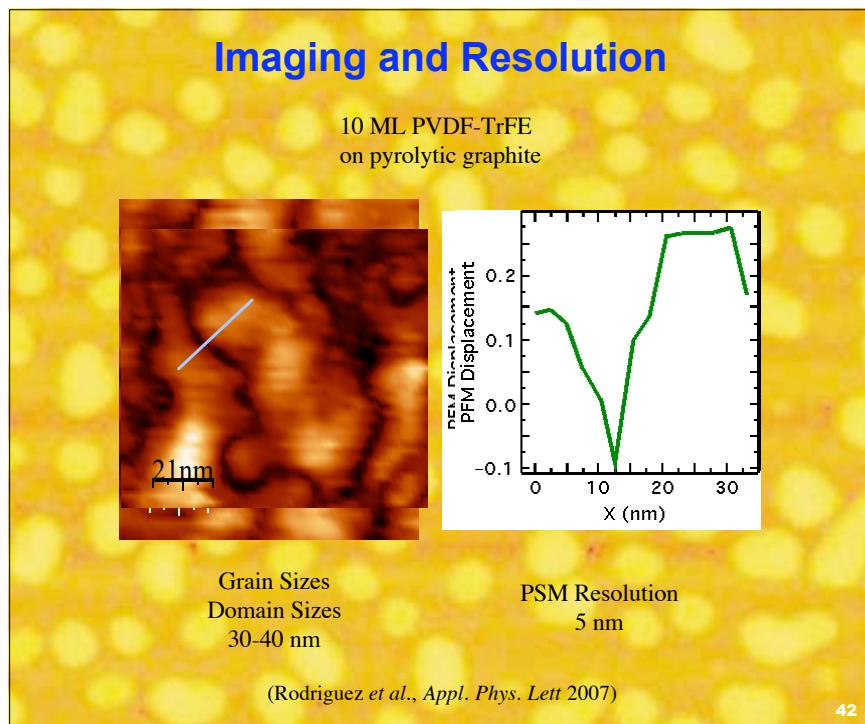


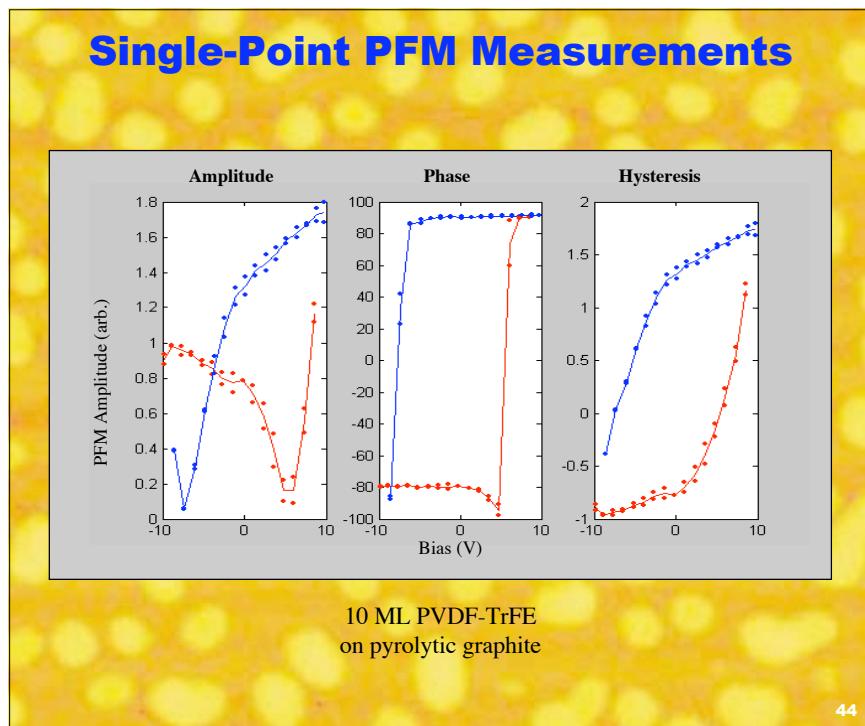
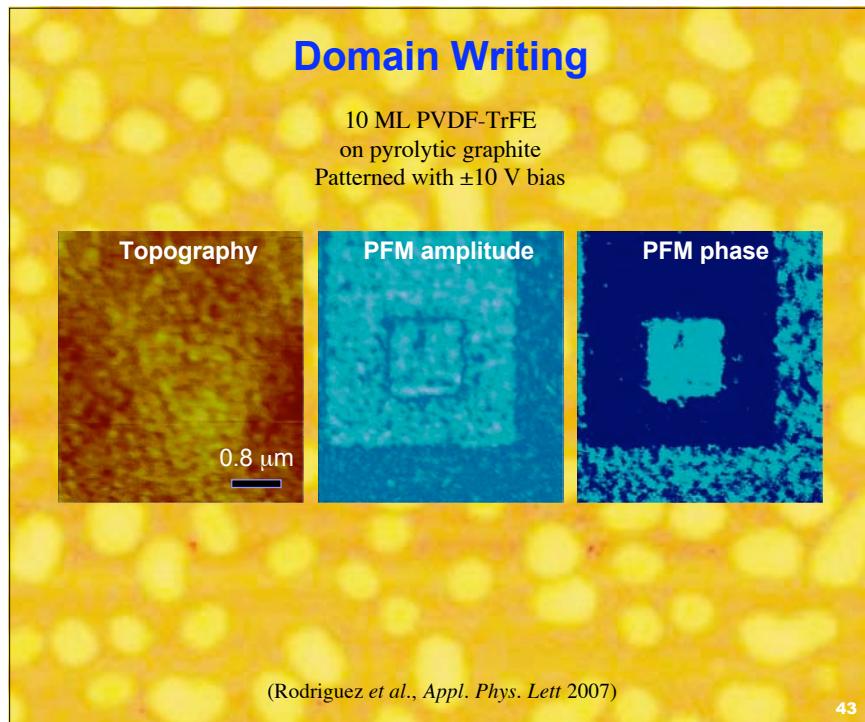
Naber et al., *Nature Materials*, 2005

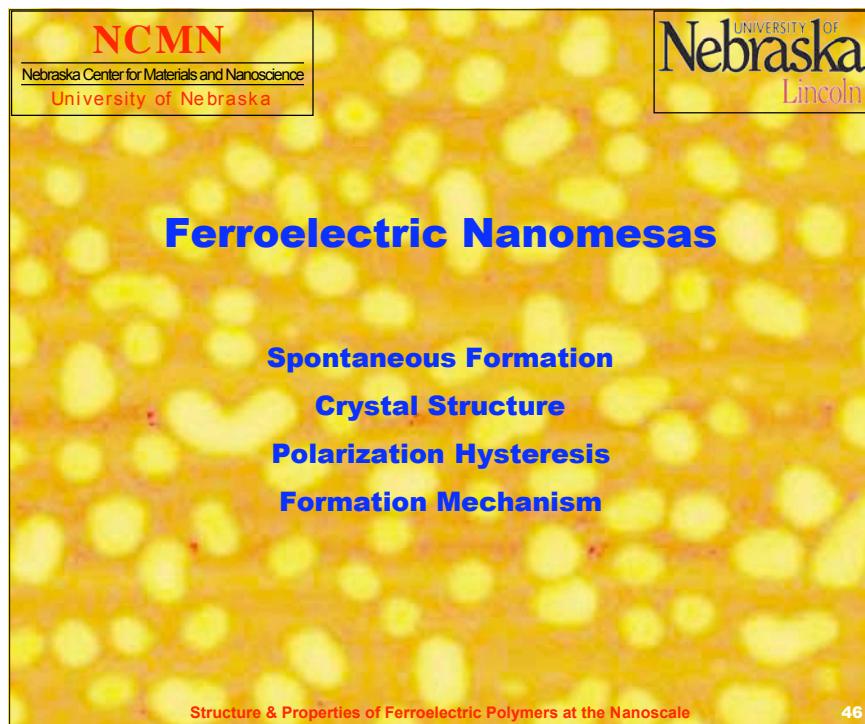
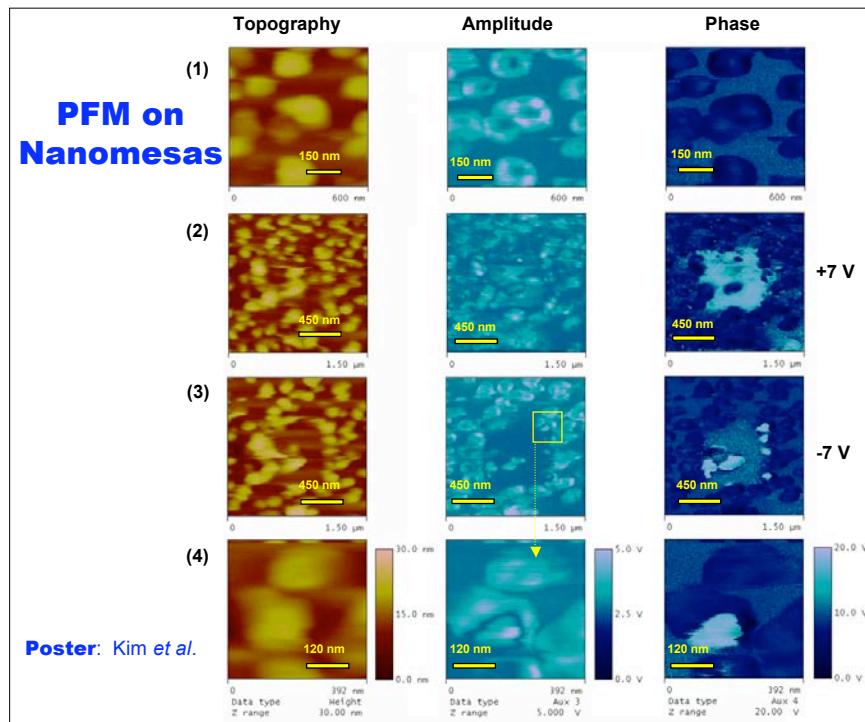
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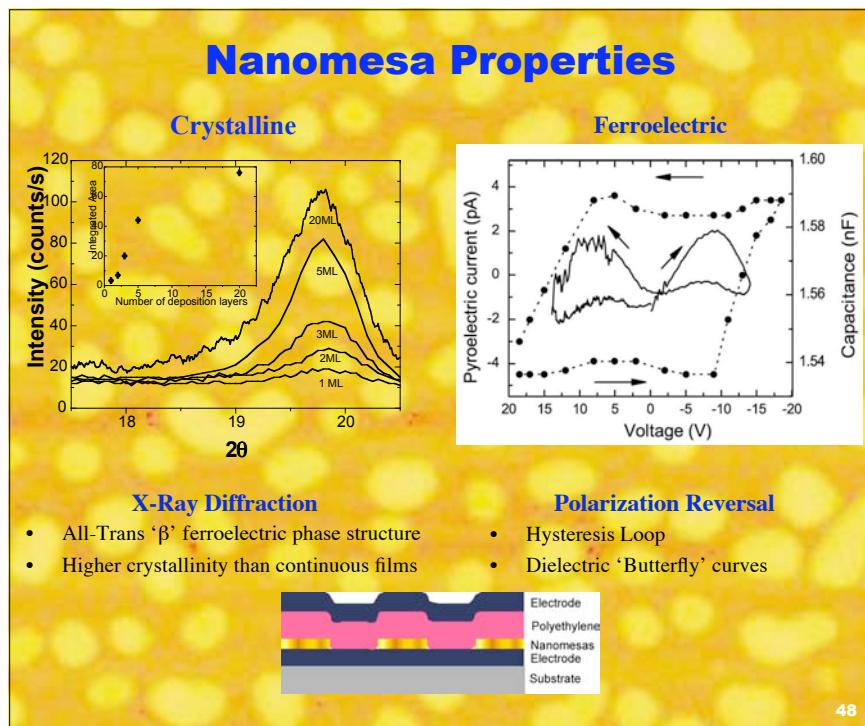
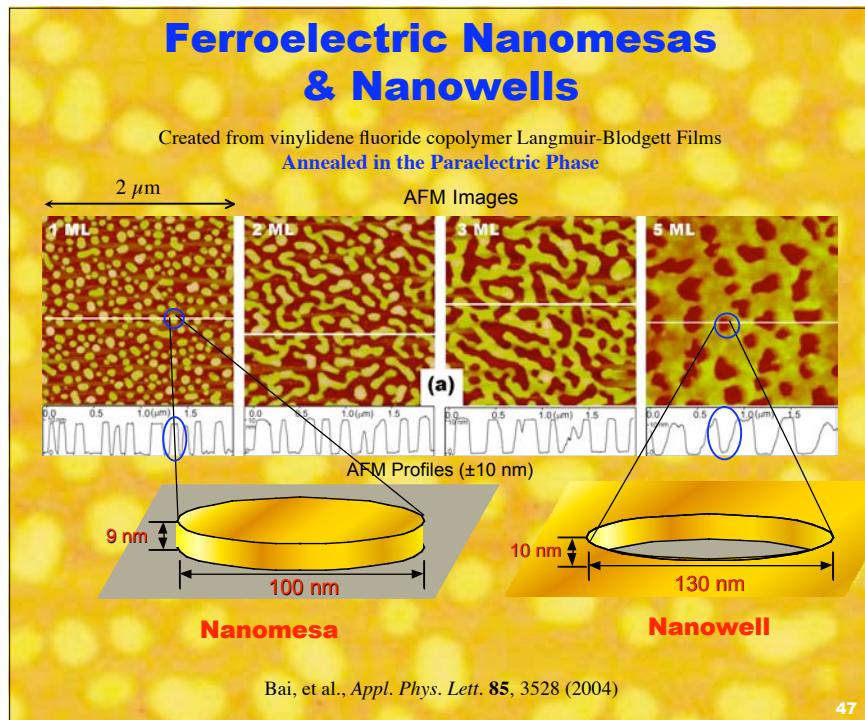


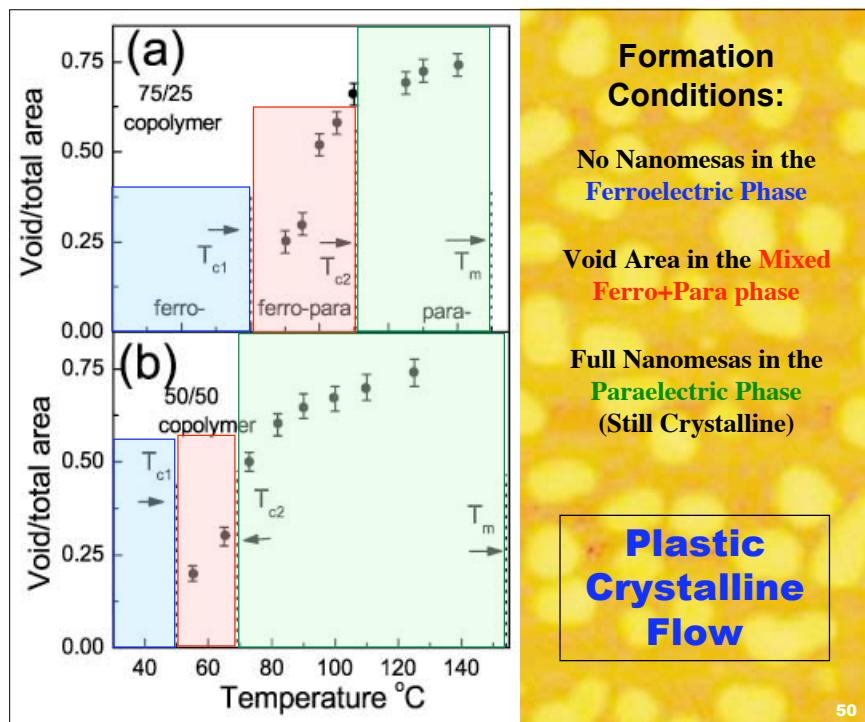
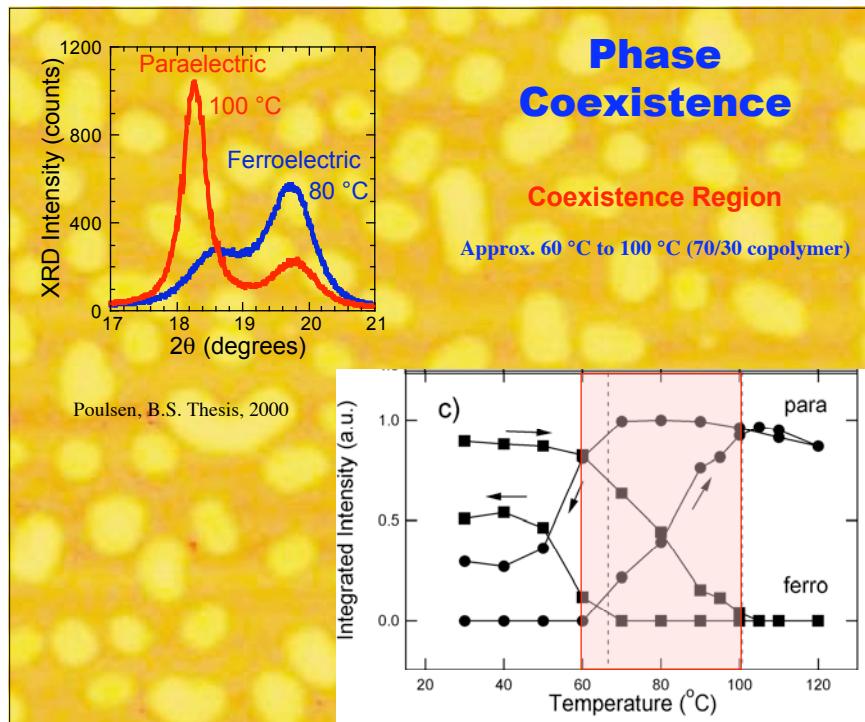








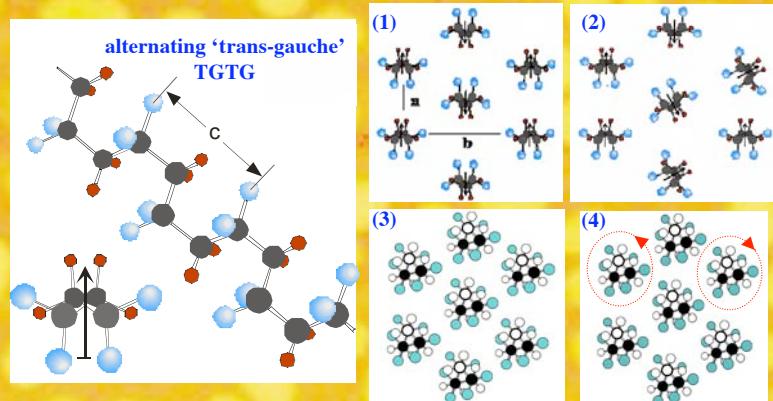




'CONDIS'-Conformational Disorder

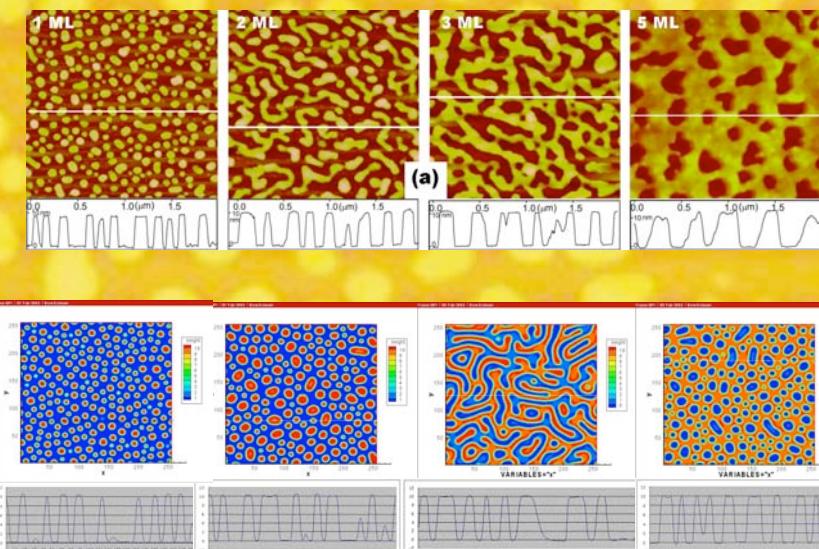
Allows Flow Perpendicular to the Chains

1. Regular TG conformation, orientational order-static
2. Regular TG conformation, orientational disorder-static
3. Conformational TG disorder-static
4. Conformational TG disorder-dynamical (CONDIS).

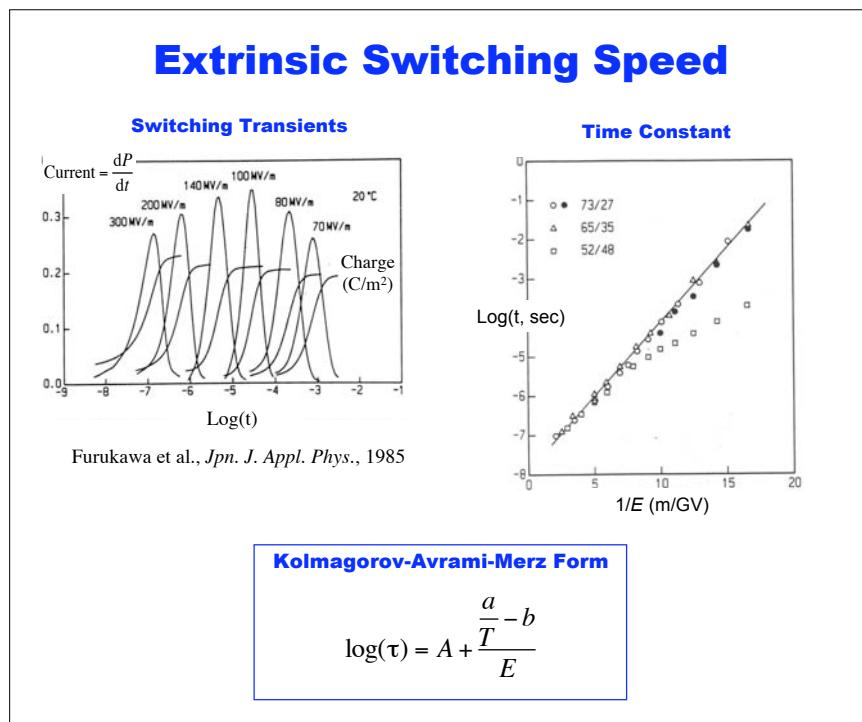
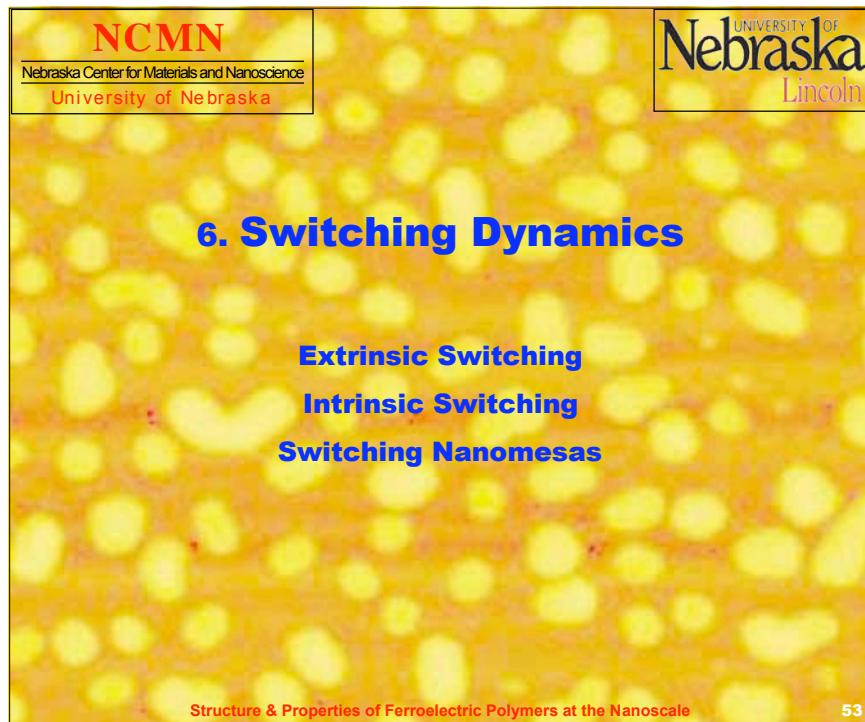


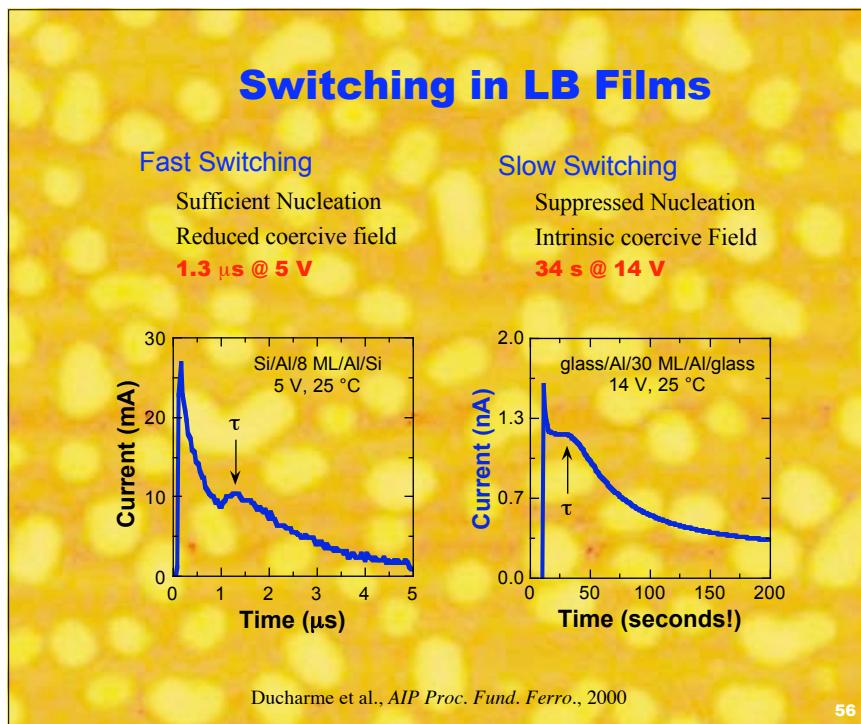
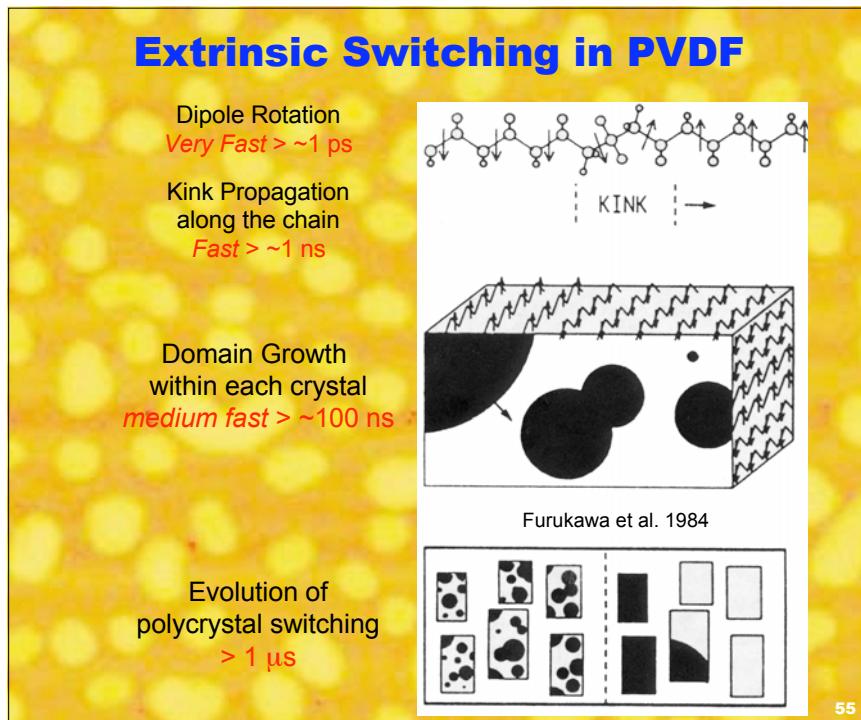
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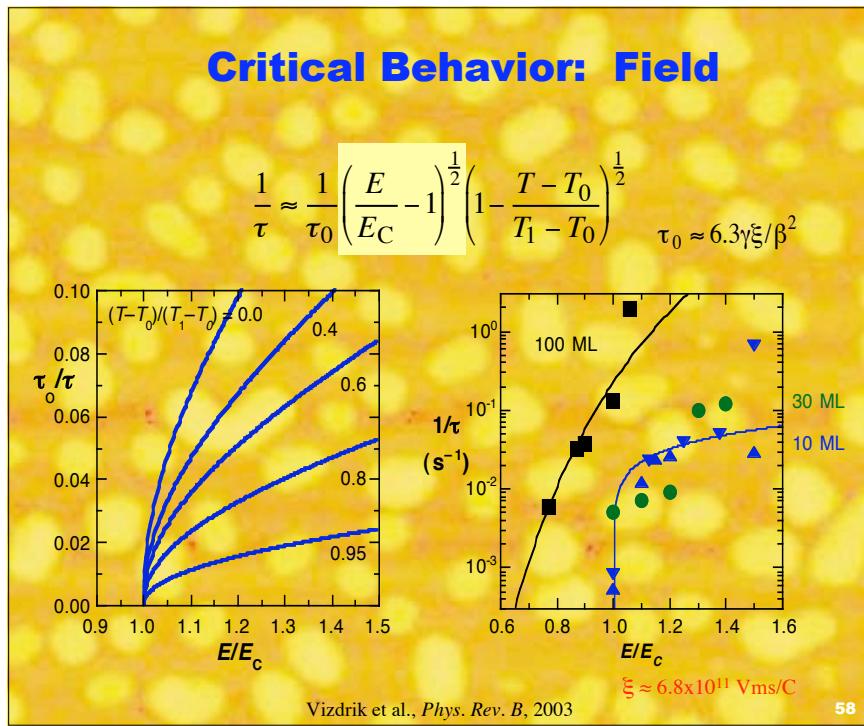
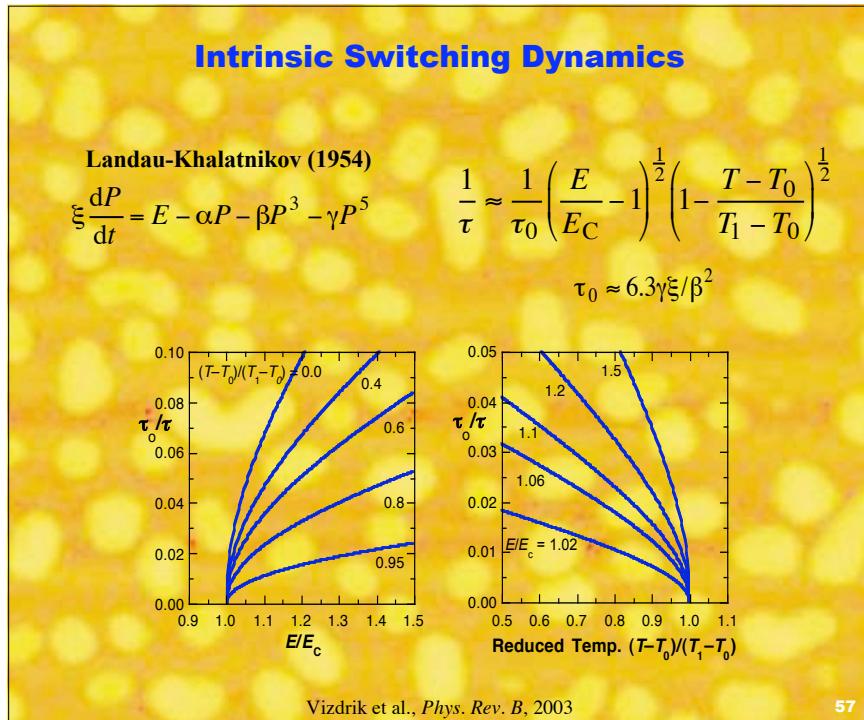
Modeling Nanomesas

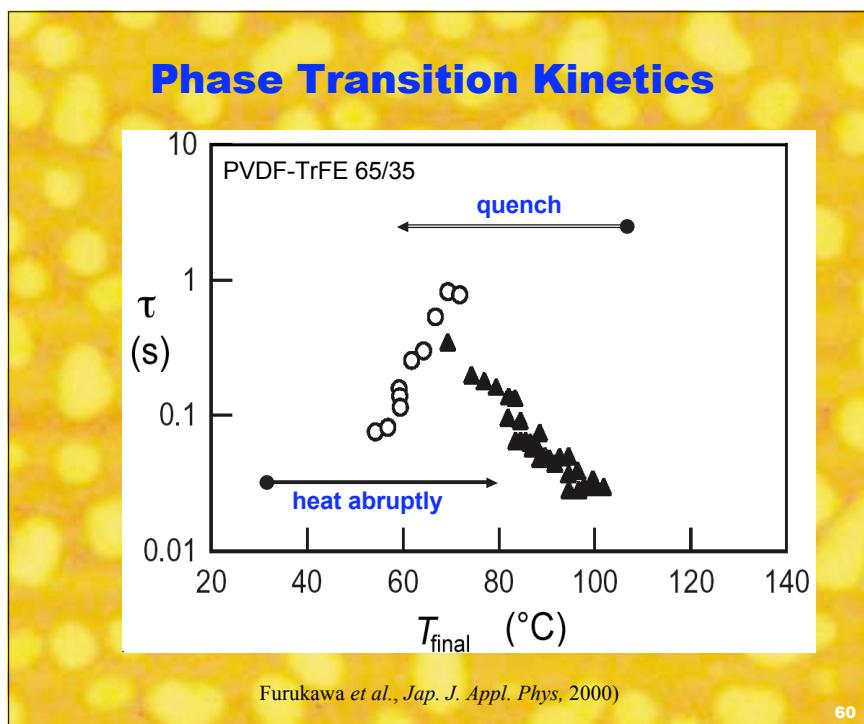
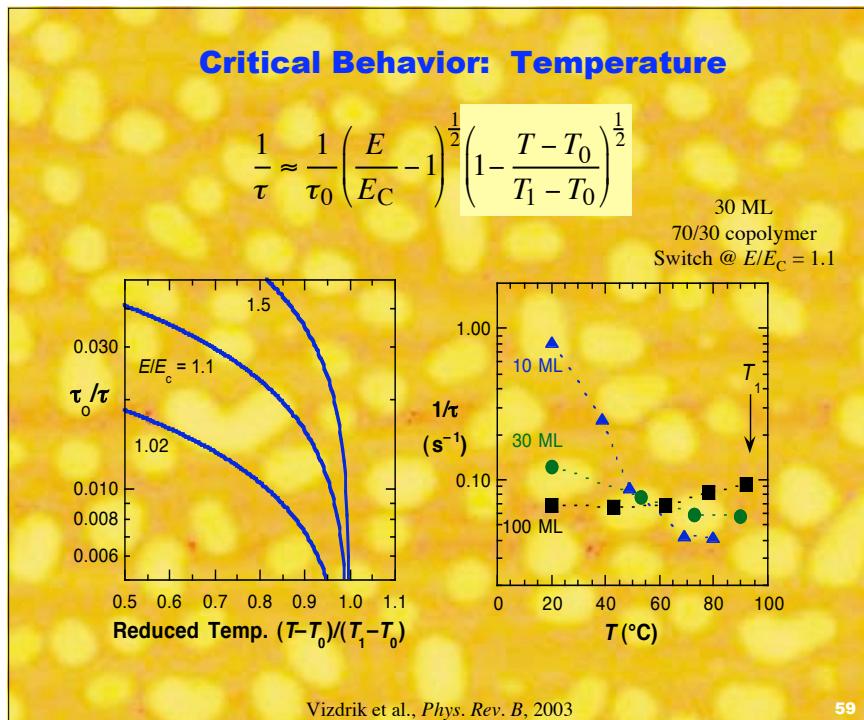


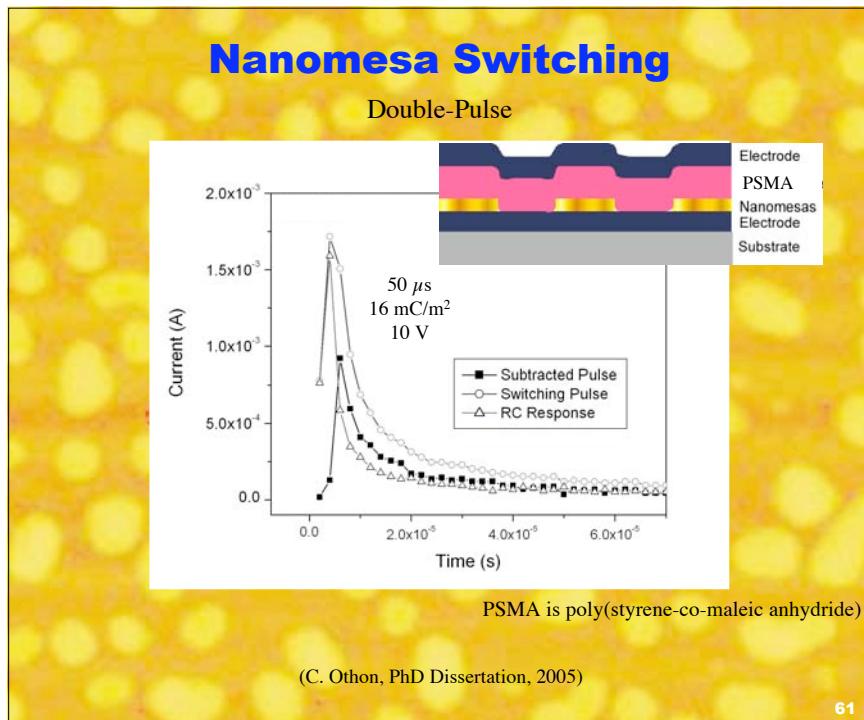
Li et al., *Appl. Phys. Lett.*, 2005

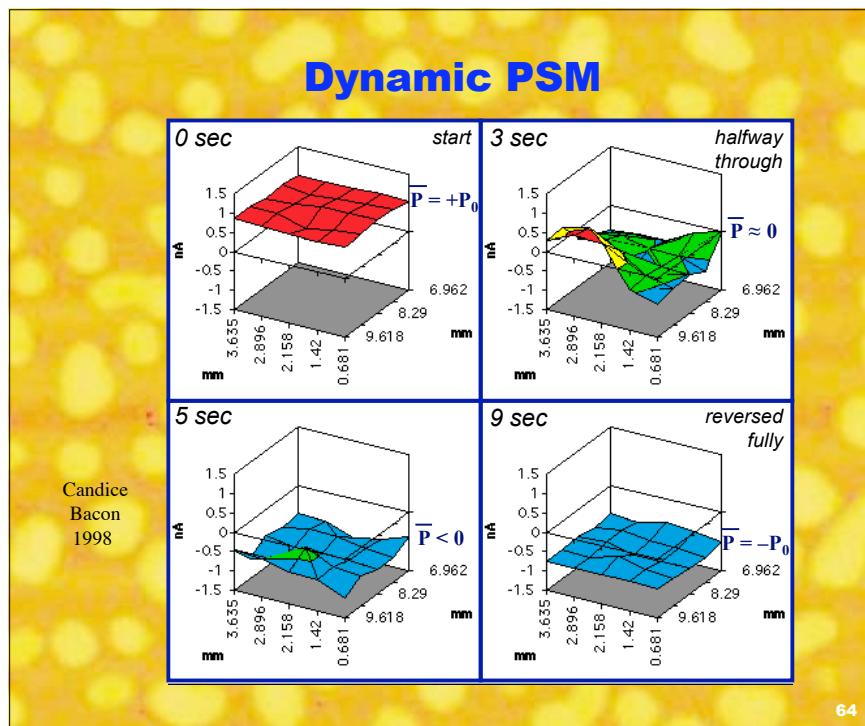
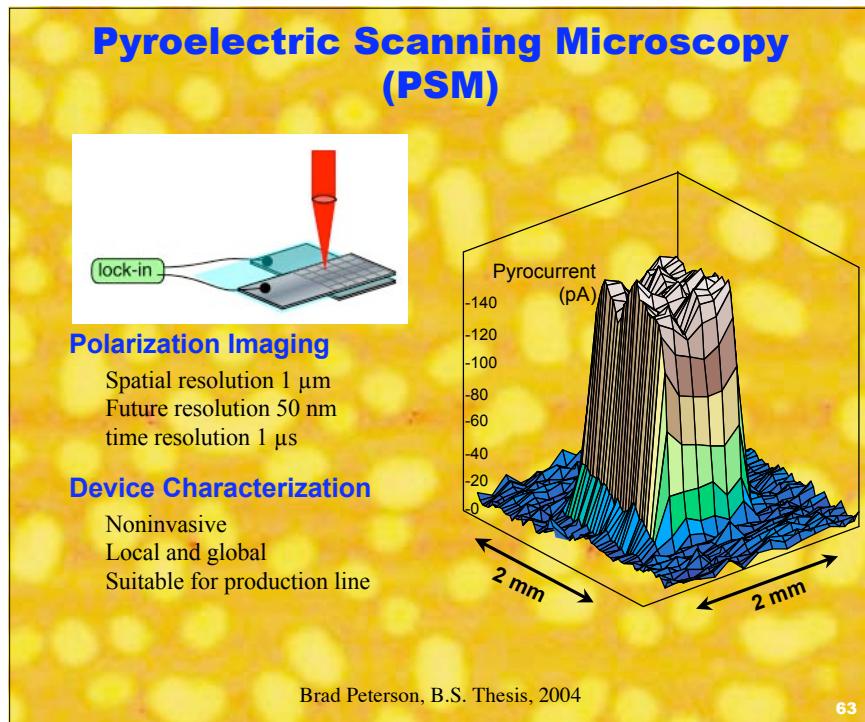




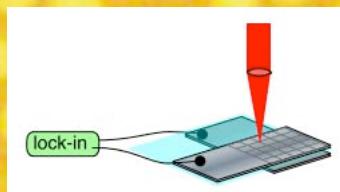






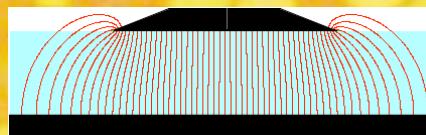
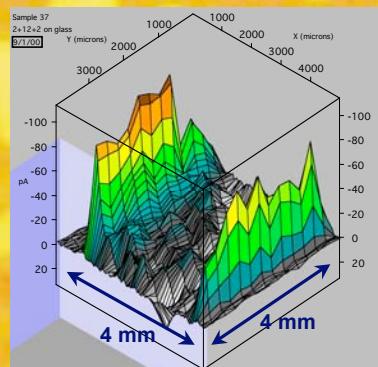


Edge Enhancement (Bat Ears)



Edges Polarize First

Partially polarized
Field Enhancement on top
electrode edges
20 ML thick

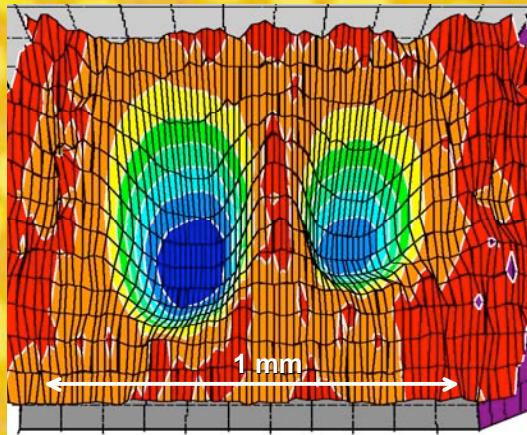


Peterson et al., *Ferroelectrics* 2004

Laser Depolarization

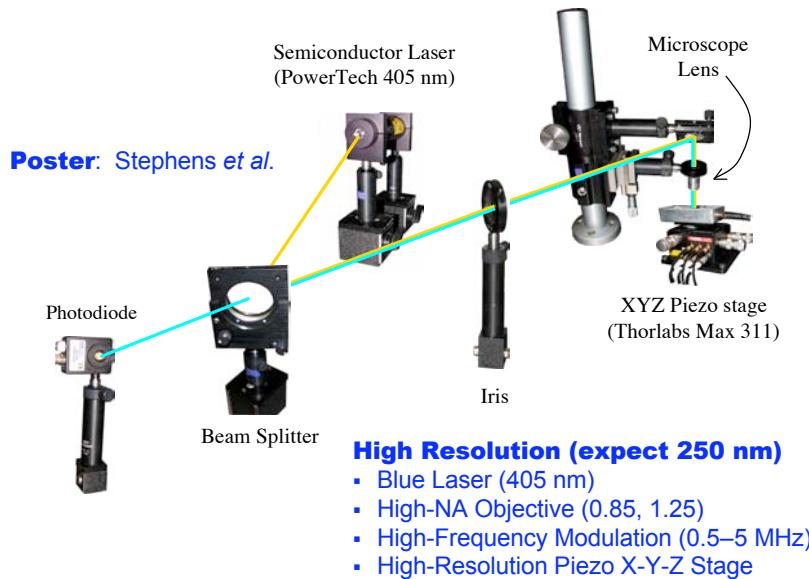
Focus Laser Beam
Heats to ~ 130 °C
Depolarizes the film
Repol polarize Electrically

PSM
Image

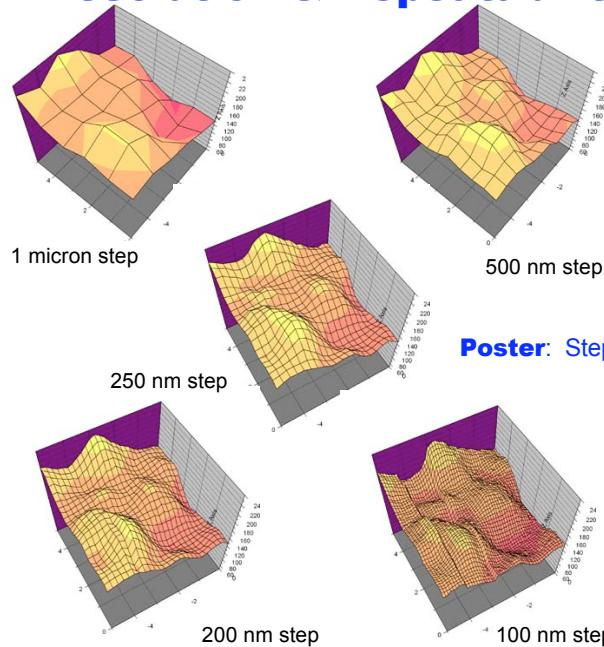


C. Othon, PhD Dissertation, 2005

Nanoscale PSM



Resolution & Repeatability





Contributors

The Real Work done by

Post Docs: Bune, Sorokin, Vizdrik, Ge, Zhang, Korlacki

Grad. Students: Bai, Choi, Kim, Kraemer, Othon, Poulsen, Reece, Wang

Undergrads: Bacon, Pebley, Peterson, Johnson, Plowman, Stephens

University of Nebraska

Shireen Adenwalla (Phys): x-ray/neutron diffraction

Peter Dowben (Phys): electron spectroscopy

Wei-Ning Mei (UNO Phys): first-principles molecular modeling

Ravi Saraf (Chem Eng): surface chemistry

Jim Takacs (Chem): organic synthesis

Institute of Crystallography-Moscow

Vladimir Fridkin: theory, switching measurements. the really good ideas

with: K. Verkhovskaya, G. Vizdrik, A. Iavlev, A. Tolstousov, A.R. Geivandov

Lev Blinov: LB deposition

with: S. P. Palto, S. G. Yudin, A. V. Sorokin, N. N. Petukhova, A. Zlatkin

Other Institutions

Craig Herzinger (J. A. Woollam Co.): ellipsometry

Sergei Kalinin (Oak Ridge Natl. lab.): piezoelectric microscopy

with: Brian Rodriguez, Stephen Jesse

Jiangyu Li (U. Washington): multiscale modeling

Hermann Kohlstedt (IFF-Jülich): ferroelectric memories

Horacio Vasquez (U. Texas-Pan Am): pyroelectric scanning microscopy

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Nebraska Research Initiative (NRI)

UNL Vice Chancellor for Research

Nebraska Center for Materials & Nanoscience

Other

Russian National Science Foundation (Moscow)

Inco-Copernicus Fund (Moscow)

Volkswagen Foundation (Jülich)

Corporate

J. A. Woollam Company

HP Research

This Space for Lease

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University of Nebraska

Future...

UNIVERSITY OF Nebraska Lincoln

Materials

- New Organic Ferroelectrics
- Nanomesa Formation Dynamics

Ferroelectricity

- Nanoscale Ferroelectricity
- Switching Processes
- Modeling

Applications

- Nonvolatile Memories
- High-Energy-Density Capacitors
- Infrared Imaging Arrays
- Ultrasonic Imaging Arrays
- Microfluidics

“I am strangely tired, not from having talked so much but at the mere thought of what I still have to say.”

--Albert Camus, *The Fall*

Structure & Properties of Ferroelectric Polymers at the Nanoscale

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