Chemical Imaging of Polymers in Real- and Reciprocal Space

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X-ray Microscopy:
X-rays have come a long way!
(Examples “biased” towards polymers/magnetic materials)
Outline

● Chemical Imaging = Spectromicroscopy
  ♦ Beamson and Turner (early 1980’s) coined the (unwieldy) term “spectromicroscopy”

● Near Edge X-ray Absorption Fine Structure (NEXAFS): The Basics
  ♦ Organic materials as examples. Magnetic materials also important class of materials

● Microscopy: Basics

● NEXAFS Microscopy of Polymers
  ♦ Some examples that exemplify applications.

● Resonant Scattering. NEXAFS “microscopy” in reciprocal space

● Future Perspective
Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy

Example: “”Richness” of Polymer NEXAFS Spectra

C 1s edge ~ 290 eV
N 1s edge ~ 405 eV
O 1s edge ~ 540 eV
Some Polymer NEXAFS Spectra

Dhez, Ade, and Urquhart

Photon Energy / eV

Data: Stony Brook STXM at NSLS

Some Polymer NEXAFS Spectra

Dhez, Ade, and Urquhart
Types of X-ray Microscopes

Scanning x-ray microscope
- Monochromator
- Undulator
- Spatial filter
- Objective Lens
- Projective Lens
- Sample
- Detector
- Micro zone plate objective
- Raster scan
- Computer

STXM
- Sample
- Detector
- Raster scan
- Computer

X-Photoemission Electron Microscope (PEEM)
- X-ray Beam
- Sample
- Aperture
- Objective Lens
- Projective Lens
- Magnified Image

Conventional x-ray microscope XM-1 at the ALS
- X-ray Beam
- Sample
- Condenser zone plate
- Plane mirror
- ALS Bending Magnet

TXM
- Sample stage
- Micro zone plate
- Mutual Indexing System with kinematic mounts

Also Scanning Photoemission X-ray Microscope (SPEM) Ade et al. 1992
X-ray imaging of polypropylene/styrene-acrylonitrile
First NEXAFS imaging in transmission (1992)

- Based on the Stony Brook X1A-STXM (1989-present)
- X1A-STXM not explicitly built to perform spectroscopy, but proved flexible enough to perform carbon NEXAFS.
  - Polymer Science was “enabled”

Data: Stony Brook STXM at NSLS
X-Linear Dichroism Microscopy

Kevlar 149 fibers, 200 nm thick, imaged at 285.5 eV

- Pattern rotates with rotation of polarization due to radial orientation of phenyl groups
- Phenyl and carbonyl groups point (on average) radially outward
- $\pi^*$ and $\sigma^*$ resonances show complementary dichroism


Data: Stony Brook STXM at NSLS
NEXAFS Microscopy:
A number of examples for organic materials

- Bilayers of thin polymer films. Can mixing be induced by physical means, i.e. confinement? - e.g. Zhu et al., Nature 40, 49 (1999)
- Organic geological materials
- Polymer surfaces
- Composition of macrophases in polyurethanes
- Polymer compatibilization with clays (ongoing)
- Semi-crystalline polymers
- Meteorites
- Diamond like carbon films
- Biofilms
- Biology
- ……..
PS/PMMA/clay nano-composites
A universal and less expensive method of polymer compatibilization?

Sample Preparation

Polystyrene (PS) Poly(methyl methacrylate) (PMMA)

1. Polystyrene (PS), Poly(methyl methacrylate) (PMMA) polymer blends and Clay are codissolved in toluene.
2. Solution are dispersed under ultra sound for 20 mins.
3. Films are spun-cast from solution onto Si$_3$N$_4$ with thickness between 800Å to 2000Å.
4. Films were annealed in 10$^{-3}$ Torr, oil free vacuum environment.
Polymer Clay Composites: PS/PMMA

- Clay works better than use of block copolymer to "compatibilize" the blend
- Observe the same in bilayer geometry

DSC suggest formation of “single” phase in the presence of clay

PS/PMMA 70/30

PS/PMMA/P(S-b-MMA) 45/45/10

PS/PMMA/Clay 45/45/10


Data: Polymer STXM at ALS

H. Ade et al., NSLS-II_ade_march2004.ppt
Compatibilization mechanism?

**TEM**

- 200 nm

**DSC**

- Set of thermograms showing PS and PMMA peaks.

**5% Cloisite 6a**

- 5% Cloisite 6a added to PMMA preannealed at 170° for 24 hrs.
- Annealed after bilayer was created for 72 hrs at 170°.

**10% Cloisite 6a**

- Data: Polymer STXM at ALS

**STXM**

- PMMA preannealed at 170° for 24 hrs.
- No preannealing.

**Why NEXAFS microscopy?**

- Lots of characterization for than tertiary and more complicated blends.
- Quantitative analysis of domains.

Formation of polymer-clay grafts.

Process is not diffusion controlled, but absorption controlled.
PS/PMMA/PEP and PS/PMMA/PVC ternary blends

Where are all the components? – Ongoing projects!

PS/PMMA/PEP

“PS” dark

“PMMA” dark

“PEP” dark

Absorption coefficient (µm^-1)

0
5
10
15
20
25

PMMA
PS
PEP

Energy (eV)

280
285
290
295
300

PS/PMMA/PVC

RGB color composite image

PS (red), PMMA (green) and PVC (blue) clearly delineating each component.

Black areas are holes.

Mixtures of PS/PMMA/PEP w/ clay would benefit from better spatial resolution

Data: Polymer STXM at ALS

H. Ade et al., NSLS-II_ade_march2004.ppt
Organic geochemistry, solid phase biomaterials
(G. Cody et al. Geophysical Laboratory, Carnegie Inst.)

- Map lignin and carbohydrate distribution and characterize their thermal/time evolution
- Also, spectacular data on evolution of coke → metallurgical coke, steel production
- Followed evolution of sporopollenin in coal → may address mechanism/timing of oil generation
- More recent wood: Some fungus rot attacks lignin selectively
- Organic sediments

Data: Stony Brook STXM
Why are copolymers so “cool”?
Patterning, selfassembly

Webster's dictionary:
co·pol·y·mer (kō-pōl'ē-mer) n.
“A polymer of two or more different monomers.”

Diblock copolymers

Triblock copolymers

ABC Block Copolymer Morphologies

 Courtesy of G. H. Fredrickson (UCSB)

Courtesy of J. Genzer, Chem. E, NCSU

H. Ade et al., NSLS-II_ade_march2004.ppt
Nanolithography for quantum dots, magnetic storage

Semi-regular Arrays of $\sim10^{11}$ holes in 1 cm$^2$


Graphoepitaxy of Spherical Domain Block Copolymer Films

Markedly enhanced coercivity
Blockcopolymers:
First attempts with ALS 5.3.2 Polymer STXM

- STXM images at 285.1 eV of 90k-PS-b-PEO.
- Hexagonally arranged PEO cylindrical microdomains are about 50 nm in size.
- Larger features are thickness variations.

Blockcopolymer/homopolymer mixtures:
Important class of materials, templating

- Morphologies could be highly complex
- Where does the homopolymer go?
- Higher resolution, higher intensity needed!!!
NEXAFS microscopy of organic materials

- NEXAFS microscopy is a powerful characterization tool for any organic nanomaterial
  - Quantitative compositional analysis (surfaces and transmission)
  - Orientational analysis (surfaces and transmission)
  - Wet (solvated) samples (special cell in transmission)
  - Relatively low radiation dose/damage

- Oxygen and nitrogen K edge NEXAFS can provide additional information if O and N present

- Still a lot of room for instrument/methodology/source improvements

- STXM
  - 50-250 nm thick samples ideal for best S/N
  - Few minutes for images or good spectra
  - Lower damage than TXM
RESONANT X-RAY SCATTERING

Ensemble-average “NEXAFS Microscopy”: Size, shape, distribution

Gary Mitchell, B. Landes, J. Lyons, B. Kern, M. Devon, I. Koprinarov, J. Kortright

Complex atomic scattering factors for carbon in the forward scattering direction

\[ f_1 = Z + \frac{1}{\pi r_e hc} \int_0^\infty \frac{\varepsilon^2 \sigma_a(\varepsilon)}{E^2 - \varepsilon^2} d\varepsilon \]

\[ f_2 = \frac{\sigma_a}{2r_e \lambda} \]

Tuning to the certain energies will switch on/off the scattering.

\[ I/I_0 \]

\[ q (1/m) \]

~1e8

~100

79 nm

PS

\[ 285.1 \text{ eV} \]

\[ 281.9 \text{ eV} \]

\[ 285.6 \text{ eV} \]

\[ 288.6 \text{ eV} \]

300 nm

PMMA
The Future:
Ingredient #1: Better spectroscopy/understanding

Sample: tetracontane

Sign of Dichroism: Molecule is “standing” up on surface, i.e. c-axis of orthorombic cell is normal to surface

(Appel, Koprinarov, Ade, unpublished. ALS 7.0 STXM)
The Future:
Ingredient #2: Better instruments

Aberration corrected Photoemission Microscope
Anticipated 2 nm spatial resolution

Interferometer based STXM’s ready for 10 nm zone plates
The future: Ingredient #3: New tools

Imaging by Coherent X-Ray Scattering

Technique of choice for dynamics

Phase problem can be solved by “oversampling” speckle image

Transmission X-ray Microscope

Reconstruction from Speckle Intensities

Figure courtesy J. Stohr

Incoherent vs. Coherent X-Ray Scattering

Small Angle Scattering
Coherence length larger than domains, but smaller than illuminated area

Speckle
Coherence length larger than illuminated area

Figure courtesy J. Stohr

Resonant scattering and resonant speckle should be excellent tools for organic materials !!!!
The future:
Ingredient #4: New sources;
NSLS-II main characteristics

- Bending magnet STXM as workhorse.
  - If optimized, >10x performance of Stony Brook STXM at X1A. (ALS 5.3.2 “Polymer” STXM is benchmark.)
- Undulator STXM, correlative microscopy
  - polarization control
  - 150-2000 eV, many elements
  - Fluorescence detection, low concentrations
- SPEM
  - Work on surfaces benefit most from increased brightness
The future: Opportunities

- **Technology:** STXM, PEEM, SPEM, dynamic speckle
  - Clearly all these techniques will benefit tremendously

- **Science**
  - Polymers! Yes, but radiation damage might set a limit
  - Polymer-inorganic bybrids
    - Templating
  - Electronic structure of single carbon nanotube (sorry, no cartoon)
    - Robust and important material
    - Back of the envelop calculations show this should be doable in transmission and/or in TEY-mode
    - Due to significantly increased S/N requirements, source stability requirements are very high
Thank you for your attention!!!!
PBrS/PS blends in thin films
1000Å thick films spun on Si (HF stripped oxide), annealed at 170°C for 12 hrs.

40/60 PBrS/PS
70/30 PBrS/PS

γ_{PS/vac} = 30.5 dyn/cm and γ_{PBrS/vac} = 33.7 dyn/cm

dispersive contribution of PBrS surface found to be γ_{PBrS/Si-H}^d < 20 dyn/cm
Surf. tension of PBrS is about 39% polar


Data: Stony Brook STXM
Dewetting of polymer bilayers
30 nm of PBrS on top of 50 nm PS

- STXM (or other technique) can not tell for sure which polymer is on surface
- Surface NEXAFS spectra via X-PEEM
  - 2-10 nm surface sensitivity, here about 200 nm spatial resolution
  - 1 week at 180° C, spectra show only PS peak, no PBrS signature

Could monitor dynamics and deduce pathways
  - PBrS gets encapsulated via plug flow, not PS diffusion through PBrS

Data: PEEM-I, ALS BL8.0
Compatibilization of PS/PMMA thin film bilayers/blends

Preferred/ideal case

Copolymer becomes trapped in micelles

Addition of PA/PMMA diblock copolymer

Reality in many cases

Copolymer locates to the interface to reduce interfacial energy.

Effects of Confinement

Theory by D. Gersappe, et al

Confinement (small $r$) increases the critical micelle concentration, $\phi_{cmc}$

Consequently, micelle size ($\eta$) is reduced which significantly increases the chemical potential of micelle formation

With high degree of confinement, ($r < \eta_{bulk}$), the creation of micelles becomes energetically unfavorable

Results

Samples annealed 4 days at 170° C.

Compositional mapping.

78 nm Top Diblock layer

Micelle formation

30 nm Top Diblock layer

Micro-emulsion

PS | PMMA | PS + PMMA

Data: Stony Brook STXM

30 nm Top PS/Diblock layer, 80 nm lower layer

Annealed for 4 days

Quantitative compositional mapping with NEXAFS microscopy reveals:

- **PS** and **PMMA** phases extend through entire film
  - Micro-emulsion phase is two dimensional
- Our approach, based on a physical phenomenon, removes limitation on the kind of polymers that can be used for thin film blends

X-ray Microscopy of Superabsorbent Polymers (SAP)

G. Mitchell, E. Rightor, et. al (Dow), S. Urquhart, H. Ade (NCSU), A. Hitchcock (McMaster) et al.

- Superabsorbent polymers absorb up to 60x their weight in water (~30x in salt water). Primarily medical and cosmetic applications
- 3rd generation SAP technology provides enhanced properties using structured crosslinking
- No conventional tool to measure surface crosslink density

- STXM has visualized crosslink density in 3rd generation superabsorbent polymers
- Understanding the actual crosslink density will help to design improved SAPs and to tailor them to particular applications
- These experiments will also provide insight into competitive processes and economics

This is actually High-Tech!

Characterize and Compare Different Surface Crosslink Processes

**Process I: “Diffusion Controlled”**

- AMOUNT OF SURFACE CROSSLINKER ADDED
- Areal Polymer Density vs. Position ($\mu$m)
- Very different crosslink density profile

**Process II: “Reaction controlled”**

- Areal Polymer Density vs. Distance from edge ($\mu$m)
- Very different crosslink density profile

G. Mitchell and E. Rightor received ALS Shirely Science Award in 2001

Data: BL7.0 STXM

NEXAFS Quantitation: Additivity

- Spectral features are “additive” if there is no change in the electronic structure due to chemical, i.e. bonding, or matrix interactions
- Generally, there are no matrix effects between molecules or polymer chains
  - Exceptions in PE and maybe all semi-crystalline polymers
Polymer STXM “community” in North America

- **NCSU**: A. P. Smith, D. A. Winesett (now EXXON), O. Dhez, G. Appel, A. Garcia, R. Spontak, R. Fornes, R. Gilbert, D. Kilcoyne, ...
- **McMaster**: A. P. Hitchcock, Ivo Koprinarov, Tolek Tyliszczak (now ALS), et al.
- **Univ. of Saskatchewan at Saskatoon**: S. Urquhart et al.
- **SUNY@Stony Brook**: M. Rafailovich, J. Sokolov, et al. ..
- **Geophysical Laboratory, Carnegie Institution**: G. Cody
- **Dow Chemical**: G. Mitchell, E. Rightor, ...
- **EXXON**: J. Das, D. A. Winesett, P. Stevens, S. Cameron, ...
- **DuPont, GE, AlliedSignal, IBM
- **Photons Unlimited**: C. Zimba
- **UMASS**: T. Russel et al.

- **Instruments**: S. Anders, T. Warwick, C. Jacobsen, J. Kirz, S. Wirick, etc.

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- DOE (DE-FG-02-98ER45737), Dow Chemical, DuPont, NCSU.
Zone Plates: Diffractive Optics for X-rays
Developed by groups in Goettingen, LBNL, Stony Brook/Lucent, a few others

  - 1978: Move to ACO
  - 1982: Move to BESSY-I
- 1982: First STXM at NSLS: Rarback and Kirz
- Circular Au, Ni, or Ge structures
- Nanofabrication with E-beam lithography (early on it was holography)
- Spatial resolution approx. outermost zone width
- Focal length is proportional to energy

Diameter: 50-200 microns
Zone widths presently as small as 20 nm

- Crosslink density about 0.1%
- hard to detect spectroscopically

Flory-Rehner equation relates swelling and crosslink density:

\[
MW_c = \frac{V_s d_p (\Phi_p^{1/3} - \Phi_p)}{(\ln (1 - \Phi_p) + \Phi_p + \chi \Phi_p)}
\]

P. Flory, and J. Rehner, Journal of Physical Chemistry, 11(1943) 512

Resulting Density Maps:

Polymer  
water

Data: BL7.0 STXM  
Images: Quantitative Analysis

We assume “ideal” behavior: The spectra of mixed phases are fitted by a linear-combination of the reference spectra and a constant:

**Component Maps**

- Average over undisturbed regions of the **matrix** and the **minority phase**.
- Normalize to get the composition of these phases:
  \[
  \Phi_{oct} = \frac{t_{oct}}{t_{oct} + t_{but}}
  \]

**OD(E, x, y) =**

\[
OD(E, x, y) = t_{oct}(x,y)R_{oct}(E) + t_{but}(x,y)R_{but}(E) + constant(x,y)
\]

*) Hitchcock A.P., AXIS 2000
Some close-up views of 5.3.2 hardware

Top view

- X-interferometer mirrors
- Sample mount
- OSA mount
- Detector

Oblique side-view

- Fine X,Y piezo stage
- OSA mount

Close-up side-view

- Zone plate mount
- Sample mount
- OSA
- Detector

Mini flange viewport to view upstream side of Si$_3$N$_4$ exit window

10-20 micron reproducible mounting. - VLM pre-indexing in the future with absolute coordinate system
The Microwave

- AFM & FM domains
- Recorded "bits"

The Nanoworld

- Media grains
- Nano-particles

Space

- $10^{-3}$ m - 1 mm
- $10^{-6}$ m - 1 μm
- $10^{-9}$ m - 1 nm

Time

- $10^{-9}$ s - 1 ns
- $10^{-12}$ s - 1 ps
- $10^{-15}$ s - 1 fs

Note: $\Delta t (\text{fs}) = 4 / \Delta E (\text{eV})$

H. Ade et al., NSLS-II_ade_march2004.ppt
Magnetic Spectroscopy and Microscopy

X-ray Magnetic Linear Dichroism: *Antiferromagnets*

\[ \theta \]
\[ I \sim \cos^2 \theta \]

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X-ray Magnetic Circular Dichroism: *Ferromagnets*

\[ \theta \]
\[ I \sim \cos \theta \]

(courtesy J. Stohr)
Dichroism in tetacontane: 
transverse to C-C backbone

Angles of crystals correspond to unit cell if crystal terminates as (1,1,0), etc.

Solution cast single crystals randomly oriented on Si3N4 membrane