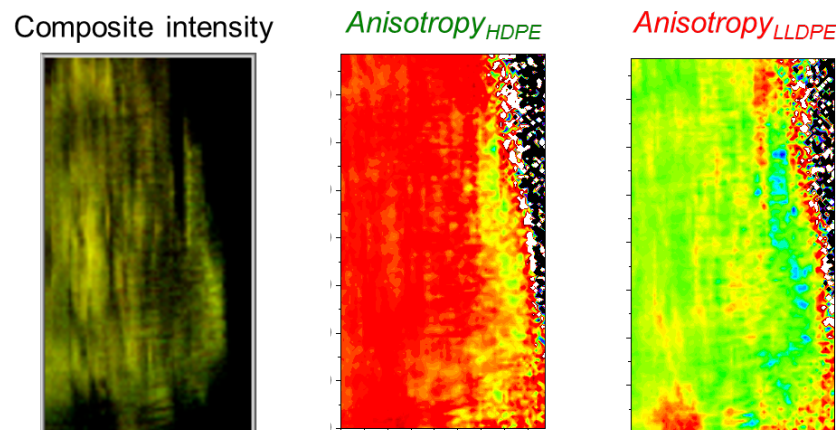


Coherent Raman Study of a Homologous PE Blend under Strain



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National Institute of Standards and Technology (NIST)



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POLYOLEFINS CONFERENCE

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Why NIST Cares ?

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NIST carries out its mission through the following programs:

- [the NIST Laboratories](#), conducting world-class research, often in close collaboration with industry, that advances the nation's technology infrastructure and helps U.S. companies continually improve products and services;
- the [Hollings Manufacturing Extension Partnership](#), a nationwide network of local centers offering technical and business assistance to smaller manufacturers to help them create and retain jobs, increase profits, and save time and money; and
- ...

www.nist.gov

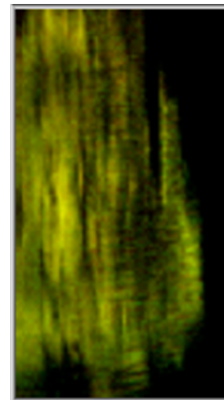
Bimodal PE Blend under stretching

- Microscopic chemical imaging
- Measure component distribution
- Analysis of chain orientation

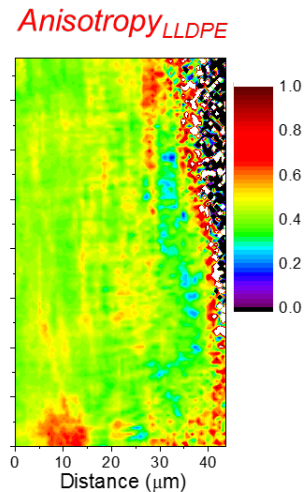
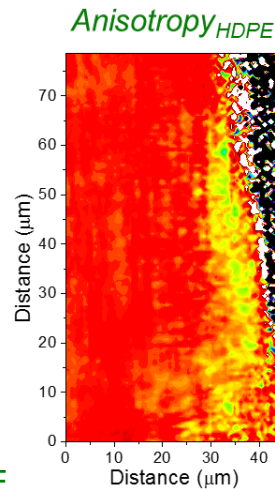
Phase transitions of polyethylene

- Will talk today

Composite intensity



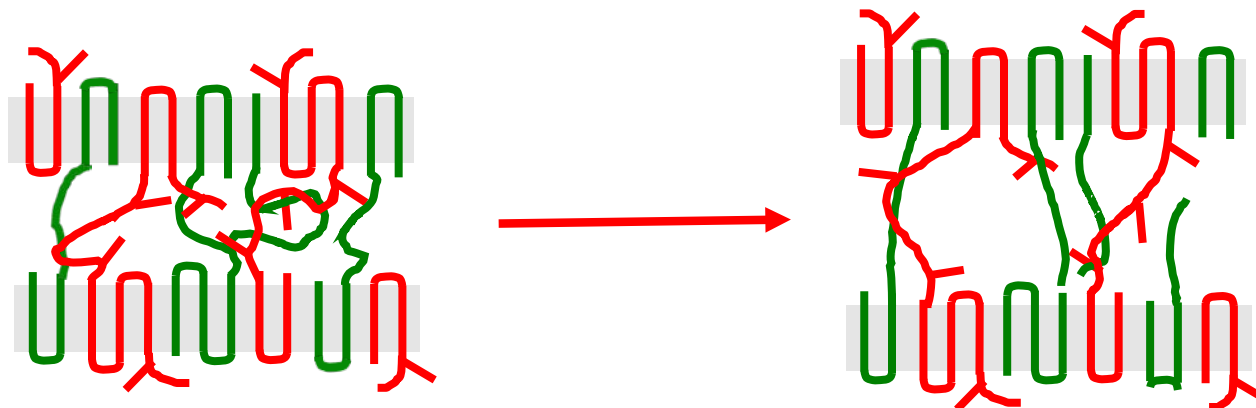
Deuterated HDPE
LLDPE



Outline

Chemical and orientation imaging of mechanical failure region

- Goal: high performance materials;
- Microscopic chemical imaging:
 - IR & Raman imaging;
- Coherent anti-stokes Raman scattering imaging
 - principle & advantages;
- Demonstrated capability on LLDPE/HDPE blend;
- Stretched bimodal PE blend;
- Measured component distribution;
- Analyzed chain orientation;
- Found the key!



LLDPE chains
for anchoring

Upgrading Water Pipes: Polyethylene (PE)



> 240,000 breaks per year, leaks wasting 1.7 trillion gallons of water and costs \$2.6 billion/year US tax-payers' money

Polyethylene (PE) pipes:

- lower cost for materials and installation (trenchless)
- negligible corrosion
- predicted service life of up to 100 years



Blending with branched LLDPE component is to increase the resistance to slow crack growth – the prevailing failure mode in today's PE pipe for potable water distribution.

WHY & HOW it works?

Limited Chemical Contrast of Current Imaging Techniques

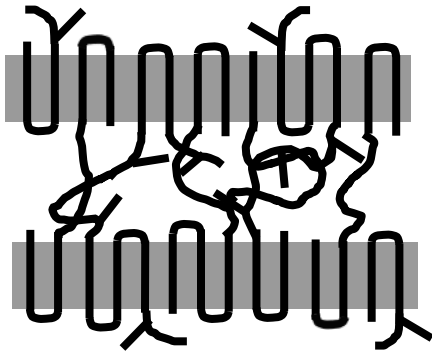
Bimodal blend linear medium MW **deuterated HDPE** and short chain branched high MW **LLDPE**



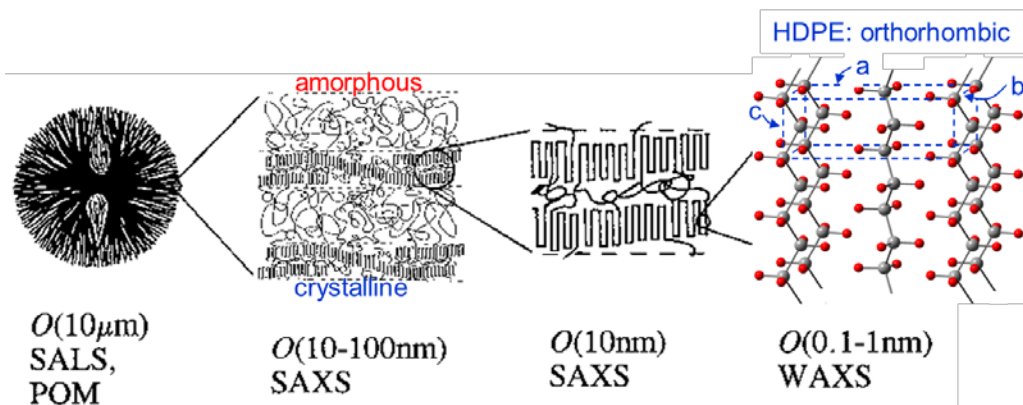
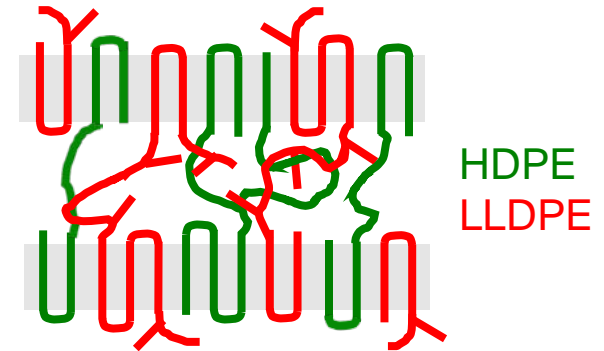
No chemical contrast

Chemical identification

AFM, TEM, SEM, X-ray, ...



IR Imaging, Raman Imaging, ...



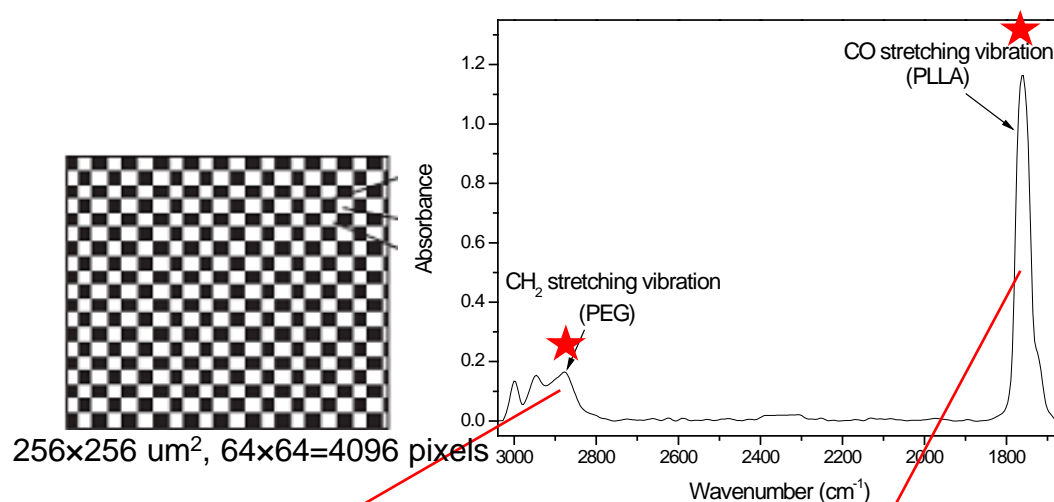
Chemical information from each component;
Both **crystalline** and **amorphous** segments;
Spatially resolved.

Microscopic Chemical Imaging

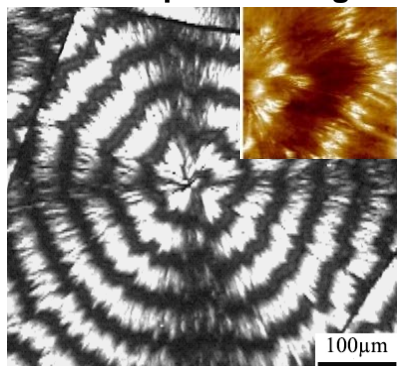
Mid-infrared spectroscopy, Near-infrared spectroscopy and Raman spectroscopy

Advantages:

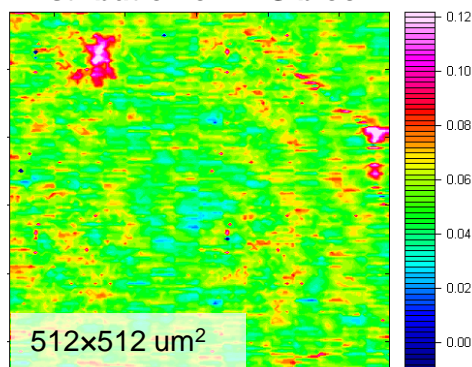
- ✓ label-free
- ✓ non-invasive
- ✓ chemical identification



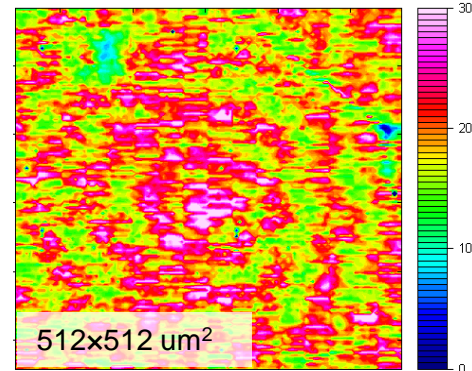
Crossed-polarized light



Distribution of PEG block



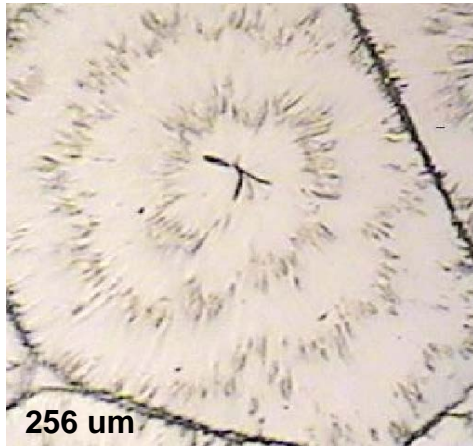
Distribution of PLLA block



- Collect thousands of IR spectra simultaneously;
- Spatially resolved chemical information (distribution);
- Spatial resolution $\sim 4 \mu\text{m}$.

Image of Orientation Function

unpolarized light

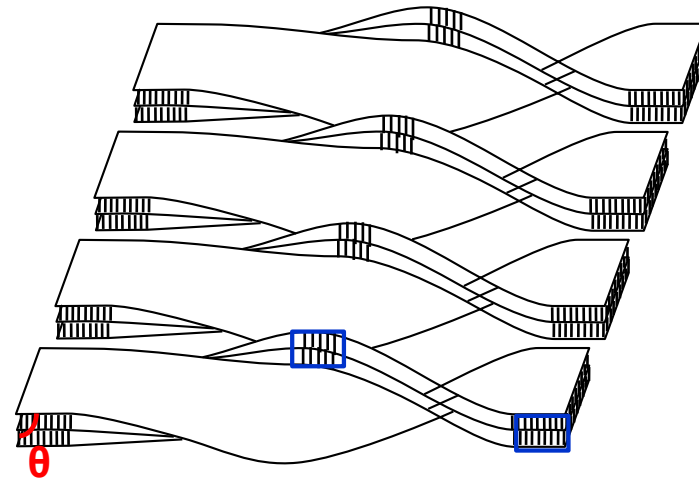
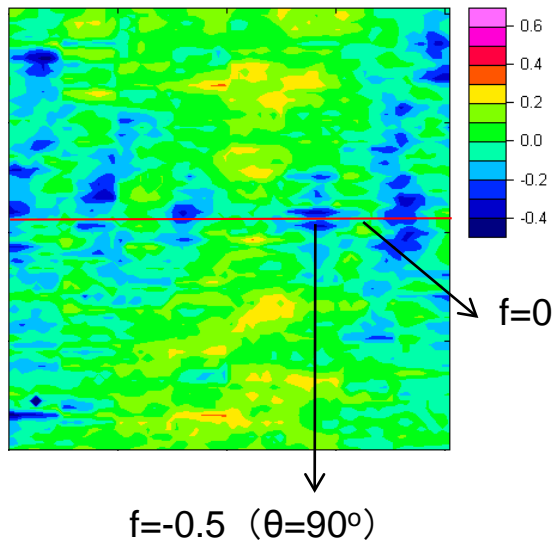


Dichroic ratio $R = A_{\parallel}/A_{\perp}$

$$f_{\text{PLLA}} = -2 \frac{R(\text{CO}) - 1}{R(\text{CO}) + 2}$$

$$f = \frac{3 \langle \cos^2 \theta \rangle - 1}{2}$$

orientation function of PLLA block

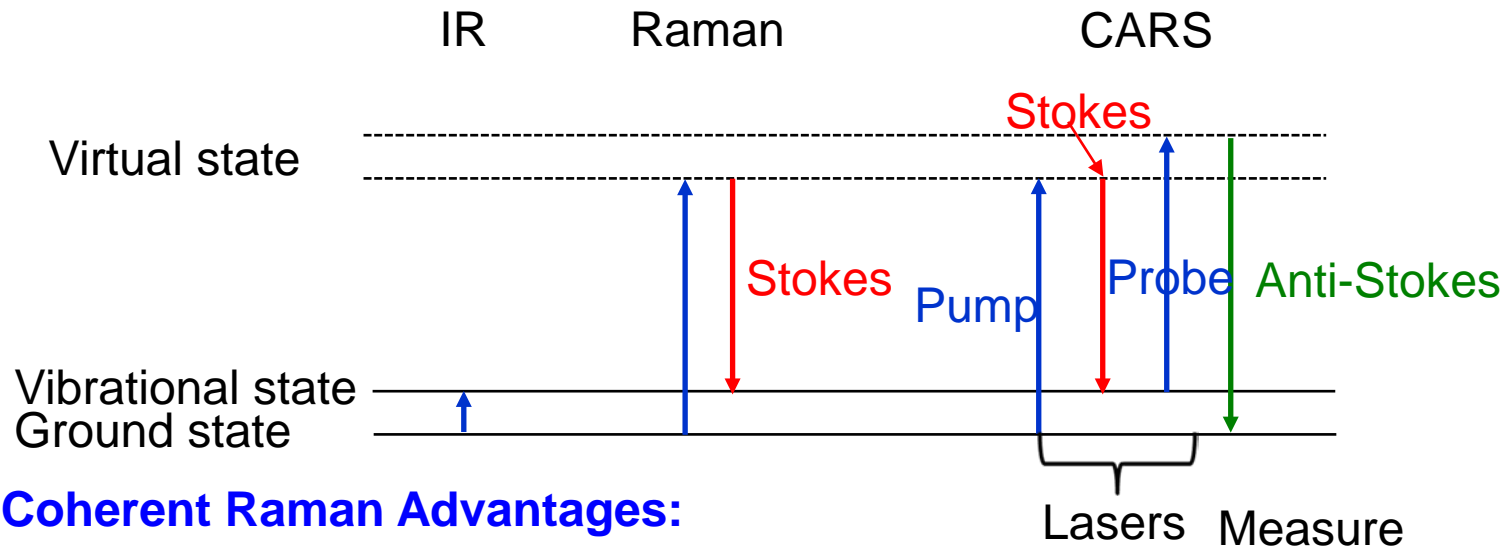


The lamellae periodically twist along the radial growth direction of the spherulite and the orientation of the PLLA chains change accordingly in between concave and convex bands.

Rapid Characterization of Complex Materials

CARS: Coherent anti-Stokes Raman Scattering

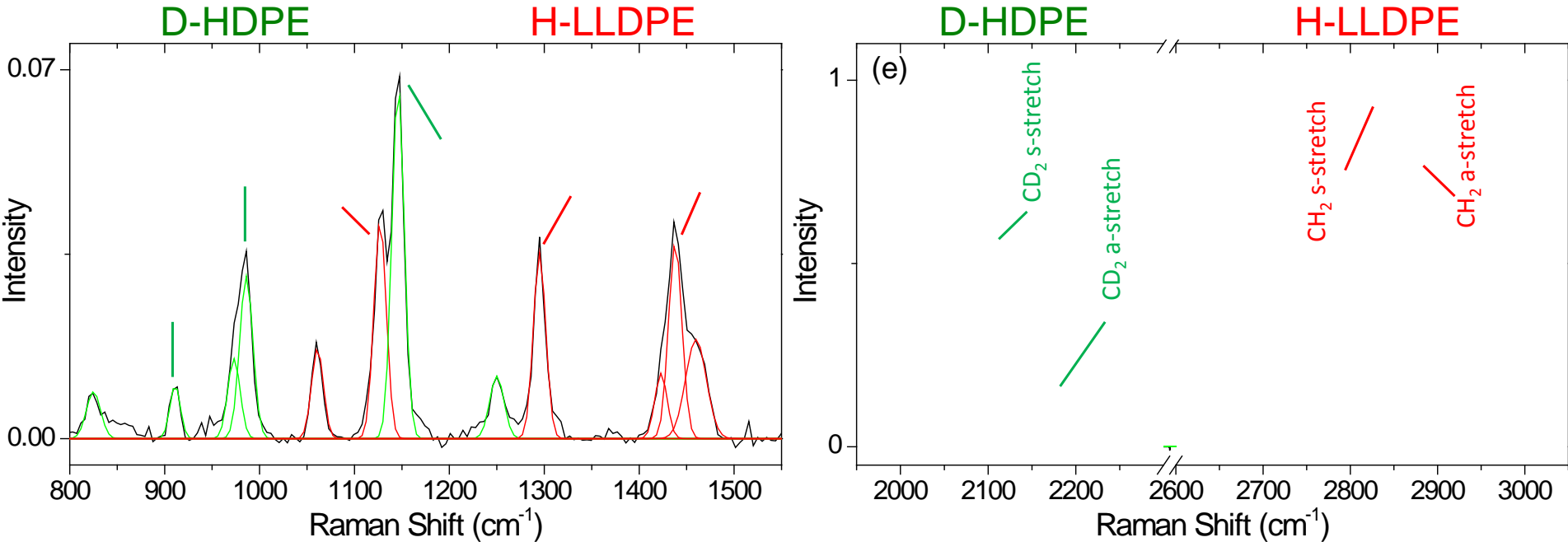
- CARS is a form of spectroscopy.
- It is sensitive to the same vibrational signatures of molecules as seen in Raman spectroscopy.
- It employs **multiple photons** to address the molecular vibration, and produces a **coherent signal**.



Coherent Raman Advantages:

- ✓ negligible water background
- ✓ signal enhancement of $>10^3$
- ✓ free of fluorescence background
- ✓ rapid Raman imaging (30 ms/pixel)
- ✓ requires a small amount of sample
- ✓ Spatial resolution ~ optical diffraction limit (0.4 μm lateral; 1.1 μm axial)

Spectral Identification of (deuterated) HDPE and LLDPE



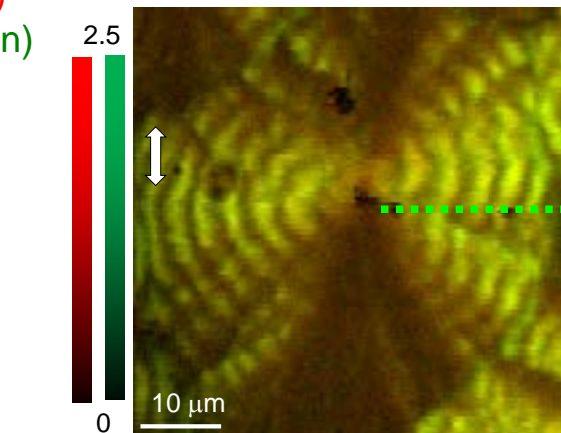
Spectrally separable!

Co-crystallization

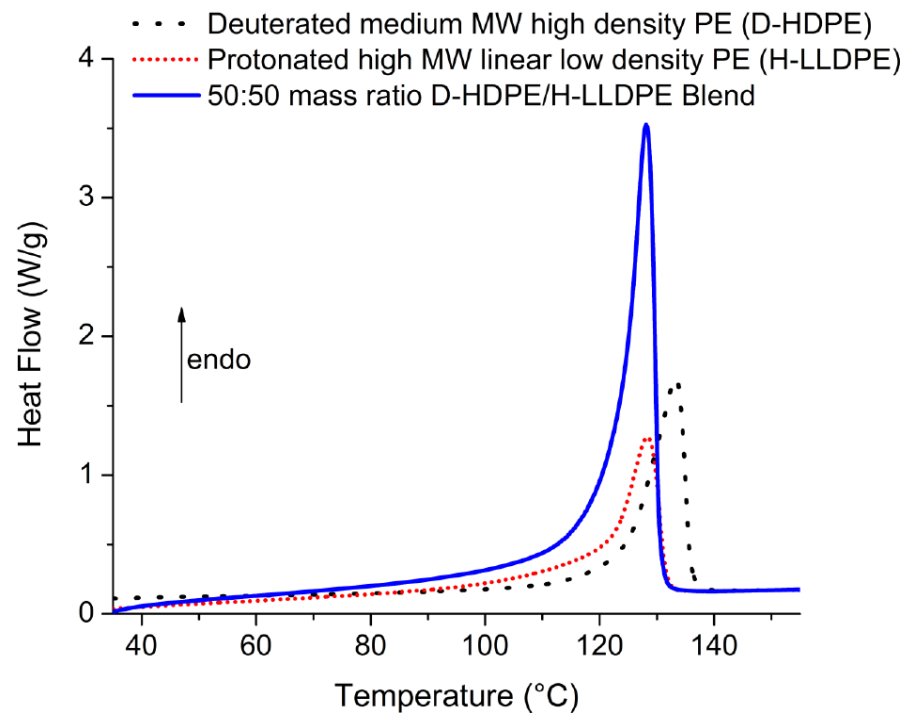
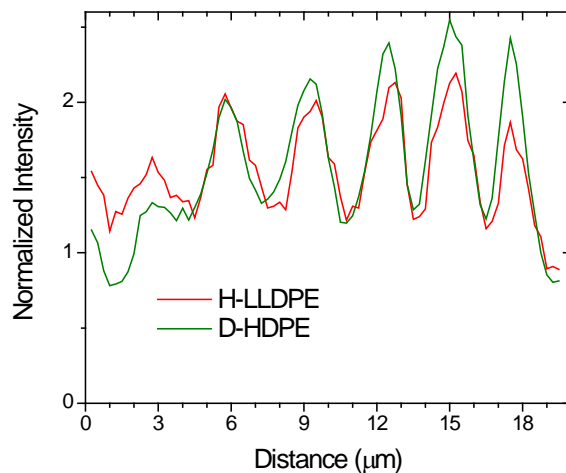
C-C stretching mode

H-LLDPE (red)

D-HDPE (green)



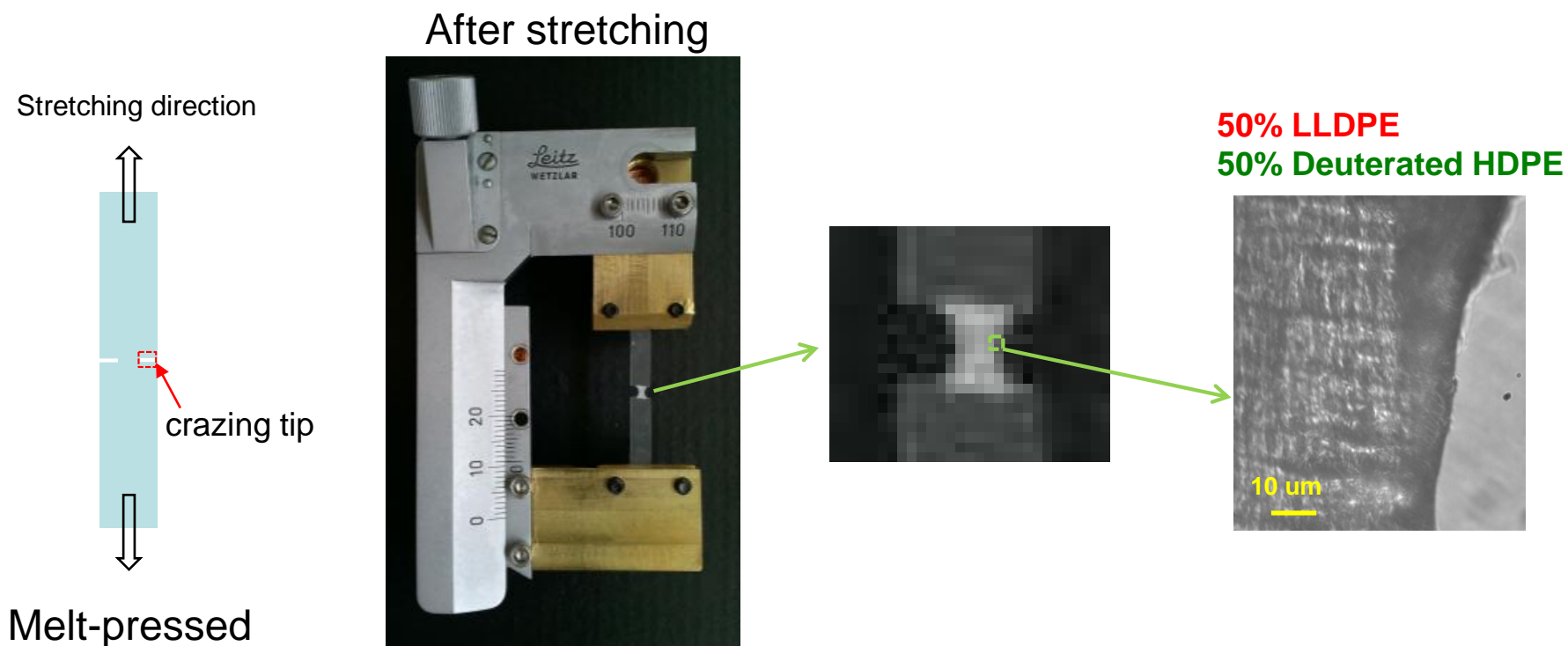
(061512-3.opi) D:\PE2-34-OL-KK-DT-xy31&32.tif



The lack of multiple peaks in the heat flows is suggestive of a single lamellar distribution formed from co-crystallization of the two components.

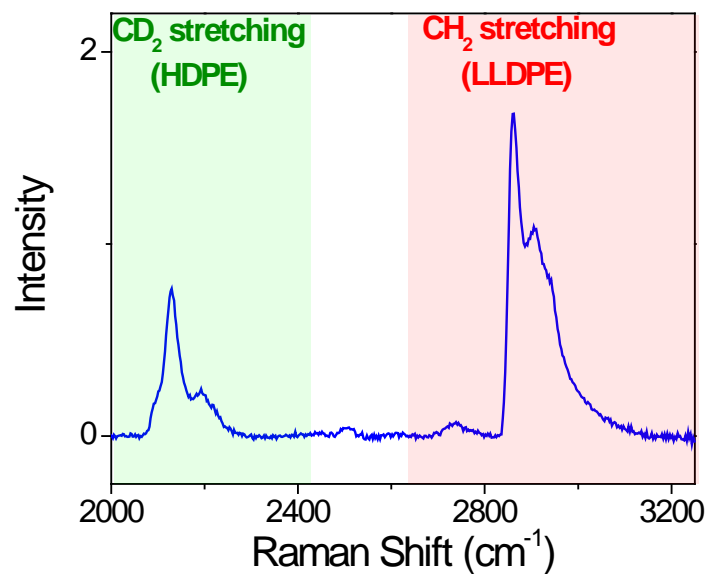
In-phase undulation suggests co-crystallization of H-LLDPE and D-HDPE.

CARS Imaging of a Mechanical Failure Region

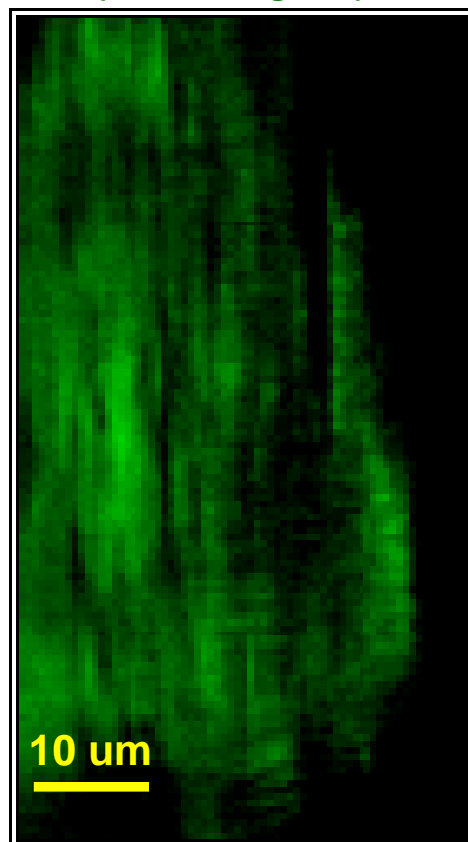


Chemical and orientation imaging of mechanical failure region

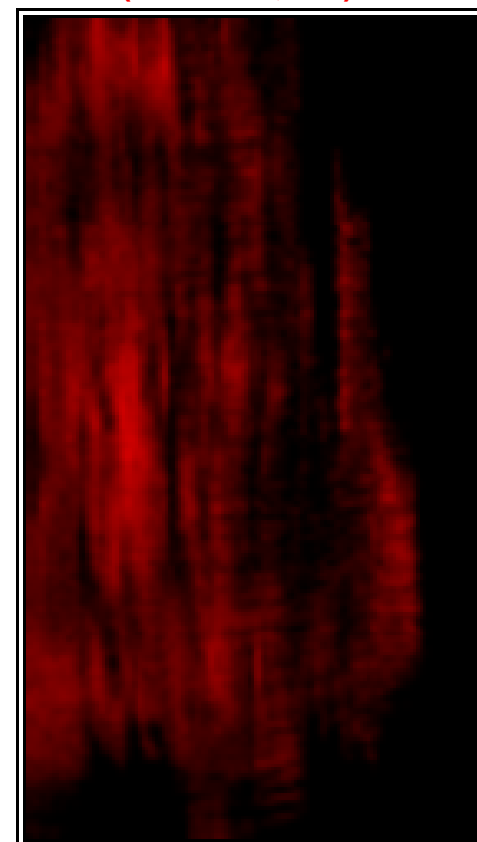
CARS Composition Distribution Image



HDPE
CD₂ stretching
(2127 cm⁻¹, green)



LLDPE
CH₂ stretching
(2858 cm⁻¹, red)

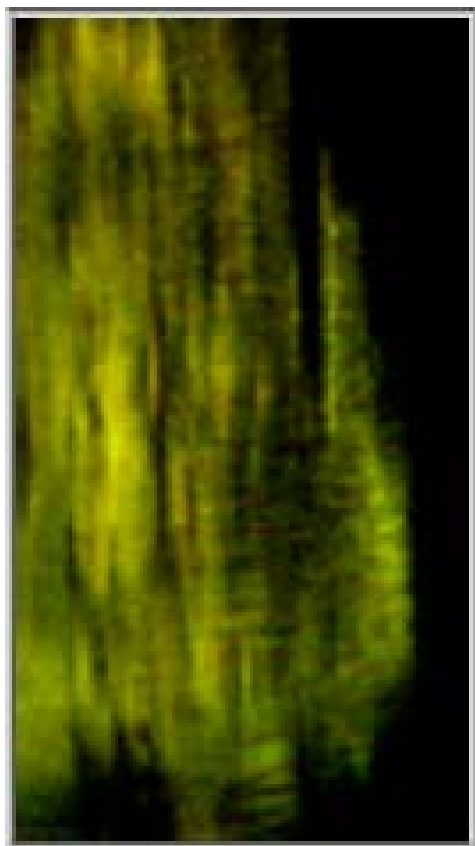


43.68 μm × 78.62 μm

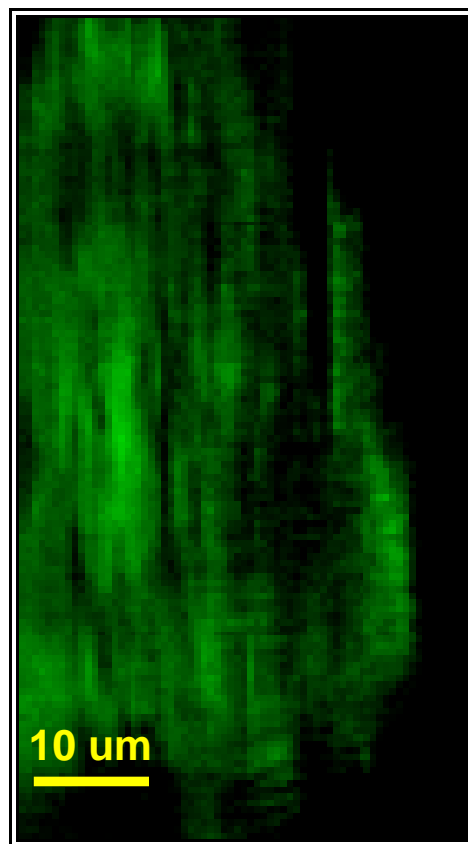
140 × 126 = 17,640 spectra

Composite Image

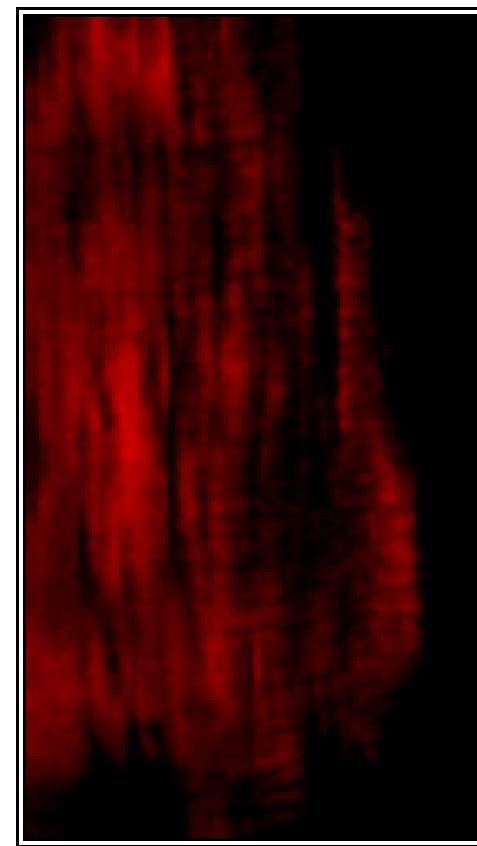
CARS composite image



HDPE
CD₂ stretching
(2127 cm⁻¹, green)



LLDPE
CH₂ stretching
(2858 cm⁻¹, red)

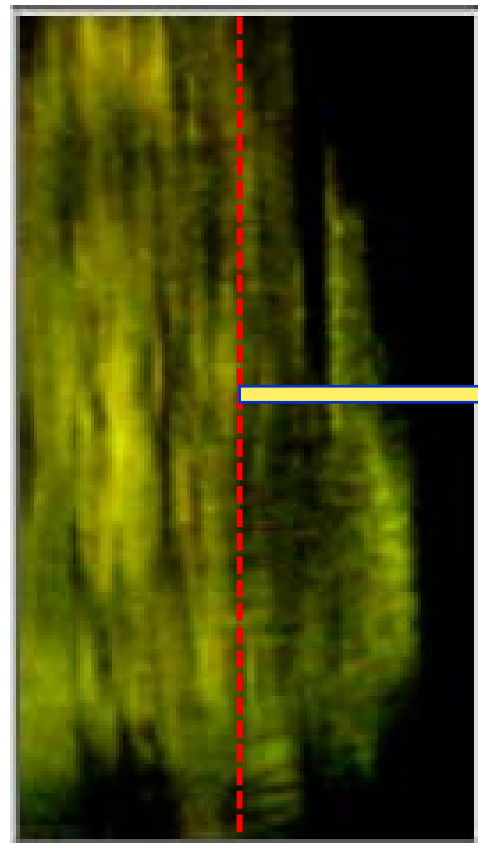


43.68 μm × 78.62 μm

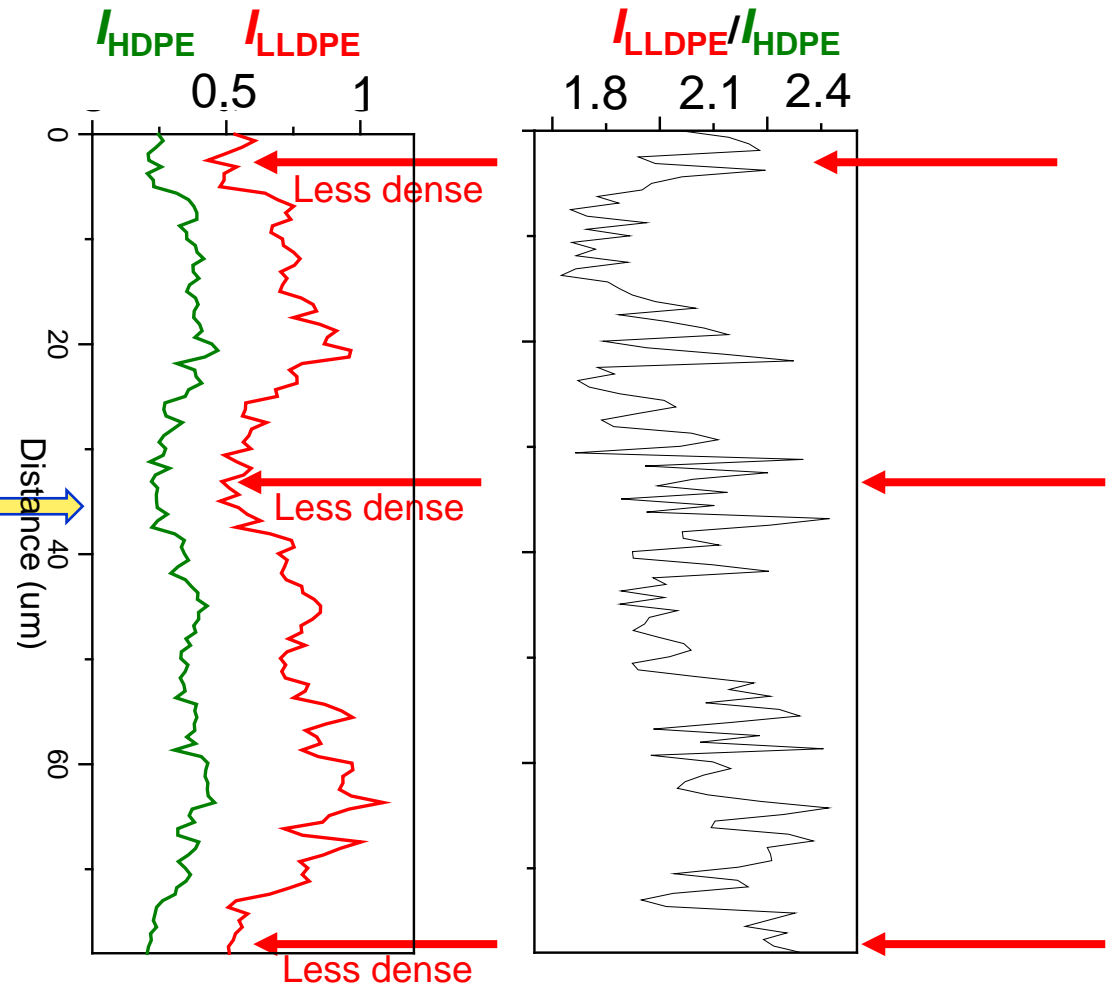
Phase separation between HDPE and LLDPE

Microphase Separation of HDPE

CARS composite image



Stretching direction
↕



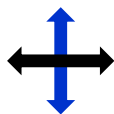
Phase separation between HDPE and LLDPE
Less dense region rich in LLDPE component

Polarization CARS

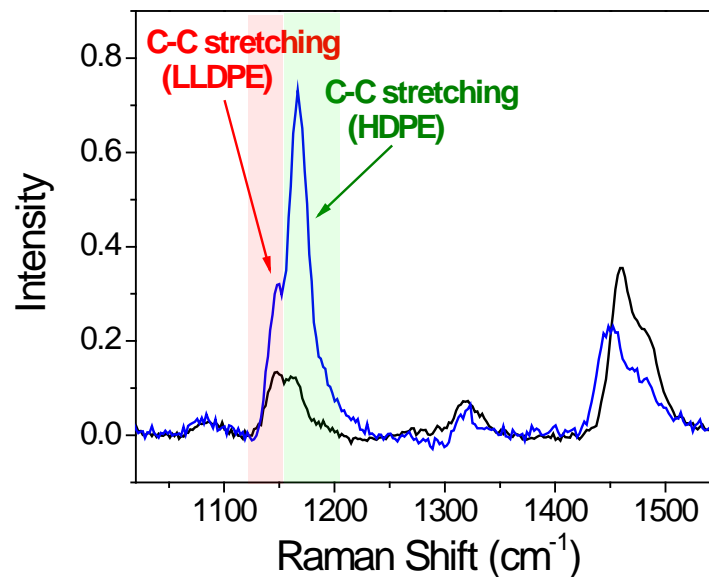
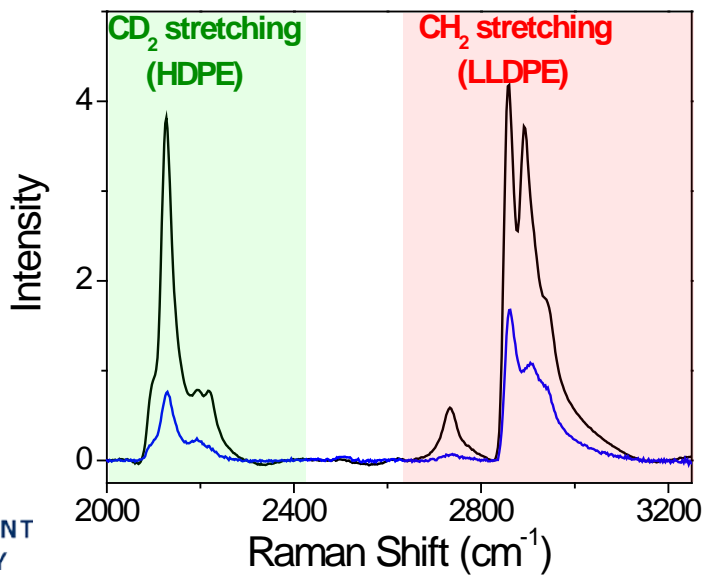
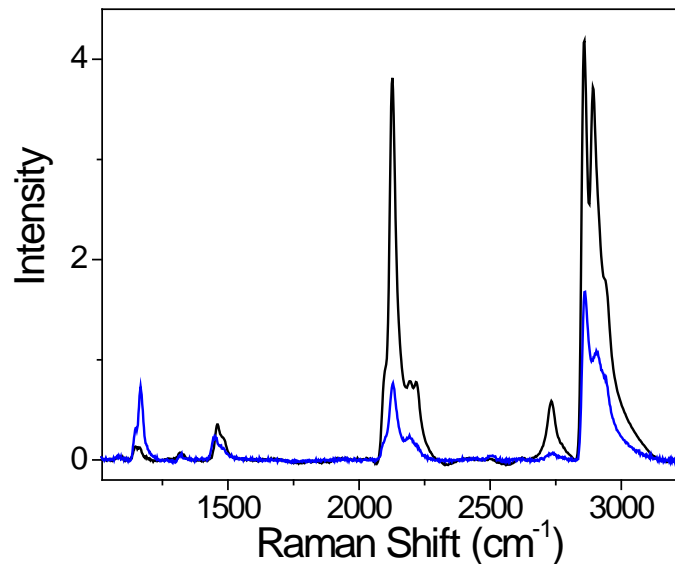
Stretching direction



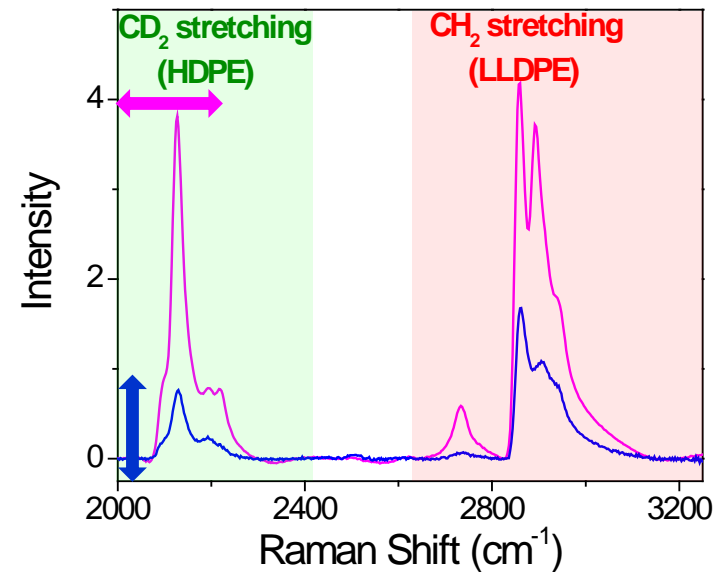
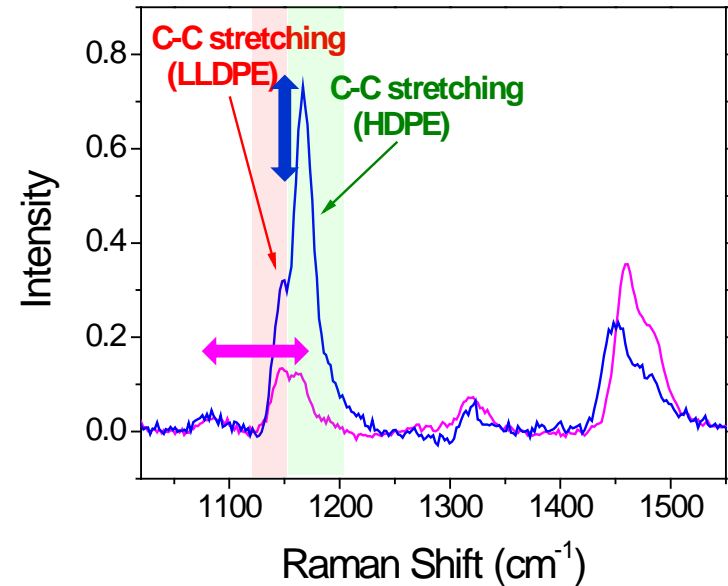
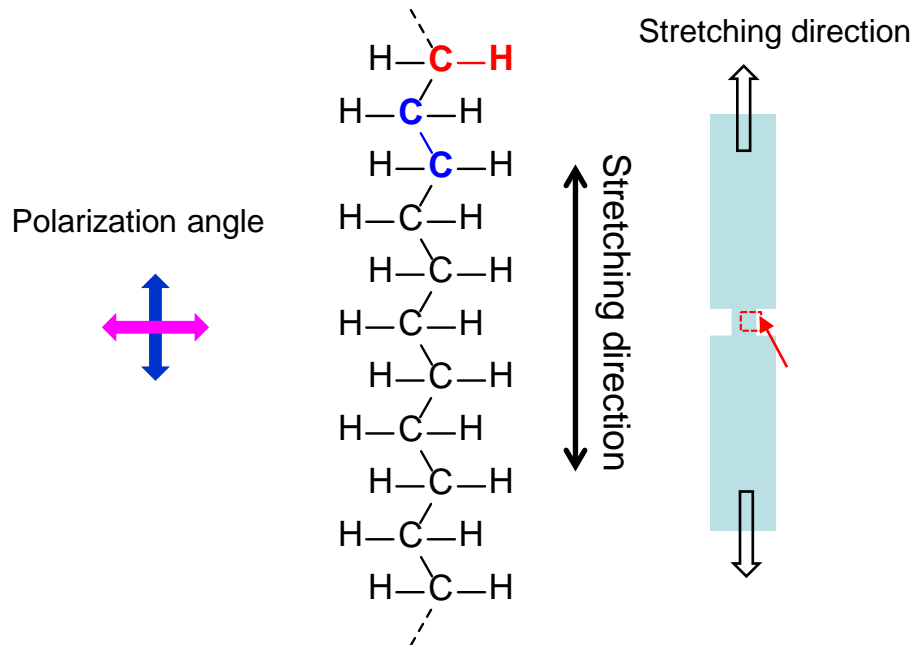
Polarization angle



— perpendicular to stretching direction
— parallel to stretching direction



Chains along Stretching Direction

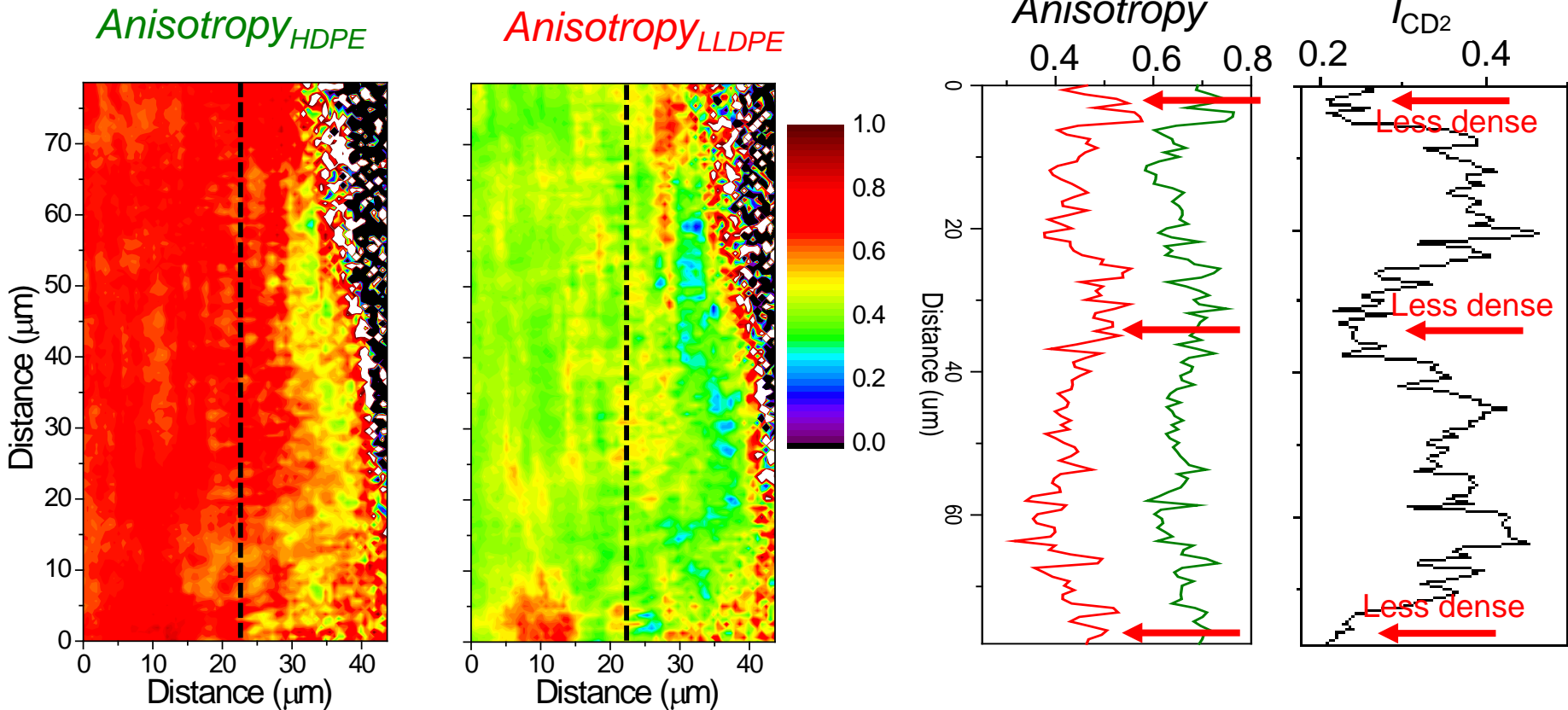


$$\text{Anisotropy} = \frac{I_{\text{perpendicular}} - I_{\text{parallel}}}{I_{\text{perpendicular}} + I_{\text{parallel}}}$$

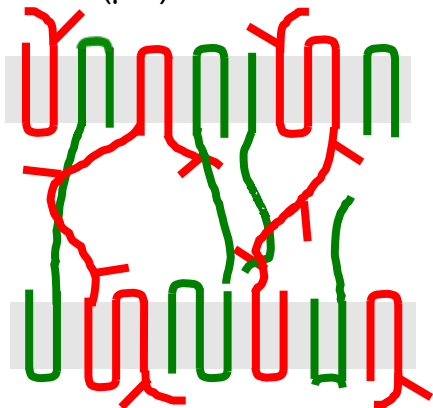
(-1,1) 0: isotropic
1 or -1: perfectly oriented

Chain oriented in the stretching direction

Different Chain Orientations



HDPE
LLDPE

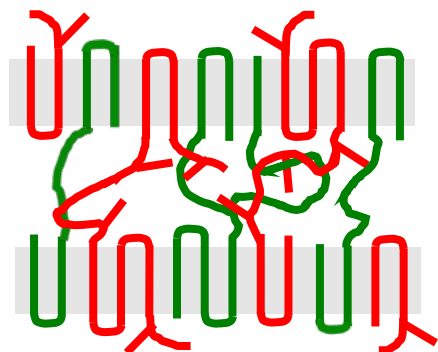


Higher orientation for HDPE

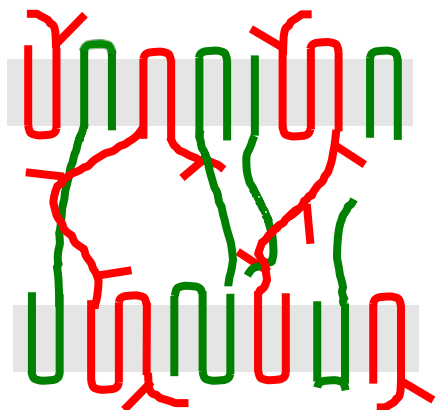
Higher orientation in less dense region

Summary

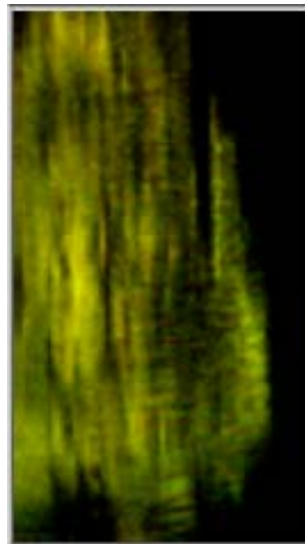
Chemical and orientation imaging of mechanical failure region



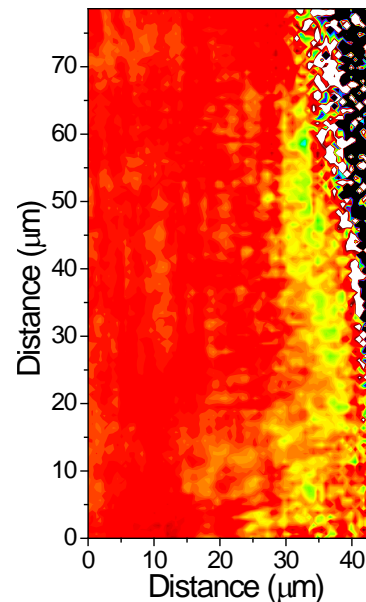
LLDPE chains
for anchoring



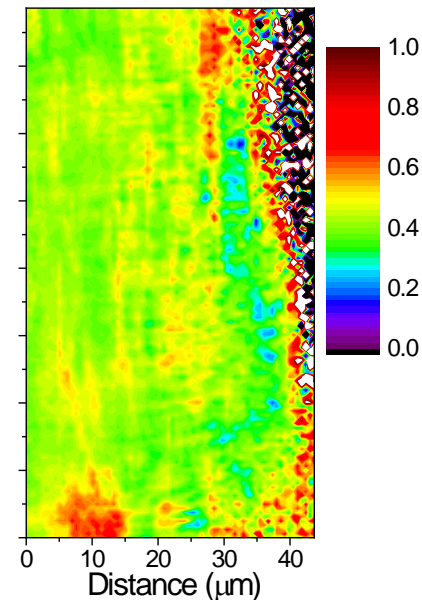
Composite intensity



*Anisotropy*_{HDPE}



*Anisotropy*_{LLDPE}



- Phase separation between HDPE and LLDPE;
- Less dense region rich in LLDPE component;
- Higher orientation in less dense region;
- Higher orientation for HDPE.

Acknowledgement

Advisor

Young Jong Lee

Raman Measurement

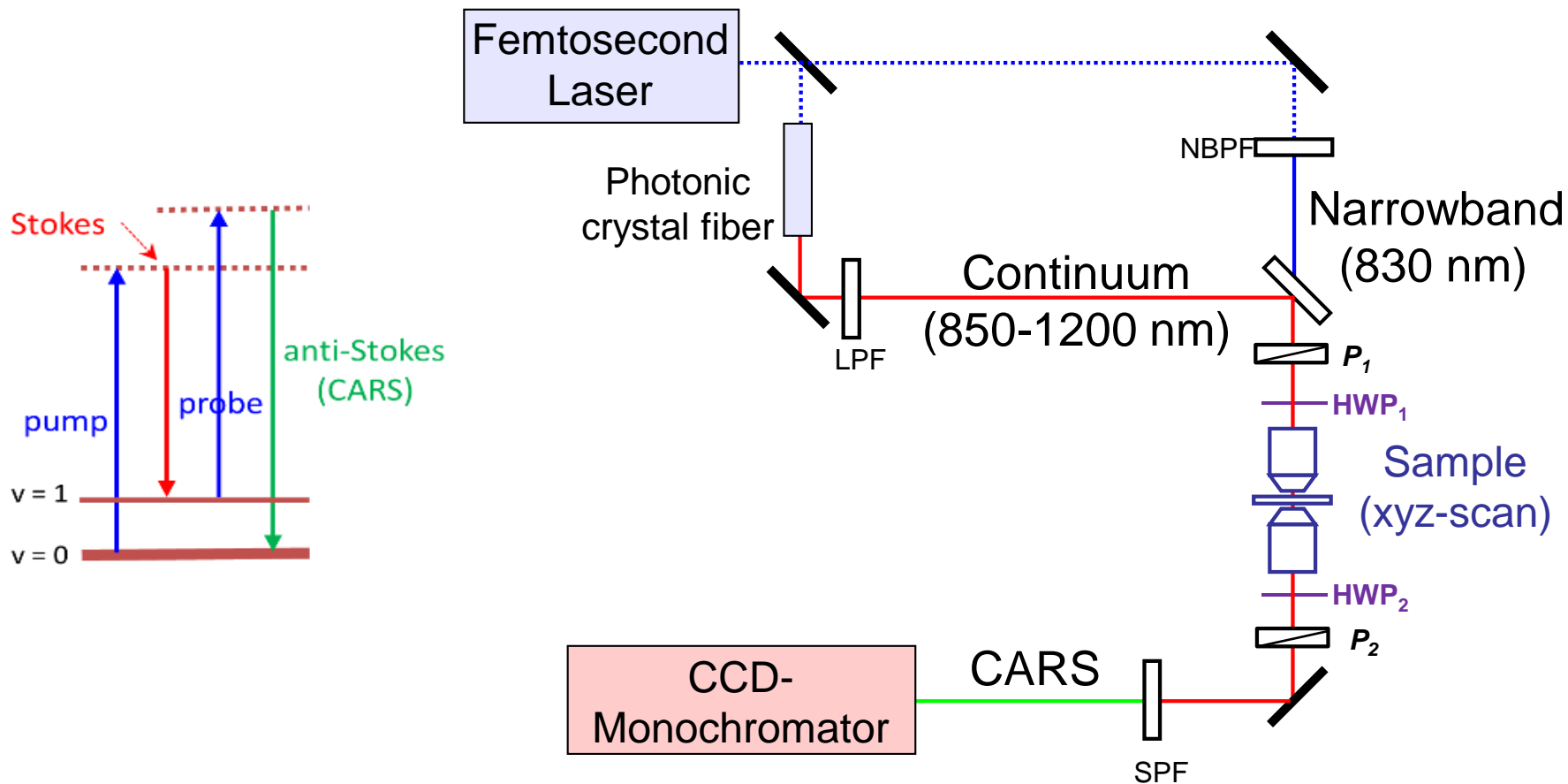
Ian S. Ryu

DSC Measurement

Chad Snyder

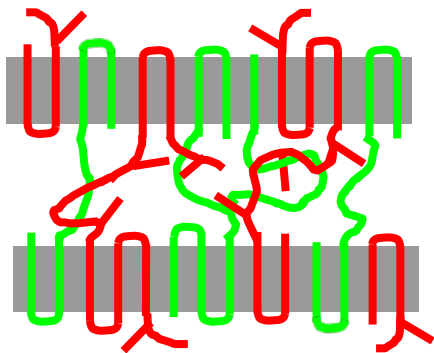
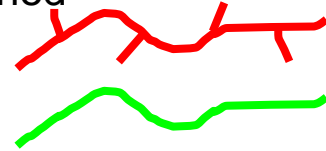
Thank you for your attention!
Questions?

Broadband CARS Microscopy by NIST

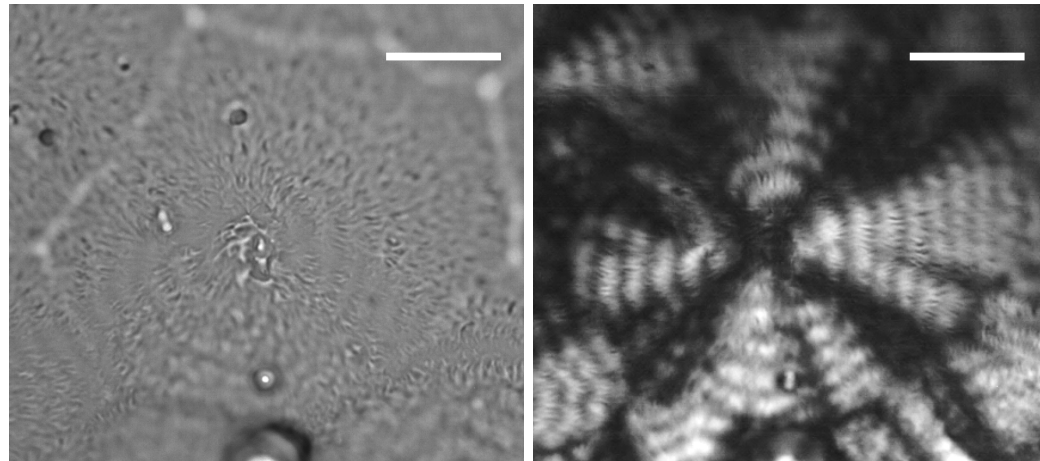


Sample

- **H-LLDPE**: high MW ($M_w \approx 1 \times 10^6$, $M_N \approx 2 \times 10^5$), short chain (hexyl) branched (5 to 7 branches per 1000 CH_2 units)
- **D-HDPE**: medium MW ($M_w \approx 2.9 \times 10^5$, $M_N \approx 1.07 \times 10^5$), linear high density (deuterated)
- 50:50 (by weight) blend of **D-HDPE** and **H-LLDPE** (mole ratio of CH_2 and CD_2 is 16:14).



HDPE
LLDPE



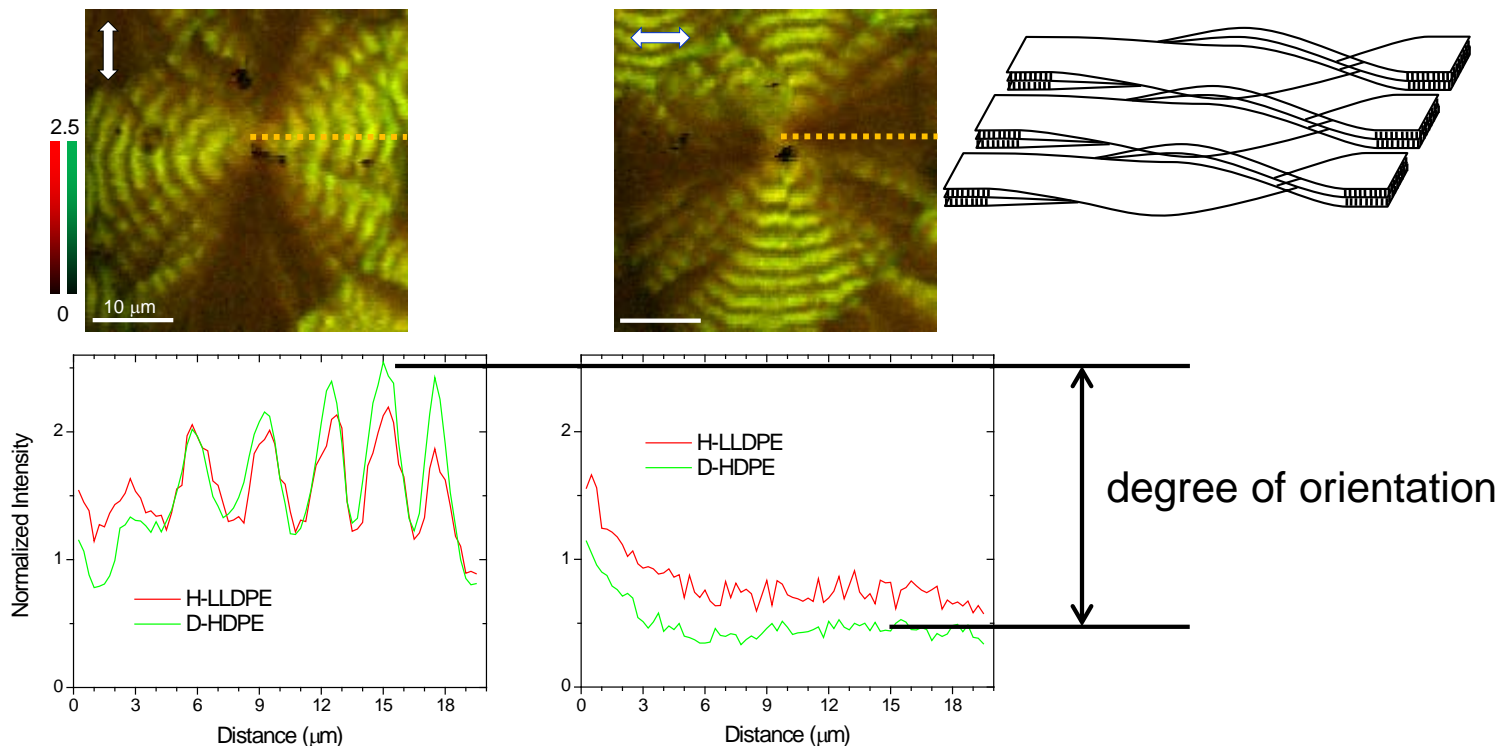
(a) Unpolarized and (b) cross-polarized bright-field images of spherulitic structures formed in the polyethylene (PE) blend film.

Quantitative Image of Chain Orientation of Both H- and D-PE

C-C stretching mode

H-LLDPE (red)

D-HDPE (green)



Greater degree of orientation for D-HDPE