Characterization and Modeling of the Interface/Interphase of Polymeric Materials and Systems Consortium

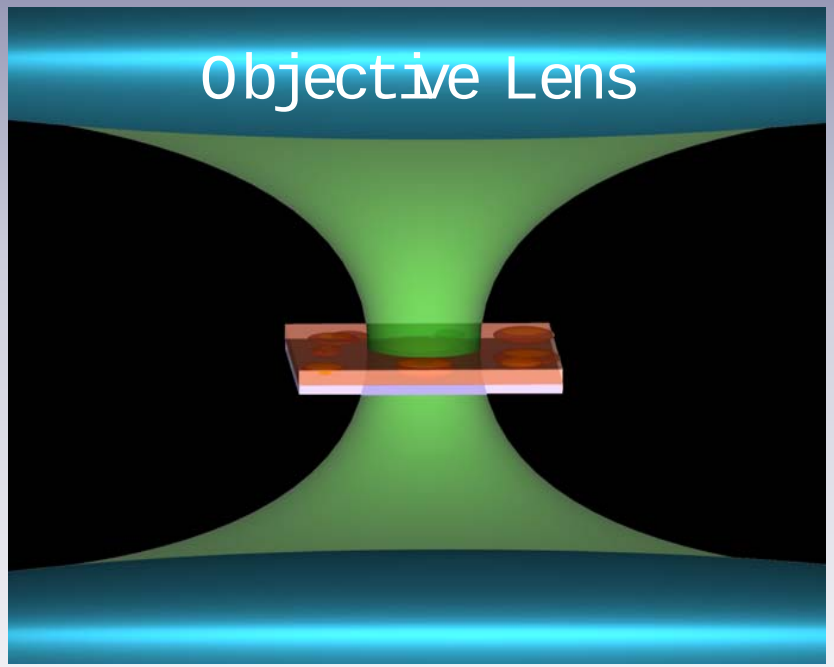
Project 3 – Milestone 4:

Development of new nanoscale techniques using Confocal Raman, NSOM, NLO, and SIMS to evaluate changes in chemical composition in interphase regions.

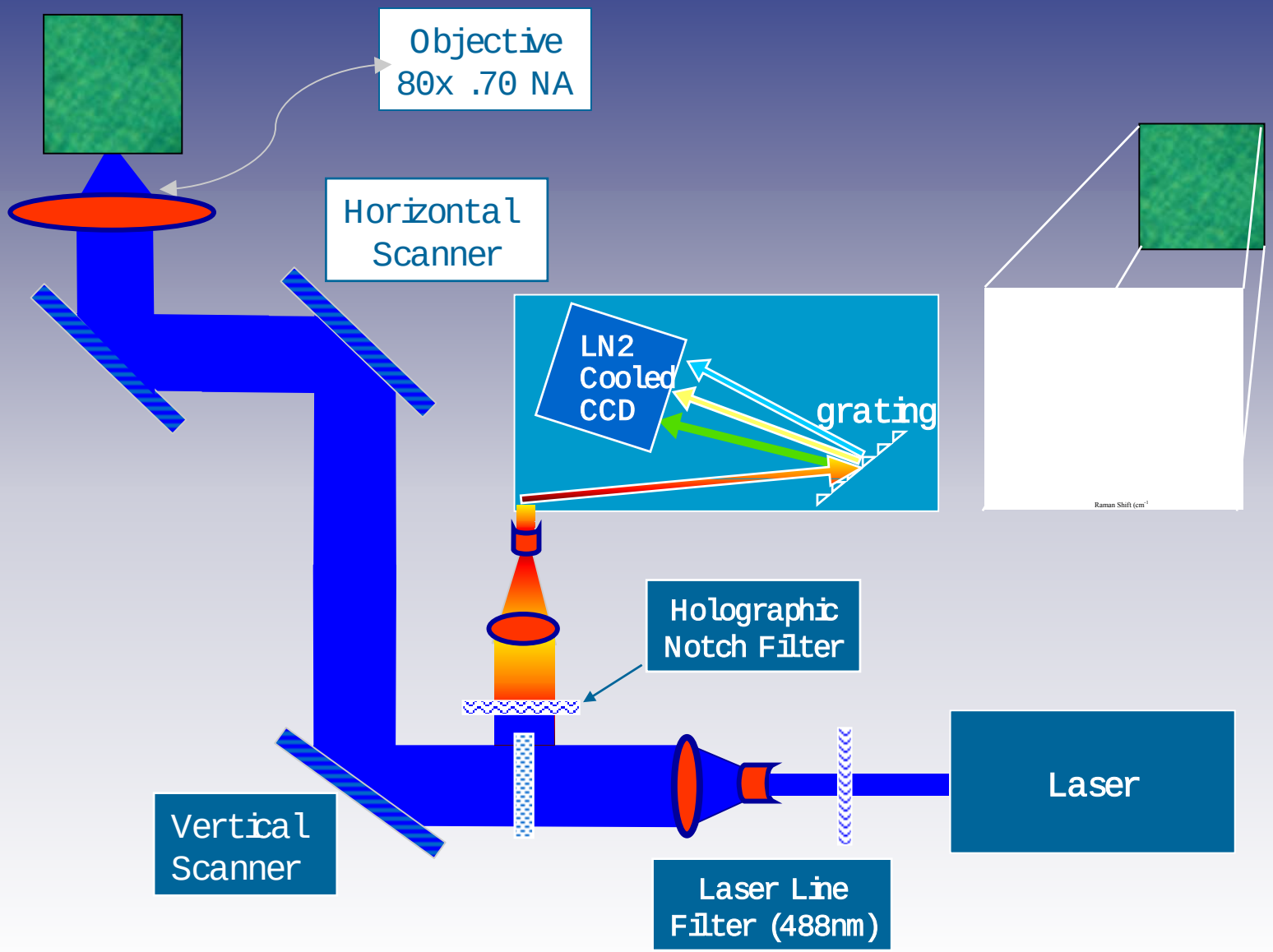
New Capabilities in Laser Scanning Confocal Raman Microscopy

Confocal Raman Microscopy

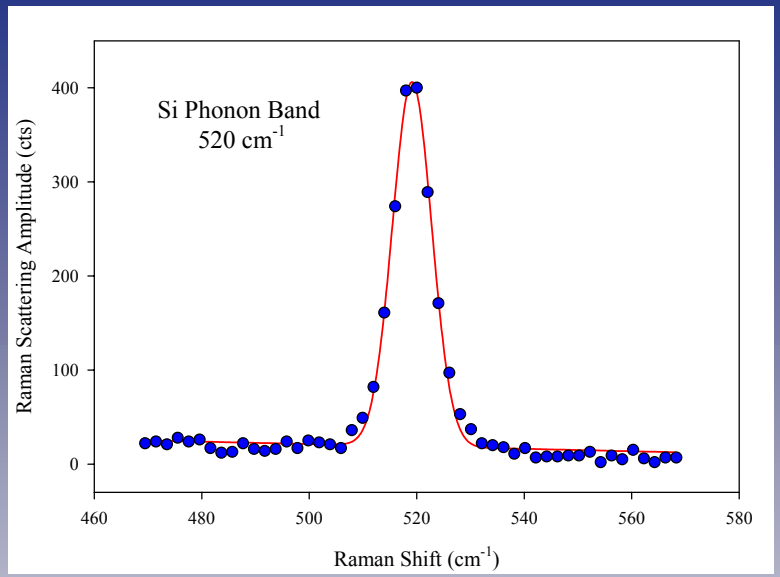
- Diffraction-limited spatial resolution
  Lateral ~ $\lambda/2NA$
  Confocal collection reduces 'out-of-focus' Raman signal $\Rightarrow$ depth profiling
- Chemical composition information from vibrational spectra
- Structural information from vibrational spectra (crystallinity, orientation, strain)

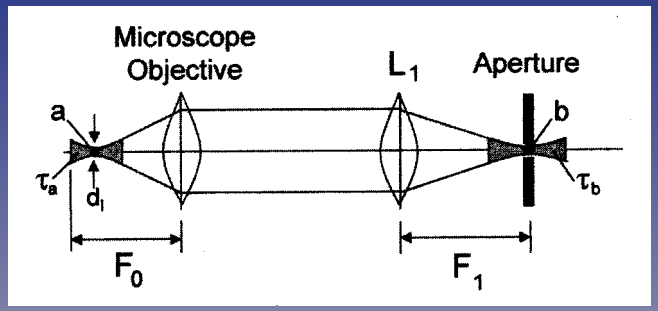


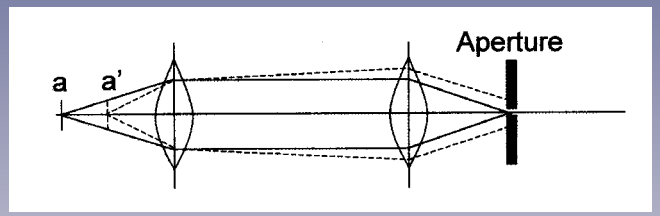
Confocal Raman Hyperspectral Imaging: 3-D Chemical and Orientation Mapping



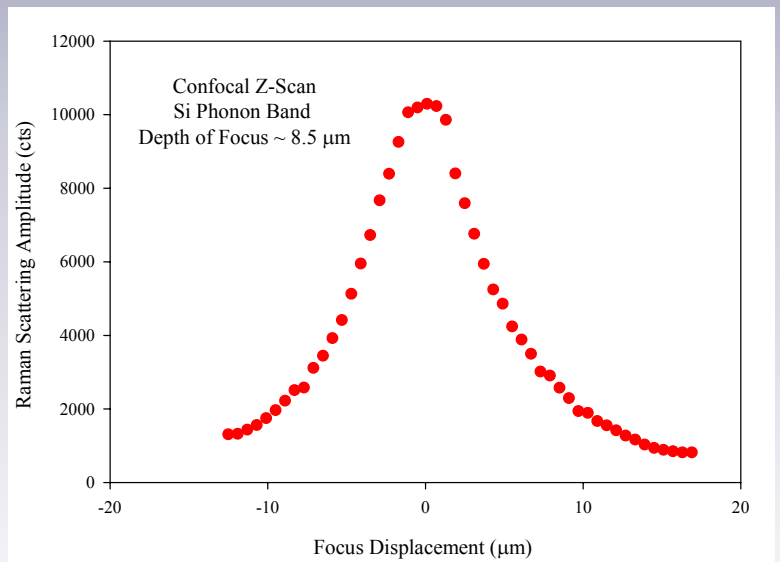
Confocal Raman Microscopy: Depth Resolution







Figures from K.J. Baldwin et al in *Handbook of Raman Spectroscopy*, Eds. I. R. Lewis and H.G.M. Edwards



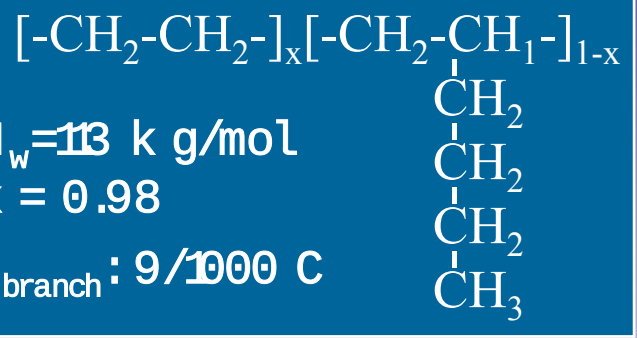
Raman Z-Scans

Raman spectra of Si phonon band at 520 cm^{-1} recorded as beam focus is scanned through Si/air interface. FWHM of z-scan function is a measure of confocal parameter (collection depth).

Confocal Raman Microscopy of Polyolefin Blends: Samples

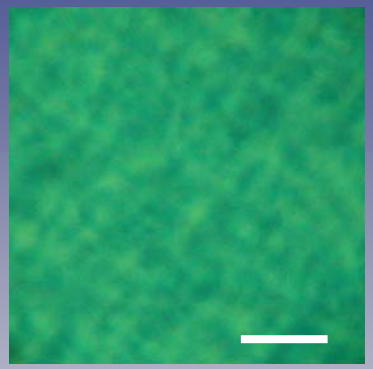
DIC Optical microscopy images 100X, 0.75 NA

PEH: ethylene/hexene

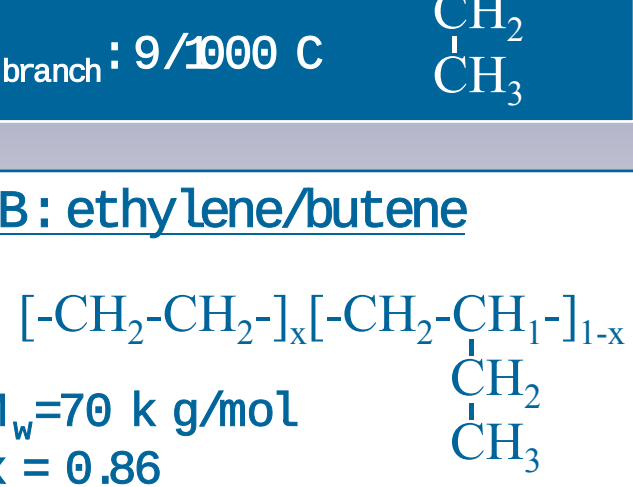


M_w=113 k g/mol
x = 0.98
ρ_{branch}: 9/1000 C

PEB:PEH
50:50
130°C/3 h

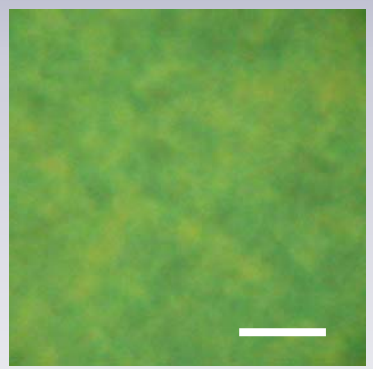


PEB: ethylene/butene



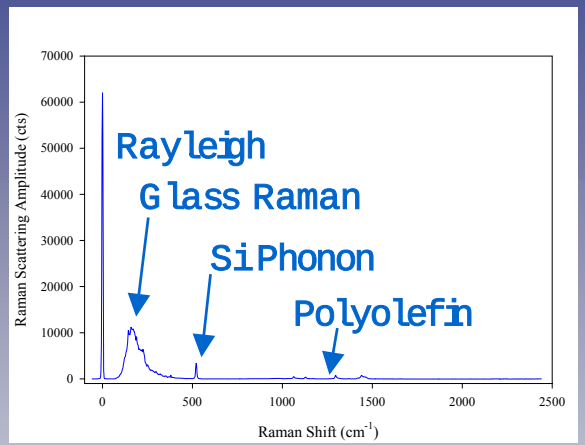
M_w=70 k g/mol
x = 0.86
ρ_{branch} : 77/1000 C

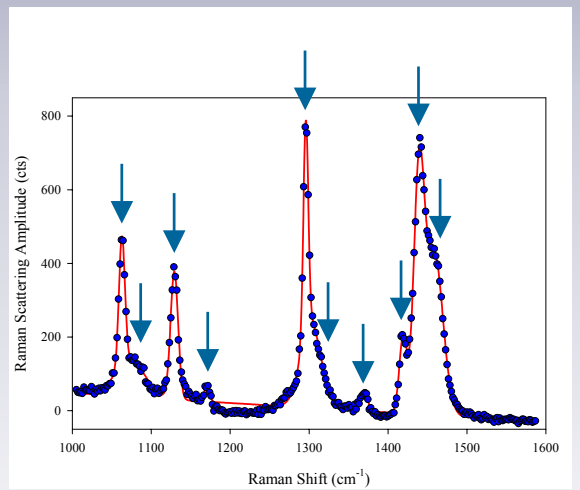
PEB:PEH
50:50
130°C/21 h



Scale bar ~ 10 µm

Confocal Raman Microscopy of Polyolefin Blends: Spectra

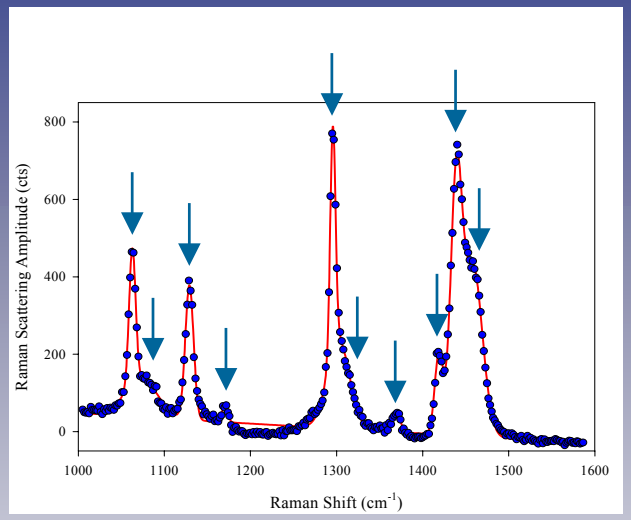




Spectral Assignments	
Band	Raman Shift (cm^{-1})
$\nu_{as}(C-C)$	1064
$\nu_{s}(C-C)$	1080
$\nu_{s}(C-C)$	1131
$\nu_{r}(CH_2)$	1170
$\nu_{t}(CH_2)$	1297
$\nu_{t}(CH_2)$	1303
$\nu_{w}(CH_2)$	1370
$\delta(CH_2)$	1418
$\delta(CH_2)$	1440
$\delta(CH_2)$	1460

Assignments compiled in C. Fagnano et al, *Polymer*, **42**, 5871 (2001).

Confocal Raman Microscopy of Semicrystalline Polyolefins: Crystalline and Amorphous Phases



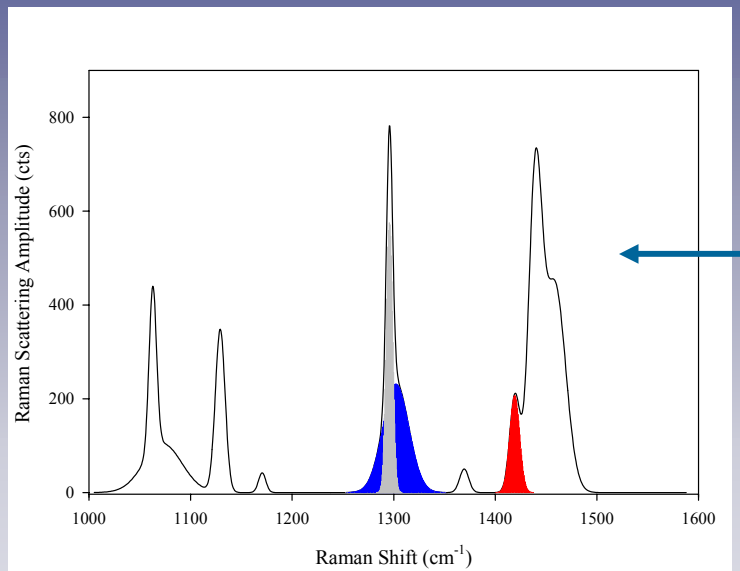
- Band assignments controversial – all-*trans* chains in amorphous phase
- Quantitative evaluation of crystalline content is problematic
- Relative changes (spatial variation) is robust

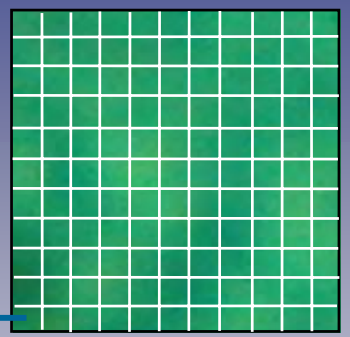
Spectral Assignments

Phase	Raman Shift (cm^{-1})
C + A_T	1064
A	1080
C + A_T	1131
C + A	1170
C	1297
A	1303
C + A	1370
C	1418
A_T	1440
A	1460

C – Crystalline, A – Amorphous, T – *trans*
Assignments compiled in C. Fagnano et al, *Polymer*, **42**, 5871 (2001).

Confocal Raman Microscopy of Semicrystalline Polyolefins: Crystallinity Mapping





32 x 32 grid
1024 spectra
Spacing – 312.5 nm

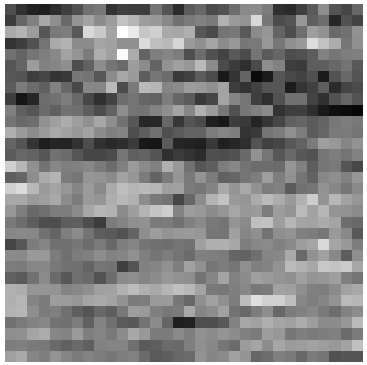
Crystallinity Map Procedure

1.) Fit each spectra for quantity $I_{418}/(I_{297} + I_{303})$

2.) $(I_{297} + I_{303})$ – Internal standard
Sum is constant from melt to pure crystalline phase

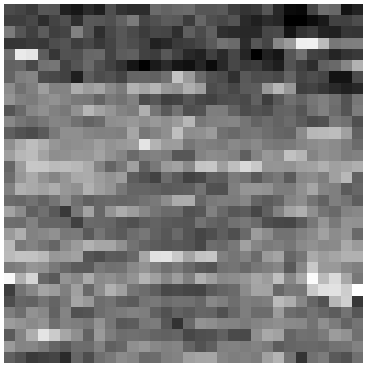
3.) Generate spatial maps

Confocal Raman Microscopy of Semicrystalline Polyolefins: Crystallinity Mapping



3H

$\langle I_{1418}/(I_{1297} + I_{1303})\rangle = 0.21$



21H

$\langle I_{1418}/(I_{1297} + I_{1303})\rangle = 0.35$

- Polyolefin blend sample amenable to study with confocal raman microscopy
- Signal levels reasonable – fluorescence largely absent
- Quantitative assessment of crystalline content problematic – study of spatial variations robust – shed light on assignments?
- Interesting regions to look for identifiable spatial variations in crystallinity?
- Depth profiling ?