

NIST

**National Institute of
Standards and Technology**

U.S. Department of Commerce

Raman Spectroscopy of 3-D Printed Polymers

Vanessa Espinoza, Erin Wood¹ and Angela Hight Walker¹

In collaboration with Jonathan Seppala², Anthony Kotula², and Kalman Migler²



About Me

- ▶ Texas Lutheran University

- ▶ Rising Senior
- ▶ Double major: Chemistry, Physics

- ▶ Previous Experience

- ▶ National Energy Technology Laboratory (DOE): Summer 2015, Spectroscopic Analysis of Metal Doped Nanoclusters
- ▶ TLU: Summer 2014, Biomimetic Modeling of Acireductone Dioxygenase's Active Site



Background-3-D Printing

- ▶ 3-D printing is an additive manufacturing process by which digital 3-D design data is used to build up a component in layers by depositing material.

- ▶ 3-D printing parameters

- ▶ Material

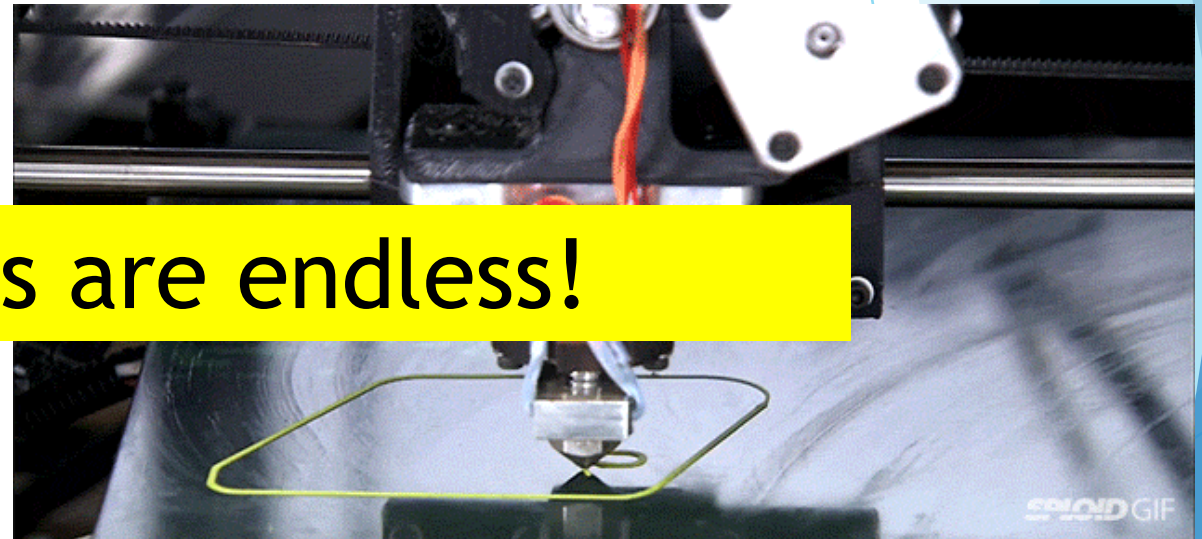


Applications are endless!

- ▶ Printer Type

- ▶ Fused Deposition Modeling

- ▶ Shear Rates
- ▶ Temperature

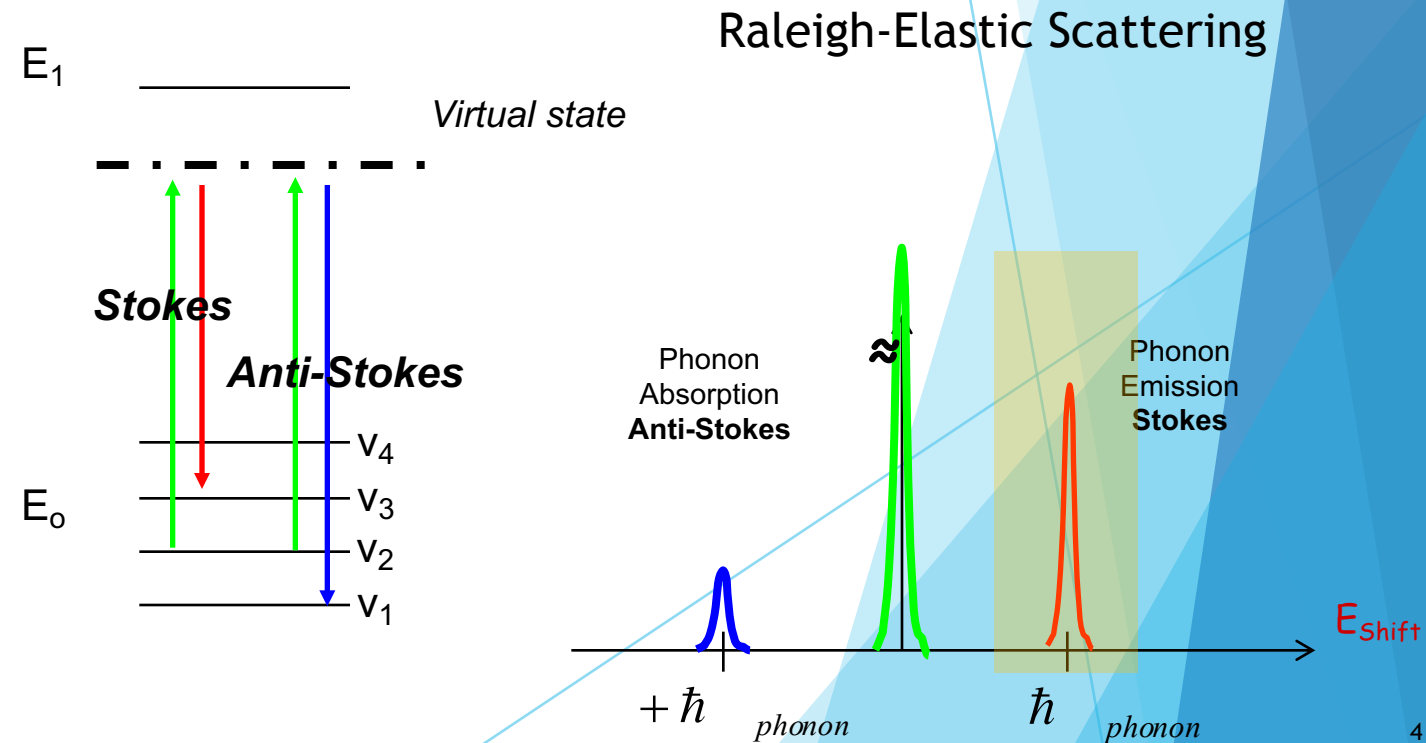
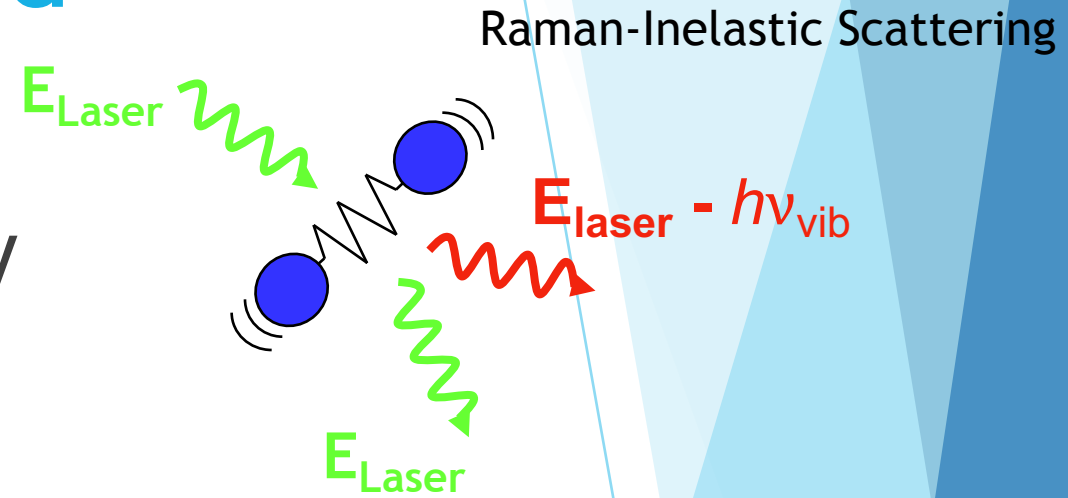
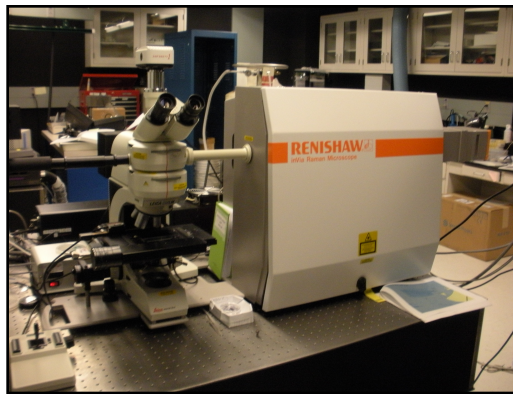


Background-Technique Used

- ▶ Raman Spectroscopy
 - ▶ Form of vibrational spectroscopy
 - ▶ Inelastic scattered light

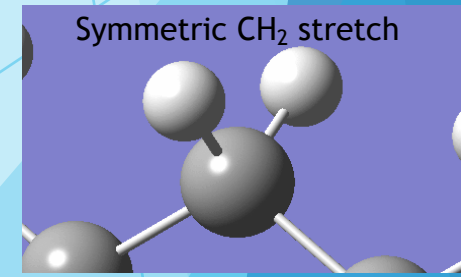
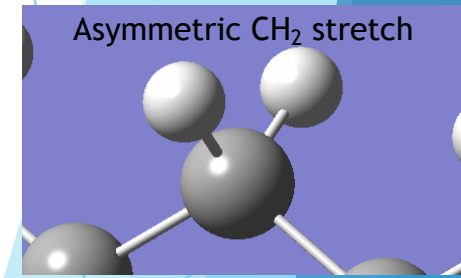
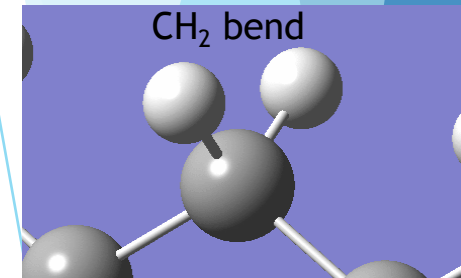
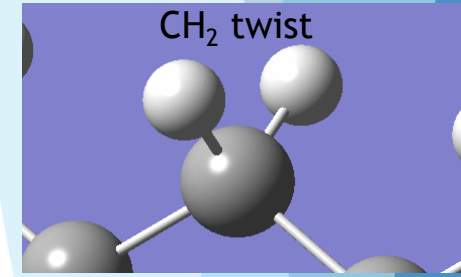
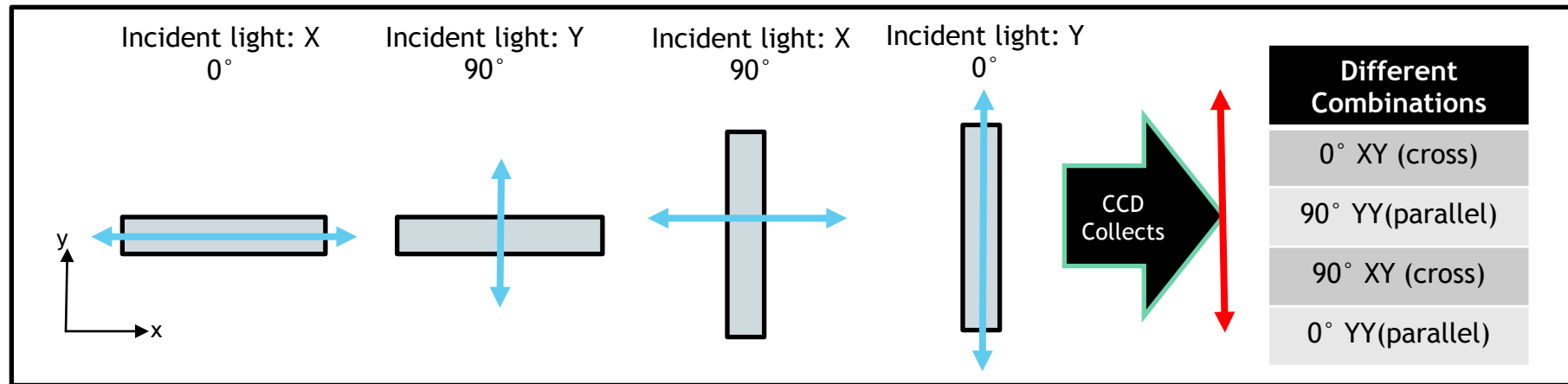


C. V. Raman
1928



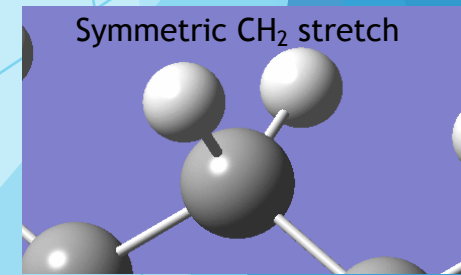
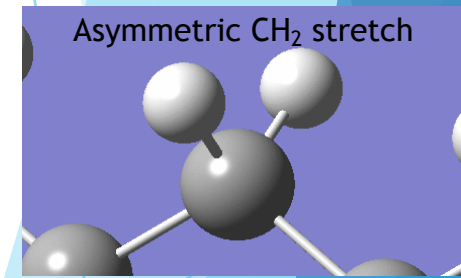
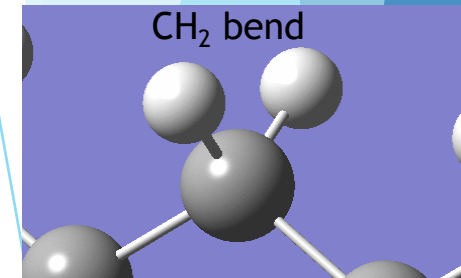
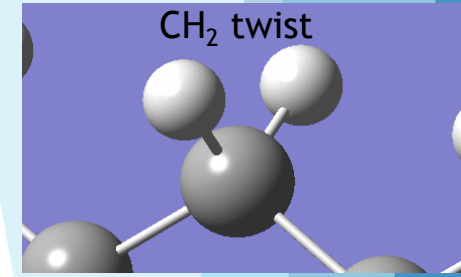
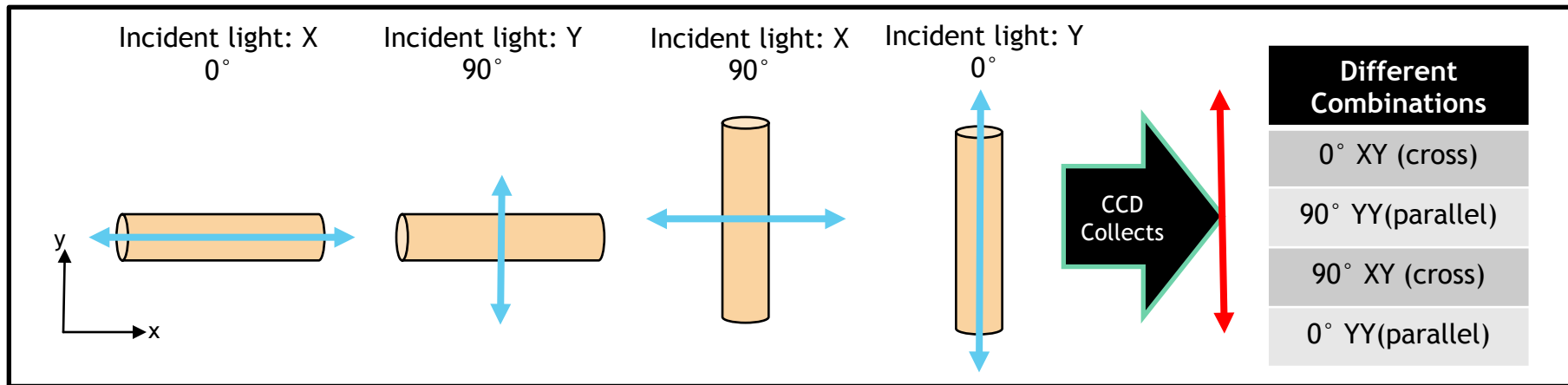
Background-Technique Used

- ▶ Polarized Raman Spectroscopy
 - ▶ A technique that quantifies alignment of polymer chains



Background-Technique Used

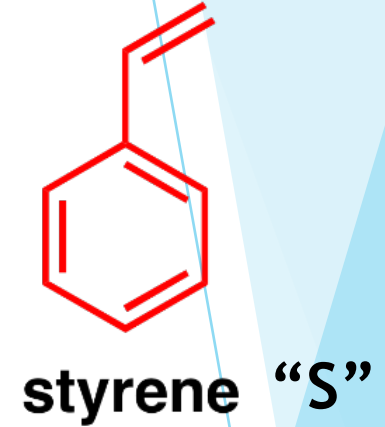
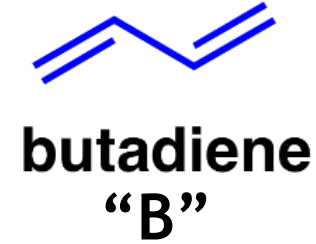
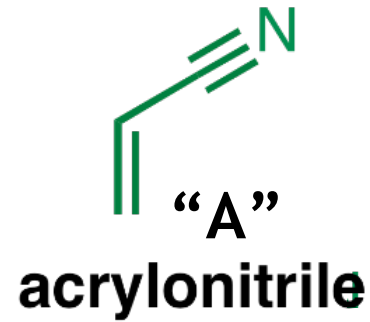
- ▶ Polarized Raman Spectroscopy
 - ▶ A technique that quantifies alignment of polymer chains



Background-Polymers Studied

▶ Acrylonitrile Butadiene Styrene

- ▶ LEGOs
- ▶ Computer keyboards



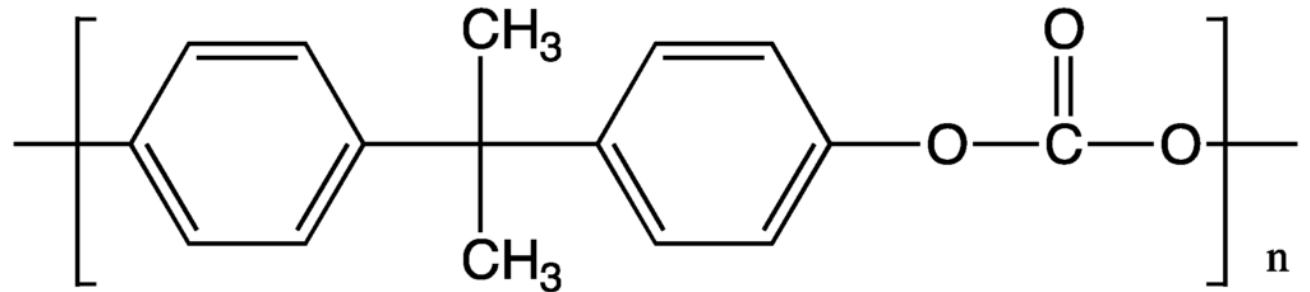
ABS

▶ Bisphenol-A-polycarbonate

- ▶ Safety glasses



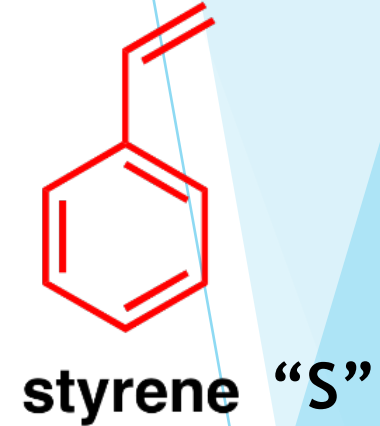
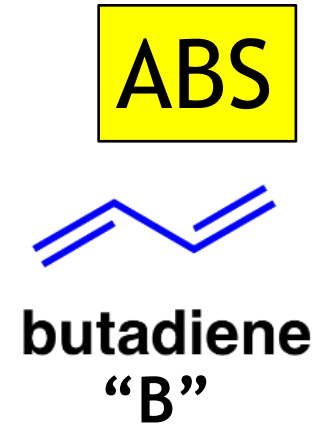
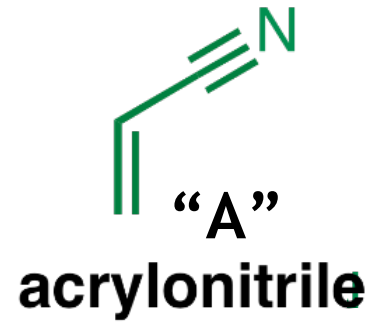
PC



1 of 2 Polymers Studied

▶ Acrylonitrile Butadiene Styrene

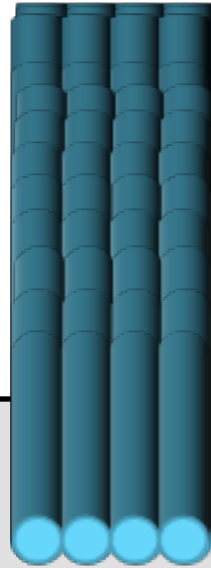
- ▶ LEGOs
- ▶ Computer keyboards



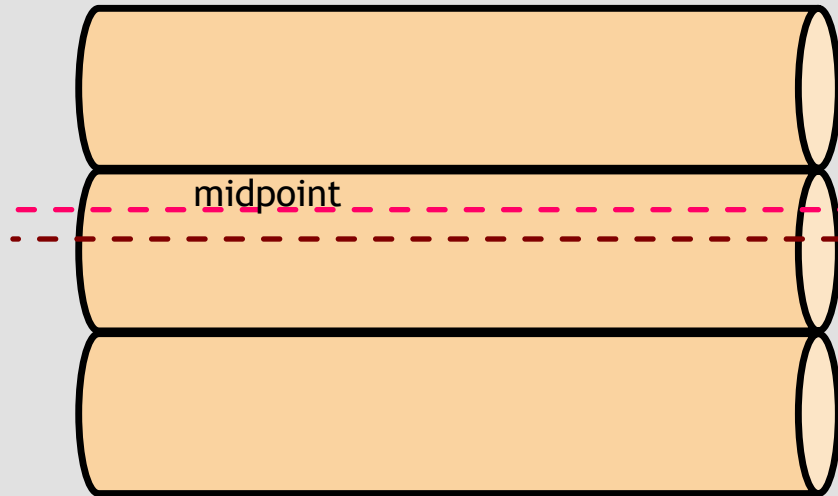
▶ Technical Project

- ▶ Determine qualitative homogeneity of components using Raman spectroscopy
- ▶ Compare experimental results to previously published work
 - ▶ Cole, Daniel P., et al. "Interfacial mechanical behavior of 3D printed ABS." *Journal of Applied Polymer Science* 133.30 (2016).

ABS- Terminology



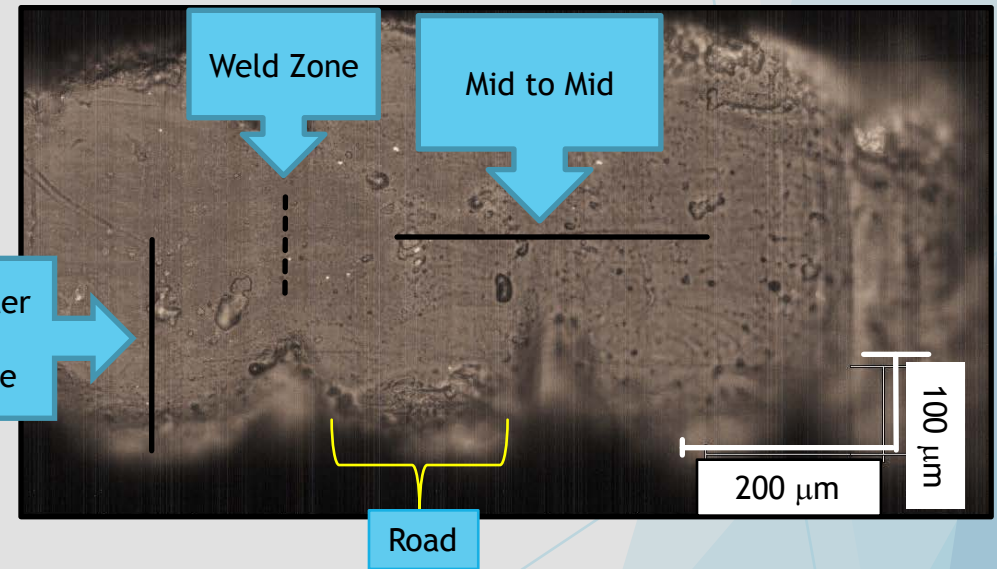
Side View



peak

Center to edge

Microtomed Cross-Sectional Area (Top View)



Technical Project

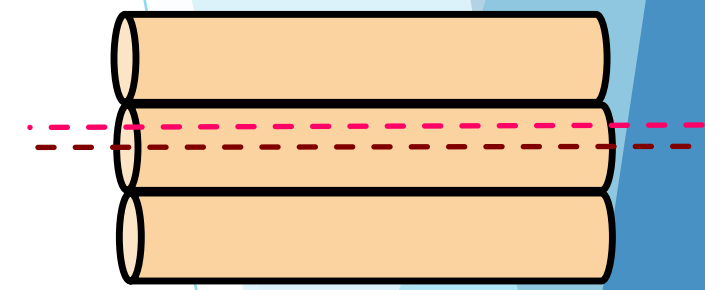
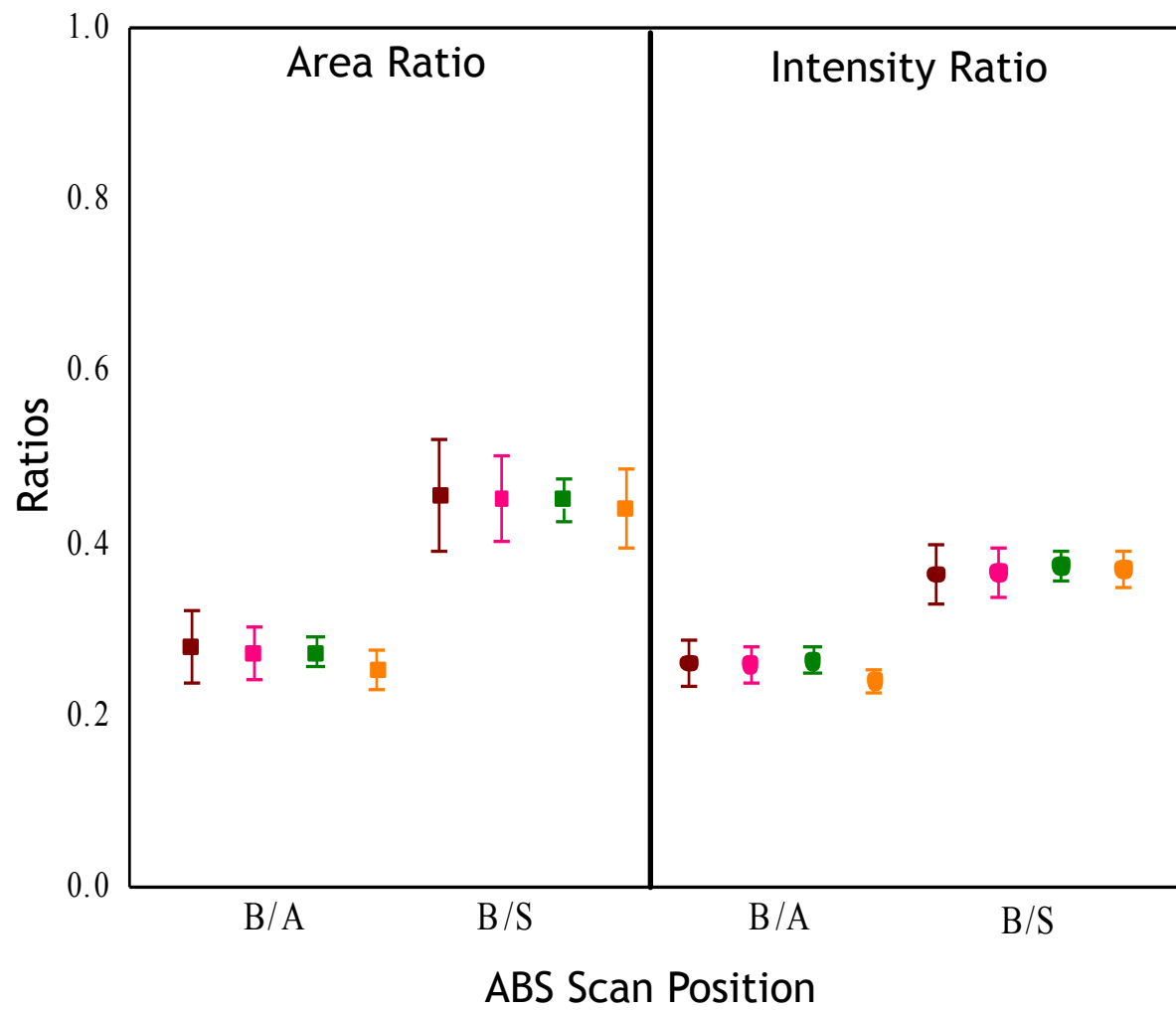
▶ ABS

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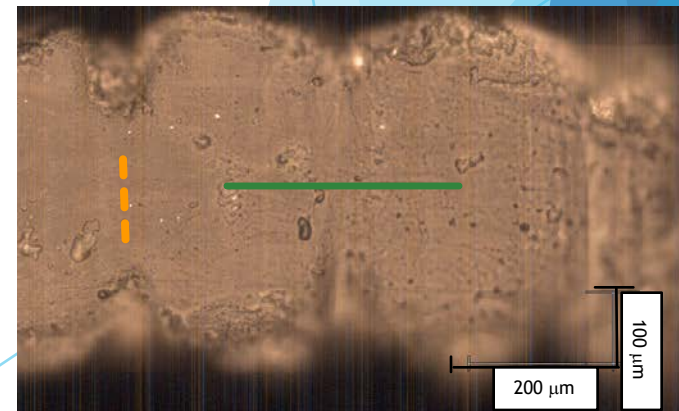


▶ BPAPC

- ▶ Use polarized Raman spectroscopy to analyze alignment of polymer chains under different conditions



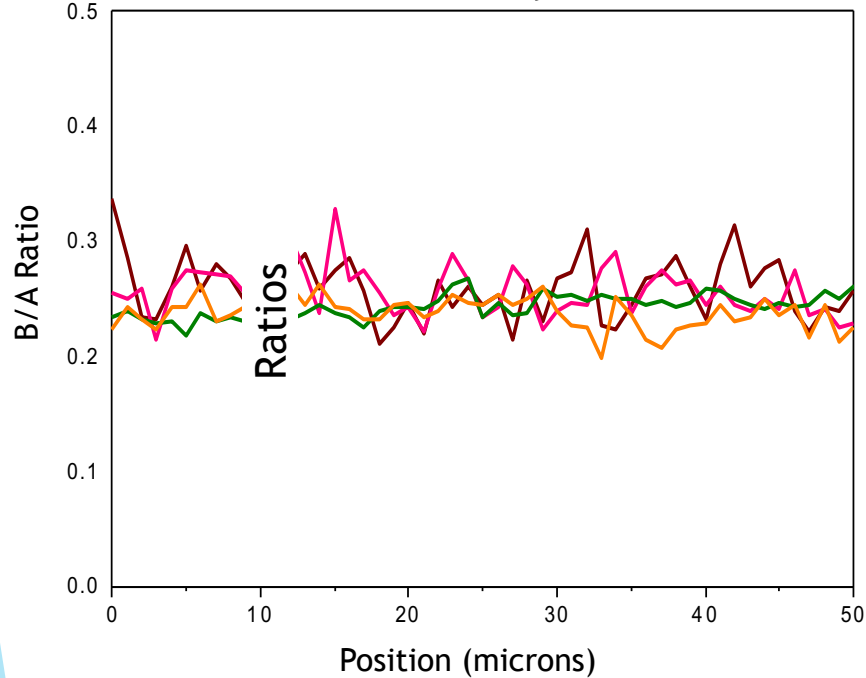
- Peak of Road
- Midpoint of Road
- CS Mid to Mid
- CS Weld Zone



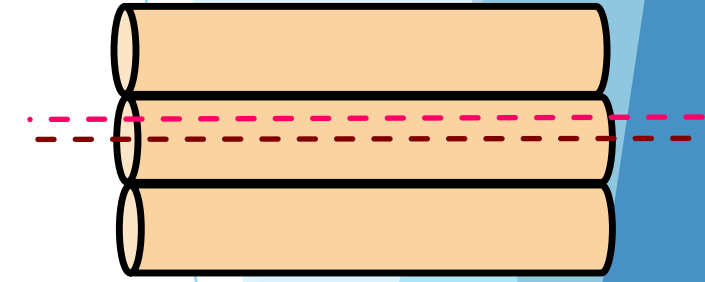
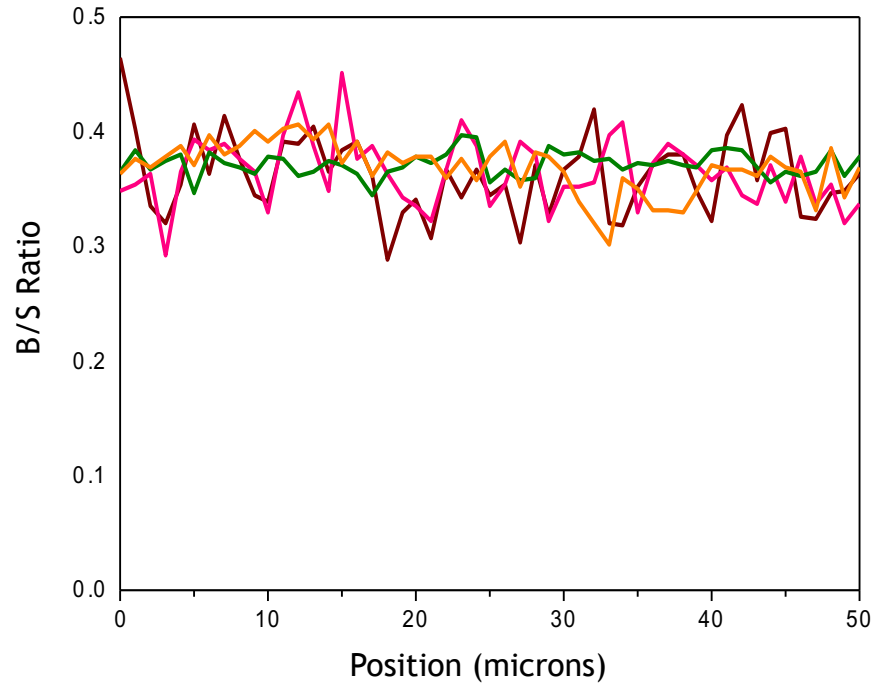
ABS

Homogeneity

B/A ABS Intensity Ratio

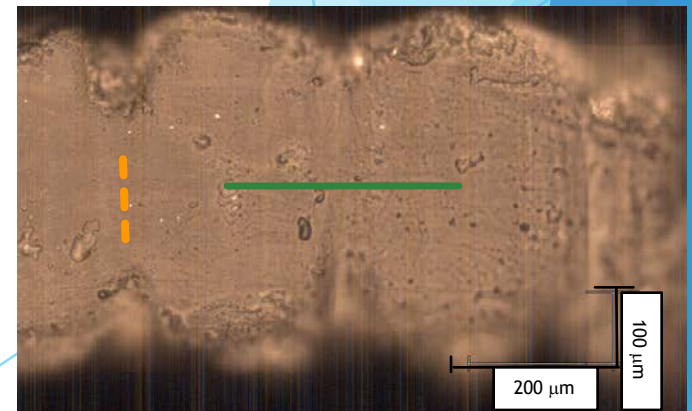


B/S ABS Intensity Ratio

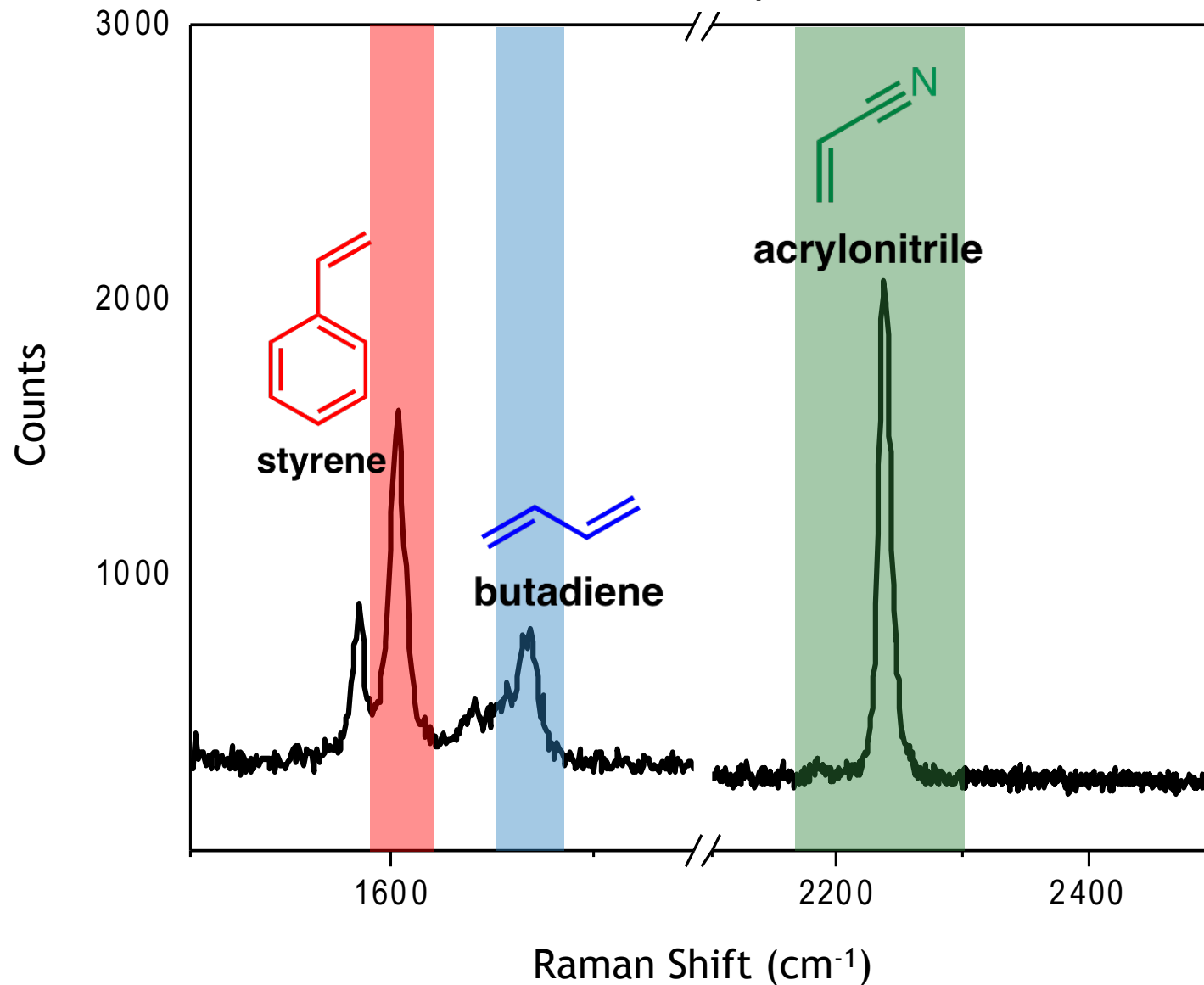


- █ Peak of Road
- █ Midpoint of Road
- █ CS Mid to Mid
- █ CS Weld Zone

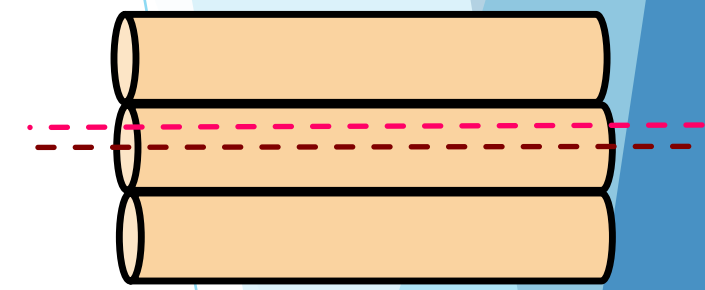
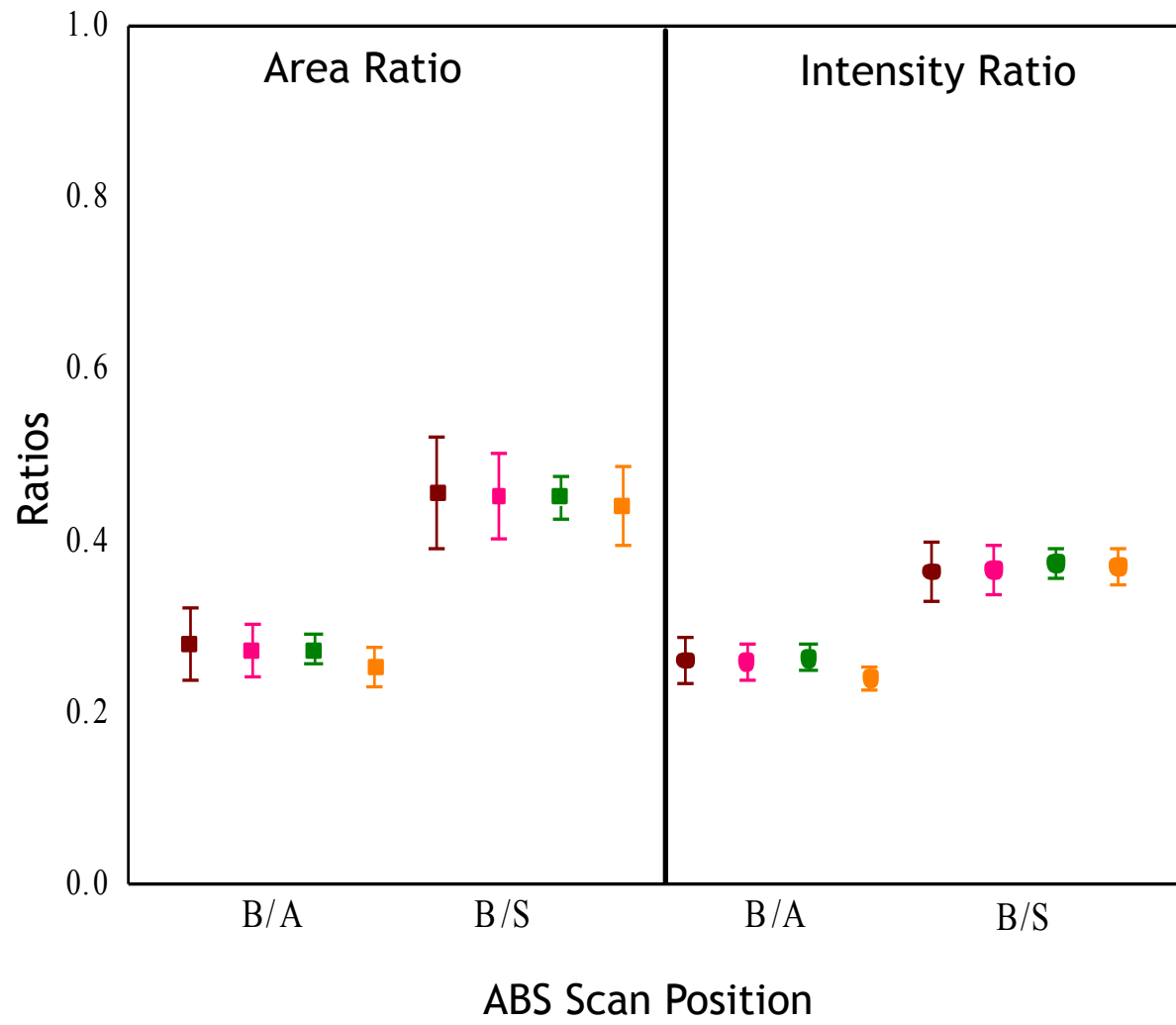
Position	B/A		B/S	
	Mean	Stnd Dev	Mean	Stnd Dev
Peak of Road	0.259	0.027	0.363	0.035
Midpoint of Road	0.267	0.022	0.365	0.030
CS Mid to Mid	0.262	0.015	0.373	0.018
CS Weld Zone	0.238	0.014	0.369	0.023



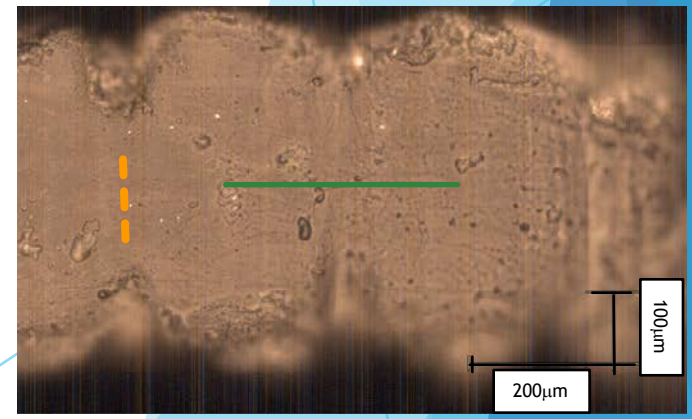
ABS Raman Spectrum



- ▶ Looked at multiple scans from line map
- ▶ Curve fit of peaks
- ▶ Peaks focused on in ABS Raman spectrum
 - ▶ A ~ 2238 cm⁻¹
 - ▶ B ~ 1667 cm⁻¹
 - ▶ S ~ 1604 cm⁻¹
- ▶ Relative ratios
 - ▶ Area
 - ▶ Intensity



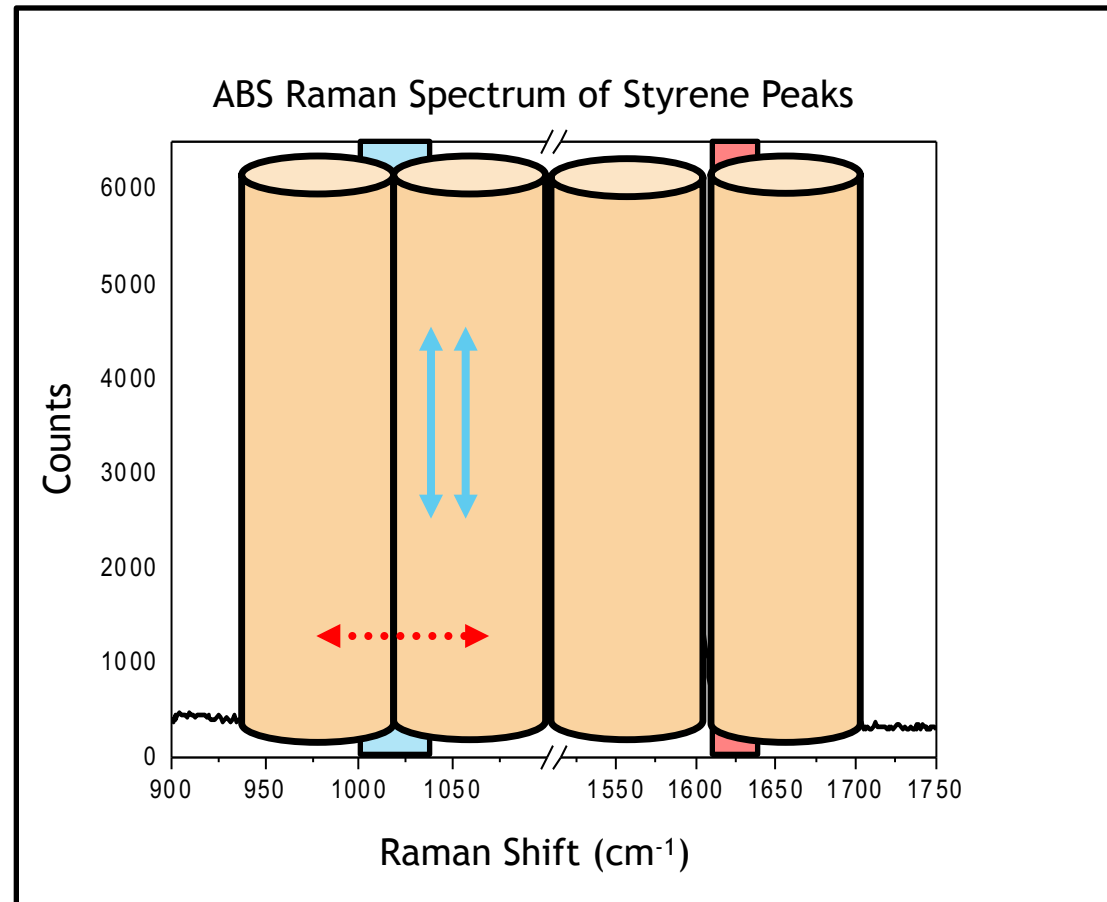
- Peak of Road
- Midpoint of Road
- CS Mid to Mid
- CS Weld Zone



ABS

Comparison with previous work

- ▶ Raman spectroscopy mapping of interfacial areas revealed ~30% less B/S and B/A ratios with respect to analysis of the build surfaces.
 - ▶ Peak selection
 - ▶ Scanning direction
 - ▶ Printing parameters
 - ▶ Printing temperature
 - ▶ 230°C vs 203°C
 - ▶ Printers used
 - ▶ Maker Bot vs Stratasys Fortus
 - ▶ Dimensions of samples

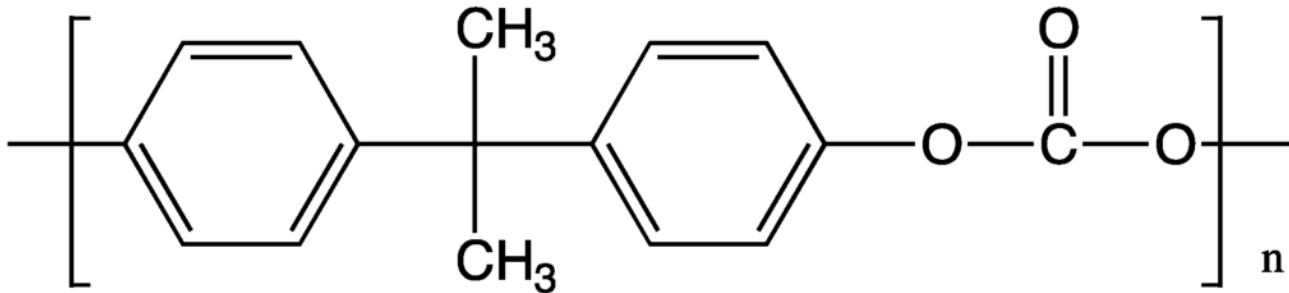


2 of 2 Polymers Studied

▶ Bisphenol-A-polycarbonate

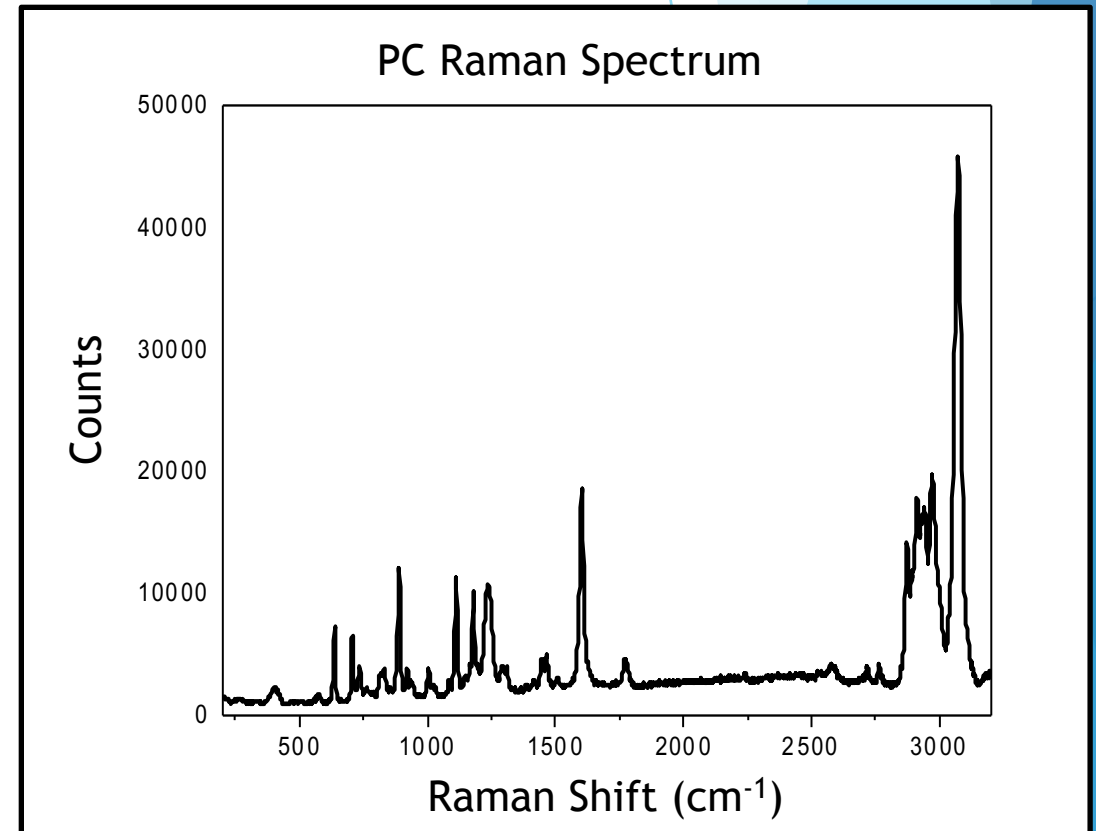
- ▶ Safety glasses

PC



▶ Technical Project

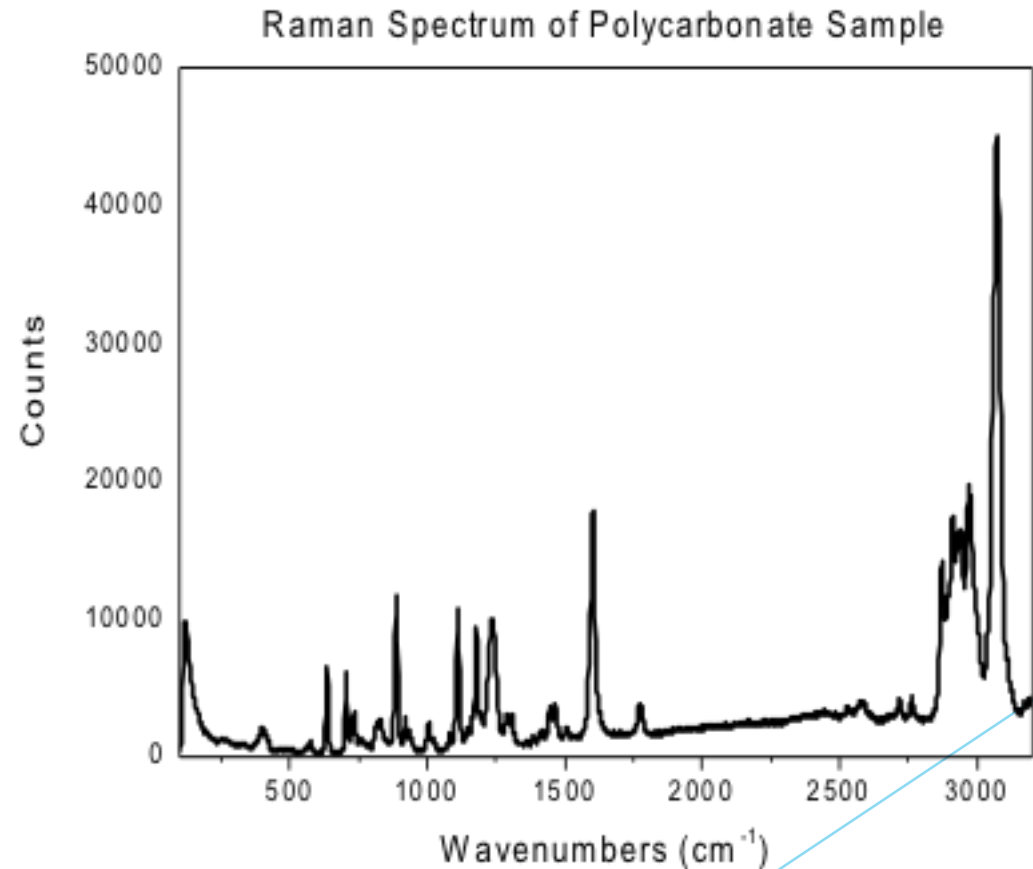
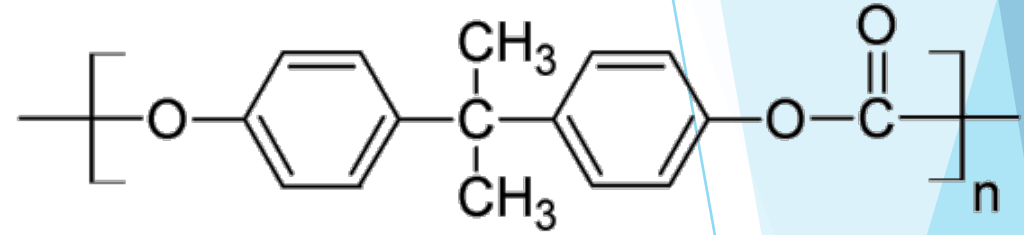
- ▶ Use polarized Raman spectroscopy to analyze alignment of polymer chains under different conditions



Polycarbonate (PC)

Sampling Parameters

- ▶ Samples of interest:
 - ▶ Extruded filament
 - ▶ Hand-drawn extruded filament
 - ▶ Neat filament
 - ▶ 100 mm/sec printed sample
 - ▶ 10 mm/sec printed sample

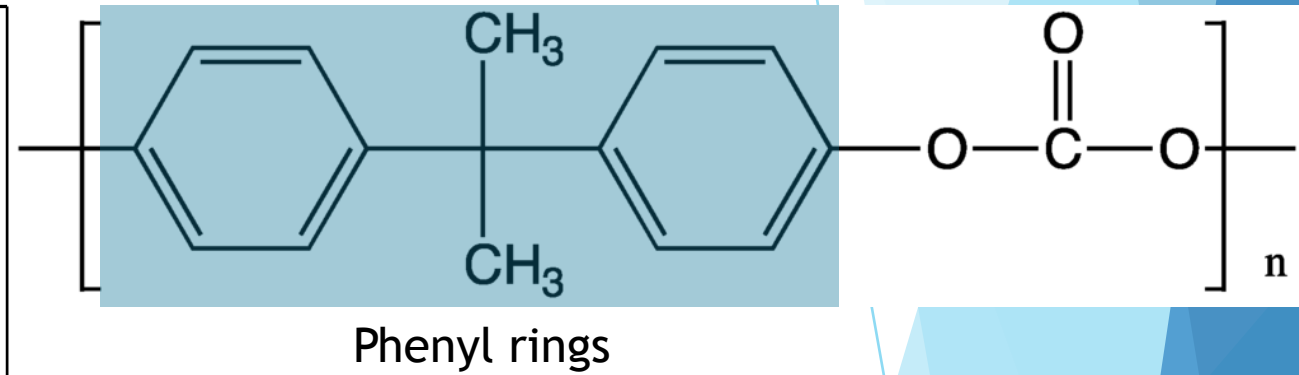
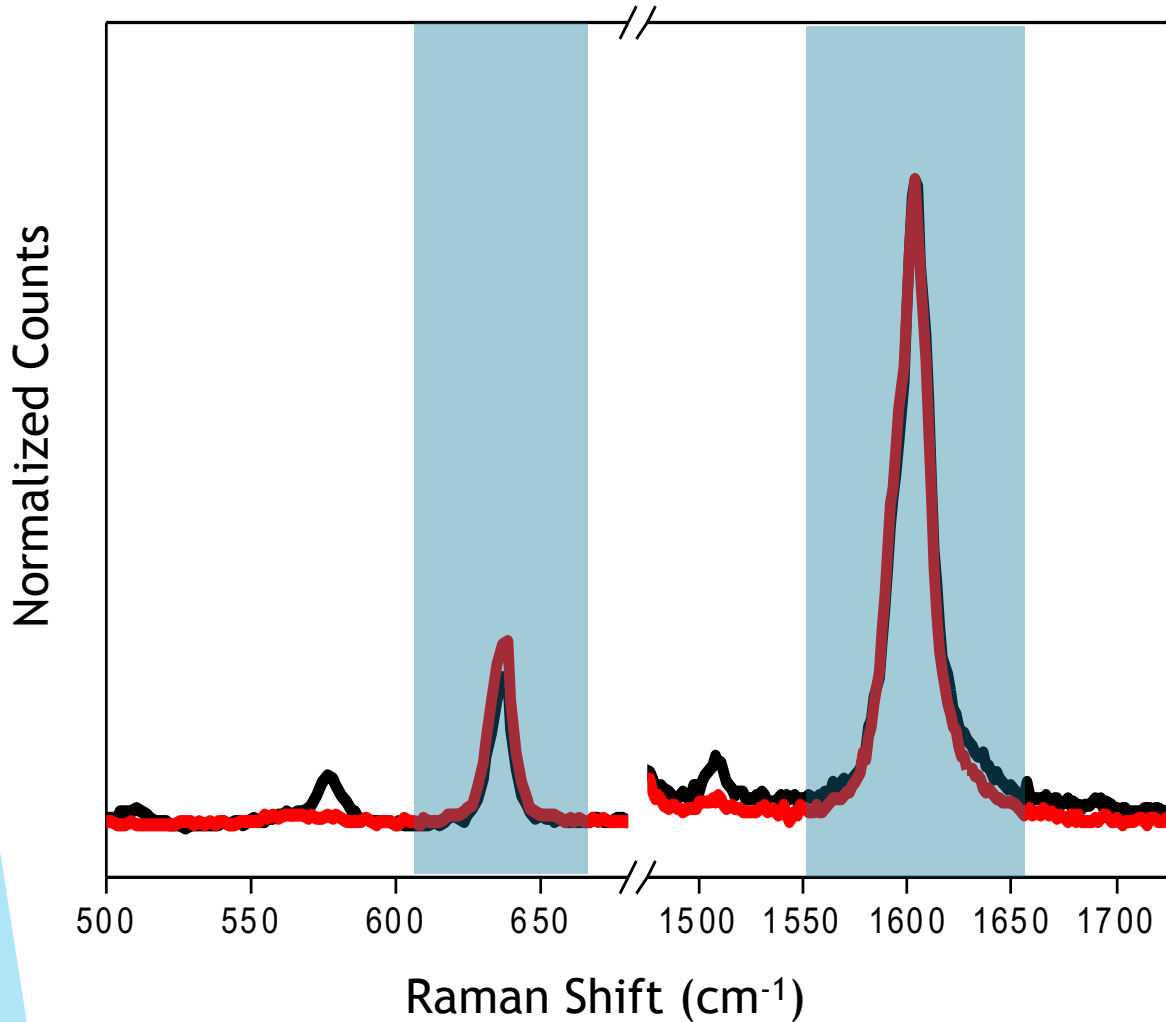


Polycarbonate

Peak Assigning

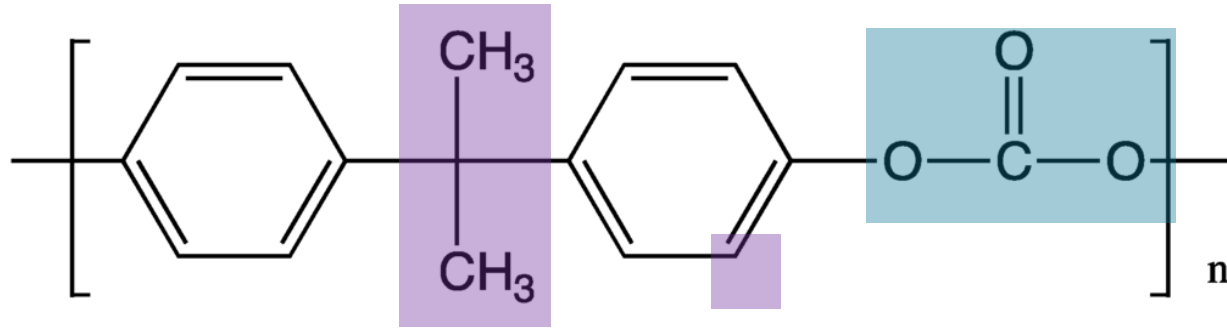
Polycarbonate-Phenyl Rings

Normalized Raman Spectra

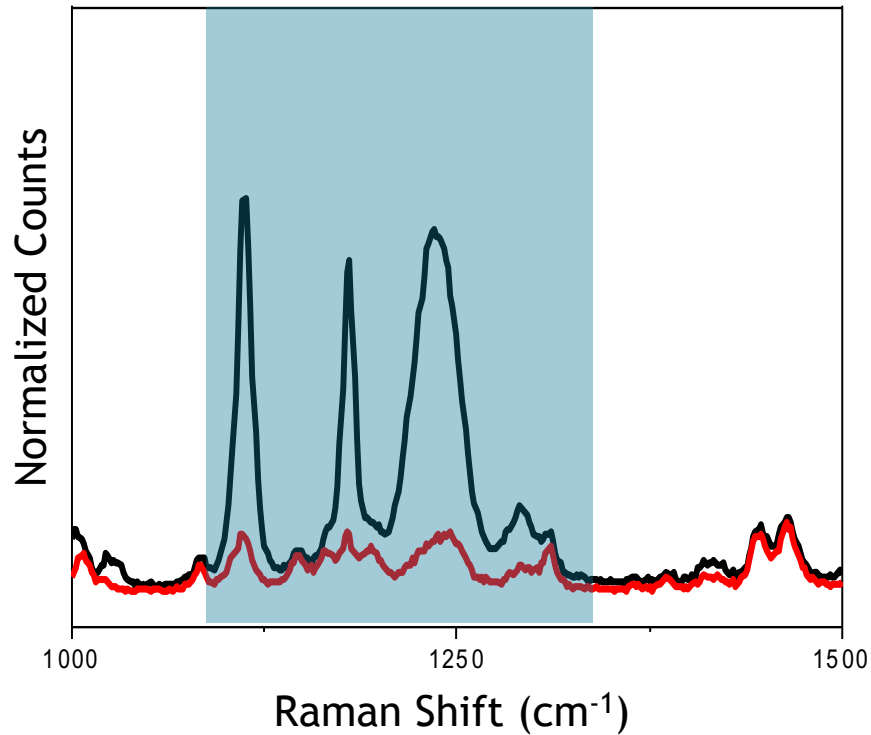


Different Combinations
0° XY (cross)
90° YY (parallel)
90° XY (cross)
0° YY (parallel)

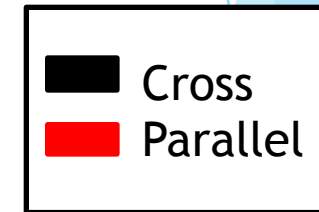
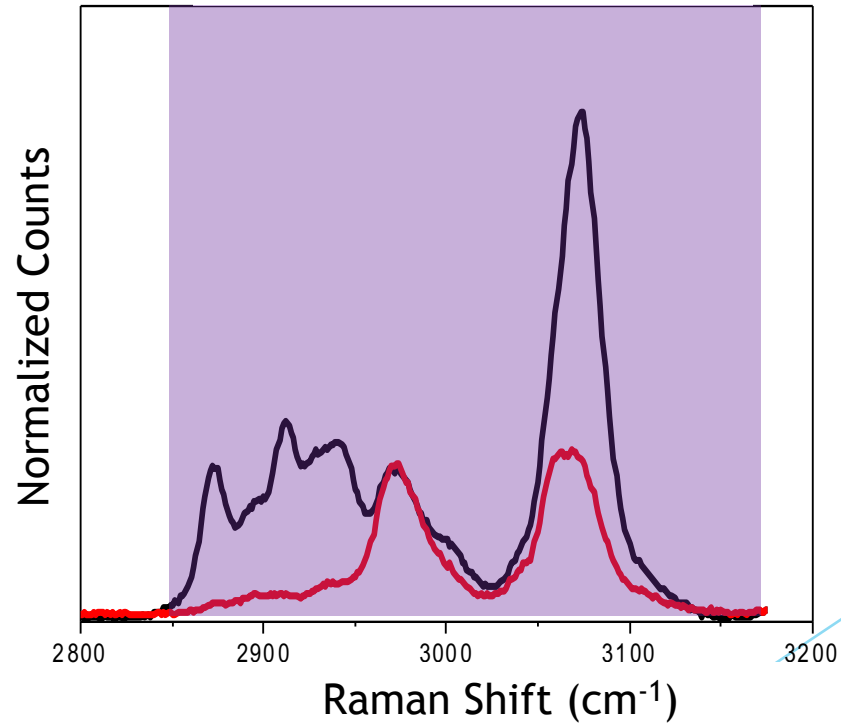
Polycarbonate-Differences in Spectra



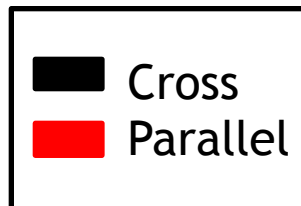
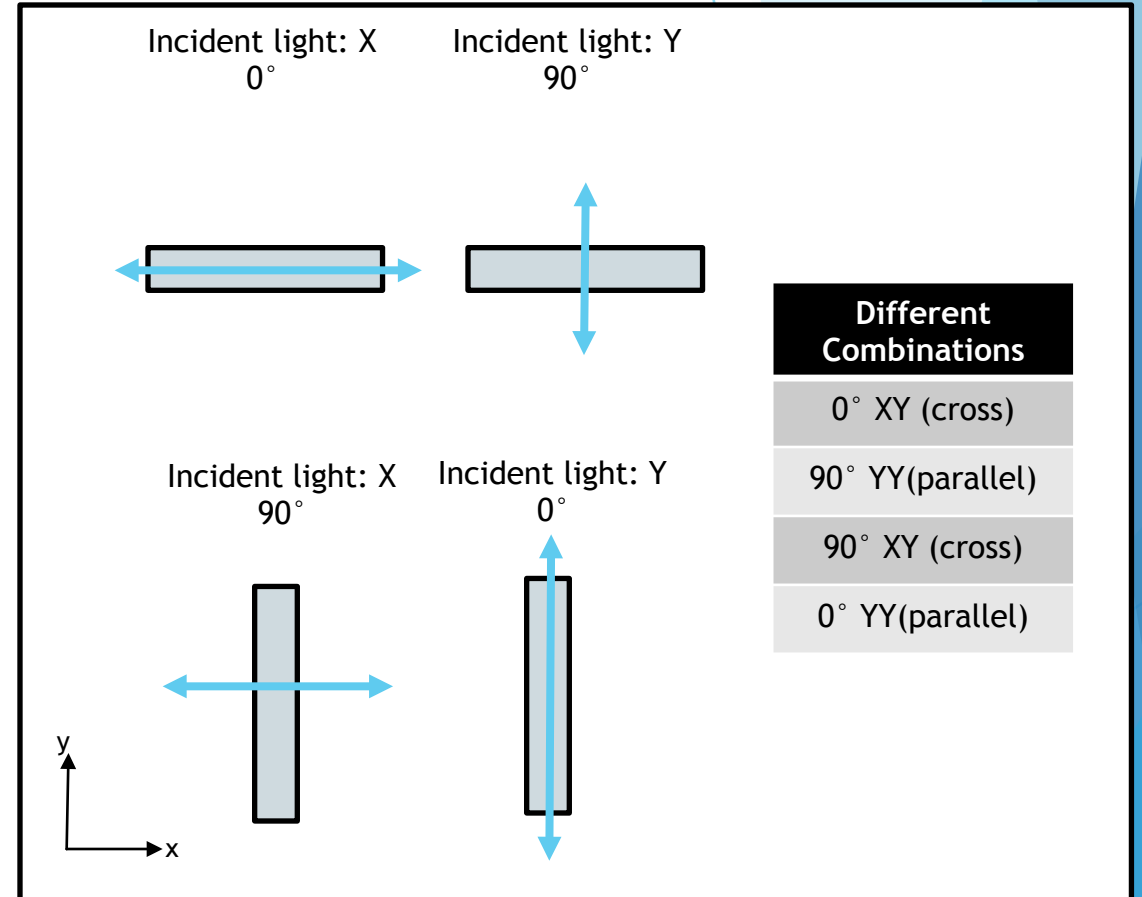
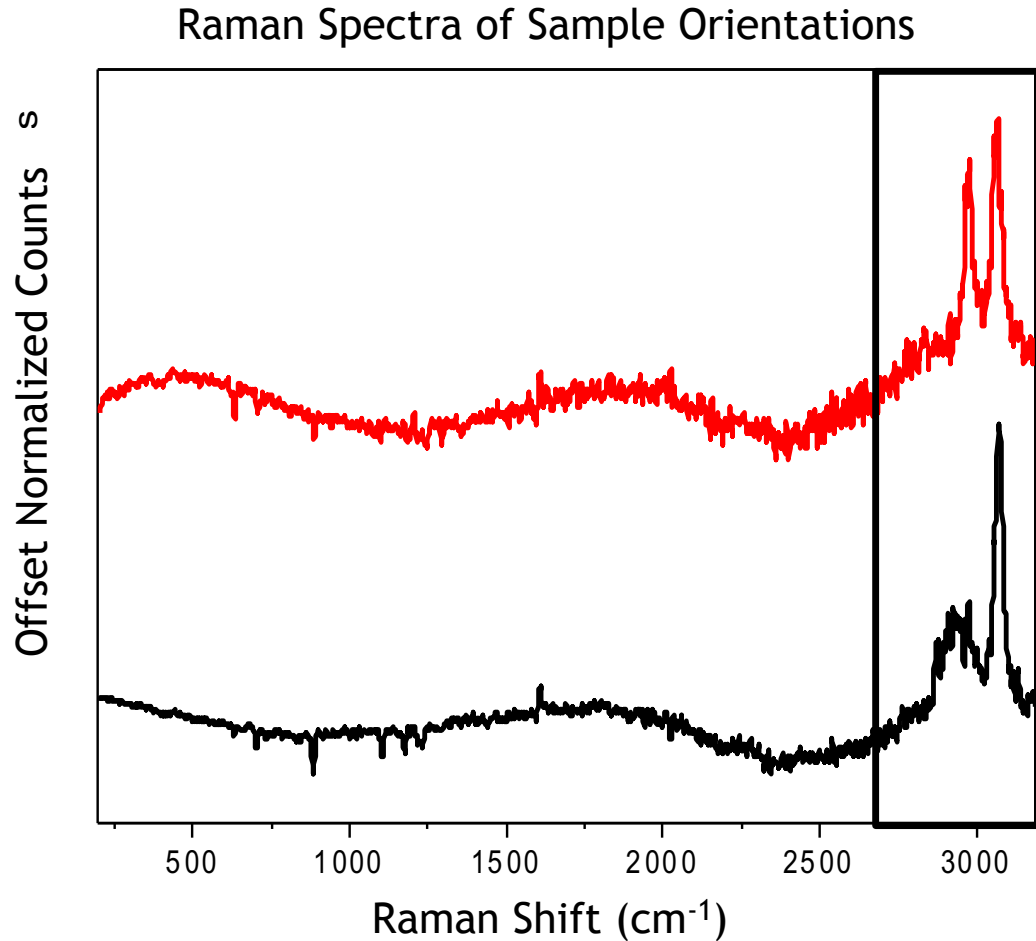
Normalized Raman Spectra



Normalized Raman Spectra

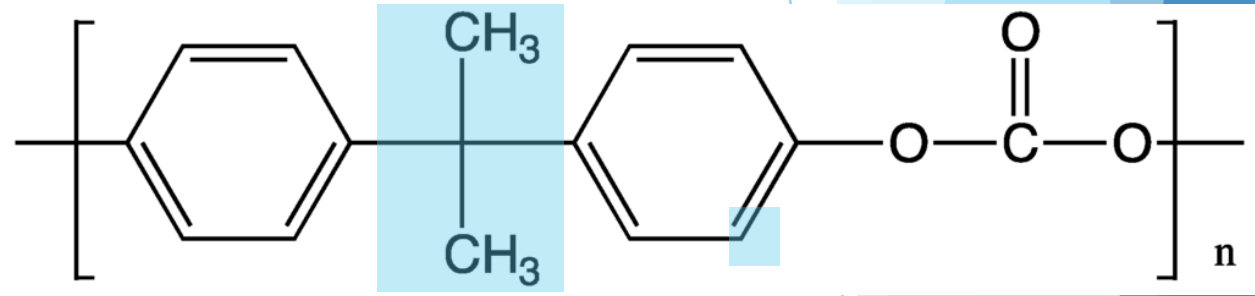
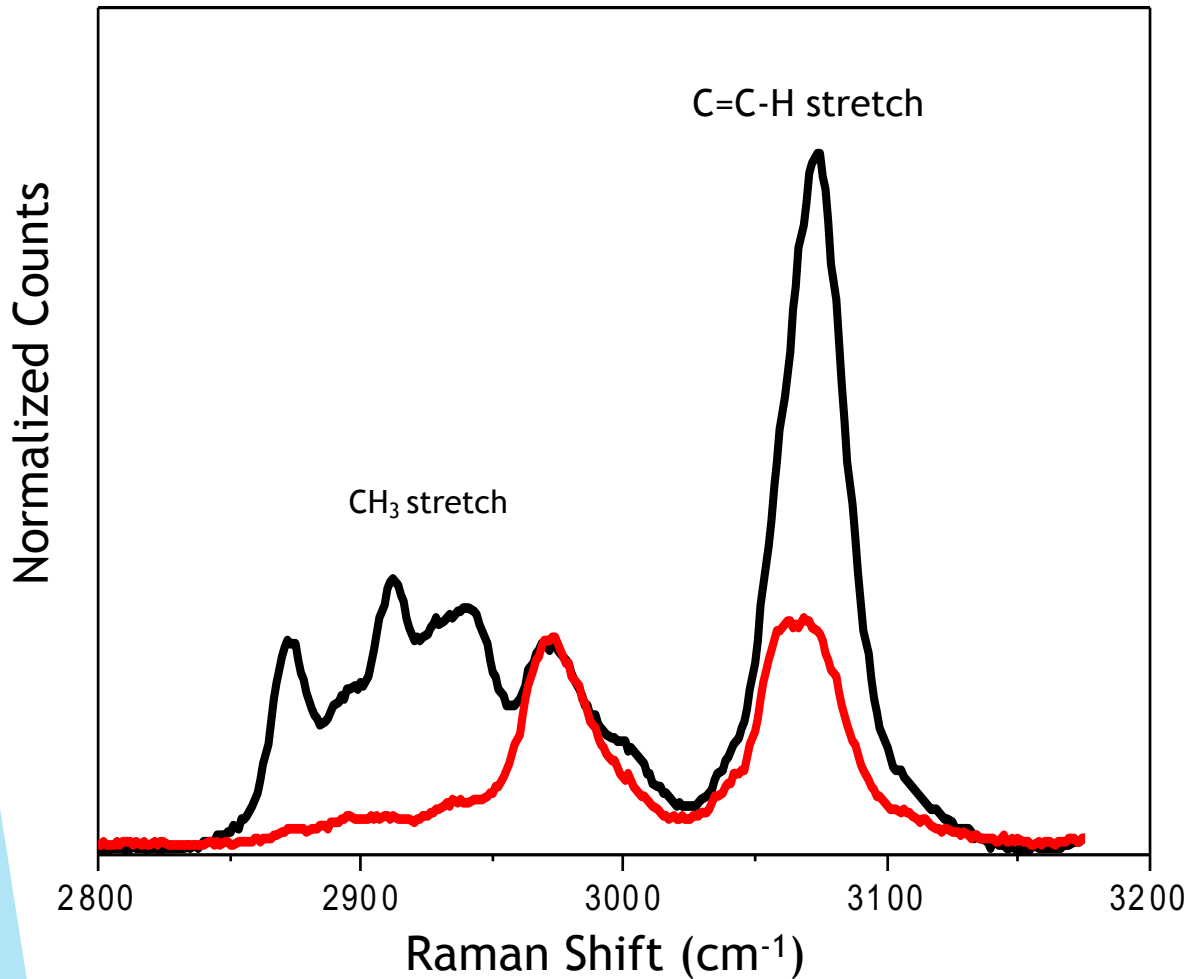


Polycarbonate-Sample Orientations



Polycarbonate- CH stretching

Normalized Raman Spectra



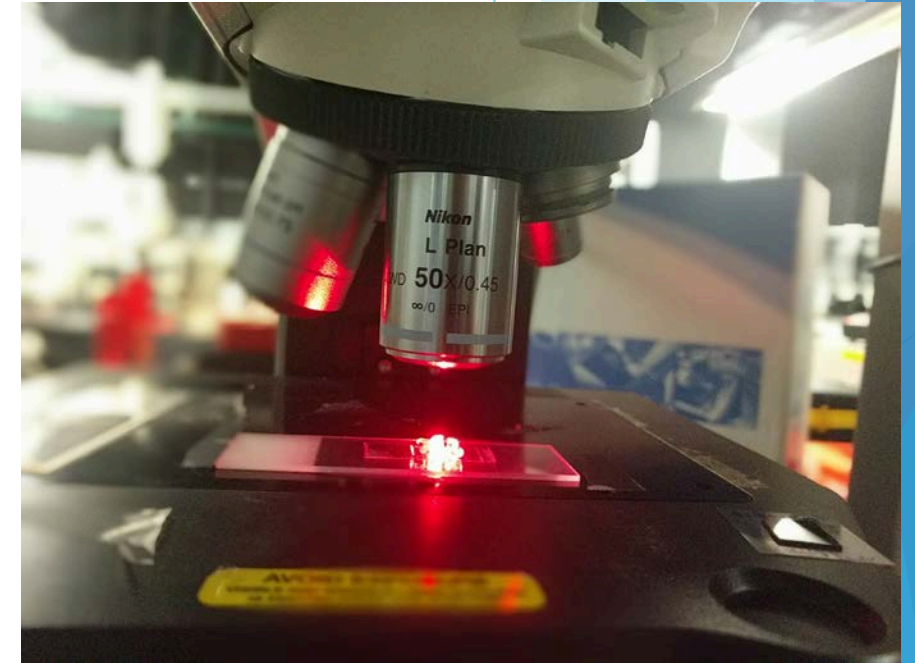
■ Cross
■ Parallel

Conclusion

- ▶ Homogeneity in ABS sample
- ▶ Polarized Raman spectroscopy shows to be useful with understanding of polymer chain alignment

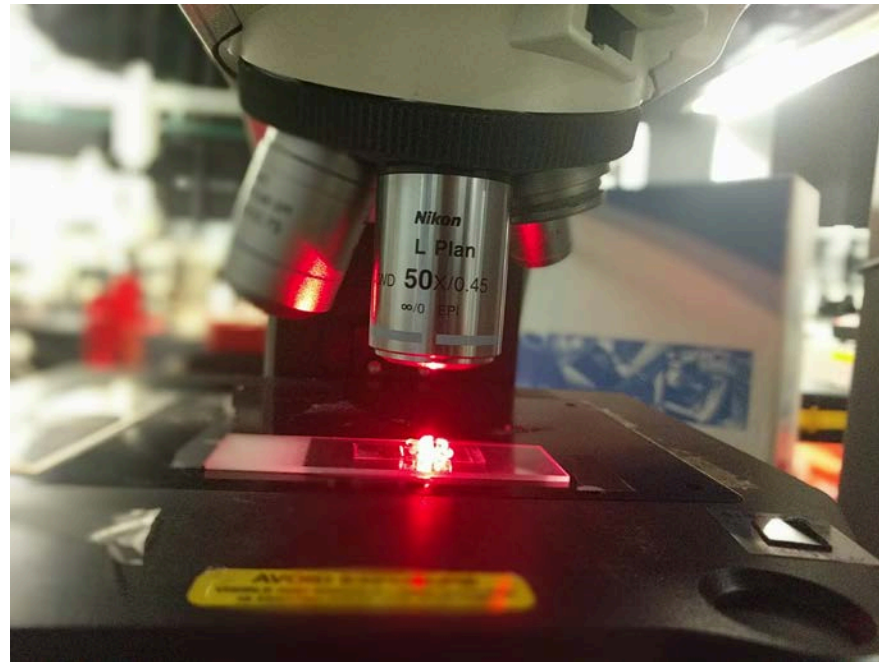
Further Experimentation

- ▶ Further explore the properties of polycarbonate
- ▶ Understanding crystallization in semi-crystalline materials
 - ▶ Polycaprolactone (PCL)
 - ▶ Polylactic acid (PLA)



Further Experimentation

- ▶ Further explore the properties of BPAPC
- ▶ Understanding crystallization in semi-crystalline materials
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Acknowledgements

- ▶ American Institute of Physics
- ▶ Society of Physics Students
- ▶ Angela Hight Walker and the Hight Walker Group
- ▶ Family and Friends
- ▶ Fellow Interns

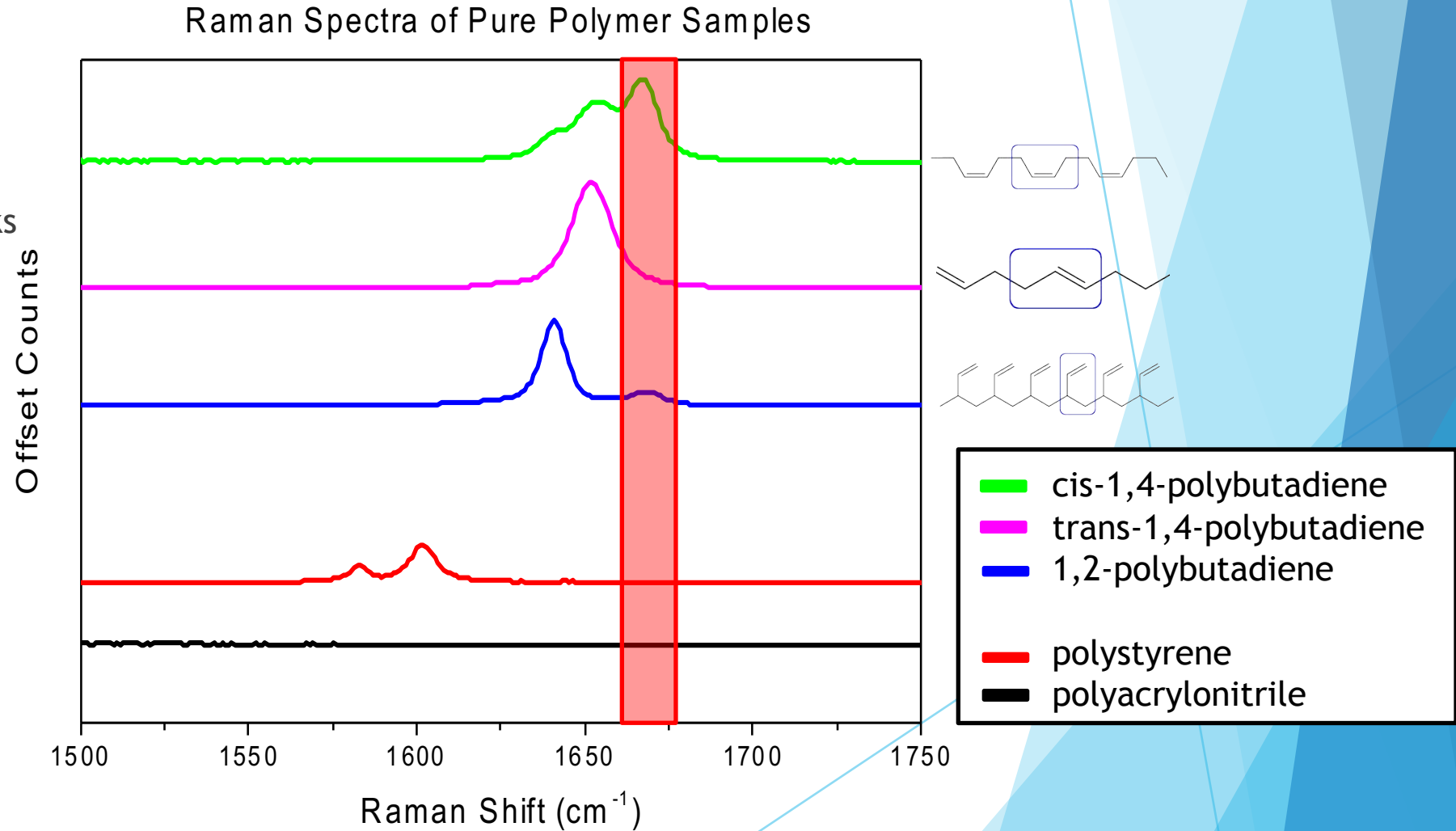


Questions?

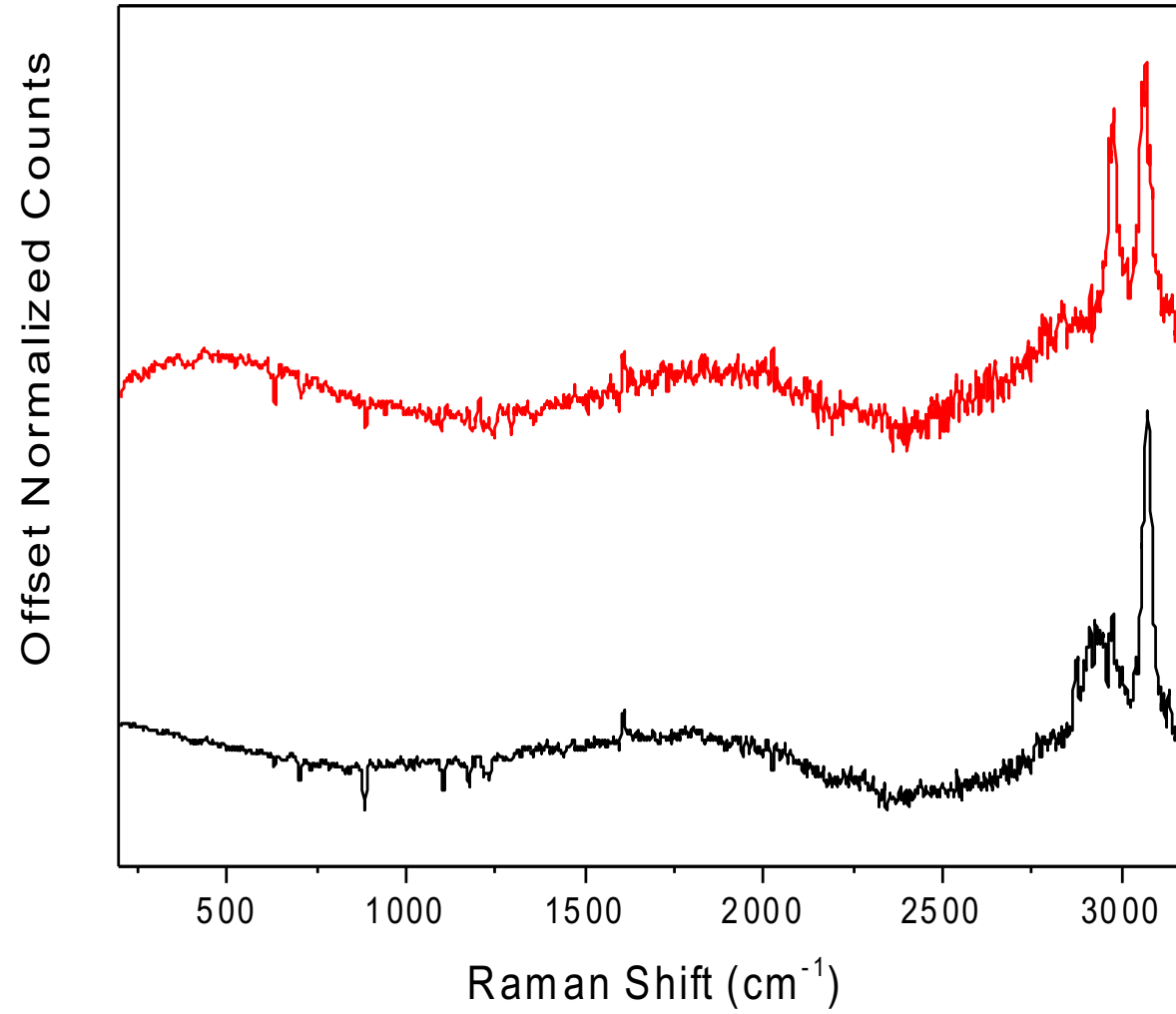
ABS

Parameter Optimization

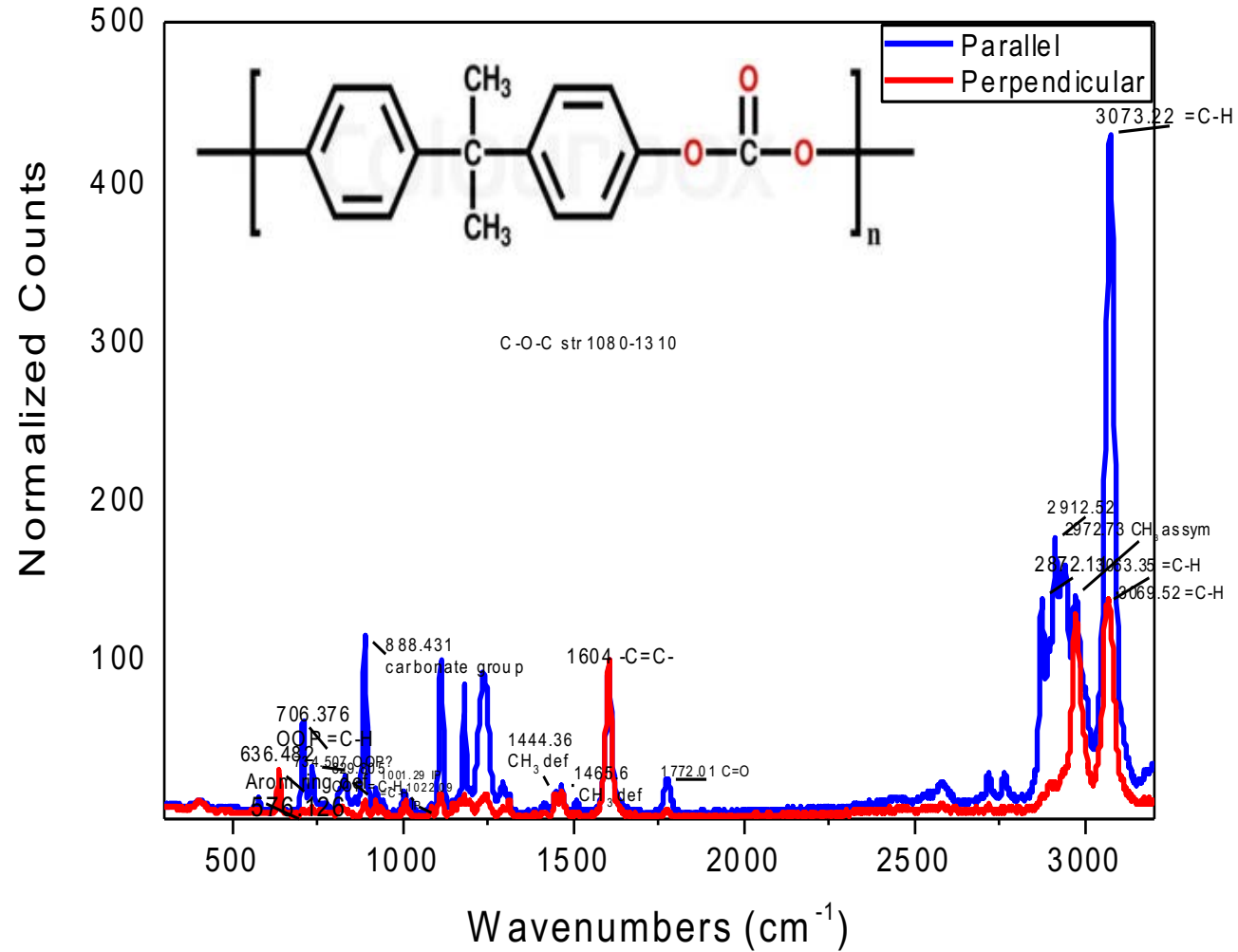
- ▶ Reasons for difficulty
 - ▶ Different isomers exist
 - ▶ Low signal to noise
 - ▶ Overlap with other peaks



Sample Orientation Raman Spectras



Polarized Raman of Polycarbonate 10 mm/s



Polarized Raman of Polycarbonate 10 mm/s

