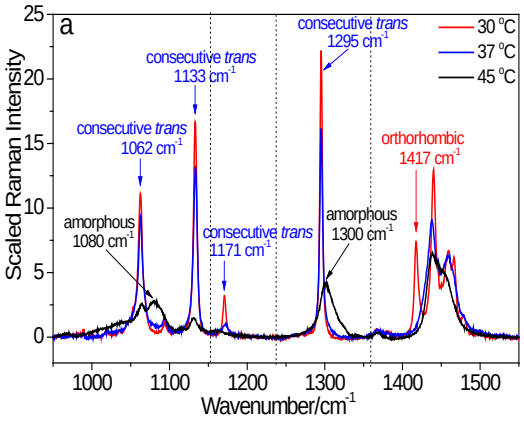
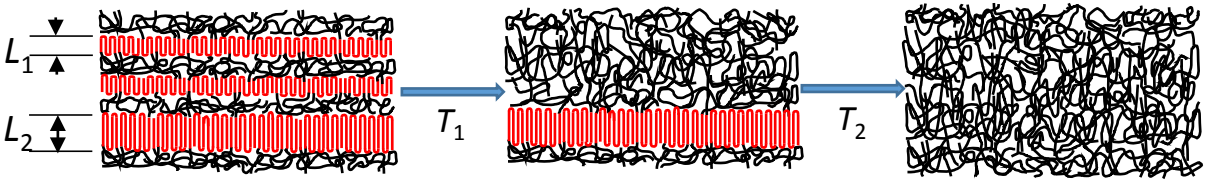
Phase transitions of polyethylene by Raman correlation spectroscopy





Ying Jin

Material Measurement Laboratory
National Institute of Standards and Technology (NIST)

2017 SPE INTERNATIONAL
POLYOLEFINS CONFERENCE
February 26 - March 1 | Houston, TX

Why NIST Cares ?

Founded in 1901, NIST is a non-regulatory federal agency within the U.S. Department of Commerce. NIST's mission is to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life.

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

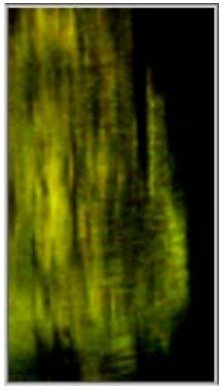
Bimodal PE Blend under stretching

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

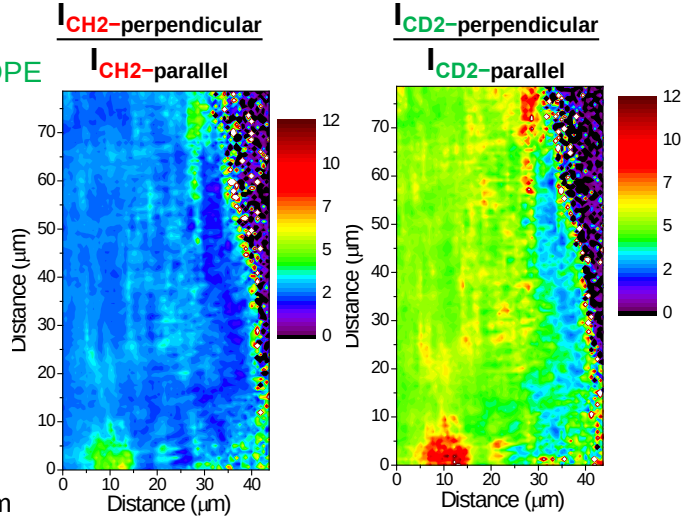
Phase transitions of polyethylene

- Will talk today

50% LLDPE
50% Deuterated HDPE



43.68 um × 78.62 um

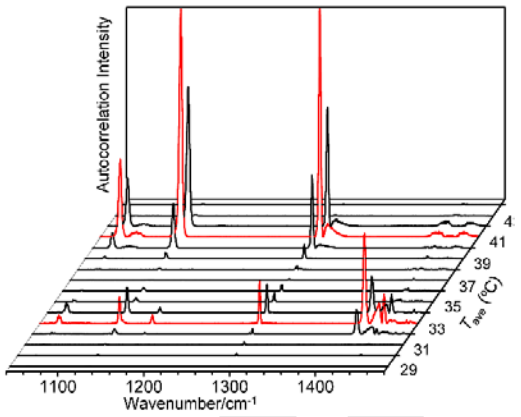


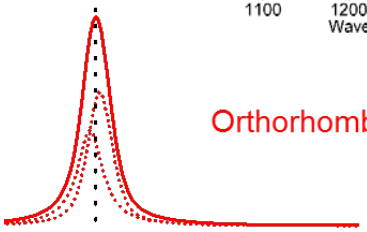
Outline

Raman spectra of alkane melting

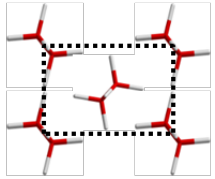
- Characterized phase-specific Raman peaks;
- Determined phase transitions;
- Identified hexagonal phase;
- Unravelled overlapped peaks.

J. Raman Spectrosc. 2016, 47, 1375–1384





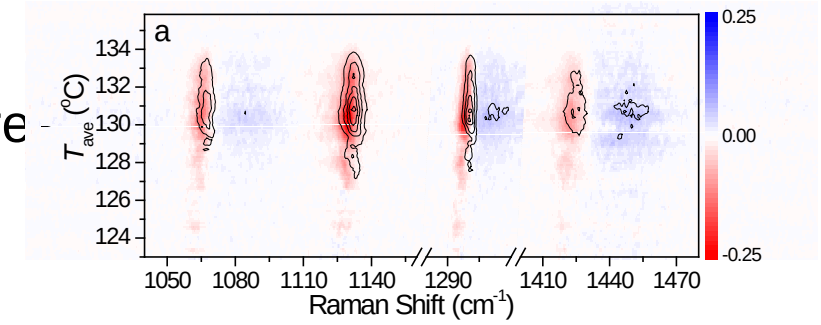
Orthorhombic

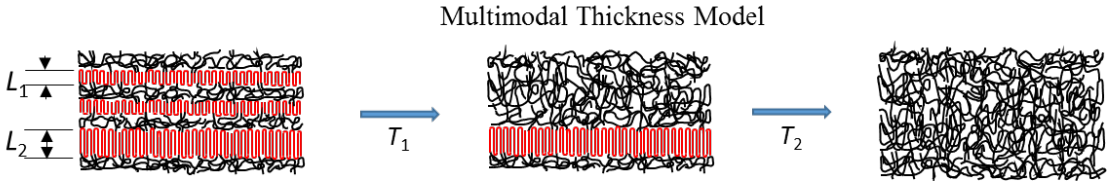


Raman spectra of HDPE melting

- Determined phase transition temperature
- Discussed melting mechanism;
- Suggested the existence of mesophase.

Submitted





PE vs *n*-alkane

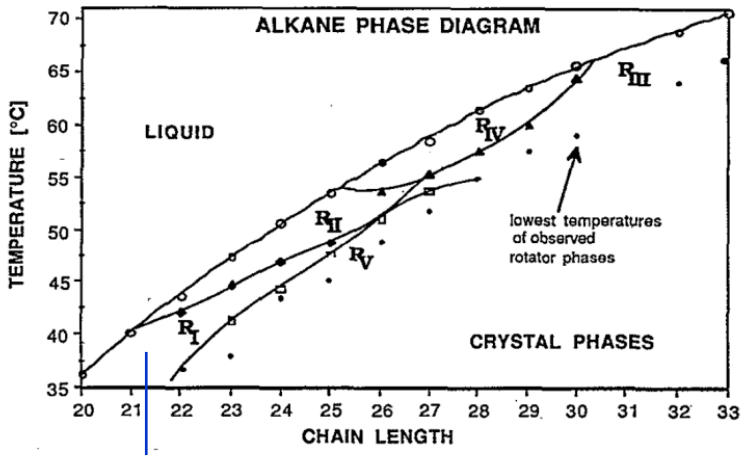
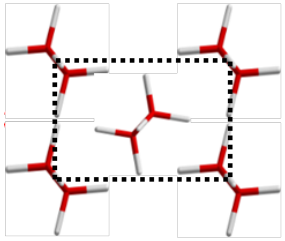


FIG. 1. Phase diagram showing the five rotator phases of the normal alkanes *C*20–30, 32, and 33. The solid dots show the lowest temperatures at which the rotator phase has been observed.

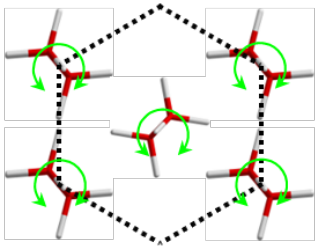
The Journal of Chemical Physics **98**, 5809 (1993)

$C_{21}H_{44}$:

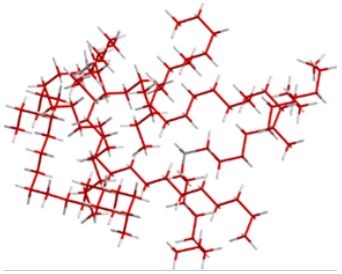
Orthorhombic



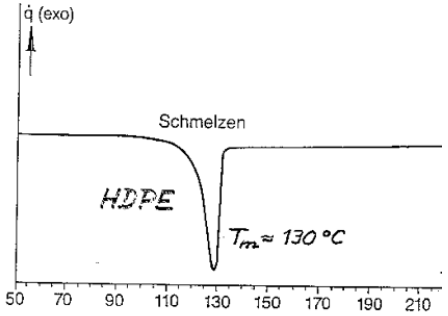
Rotator: hexagonal lattice

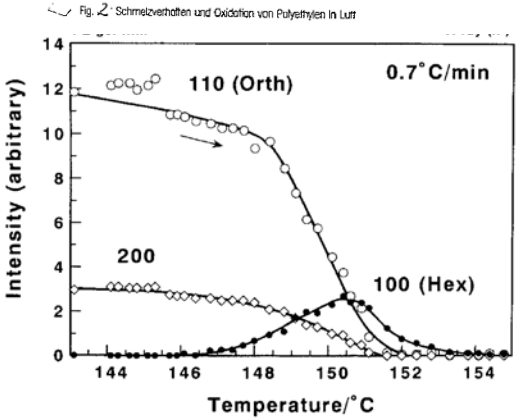


Amorphous



PE:

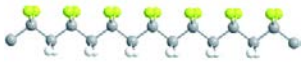




Hexagonal phase plays an important role as an intermediate phase in the crystallization process from the melt to the extended chain crystal

- under high pressure condition
- ultradrawn high-modulus PE

Intermediate phases: rotator phase



- predominantly *trans* chains
- rotate along the chain axis
- packed in lattice with long range order

Phys. Chem. Chem. Phys., 2011, 13, 15031-15036

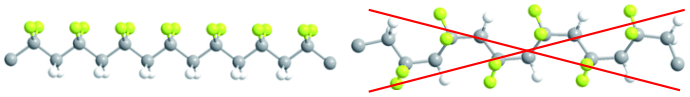
Raman Spectroscopy

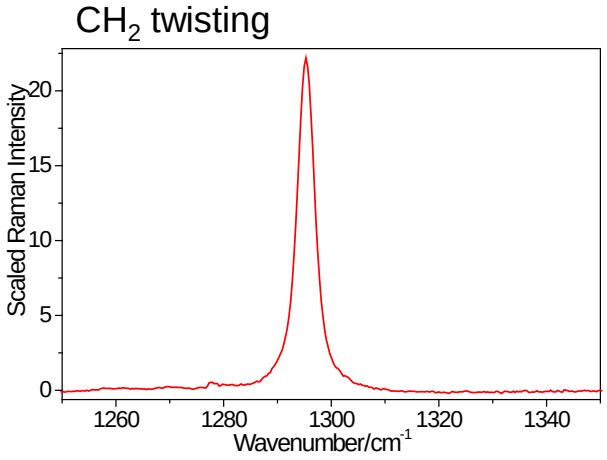
Measure vibration frequencies affected by chain **conformations** (*trans* vs *gauche*) and short-range interchain **interactions**.

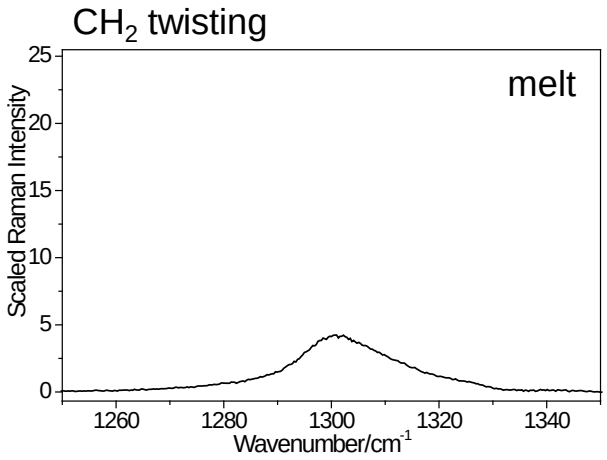
consecutive *trans* **conformation**: orthorhombic and rotator

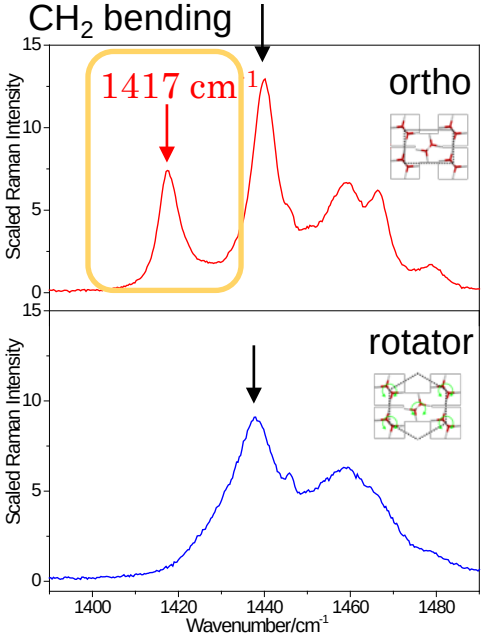
amorphous phase

two types/bands of interchain **interactions** in the orthorhombic unit









Consecutive trans = orthorhombic + mesomorphic
= crystalline + non-crystalline consecutive trans

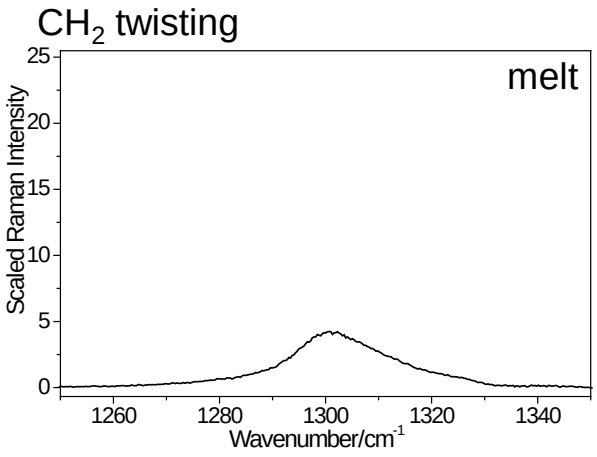
Splitting Peaks

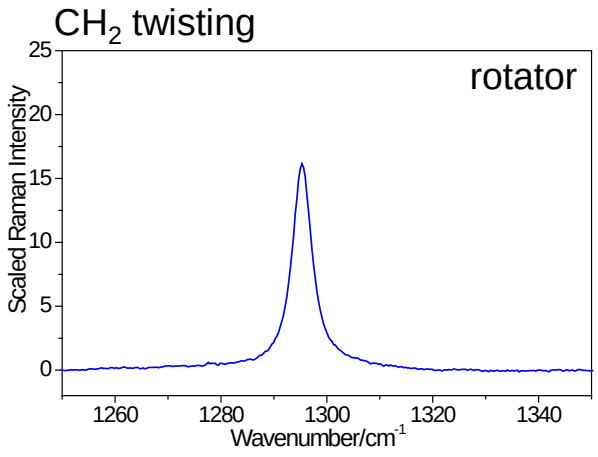
The crystal-field splitting for other bands:
Peak splitting in the orthorhombic phase is smaller than the Raman bandwidth at room temp;
Observed only at extreme conditions (at liquid nitrogen temperature or from single crystals).

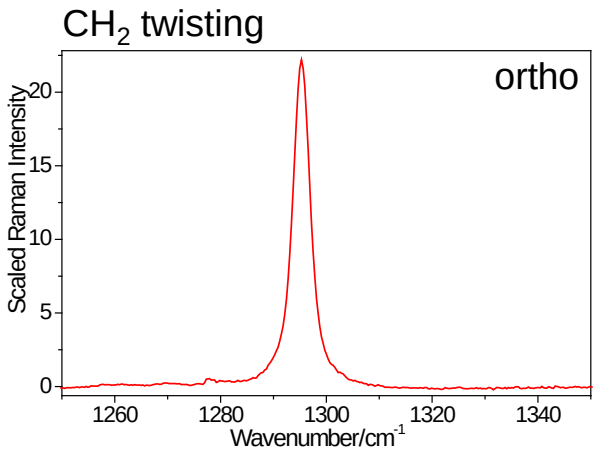
amorphous phase

rotator phase

two types/bands of interchain **interactions** in the orthorhombic unit



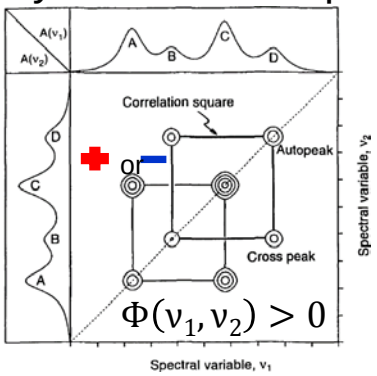




Such subtle spectral changes are challenging for conventional fitting based individual peak analysis to decipher.

2D Correlation Spectroscopy

Synchronous map

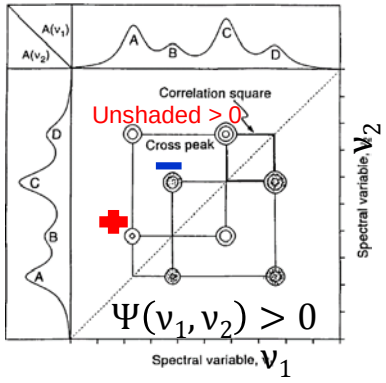


Represent the simultaneous or coincidental changes of spectral intensities measured at ν_1 and ν_2

Advantages:

1. Simplify the overlapped peaks, enhance the resolution
2. to determine the sequence of spectral changes
3. to identify various inter- and intramolecular interactions
4. band assignments of reacting groups

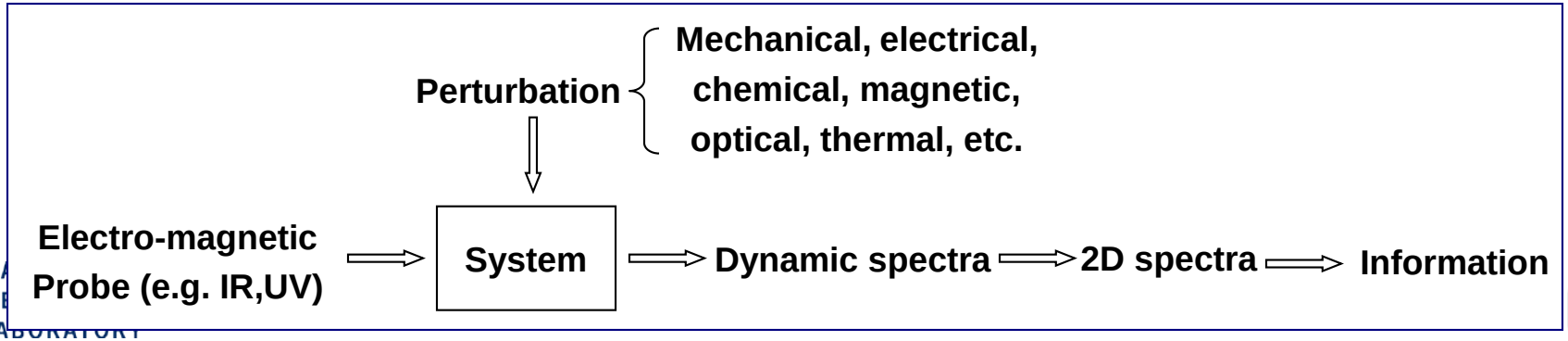
Asynchronous map



Represent the sequential, or unsynchronized changes of spectral intensities measured at ν_1 and ν_2

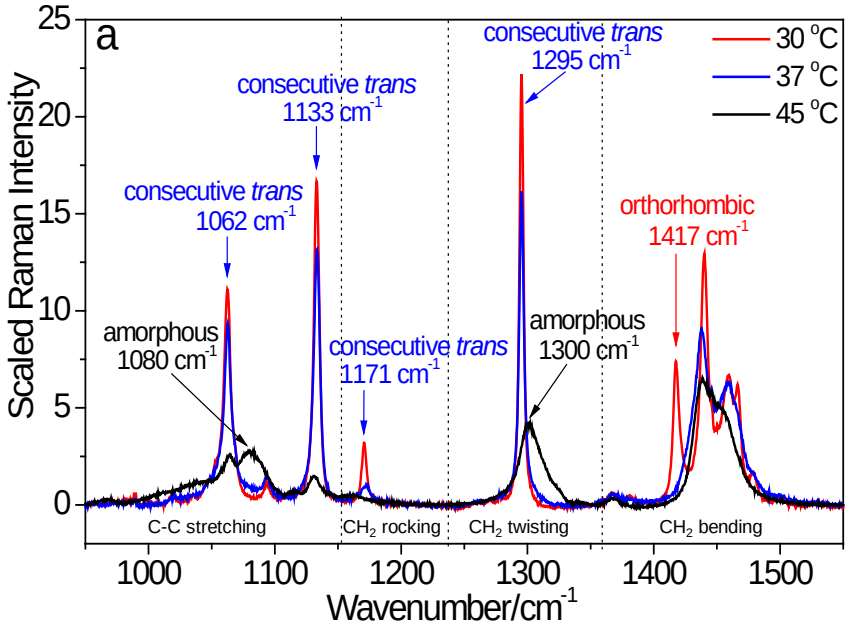
Moving-window 2DCOS:

- a small subset or window of spectra is scanned over the whole perturbation range
- previously demonstrated to determine phase transition temperature and the associated spectral features

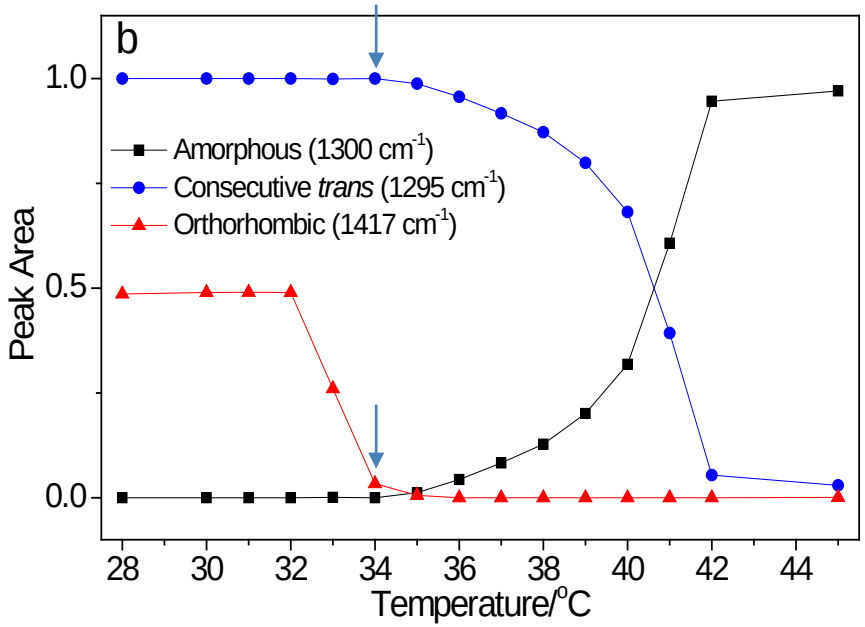


Variable Temperature Raman Spectra of Alkane (*n*-$C_{21}H_{44}$)

Selected Raman spectra acquired from n-$C_{21}H_{44}$ (28 °C to 45 °C)



Single peak analysis



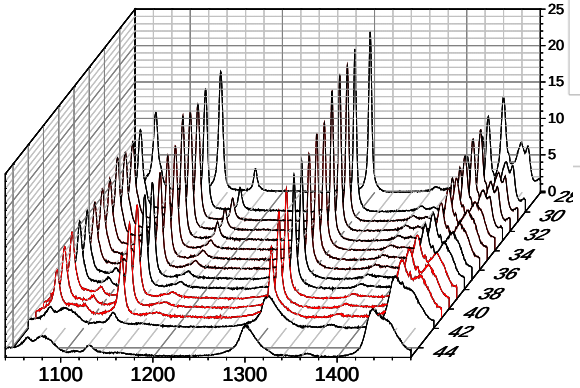
32 °C-34 °C 34 °C-42 °C

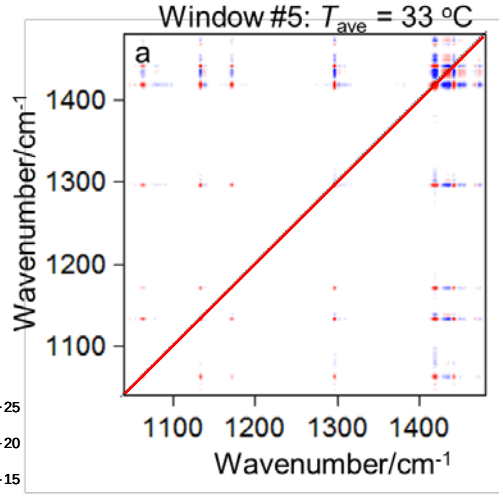
(orthorhombic phase) → (rotator phase) → (amorphous phase)

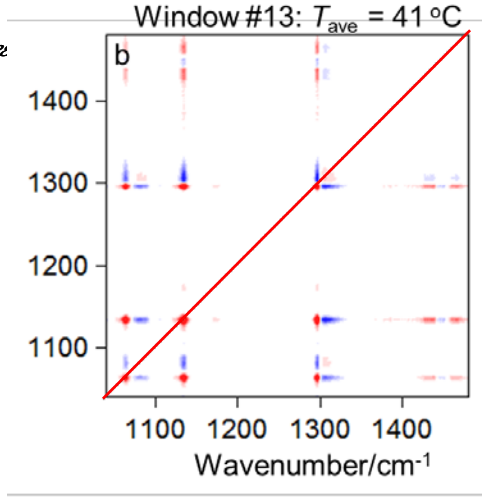
Autocorrelation MW of Alkane Raman

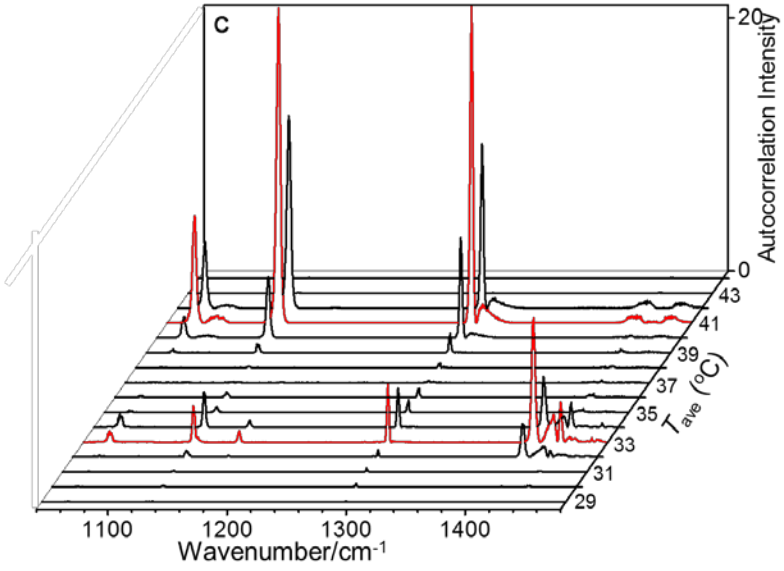
MW-2DCOS

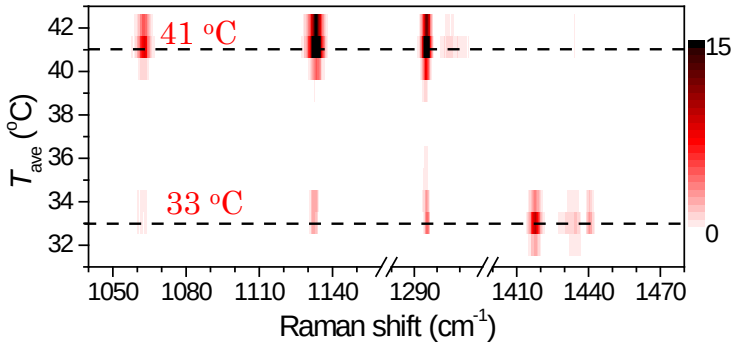
three temperatur e steps (ΔT = 2 °C)





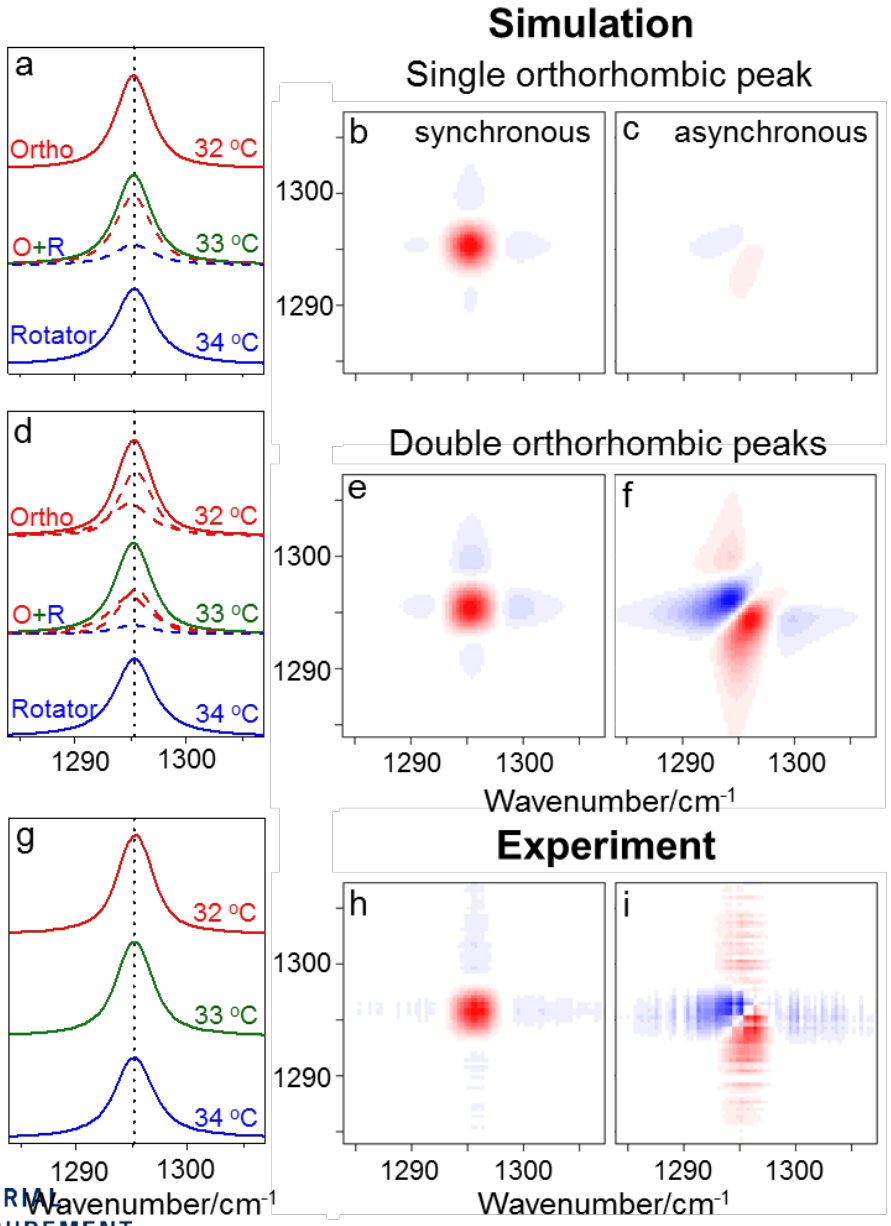


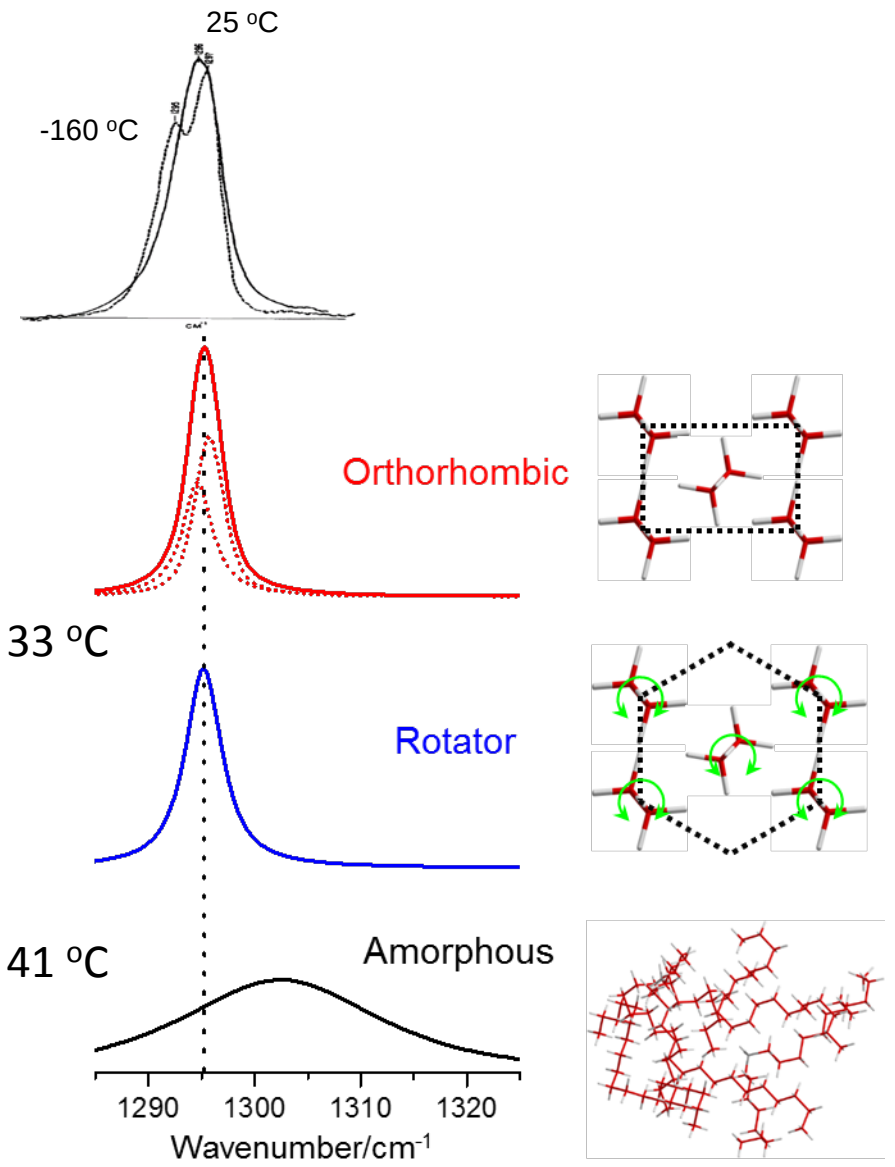




high resolving power

Resolving Splitting Peaks @ RT





MATERIAL MEASUREMENT LABORATORY
NIST

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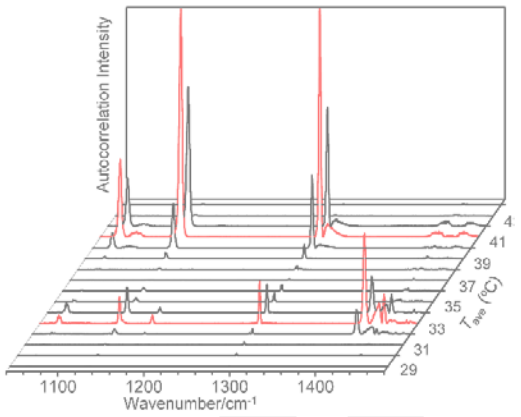
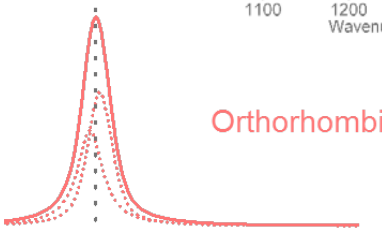
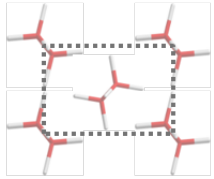
J. Raman Spectrosc. 2016, 47, 1375–1384





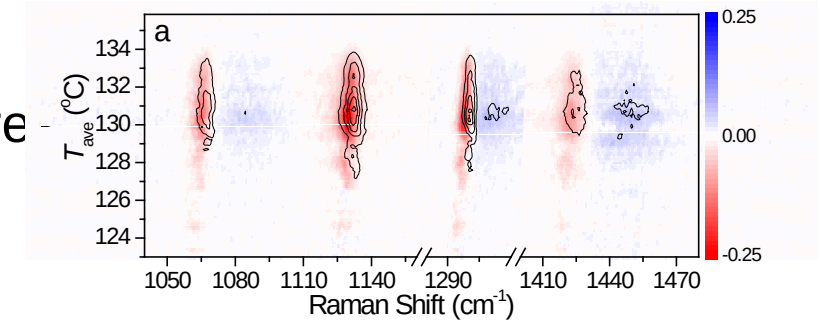
Orthorhombic

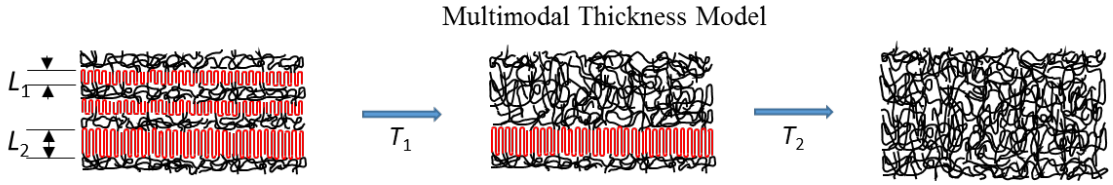


Raman spectra of HDPE melting

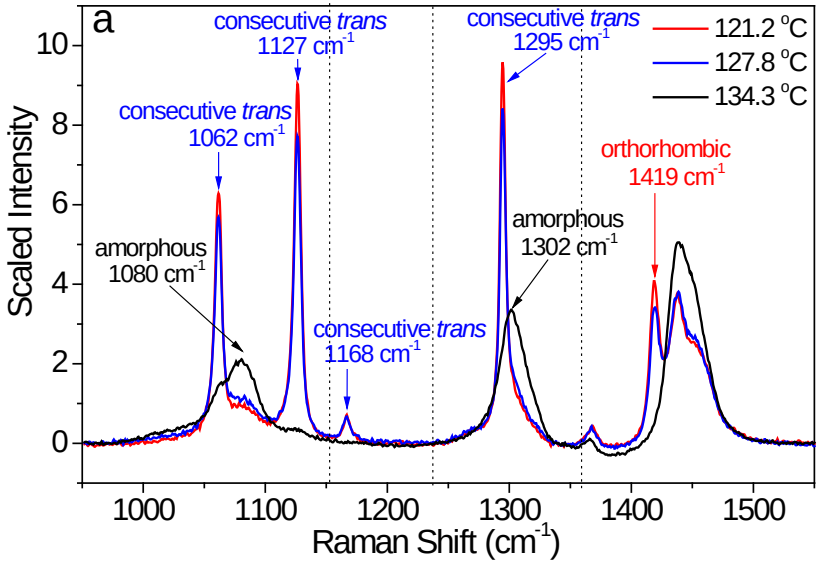
- Determined phase transition temperature
- Discussed melting mechanism;
- Suggested the existence of mesophase.

Submitted

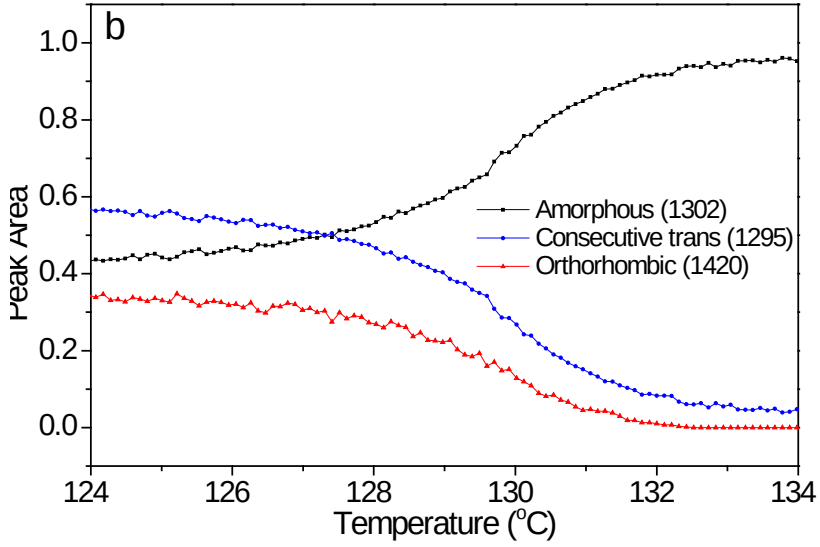




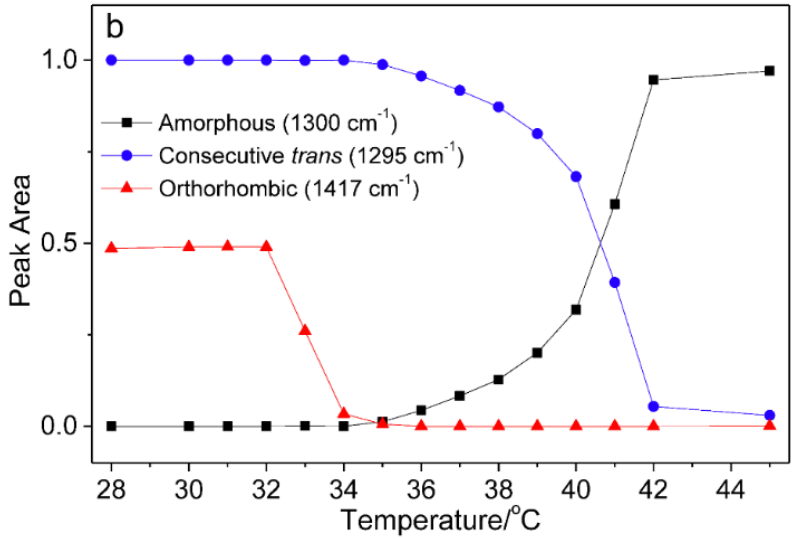
Variable Temperature Raman Spectra of HDPE



HDPE

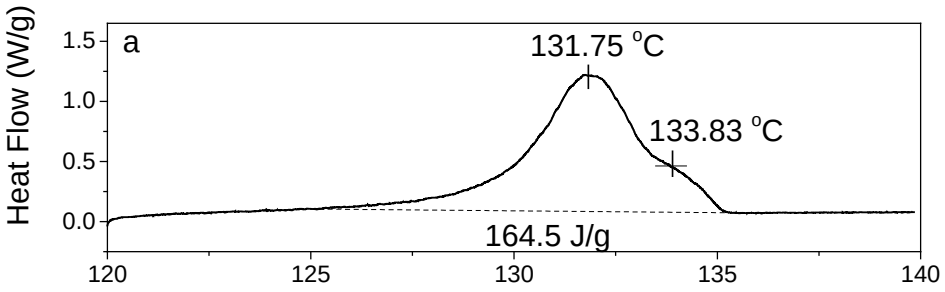


cf. alkane



Mechanisms of Heterogeneous Melting of HDPE

Differential Scanning Calorimetry (DSC)

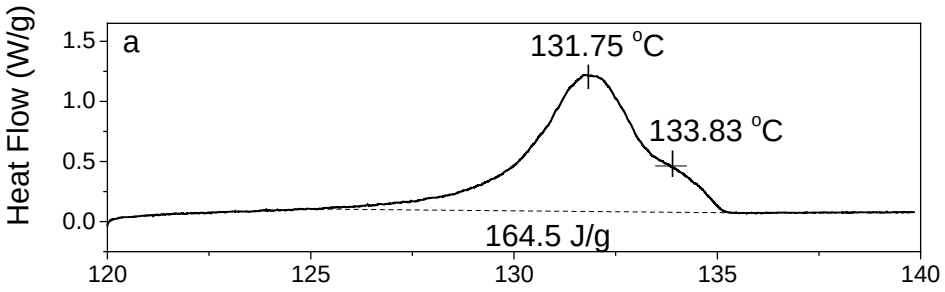


- Two phase transition temperatures.
- Are they qualitatively different?
- What are the possible origins?

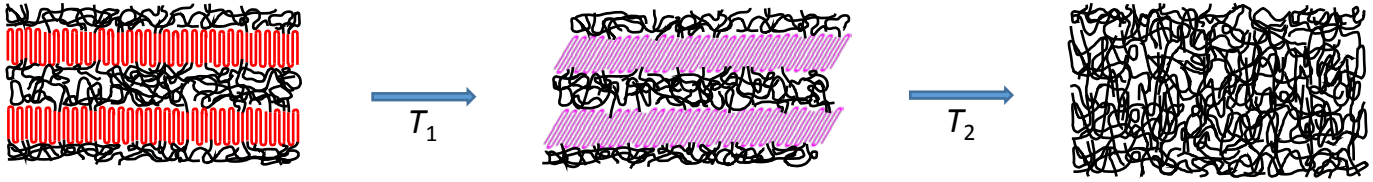
Crystalline phase
Amorphous phase
X_c = 60%

Mechanisms of Heterogeneous Melting of HDPE

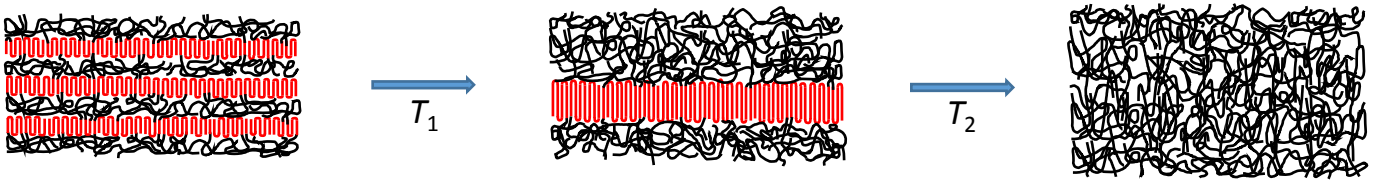
Differential Scanning Calorimetry (DSC)



Mesophase Model

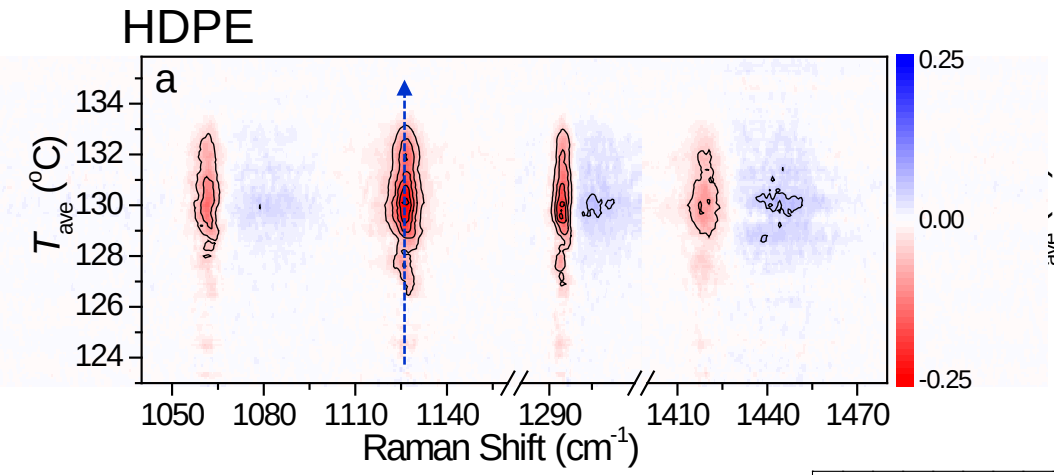


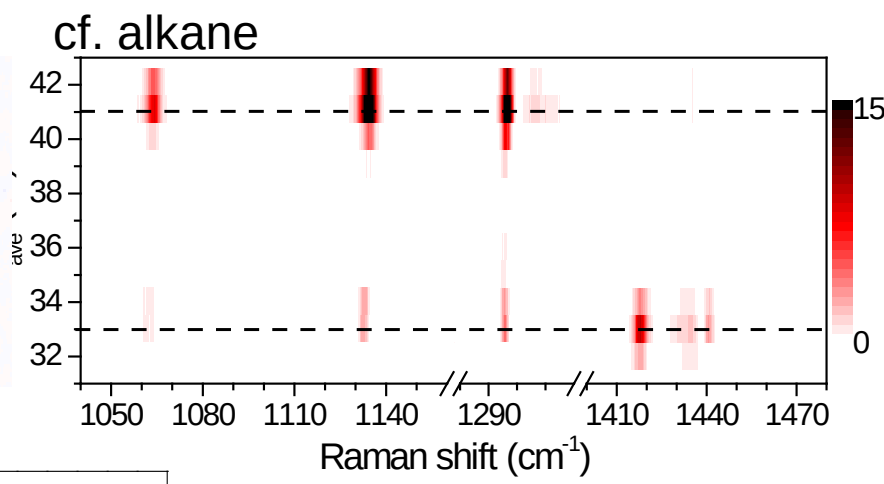
Recrystallization Model

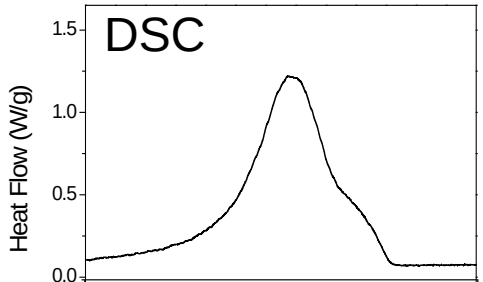


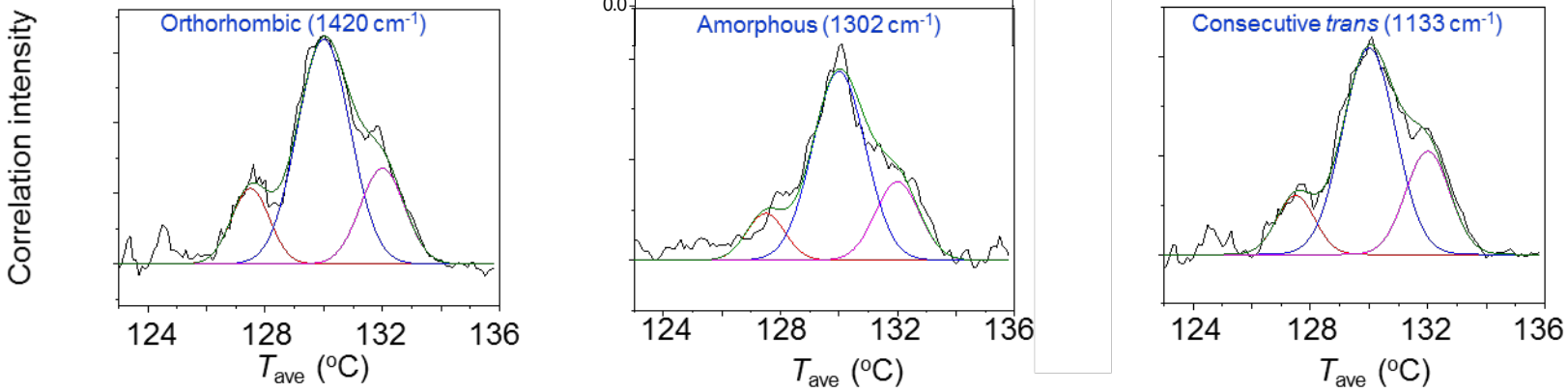
Multimodal Thickness Model

MW-2DCOS of HDPE



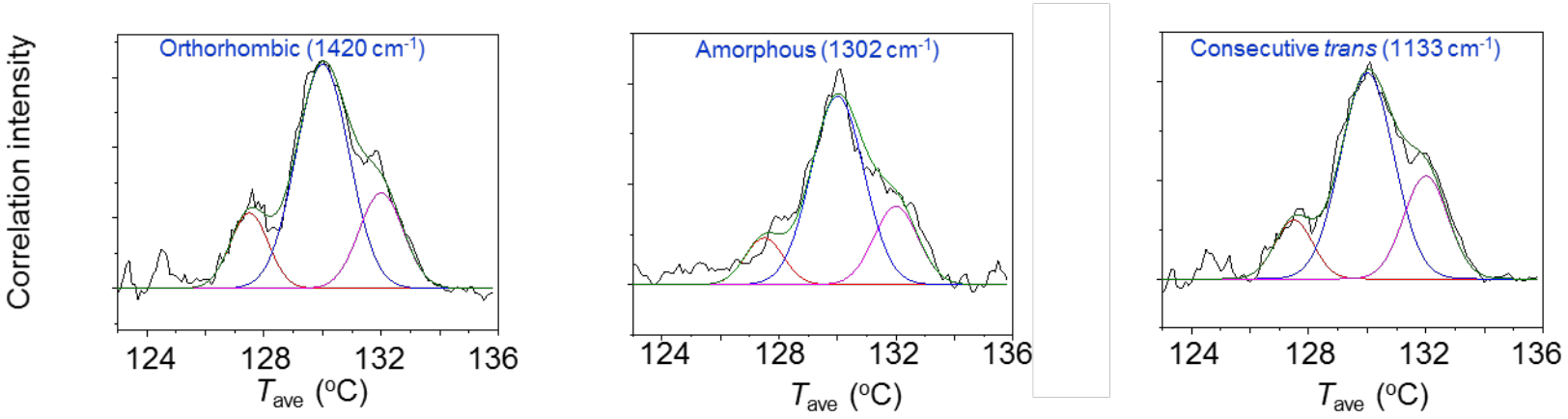






Three overlapping phase transition temperatures are observed

Quantitative Analysis of MW-2DCOS from HDPE Raman

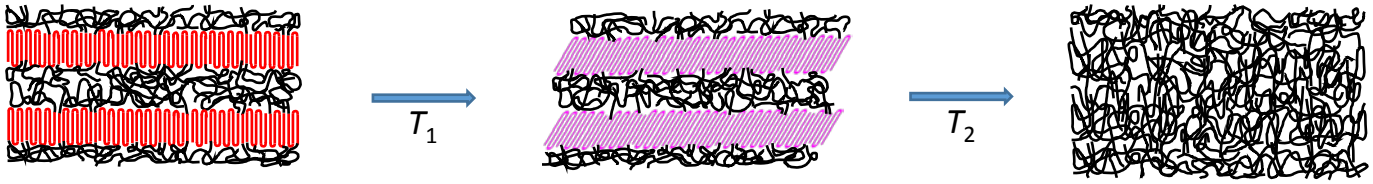


Frequency	Assignment	$A_{127.5}/A_{130.0}$	$A_{132.0}/A_{130.0}$
1133	Consecutive *trans*	0.19	0.42
1420	Orthorhombic	0.23	0.35
1302	Amorphous	0.17	0.35

Area ratios are similar among different, phase-specific Raman peaks

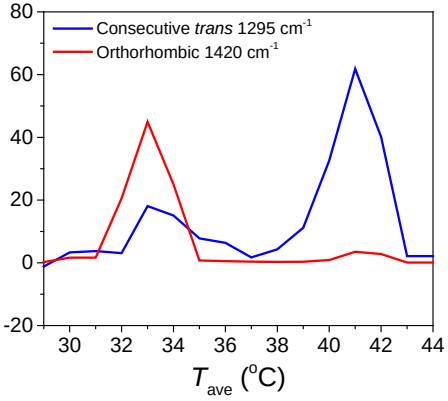
Mechanisms of Heterogeneous Melting of HDPE

Mesophase Model

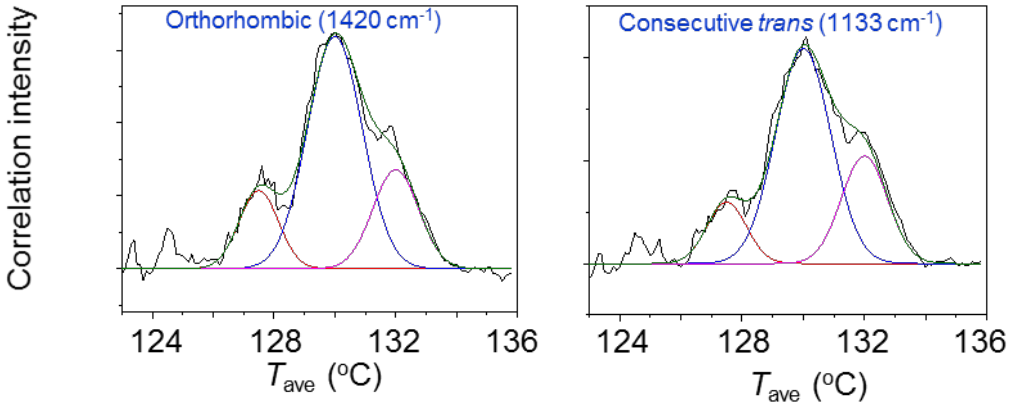


Because the two transitions are qualitatively different, changes in Raman characteristics at the two transitions are expected to be different.

Alkane (C21)

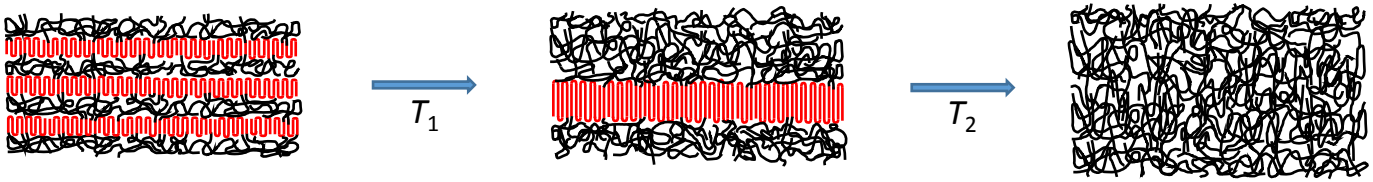


HDPE



Mechanisms of Heterogeneous Melting of HDPE

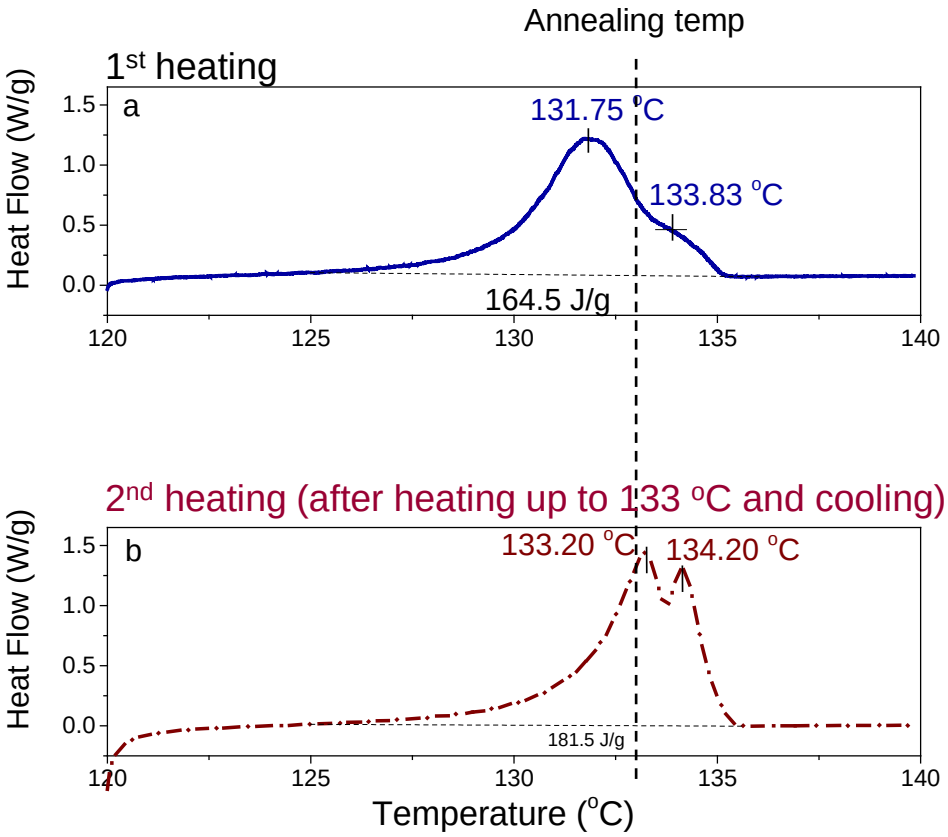
Recrystallization Model ?



Multimodal thickness Model ?

Annealing of HDPE

Differential Scanning Calorimetry (DSC) of HDPE

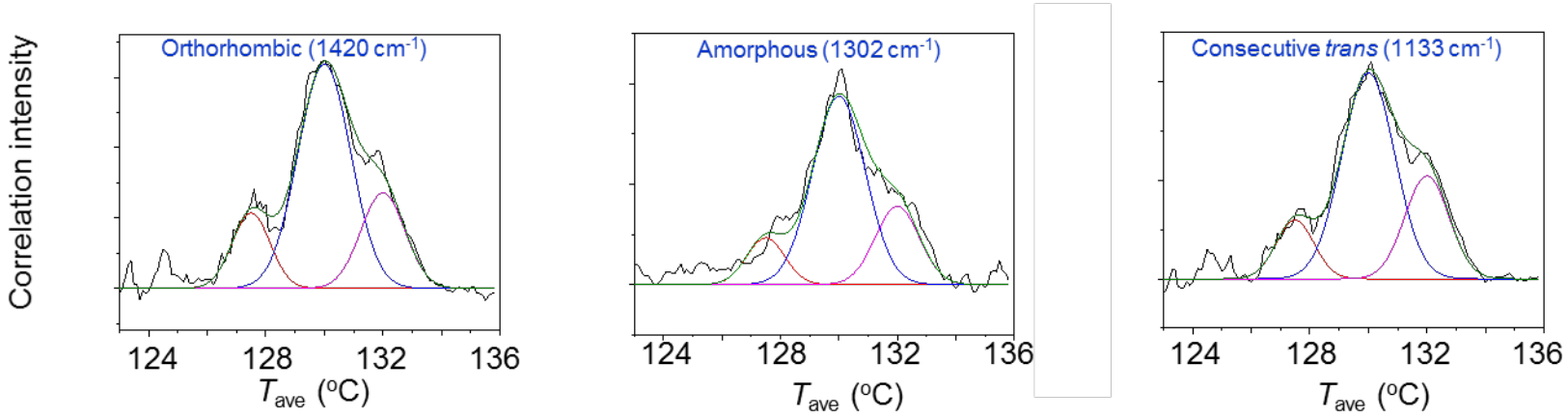


Two shifted transition temperatures

Dominant HDPE Melting Mechanisms

Multimodal thickness Model

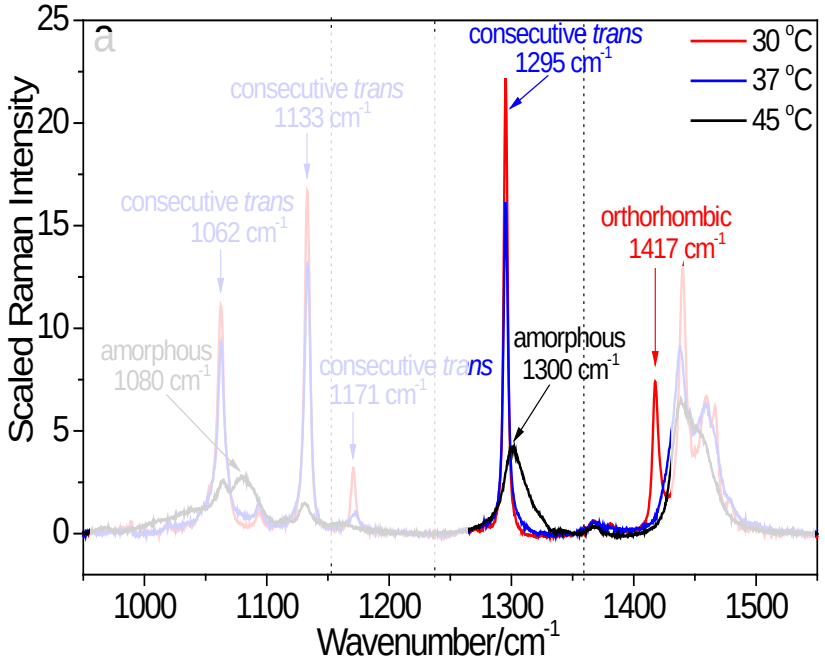
Initial distribution of lamellar thickness determines the transition temperature.
The density of each sub-population determines the amplitude of the spectral change. However, all transitions are qualitatively the same, and relative Raman intensity changes among different Raman modes will be the same at all transitions.



Mesophase (non-crystalline consecutive *trans*)

NCCT (non-crystalline consecutive trans) + Crystalline = Consecutive *trans*

NCCT (non-crystalline consecutive trans) = Consecutive *trans* - Crystalline



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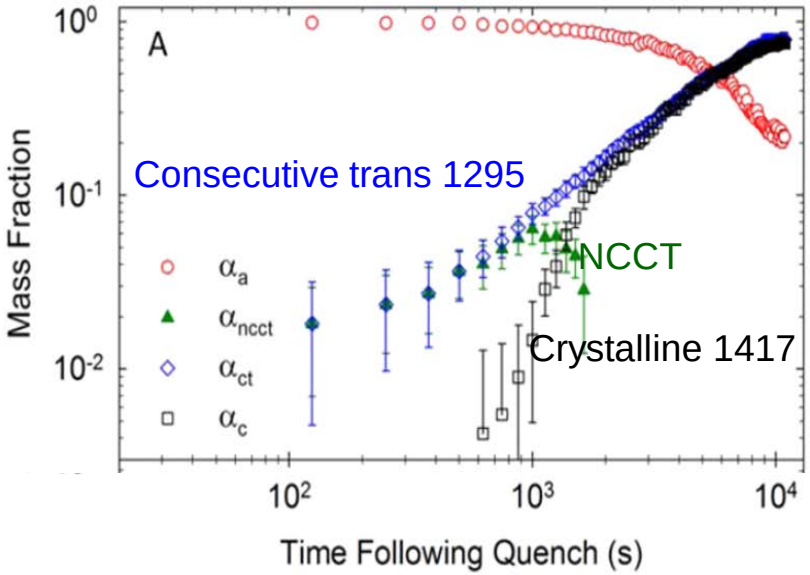
***Trans*-Rich Structures in Early Stage Crystallization of Polyethylene**

Kalman B. Migler,*,† Anthony P. Kotula,† and Angela R. Hight Walker‡

†Materials Science & Engineering Division and ‡Physical Measurements Laboratory, NIST, Gaithersburg, Maryland 20899, United States

Single peak analysis



Similar Melting & Crstallization

HDPE melting

Macromolecules
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Trans-Rich Structures in Early Stage Crystallization of Polyethylene

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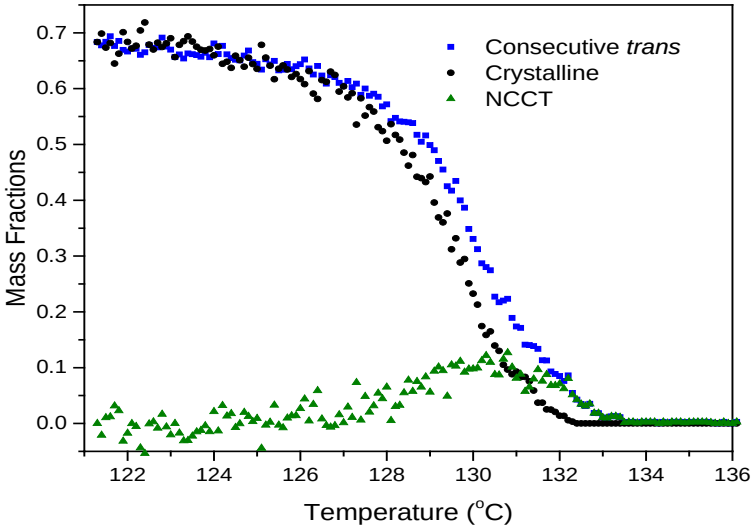
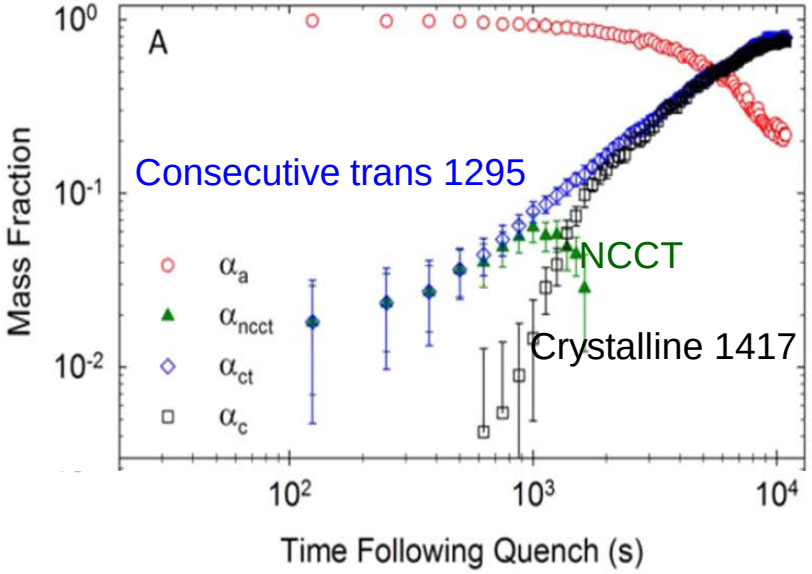


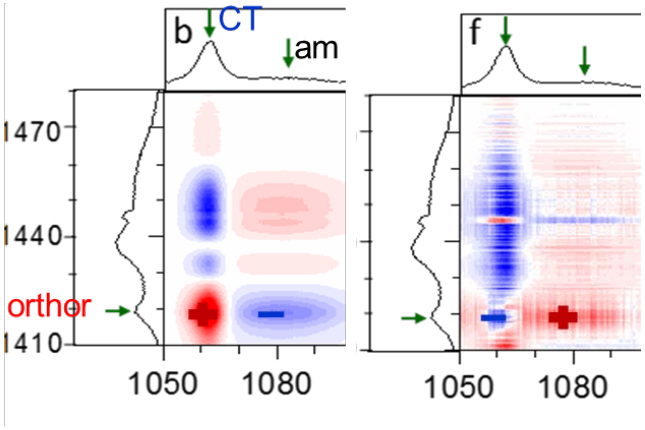
Single peak analysis

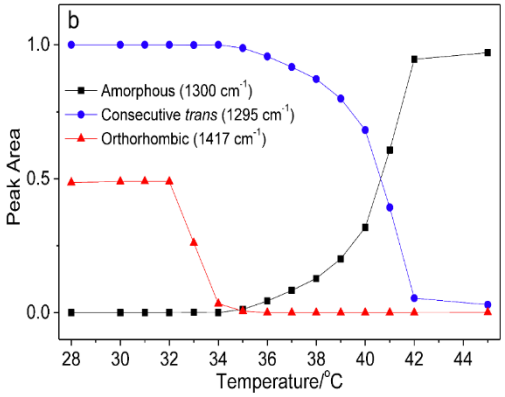


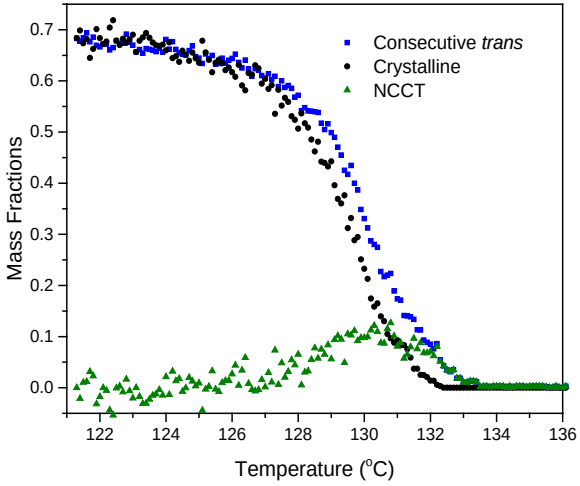
<10% non-crystalline consecutive *trans*

Minor HDPE Melting Mechanism

2DCOS-sequecial changes

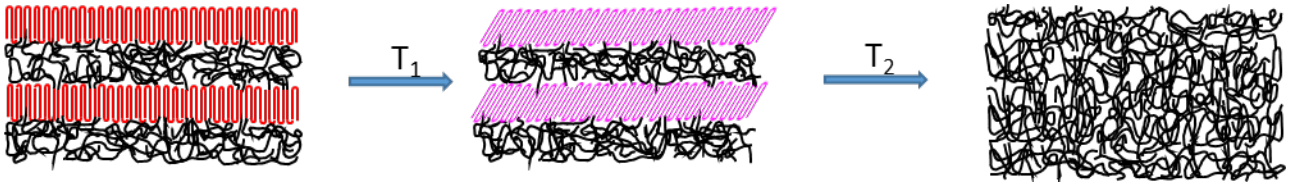






Possible existence of mesophase

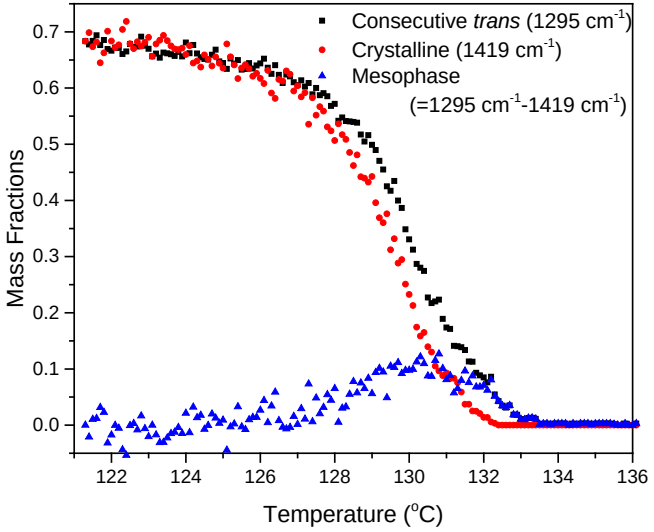
Mesophase Model



Summary

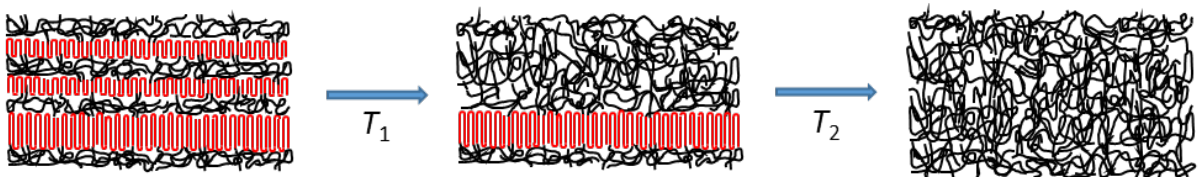
Raman spectra of HDPE melting

- Determined phase transition temperatures;
- Discussed dominant melting mechanism;
- Suggested the existence of mesophase.



Consecutive trans
= orthorhombic + mesophase

Heterogeneous Melting of Polyethylene



Acknowledgement

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Raman Measurement

Anthony Kotula

Kalman Migler

Angela Hight Walker

DSC Measurement

Chad Snyder

Thank you for your attention!

Questions?

2D Correlation Theory

The dynamic spectrum is defined as

$$\tilde{y}(v,t) = \begin{cases} y(v,t) - \bar{y}(v) & \text{for} \quad T_{min} \leqslant t \leqslant T_{max} \\ 0 & otherwise \end{cases}$$

Reference spectrum

$$\bar{y}(v) = \frac{1}{T_{max} - T_{min}} \int_{T_{min}}^{T_{max}} y(v,t)\,dt$$

Generalized 2D correlation function is defined as

$$X(v_1, v_2) = \frac{1}{(\pi T_{max} - T_{min})} \times \int_0^{\infty} \tilde{Y}_1(\omega) \cdot \tilde{Y}_1^*(\omega)\,d\omega$$

$$\tilde{Y}_1(\omega) = \int_{-\infty}^{\infty} \tilde{y}(\nu_1, t) e^{-i\omega t}\,dt$$

$$\tilde{Y}_2^*(\omega) = \int_{-\infty}^{\infty} \tilde{y}(\nu_2, t) e^{+i\omega t}\,dt$$

$$X(v_1, v_2) = \Phi(v_1, v_2) + i\Psi(v_1, v_2)$$

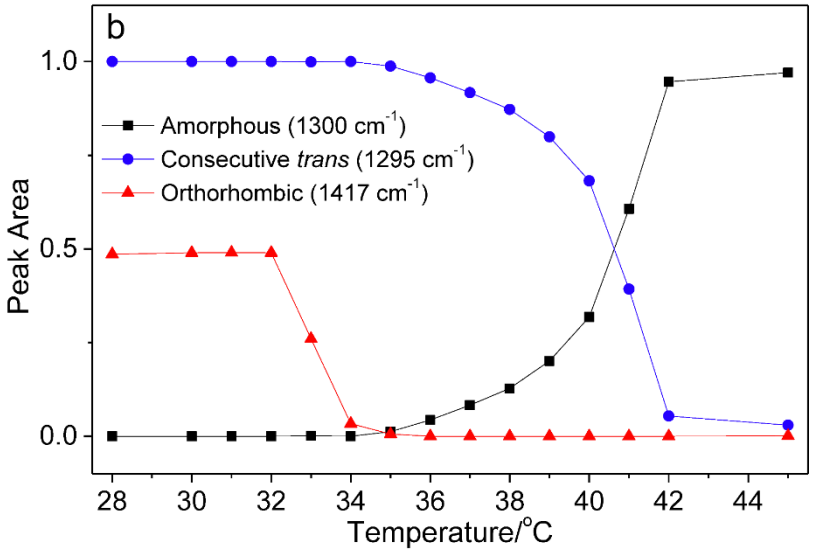
Real $$\Phi(\nu_1, \nu_2) = \frac{1}{m-1} \sum_{j=1}^{m} \tilde{y}_j(\nu_1) \cdot \tilde{y}_j(\nu_2)$$

Imaginary $$\Psi(\nu_1, \nu_2) = \frac{1}{m-1} \sum_{j=1}^{m} \tilde{y}_j(\nu_1) \sum_{k=1}^{m} N_{jk} \cdot \tilde{y}_k(\nu_2)$$

The elements of the Hilbert-Noda transformation matrix is defined as

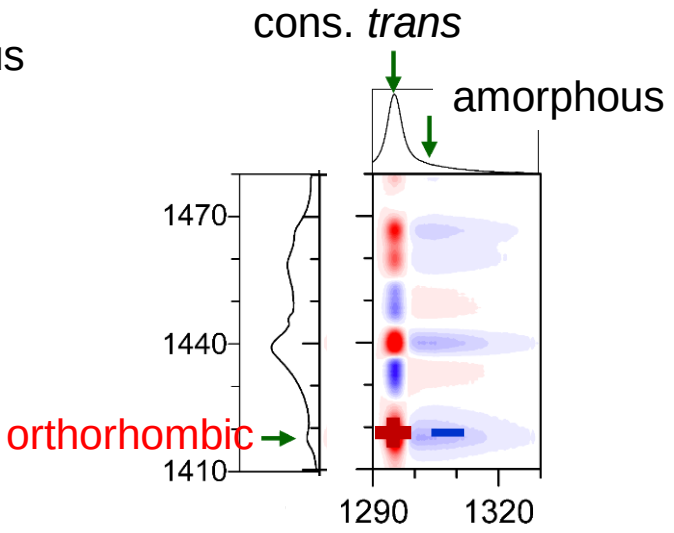
$$N_{jk} = \begin{cases} 0, & \text{if } j = k \\ \frac{1}{\pi(k-j)}, & \text{otherwise} \end{cases}$$

2DCOS of Alkane Raman

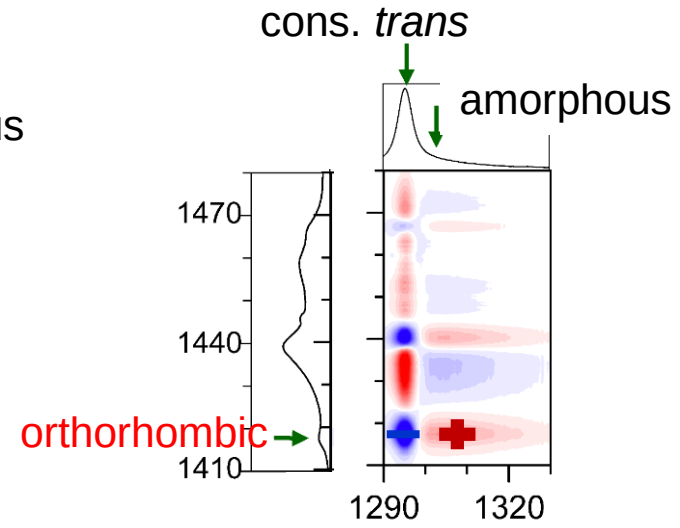


Ortho is prior to CT, am

Synchronous



Asynchronous

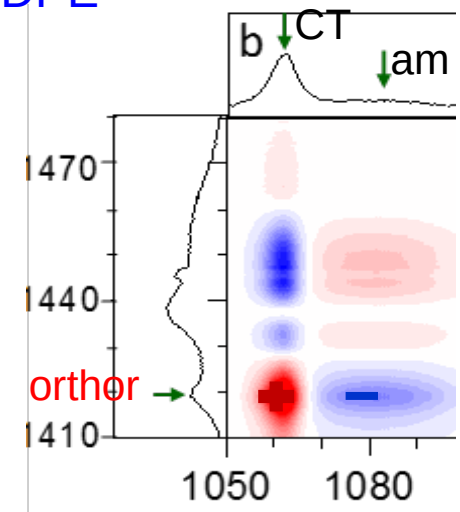


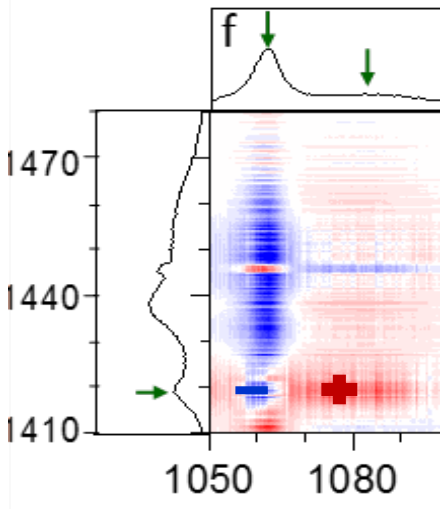
32 °C-34 °C 39 °C-42 °C

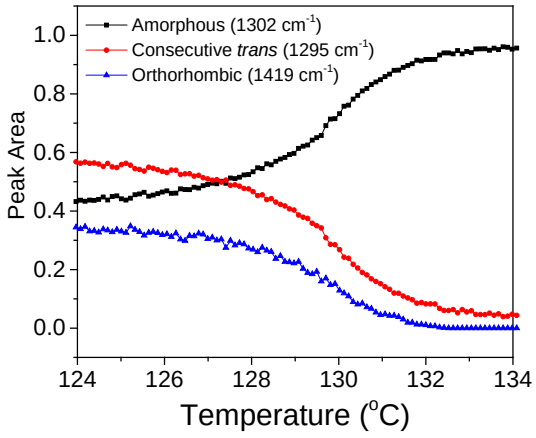
(orthorhombic phase) → (rotator phase) → (amorphous phase)

2DCOS of Raman Spectra of HDPE

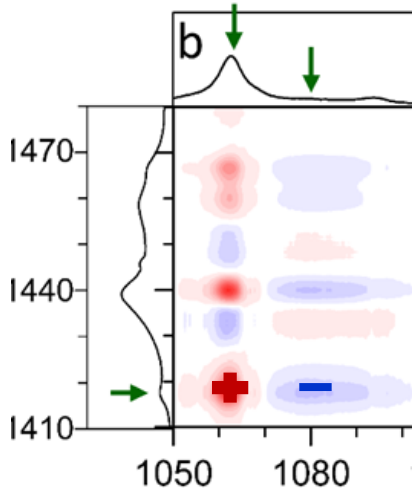
HDPE

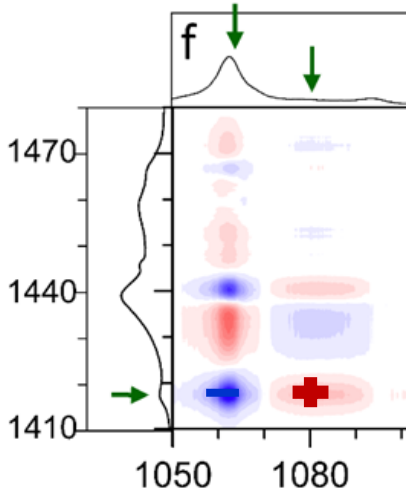


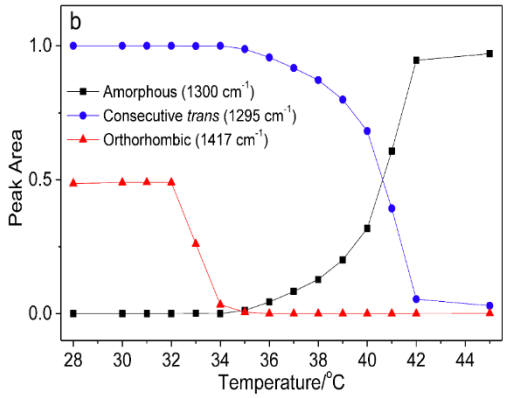




Alkane







Possible existence of mesophase