Rheo-Raman measurements for improved structure-property relationships in crystallizing polymers

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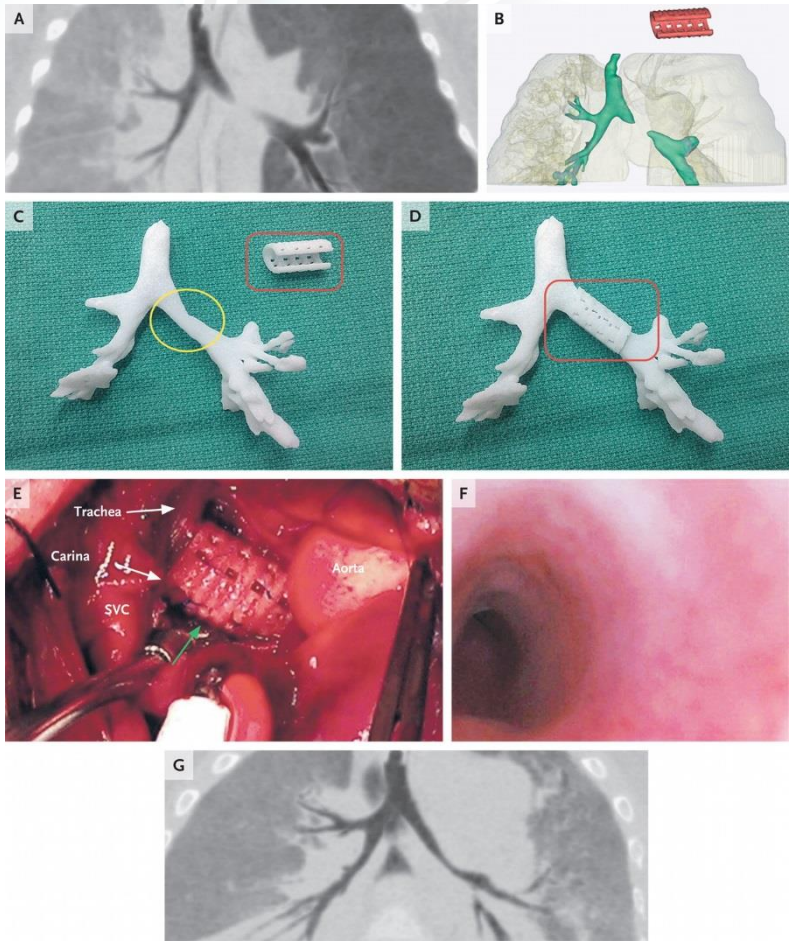
U.S. Department of Commerce

MATERIAL MEASUREMENT LABORATORY

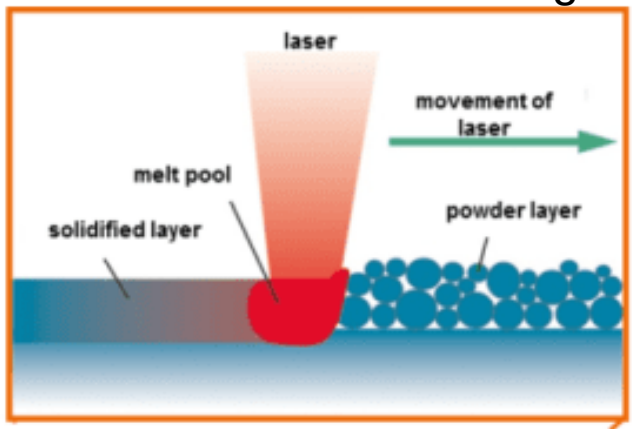
SEMICRYSTALLINE POLYMERS IN ADDITIVE MANUFACTURING

Customized Parts, Rapid Prototyping



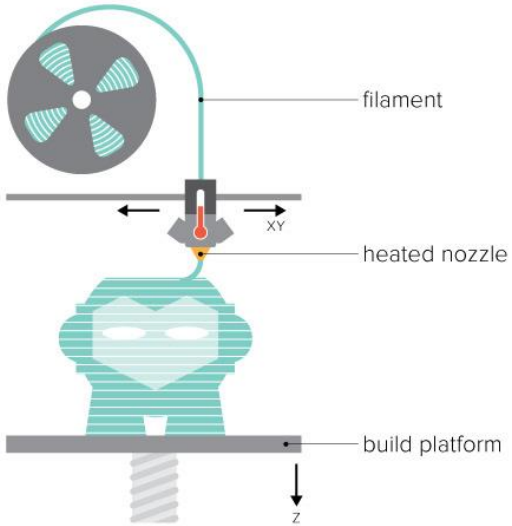
Zopf and Hollister, *N. Engl. J. Med.* (2013)

Selective Laser Sintering



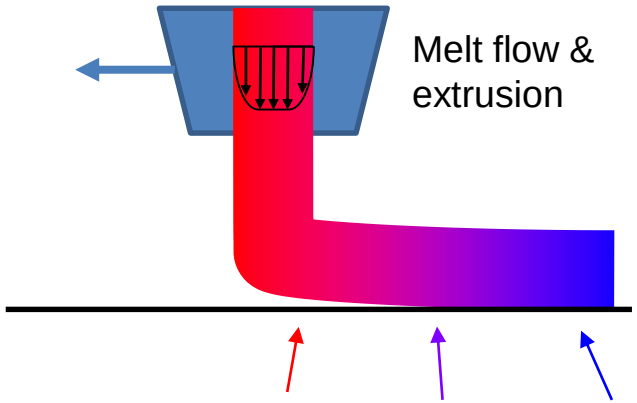
bintoa.com

Materials Extrusion



A COMMON PROCESSING PROBLEM: FLOW AND CRYSTALLIZATION

Control: temperature and feed rate

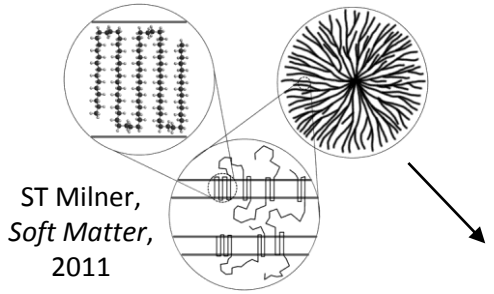


Modulus and crystallinity?

Melt

Cooling &
crystallization

Semicrystalline



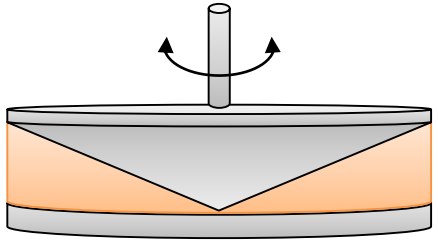
ST Milner,
Soft Matter,
2011

1 frame per 60 s.

MATERIALS CHARACTERIZATION CHALLENGE

How do we relate flow properties to crystallinity during crystallization?

Rheology

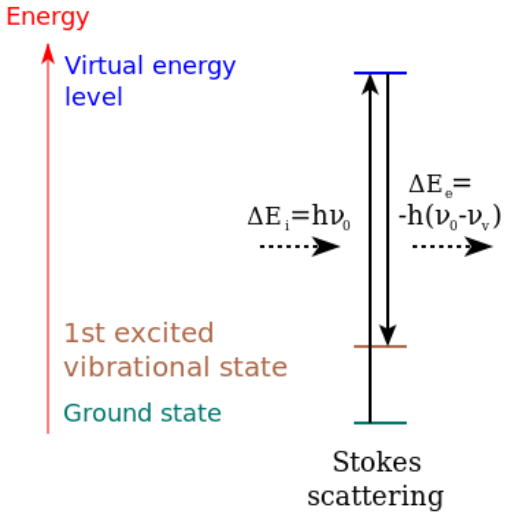


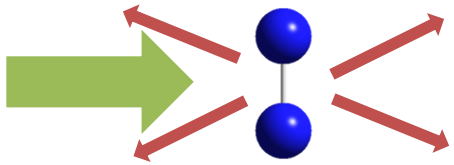
$$\frac{\text{Stress}}{\text{Strain}} = \text{Viscoelastic modulus}$$

$$\frac{\sigma_{12}(\omega)}{\gamma(\omega)} = G^*(\omega) = G'(\omega) + iG''(\omega)$$

Viscosity, relaxation timescales…

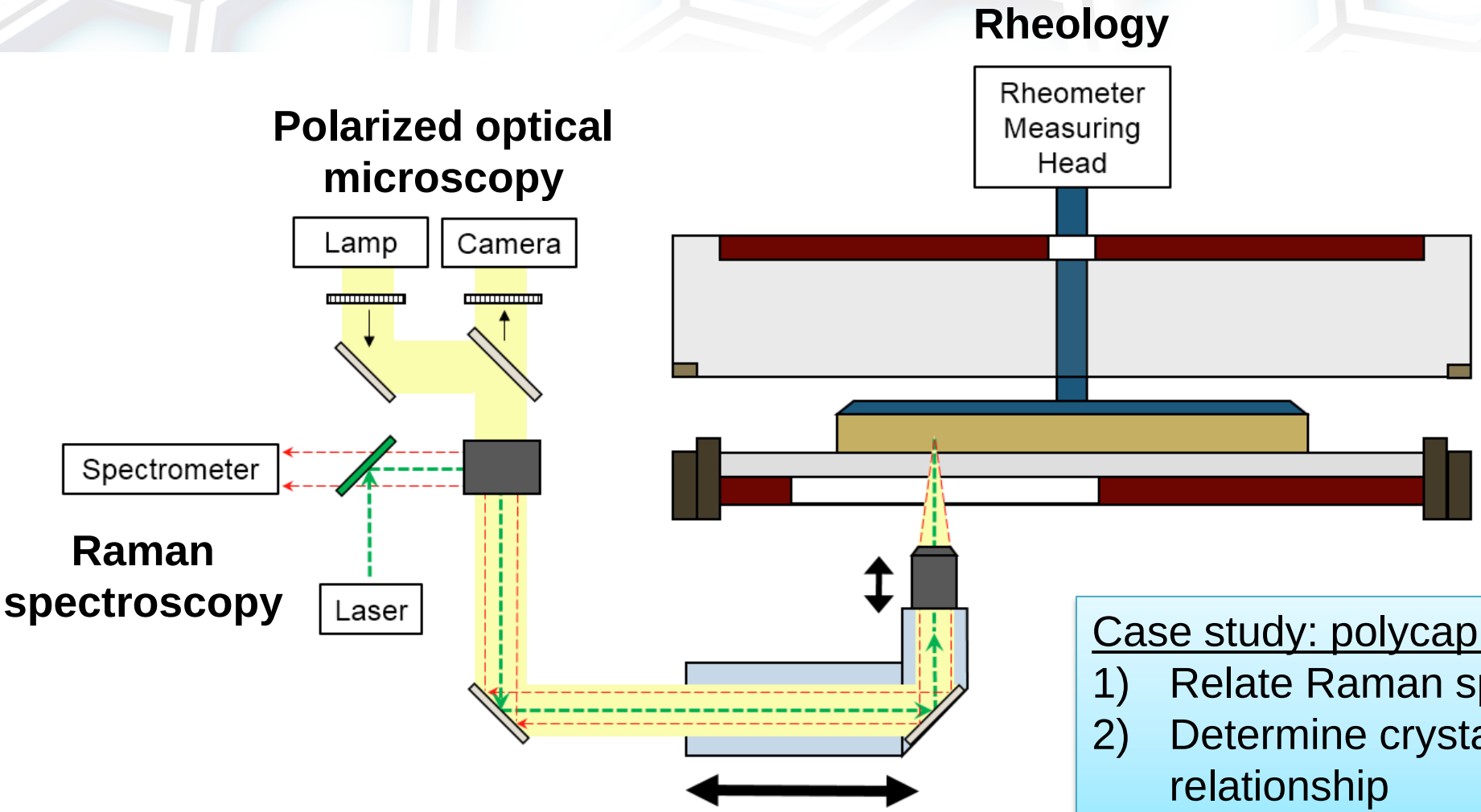
Raman spectroscopy





Covalent bonds, chain conformation…

RHEO-RAMAN MICROSCOPY



Case study: polycaprolactone

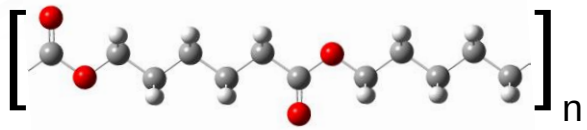
1) Relate Raman spectrum to crystallinity
2) Determine crystallinity-rheology relationship

Kotula, Meyer, De Vito, Plog, Hight Walker, Migler. *Rev. Sci. Inst.* (2016)

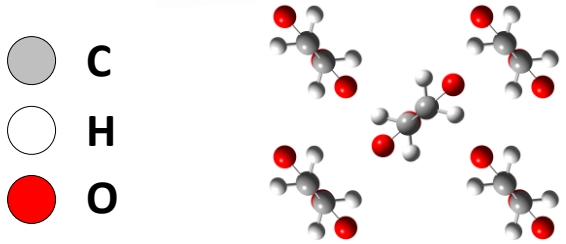
REGULAR SINGLE CHAIN VS. CRYSTALLINE EFFECTS IN PCL

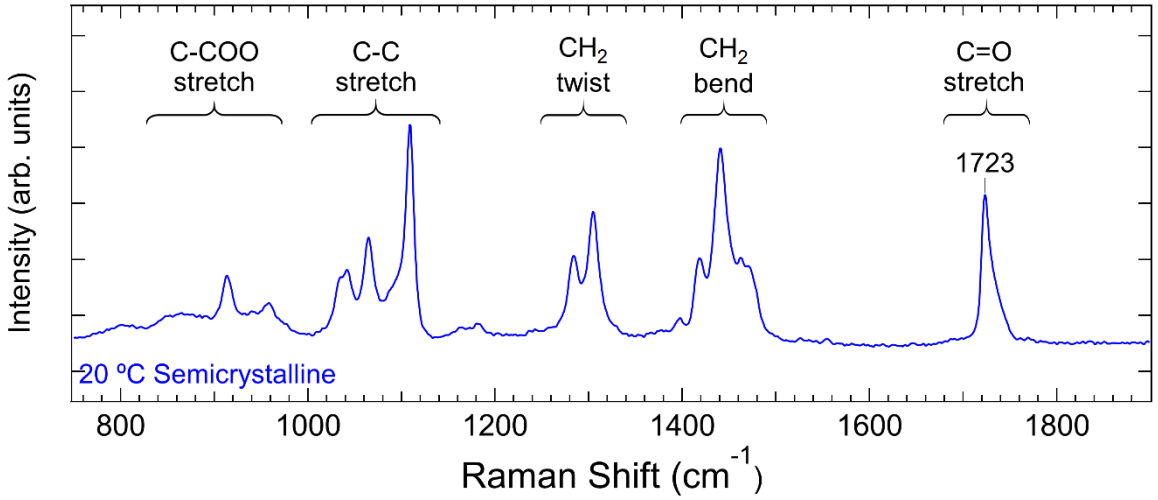
Semicrystalline spectrum – both single chain and *inter*chain effects

Single chain

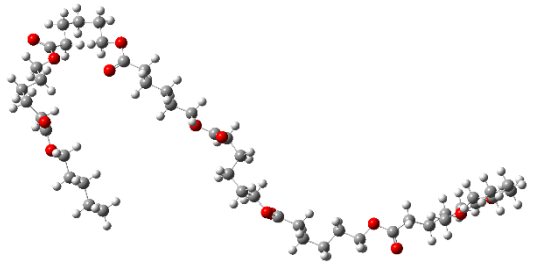


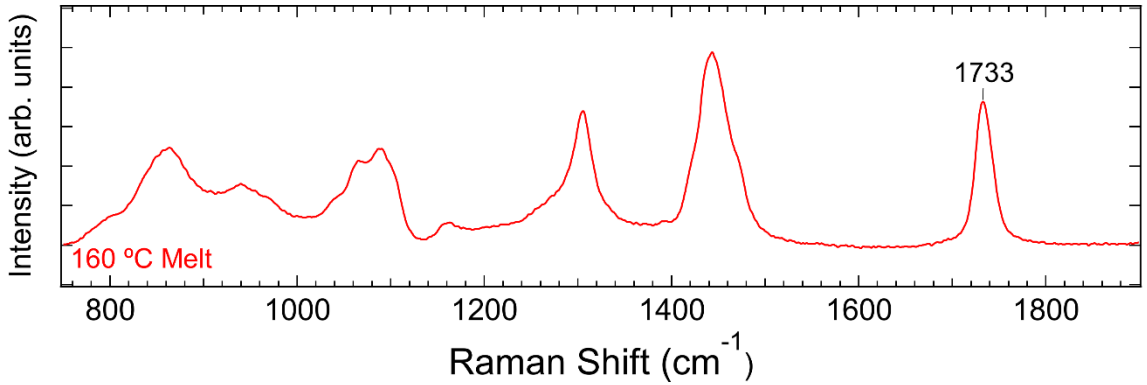
Crystal





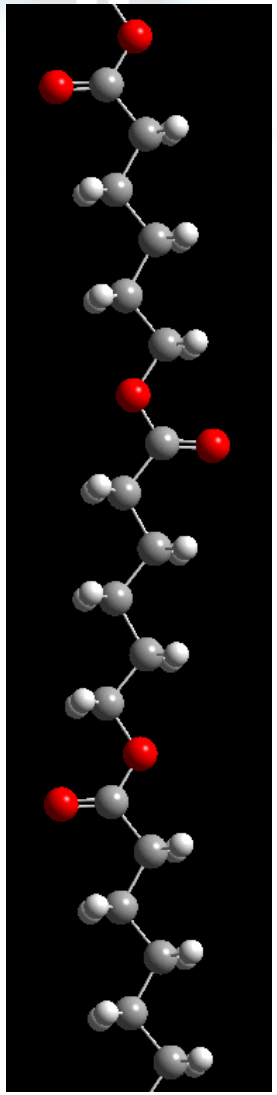
Melt spectrum – many chain conformations, broad features

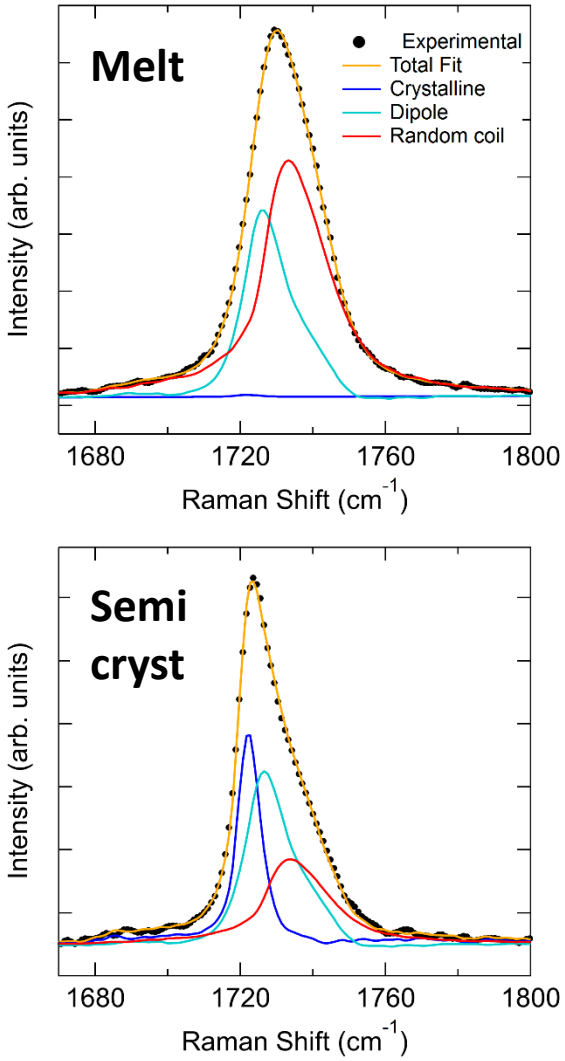




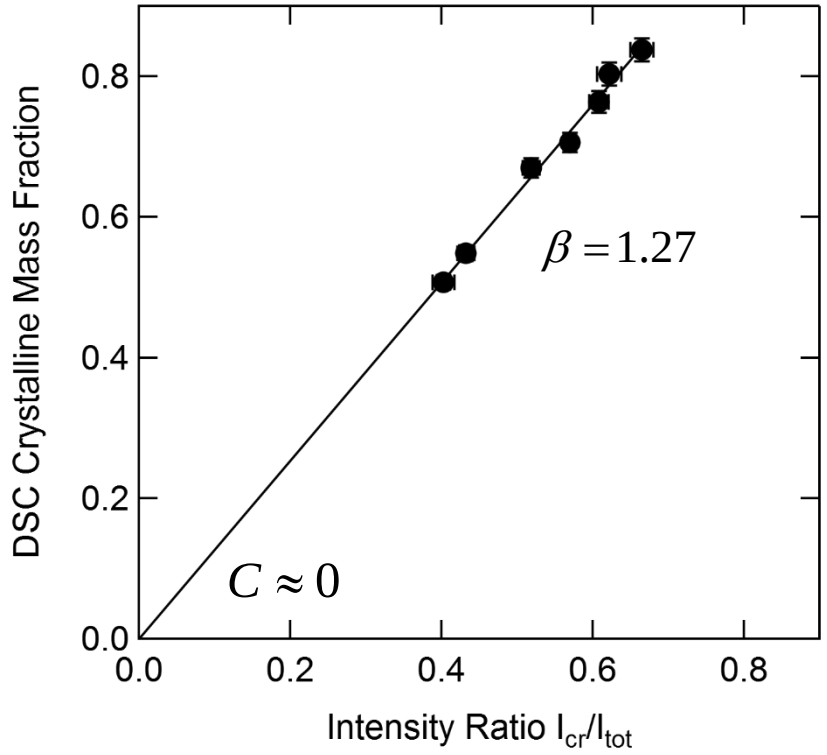
Need a simple method to find crystalline bands

CHEMOMETRICS TO QUANTIFY CRYSTALLINITY IN C=O STRETCH REGION





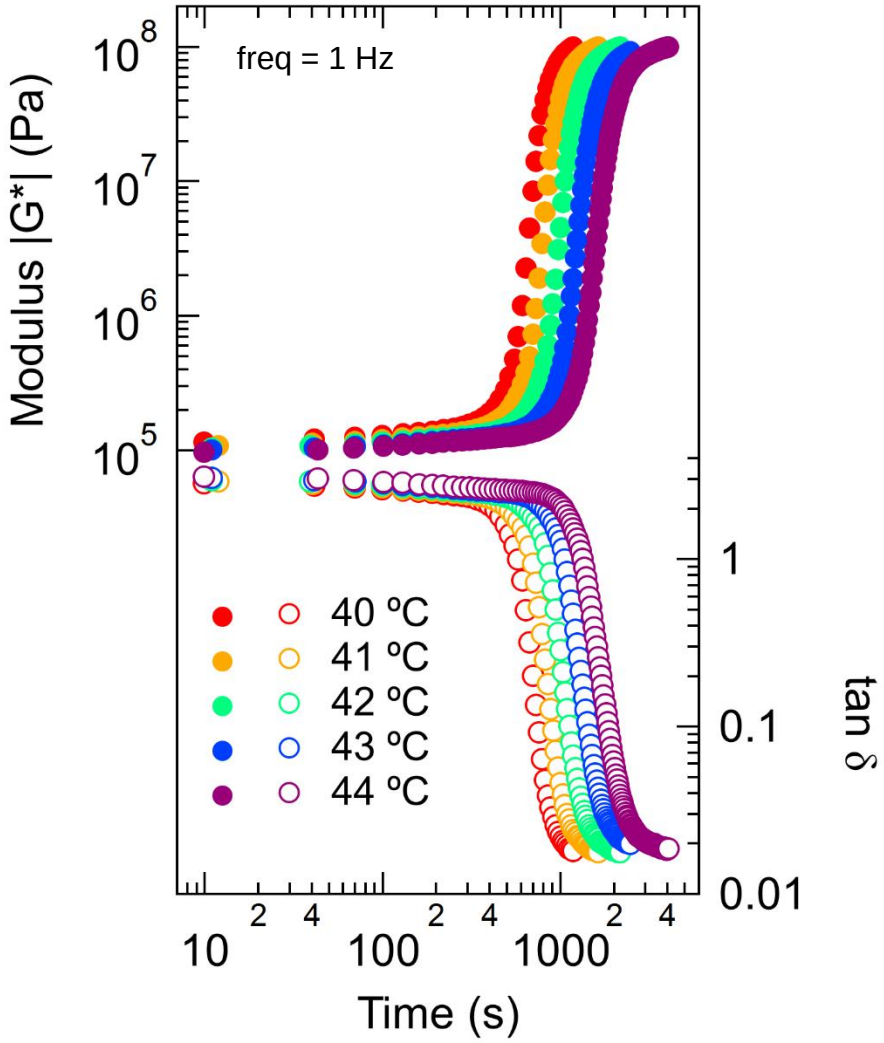
$$\alpha_c = \beta \frac{I_{cr}}{I_{tot}} + C$$



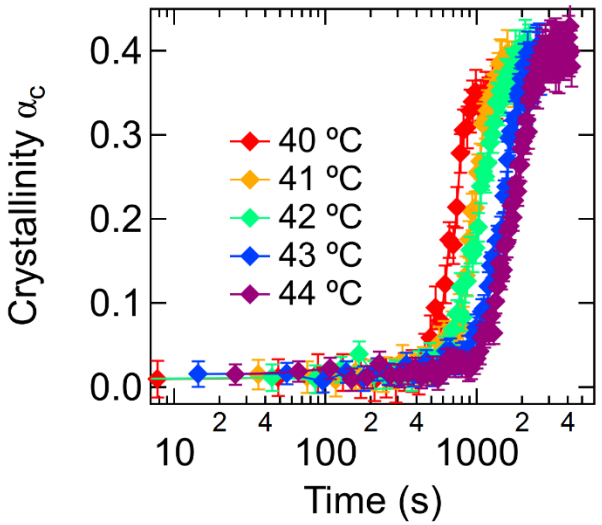
Kotula, Snyder, Migler, *Polymer* (2017)

PCL ISOTHERMAL CRYSTALLIZATION MEASUREMENTS

Rheology



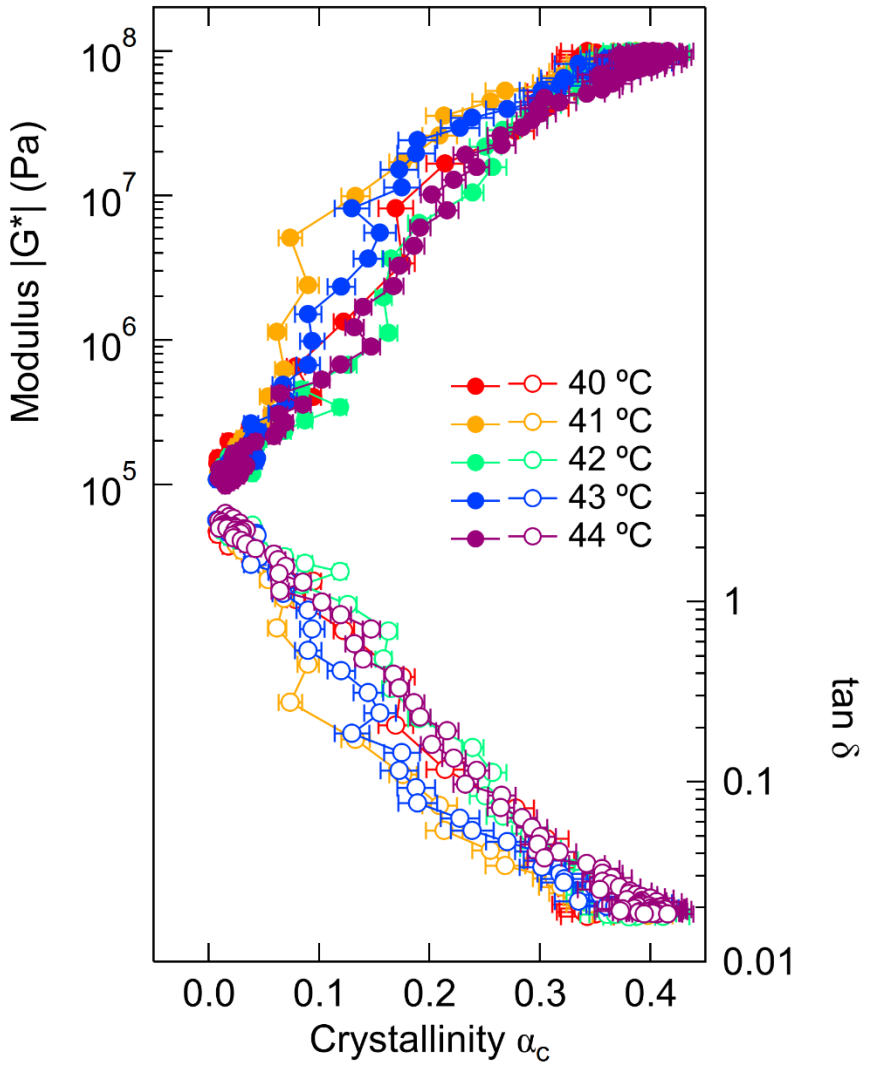
Raman Spectroscopy

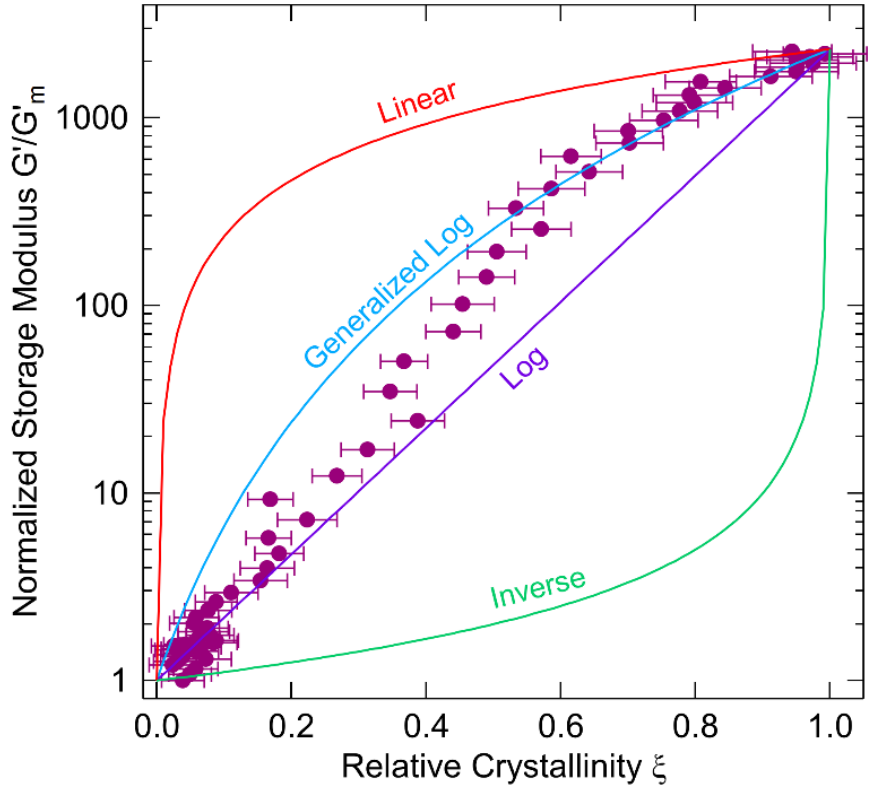


Simultaneous measurement of crystallinity and rheology

Kotula and Migler, *J. Rheol.* (2018)

VISCOELASTICITY AS A FUNCTION OF CRYSTALLINITY

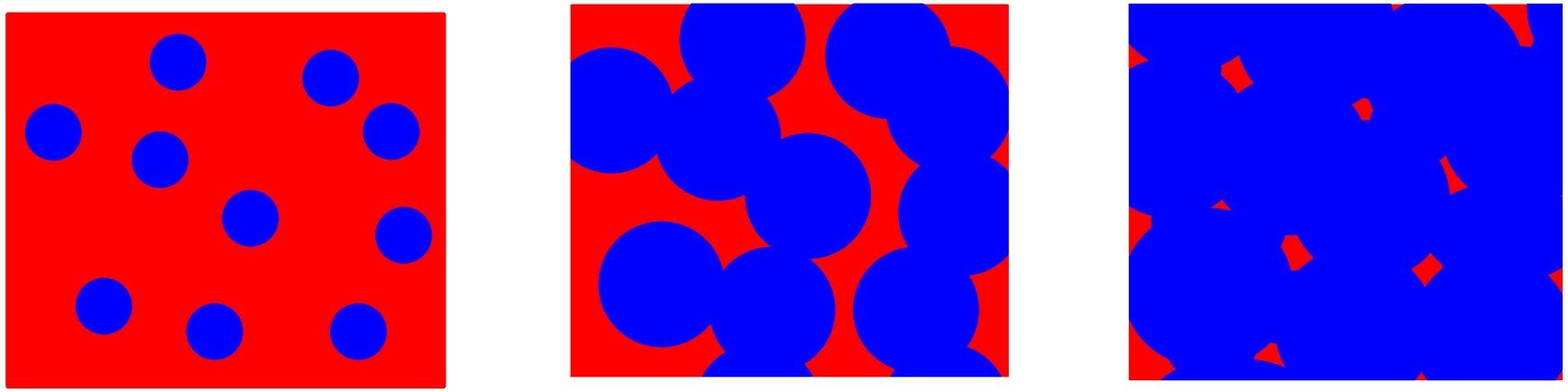




Current models do not capture structure development during crystallization

POLYMER CRYSTALLIZATION IS A PERCOLATION PROBLEM

Growth of semicrystalline domains



Dispersed
semicrystalline solids
in a polymer melt

Percolating network of
semicrystalline domains

Dispersed
melt domains in a
semicrystalline solid

Need a modulus dependence on solid fraction that crosses the *percolation threshold*

SUSPENSION-BASED MODEL ACROSS PERCOLATION THRESHOLD

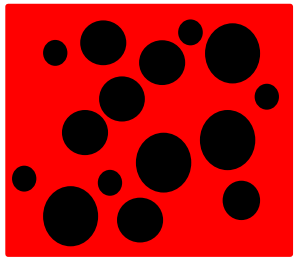
Hard particle composites

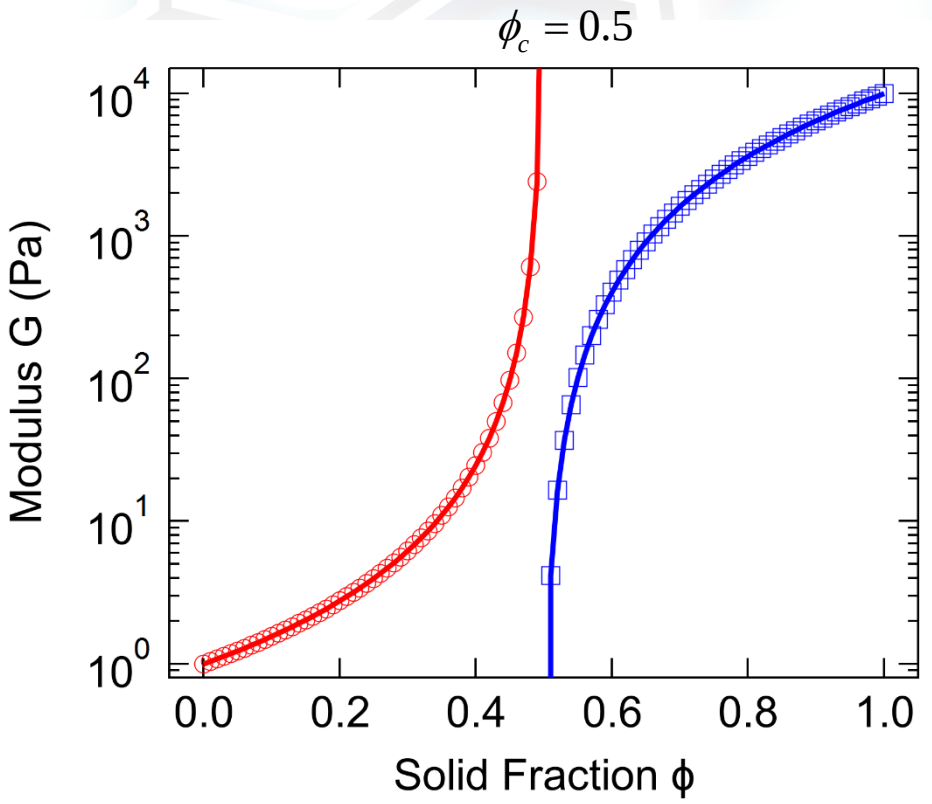
(~Krieger-Dougherty)

$$G = G_0 \left(1 - \frac{\phi}{\phi_c}\right)^{-s}$$

$$s \approx 2$$

Maron & Pierce (1956)



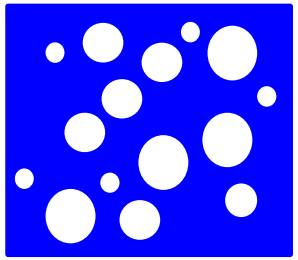


Porous elastic solids

$$G = G_s \left(\frac{\phi - \phi_c}{1 - \phi_c}\right)^t$$

$$1.6 < t < 2.3$$

Roberts & Garboczi (2002)



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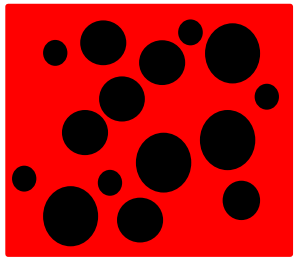
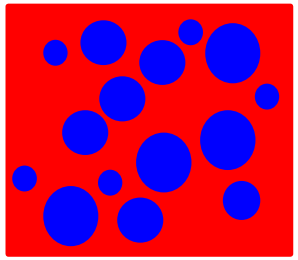
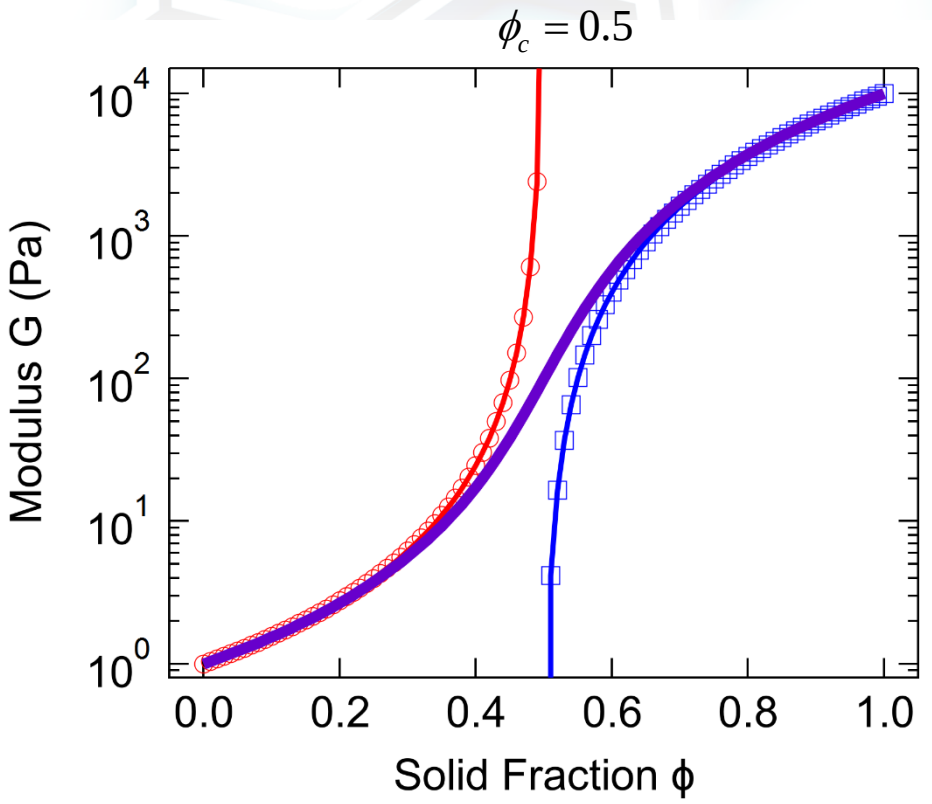
Maron & Pierce (1956)







General effective medium theory

$$(1-\phi)\frac{(G_0)^{1/q}-(G)^{1/q}}{(G_0)^{1/q}+A(G)^{1/q}}+\phi\frac{(G_s)^{1/q}-(G)^{1/q}}{(G_s)^{1/q}+A(G)^{1/q}}=0$$

Assuming $s = t = q$

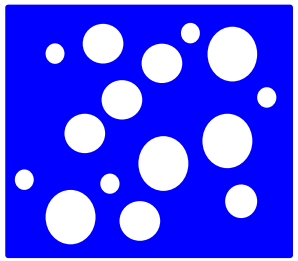
$$A = \frac{1-\phi_c}{\phi_c}$$

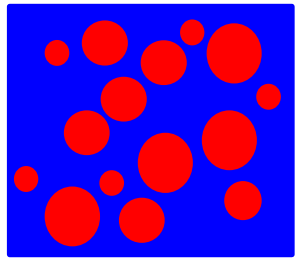
Porous elastic solids

$$G = G_s\left(\frac{\phi-\phi_c}{1-\phi_c}\right)^t$$

$1.6 < t < 2.3$

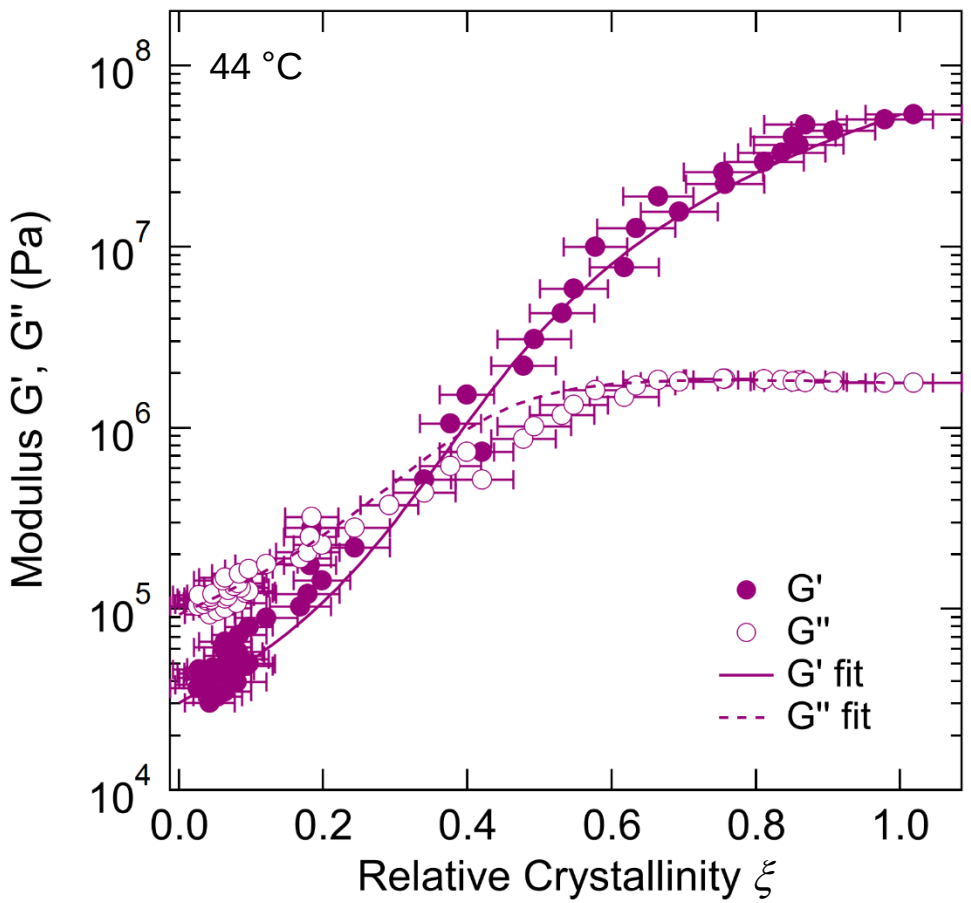
Roberts & Garboczi (2002)

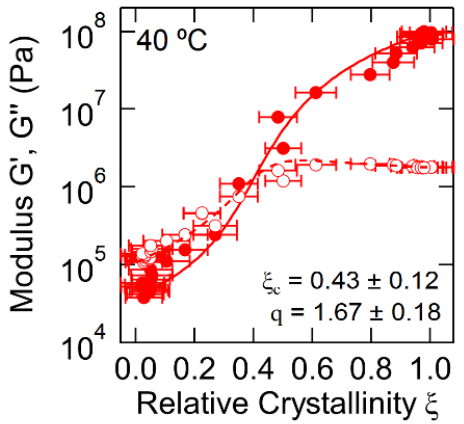


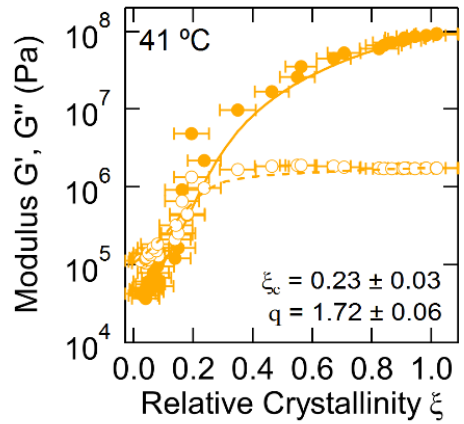


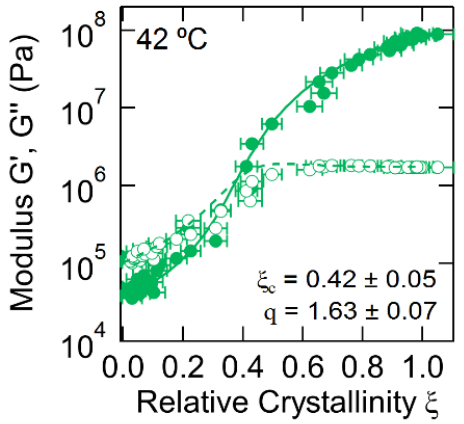
Kotula and Migler, *J. Rheol.* (2018)

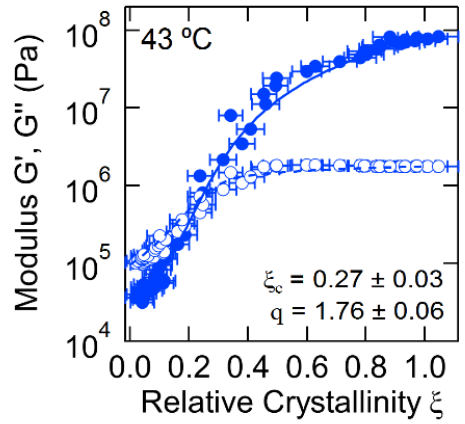
MODULUS VS CRYSTALLINITY FOLLOWS EFFECTIVE MEDIUM THEORY







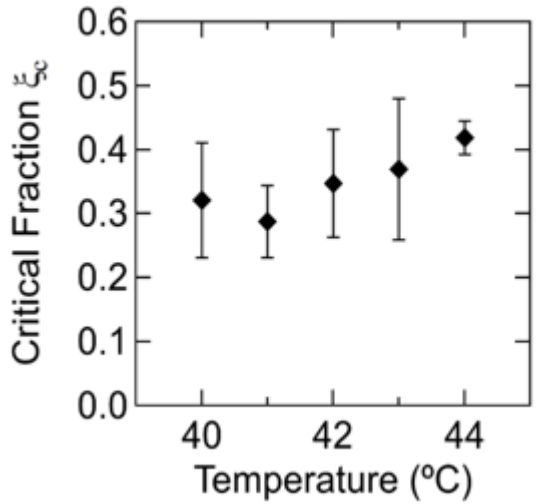


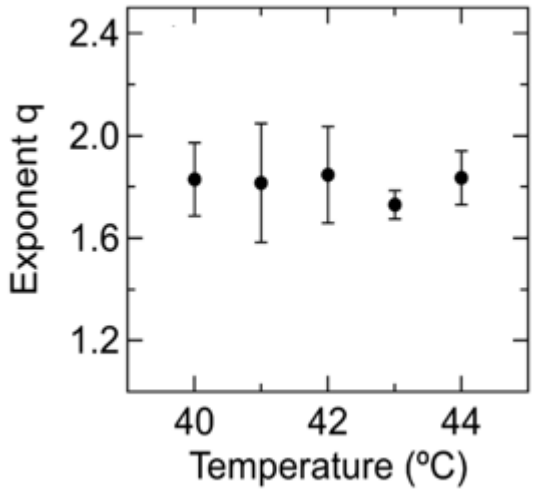


$$(1-\xi)\frac{\left(G_m^*\right)^{1/q}-\left(G^*\right)^{1/q}}{\left(G_m^*\right)^{1/q}+A\left(G^*\right)^{1/q}}+\xi\frac{\left(G_\infty^*\right)^{1/q}-\left(G^*\right)^{1/q}}{\left(G_\infty^*\right)^{1/q}+A\left(G^*\right)^{1/q}}=0$$

Kotula and Migler, *J. Rheol.* (2018)

PUTTING EFFECTIVE MEDIUM FIT PARAMETERS IN CONTEXT



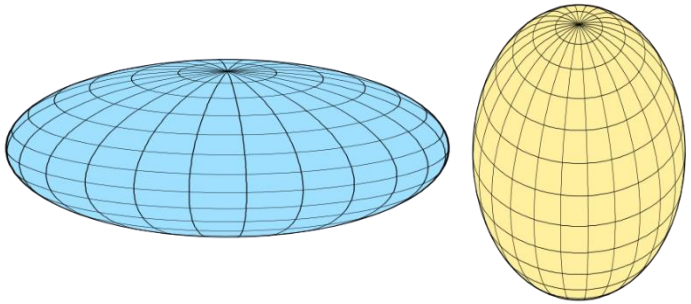


Critical percolation fraction

- Monodisperse hard spheres

$$\xi_c = 0.64$$

- Lower percolation fractions
  - **Nonspherical shapes**
  - **Aggregates**



Exponent

- Krieger-Dougherty

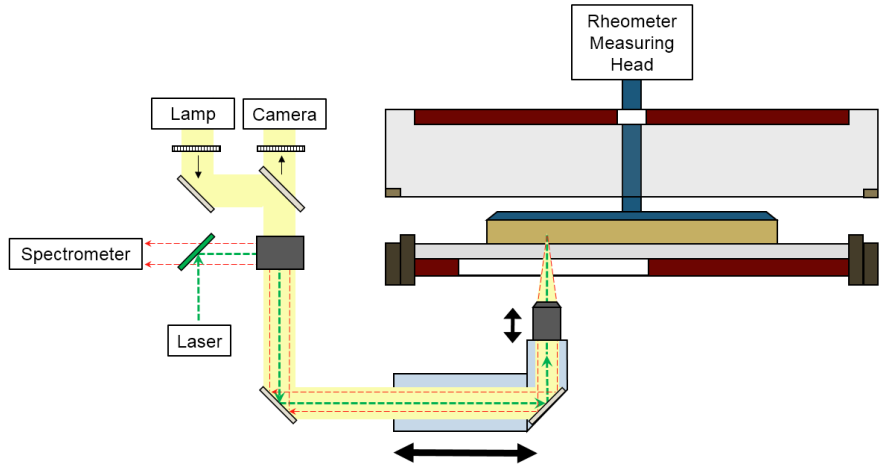
$$\eta = \eta_0 \left(1 - \frac{\xi}{\xi_c}\right)^{-s} \qquad s = [\eta]\xi_c$$

- **Hard spheres** $s = 1.6$
- **Ellipsoidal** $s \approx 2$

Kotula and Migler, *J. Rheol.* (2018)

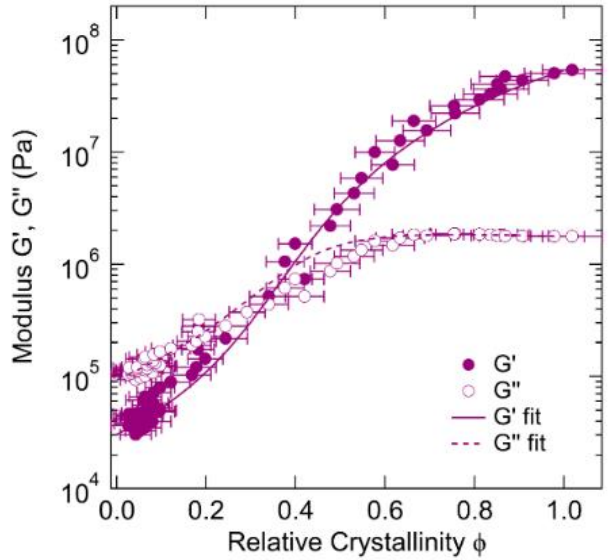
CONCLUSIONS

The rheo-Raman microscope provides simultaneous investigation of mechanical, chemical, and structural properties



Simultaneous rheology and Raman reveal that modulus-crystallinity follows generalized effective medium equation

– *a suspension-based model*



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