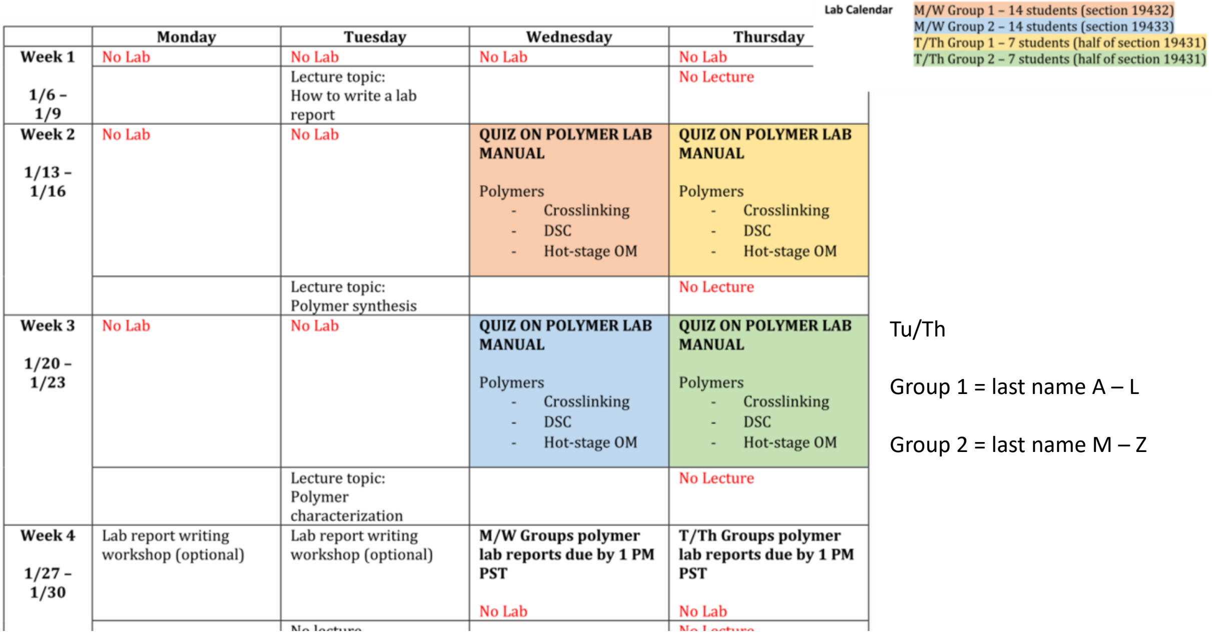
MSE 160 – Polymer characterization

Labs this week (details here: bowmanlab.eng.uci.edu/class)



Lab Calendar

M/W Group 1 – 14 students (section 19432)
M/W Group 2 – 14 students (section 19433)
T/Th Group 1 – 7 students (half of section 19431)
T/Th Group 2 – 7 students (half of section 19431)

	Monday	Tuesday	Wednesday	Thursday
Week 1 **1/6 – 1/9**	No Lab	No Lab	No Lab	No Lab
		Lecture topic: How to write a lab report		No Lecture
Week 2 **1/13 – 1/16**	No Lab	No Lab	**QUIZ ON POLYMER LAB MANUAL** Polymers - Crosslinking - DSC - Hot-stage OM	**QUIZ ON POLYMER LAB MANUAL** Polymers - Crosslinking - DSC - Hot-stage OM
		Lecture topic: Polymer synthesis		No Lecture
Week 3 **1/20 – 1/23**	No Lab	No Lab	**QUIZ ON POLYMER LAB MANUAL** Polymers - Crosslinking - DSC - Hot-stage OM	**QUIZ ON POLYMER LAB MANUAL** Polymers - Crosslinking - DSC - Hot-stage OM
		Lecture topic: Polymer characterization		No Lecture
Week 4 **1/27 – 1/30**	Lab report writing workshop (optional)	Lab report writing workshop (optional)	**M/W Groups polymer lab reports due by 1 PM PST** No Lab	**T/Th Groups polymer lab reports due by 1 PM PST** No Lab
		No lecture		No Lecture

Tu/Th

Group 1 = last name A – L

Group 2 = last name M – Z

Lecture outline

Outline

- Characterization
  - Differential scanning calorimetry
  - Polarized light microscopy

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Differential scanning calorimetry (DSC)

Calorimetry measures thermal properties of materials

Connects temperature and specific physical properties of substances

Only method for direct determination of enthalpy associated with a process

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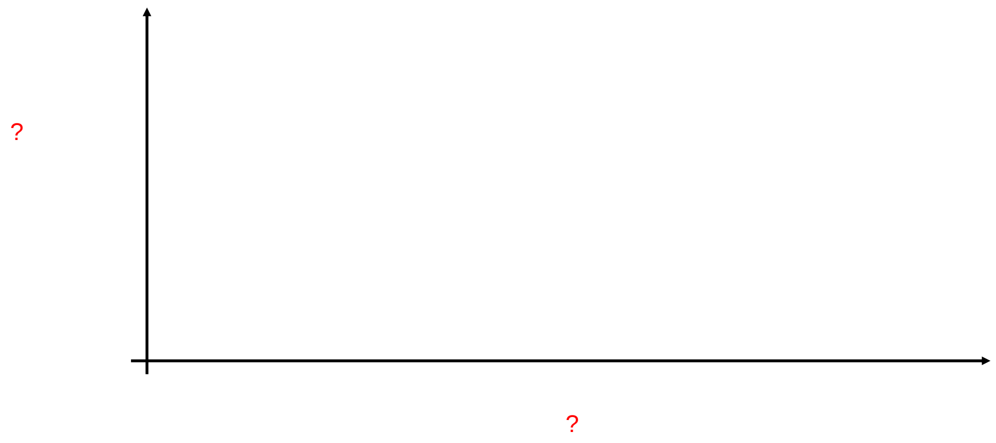
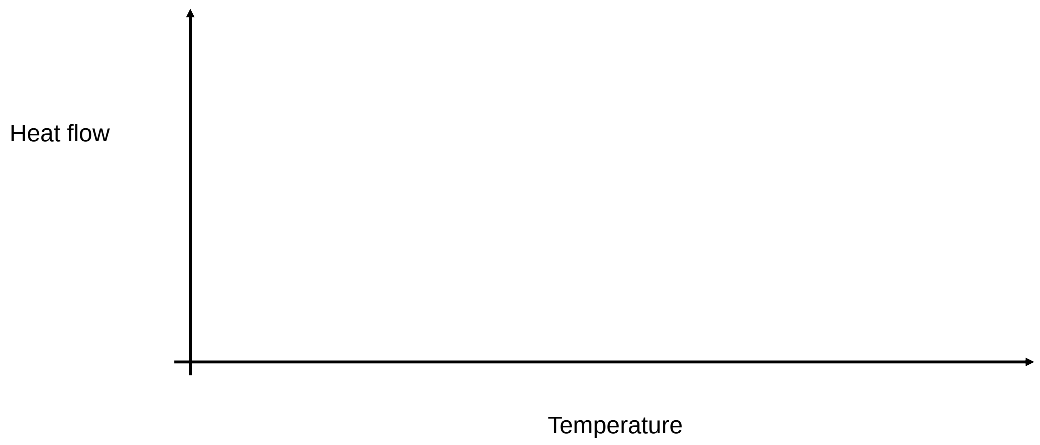
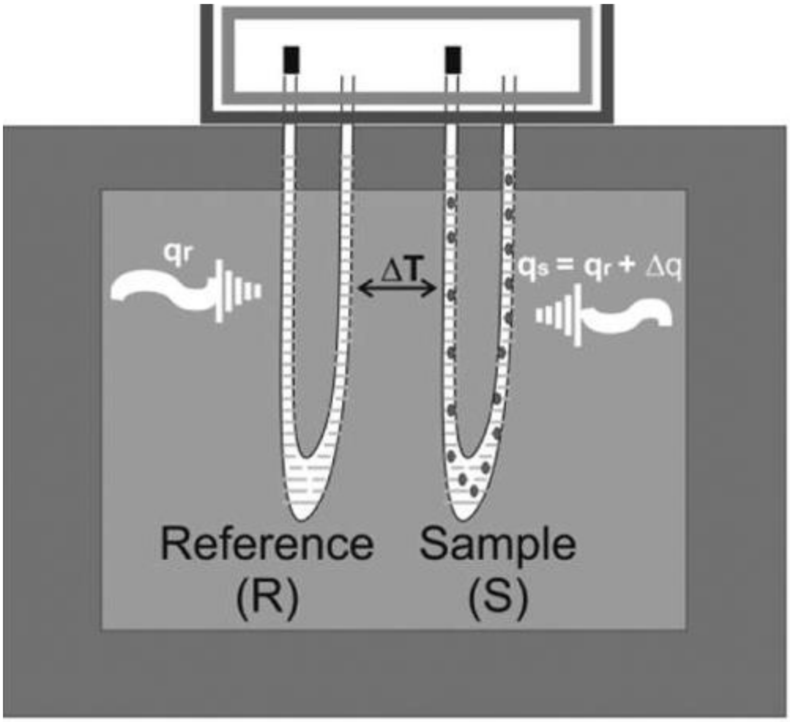
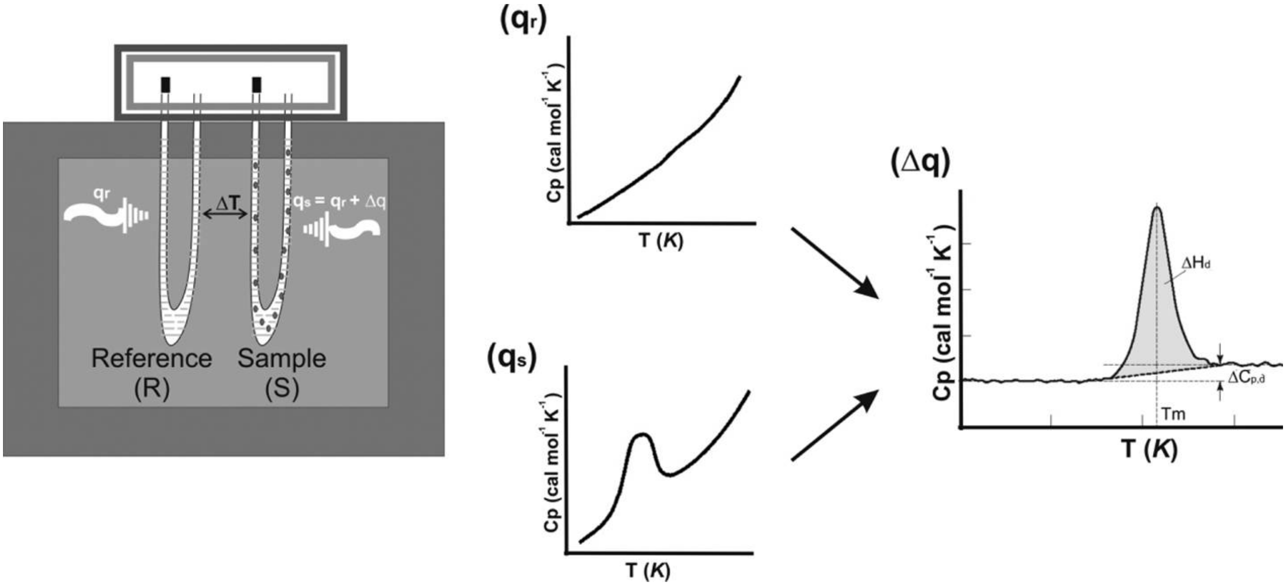
What are the dependent and independent variables in DSC?



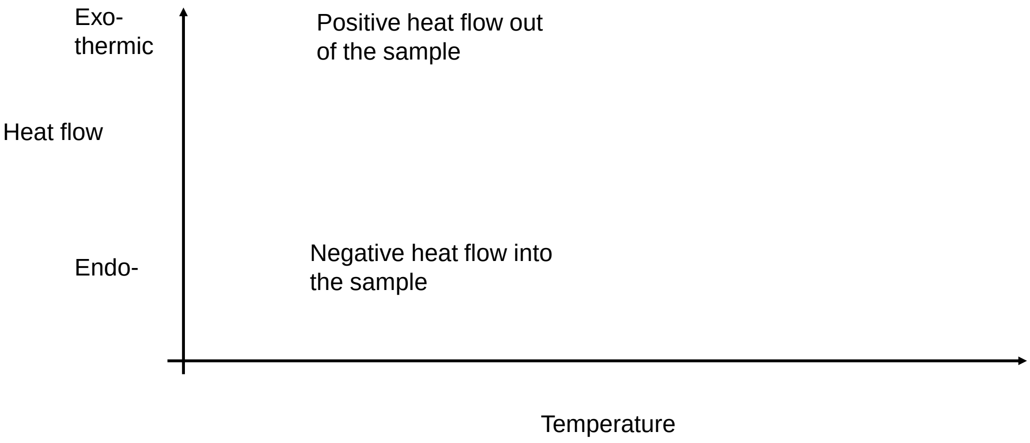
DSC measures heat flow vs. temperature



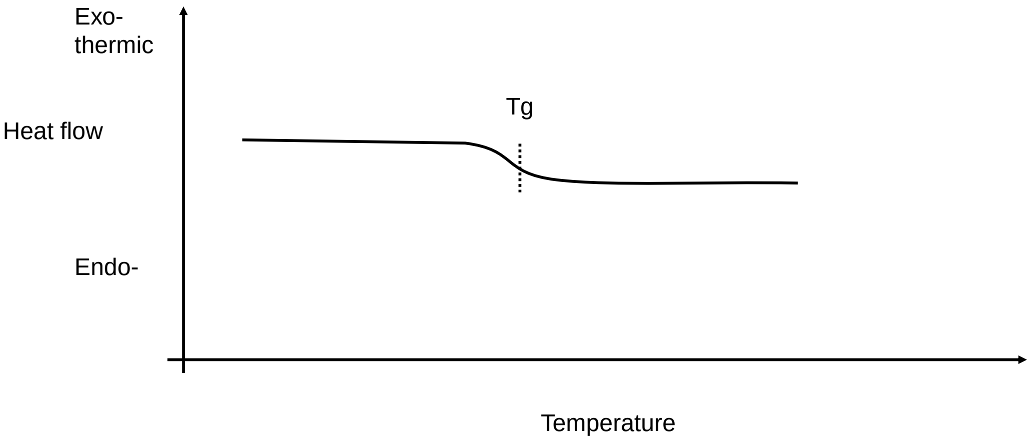

qr
ΔT
qs = qr + Δq
Reference
(R)
Sample
(S)


qr
ΔT
qs = qr + Δq
Reference
(R)
Sample
(S)
(qr)
Cp (cal mol-1 K-1)
T (K)
(qs)
Cp (cal mol-1 K-1)
T (K)
(Δq)
Cp (cal mol-1 K-1)
ΔHd
ΔCp,d
Tm
T (K)

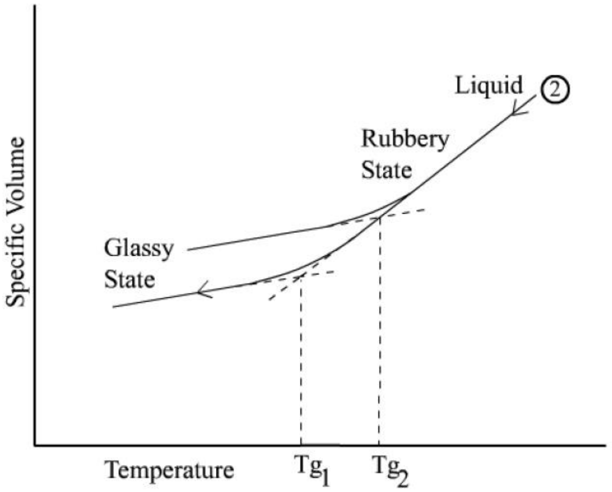
Differential scanning calorimetry (DSC)



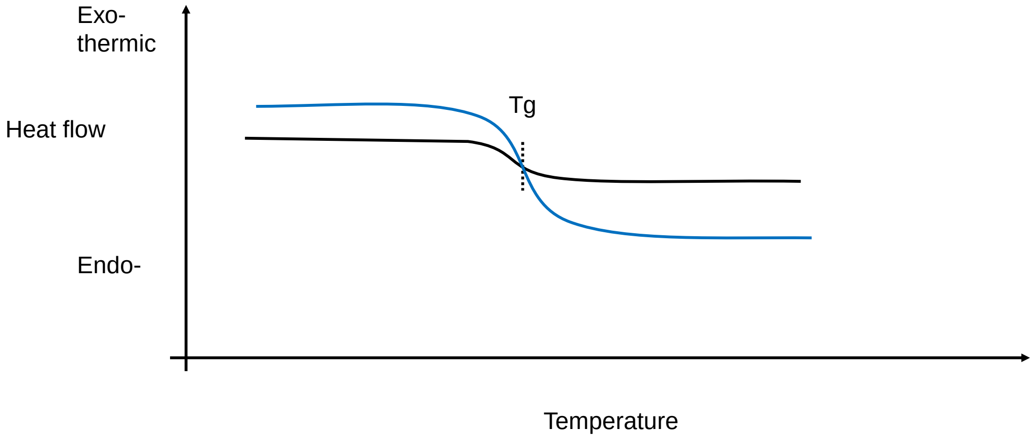
Differential scanning calorimetry (DSC)



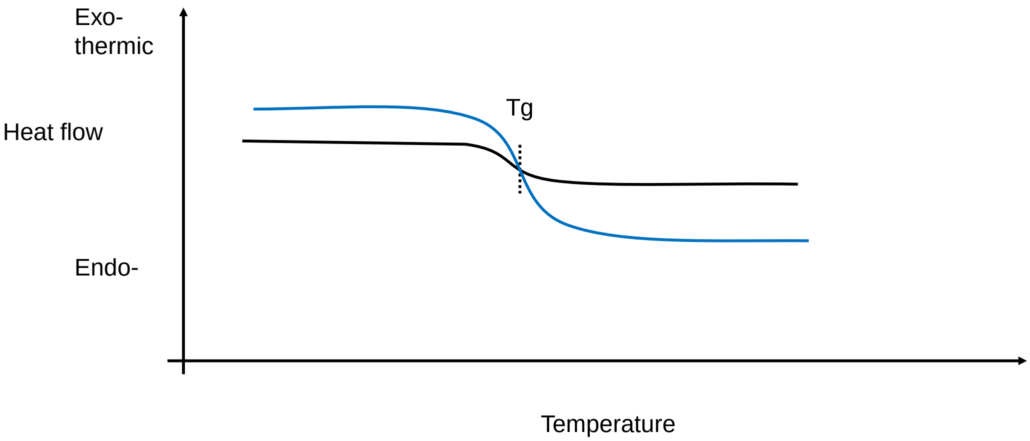
Above Tg the amorphous phase softens, but the material is still solid



Differential scanning calorimetry (DSC)

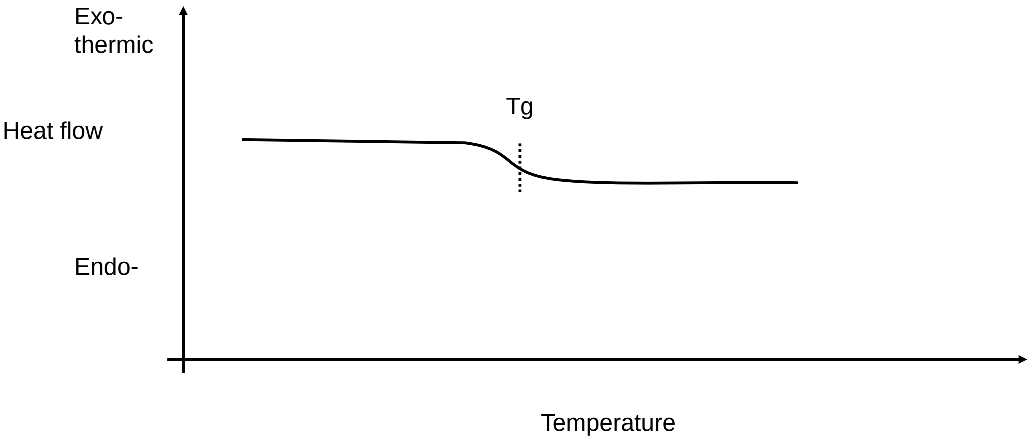


Magnitude of heat flow at Tg indicates a change in the amount of amorphous material

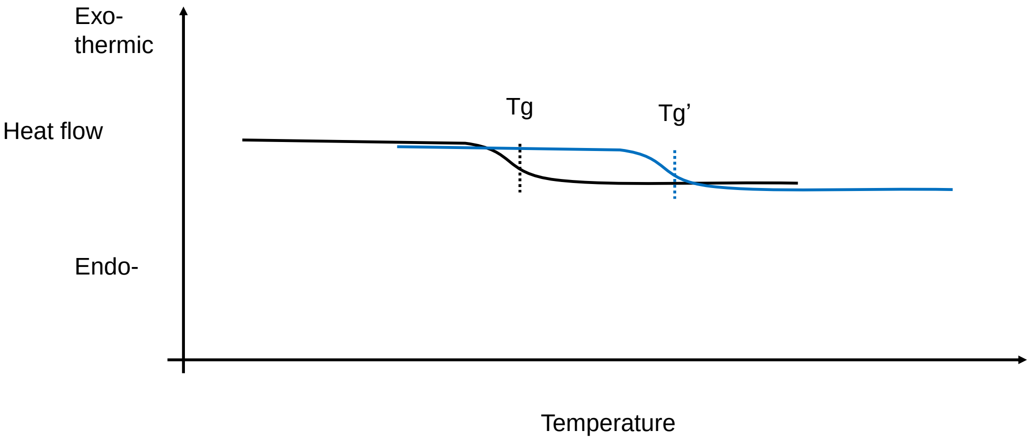


Differential scanning calorimetry (DSC)

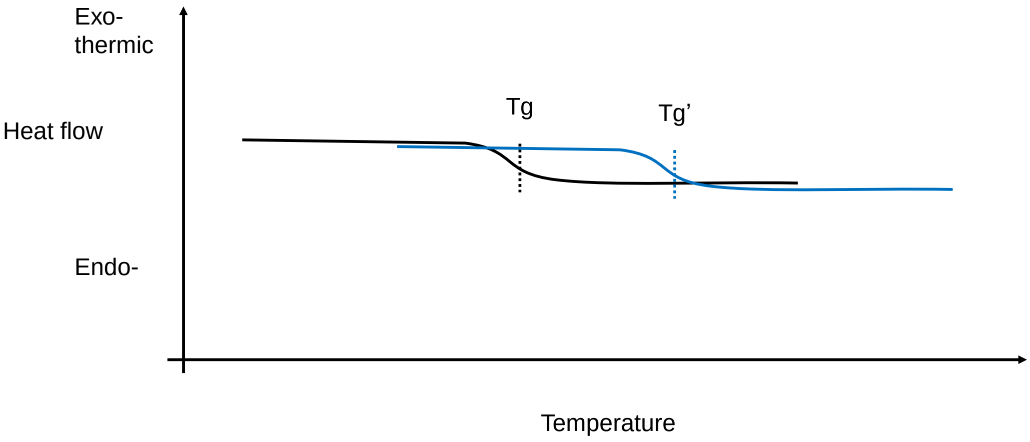
How else can Tg change?



Differential scanning calorimetry (DSC)



Shift of Tg indicates a change in the mobility of molecules



Exotherm or endotherm DSC signals result from phase change or chemical reaction

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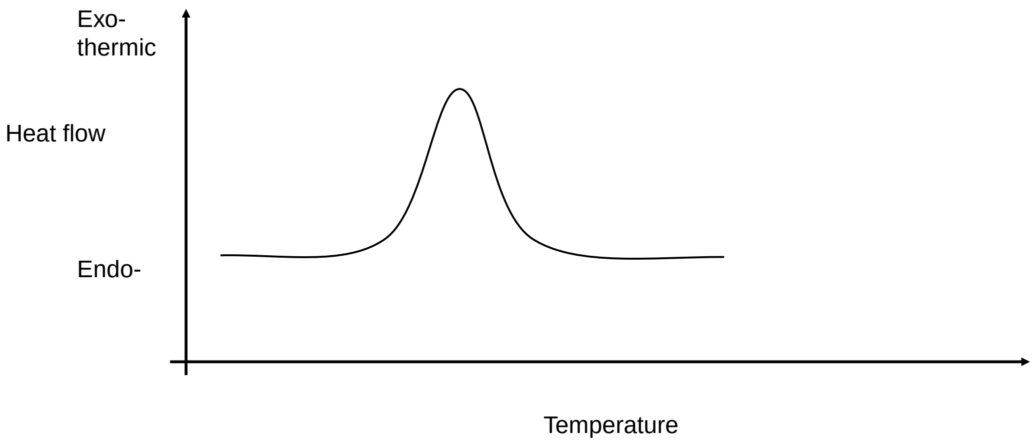
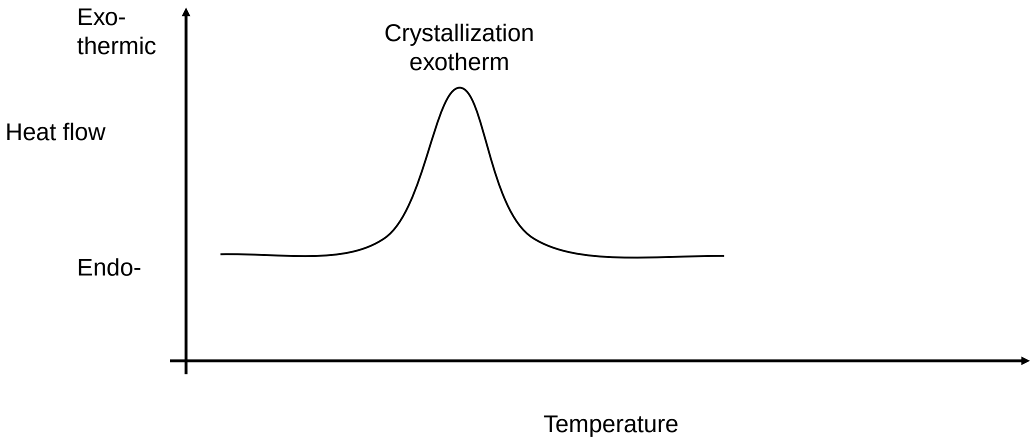
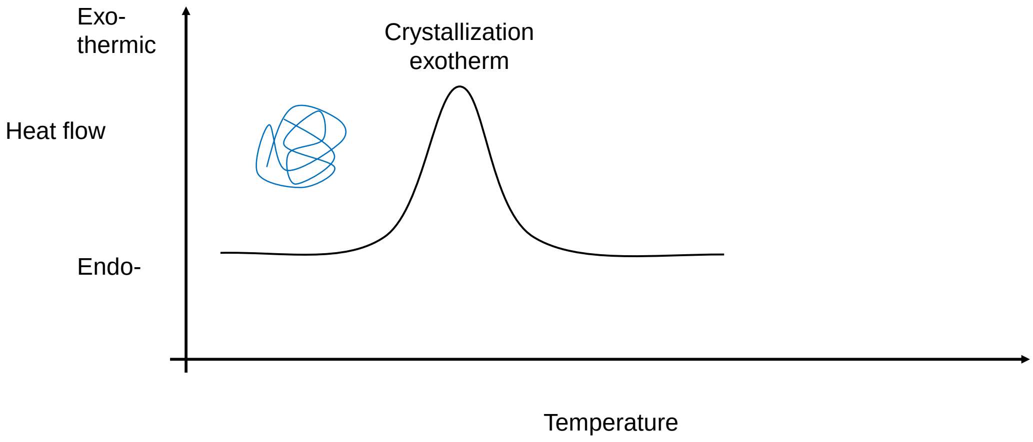


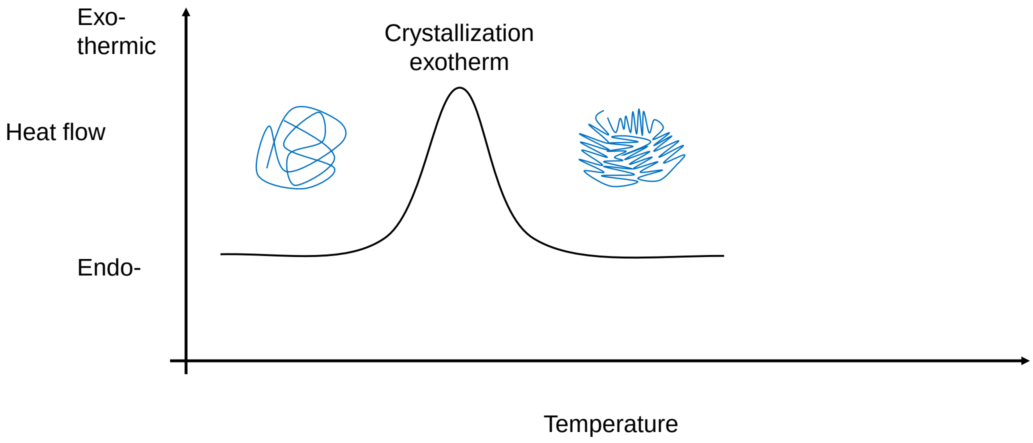
Crystallization releases heat
as a lower-energy, higher-order state is formed

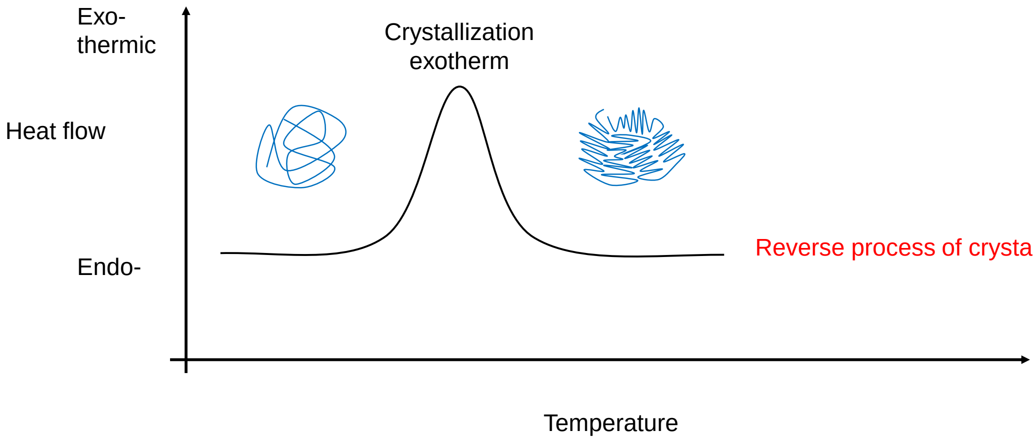


Molecular ordering releases excess free energy
associated with disorder



Molecular ordering releases excess free energy associated with disorder

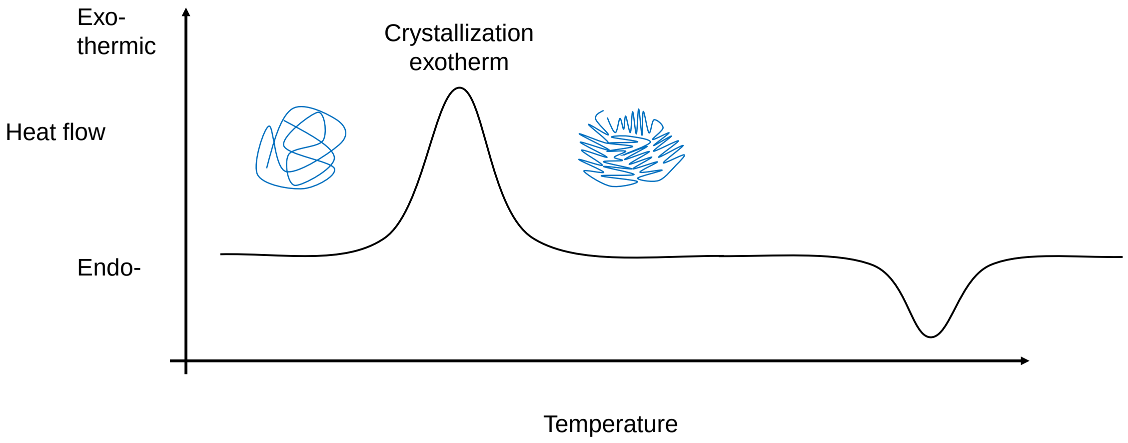




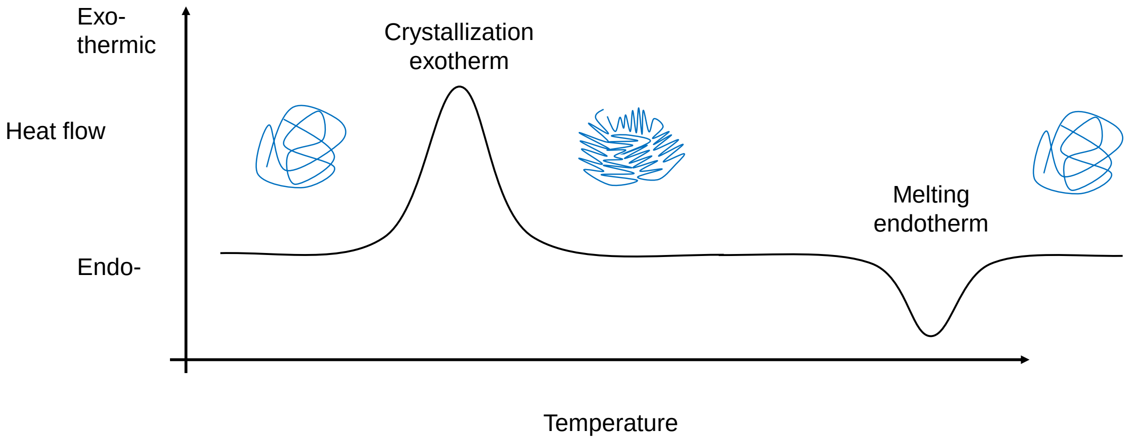
Reverse process of crystallization is ?

Differential scanning calorimetry (DSC)

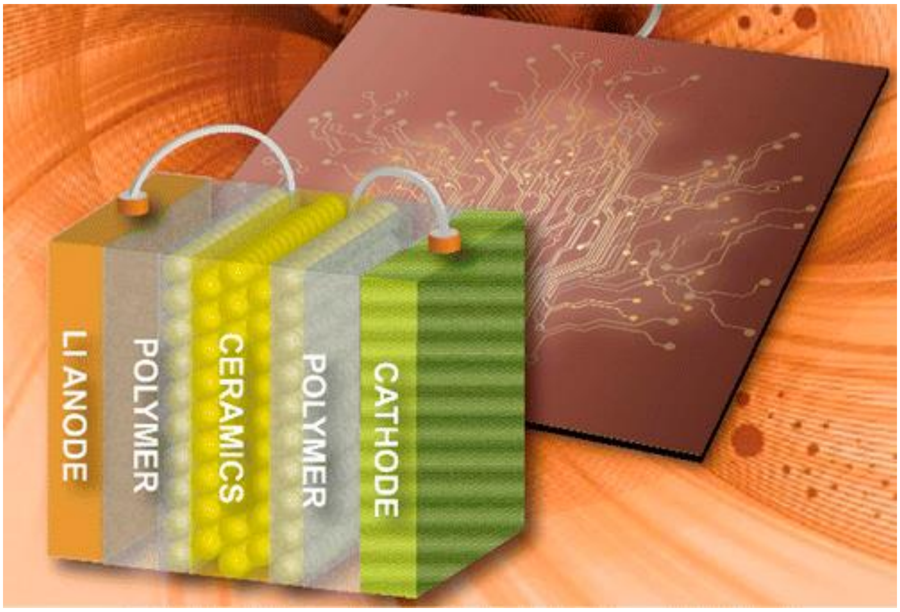
Reverse process of crystallization is ?

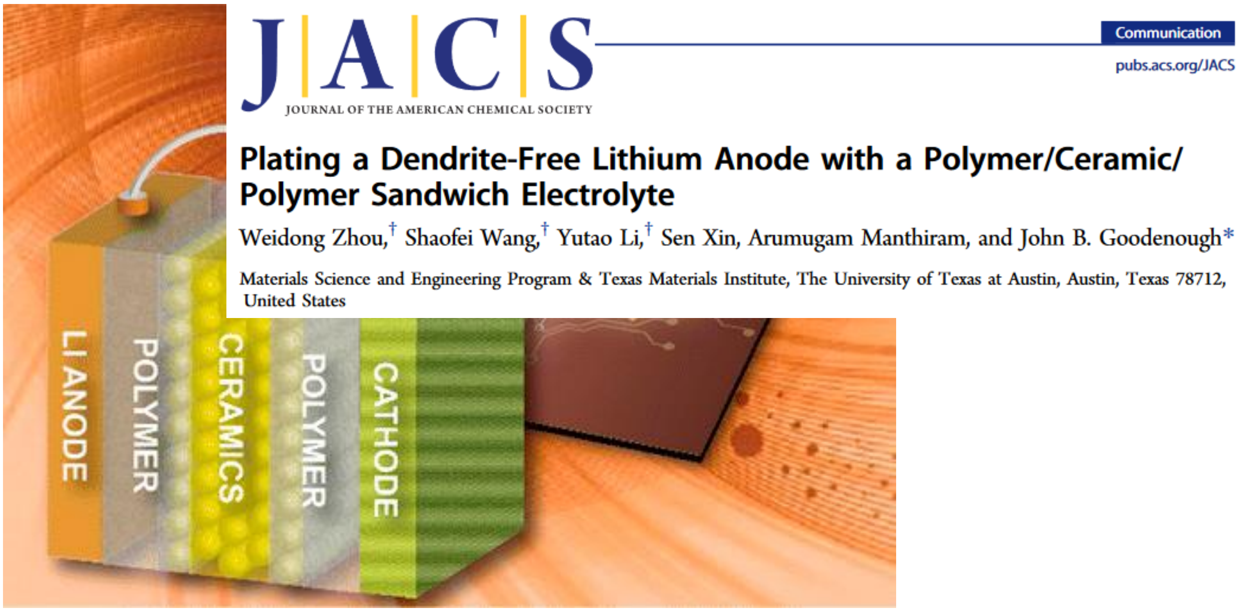


Disordering of the molecules requires excess free energy



DSC application in battery research

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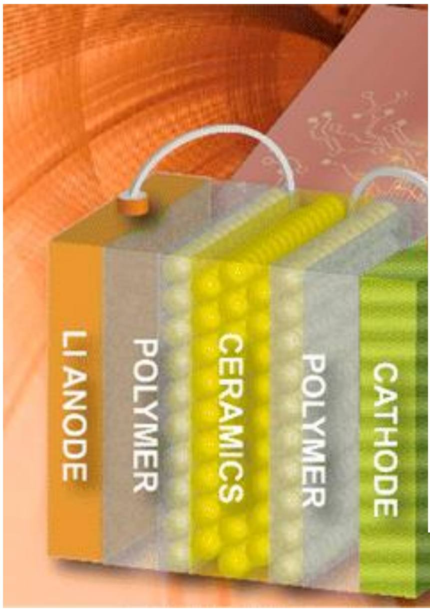
Communication
pubs.acs.org/JACS

Plating a Dendrite-Free Lithium Anode with a Polymer/Ceramic/Polymer Sandwich Electrolyte

Weidong Zhou,[†] Shaofei Wang,[†] Yutao Li,[†] Sen Xin, Arumugam Manthiram, and John B. Goodenough*

Materials Science and Engineering Program & Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712, United States



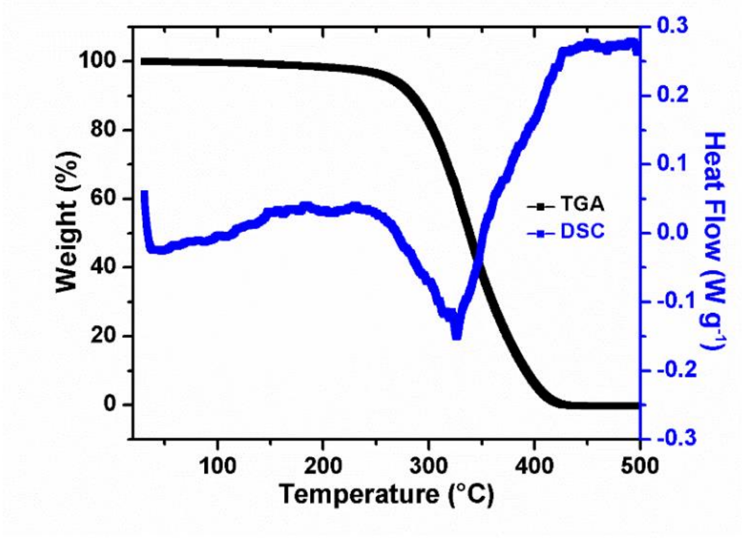


Figure S2. TGA and DSC curves of the polymer CPMEA.

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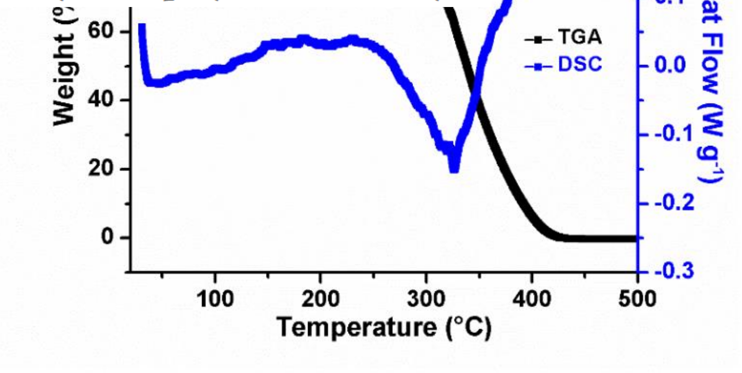
swing freely, facilitating the ionic transfer of Li^+. Thermogravimetric analysis showed that the CPMEA did not exhibit an obvious weight loss until 270 °C, and the differential scanning calorimetry curve did not give an obvious endothermal melting process until 270 °C (Figure S2), indicating that the CPMEA-based membranes should have sufficient thermal stability to remain solid in a lithium metal battery. The polymer−electrolyte



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Exotherm can result from chemical reaction or “curing”

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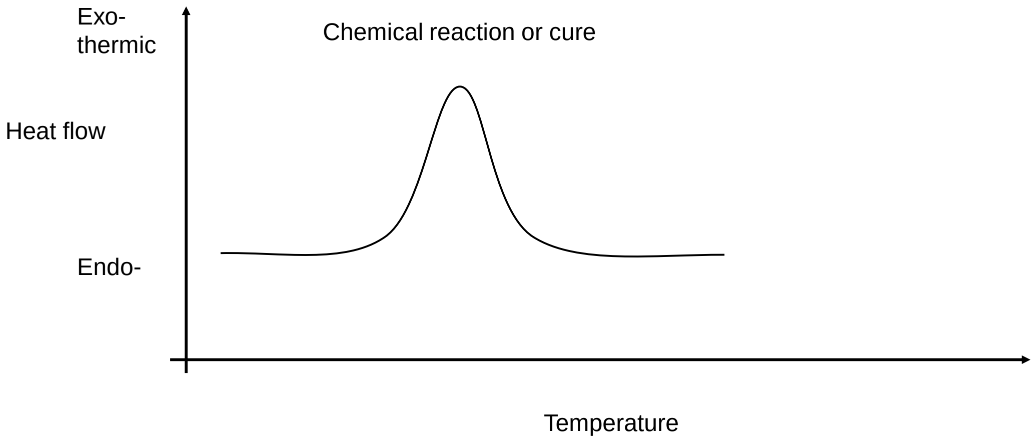
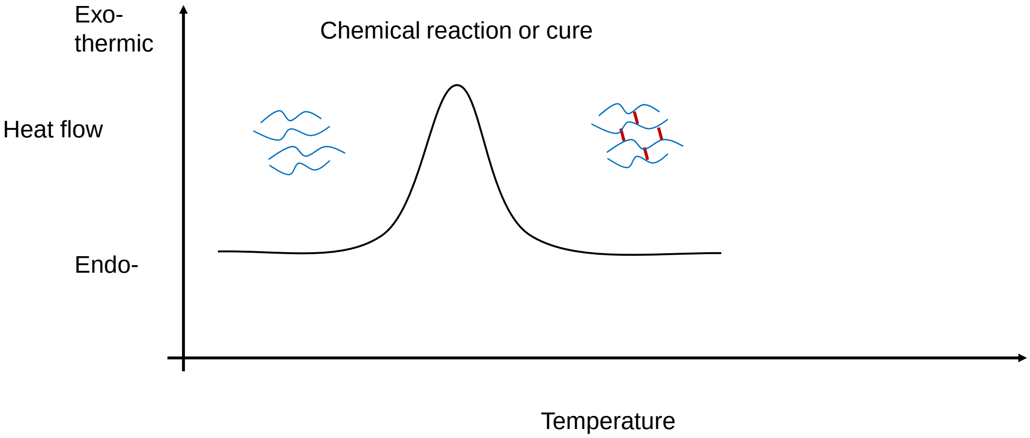
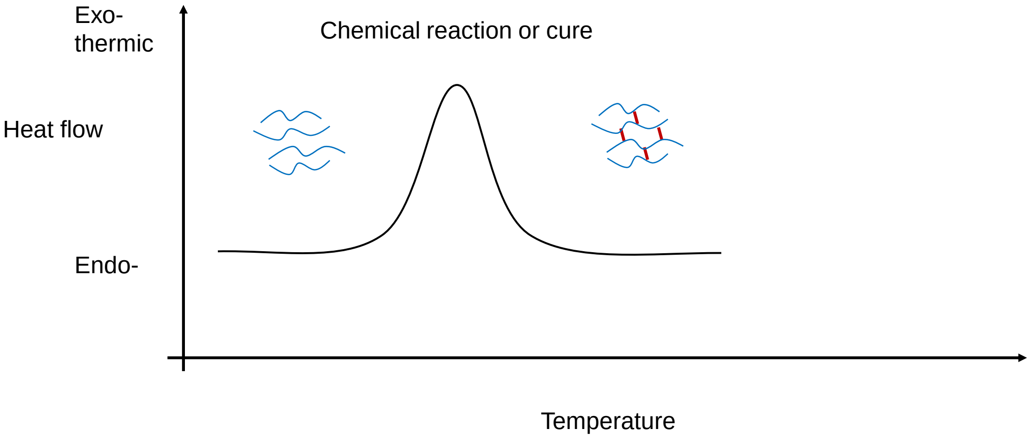


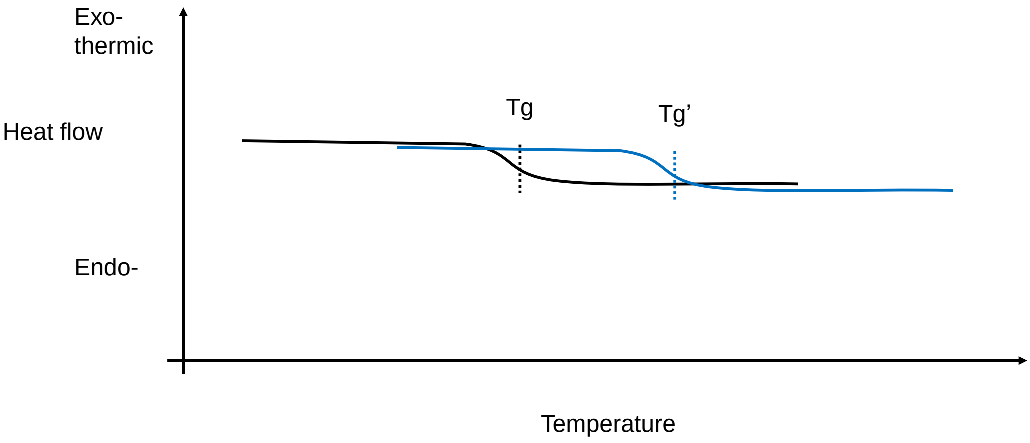
Bond formation between molecular segments forms a tighter network



At higher temperature there is no endotherm because no melting



Curing shifts Tg to higher values
by lowering molecular mobility



Area under an exotherm is the energy released during a reaction or phase change

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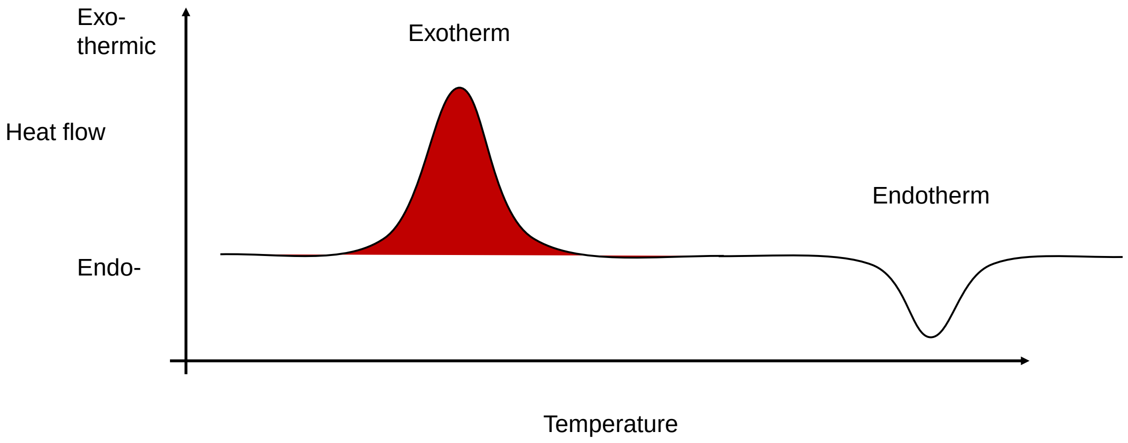
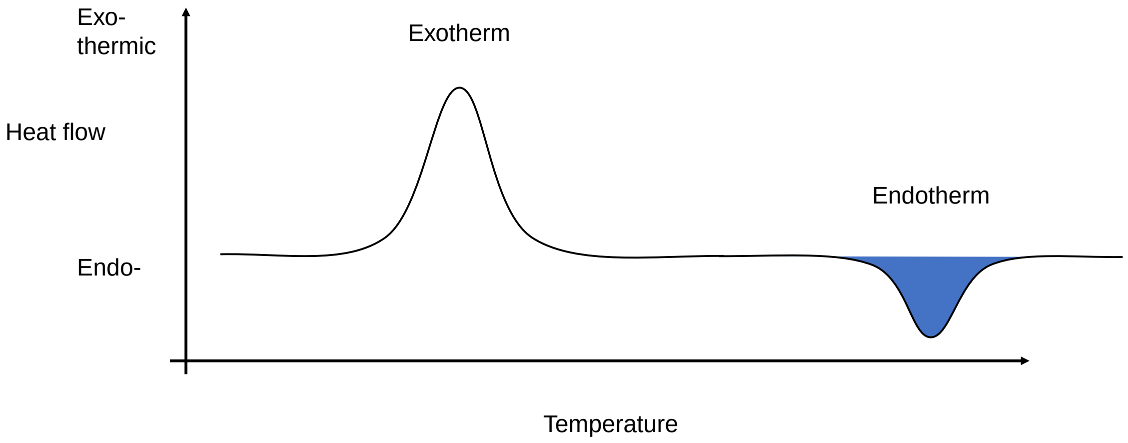


Area above an endotherm is the energy required for a phase change

Area above an endotherm is the energy required for a phase change



Semi-crystalline polymers can have multiple DSC signals

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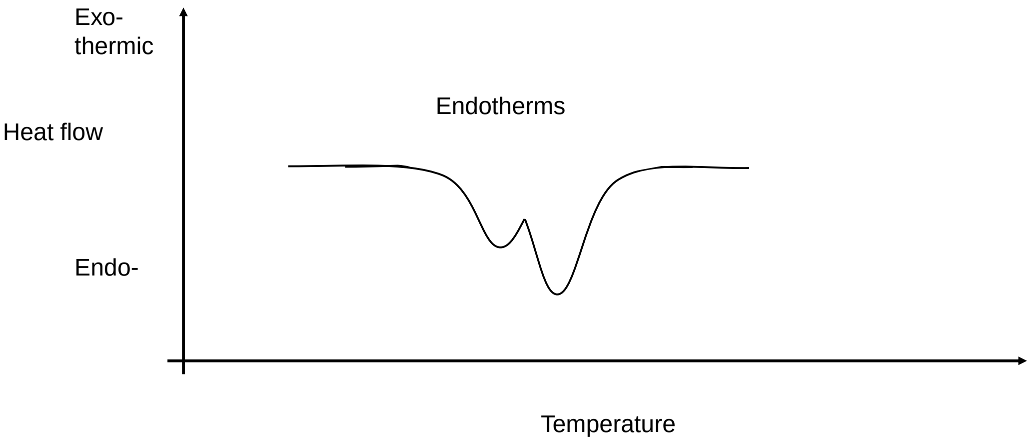
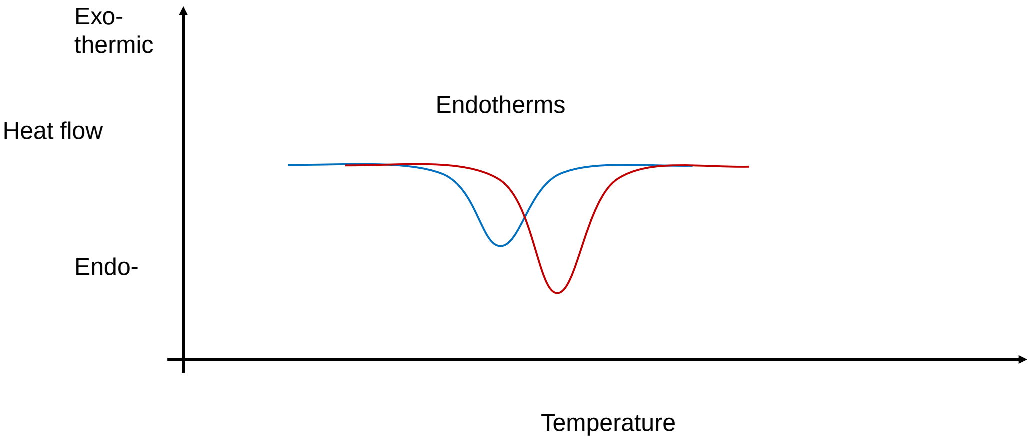
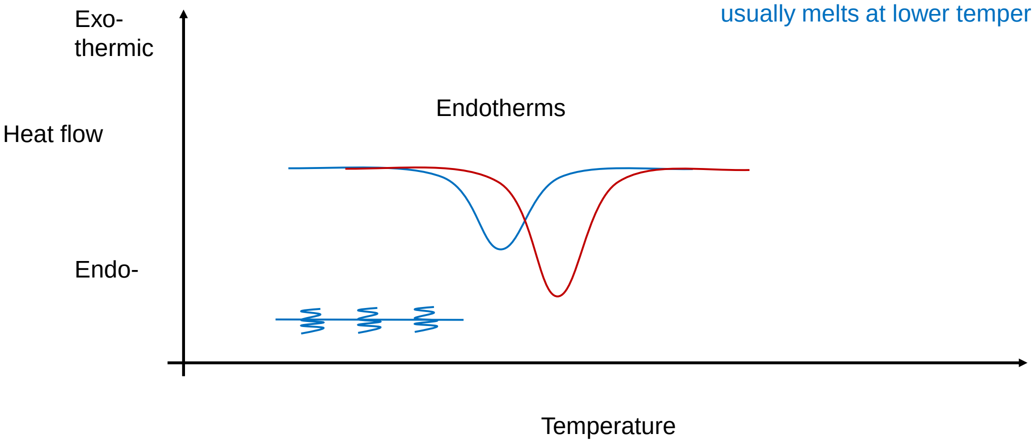
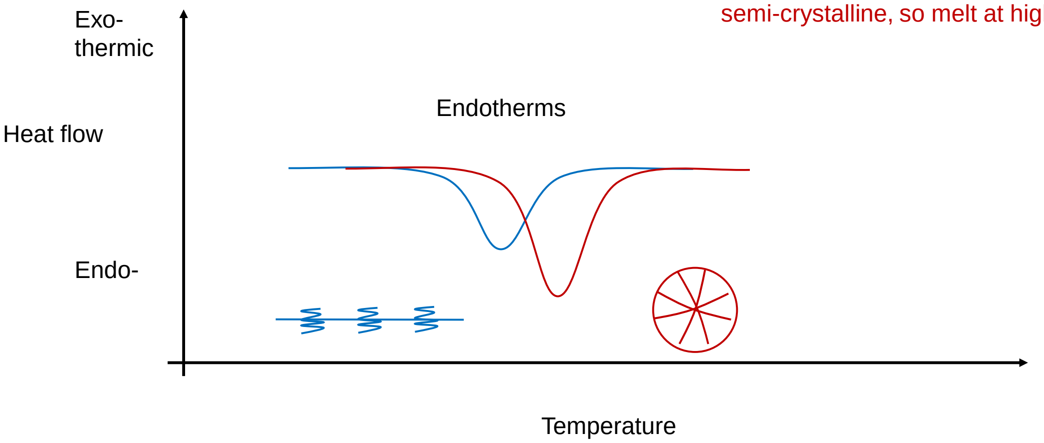


Two different crystal morphologies yield two melting endotherms

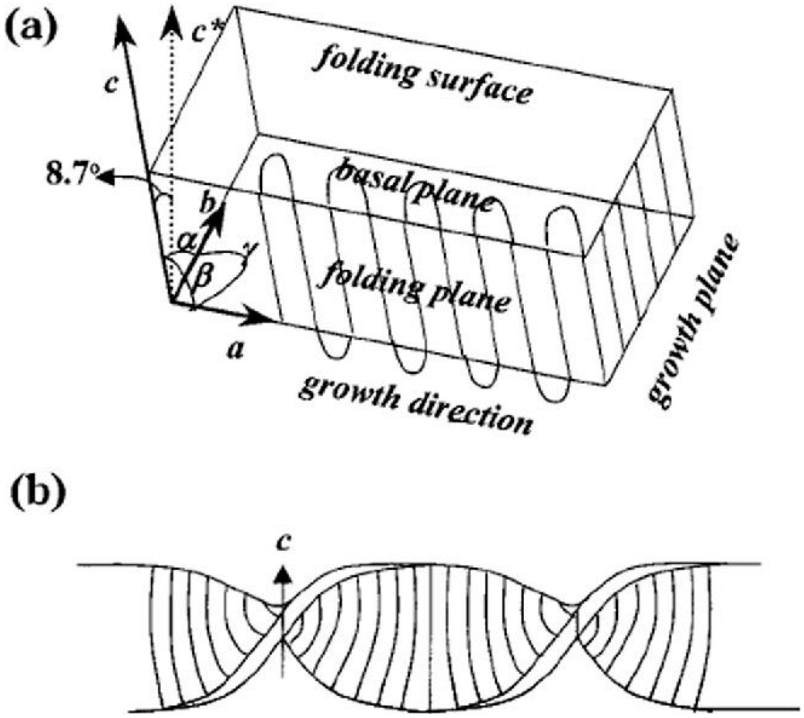




Row-nucleated structure is higher energy, so usually melts at lower temperature



Spherulitic structure is highly ordered and semi-crystalline, so melt at higher temperature



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Copolymer or blend of two semi-crystalline polymers would show two DSC endotherms

Two polymers can combine into one, giving new DSC endotherm

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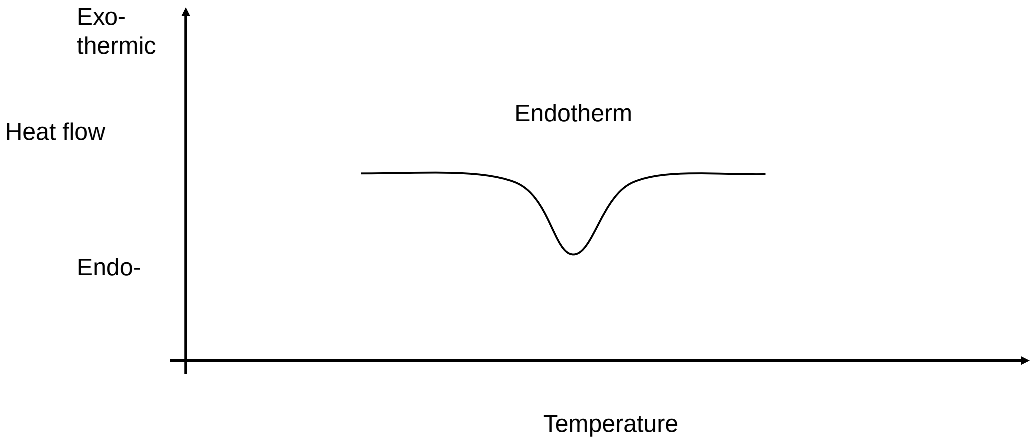
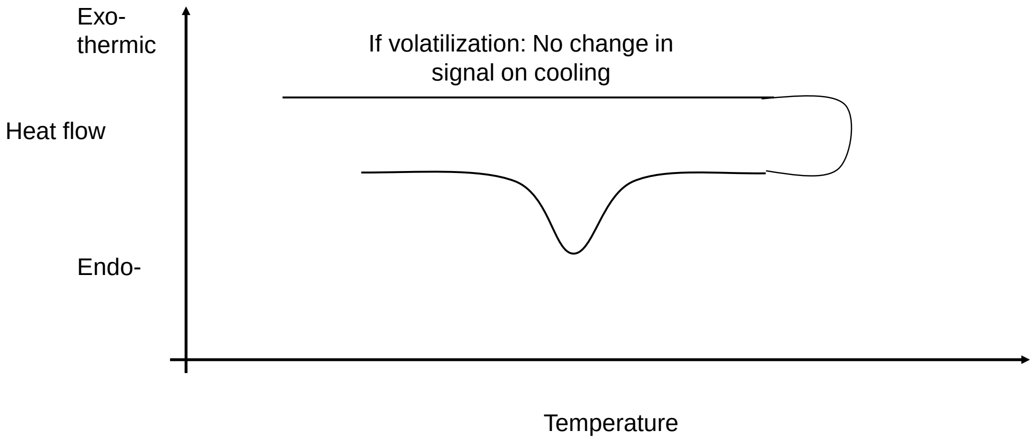
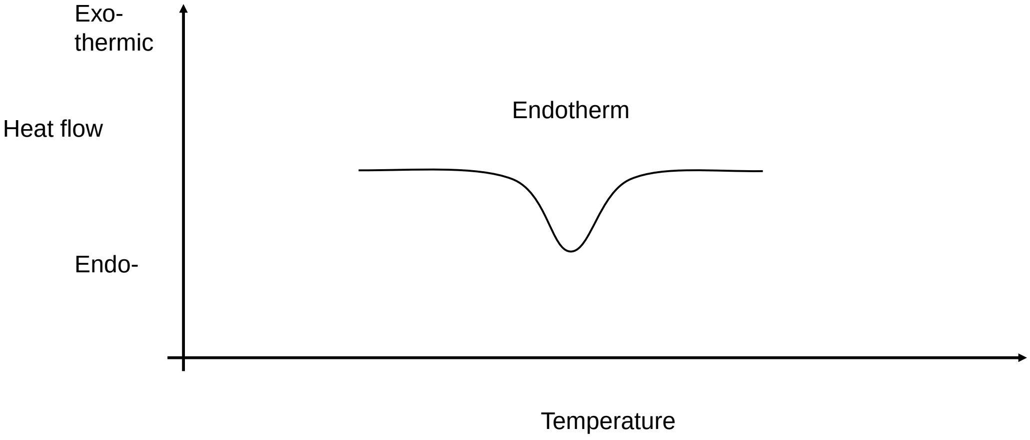
Endotherm signal on first heating



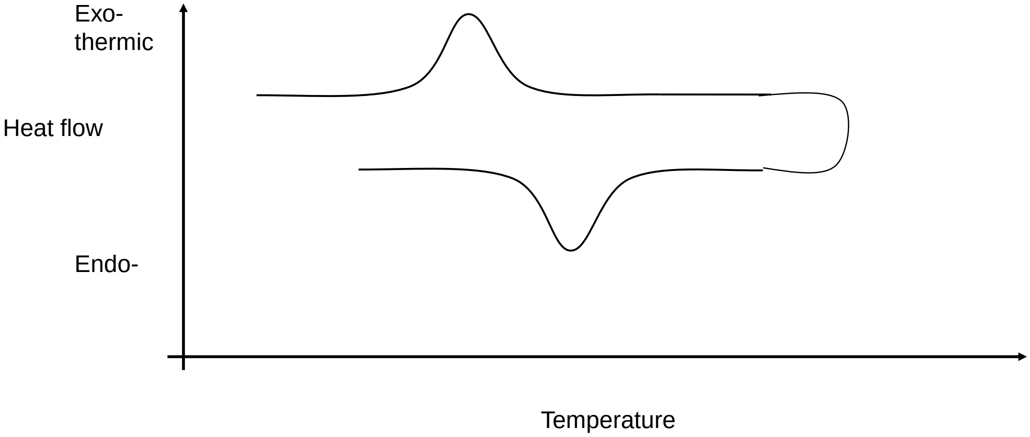


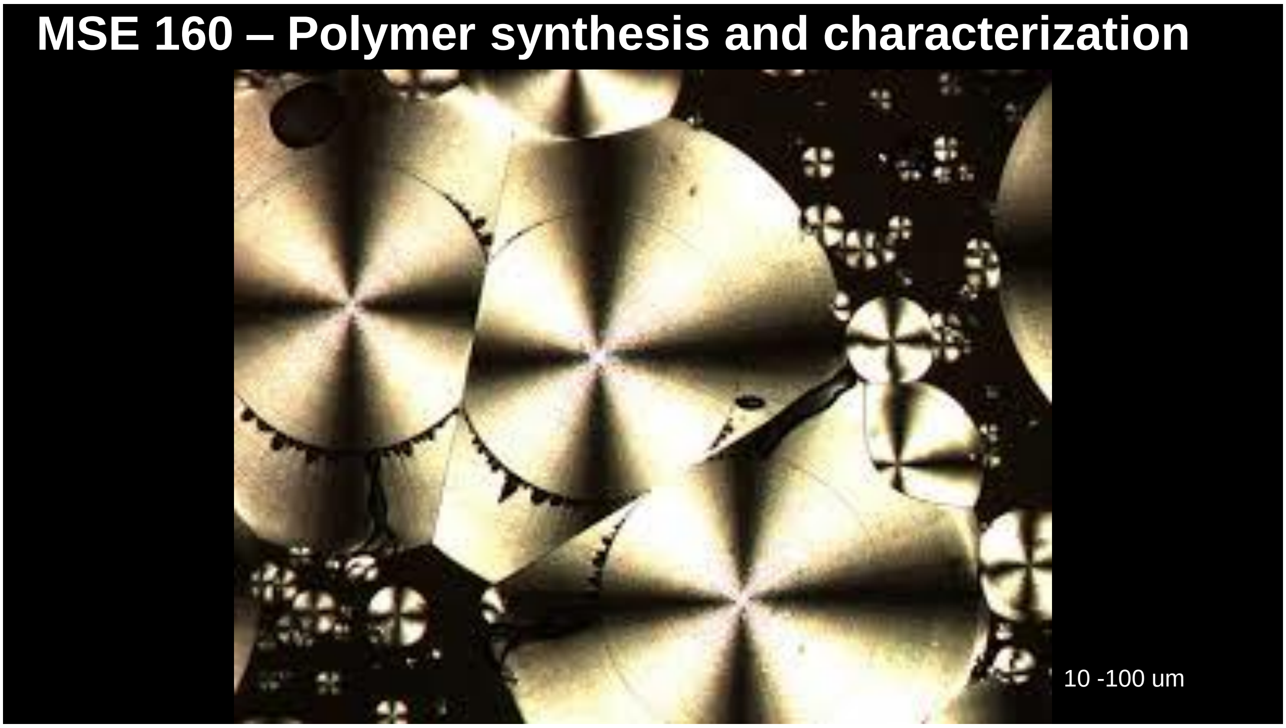
If volatilization: No change in signal on cooling

Endotherm signal on first heating



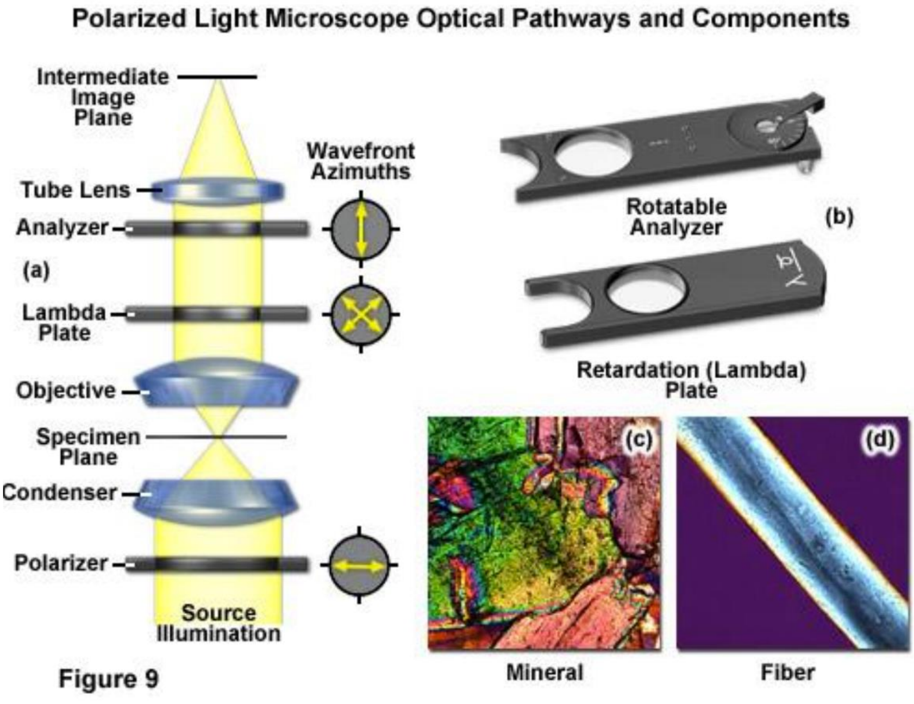
If melting: crystallization exotherm signal on cooling





MSE 160 – Polymer synthesis and characterization

10 -100 um

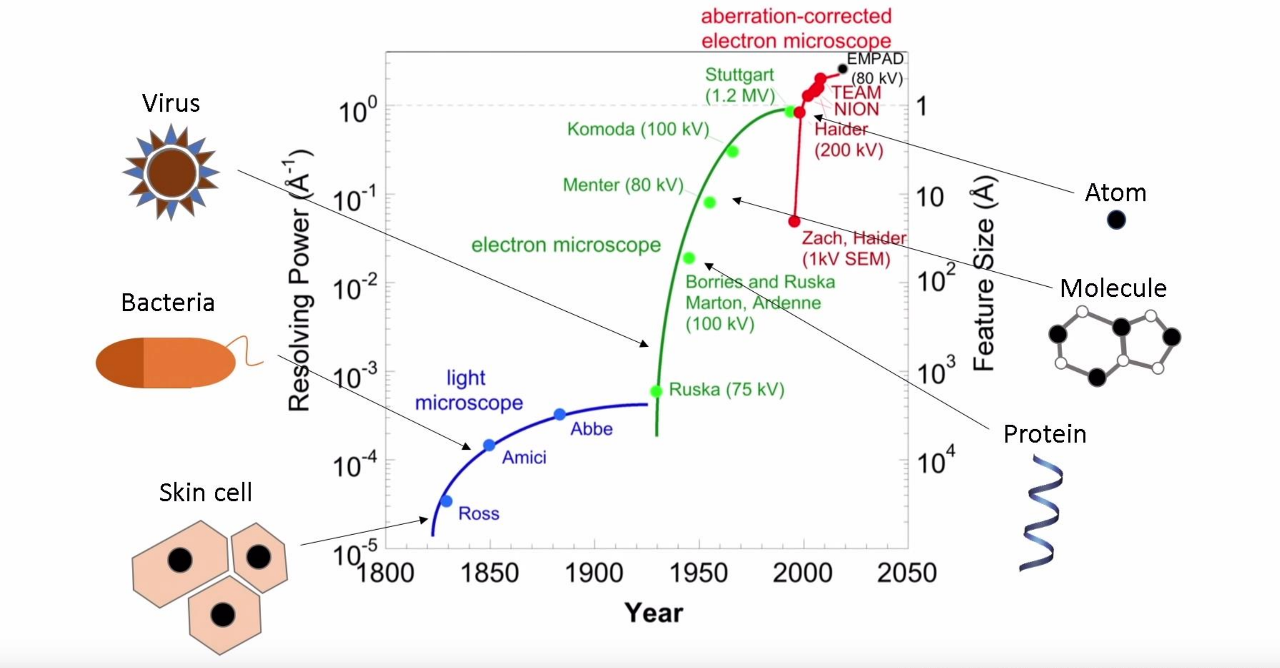


Polarized Light Microscope Optical Pathways and Components

Figure 9

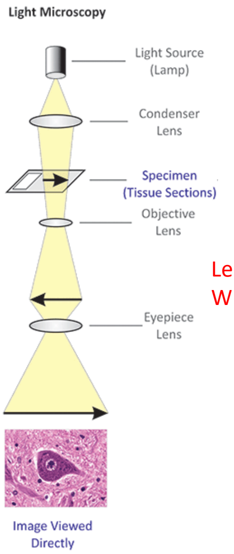
There are many microscopes at UCI

JEOL JEM-ARM300F Grand ARM



Muller, DA et al. *Nature Materials*, **8**(2009)

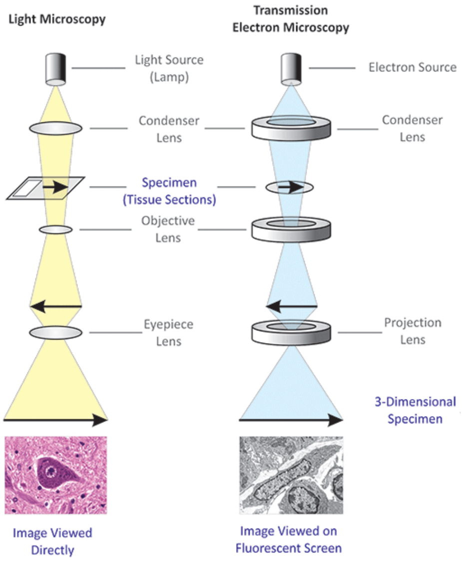
Visible light is the most common microscopy



Lenses (de)magnify beams.
What lenses did you bring to this lecture?

microbiologyinfo.com

Electron microscopy is analogous to visible-light microscopy, but with higher ***resolution***



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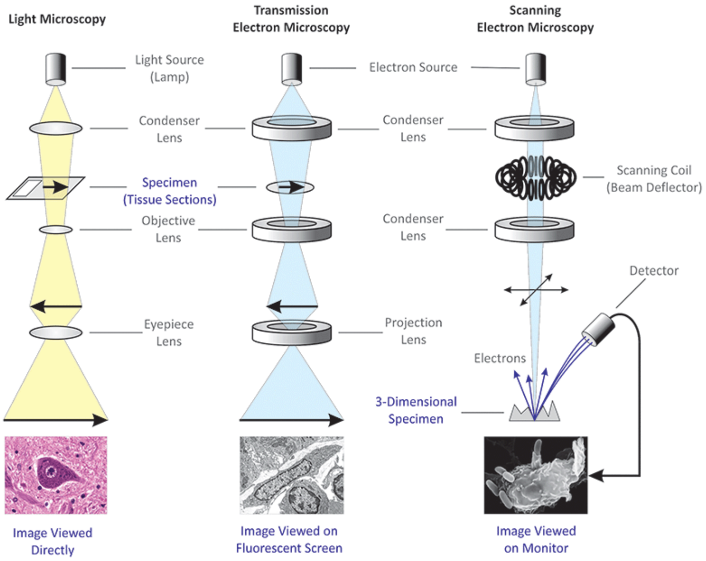

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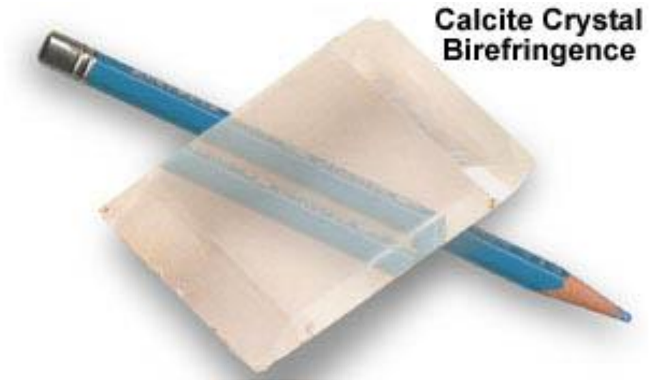
Spherulites are birefringent, or “doubly-refracting”

Anisotropic crystals with two independent refractive indices, n

B = $|n_{high} - n_{low}|$



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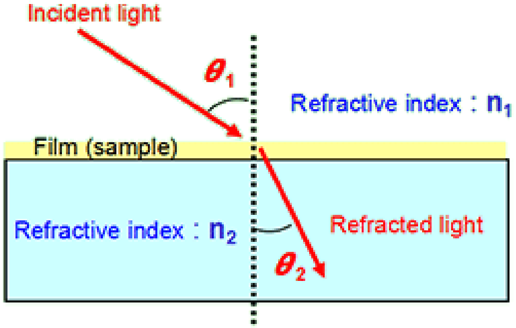
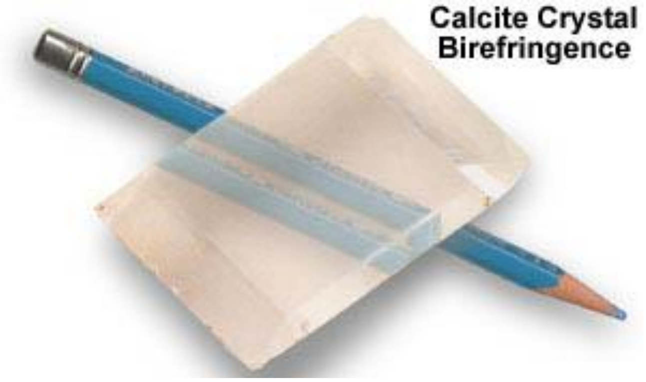
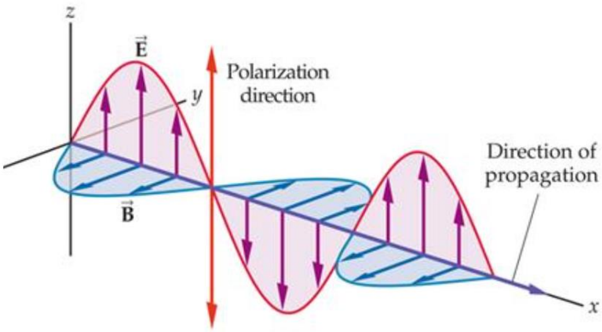


Snell's formula :

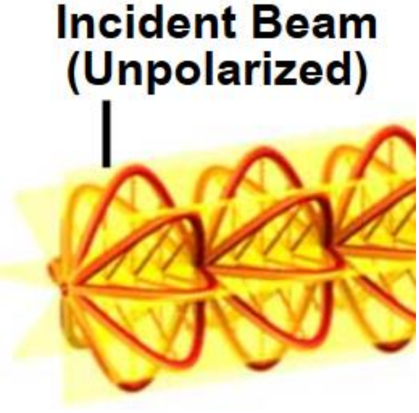
$n_1 \sin \theta_1 = n_2 \sin \theta_2$



Illumination produces light waves with electric field vectors vibrate in all planes perpendicular to the direction of propagation



This wave **is polarized** in z -direction



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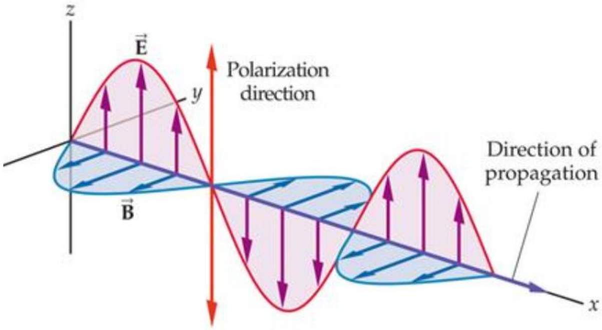
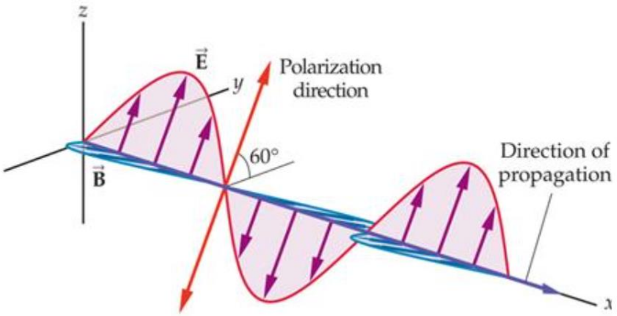
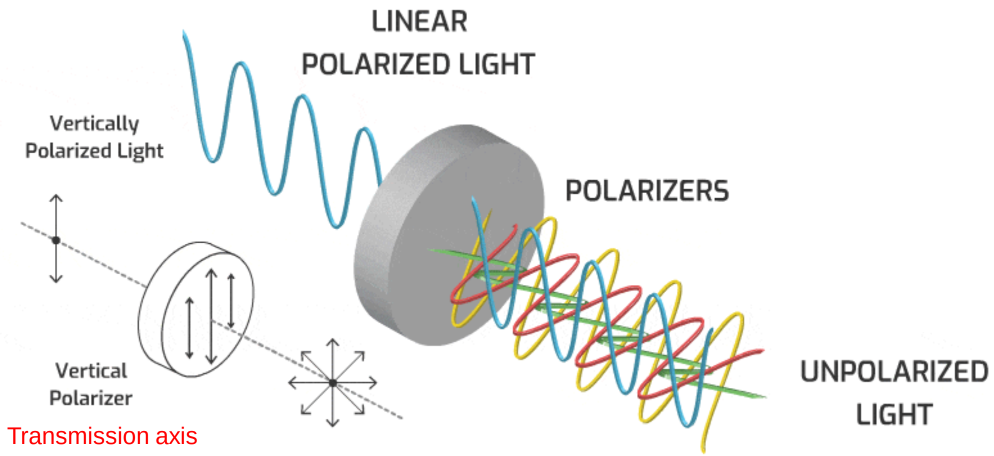


This wave **<u>is polarized</u>** in z -direction



This wave **<u>is polarized</u>** in a direction at an angle of 60° with y-axis



Transmission axis

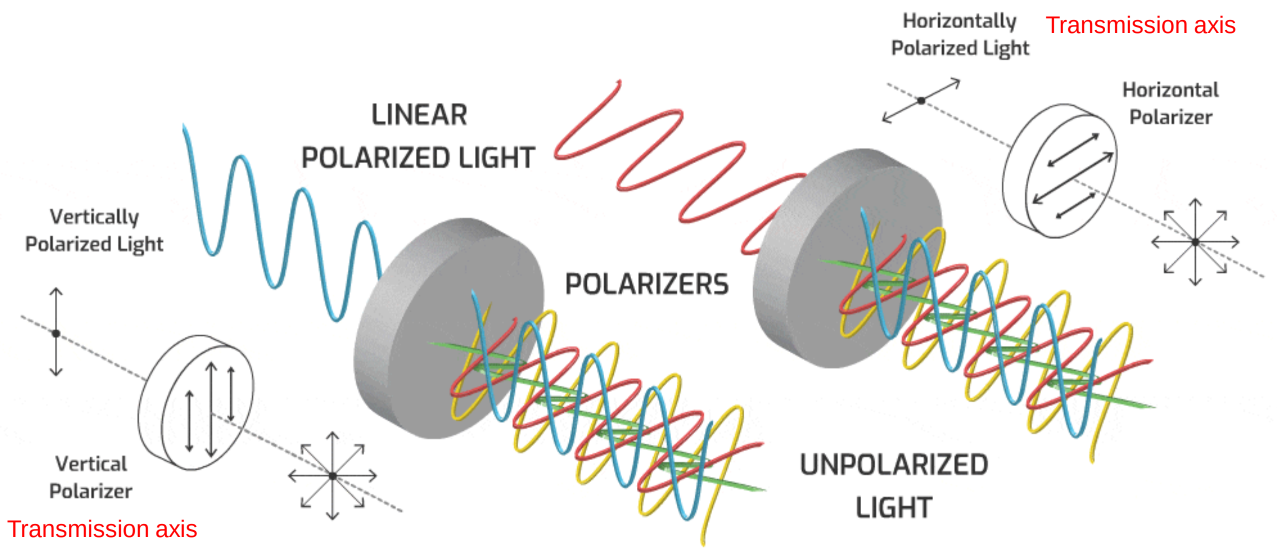
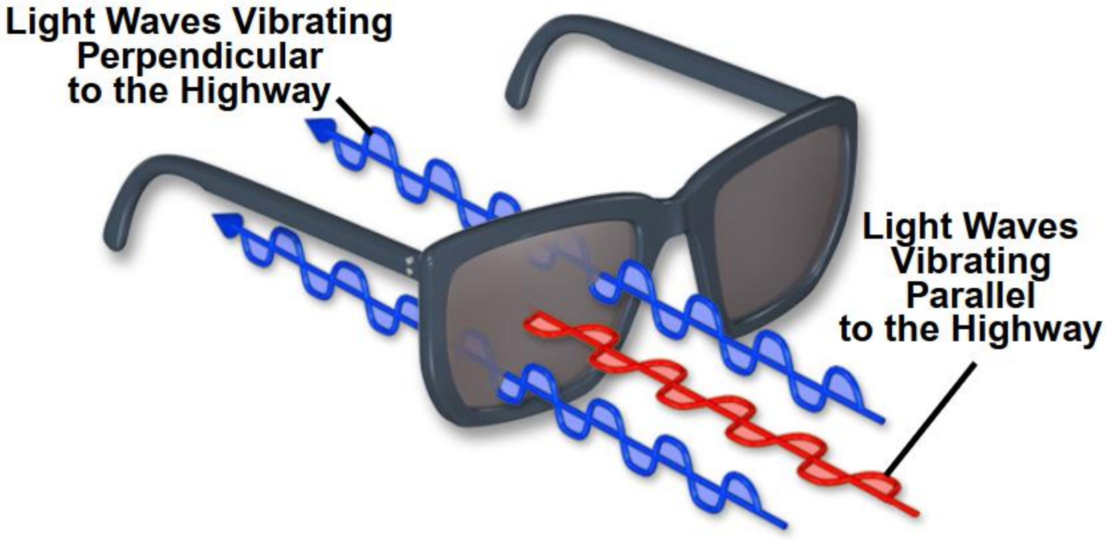
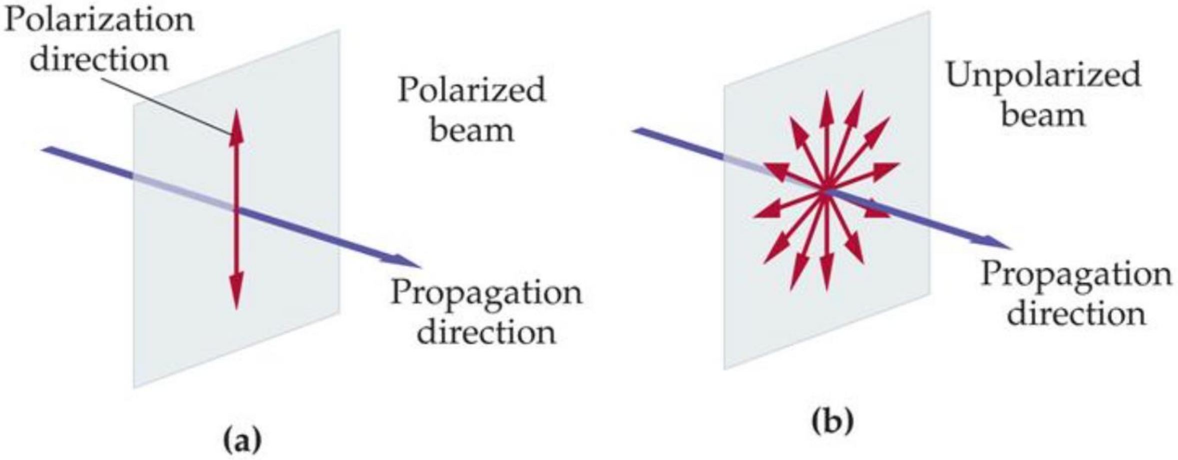
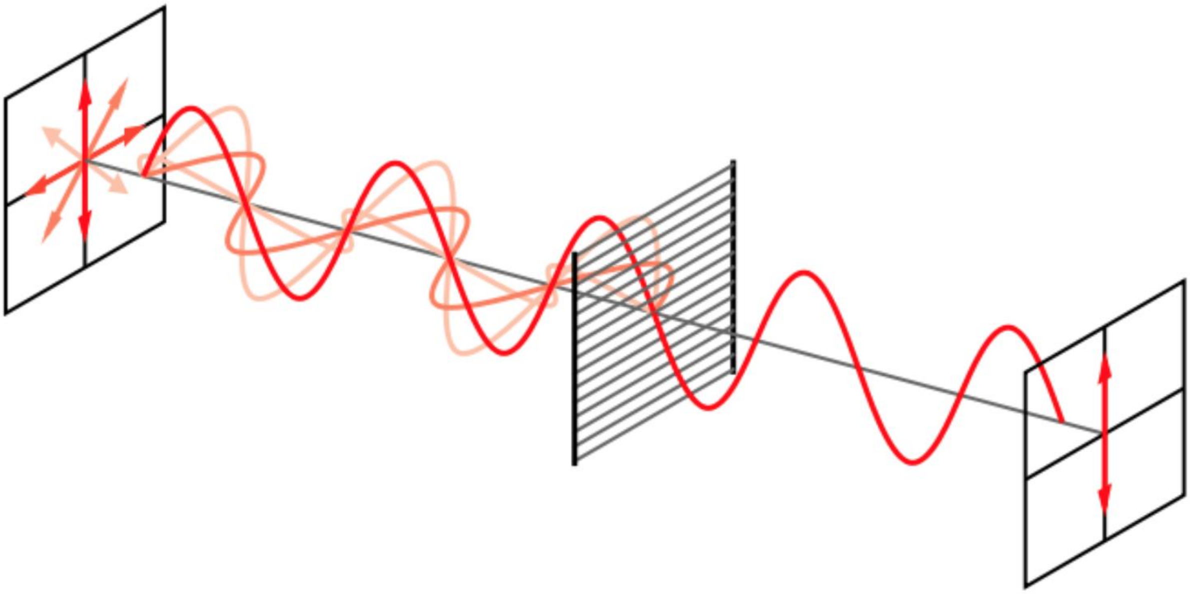


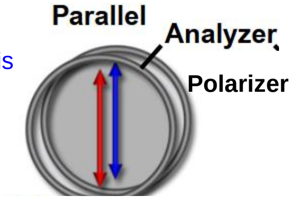
Figure 4 - Action of Polarized Sunglasses




Polarization direction
Polarized beam
Propagation direction
(a)
Unpolarized beam
Propagation direction
(b)



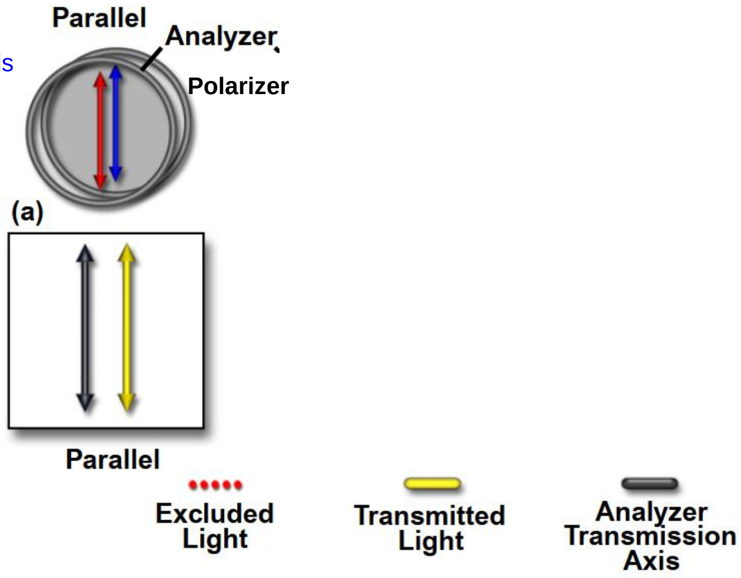
The amount of transmitted light through a pair of polarizers depends on transmission axes' orientation



Transmission axis

Transmission axis

The amount of transmitted light through a pair of polarizers depends on transmission axes' orientation

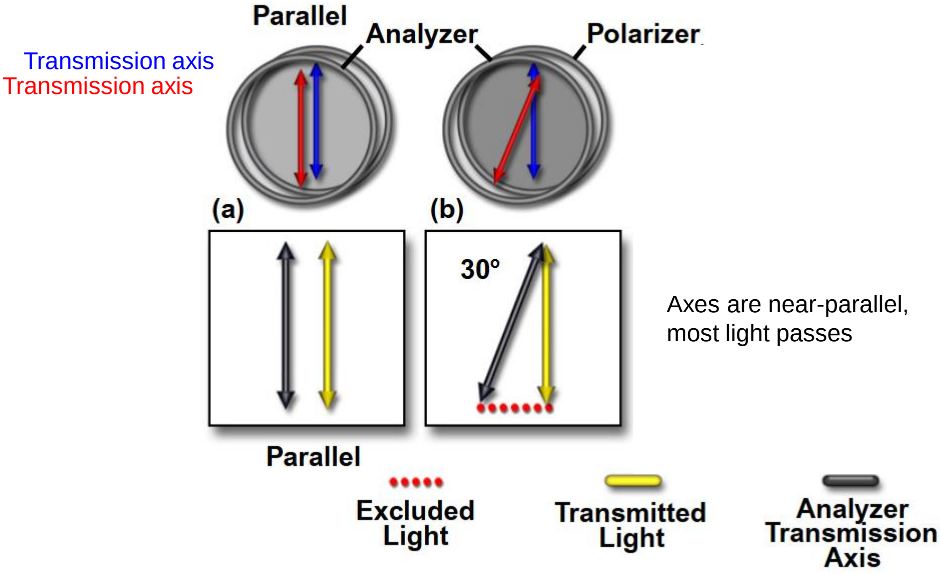


Transmission axis

Transmission axis

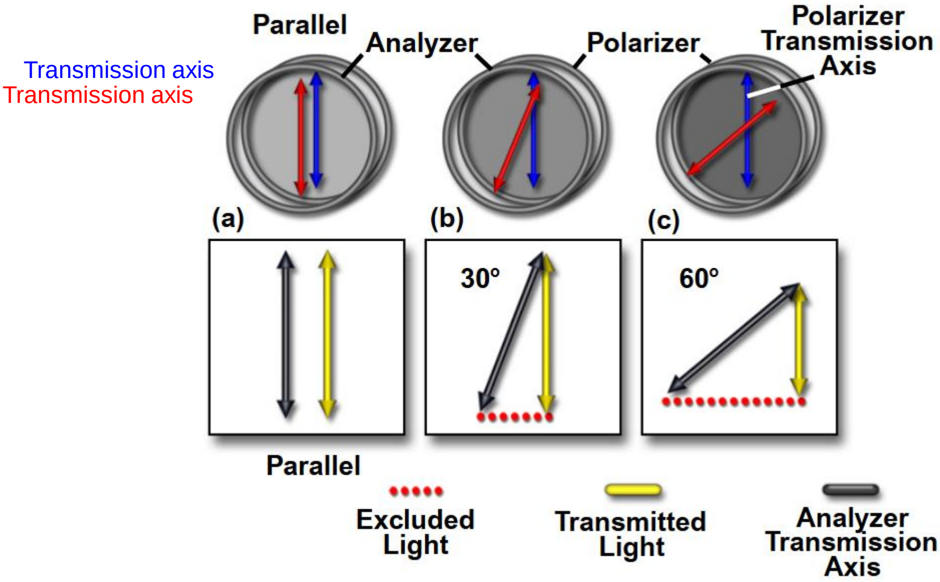
Axes are parallel, all light passes

The amount of transmitted light through a pair of polarizers depends on transmission axes’ orientation



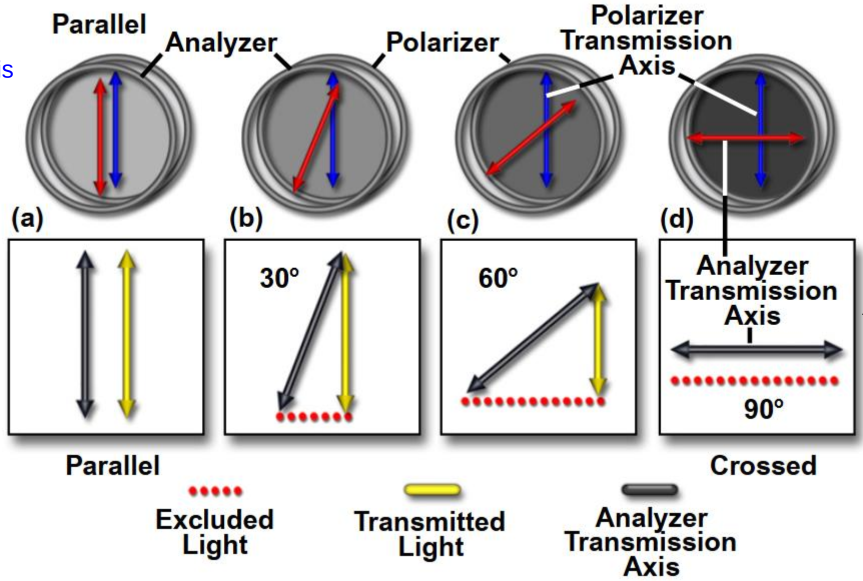
Axes are near-parallel, most light passes

The amount of transmitted light through a pair of polarizers depends on transmission axes’ orientation



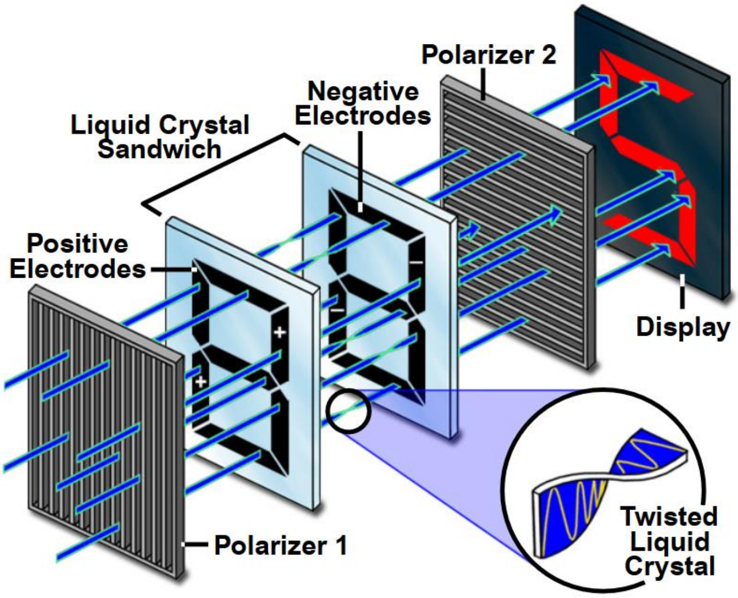
The amount of transmitted light through a pair of polarizers depends on transmission axes' orientation

Transmission axis
Transmission axis

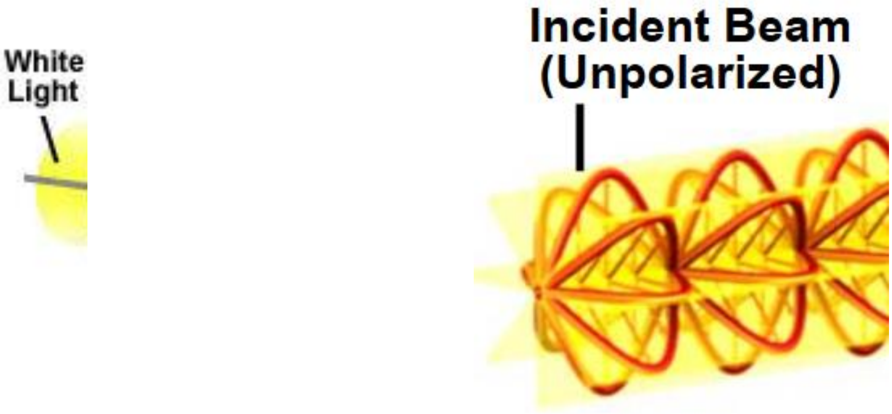


Axes perpendicular
no light passes

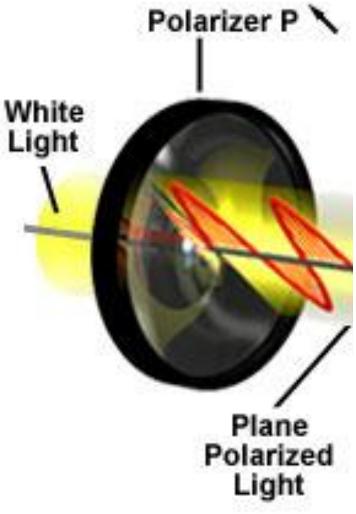
Seven-Segment Liquid Crystal Display (LCD)



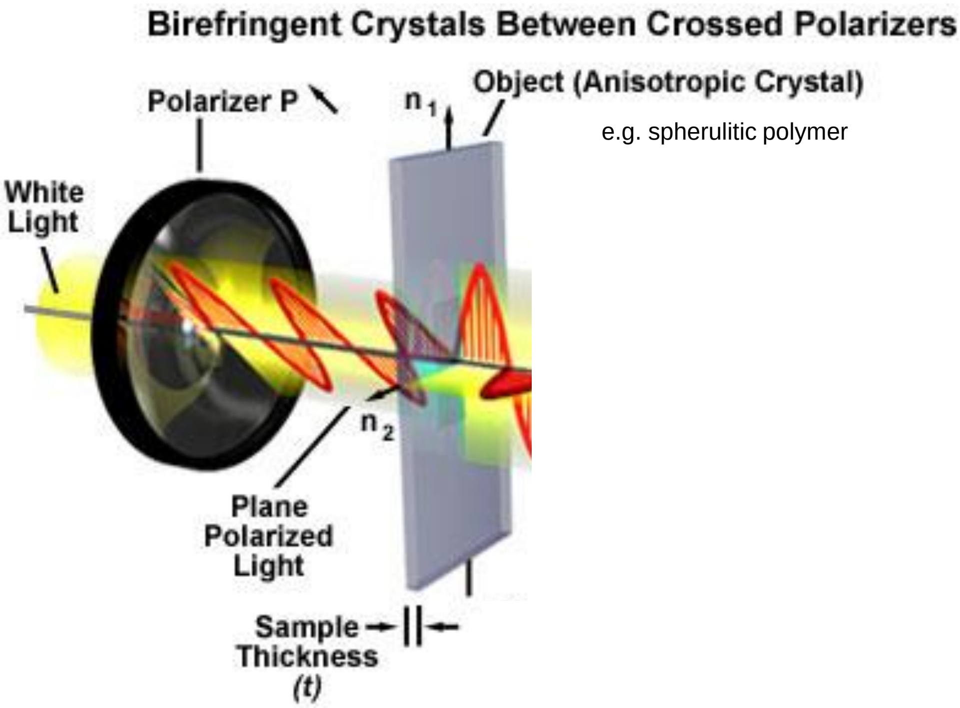
Birefringent Crystals Between Crossed Polarizers



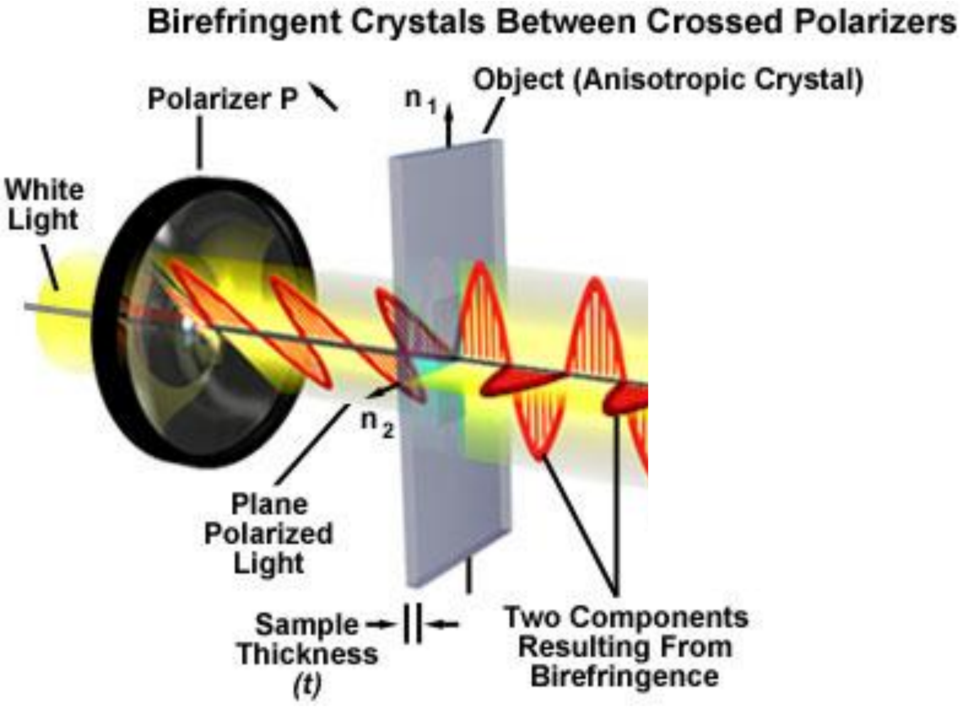
Birefringent Crystals Between Crossed Polarizers



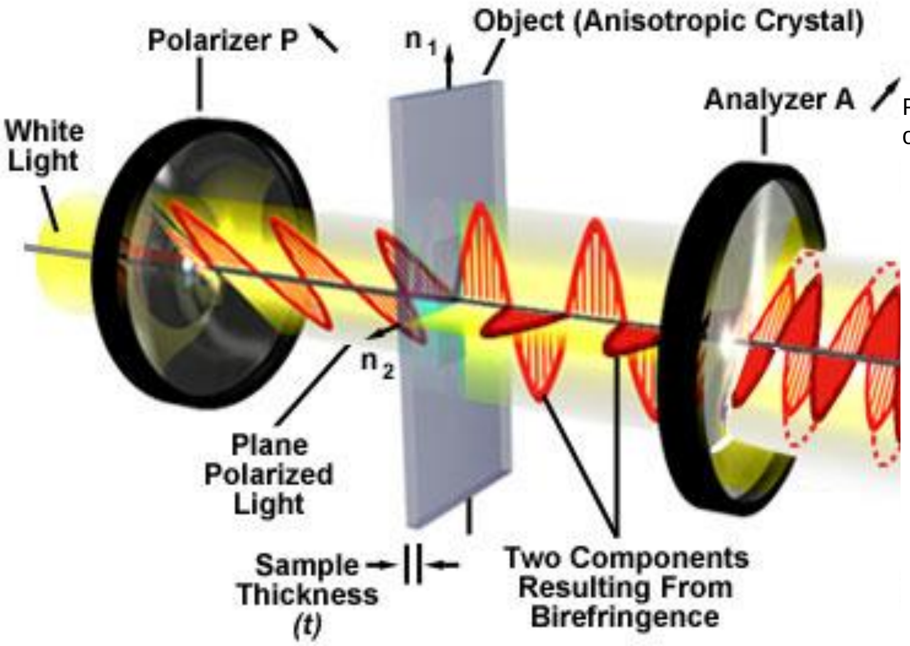
Transmission axis



e.g. spherulitic polymer

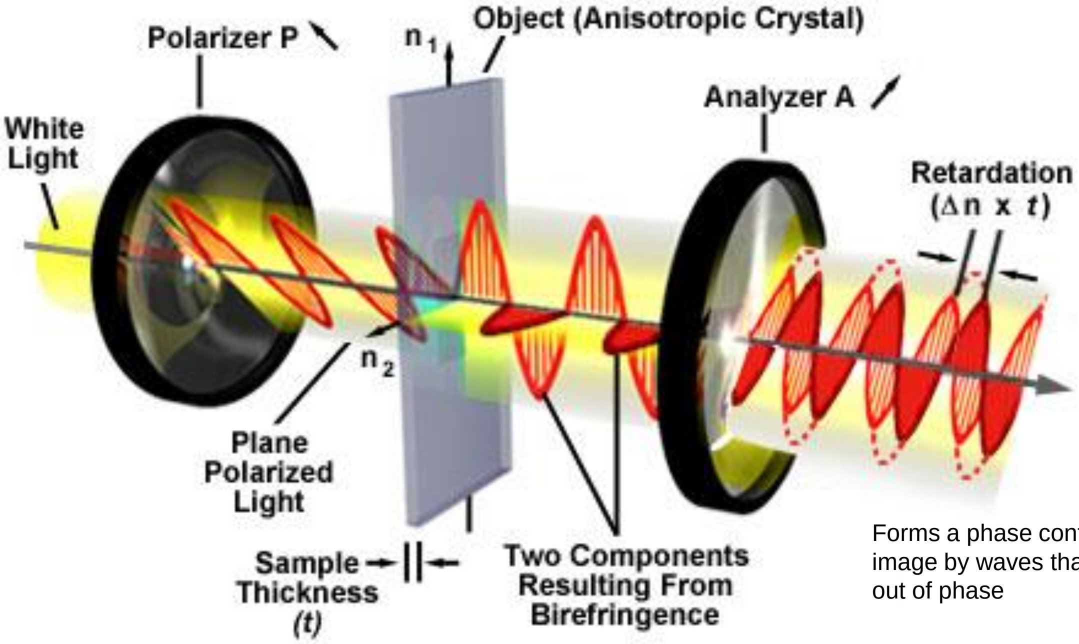


Birefringent Crystals Between Crossed Polarizers

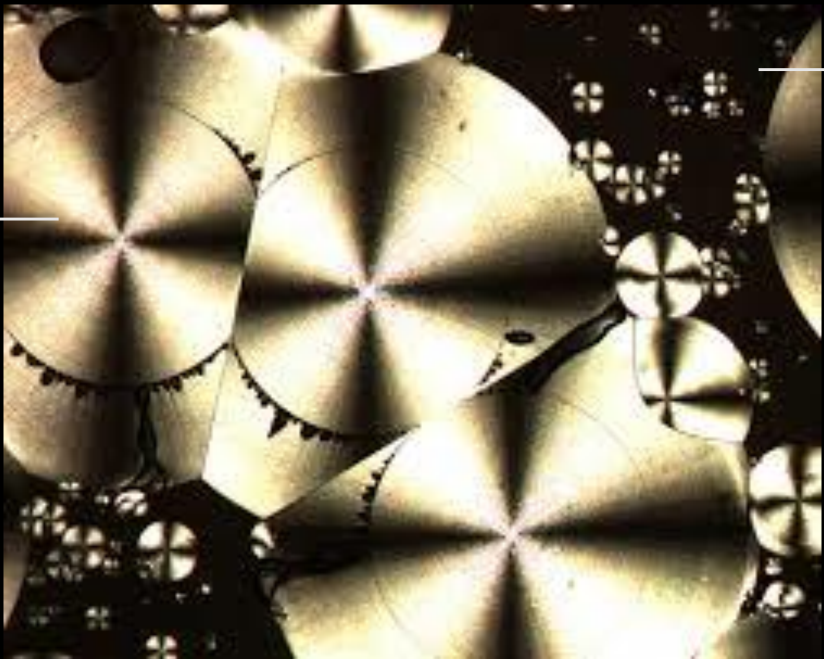


Polarizes both components of the resulting light

Birefringent Crystals Between Crossed Polarizers

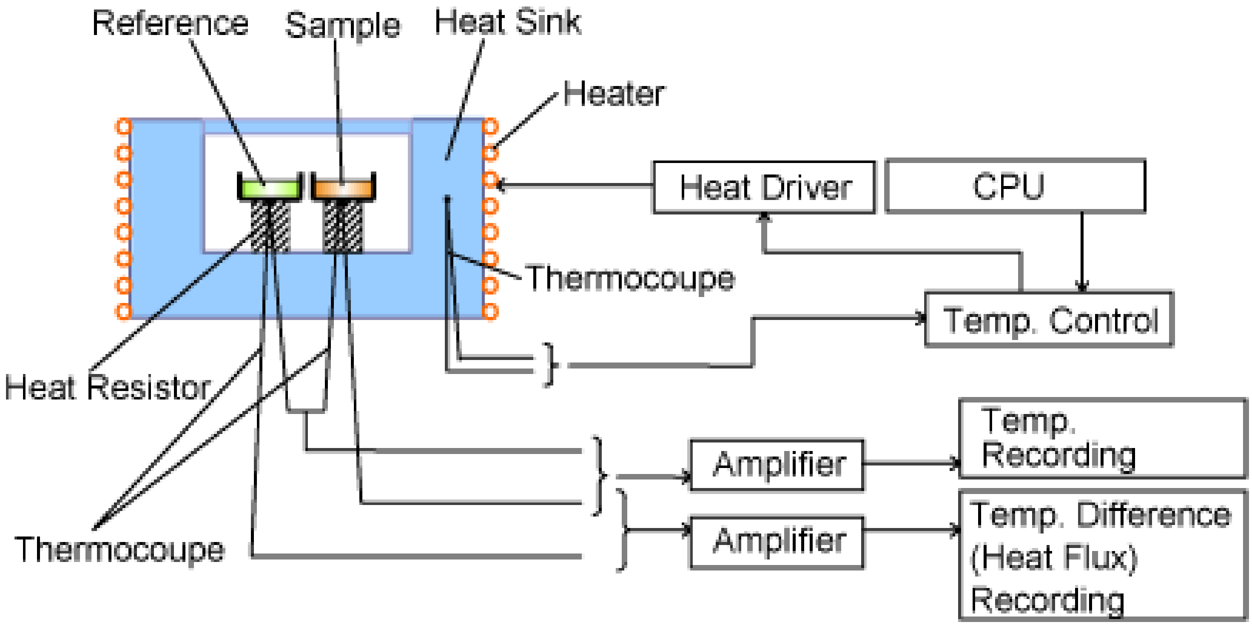


Forms a phase contrast image by waves that are out of phase



Spherulitic: Polarizer-analyzer pair transmits some illumination; sample appears dark and bright (i.e. imaged with phase contrast)

Amorphous: Polarizer-analyzer pair blocks illumination; sample appears dark



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