Thermal Transitions: Crystallization, Melting and the Glass Transition

• This lecture: Crystallization and Melting

• Next Lecture: The Glass Transition Temperature

Today:

• Why do polymers crystallize in a chain folded fashion?

• Why do polymers melt over a range of temperatures?

• What are the factors that affect the Tm?

Chapter 8 in CD (Polymer Science and Engineering)
Thermal Transitions

- Viscoelastic
- Liquid
- Semi-crystalline Solid
- Crystallization
- Melting
- Glass Transition
- Glassy Solid

Temperature
Crystallization and the Glass Transition
Kinetics, Crystallization and the Glass Transition

Volume

Temperature

Crystallizable Polymer

Non-Crystallizable Polymer

Cool Quickly

Cool Slowly

Glassy Solid

Liquid or Melt

Does not Crystallize!

Cool Quickly

T_g

T_g

T_g

T_g
Polymer Crystallization

WHAT DO WE KNOW FROM EXPERIMENTAL OBSERVATION?

- Crystallization occurs relatively slowly
- At high undercoolings
- And results in the formation of chain folded lamellae
What is undercooling?
Crystallization Kinetics

General Features

- Induction period - formation of primary nuclei
- Primary crystallization - a period of fast spherulitic growth
- Secondary crystallization - a period of slower crystallization that occurs once the spherulites have impinged on one another
Thermodynamic Considerations

The free energy of this primary nucleus is given by

\[ \Delta G_{\text{cryst}} = (4xl}\sigma + (2x^2)\sigma_e - (x^2l)\Delta g \]

- The last term represents the free energy that we would obtain if all the segments were in the bulk.
- The first two terms are the excess free energy that must be “added in” to account for those segments at the surface.
Extended Chain Crystals and Annealing

Thermodynamically most stable form

Crystals irreversibly thicken on annealing - so they would like to get to the extended form

Courtesy of I.R. Harrison, Penn State
So why don’t polymers crystallize in the extended chain form to begin with? To answer this let’s calculate the critical nucleus size.

\[ T_m = T_m^0 \]
The critical nucleus size is given by the values of \( l \) and \( x \) that minimize \( \Delta G_{\text{cryst}} \):

\[
\frac{\partial \Delta G}{\partial l} = \frac{\partial \Delta G}{\partial x} = 0
\]

Solving the two simultaneous equations

\[
l^* = \frac{4\sigma_e}{\Delta g}
\]
Critical Nucleus Size

Substituting for $\Delta g$:

$$l^* = \frac{4\sigma_e T_m^0}{\Delta h_f \Delta T}$$

where $\Delta T$ is the undercooling:

$$\Delta T = T_m^0 - T_c$$

Note the inverse dependence of fold period on $\Delta T$.

Also, at the equilibrium melting temperature, $T_c = T_m^0$, and only lamellae with infinite fold periods could grow.
The Rate of Primary Nucleation

An expression for the rate of nucleation can also be obtained:

\[ v_{\text{nuc}} \sim \exp\left( -\frac{\text{const}\cdot \sigma^2 \sigma_e [T_m^0]^2}{\Delta h_f kT_c [\Delta T]^2} \right) \]

Note that the rate of nucleation is vanishingly small at low undercoolings. Only nuclei with relatively short fold periods (compared to chain length) form at an appreciable rate.
Primary Crystallization:

- Once a nucleus has been formed, growth is predominantly in the lateral direction.
- There is a considerable increase in the fold period behind the lamellar front during crystallization from the melt.
The Crystalline Melting Temperature

Semi-crystalline Solid

Heat

Melt
Characteristics:
Melting Temperatures

- Melting is Complete
- Melting Starts
- Crystallization
The Melting Temperature of Polymer Crystals

\[ T_m = T_m^0 \left[ 1 - \frac{2\sigma_e}{l\Delta h_f} \right] \]
Factors that Affect the Melting Temperature of Polymer Crystals

Why?

\[ T_m \approx 135^0C \]

\[ T_m \approx 370^0C \]
The Effect of Chemical Structure

Equilibrium at temperature $T_m$

$T_m = \Delta H_f / \Delta S_f$

$\Delta G_f = \Delta H_f - T \Delta S_f$

And at Equilibrium

$\Delta G_f = 0$

Hence $T_m = \Delta H_f / \Delta S_f$

The subscript “f” stands for fusion.
Intermolecular Interactions

\[ \begin{align*}
\text{CH}_2 & \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \\
T_m & \sim 135^0C
\end{align*} \]

\[ \begin{align*}
\text{CH}_2 & \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{C} \text{N} \\
T_m & \sim 265^0C
\end{align*} \]

Is this nylon 6 or nylon 66?
OK, now it’s your turn!
Supposing you could synthesize such beasts, would you expect syndiotactic poly(propylene) or syndiotactic PVC to have the higher melting point?

A. \(-\text{CH}_{2}-\text{CH}-\text{Cl}\)
B. \(-\text{CH}_{2}-\text{CH}-\text{CH}_{3}\)
Entropy and Chain Flexibility

\[ T_m = \frac{\Delta H_f}{\Delta S_f} \]
Entropy and Chain Flexibility

\[ S = k \ln \Omega \]

\[ \Delta S_f = k (\ln \Omega_{\text{melt}} - \ln \Omega_{\text{crystal}}) = \text{Large} \]
Conformational Entropy and the Melting Point

\[ \Delta S_f = k \left( \ln \Omega_{\text{melt}} - \ln \Omega_{\text{crystal}} \right) = \text{Small} \]

\[ T_m = \frac{\Delta H_f}{\Delta S_f} \]
Entropy and the Melting Point

- **Polyethylene**
  - CH₂ - CH₂ -
  \[ T_m \sim 135^0C \]

- **Poly (ethylene oxide)**
  - CH₂ - CH₂ - O -
  \[ T_m \sim 65^0C \]

- **Poly (p-xylene)**
  - CH₂ - CH₂ -
  \[ T_m \sim 400^0C \]
Entropy and the Melting Point

- CH$_2$ - CH$_2$ -
  Polyethylene  $T_m \sim 135^0C$

- CH$_2$ - CH -
  CH$_3$
  Isotactic Polypropylene  $T_m \sim ?$

- CH$_2$ - CH -
  Isotactic Polystyrene  $T_m \sim ?$
The Effect of Diluents

\[ \Delta S_2 > \Delta S_1 \]
The Effect of Copolymerization and Molecular Weight