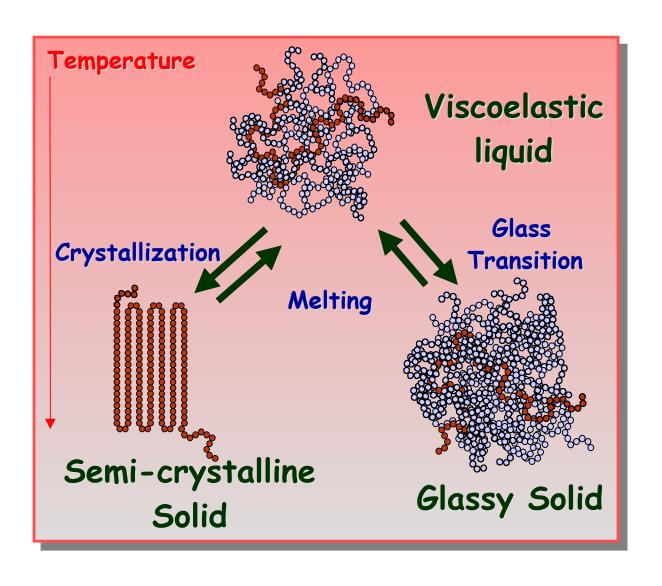
Thermal Transitions: Crystallization, Melting and the Glass Transition

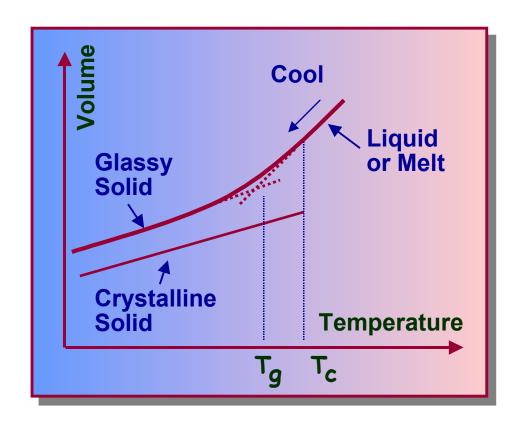
- This lecture: Crystallization and Melting
- Next Lecture: The Glass Transition Temperature Today:
 - Why do polymers crystallize in a chain folded fashion?
 - Why do polymers melt over a range of temperatures?
 - What are the factors that affect the Tm?

Chapter 8 in CD (Polymer Science and Engineering)

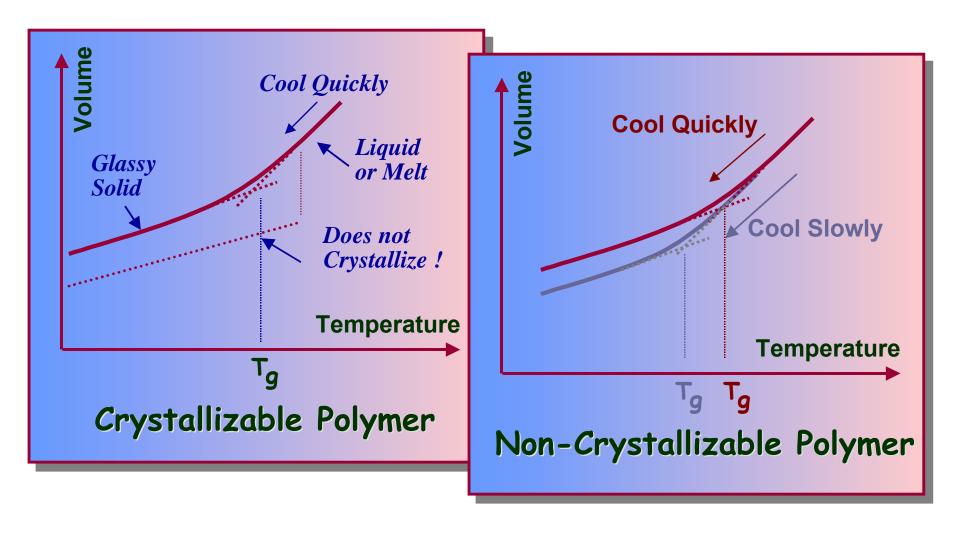
Thermal Transitions



Crystallization and the Glass Transition



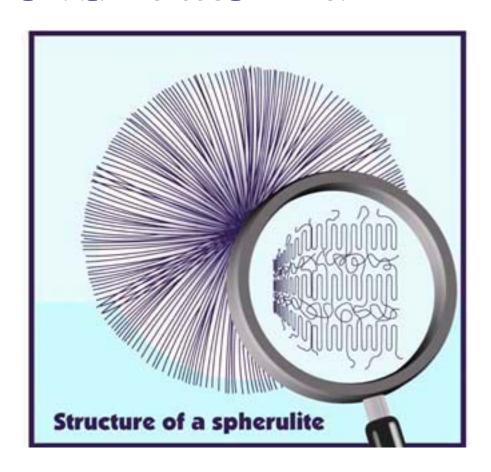
Kinetics, Crystallization and the Glass Transition



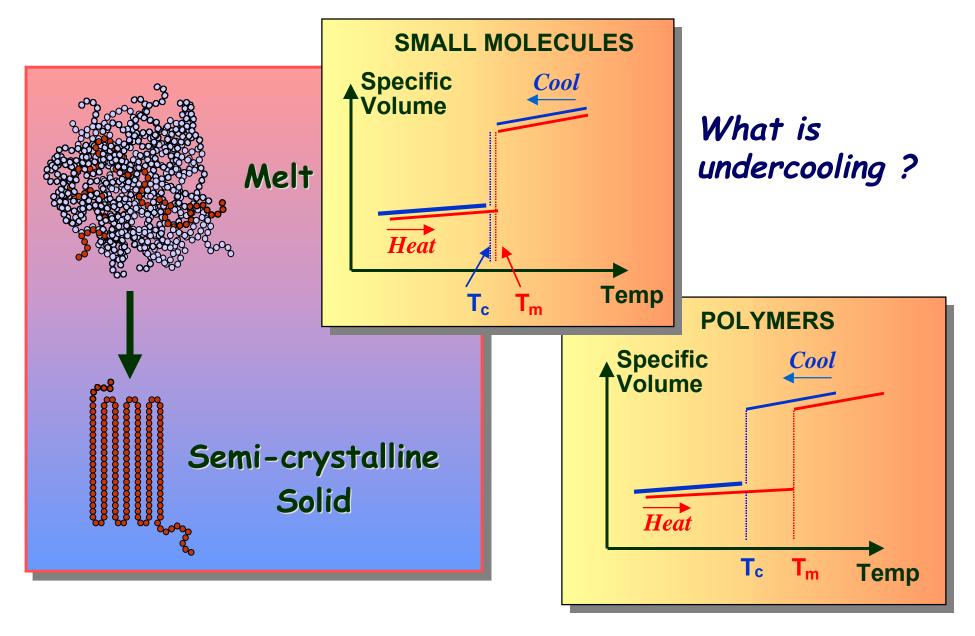
Polymer Crystallization

WHAT DO WE KNOW FROM EXPERIMENTAL OBSERVATION?

- Crystallization occurs relatively slowly
- At high undercoolings
- And results in the formation of chain folded lamellae

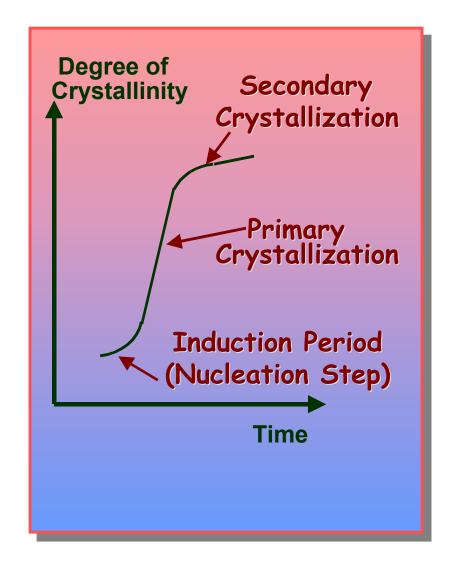


Polymer Crystallization



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

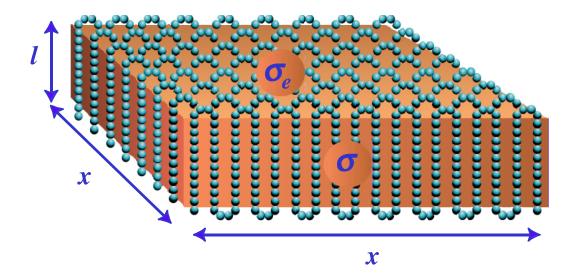


Thermodynamic Considerations

The free energy of this primary nucleus is given by

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

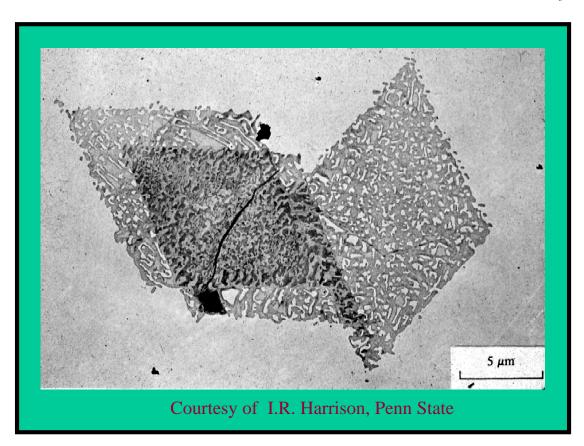
- The last term represents the free energy that we would obtain if all the segments were in the bulk.
- The first two terms are the excess free energy that must be "added in" to account for those segments at the surface.



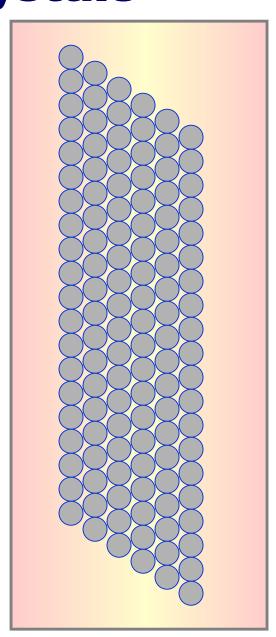
Extended Chain Crystals

and Annealing

Thermodynamically most stable form

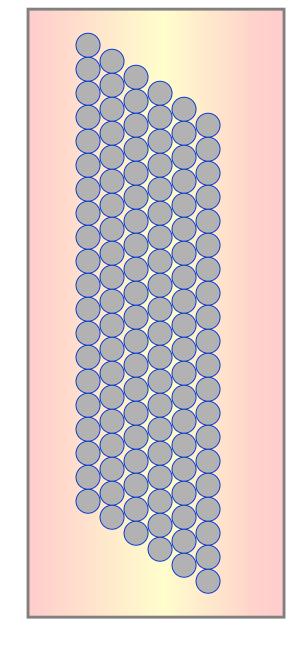






Critical Nucleus Size

So why don't polymers crystallize in the extended chain form to begin with? To answer this let's calculate the critical nucleus size.



$$T_m = T_m^0$$

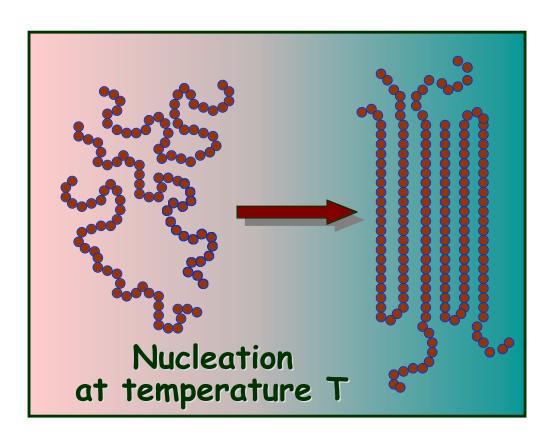
Critical Nucleus Size

The critical nucleus size is given by the values of I and x that minimize ΔG_{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

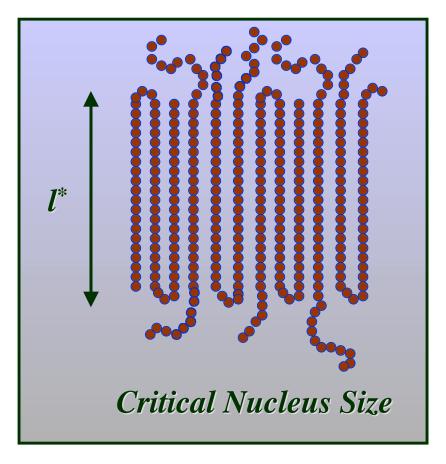
Substituting for Δg ;

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

where ΔT is the undercooling;

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

Note the inverse dependence of fold period on ΔT .



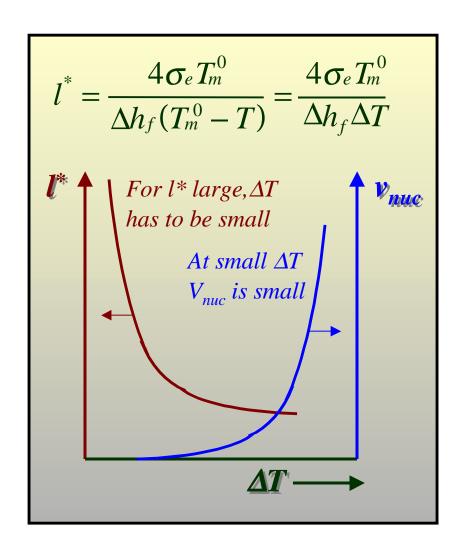
Also, at the equilibrium melting temperature, $T_c = T_m^0$, and only lamellae with infinite fold periods could grow.

The Rate of Primary Nucleation

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

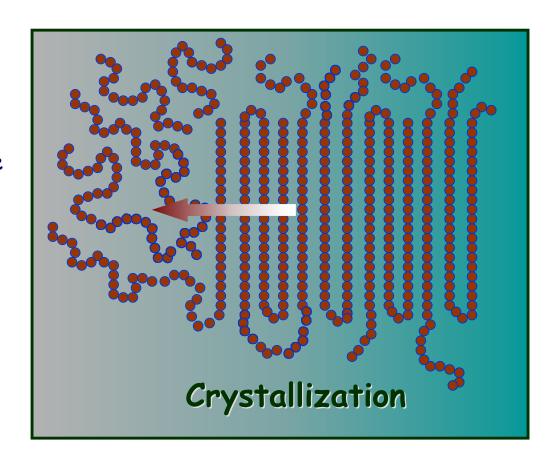
$$V_{nuc} \sim \exp{-\frac{const.\sigma^2\sigma_e[T_m^0]^2}{\Delta h_f^2 k T_c[\Delta T]^2}}$$

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.

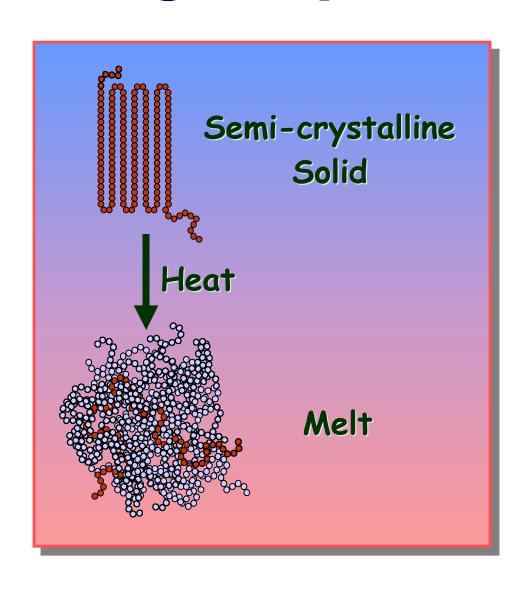


Primary Crystallization:

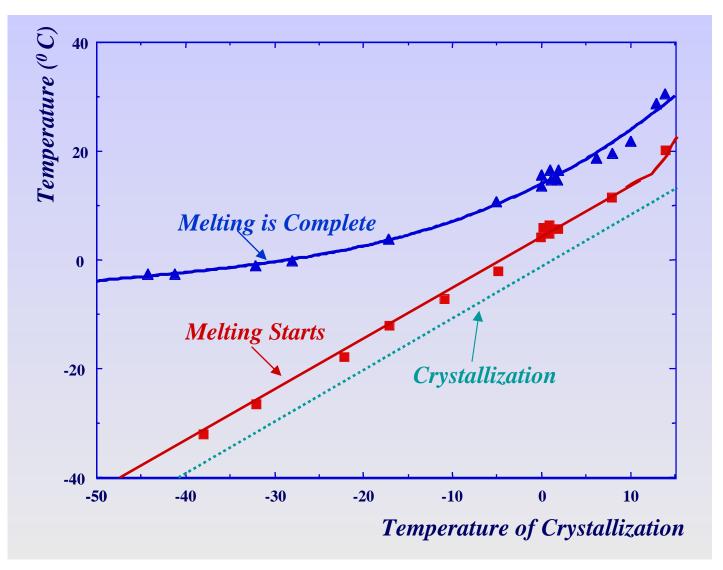
- Once a nucleus has been formed growth is predominantly in the lateral direction.
- There is a considerable increase in the fold period behind the lamellar front during crystallization from the melt



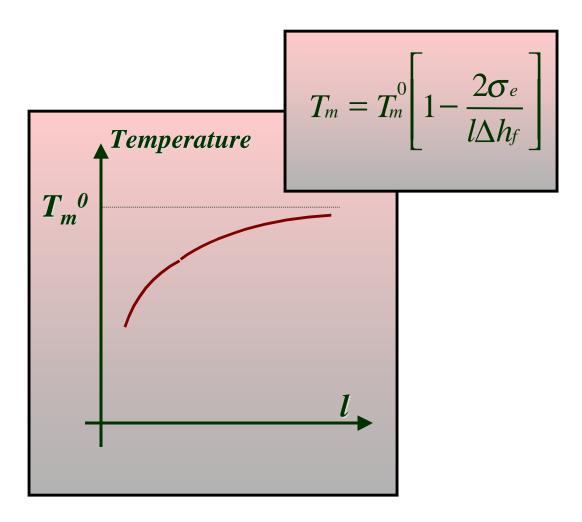
The Crystalline Melting Temperature



Characteristics: Melting Temperatures



The Melting Temperature of Polymer Crystals

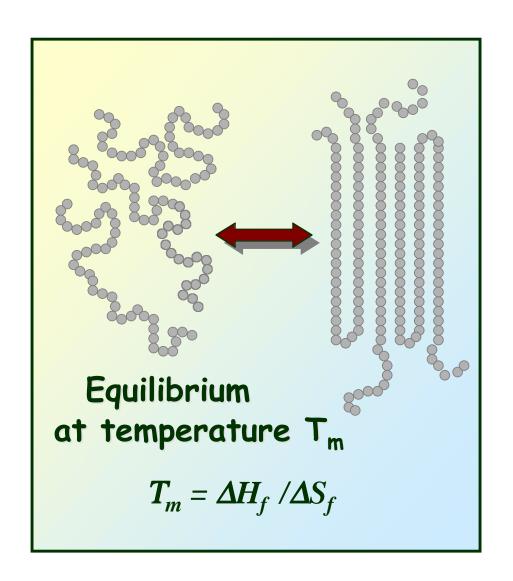


Factors that Affect the Melting Temperature of Polymer Crystals

$$CH_2$$
, CH_2

Why?

The Effect of Chemical Structure



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

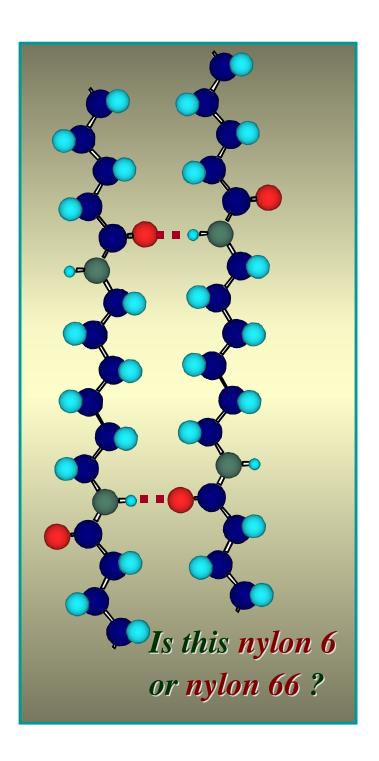
And at Equilibrium

 $\Delta G_f = 0$

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

Intermolecular Interactions

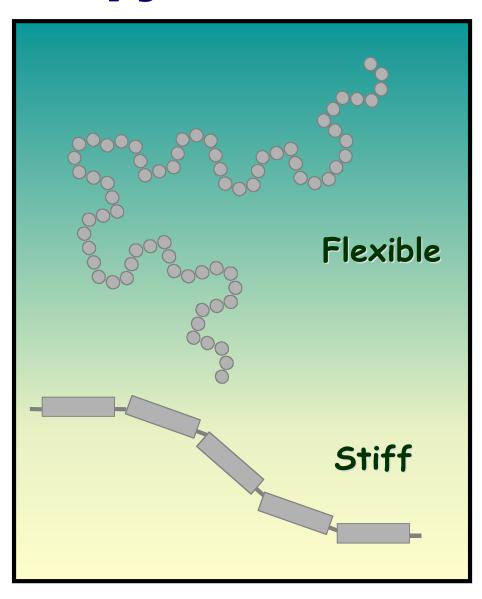
$$CH_{2}$$
, CH_{2} , $CH_{$



The Effect of Intermolecular Interactions

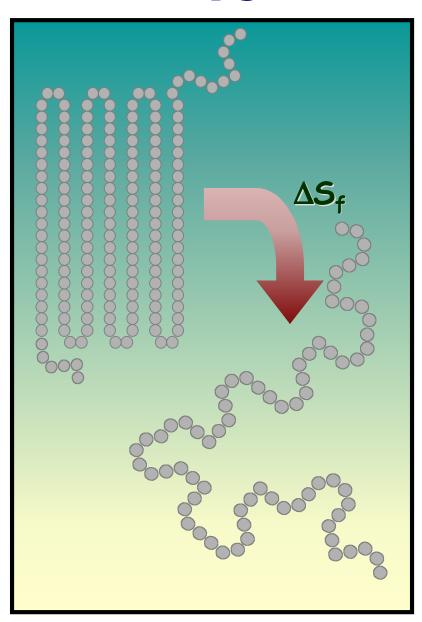
OK, now it's your turn!
Supposing you could synthesize such beasts, would you expect syndiotactic poly(propylene) or syndiotactic PVC to have the higher melting point?

Entropy and Chain Flexibility



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

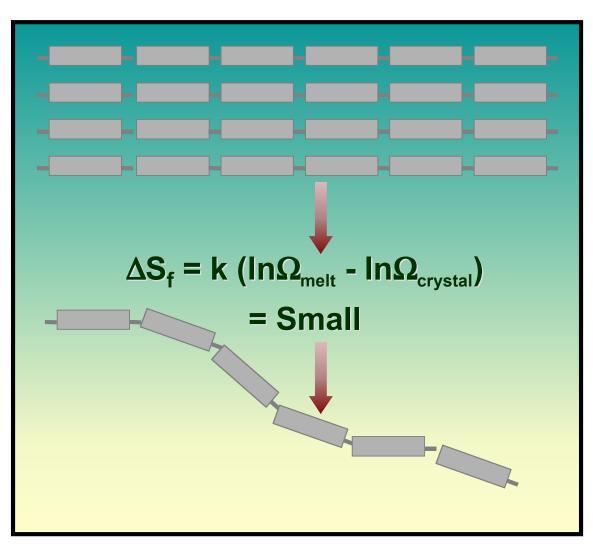
Entropy and Chain Flexibility



$$S = k \ln \Omega$$

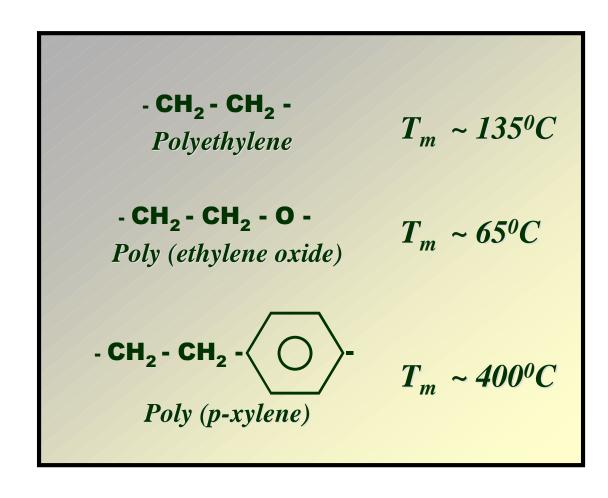
$$\Delta S_f = k \left(ln \Omega_{melt} - ln \Omega_{crystal} \right) = Large$$

Conformational Entropy and the Melting Point

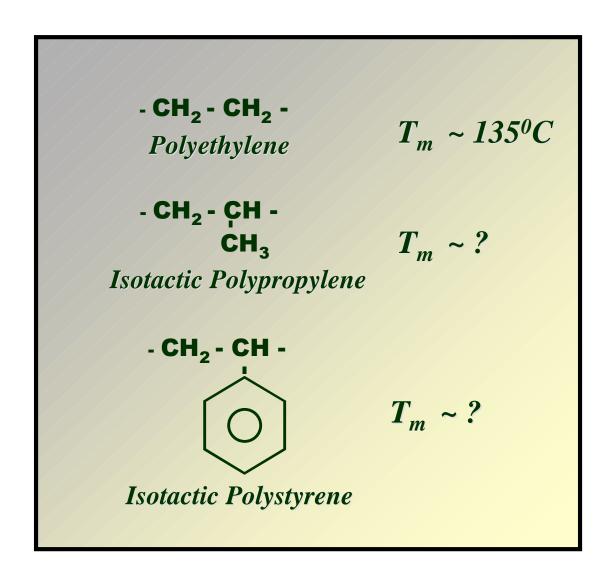


$$T_{\rm m} = \Delta H_{\rm f} / \Delta S_{\rm f}$$

Entropy and the Melting Point



Entropy and the Melting Point



$\Delta S_2 > \Delta S_1$

The Effect of Diluents

The Effect of Copolymerization and Molecular Weight

