

**Chemical Engineering 160/260**  
**Polymer Science and Engineering**

**Lecture 17: Kinetics and  
Thermodynamics of Crystallization**

**February 26, 2001**

*Sperling, Chapter 6*

# Objectives

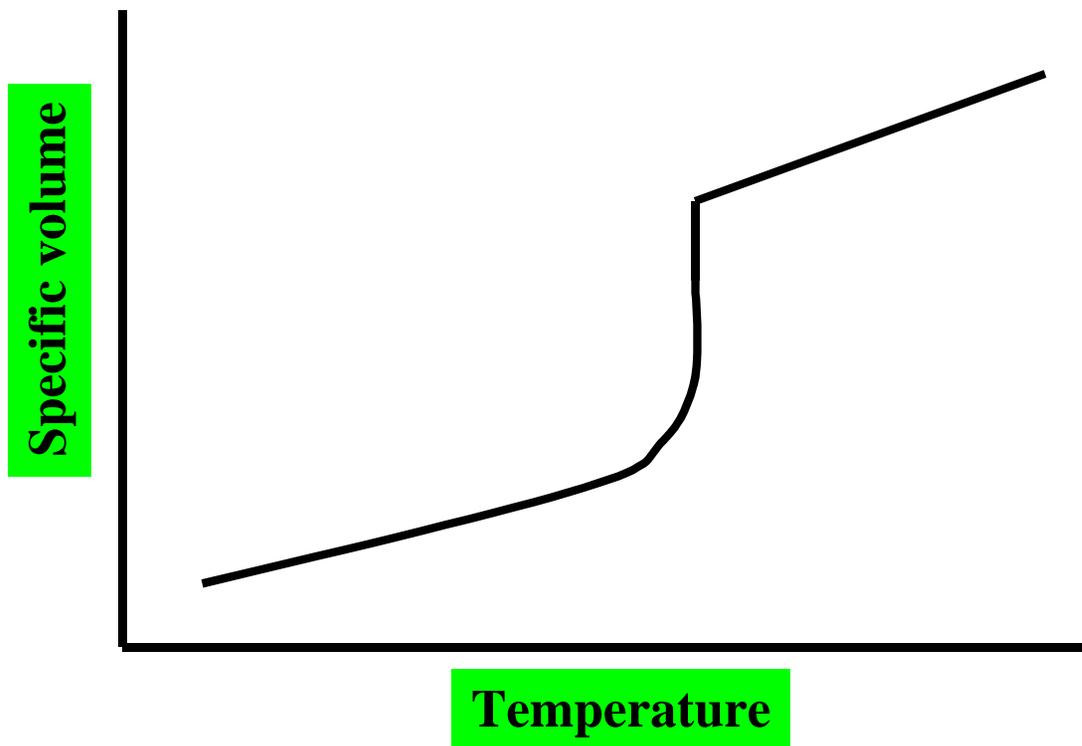
- To rationalize the observed morphology of semicrystalline polymers in terms of kinetic and thermodynamic considerations.
- To illustrate the relationship between molecular structure and morphology for a new class of polyolefins prepared with metallocene catalysts.

# Outline

- Degree of crystallinity
  - Dilatometric measurements
  - Melting point depression
- Radial growth rate and the Avrami Equation
- Spherulitic growth morphology
  - Effect of impurities
  - Effect of temperature
  - Model of Keith and Padden
- Structure-property relationships for polyolefins prepared with single site catalysts

# Experimental Observations of Crystallization Behavior

The specific volume decreases sharply upon melting.



*Due to more efficient packing, the crystalline regions will have a lower specific volume than the amorphous.*

# Measurement of Degree of Crystallinity

## Specific volume

Assume that the specific volumes of the crystalline and amorphous phases are additive.

$$V_{sp} = \theta V_c + (1 - \theta) V_a$$

$V_{sp}$  = specific volume of partially crystalline polymer

$V_a, V_c$  = specific volumes of purely amorphous and purely crystalline regions

$\theta$  = weight fraction of crystalline phase (degree of crystallinity)

$$\theta = \frac{V_a - V_{sp}}{V_a - V_c} = \frac{\frac{1}{\rho_a} - \frac{1}{\rho_{sp}}}{\frac{1}{\rho_a} - \frac{1}{\rho_c}}$$

$V_c$  may be determined from unit cell geometry using x-ray data.

If the glass transition is higher than the temperature at which  $\theta$  is measured,  $V_a$  may be obtained by rapid quenching of the melt.

# Melting Point Depression

## Due to presence of noncrystallizable monomer

$$\frac{1}{T_f} - \frac{1}{T_f^0} = \frac{R}{\Delta H_f} X_B$$

$X_B$  = mole fraction of noncrystallizable comonomer “impurity”

$\Delta H_f$  = heat of fusion per mole of crystalline mers

## Due to presence of chain ends

$$\frac{1}{T_f} - \frac{1}{T_f^0} = \frac{R}{\Delta H_f} \frac{2M_0}{M_n}$$

$M_0$  = molecular weight of end mer

$M_n$  = molecular weight of polymer

## Due to presence of solvent or plasticizer

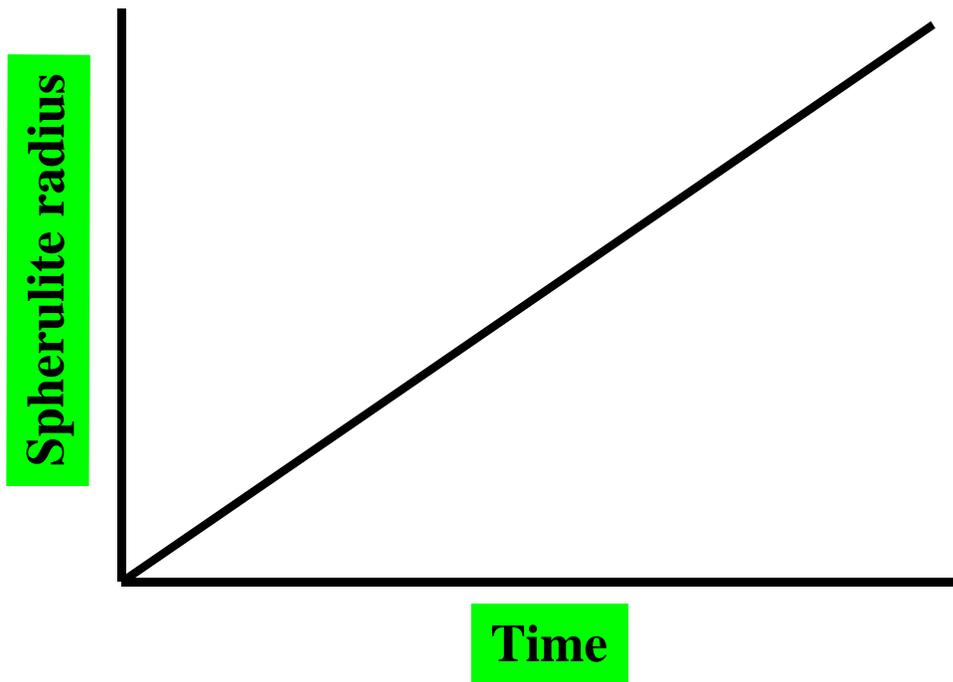
$$\frac{1}{T_f} - \frac{1}{T_f^0} = \frac{R}{\Delta H_f} \frac{V_u}{V_1} (v_1 - \chi_1 v_1^2)$$

$v_1$  = volume fraction of diluent

$$\chi_1 = \frac{(\delta_1 - \delta_2)^2 V_1}{RT}$$

# Experimental Observations of Crystallization Behavior

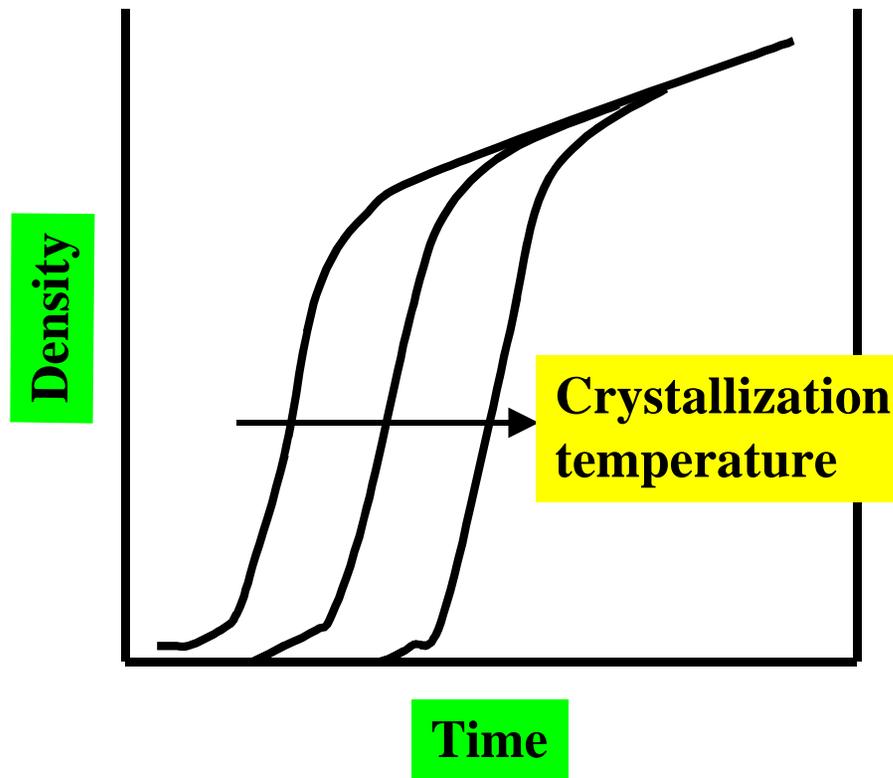
The spherulite radius increases linearly with time for isothermal crystallization.



*Linear growth rates occur except when spherulites are near impingement.*

# Experimental Observations of Crystallization Behavior

The sample density increases in a sigmoidal fashion with time.



# Avrami Equation

This phenomenological model applies to the bulk crystallization rate of a supercooled melt with spherically symmetric growth.

## Assumptions

- All nuclei are randomly distributed.
- The spherulites do not interact (valid only in the early stages).
- The rate of radial expansion is uniform.
- The density of the spherulite is independent of the radius.

$$\theta = \theta_{\infty} \left[ 1 - \exp(-Kt^n) \right]$$

$\theta$  = weight fraction of crystalline material at time  $t$

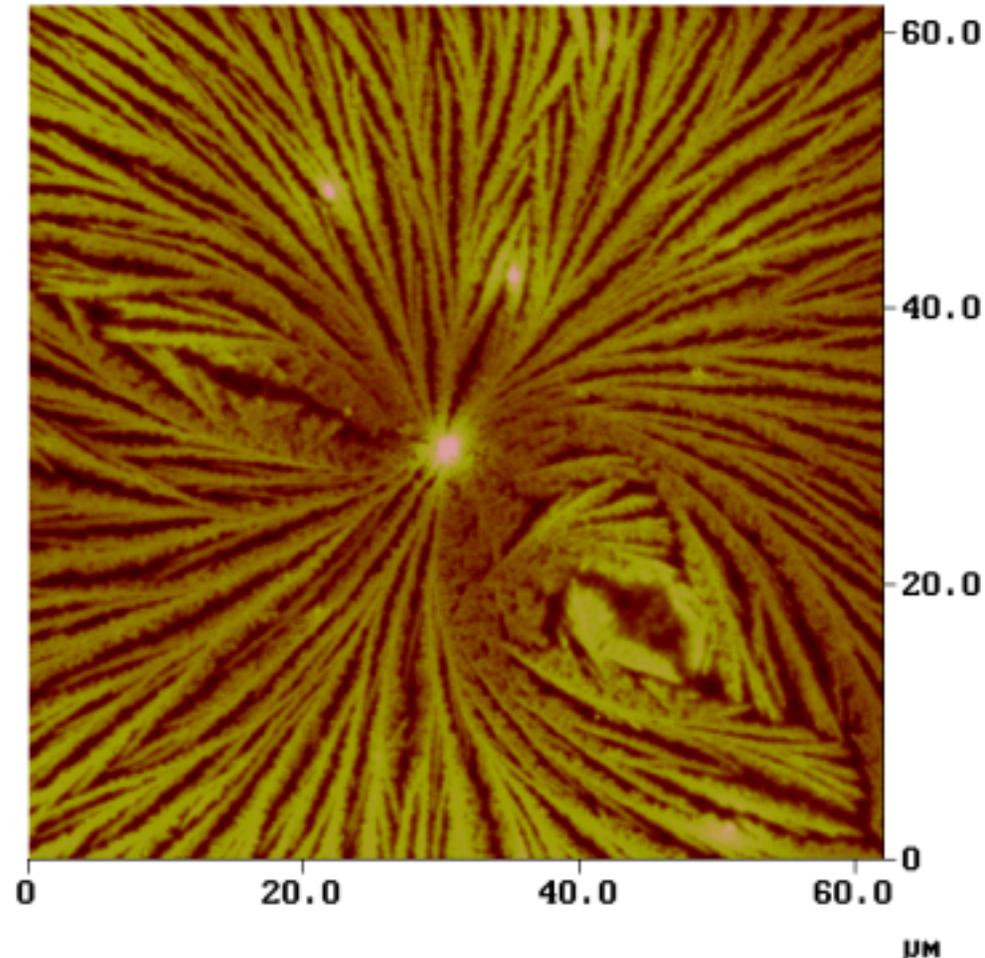
$\theta_{\infty}$  = weight fraction of crystalline material at equilibrium

$K$  = constant containing nucleation and growth parameters

$n$  = integral valued constant, which depends on the mechanism of nucleation and the form of crystal growth

**$n$  is usually in the range of 2.0 to 4.0**

# Spherulitic Growth of Fibrils



Tapping Mode Atomic Force Microscopy: Height image of elastomeric polypropylene crystallized isothermally at 130°C in a 200 nm thin film on Si (z scale from dark to bright 200 nm).

# Experimental Observations of Crystallization Behavior

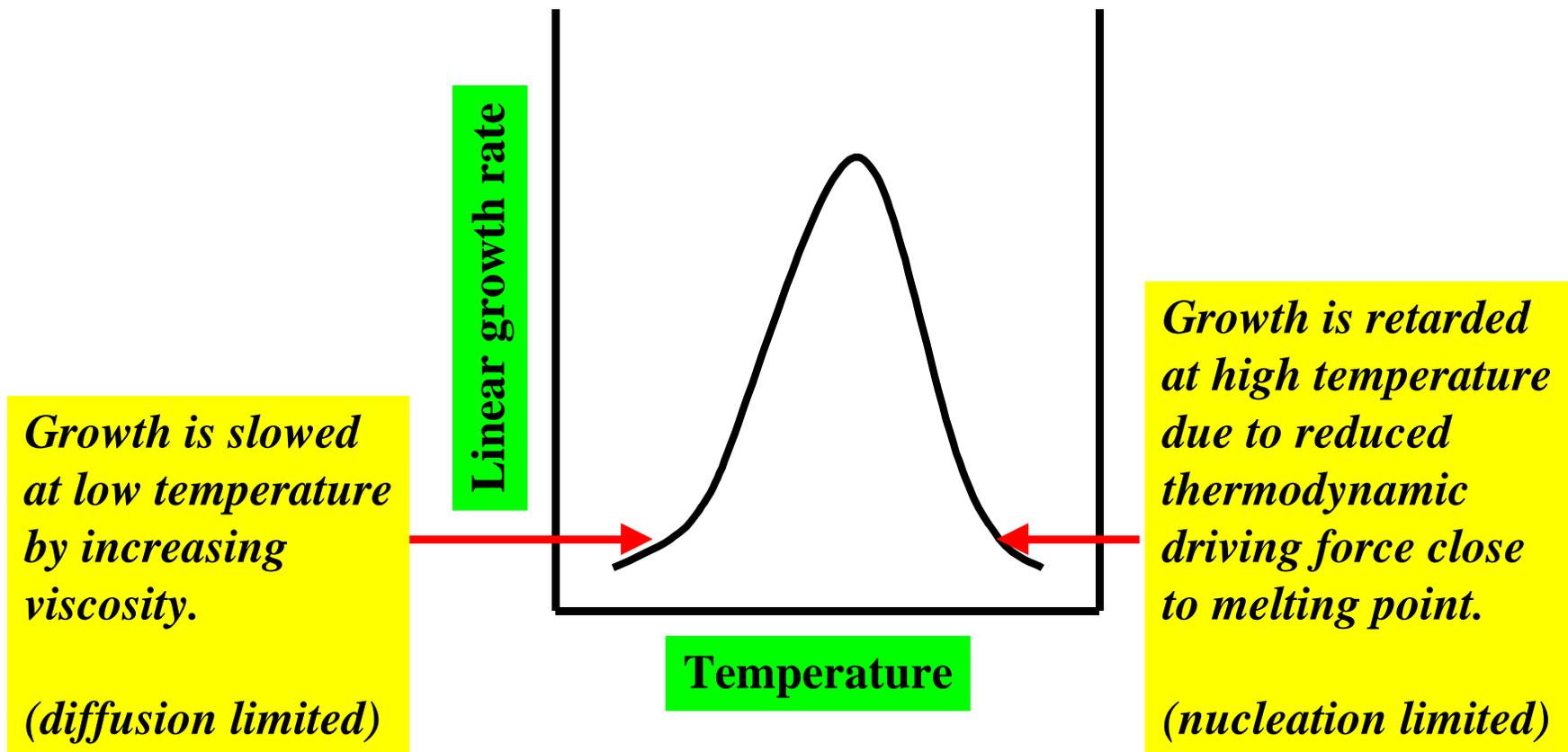
Radial growth rates are retarded by impurities.

Temperature, °C	Radial growth rates of mixtures of isotactic and atactic polypropylene (micron/min)				
	100%	90%	80%	60%	40% isotactic
120	29.4	29.4	26.4	22.8	21.2
125	13.0	12.0	11.0	8.90	8.57
131	3.88	3.60	3.03	2.37	2.40
135	1.63	1.57	1.35	1.18	1.12
Melting point, °C	171	169	167	165	162

Data from L.H. Sperling, Introduction to Physical Polymer Science, 2nd Ed., Table 6.3, p 231.

# Experimental Observations of Crystallization Behavior

The spherulite linear growth rate goes through a maximum with increasing temperature.



# Nucleation Mechanisms for Bulk Crystallization

## Homogeneous (sporadic)

- Chance collisional encounters of molecules of suitable orientation
- For polyethylene, this is effective only for supercooling of 50 - 80 °C

## Heterogeneous

- Adventitious impurities, residual crystalline polymer that has not completely melted, finely dispersed solids (carbon black, silica, talc) or the container wall may serve as nucleating agents.
- For polyethylene, this is effective for supercooling of 20 - 25 °C.

# Stability of Nuclei

- Nuclei will grow due to the orienting effect of a molecule in the nucleus on those surrounding it.
- Nuclei will disperse as a result of thermal agitation.
- A critical size is required for a stable nucleus.
  - As the crystallization temperature for sporadic nucleation approaches the melting temperature, the critical size increases.
  - As the crystallization temperature is reduced, the average size of chance clusters increases and the critical nuclear size drops.
- No minimum nuclear size is required for heterogeneous nucleation.
- Nuclei beyond the critical size lead irreversibly to form the crystal.
- Under steady state conditions for homogeneous nucleation, fresh nuclei of the critical size replace those lost by crystallization.
- If the critical nuclear size is still large when the viscosity hinders molecular motion, an amorphous glass will be formed.

# Model of Keith and Padden

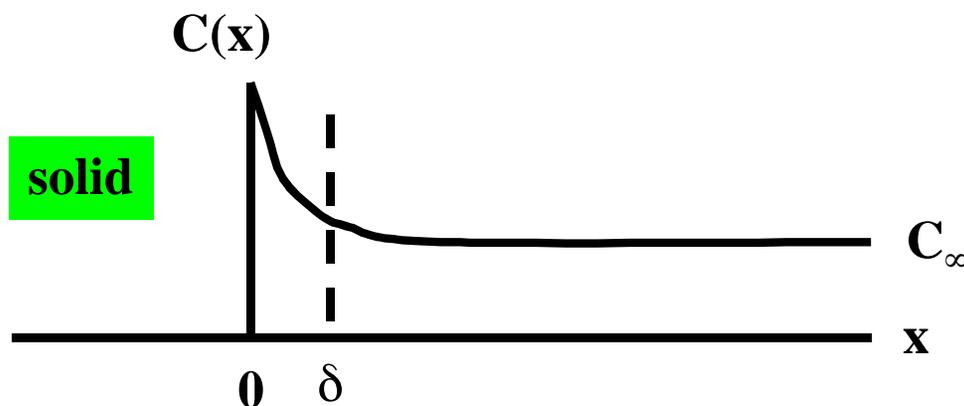
This model attempted to explain the tendency for spherulites to fill space uniformly and maintain spherical symmetry (as opposed, for example, to creating dendritic structures). It applies to a supercooled polymer melt undergoing isothermal crystallization.

An important parameter in the KP approach is the quantity

$$\delta = \frac{D}{G}$$

$D$  = diffusion coefficient for impurity in the melt  
(atactic species, branched species, entangled chain segments)

$G$  = radial growth rate of the spherulite

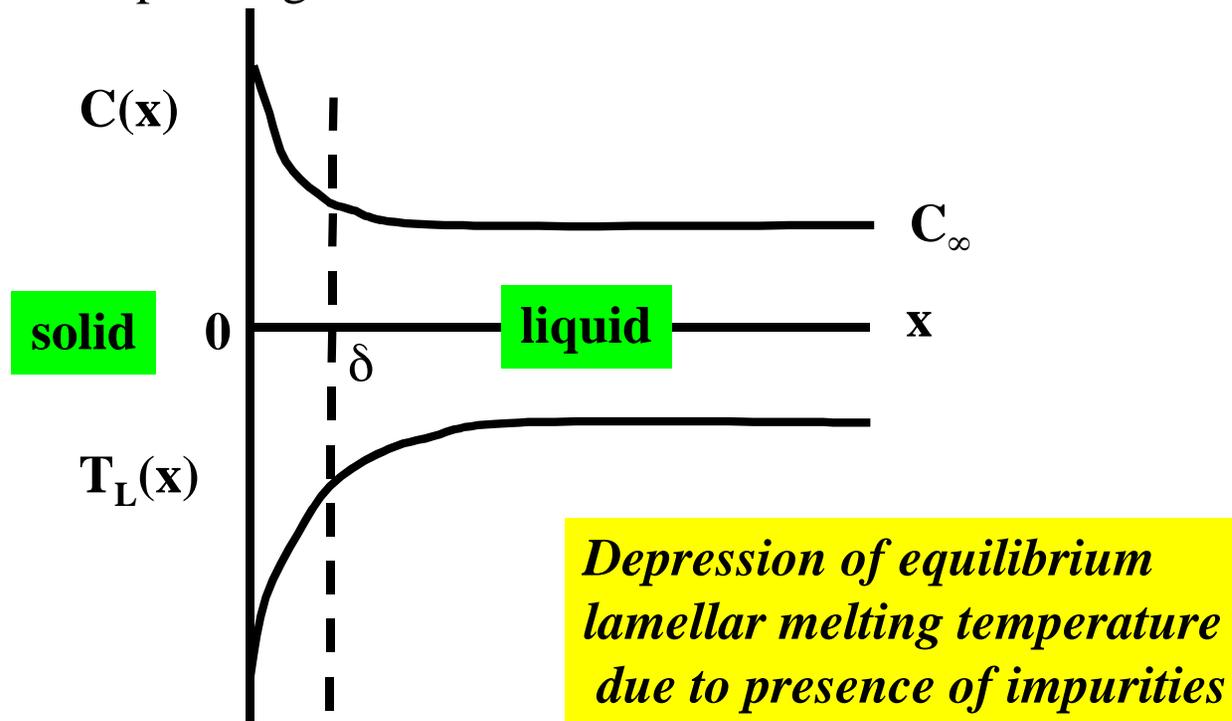


$$\exp\left(-\frac{x}{\delta}\right)$$

$C(x)$  = impurity concentration  
 $C_\infty$  = impurity concentration  
far from growing crystal

# Keith and Padden - Planar Instability

Consider a planar growth front:



- Impurities cause the effective supercooling to be decreased, thus reducing the thermodynamic driving force for crystallization.
- If a protuberance developed due to instability, it would be at a larger value of  $x$  (with fewer impurities) and have a larger supercooling. Thus, it would grow faster. As a consequence, a planar surface is unstable.

# Keith and Padden - Fibril Formation

- Fibrils result because uncrystallizable material is segregated between fibrils, stopping crystallization of the melt in between. The fibril diameter is of the order of  $\delta$  (the scale of the diffusion field at each growing tip).
- The kinetics of crystallization involves two regimes:

**Primary crystallization** - outward growth of fibrils until impingement

**Secondary crystallization** - growth filling in the interstices

- Keith and Padden predicted that spherulitic growth will occur when the scale of the growing unit reaches  $\delta$ . This is about 1 micron in polymer melts. Impurities are localized by being unable to diffuse away from the interface at rates comparable to the radial growth rate.

# Keith and Padden - Radial Growth Rate

$$G = G_0 \exp\left(\frac{\Delta E}{RT}\right) \exp\left(-\frac{\Delta F^*}{RT}\right)$$

$\Delta E$  = free energy of activation for a transporting a polymer segment across the impurity barrier to the growing crystal face

$\Delta F^*$  = free energy of formation of a surface nucleus of critical size

## There are two opposing phenomena:

- Rate of molecular transport in the melt (increases with increasing temperature)
- Rate of nucleation (decreases with increasing temperature)

Crystallization typically occurs over the range  $T_g + 30 < T_{cryst} < T_m - 10$

As the molecular weight is lowered, the viscosity drops, causing the molecular mobility and radial growth rate to increase.

# Polyolefin Copolymers Made by Single-Site Catalyst Technology

- **Polyolefin Elastomers**
  - ENGAGE (DuPont Dow Elastomers)
- **Polyolefin Plastomers**
  - AFFINITY (Dow Chemical)
  - EXACT (Exxon Chemical)
  - EPDM (NORDEL IP from DuPont Dow Elastomers)
- **Enhanced Polyethylene**
  - ELITE (Dow Chemical)
- **Gas-phase LLDPE**
  - EXCEED (Exxon Chemical)
- **Polypropylenes**
  - ACHIEVE (Exxon Chemical)

# Structure-Property Relationships for Ethylene- $\alpha$ -olefin SSC Copolymers

## Molecular Weight Distribution

Typically narrower composition distribution than for copolymers prepared from Ziegler-Natta catalysts, e.g.  $M_w/M_n = 2.0$  for homogeneous ethylene-octene copolymer compared to  $M_w/M_n = 3.7$  for conventional heterogeneous LLDPE

Polymers with a narrow molecular weight distribution have:

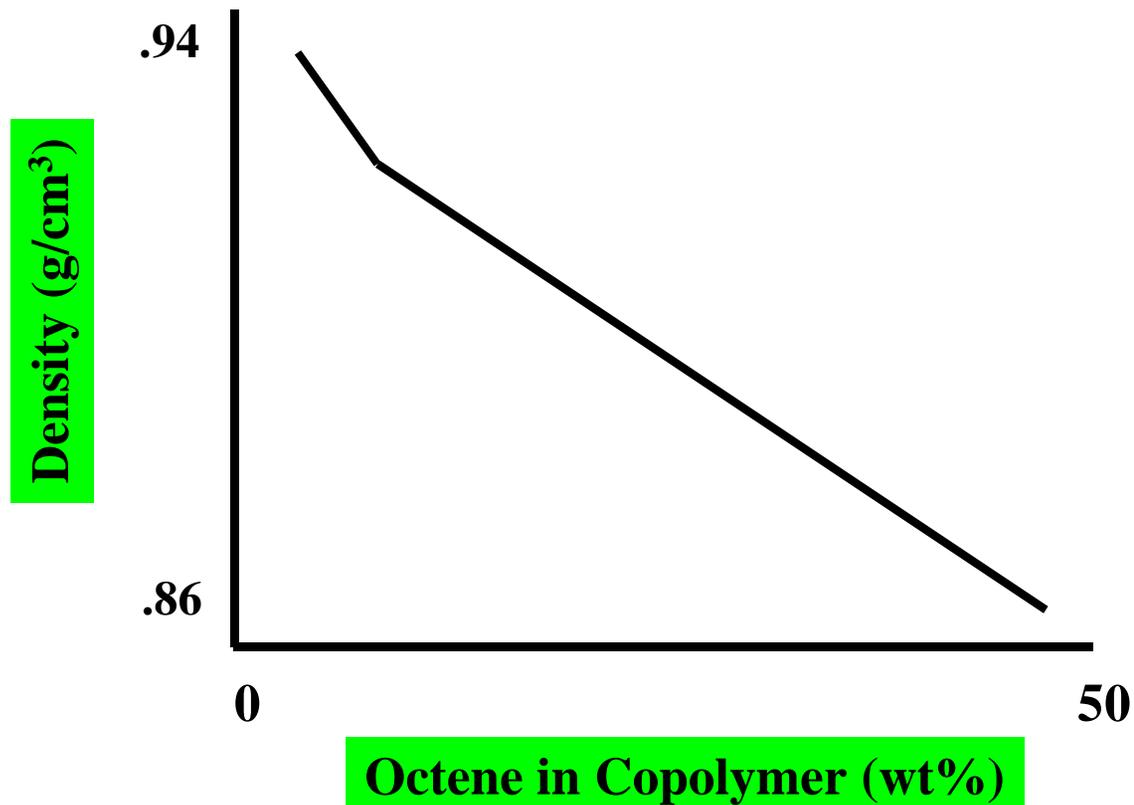
- Increased toughness
- Less solvent extractables

Polymers with a narrow molecular weight distribution can also show poor melt processability:

- Low melt strength
- High extruded back pressure
- High energy consumption during extrusion

# Structure-Property Relationships for Ethylene- $\alpha$ -olefin SSC Copolymers

Density



S.P. Chum, C.I. Kao, G. W. Knight; Ch 12; Metallocene-Based Polyolefins, J. Scheirs, W. Kaminsky, eds.

# Structure-Property Relationships for Ethylene- $\alpha$ -olefin SSC Copolymers

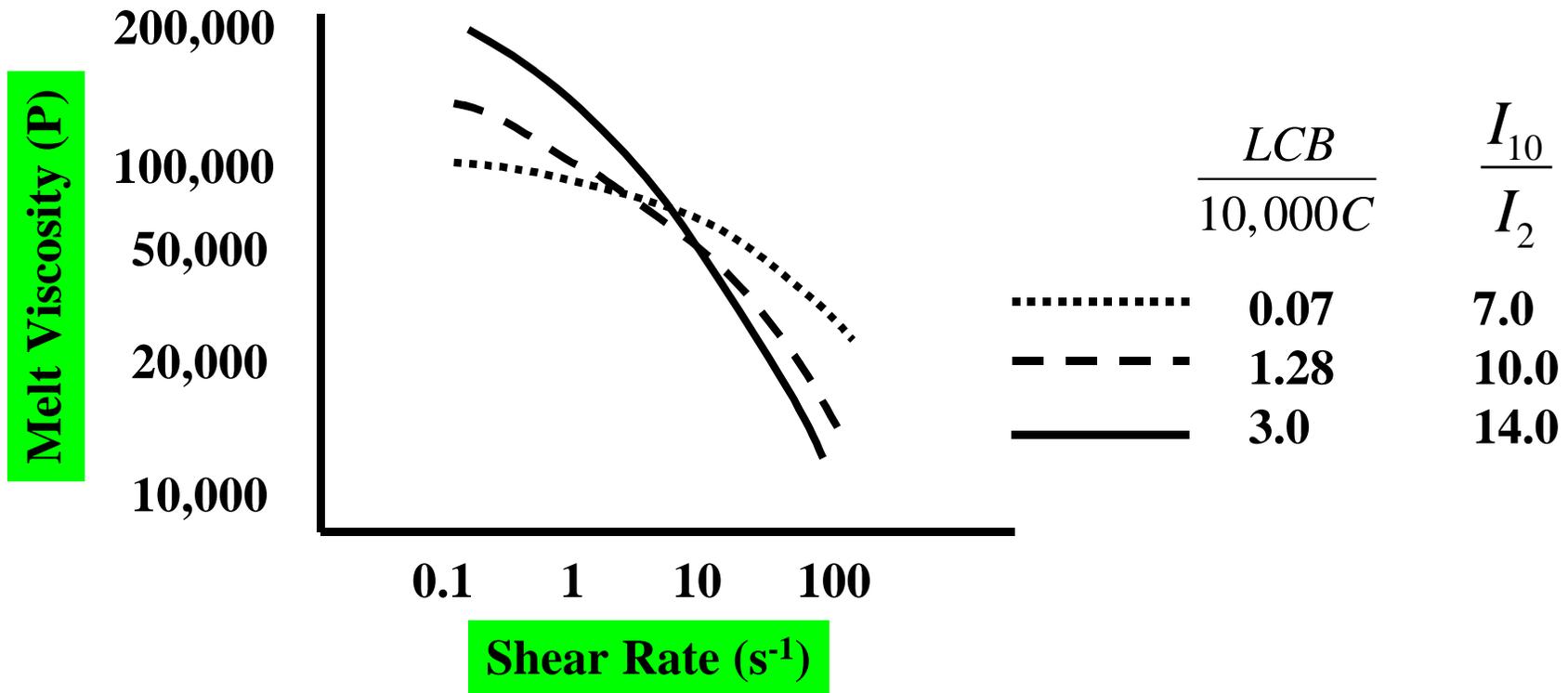
## Comonomer Distribution

- The number of comonomer units per unit chain length is very similar for homogeneous SSC copolymers, but is rather different for conventional heterogeneous ZN copolymers.
- The uniformity influences the solid-state thermal and dynamic mechanical properties.

# Structure-Property Relationships for Ethylene- $\alpha$ -olefin SSC Copolymers

## Long-chain Branching

The occurrence of long-chain branching influences the melt fracture resistance and the shear thinning behavior.



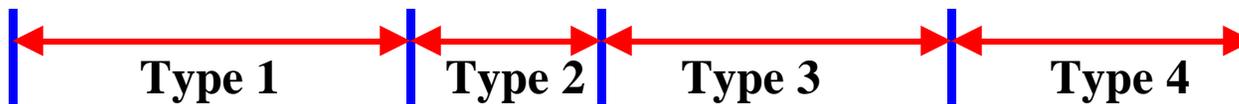
# Classification of SSC Technology Ethylene- $\alpha$ -olefin Copolymers

Crystallinity (%)

10      20      30      40      50      60      70

Density (g/cm<sup>3</sup>)

0.86      0.88      0.90      0.92      0.94      0.96



Morphology

Bundle-like crystals

Mixed

Lamellae

Spherulites

Descriptor

Elastomer      Plastomer      LLDPE-like      HDPE

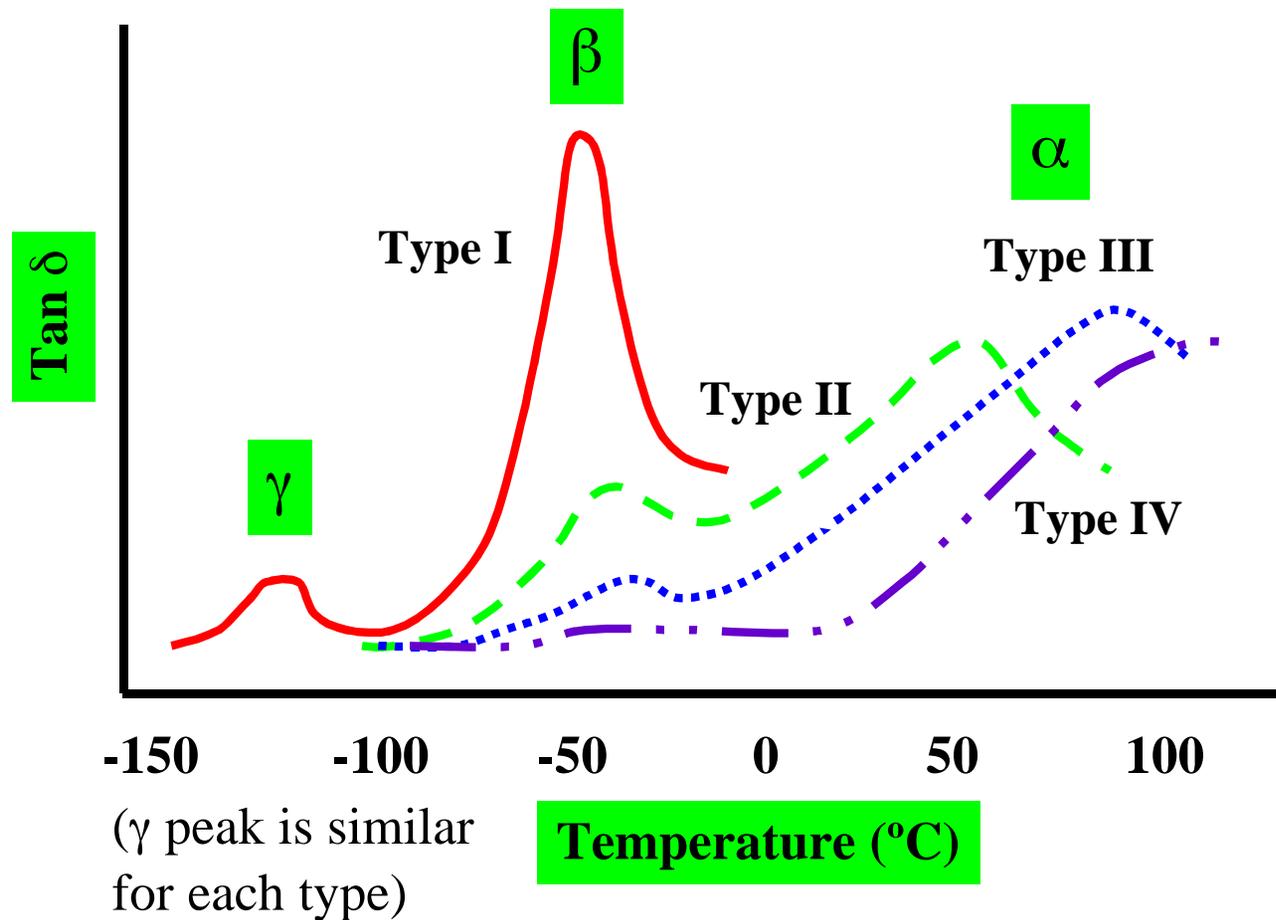
# Structure-Property Relationships for Ethylene- $\alpha$ -olefin SSC Copolymers

## Melting Behavior

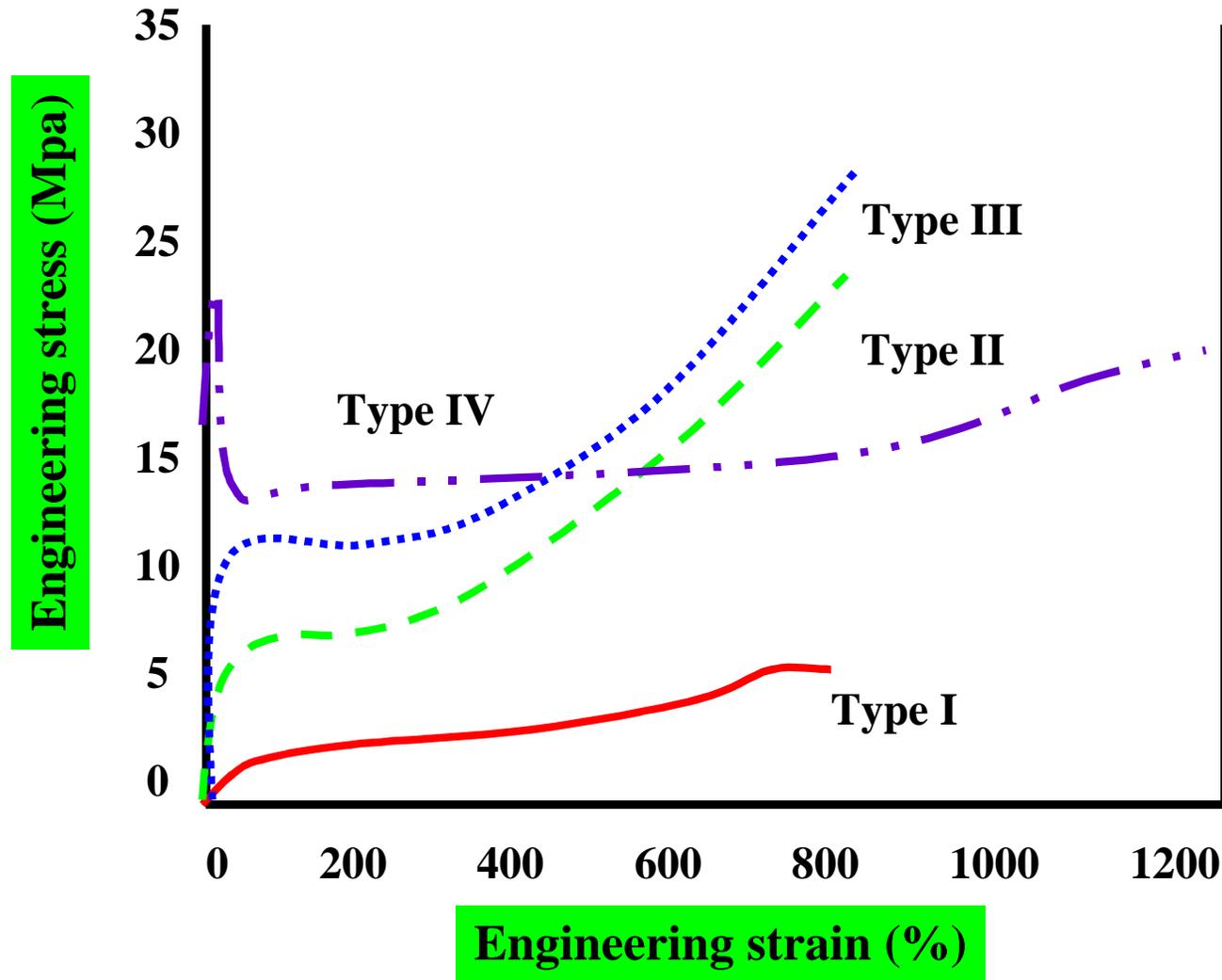
SSC copolymers typically have much narrower melting peaks than their heterogeneous counterparts prepared from multiple-site ZN catalysts.

Polyolefin Type	Density (g/cm <sup>3</sup> )	Melting Temp. (°C)
Type I	0.870	47, 63
Type II	0.902	101
Type III	0.918	118, 114 sh
Type IV	0.960	136

# Dynamic Mechanical Properties of Type I to IV Homogeneous SSC Ethylene-Octene Copolymers



# Engineering Stress-strain Properties of Homogeneous Ethylene-Octene Copolymers



S.P. Chum, C.I. Kao, G. W. Knight; Ch 12; Metallocene-Based Polyolefins, J. Scheirs, W. Kaminsky, eds.

# General Comments on Modulus and Yield Strength

- Initial modulus is a complicated function of polymer crystallinity, molecular weight, thermal history, and fabrication conditions.
- Initial modulus increases with increasing density and crystallinity, and there is a direct relationship between initial modulus and crystallite size.
- Young's modulus is generally a simple function of the polymer density, with SSC and ZN-formed materials falling on the same curve.

# General Comments on Elastic Properties of Type I Polyolefin Elastomers

- Type I, high  $\alpha$ -olefin content, very low density, homogeneous copolymers have a fringed micelle or quasi-nematic bundle morphology, in contrast to Types II - IV, which have lamellar morphology.
- Small, fringed-micelle crystals dispersed in the amorphous matrix act as anchoring points for elastic deformation.