Chapter 5.

Crystalline Polymers

1. Introduction
2. Transition btw Crystallization & Melting (Thermodynamics)
3. Kinetics of Crystallization
4. Morphology and Structure (Model of Crystallites)
5. Factors Affecting Crystallization & $T_m$
References


1. Introduction

Depending on physical states

- **Amorphous polymer;** PVA, PS
  ① Transparent
  ② Bulky side chain and irregular structure (atactic)

- **Crystalline polymer;**
  ① opaque in general
  ② chemically and geometrically regular
  - linear homopolymers:
    PE, PP, Poly(amide), PVC (syndio-), PVA (atactic-)
  - Copolymer; exceptional case (random)
    Ethylene/TFE (tetrafluoro ethylene), Ethylene/VA
1. Introduction
1. Introduction

◆ Uses of crystalline polymer
→ plastics & fibers

ex) PE: 농업용 film, container for H₂O, solvent
film to cover dry-cleaned clothes

PP: highly extensible rope (in marine industry)

polyamide, PET: clothing

cellulose: fibers (cotton, rayon)
PE were crystallized for 40 days at a temperature of 131.5 °C, just below $T_m$. 
1. Introduction
1. Introduction

1) Stereoregularity

2) Local conformation

3) Molecular packing
1. Introduction

1) Stereoregularity

- Chemically + Sterically $\rightarrow$ “Regular”

a) Recurrence regularity

● Head to tail (most probable)
● Head to head
● Tail to tail

$\rightarrow$ not sufficient to become crystallinity in polymers
1. Introduction

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b) Spatial regularity

- tacticity in mono-substituted vinyl polymers

\[
\begin{align*}
\text{cis, trans in diolefin} \\
- \text{cis- poly(isoprene)} : T_m \sim 25 \degree C \text{ (soft rubber)} \\
- \text{trans- poly(isoprene)} : T_m \sim 56\sim 65 \degree C \text{ (hard rubber)}
\end{align*}
\]
1. Introduction
1. Introduction

2) Local conformation

- geometrical arrangement of neighboring groups which can be altered by rotation around primary valence bonds

random coil

(gauche/trans)

helix

alternative gauche/trans mostly isotactic

fully extended

(all trans)

- dissolved in solvent
- molten state
- amorphous
- glassy

- PVA, PB
- PAmide, cellulose
poly(2-vinylpyridine) at the solid–liquid interface at different pH of aqueous solutions: AFM
Microcrystalline regions of a polymer are composed of individual chains (or different segments of the same chain) packed side by side in a regular manner.
Fig. 4.6 Schematic representation of the 3/1 helix found for isotactic vinyl polymers of the type (—CH₂—CHX—)_ₙ. (a) Side view of helix. (b) View along helix. The X groups are —CH₃, —CH₂=CH₂, etc.
Helix types of some isotactic poly(α-olefin)s

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1. Introduction

PP  poly(4-methyl-1-pentene)  poly(3-methyl-1-butene)

<chain atoms (○), substituents (●) and short periodicity (C); hydrogen atoms are not shown>
1. Introduction

3) Molecular packing

- Arrangement of molecules in crystal in term of unit cell and its contents
- Aggregate of molecules
2. Transition between Crystallization & Melting

1) First order transition

2) Equilibrium melting $T \left( T_{m^\infty} \right)$

3) Thermodynamics point of view
2. Transition between Crystallization & Melting

1) First order transition of polymers
   melting $\leftrightarrow$ crystallization

- essentially reverse process but more complicated than low $M_w$ materials
2. Transition between Crystallization & Melting

1) First order transition
2. Transition between Crystallization & Melting

\[ \Delta G_f = G_l - G_c \]

\[ \Delta G_f = 0 \]

Behavior of thermodynamic variables at \( T_m \) for an idealized phase transition: (a) Gibbs free energy and (b) entropy and volume.
2. Transition between Crystallization & Melting

First order: melting of an infinitely large, perfect crystal; melting of a crystal with defects.
Second order: transition with dominating intermolecular cooperative effects; transition with exclusively intermolecular-cooperative effects.
Glass transformation: conventional experiment; infinitely slow measurement.
2. Transition between Crystallization & Melting

2) Equilibrium Melting $T$ ($T_m^\infty$, $T_e^\infty$)

- $T_m^\infty$: equilibrium $T_m$ for finite MW
- $T_e^\infty$: equilibrium $T_m$ for infinite MW & crystal size

a) Small molecules

  Experimental thermodynamics for true equilibrium is to approach the state of interest from opposite direction

  $\Rightarrow T_m = T_c$

  (equil. melting point of crystal
   = equil. freezing point of liquid)

b) Polymer crystals: this is not the case.

  $T_m \neq T_c \neq T_e^\infty$
2. Transition between Crystallization & Melting

Effect of Cooling Rate on $T_g$

PVAc Mn = 60,000
poly(1,4 cis isoprene): $T_m$ vs. $T_c$

temperature range over which melting occurs
2. Transition between Crystallization & Melting

\[ T_m > T_c \]

\( T_m \) against \( T_c \) for poly (propylene oxide)
Idealized Hoffman-Weeks Plot

\[ T_m^\infty = T_c = T_m \]

equilibrium at finite MW and infinite crystal size
(or infinitely slowly cooled)
2. Transition between Crystallization & Melting

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If polymer has infinite MW and infinite crystal size, we can define equil. $T$ ($T_e^\infty$) between crystal and melt.

Since actual MW crystal size are less than, this fact lowers $T_m^\infty$ than $T_e^\infty$.

① The lower $T_c$, the lower $T_m$

② Melting occurs over a range of $T$

③ Convergence of lines in the upper right-hand portion ($T_m^\infty = 75\ ^\circC$)

④ Melting behavior depends on heating rate.
2. Transition between Crystallization & Melting

- Melting temperature is related to size of crystals.
  
  \((\text{the larger, the higher } T_m)\)
  
  \((\text{range of } T_m \text{ due to different sizes of crystals})\)

- quenching: rapid cooling
  
  \(\text{T drops below } T_e^\infty \text{ without crystallization}\)

- slow crystallization due to intricate mode of crystallization coupled with mobility of chains due to viscous effect

- thickness depends on super-cooling and is related to \(T_c\)

\[
T_m < T_m^\infty < T_e^\infty
\]

\(\infty: \text{ infinite crystal size}
\)

\(\text{(or infinitely slowly cooled)}\)

truer approximation to valid equilibrium parameter

\(\text{(for finite crystal dimension and MW)}\)
2. Transition between Crystallization & Melting

\[ T_m = T_e^{\infty} - \frac{2 \gamma_e T_m}{\ell \Delta H_v} \]

- \( T_e^{\infty} \): melting point of crystal with infinite size
- \( \Delta H_v \): enthalpy of fusion \( p_u V \) of crystal
- \( \ell \): thickness of crystal
- \( \gamma_e \): surface energy of top & bottom surface
2. Transition between Crystallization & Melting

\[ T_m = T_e^\infty - \frac{k}{\ell} \]

\( \gamma_e : \text{calculated} \)

\( T_m: \) truer approximate to valid equil parameter (for finite \( M_w \) and crystal size)
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2. Transition between Crystallization & Melting

Crystal thickness vs. $T_m/\Delta T$ for PE
2. Transition between Crystallization & Melting

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3) Thermodynamic point of view

at equilibrium

\[ \Delta G = \Delta H - T\Delta S = 0 \]

\[ T_m^\infty = \frac{\Delta H_m}{\Delta S_m} \sim T_m \]

\[ \Delta H_m = \Delta H_0 + n\Delta H_{m1} \]

\[ \Delta S_m = \Delta S_0 + n\Delta S_{m1} \]

If \( n \to \infty \)

\[ \begin{cases} \Delta H_m = n\Delta H_{m1} \\ \Delta S_m = n\Delta S_{m1} \end{cases} \]

\[ T_m^\infty = \frac{\Delta H_{m1}}{\Delta S_{m1}} \]
### Values of $T_m$, $\Delta H_{f1}$ and $\Delta S_{f1}$ for Several Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_{f1}$ (J mol$^{-1}$)</th>
<th>$\Delta S_{f1}$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Polyethylene</td>
<td></td>
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<tr>
<td>2. Poly(1, 4-cis-isoprene)</td>
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<tr>
<td>3. Poly(ethylene oxide)</td>
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<tr>
<td>4. Poly(decamethylene sebacate)</td>
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<tr>
<td>5. Poly(decamethylene sebacamide)</td>
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<tr>
<td>6. Poly(decamethylene azelate)</td>
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<tr>
<td>7. Poly(decamethylene azelamide)</td>
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</tbody>
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