

# An introduction to polymer physics

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## 4. Condensed State Structure

~10 hours

- Contents:
  - 4.1 Basic ideas of condensed state structure
  - 4.2 Polymer macro-conformation
  - 4.3 Crystalline structure

Objective: to establish the idea of polymer morphology

- Requirement: random coil, crystallites, macro-conformation of polymer

### 4.1 Basic ideas of condensed state structure

Key point

#### 4.1.1 Concept

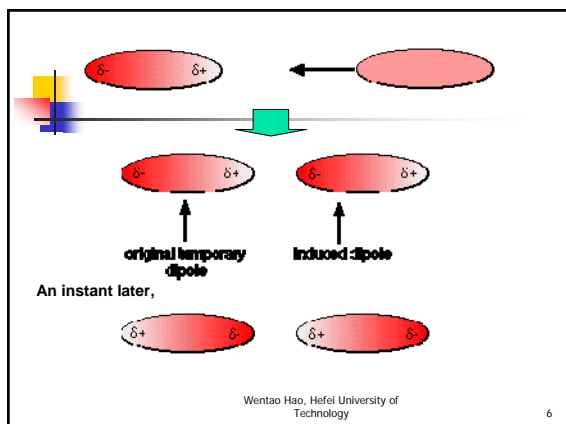
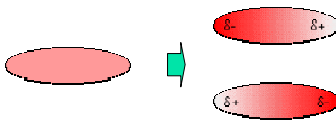
- Sometimes, condensed state structure of polymer is called the super-molecular structure. That is, how the polymer chains arrange themselves when they meet together.
- 高分子的聚集态结构是指高分子链之间的排列和堆砌结构，也称为超分子结构。

### Comparison between the condensed state structure of small molecules and polymer

	Small molecules	Macromolecules
	Crystalline state	Crystalline state
	liquid state	liquid state
	gaseous state	gaseous state
Transition state	Liquid-crystalline state	Liquid-crystalline state
	Glass state	Glass state

### 4.1.2 Interaction between polymer chains

- A. Van der Waals forces (范德华力)
  - van der Waals forces: dispersion forces



As long as the molecules are close together this synchronised movement of the electrons can occur over huge numbers of molecules.

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## B. Hydrogen bonds

Fig. 4-1 illustration of hydrogen bonds

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### 4.1.3 Isolated chains to condensed state structure

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### 4.1.4 contents of condensed state structure

- 1. non-crystalline structure
- 2. crystalline structure
- 3. liquid-crystalline structure
- 4. condensed state of single chain
- 5. orientation structure
- 6. textile structure

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### 4.1.5 Cohesion energy density (内聚能密度)

■ COHESION ENERGY is defined as energy used to overcome the intermolecular force and evaporate one molar aggregated molecules.

■ CED -- Cohesion energy located in one unit volume is called CED.

$$CED = \frac{\Delta E}{\tilde{V}}$$

$\Delta E = \Delta H_v - RT$

$\Delta H_v$  – Evaporation Heat per mole,  
 $RT$  – Inflation Work

$\tilde{V}$  Volume per mole

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### Table 4-1 CED for linear polymers

polymer	CED (J/cm <sup>3</sup> )	polymer	CED (J/cm <sup>3</sup> )
PE*	259	PMMA	347
PIB	272	EVA	368
NR	280	PVC	380
PB	276	PET	477
SBR	276	PA-66	773
PS	305	PAN	991

高聚物的结构与性能, p90

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Table 4-2 Comparison of polymer with different CED

CED	polarity	interaction	flexibility	usage
CED < 300	Non-polar	Weak interaction	Soft chains	Rubber materials
CED > 400	Polar or with H-bonding	Strong interaction	Rigid chains	Fiber materials
300 < CED < 400	middle	middle	middle	Plastic materials

Interaction will determine the strength, thermal stability and aggregation structure, and further determine the properties and possible usage.

\*PE is a easily crystallized polymer and is used as plastics

## 4.1.6 Crystalline structure of polymer

### Nature of crystallization

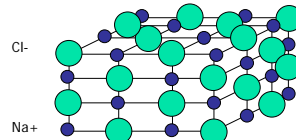


Fig. 4-2 Crystal of Sodium Chloride – NaCl

What can be inferred from this picture?

Ideal crystals are regularly or periodically repeating three-dimensional arrays of atoms.

## Crystallization of polymer

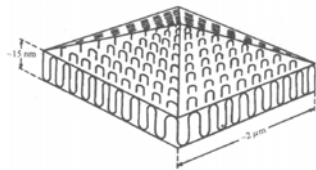


Fig. 4-3 illustration of polymer single crystal

The nature of polymer crystallization is .....

The polymer chains or segments regularly packed up together.

## Wide Angle X-ray Scattering

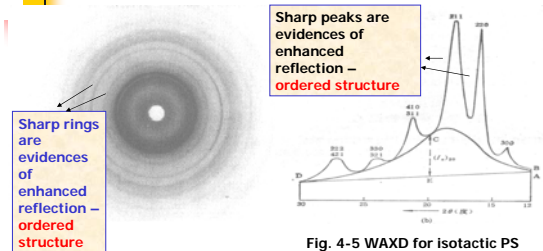


Fig. 4-5 WAXD for isotactic PS

Fig. 4-4 WAXS from PE – highly crystalline sample

Textbook, p81

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## Thermal analysis

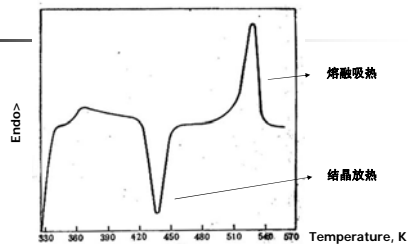


Fig. 4-6 DSC for non-crystalline PET thick sheet

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## Optical observation

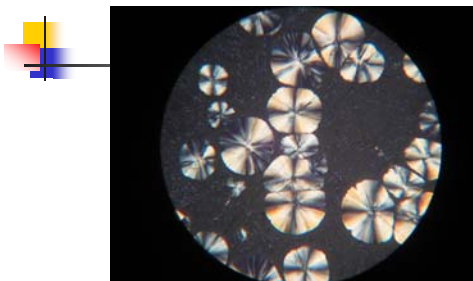


Fig. 4-7 spherulites of polypropylene after isothermal crystallization

### Conformation of chains in crystallites – Helix

**Fig. 4-8 strong repulsion of large substitutes of vinyl polymer**

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**Fig. 4-9 Helical conformation of chains**

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### Structure of polymer crystals

**Fig. 4-10 Ordered 3-D structure of polymer crystallite**

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**Fig. 4-11 Crystal structure of PE**

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### 4.1.7 non-crystalline structure

- While polymer is in the liquid, elastomer or glass state, it is totally **non-crystalline**
- The feature is that lots of polymer chains **entangled** with each other randomly
- The **entangled mass** – non-crystalline phase

《高聚物的结构与性能》，P90-95

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For glassy or rubbery polymer, **no crystallinity** can be found and only short-range regularity is presented, then the diffraction figure will be a **diffused halo**.

**Fig. 4-12 WAXD for isotactic PS**

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**Fig. 4-13 WAXS from PS – amorphous sample**

## 4.2. polymer macro-conformation

- 4.2.1 introduction
- 4.2.2 crystallites
- 4.2.3 non-crystalline regions
- 4.2.4 Macro-conformation of polymer

### 4.2.1 introduction

- Condensed state structure is complicated
  - Crystalline, non-crystalline, orientation, liquid crystalline, textile structure.....
- Size of crystallite (微晶) is much less than the length of polymer chains
  - 10nm Thickness of crystal compared to the 3000nm length of polymer chain

### Questions arose ...

- How can long molecules give rise to small crystallites?
- What are the sizes and shapes of polymer crystallites?
- How are the crystallites disposed (安置) with respect to each other and to the non-crystalline material?
- What is the nature of the non-crystalline material?
- The directions of the chain axes (轴) with respect to the crystallite faces.
- The relationship between the crystallites and the non-crystalline material, especially the nature of the crystalline – ‘amorphous’ interface.

### 4.2.2 crystallites (微晶)

Key point

- How can long molecules give rise to small crystallites? (what do you think?)
- The answer is:
  - Polymer chain will be folded in some way
    - Fringed-micelle model (缨状-微束模型)
    - Chain-fold model (折叠链模型)

### 1. Fringed-micelle model

缨状-微束模型 (两相模型)

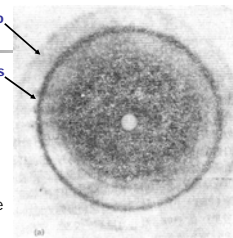
- history:
  - An early attempts to inter-relate long molecules, small crystals and a ‘sea’ of amorphous materials
  - Proposed by *Hermans* and others in 1930 according to the results from X-ray diffraction
  - Though it is now believed to be incorrect as the fundamental model for polymer crystallites, but has its own historical significance
  - can be applied in some special cases

高分子物理, P58-59

### Results from XRD

Diffused halo  
弥散光晕  
concentric rings  
同心圆环

The crystalline material is not composed of randomly arranged polymer chains, but a mixture of ordered structure and amorphous structure in the whole.



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Fig. 4-14 XRD for POM sample

## The model is ...

Amorphous structure, non-crystalline regions

Ordered structure, crystallites

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Fig. 4-15 Schematic diagram of Fringed-micelle model

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## It was supposed that ...

- ① crystalline region and non-crystalline region coexist together 共存
- ② Some parallel polymer chains packed up one by one to form ordered structure 平行
- ③ One molecular chain may pass through several crystalline regions and non-crystalline regions 穿越
- ④ Generally, the crystalline regions are randomly oriented 晶区无规取向
- ⑤ The non-crystalline regions are composed of randomly packed polymer chains 非晶区无规堆积

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## Historical significance

- It explained many results from XRD and other experiments
  - Arcs (圆弧) on the XRD of extended samples (due to orientation of crystallites)
  - Melting temperature range 熔限 (due to the size distribution of crystallites)
  - The density of the whole polymer material is less than the density of pure crystals (calculated from unit cell)

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## Arcs on the XRD of extended samples

圆弧

Arcs, depriving from rings  
Due to the orientation of crystallites

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Fig. 4-16 XRD for uniaxially oriented POM sample

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## Melting temperature range

熔限

$T_m$

(a) (b)

Fig. 4-17 Melting of crystalline polymer (a) and small molecules (b)

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## 2. Chain-fold crystallites

- Time: 1938
- Proposer: Storks
- Experiments:
  - gutta percha of 27nm thick
  - electron diffraction
- Results:
  - Large size of crystallites were observed
  - the chain axes were normal to the plane of the film.
- Conclusion:
  - The only possibility was that the chains fold back and forth upon themselves
- single crystals, found in early 1950s, thickness of 12 nm
  - chain axes found to be parallel to the thickness direction of these lamellar crystals,
  - by Keller, electron diffraction
- crystallites in melt-down spherulites of PE and nylon
  - to be lamellar rather than fibrillar, in 1957,
  - by Fisher, electron microscopy
- Great challenge to Fringed-micelle model!
- Chain-fold model established

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## Chain-fold model

Chains or chain bundles

Fig. 4-18 Schematic diagram shows regular chain-folding with adjacent re-entry (1)

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## Topic1. the production of single crystals from solution

- Linear PE was first used to obtain single crystals in super-cooled diluted solution, e.g. 0.01% in *p*-xylene at 70°C.
- Then other polymers such as POM etc. were used to produce single crystal in a similar way.

Fig. 4-19 Electron micrographs of single crystals of polyethylene crystallized from dilute solution of xylene:

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## Topic 2. illustration of solution-grown crystals of polyethylene

12nm

nuclear

Chains or chain bundles

1. The thickness of single crystal of PE is only about 12 nm
2. Electron diffraction results – chain axes are approximately perpendicular to the planes of lamellae

Fig. 4-20 relationship between single crystal and polymer chains

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Small molecules

Polymers

Fig. 4-21 illustration of growth of single crystals

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## 3. Switch board model

■ Question

- For the single crystal growing in the ultra-dilute solutions, the chain-fold model can be applied. However, for the crystals formed in the viscous melt, it is not applicable.
- How can entangled molecular chains form crystals in the melt?

■ Remember

- Lamellar crystallites can be found in the melt-down crystal
- Amorphous phases are coexist with crystalline structures

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## Switch board model based on Flory's random coil theory was proposed

Fig. 4-22 'Solidification model' of the crystallization process

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#### 4. Switch board model based on Flory's random coil theory was proposed

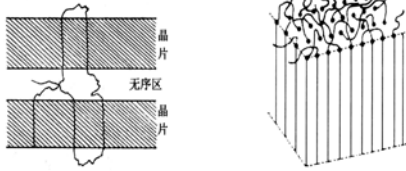


Fig. 4-23 Schematic diagram shows switch board model with non-adjacent re-entry

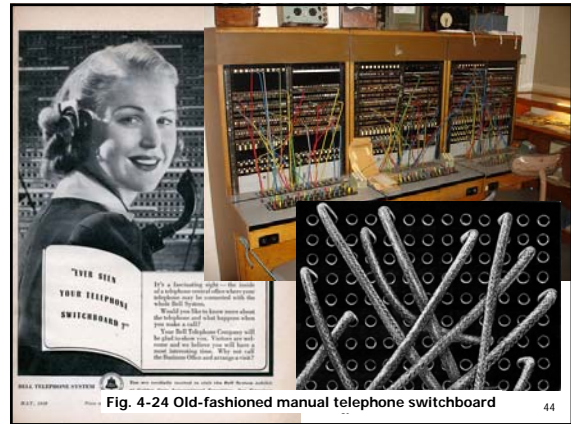


Fig. 4-24 Old-fashioned manual telephone switchboard

#### 4. Switch board model

- Molecular chains enter crystal lattice in a random way
- Adjacent segments in the unit cell may be not the adjacently jointed segments
- Or they may be not belong to one molecular chain
- One molecule can pass through crystallites and non-crystalline region back and forth several times
- Molecular chain on the lamellae surface are like criss-crossing of wires on an old-fashioned manual telephone switchboard

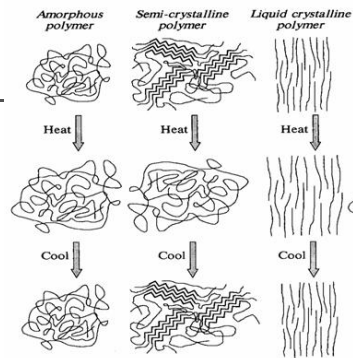
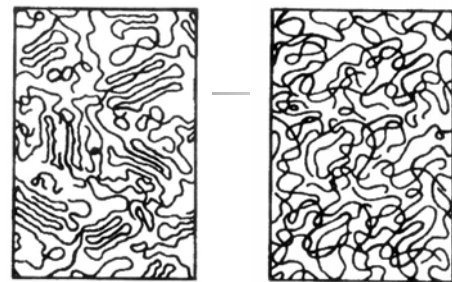


Fig. 4-25 Crystallization of polymers

#### 4.2.3 Non-crystalline regions

- Non-crystalline regions – are usually called amorphous, represented by tangled mass of polymer chains rather like a bowl of spaghetti
- Exists in melted polymers, totally amorphous polymers in the glassy or rubbery states, also as a component of semi-crystalline polymers.
- Non-crystalline regions may sometimes have some kind of organization and they may certainly be oriented
- They are the component of polymer morphology that is least well understood



Left: the bundle model

Right: the random coil model

Fig. 4-26 proposed structure for the non-crystalline regions



## 1. the bundle model



两相球粒模型

- High packing density of non-crystalline region – 85~95% of the crystalline material
- It was supposed to be the **existence of short-range ordered structure**

可参阅《高分子物理》p66

## 1. the bundle model

- However, the results from SAXS experiment **did not support** such hypothesis
- Because electron density was the **same** everywhere
- There is **no difference** between the postulated bundles and the rest regions
- Such a model is not perfect

## 2. The random coil model



(c)

- Computer modeling has shown that randomly coiled chains can pack together **at the required densities**
- in agreement with the Flory theorem.
- So that, **random-coil model** for un-oriented non-crystalline material become more and more **popular**.

Theorem – 定理, 法则

## 4.2.4 Macro-conformation of polymer

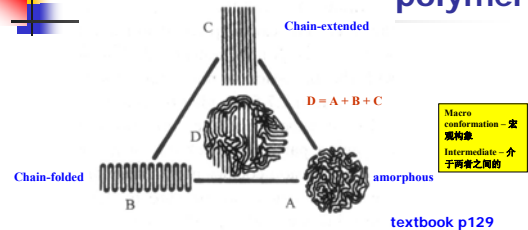


Fig. 4-27 Schematic representation of the macro-conformation of polymer chains

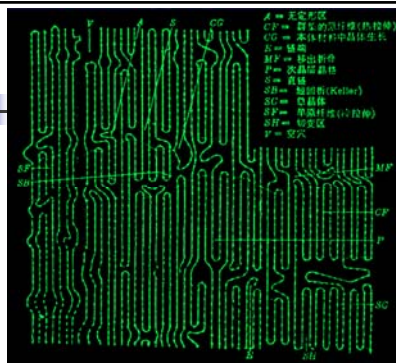


Fig. 4-28 the tunnel folding-chain model

## 4.3 Crystalline structure

- 4.3.1 crystalline morphology
- 4.3.2 Crystallization and melting
- 4.3.3 Crystallization capacity
- 4.3.4 Crystallinity
- 4.3.5 Crystallization to property

### 4.3.1 crystalline morphology

#### 1. Spherulites

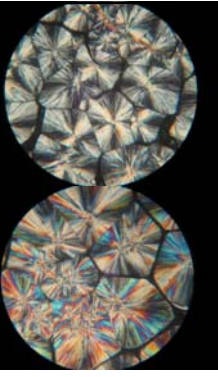
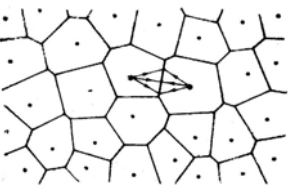



Fig. 4-29 spherulites of isotactic polypropylene

Fig. 4-30 Sketch of spherulites growing at same speed

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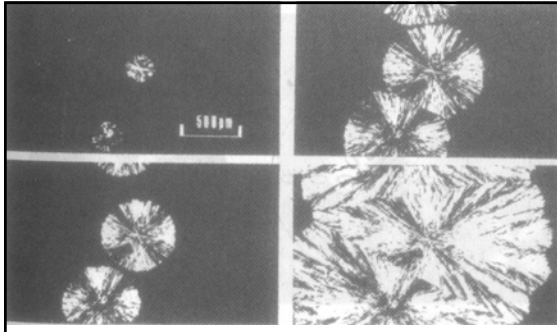


Figure 4-31 illustration of growth of spherulites  
Being found in very many polymers crystallized from melt

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### First observation

- The spherulites consists of 'fibrils' growing out in a radial direction
- It suggests that the fibrils probably branch at fairly small angles as they grow outwards

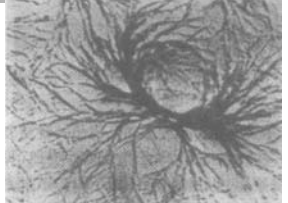


Fig. 4-32 Bundle-like crystal of Nylon spherulite during the early period

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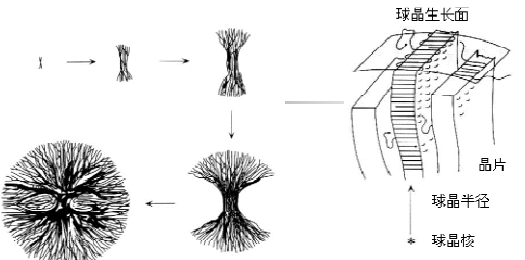


图 6-15 球晶的结构和生长过程示意图<sup>[9]</sup>

图 6-16 从熔体生长的球晶内晶片的示意图<sup>[9]</sup>

Fig. 4-33 Illustration of growth of spherulites

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### Second observation

#### Maltese-cross

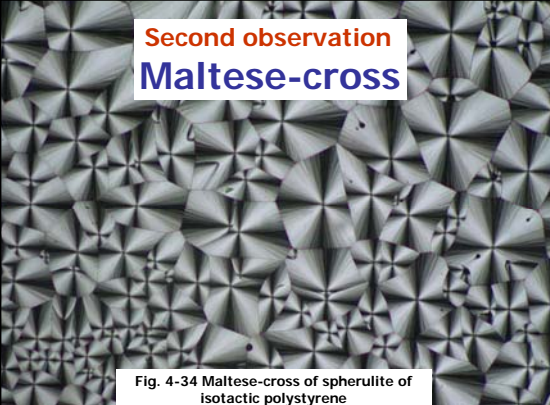
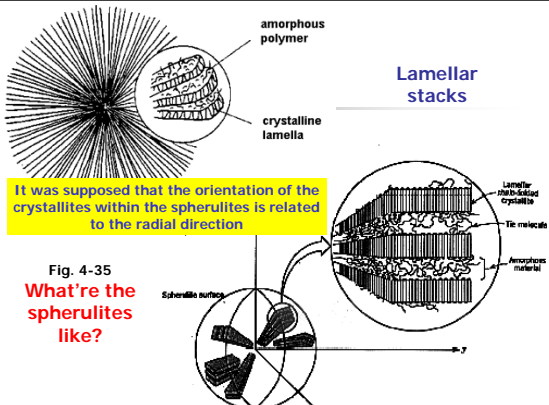


Fig. 4-34 Maltese-cross of spherulite of isotactic polystyrene



amorphous polymer

crystalline lamella

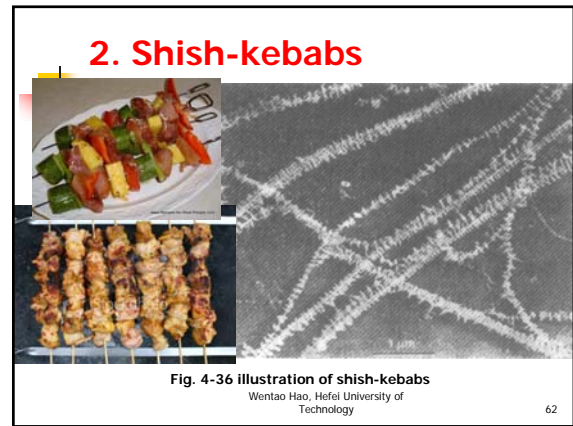
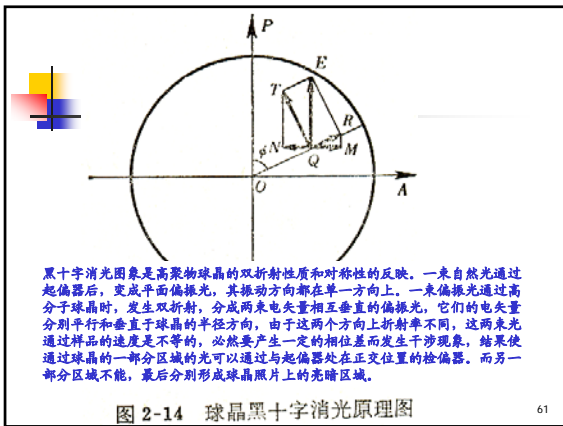
Lamellar stacks

Lamellar phase-crystallite

Amorphous material

Fig. 4-35 What're the spherulites like?

It was supposed that the orientation of the crystallites within the spherulites is related to the radial direction



### Schematic figure for shish-kebabs

- Shish-kebabs are generally produced only when crystallization occurs **under strain**
- for instance when a crystallizing solution or melt is stirred or flows.

Shish-kebabs - 串型多晶

Fig. 4-37 sketch of shish-kebabs

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### 3. Extended-chain crystallites

- Extended-chain crystallites can be obtained from only a few polymers like PE, PTFE using special crystallization techniques
- Extended-chain PTFE – slow crystallization from melt
- PE – from melt under elevated pressure

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Fig. 4-38 Extended chain crystals of polyethylene crystallized on graphite substrate

Fig. 4-39 Extended-chain crystallites of Polychlorotrifluoroethylene

- Very bristle – there were not so many inter-crystallite linking molecules
- Size – Lamellae may be about 1-2  $\mu\text{m}$  thick and no limit on the lateral dimensions of the crystallites

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### Summary of crystalline morphology

- Single crystal – in ultra-dilute solutions
- Spherulite – in melt, condensed solutions
- Shish-kebab – under strain
- Extended crystal – extremely high-pressure

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## 4.3.2 crystallization and melting

- The previous sections
  - focused on description of the morphological features, on what had been observed
- The present section
  - focused on why some of the observed features are as they are, and at what rate they appear
- It involves .....
  - The melting temperature  $T_m$
  - The factors determining the overall crystallinity achievable
  - the rate of growth of crystallites
  - Factors affecting the fold length in lamellar crystallites

## 1. Melting temperature or melting point

- Generally, the melting point is defined as the temperature at which the change of Gibbs free energy per unit mass is zero.

$$\Delta G = \Delta H - T_m \Delta S = 0$$

- $\Delta H$  – the increases in enthalpy per unit mass
- $\Delta S$  – the increases in entropy per unit mass

$$T_m = \Delta H / \Delta S$$

Gibbs free energy – 吉布斯自由能

Enthalpy – 焓; Entropy – 熵

## Examples

- High  $\Delta H$ , low  $\Delta S$ , results in high  $T_m$
- Polyethylene,
  - weak intermolecular force, low  $\Delta H$
  - high flexibility, high  $\Delta S$
  - $T_m = 418 \text{ K}$
- Nylon-6,6
  - hydrogen bonding, high  $\Delta H$
  - similar chain flexibility, same  $\Delta S$
  - $T_m = 543 \text{ K}$

## Approximate equilibrium melting points of some commonly used polymers

Polymer	Melting point (°C)
Polyisoprene (cis form)	28
Poly(ethylene oxide)	66
Polyisoprene (trans form)	80
1,2-polybutadiene (isotactic form)	120
Polyethylene (linear)	135
1,2-polybutadiene (syndiotactic form)	154
Polypropylene (syndiotactic form)	163
Polyoxymethylene	183
Polypropylene (isotactic form)	187
Poly(vinyl chloride)	212
Polystyrene (isotactic form)	240
Poly(vinyl alcohol)	250
Nylon-6	260
Poly(ethylene terephthalate)	270
Nylon-6,6	270
Polytetrafluoroethylene	332
Polyacrylonitrile (syndiotactic)	341

## 2. $T_m$ , talking more

- The  $T_m$  mentioned above is the equilibrium melting point  $T_m^0$
- If the lamella is infinitely large and perfect, the melting point will be equilibrium melting temperature  $T_m^0$
- Usually obtained by extrapolation

equilibrium melting point  $T_m^0$  – 平衡熔点

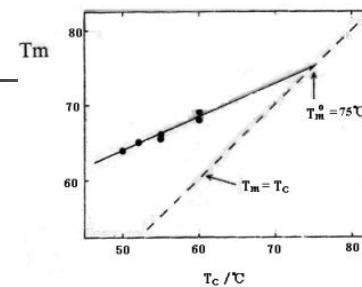


Fig. 4-40 How to determine the equilibrium melting point  $T_m^0$

### 3. $T_m$ and size of crystallites

- For smaller crystallites,  $T_m$  will be less (?)
- For polymer material, size of crystallites are not the same; distribution exists.
- Fixed melting points are replaced by melting temperature range

### 3. $T_m$ and size of crystallites

- For any crystallite, the total Gibbs free energy is the sum of a part proportional to its volume and a part due to the extra energy involved in forming its surfaces.
- As the crystallite becomes larger, the ratio of volume to surface area increases and the contribution due to the surfaces becomes negligible compared with that due to the volume.
- For a small crystallite, however, the surface energy contributes significantly to the enthalpy, so that the effective enthalpy per unit mass is higher.
- This means that the increase in enthalpy required to melt the crystallite is lower and, assuming that  $\Delta s$  is temperature-independent,  $T_m$  is lower than that of larger crystals.
- For lamellar polymer crystals the fold surfaces contribute by far the larger part to the surface energy, both because they are much larger in area than the other surfaces and because the surface energy per unit area is much higher owing to the high energy required to make the folds.

### 熔融温度与晶体尺寸

- 对于任何晶体而言，总的吉布斯自由能都是两部分能量之和。其中一部分正比于其体积，另一部分是由于形成微晶表面而必需的额外能量。
- 当晶体变大时，体积与表面之比变大。与表面相关那部分能量相对于与体积相关能量而变得可忽略不计。
- 然而，对于一个小晶体，表面能对于热焓贡献较多，因此单位质量的有效热焓更高。
- 这意味着为了熔融晶体而需要增加的热焓较少，同时假定熵变与温度无关，小晶体的 $T_m$ 就比大晶体的 $T_m$ 低。
- 对于片晶状聚合物晶体，折叠表面对表面能贡献更大，一方面由于它们的表面积较其他表面更大，另一方面由于形成这些折叠所需的较高能量而使每单位面积表面能更高。

### Thompson-Gibbs equation – relationship between $T_m$ and thickness of lamellae

$$T_m = T_m^0 [1 - 2\sigma / (l\rho\Delta h)]$$

where  $l$  is the thickness of the lamellae  
 $\sigma$  is the surface free energy per unit area  
 $\Delta h$  is the increase in enthalpy per unit mass on melting for an infinitely thick crystal

The larger  $l$ , the higher the  $T_m$   
 Or it can be said, the better the perfection of the crystal, the higher the  $T_m$

Textbook, P139

### 4. Is the melting process of polymer different from that of small molecules?

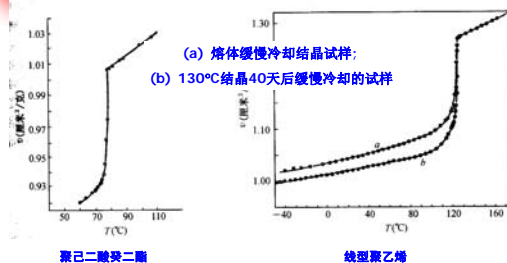


Fig. 4-41 examples of polymer melting 《高分子物理》, p85

### What can be inferred from the previous page

- Under very low heating rate ( $1^\circ\text{C}/24\text{h}$ ), the melting process of polymer is like that of small molecules – a jumping process – an absolute melting point can be seen
- The larger the crystallites, the narrower the melting temperature range, the higher the melting point
- In fact, the melting process for polymer and small molecule is the same in nature – they are all thermodynamic first-order phase transition

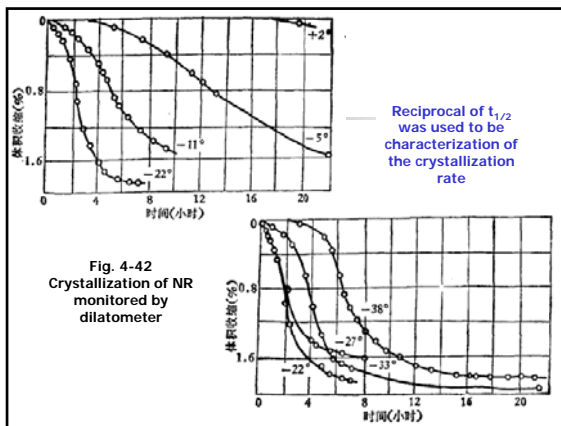
## 5. Kinetics – The rate of crystallization

- The crystallization rate is depending on Degree of Supercooling  $\Delta T$
- $\Delta T = T_m^0 - T_c$ 
  - Where  $T_c$  is the temperature at which crystallization takes place

Degree of supercooling – 过冷(程)度  
 $T_c$  – 结晶温度

## Crystallization rate – Temperature Relationship

- $\Delta G_c = \Delta H - T_c \Delta S$ ,
- $\Delta G_m = \Delta H - T_m^0 \Delta S = 0$
- $\Delta G_c = \Delta H (T_m^0 - T_c) / T_m^0$   
 $= \Delta H \cdot \Delta T / T_m^0$
- $T_c \downarrow, \Delta T \uparrow, \Delta G_c \uparrow$
- More favorable for crystallization



## Maximum crystallization rate

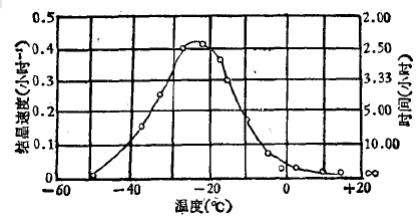


Fig. 4-43 the maximum rate of crystallization

## Nucleation and crystallization rate

- Crystallization of polymers can be seen as a combination of nucleation process and crystallite growing process
- Nucleation includes homogeneous nucleation and heterogeneous nucleation
  - Homogeneous nucleation is due to the formation of fibrils of folded chains in the melt or chain ends
  - Heterogeneous nucleation is due to the impurities, crystallite remains and dispersed solid particles
- crystallization rate = nucleation rate + crystallite growing rate

Homogeneous 均相的  
Heterogeneous 非相的

## Explanation

- At temperature **not far below** from the  $T_m$ , nuclei forming rate is **low** because of the instability of nuclei, the crystallization rate is **low**;
- At temperature **far below** from the  $T_m$ , but near  $T_g$ , molecular chains will have not so much energy to move, the crystallization rate is **low** again.
- So that, there must be a temperature, at which the nuclei are fairly stable and the mobility of chains is fairly good too and the crystallization rate reach the maximum.

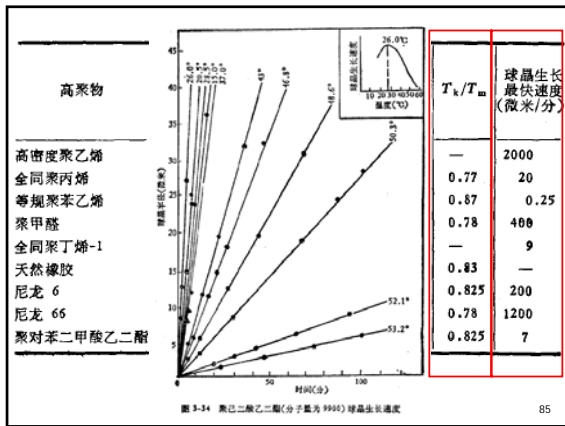


图 3-34 聚己二酸乙二酯(分子量为 9999) 球晶生长速度

## 6. Avrami equation

– about growth rate of crystallinity

- $1 - v_s(t) = \exp(-Kt^n)$ 
    - Where  $v_s$  is the volume fraction occupied by spherulites;
    - $t$  is time;
    - $K$  and  $n$  depend on the nucleation and growth mechanism.
  - Suitable for all kinds of crystallization, not only for polymers
  - $v_s(t) = v_c(t) / v_c(\infty)$ 
    - $v_c(t)$  is the volume-fraction crystallinity at time  $t$
- $\Rightarrow v_c(t) = v_c(\infty)[1 - \exp(-Kt^n)]$

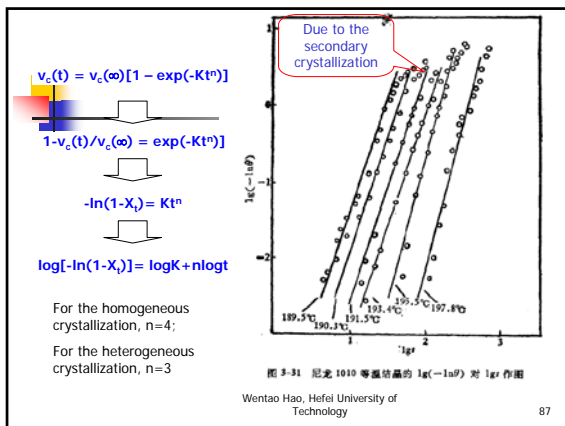


图 3-31 尼龙 1010 等温结晶的  $\lg(-\ln(1-X_t))$  对  $\lg t$  作图

## 4.3.3 Crystallization Capability

1. Symmetric structure
2. Regularity
3. Copolymer
4. Talking more

## 4.3.3 Crystallization Capability

### 1. Symmetric structure

- PE [-CH2-CH2-]\_n
- PTFE [-CF2-CF2-]\_n
- PVDC [-CH2-CHCl-CH2-CHCl-]\_n
- Any other samples?  
PIB, POM, PA, Polyester .....

## 4.3.3 Crystallization Capability

### 2. Regularity

- ASYMMETRIC, not Crystallizable
- PS
  - PMMA
  - PVAc
  - PP
- Randomly polymerized NOT

**Stereoregular polymers are crystallizable**

All Cis-PB and All Trans-PB (stronger)  
PCTFE (90%), PVOH (weak), PVC (very weak)

### 4.3.3 Crystallization Capability

#### 3. Copolymer

- Block copolymer – MAYBE
  - PP copolymer
- Random copolymer – usually NOT
  - EPR

### 4.3.3 Crystallization Capability

#### 4. Talking more

- Flexibility
    - PE > PET > PC
  - Crosslinking
- } Mobility of polymer chains
- Branching
  - LDPE < HDPE
- Regularly pack

### 4.3.4 Crystallinity

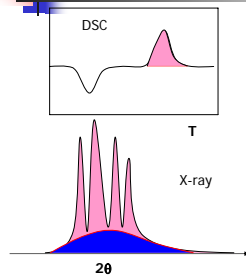
★ 了解结晶度的实验测定方法和计算公式

- Polymer morphology is not only composed of crystalline region and non-crystalline region (amorphous region)
- Intermediate region exists!
- But we assume the morphology is only a two-phase model to simplify it ☺

### 4.3.4 Crystallinity

- Degree of crystallinity is always labeled as  $x$ , and usually being simply called **crystallinity**.
- Volume crystallinity,  $x_v = v_c / (v_c + v_a)$
- Mass crystallinity,  $x_m = m_c / (m_c + m_a)$
- $x_m = x_v \cdot (\rho_c / \rho_s)$ 
  - $\rho$  – density,  $s$  – sample

### Most commonly used methods to determine the crystallinity



- **Important !**
  - The crystallinity obtained relies on the **methods** being used **greatly**;
  - Every time the crystallinity being given, the **methods** used must be labeled **at the same time**.

### Experimental determination of crystallinity

- $x_v = (\rho_s - \rho_a) / (\rho_c - \rho_a)$ , why ?
- The density of the sample is usually obtained by means of a **density-gradient column**.

density-gradient column  
— 密度梯度管



$$\rho_s = \frac{m_c + m_a}{V_c + V_a}$$

$$\rho_s(V_c + V_a) = m_c + m_a = \rho_c V_c + \rho_a V_a$$

$$\rho_s V_a - \rho_a V_a = \rho_c V_c - \rho_s V_c$$

$$\frac{V_a}{V_c} = \frac{\rho_c - \rho_s}{\rho_s - \rho_a}$$

$$X_v = \frac{V_c}{V_c + V_a} = \frac{1}{1 + \frac{V_a}{V_c}} = \frac{1}{1 + \frac{\rho_c - \rho_s}{\rho_s - \rho_a}} = \frac{\rho_s - \rho_a}{\rho_c - \rho_a}$$

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### Question

It has been summarized from many experiments that

$$\rho_c / \rho_a = 1.13$$

Please deduct the following equation

$$\rho / \rho_a = 1 + 0.13 X_c^V$$

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### 4.3.5 Crystallization to property

- **例4-1** 有两种乙烯和丙烯的共聚物，其组成相同（均为65% 乙烯和35% 丙烯），但其中一种室温时是橡胶状的，一直到稳定降至约-70℃时才变硬，另一种室温时却是硬而韧又不透明的材料。试解释它们内在结构上的差别。
- **解：**前者是无规共聚物，丙烯上的甲基在分子链上是无规排列的，这样在晶格中难以堆砌整齐，所以得到一个无定形的橡胶状的透明聚合物。  
后者是乙烯和有规立构聚丙烯的嵌段共聚物，乙烯的长嵌段堆砌入聚乙烯晶格，而丙烯嵌段堆砌入聚丙烯晶格。由于能结晶从而是硬而韧的塑料，且不透明。
- **错误分析：**“前者是交替共聚物”。交替共聚物的结构规则性也很好，也易结晶。

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### 4.3.5 Crystallization to property

- **例4-2** 为什么聚对苯二甲酸乙二醇酯从熔体淬火时得到透明体？为什么IPMMA是不透明的？
- **解：**聚对苯二甲酸乙二醇酯的结晶速度很慢，快速冷却时来不及结晶，所以透明。等规PMMA结晶能力大，结晶快，所以它的试样是不透明的。
- **例4-3** 试分析聚三氟氯乙烯是否结晶性聚合物？要制成透明薄板制品，问成型过程中要注意什么条件的控制？
- **解：**是结晶性聚合物，由于氯原子与氟原子大小差不多，分子结构的对称性好，所以易结晶。  
成型过程中要使制品快速冷却，以降低结晶度并使晶粒更细小，才能得到透明薄板。

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