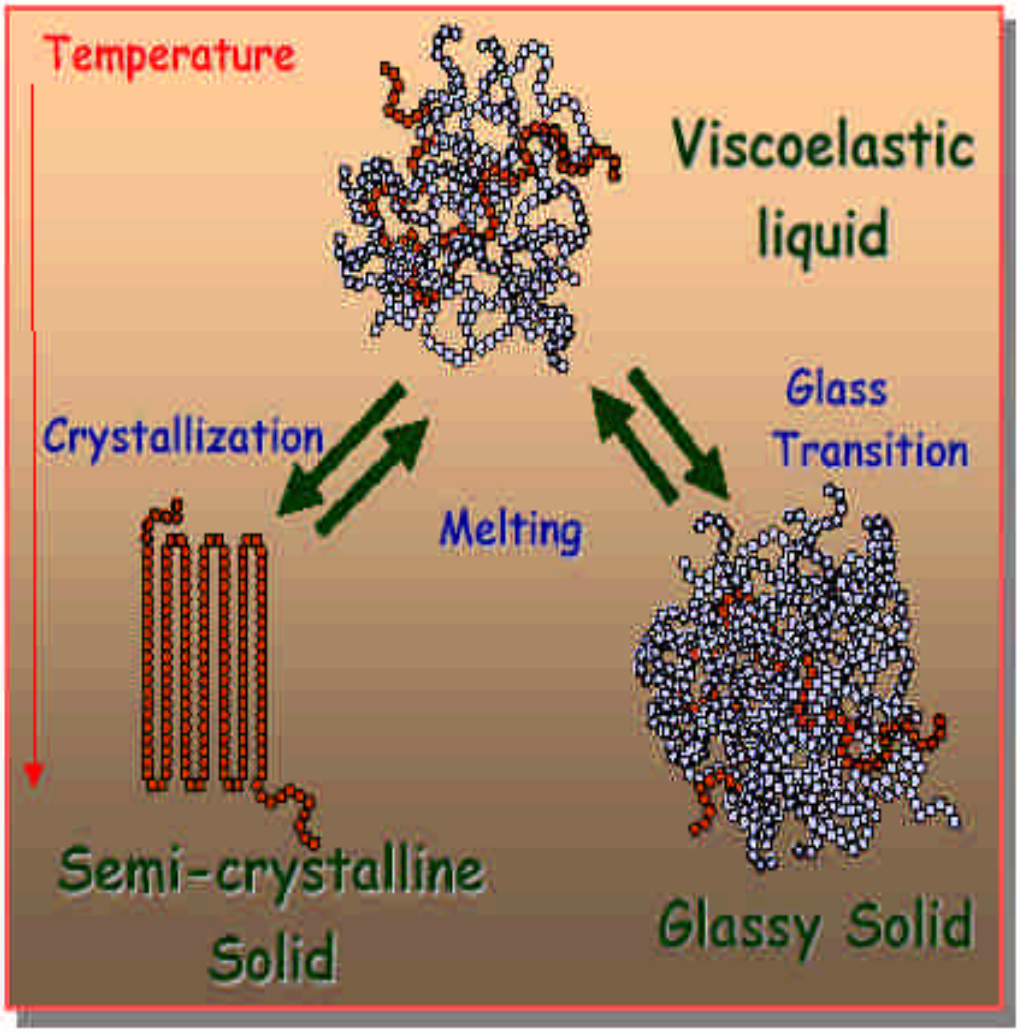
Chapter 3

MORPHOLOGY AND ORDER IN CRYSTALLINE POLYMERS

Polymer Solid State

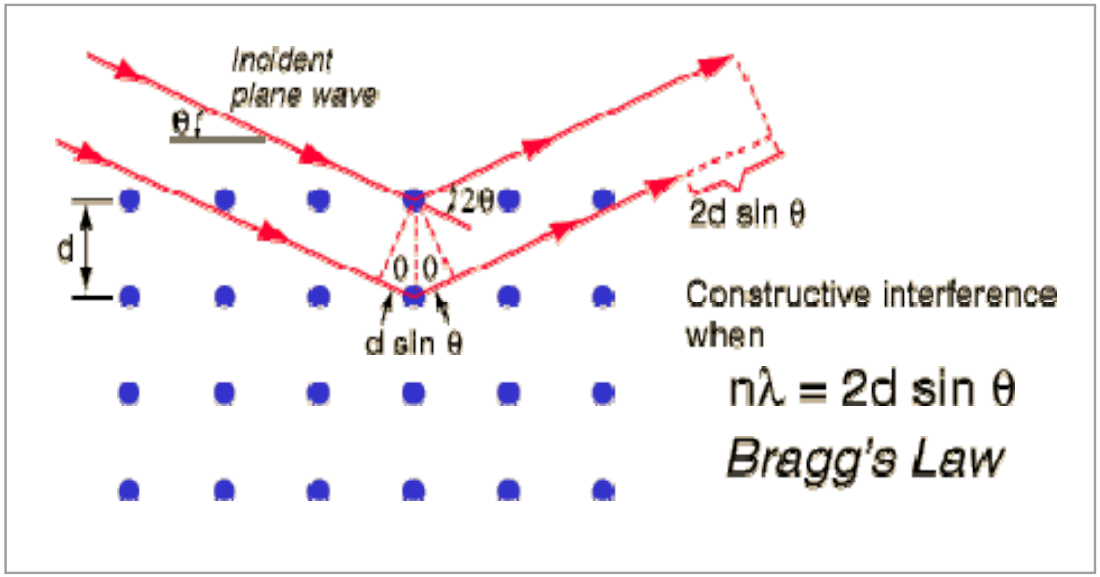


- What is the arrangement of the chains in the crystalline domains and the morphology of these crystal?

Polymers yield X-ray diffraction patterns?

- In 1920s, it was found that some polymers did yield x-ray diffraction pattern!
- Metals and inorganic salts exhibit well-defined patterns
- Polymers produced only a few broad Bragg diffraction peaks pattern
- Small, relatively perfect crystallites existed in an amorphous matrix

Bragg's Law



Schematic diagram for determining Bragg's law

$$n\lambda = 2d\sin\theta,\ n=1,2,3\ldots$$

λ :**wavelength**

θ :**Angle between x-ray beam**

n :**Any whole number**

Fringed micelle model

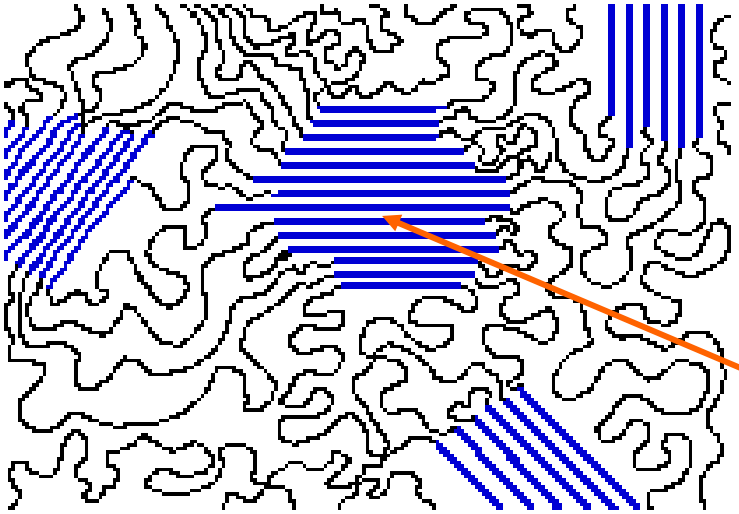
- X-ray deffraction showed their dimensions to be on the order of ***several hundred Anstroms***

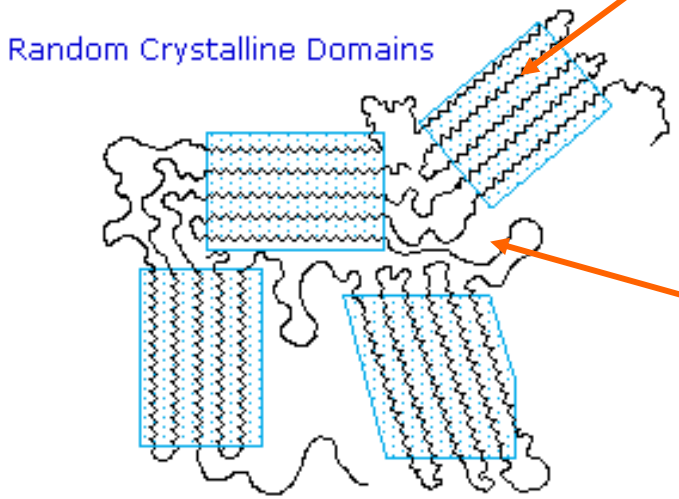
- The crystallites were though to serve as ***mechanical crosslinks*** and to affect the physical properties in much the same way as **chemical crosslinks in vulcanized rubber**

Crystallographic structures of polymers

結晶學構造

- Configuration: defined in terms of its chemical repeat unit and a statement of molecular architecture
- Local conformation: refer to geometrical arrangements of neighboring groups in molecule, which can be altered only by rotation about primary valence bonds
- Molecular packing: refer to the arrangement of the molecules in the crystal in terms of ***unit cell*** and its contents





- **As you can also see in the picture, a single polymer chain may be partly in *a crystalline lamella*, and partly in the amorphous state. Some chains even start in one lamella, cross the amorphous region, and then join another lamella. These chains are called *tie molecules*.**

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No polymer is completely crystalline. If you're making plastics, this is a good thing. Crystallinity makes a material strong, but it also makes it brittle. A completely crystalline polymer would be too brittle to be used as plastic. The amorphous regions give a polymer *toughness*, that is, the ability to bend without breaking.

Amorphousness and Crystallinity

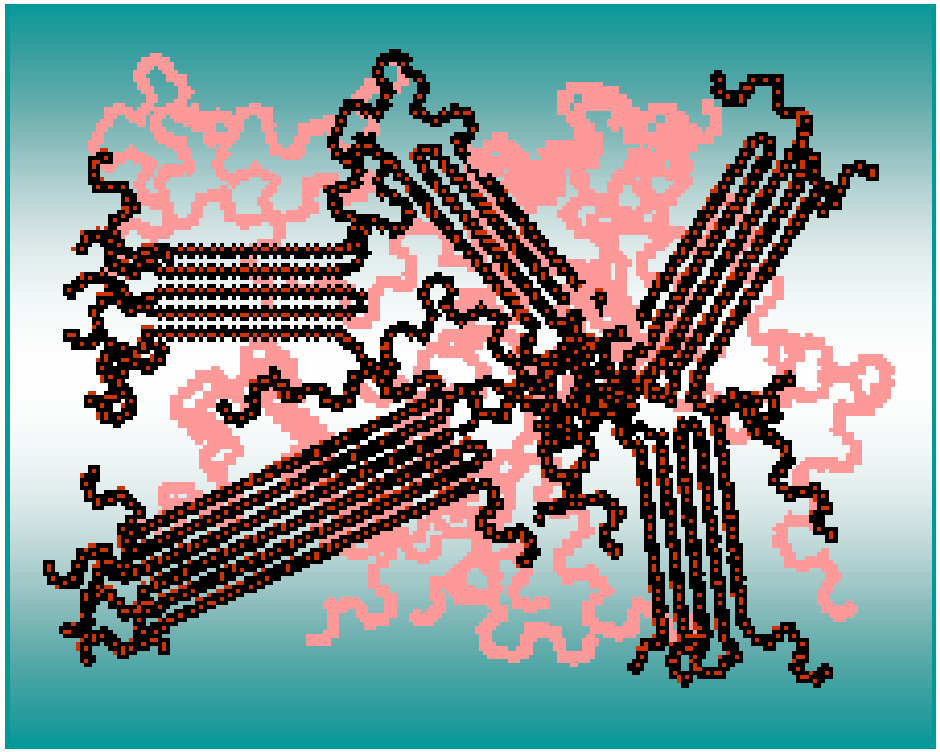
Are you wondering about something? If you look at those pictures up there, you can see that some of the polymer is crystalline, and some is not! *Most crystalline polymers are not entirely crystalline.* The chains, or parts of chains, that aren't in the crystals have no order to the arrangement of their chains. They are in the *amorphous state*. So a crystalline polymer really has two components: *the crystalline portion* and *the amorphous portion*. The crystalline portion is in the *lamellae*, and the amorphous potion is *outside the lamellae*. If we look at a wide-angle picture of what a lamella looks like, we can see how the crystalline and amorphous portions are arranged.

Three factors that influence the degree of crystallinity

- Chain length
- Chain branching
- Interchain bonding

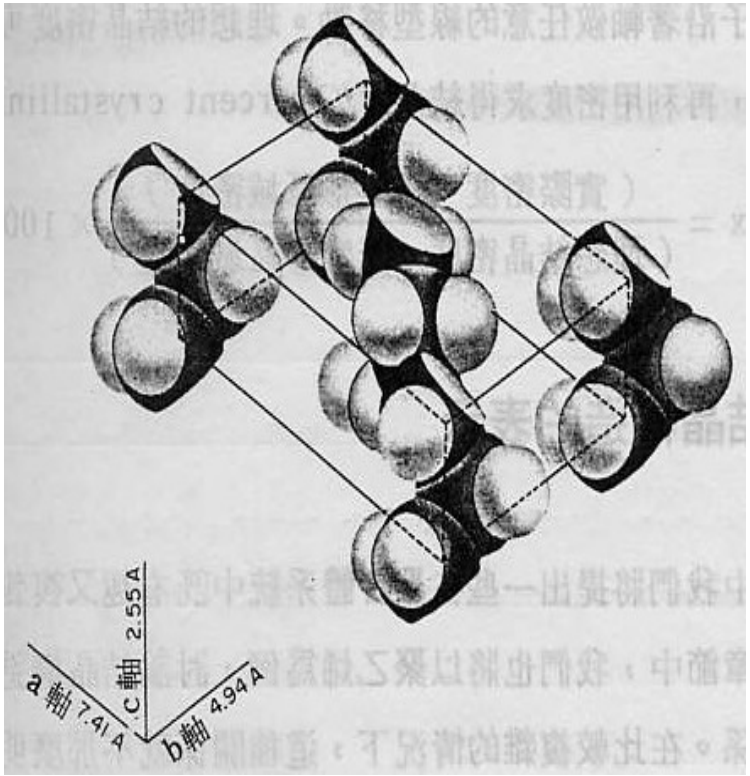
The fringed micelle model

纓狀膠束模型



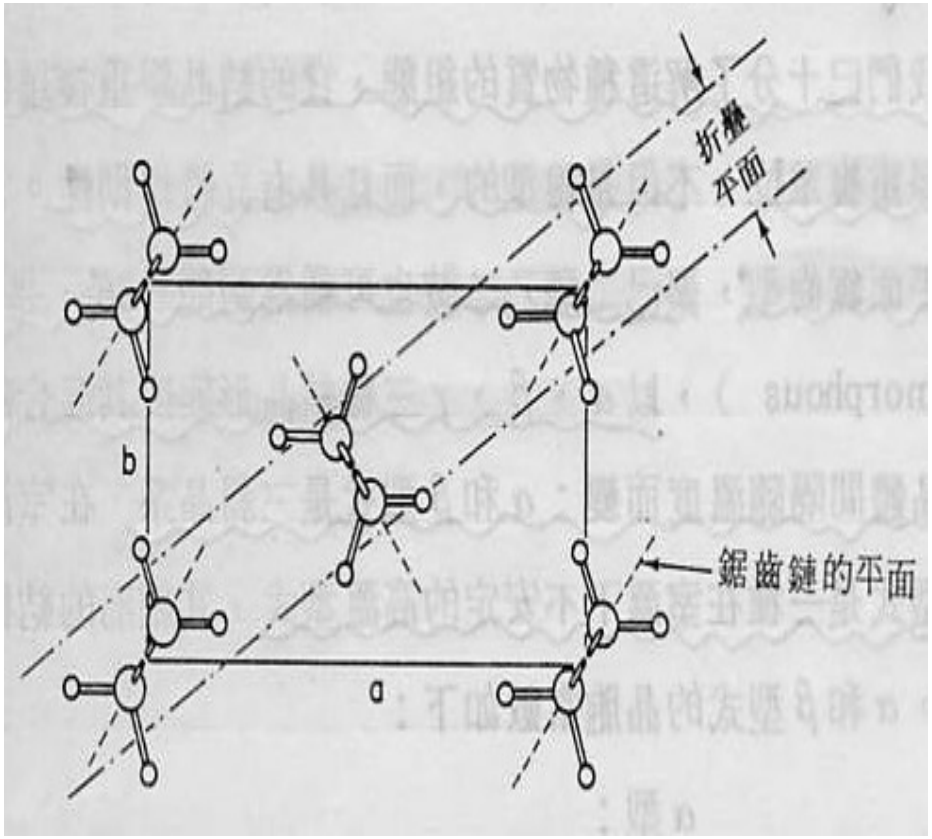
- The molecules passed successively through a number of these crystalline and intervening amorphous region
- The crystallites were pictured as sheaves of chains aligned in a parallel fashion
- X-ray diffraction pattern showed their dimensions to be on the order of *several hundred angstroms*

Arrangement of chains in unit cell of Polyethylene



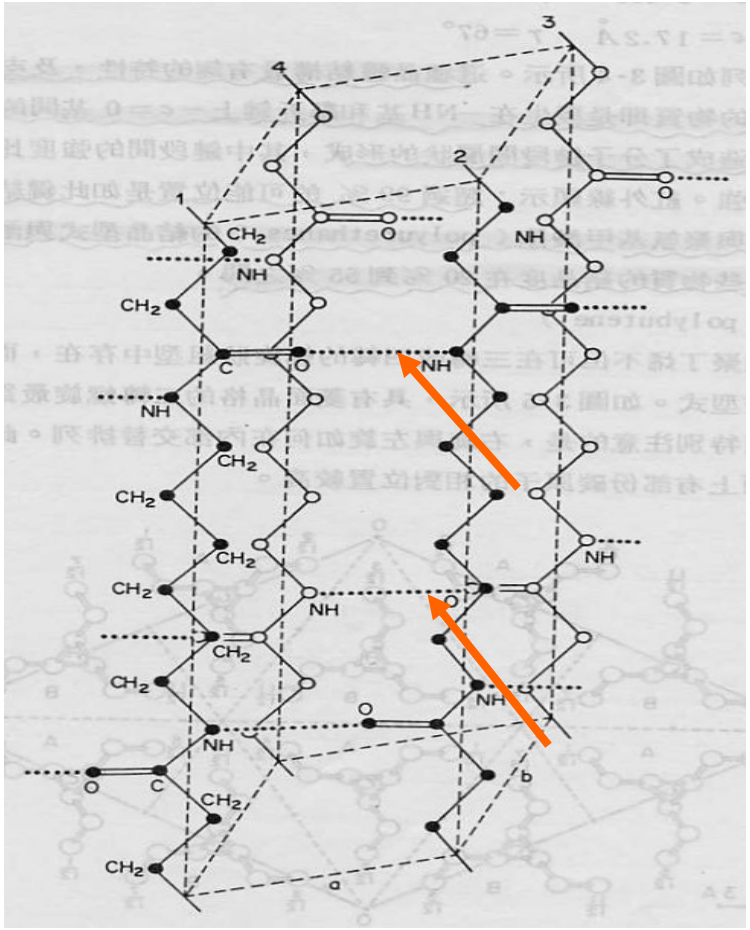
- **Parallelepiped(平行六面體) with axes *a*, *b*, *c* (*T* dependent) and angle α, β, γ**
- ***a* = 7.41 Å**
  ***b* = 4.94 Å**
  ***c* = 2.55 Å(chain axis)**
- **$\alpha = \beta = \gamma = 90^{o}$**
- **Length of *c*-axis = crystallographic repeat unit**

Packing in crystal structure of PE as viewed along the *c-axis*



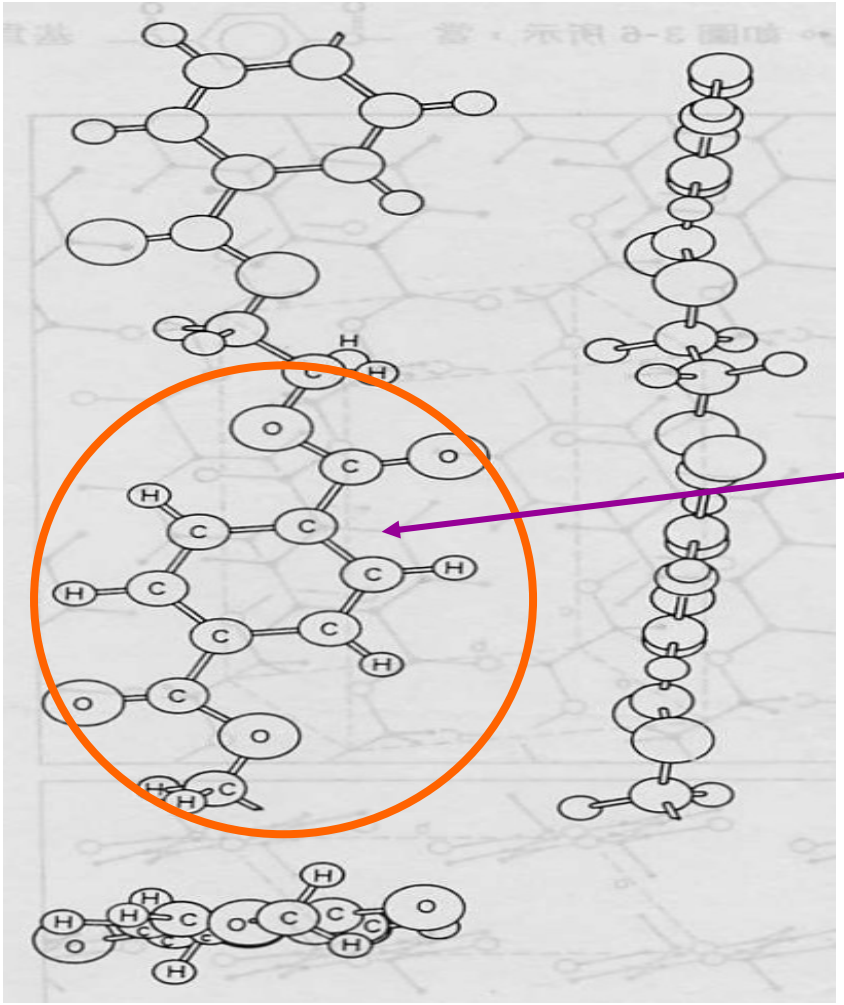
- Top view of unit cell
- The planes of *chain zigzag* and the plane containing the consecutively folded chain are shown as they pass through the unit cell

Packing of Nylon 66 molecules in triclinic unit cell(三斜晶系)



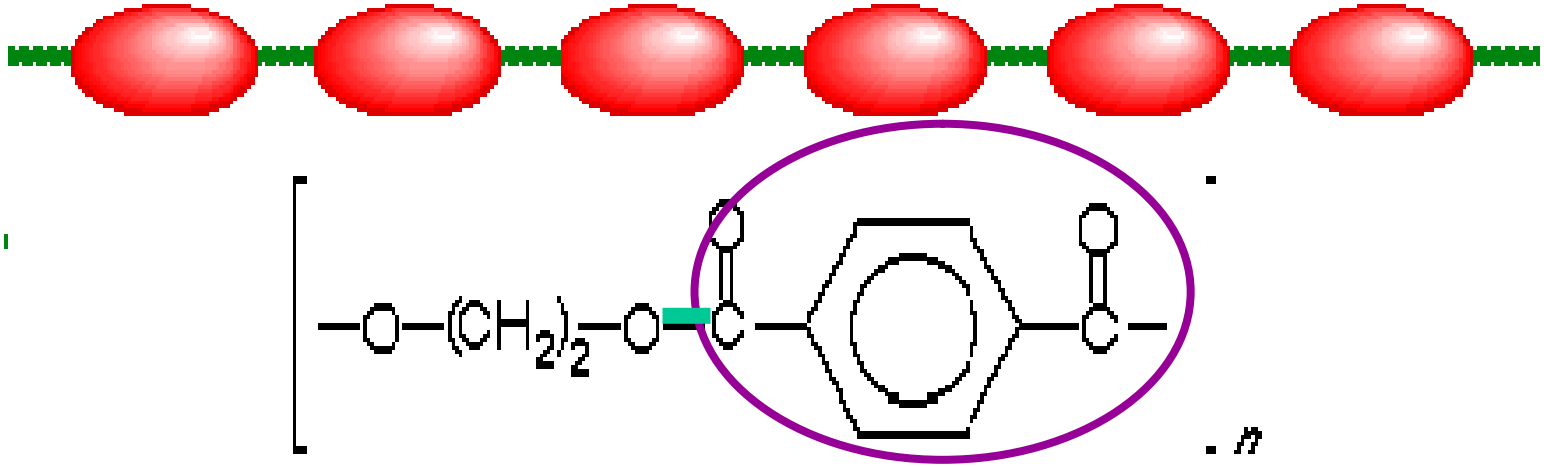
- Its *crystallographic repeat unit* (結晶學重複單位)corresponds to its chemical repeat unit(化學重複單位)
- Its conformation is essentially *planar zigzag*(平面鋸齒型)
- Left(-form) is the most interesting feature of this crystal structure which dominates the properties of *Nylon 66*

Molecular conformation of polyethylene terephthalate
聚對苯二甲酸乙烯酯

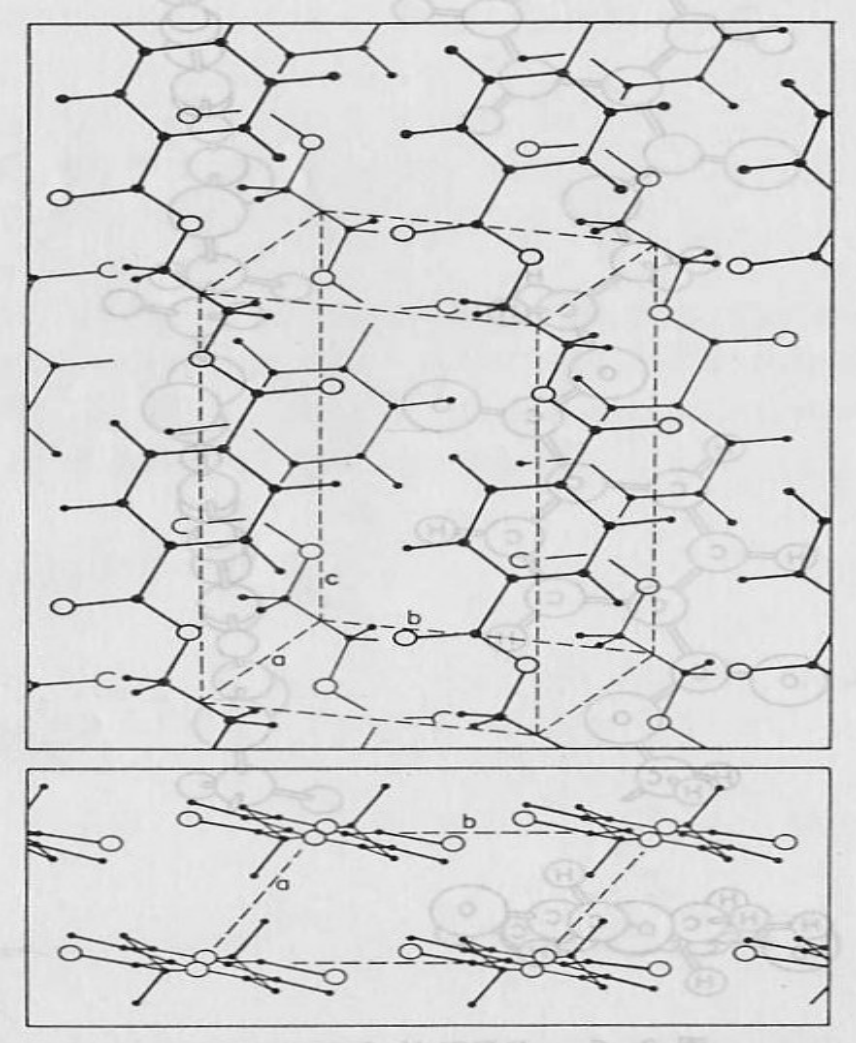


- **Its conformation is nearly a planar zigzag with the benzene ring in the plane of the *zigzag*. As shown, there is some *distortion* along the axis of the chain as the –CO-(C_6H_6)-CO- group make a slight angle with axis by rotation about the C-O bond in order to allow for close packing**

Polyethylene terephthalate

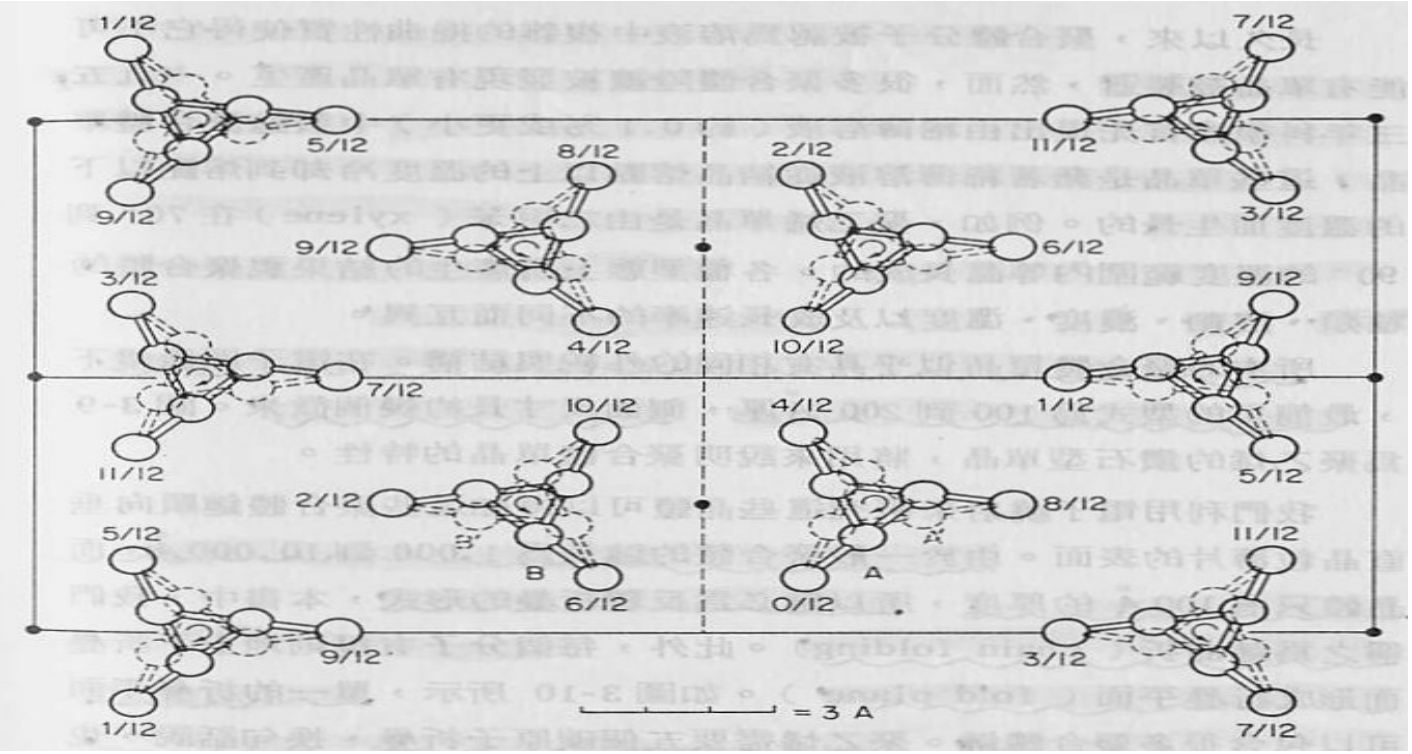


Molecular packing of polyethylene terephthalate



- **Unit cell of PET**
- a = 4.56 Å α = 90°
- b = 5.94 Å β = 118°
- c = 10.75 Å γ = 112°

Projection of the monoclinic unit cell (單斜晶胞) of polypropylene along the chain-axis

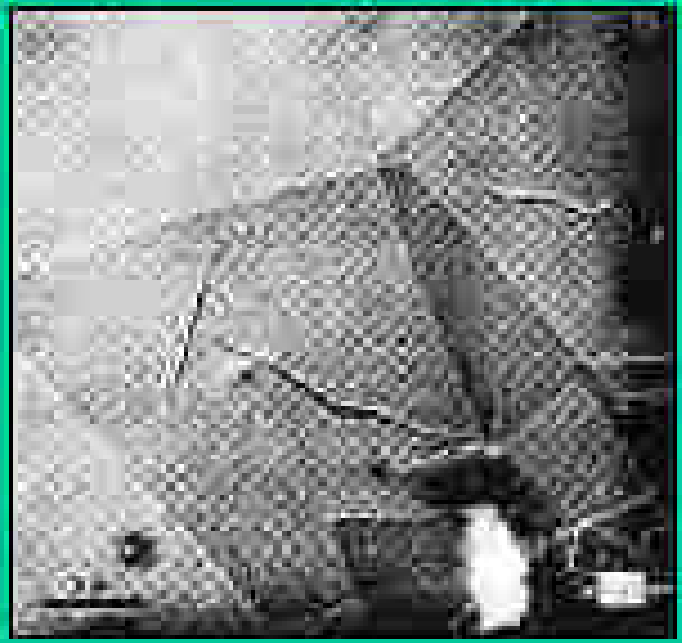


- *Isotactic polypropylene* can crystallize under normal conditions in two forms(hexagonal & monoclinic), both with a conformation of *3 units in one turn*

Single crystals or linear PE

- ***All polymer single crystals seem to have the same general appearance and structure*. In their simplest form, they appear in the electron microscope as thin, flat platelets on the order of *100 to 200 Å* thick and several microns in lateral dimensions**

Single Crystal Lamellae



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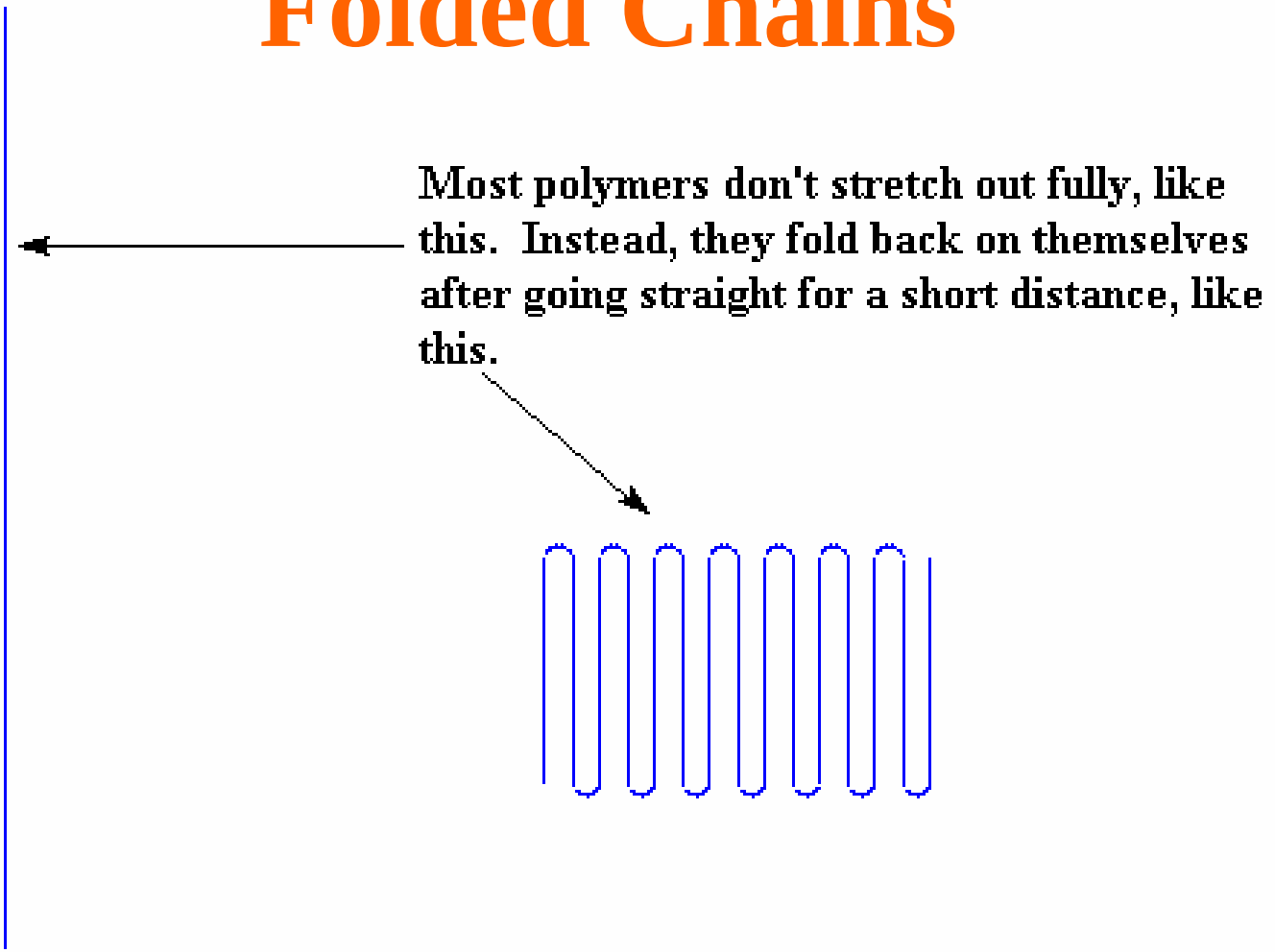
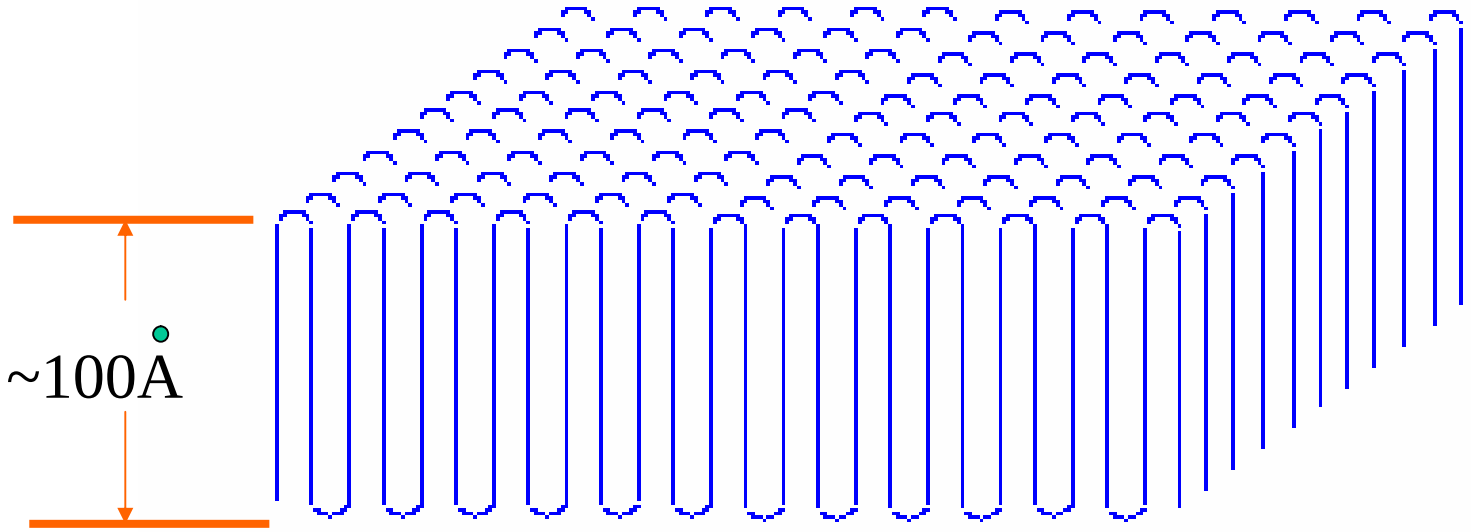
Courtesy of L.B. Gleeson, Penn State

Folded Chains

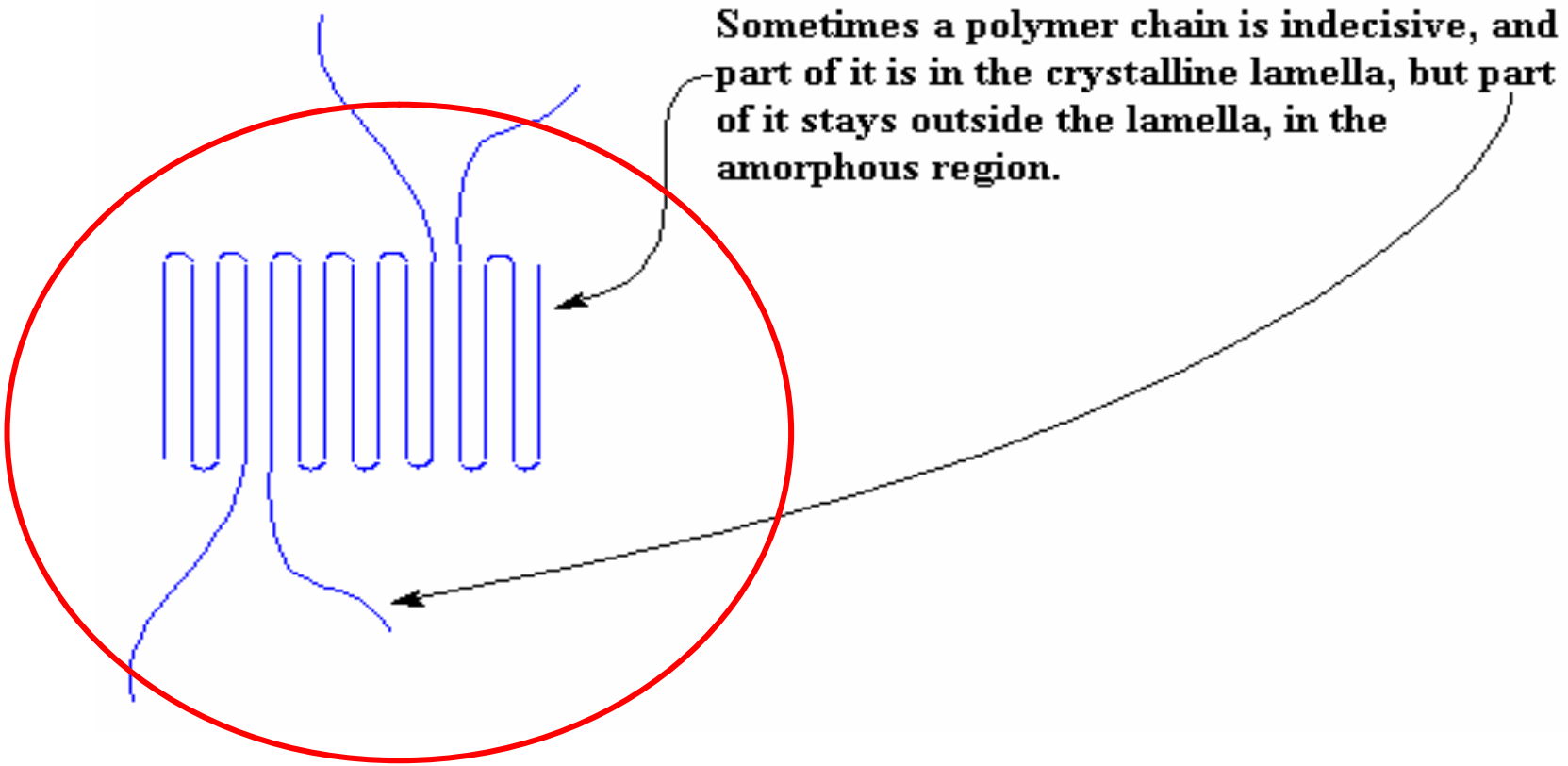


Polymers form stacks of these folded chains. There is a picture of a stack, called a *lamella*, right below.

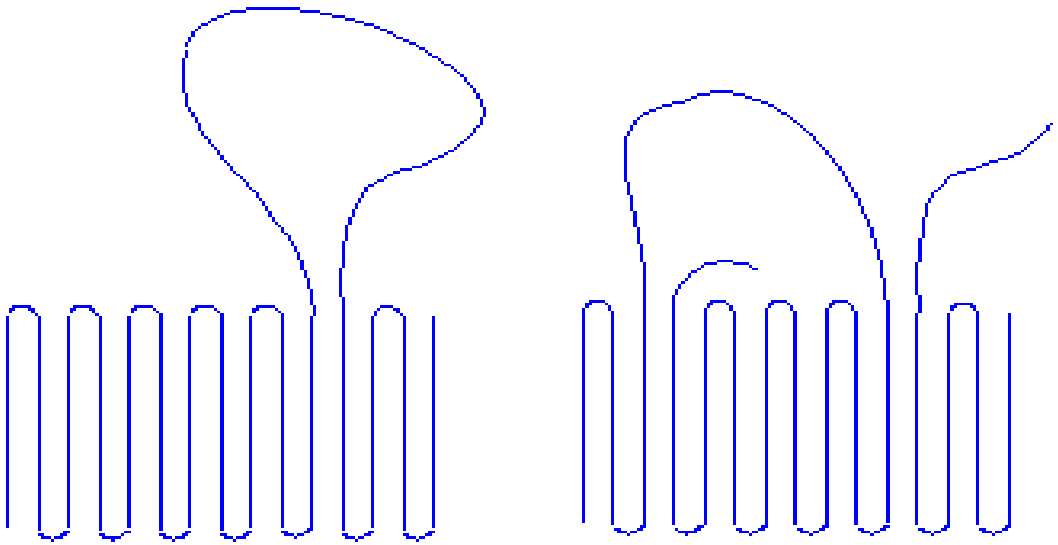


They can fold, and they can stack. A stack of polymer chains folded back on themselves like this is called a *lamella*.

Of course, it isn't always as neat as this. Sometimes part of a chain is included in this crystal, and part of it isn't. When this happens we get the kind of mess you see below. our lamella is no longer neat and tidy, but sloppy, with chains hanging out of it everywhere!

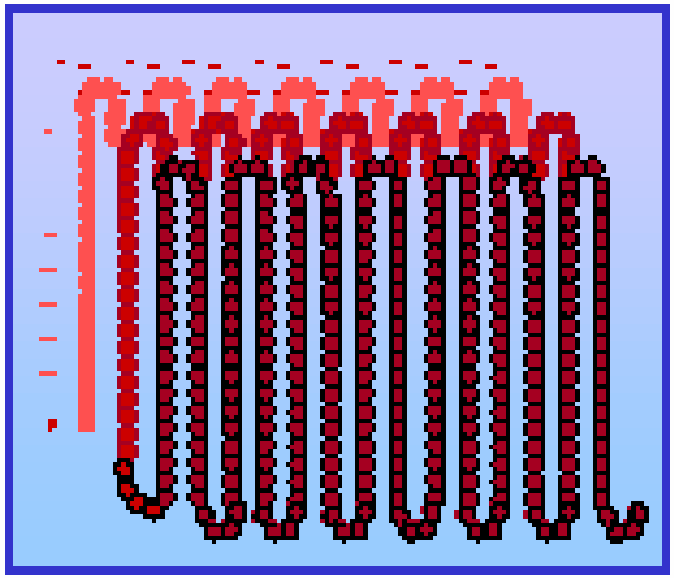


Of course, being indecisive, the polymer chains will often decide they want to come back into the lamella after wandering around outside for awhile. When this happens, we get a picture like this:

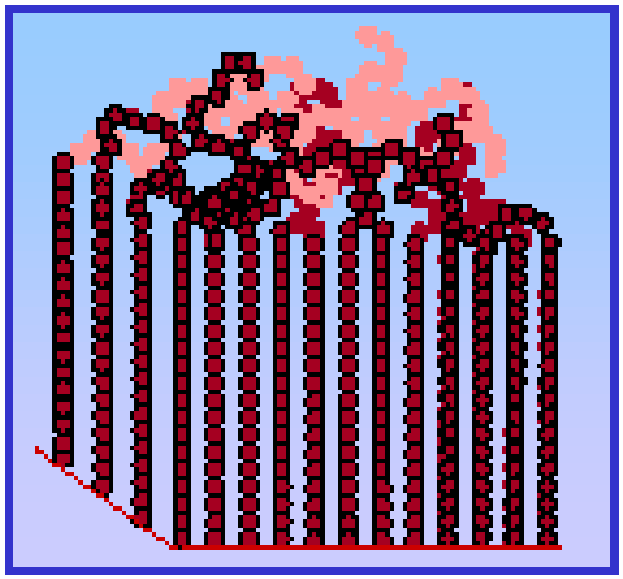


These lamellae have chains that go out for awhile, then come back in. On the left, the chain re-enters the lamellae right next to where it left. On the right our outgoing chain comes back in some distance away from where it left. Both are possible. These two pictures both show what is called the ***switchboard model*** of a polymer crystalline lamella.

The Flory Switchboard Model

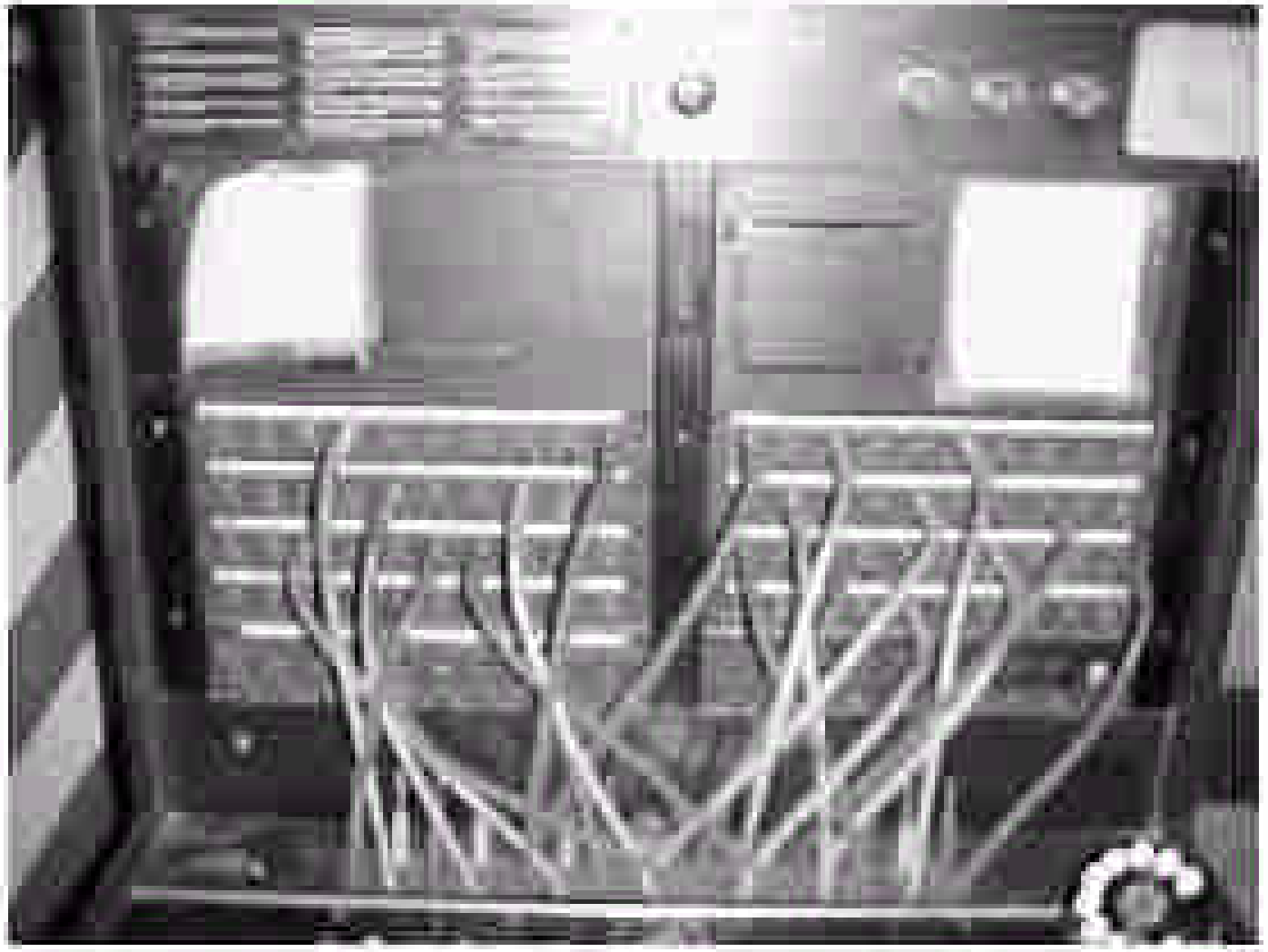


Regular Folding Chain
(Adjacent Re-entry)

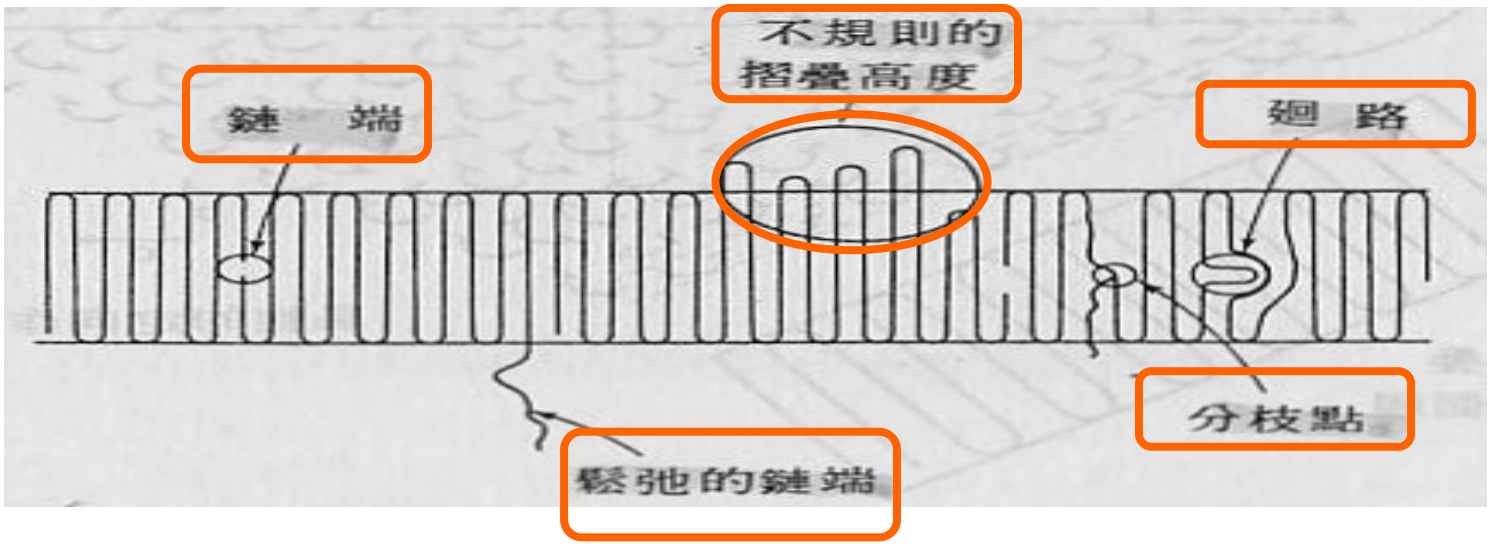


Irregular Chain Folding
(Random Re-entry)

The Flory Switchboard Model

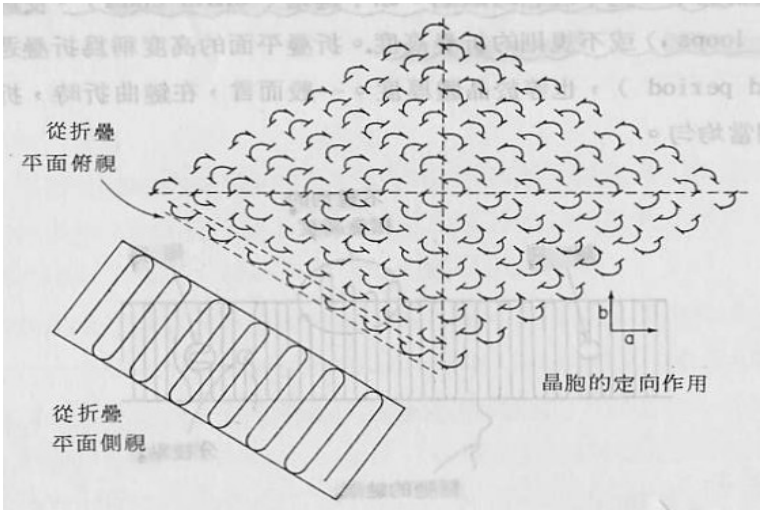


Model of fold plane illustrating chain folding with imperfections which may occur in the structure



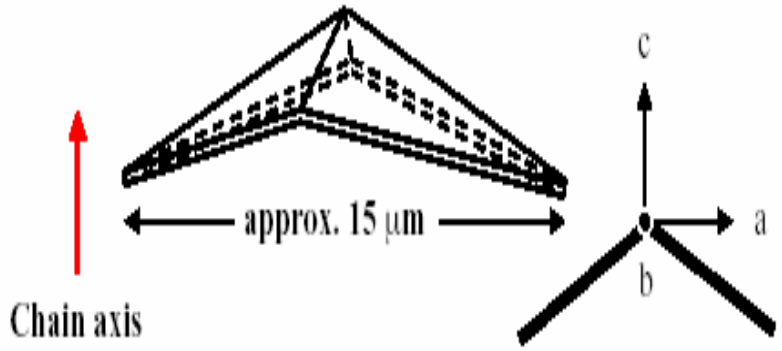
- **Electron-diffraction studies of these crystals indicate that the polymer chains are oriented perpendicular to the plane of the lamellae. Since the crystals are only 100 Å or so thick and the polymer chains are generally on the order of 1,000 to 10,000 Å long, the chain must be folded back and forth on themselves**

Fold packing in a PE single crystal



- Top view of an idealized model of a diamond-shaped PE single crystal, showing its skeletal structure as viewed along the c-axis

Solution Crystallization: Chain Folding

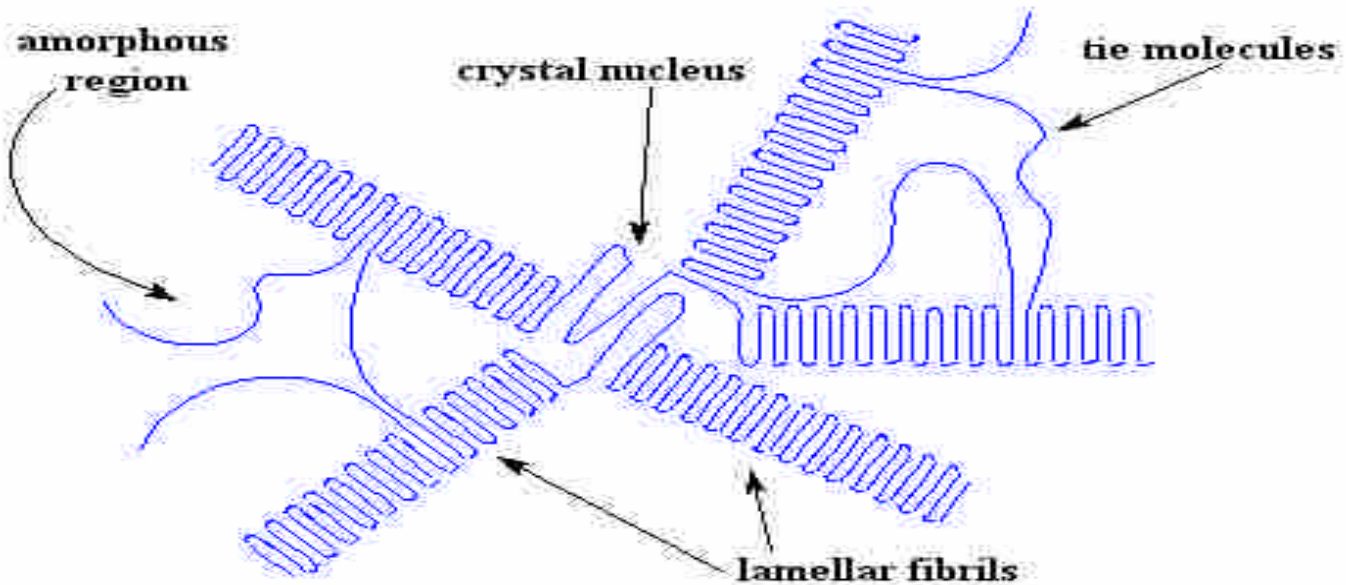


- Side view shows this fold plane

The morphology of polymers crystallized from the melt

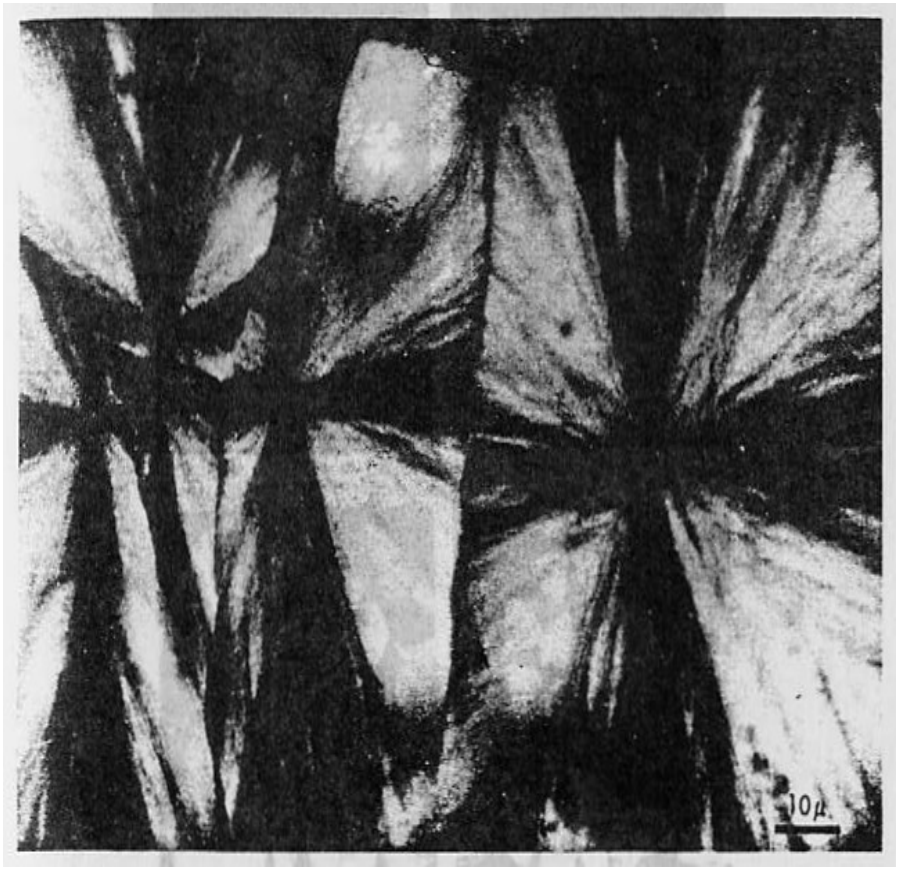
- Polymers crystallized from the melt seem to maintain the two most prominent structural features of single polymer crystals: **aggregates of 100 Å-thick lamellae of different degree of perfection are observed, and the chains are oriented perpendicular to the face of the lamellae so that chain folding must also be inherent in melt-crystallized materials**

Lamella grow like the spokes(輻條) of a bicycle wheel from a central nucleus. (Sometimes scientists like to call the "spokes" lamellar fibrils.) The fibrils grow out in three dimensions, so they really look more like spheres than wheels. The whole assembly is called a "*spherulite*" 球晶. In a sample of a crystalline polymer weighing only a few grams there are many billions of spherulites.



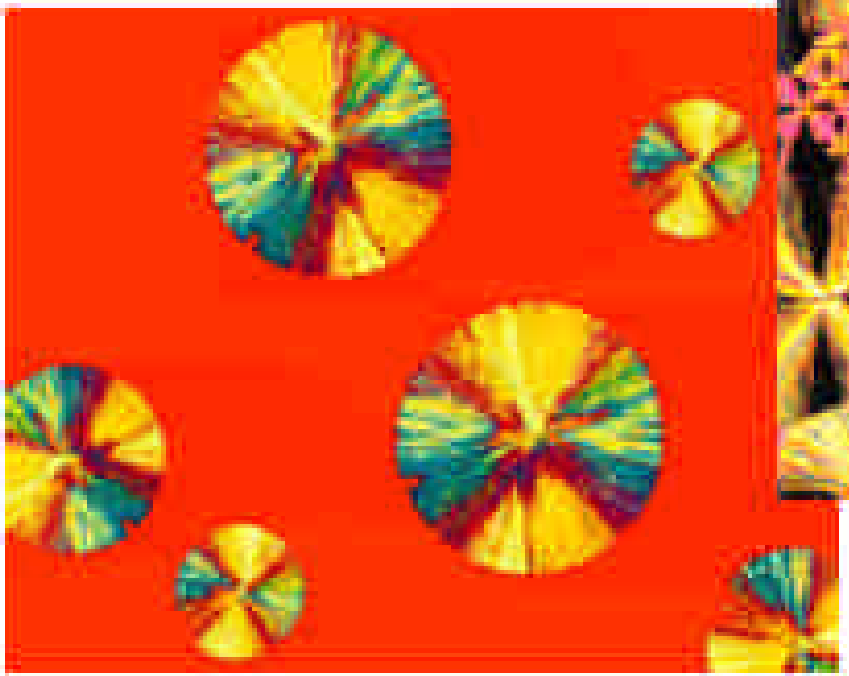
a polymer crystalline spherulite

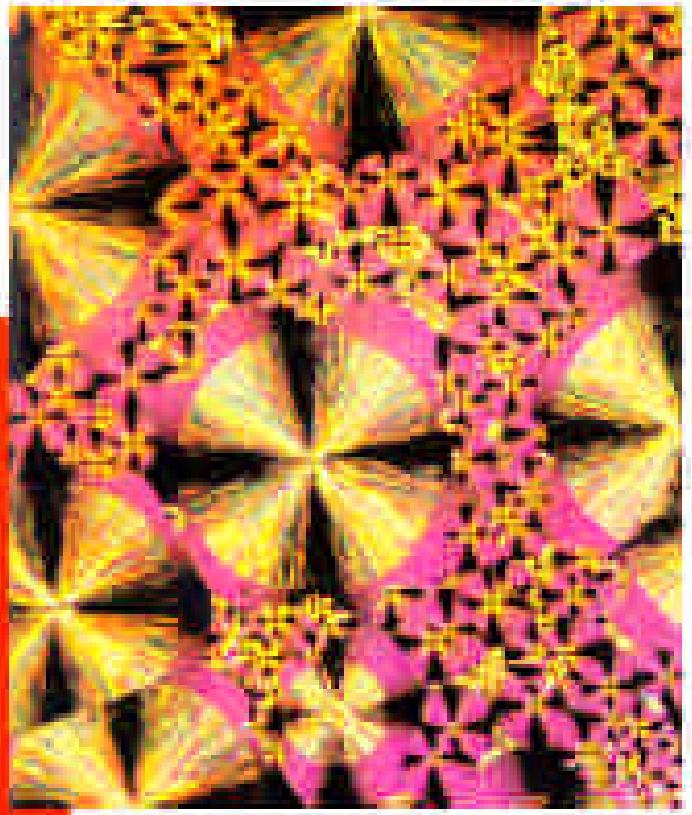
Spherulite(球晶)of a low density polyethylene crystallized from a molten thin film as observed between crossed polarizers



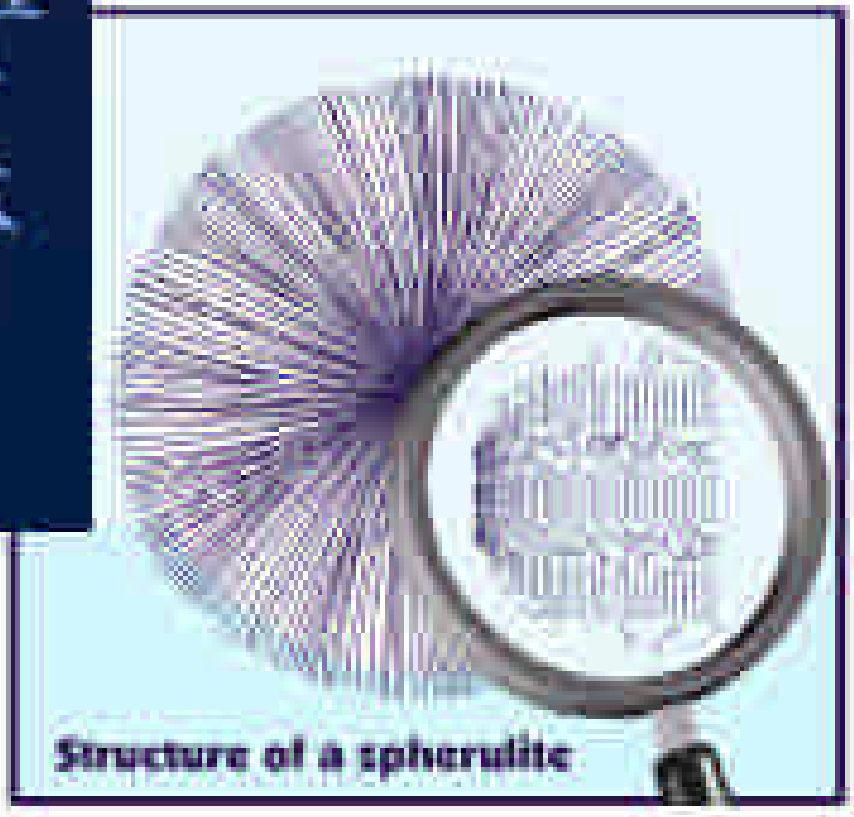
- The characteristic ***Maltese-cross pattern***馬爾它交叉 results from the *birefringent nature* of the polymer film
- Crystal growth can be observed if a temp-controlled mounting stage is used

Spherulites

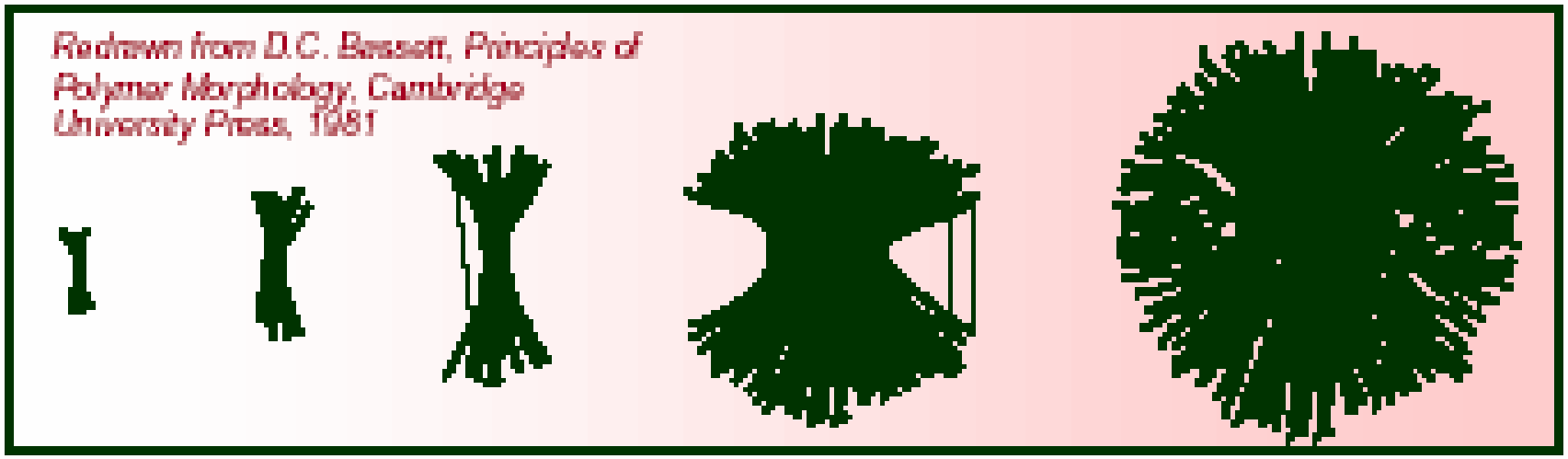




Spherulites

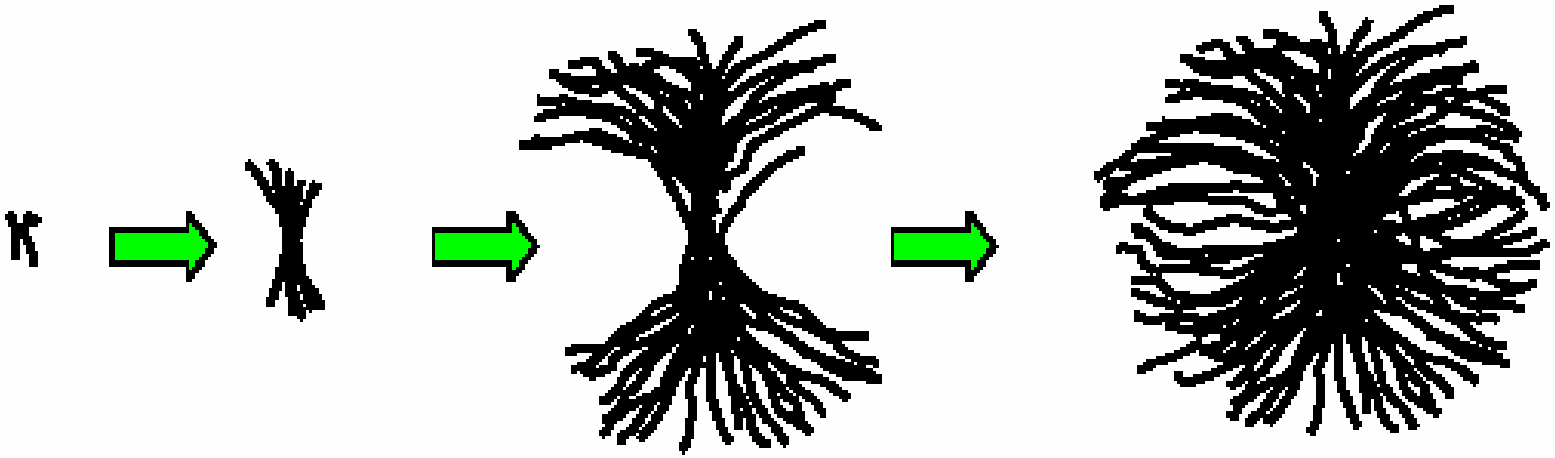


Initial growth of Spherulites

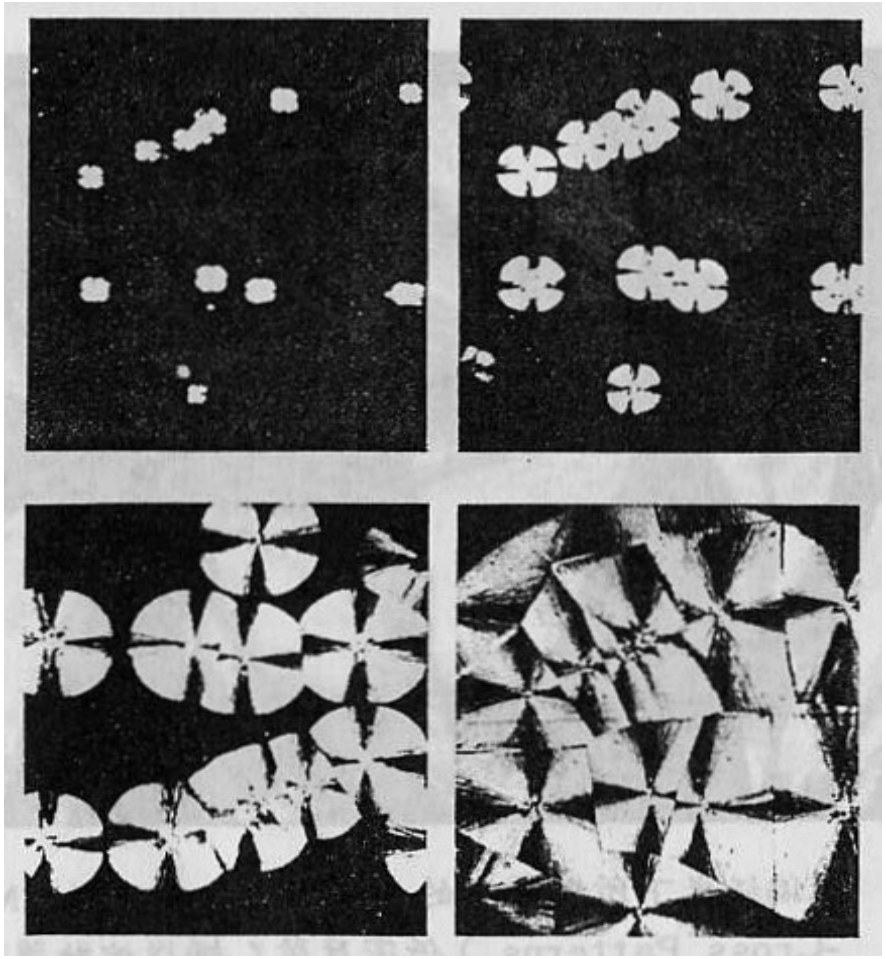


- The initial development of spherulites depends on how they are nucleated (homogeneous vs. heterogeneous).
- Some appear to develop from single crystal lamellar type structures.
- Others show a sheaf-like stage that begins with a fiber-like structure.

Initial Stages of Spherulite Growth

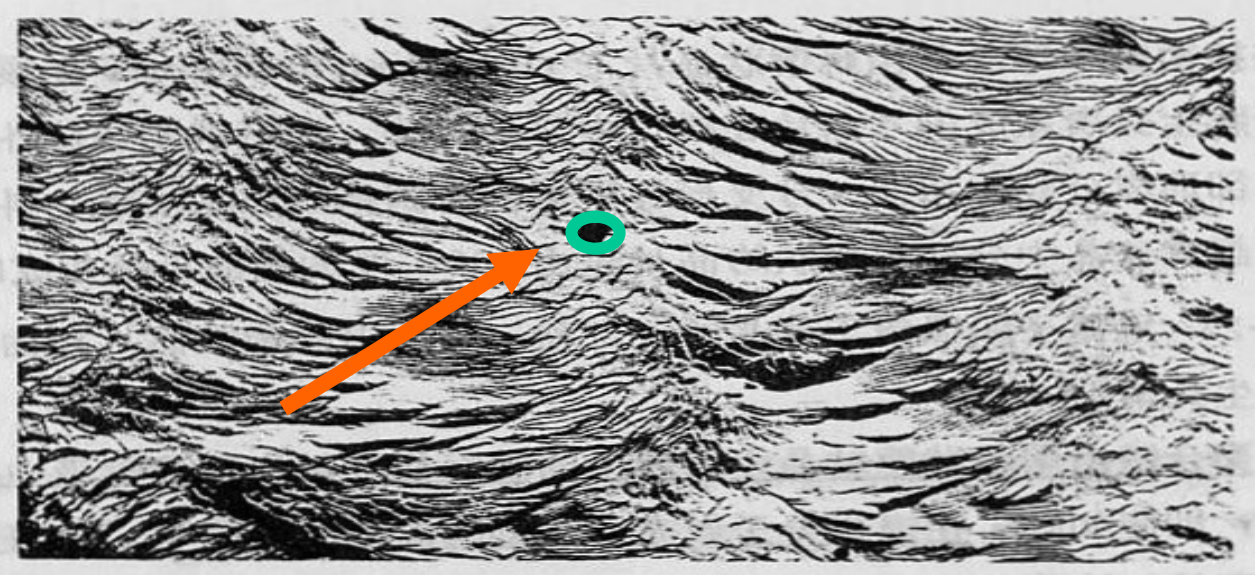


Sequence of growth of spherulites in polypropylene



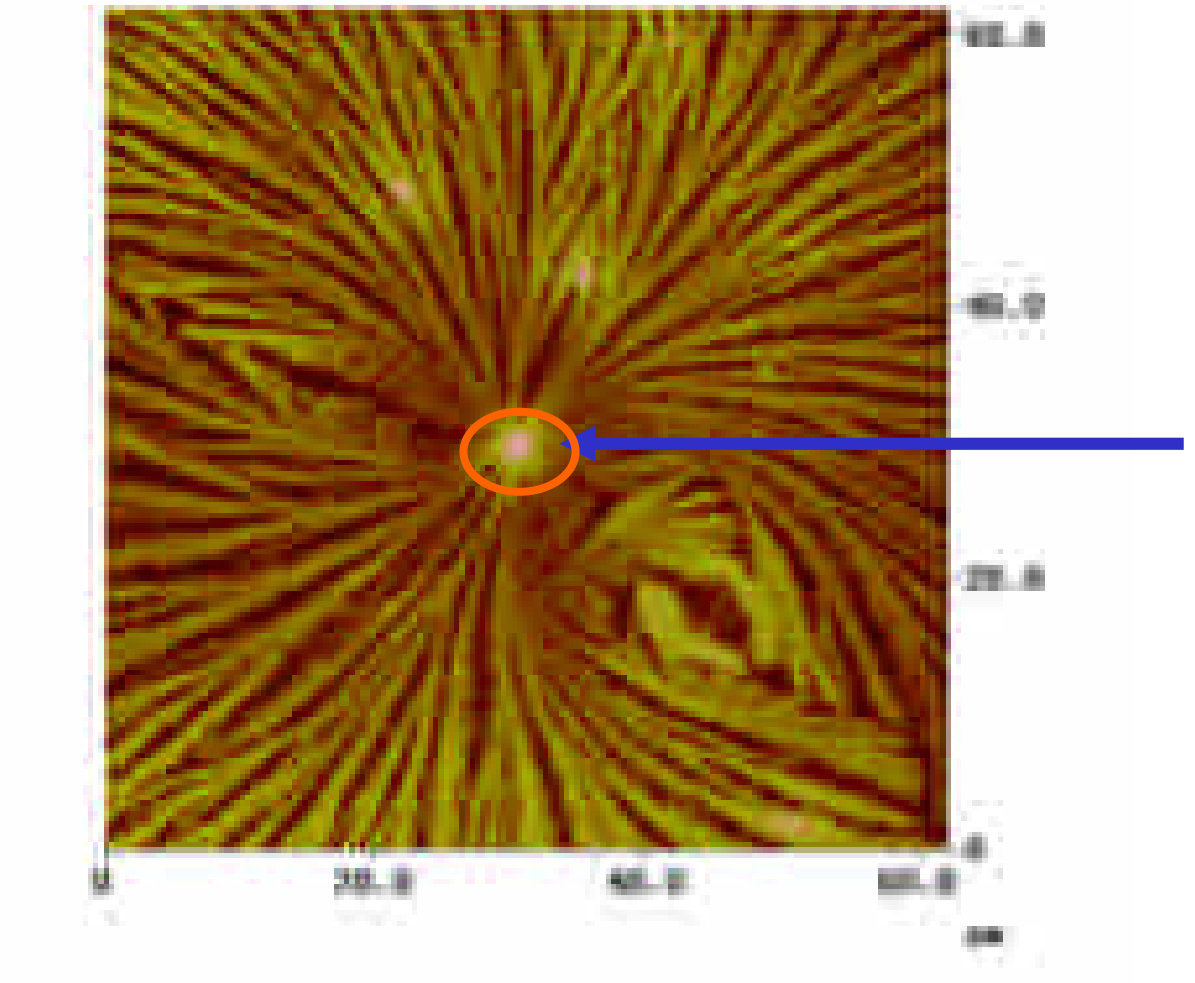
- The sample is first heated above its Tm and then supercooled by 10 or 15°C
- Rate of crystallization can be measured from such micrographs by comparing the area occupied by the spherulites to the total area

Surface replica of a portion of a linear polyethylene spherulite球晶表面的複製



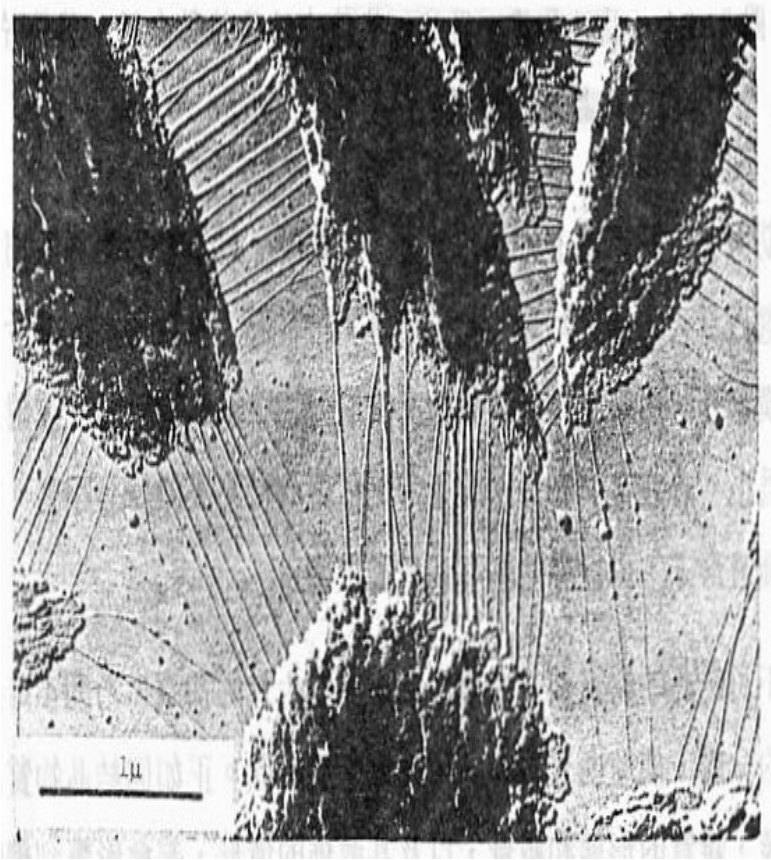
- The spherulites are comprised of ribbonlike lamellae which grow radially from a central nucleus
- The lamellae are parallel at the nucleus, but as they begin to grow outward, they diverge, twist, and branch to form an overall structure being radially symmetric spherulite

Tapping Mode Atomic Force Microscopy:



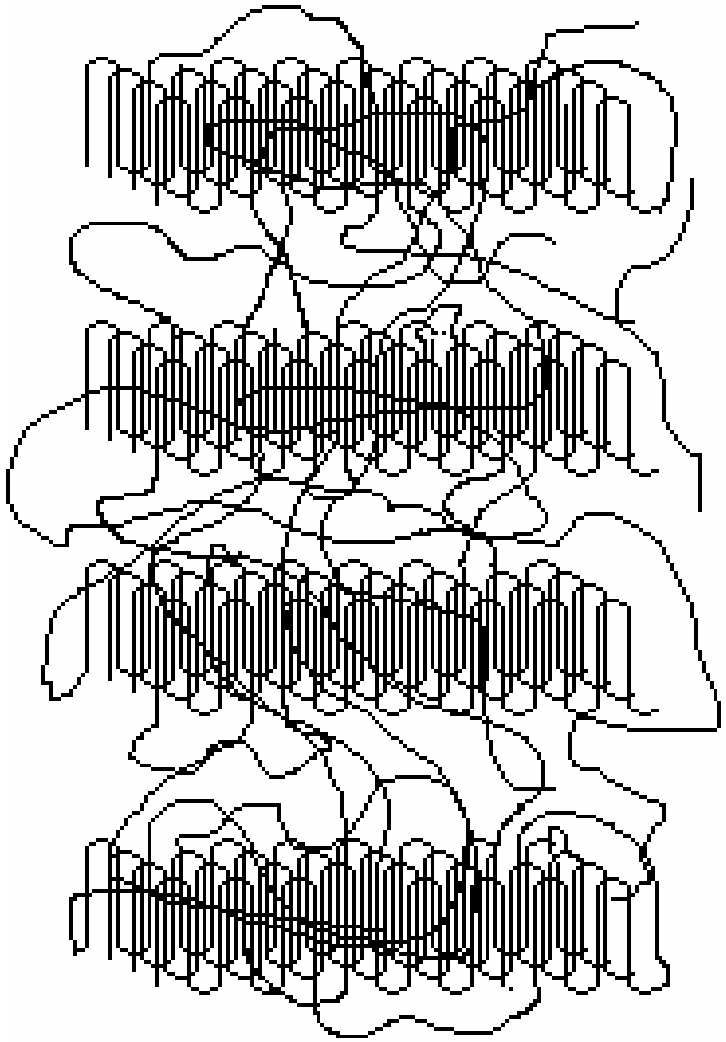
Interlamellar ties 晶片間的接合

Boundary region between spherulite grown at 95°C in a PE fraction



- The links are *highly oriented and strongly anchored to* the neighboring lamellae
- These links should possess *considerable strength*

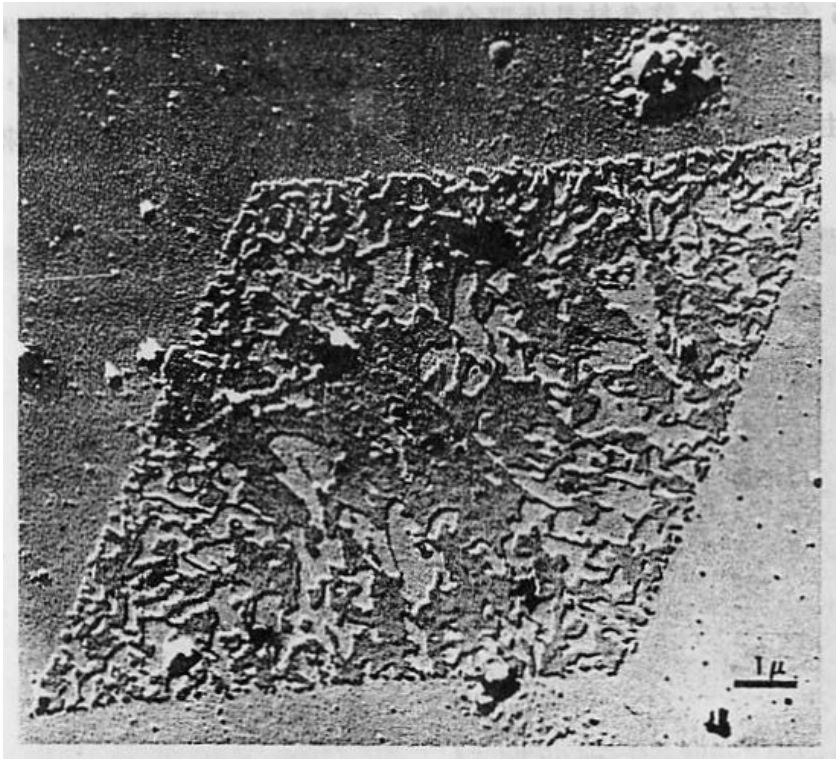
Interlamellar ties



PE Crystallized under Pressure

- Fracture surface of a polyethylene spherulite center
- At about 5000 atm and a T_c at 236 ^oC, the density ~0.997
- All molecules crystallize, not in a folded fashion, but in paraffinlike crystals in which the chains are *fully extended*

Annealing Polymer Crystals



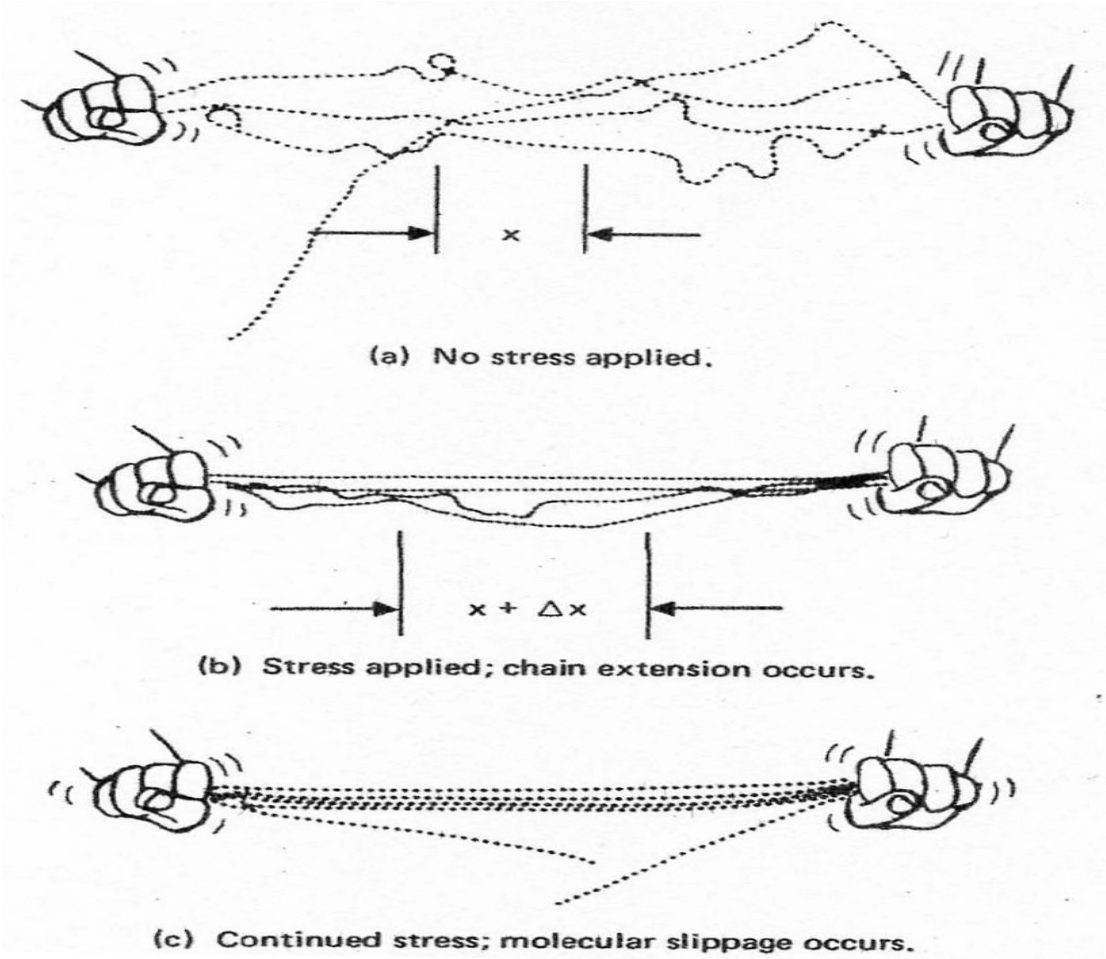
Thickness increase from 100 Å to ~200 Å during annealing

- Annealing a formed crystal is accomplished by maintaining the crystal at a T above its Tc
- Upon annealing, extensive *remelting and recrystallization* take place and lead rapidly to a severalfold increase in the fold period of lamellae
- A single crystal of linear PE crystallized from perchloroethylene solution, then annealed for 30 min at 125°C, 10° below T_m

Orientation and Drawing

- **No preferred orientation of crystallites or molecules when bulk polymer is crystallized in the absence of external forces**
- **The crystallites and molecules become *oriented* if it is subjected to an external force, such as mechanical drawing**
- **The polymer *is stronger in the draw direction* than in any other direction, and it will be weakest in directions 90 deg to the draw direction**

Effect of tensile stress on molecular configuration

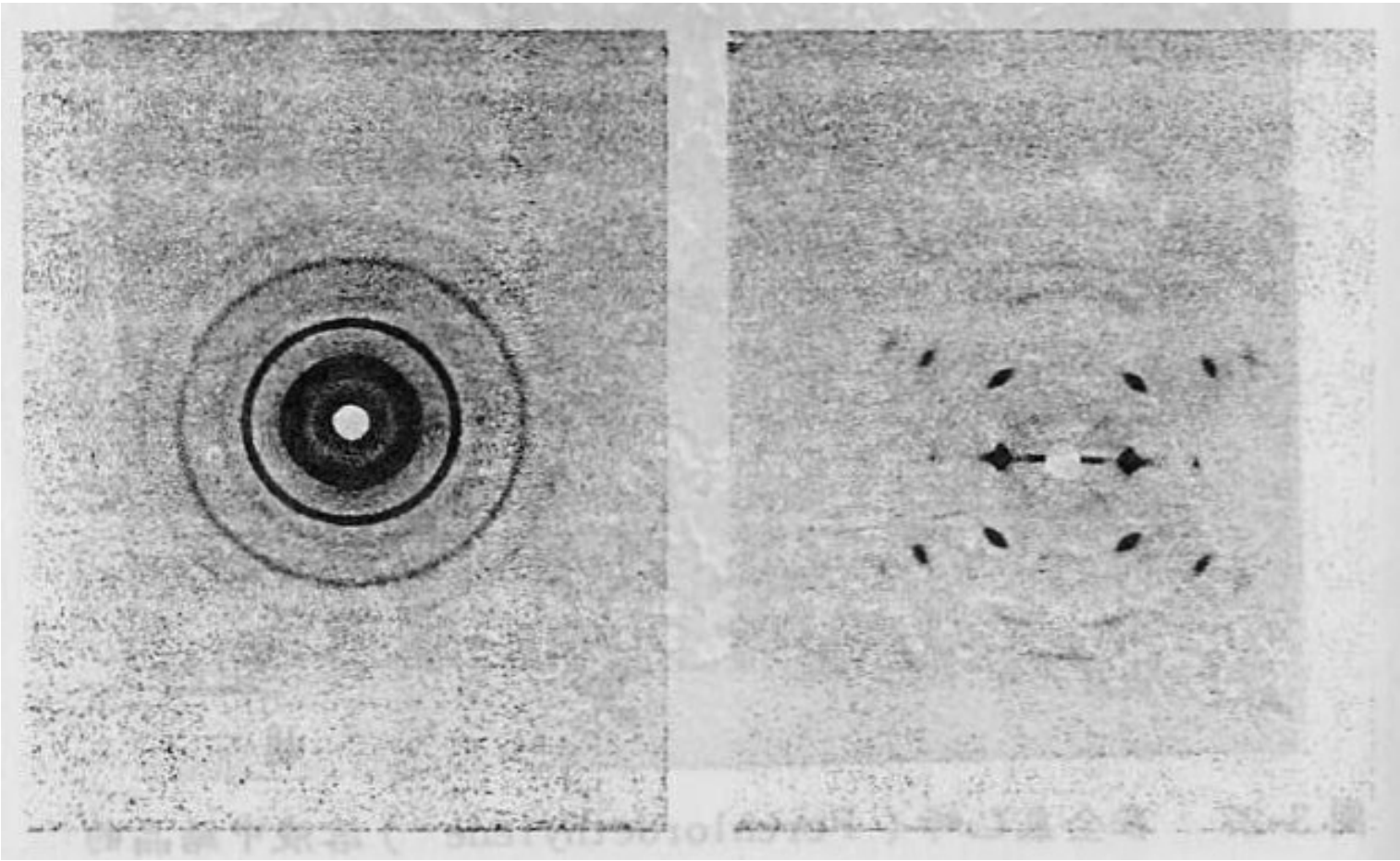


(a) No stress applied.

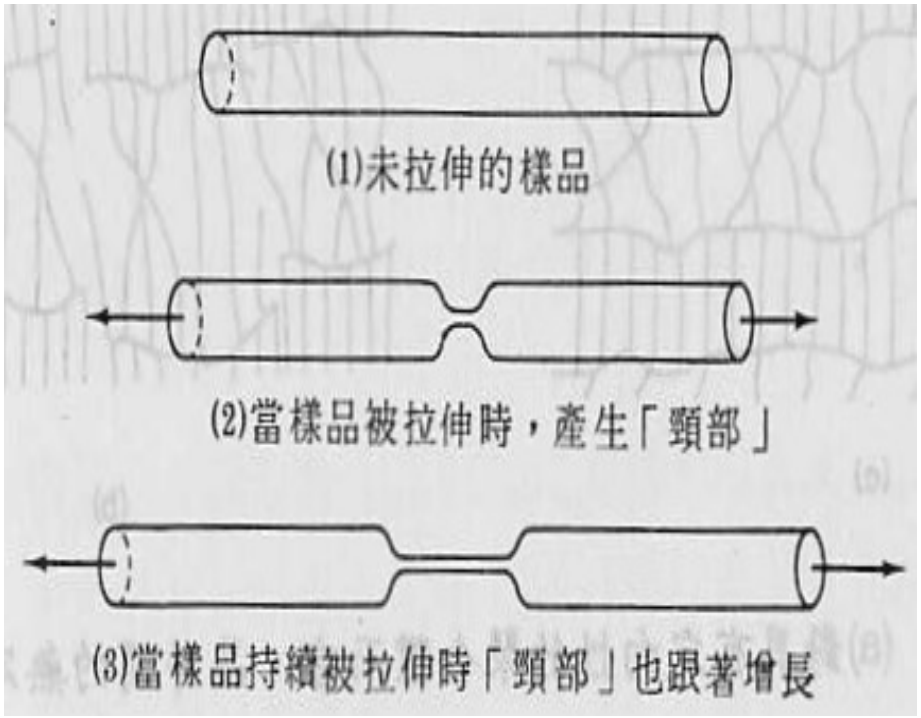
(b) Stress applied; chain extension occurs.

(c) Continued stress; molecular slippage occurs.

X-ray diffraction patterns for (a) unoriented and (b) oriented polyoxymethylene

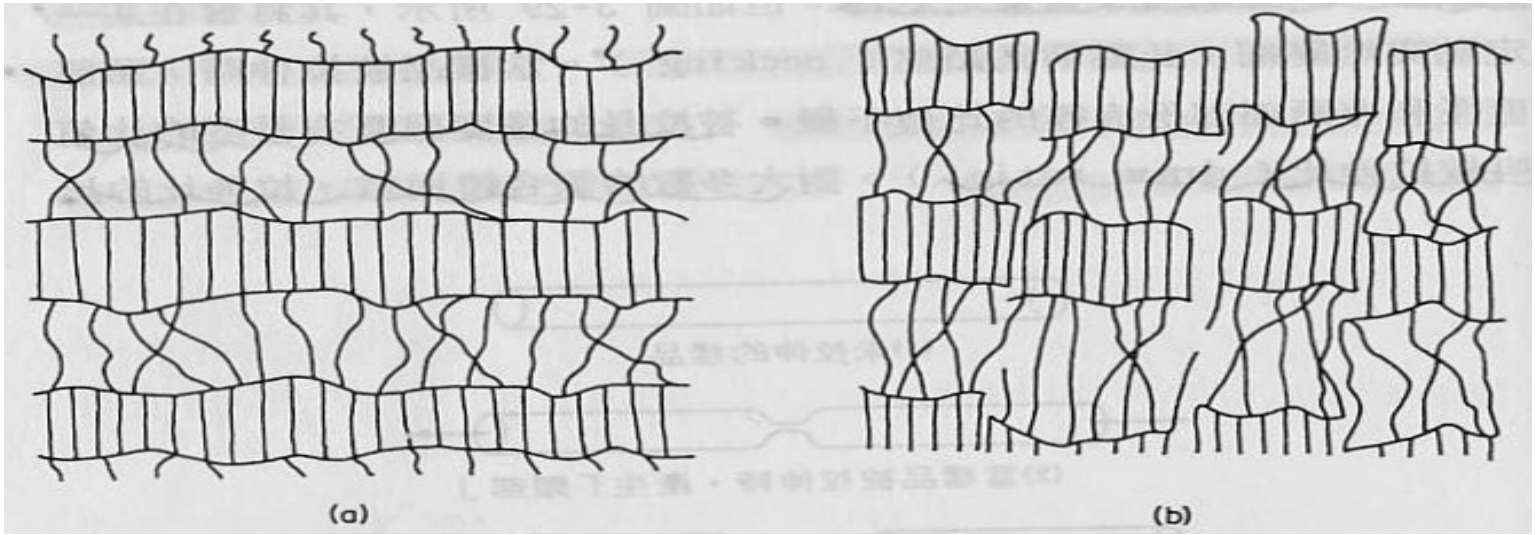


Schematic illustrating the necking process in a crystalline filament

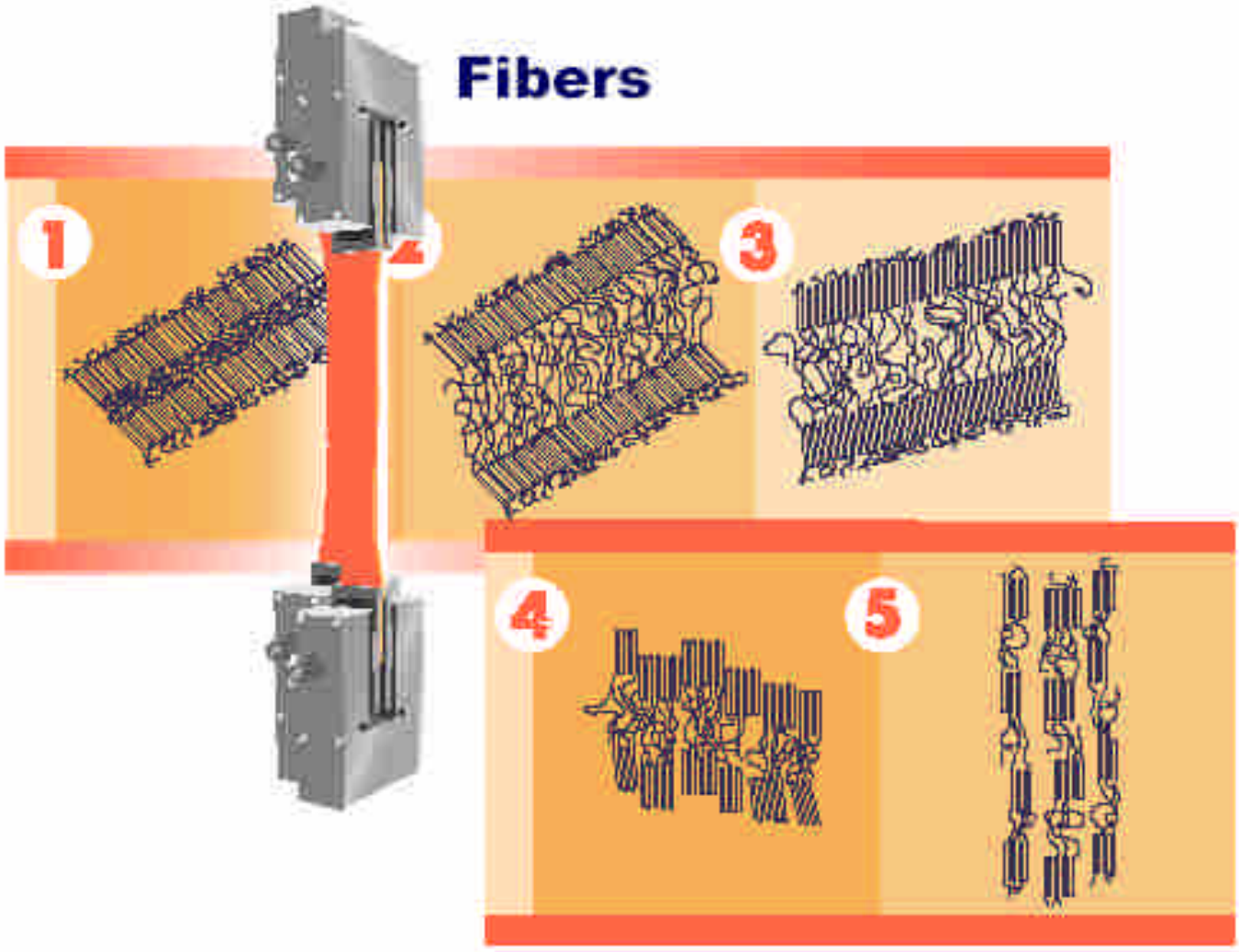


- Many crystalline polymers, such as *fibers and films*, are oriented.
- Films can be biaxially oriented
- Orientation can be accomplished by mechanical drawing or rolling
- Drawing is liable to increase the crystallinity

Two suggested models for an oriented polymer

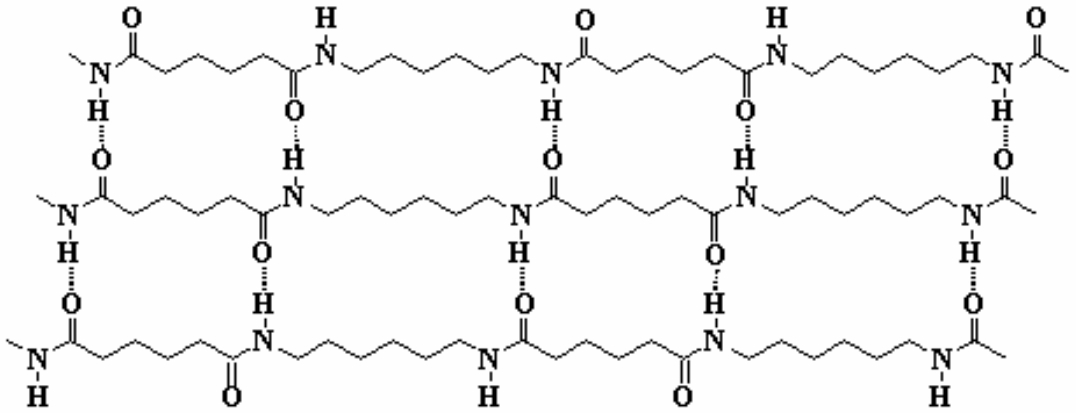


- **(a)Interlamellar amorphous model for an oriented polymer (b) Fibrils in drawn crystalline polymer**
- **(a) is appropriate for polymers being hot drawn or annealed after drawing at RT*(cold drawn*) Cold drawing by itself causes the original lamellae to break up into blocks accompanied by the formation of long fibrils**


Fibers
1
2
3
4
5

Crystallinity and intermolecular forces

Intermolecular forces can be a big help for a polymer if it wants to form crystals. A good example is nylon. You can see from the picture that the polar amide groups in the backbone chain of nylon 6,6 are strongly attracted to each other. They form strong hydrogen bonds. This strong binding holds crystals together.



In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

Polymer Chains

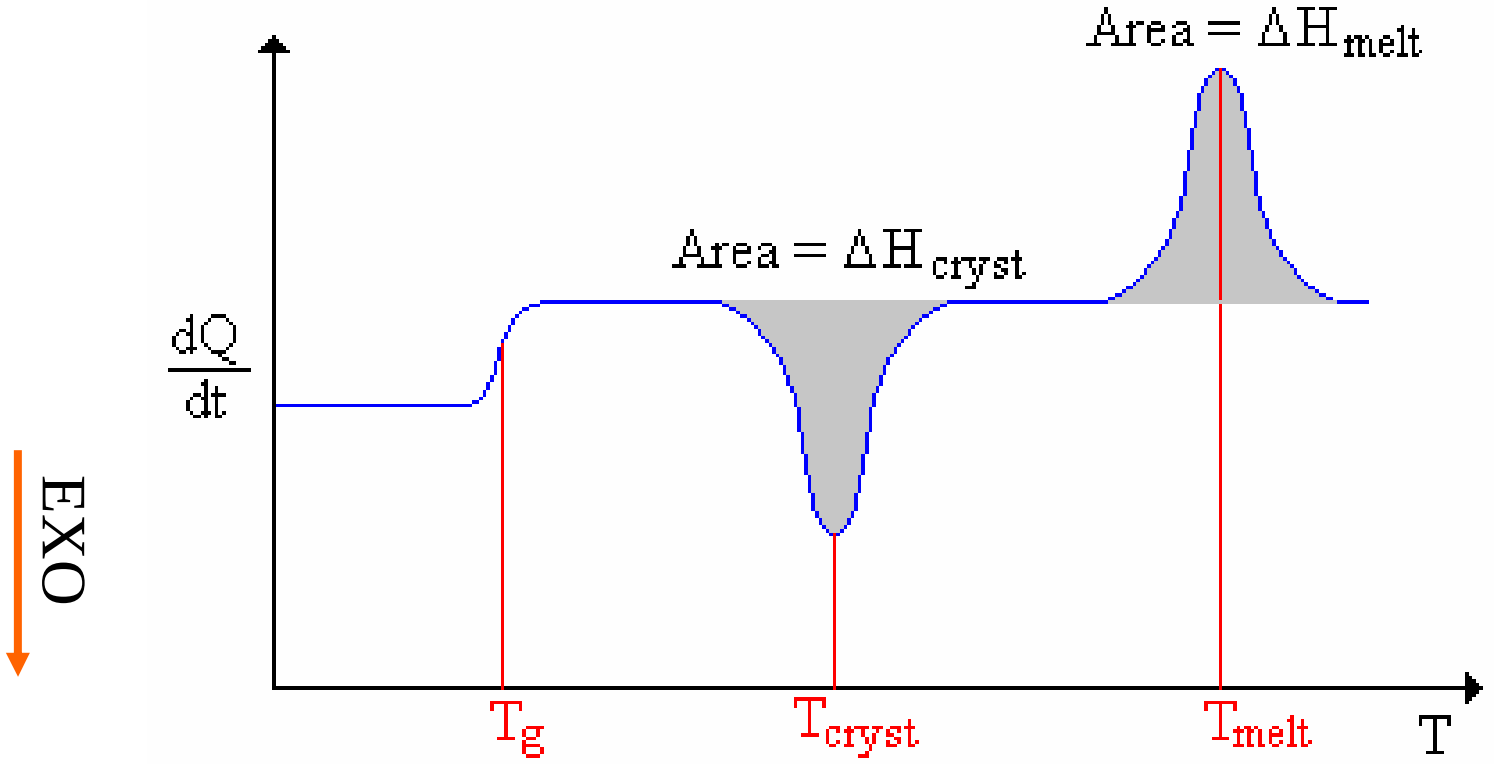
In fact, very few polymers can stretch out perfectly straight, and those are *ultra-high molecular weight*, and *aramids* like *Kevlar and Nomex*. Most polymers can only stretch out for a short distance before they fold back on themselves.

For polyethylene, the length the chains will stretch before they fold is about 100 angstroms.

How Much Crystallinity?

Remember we said that many polymers contain lots of crystalline material and lots of amorphous material. There's a way we can find out how much of a polymer sample is amorphous and how much is crystalline. This method is called *differential scanning calorimetry(DSC)(will be discussed in next chapter)*.

DSC



For making fibers, we like our polymers to be as crystalline as possible. This is because a fiber is really a long crystal.

Many polymers are a mix of amorphous and crystalline regions, but some are highly crystalline and some are highly amorphous. Here are some of the polymers that tend toward the extremes:

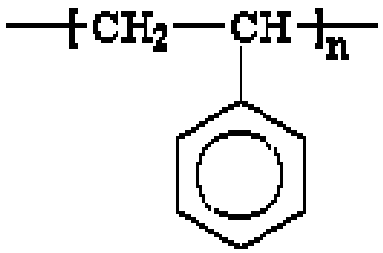
Some Highly Crystalline Polymers:	Some Highly Amorphous Polymers:
polypropylene	Poly(methyl methacrylate)
Syndiotactic polystyrene	Atactic polystyrene
Nylon	Polycarbonate
Kevlar and Nomex	Polyisoprene
Polyketones	Polybutadiene

Why?

So why is it that some polymers are highly crystalline and some are highly amorphous? There are two important factors, polymer structure and intermolecular forces.

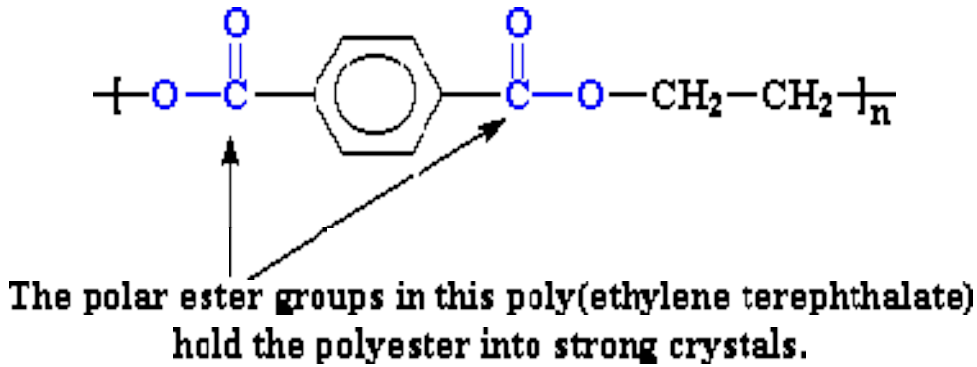
Crystallinity and polymer structure

A polymer's structure affects crystallinity a good deal. If it is regular and orderly, it will pack into crystals easily. If not, it won't. It helps to look at polystyrene to understand how this works.



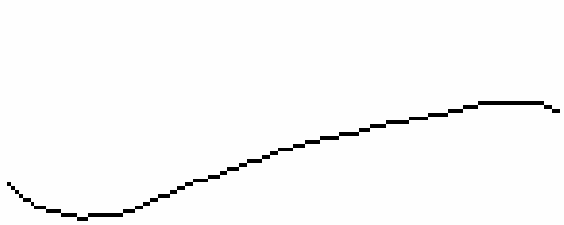
polystyrene

Polyesters are another example. Let's look at the polyester : poly(ethylene terephthalate)

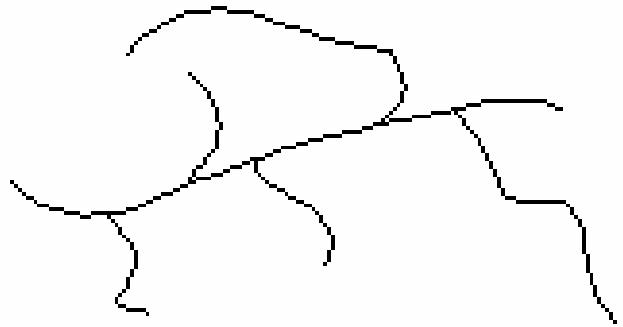


The polar ester groups make for strong crystals. In addition, the aromatic rings like to stack together in an orderly fashion, making the crystal even stronger.

Polyethylene is another good example. It can be crystalline or amorphous. Linear polyethylene is nearly 100% crystalline. But the branched stuff just can't pack the way the linear stuff can, so it is highly amorphous.

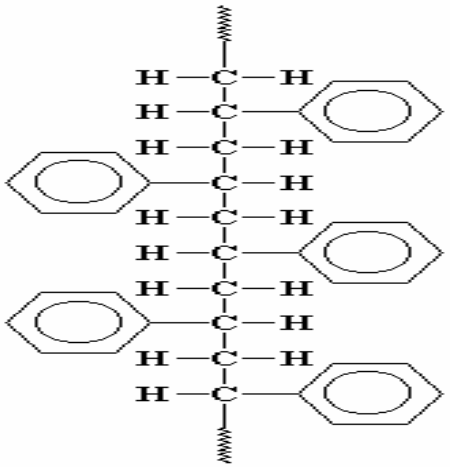


linear polyethylene

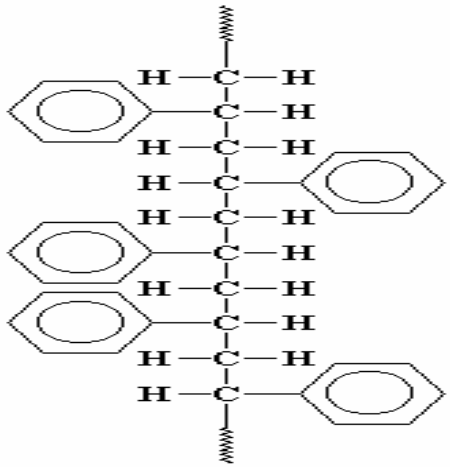


branched polyethylene

As you can see on the lists above, there are two kinds of polystyrene. There is atactic polystyrene, and there is syndiotactic polystyrene. One is very crystalline, and one is very amorphous.



syndiotactic
polystyrene



atactic
polystyrene

Syndiotactic polystyrene has a regular structure, so it can pack into crystal structures. The irregular atactic polystyrene can't.

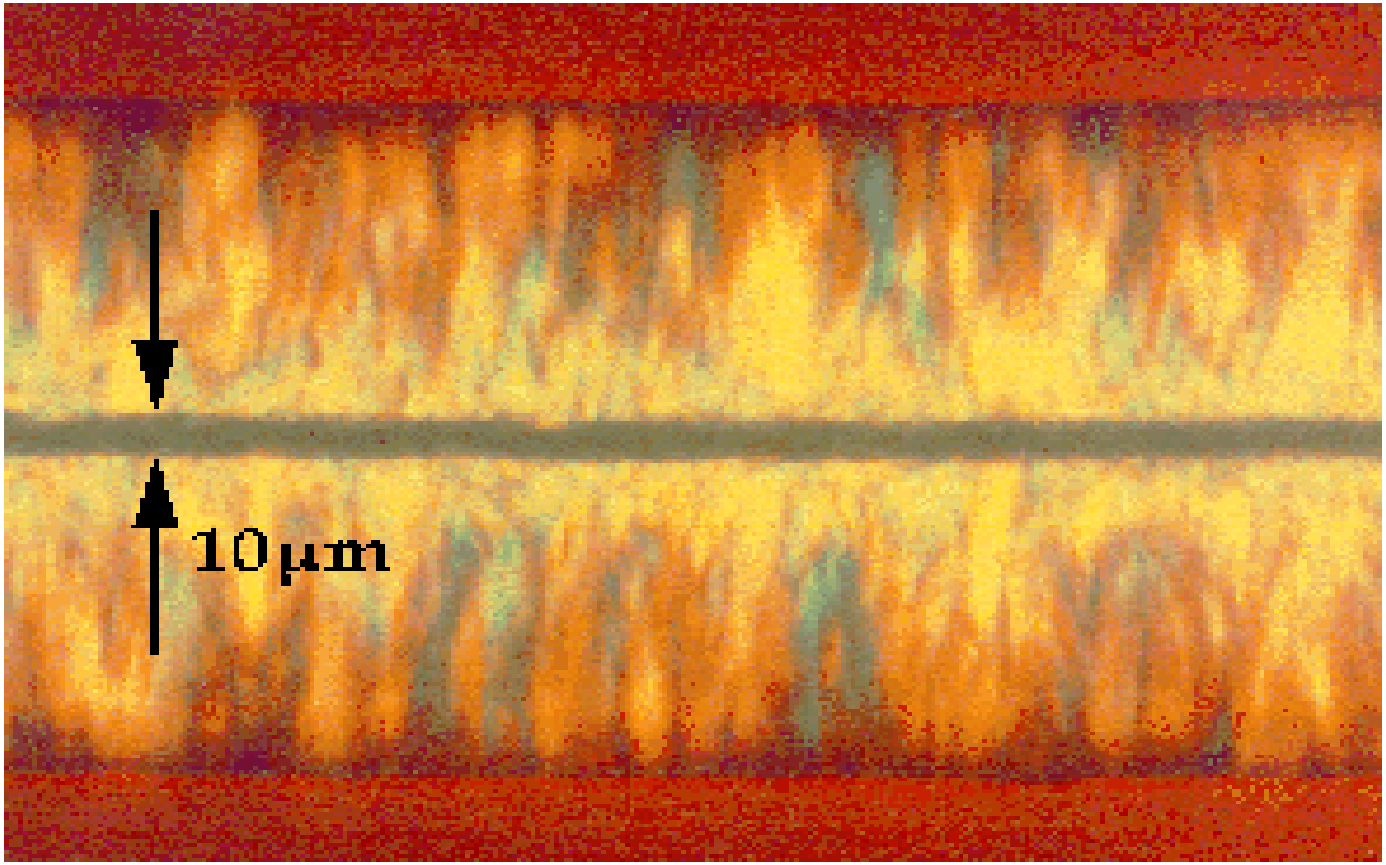
Order and disorder molecular chains

Syndiotactic polystyrene is very orderly, with the phenyl groups falling on alternating sides of the chain. This means it can pack very easily into crystals.

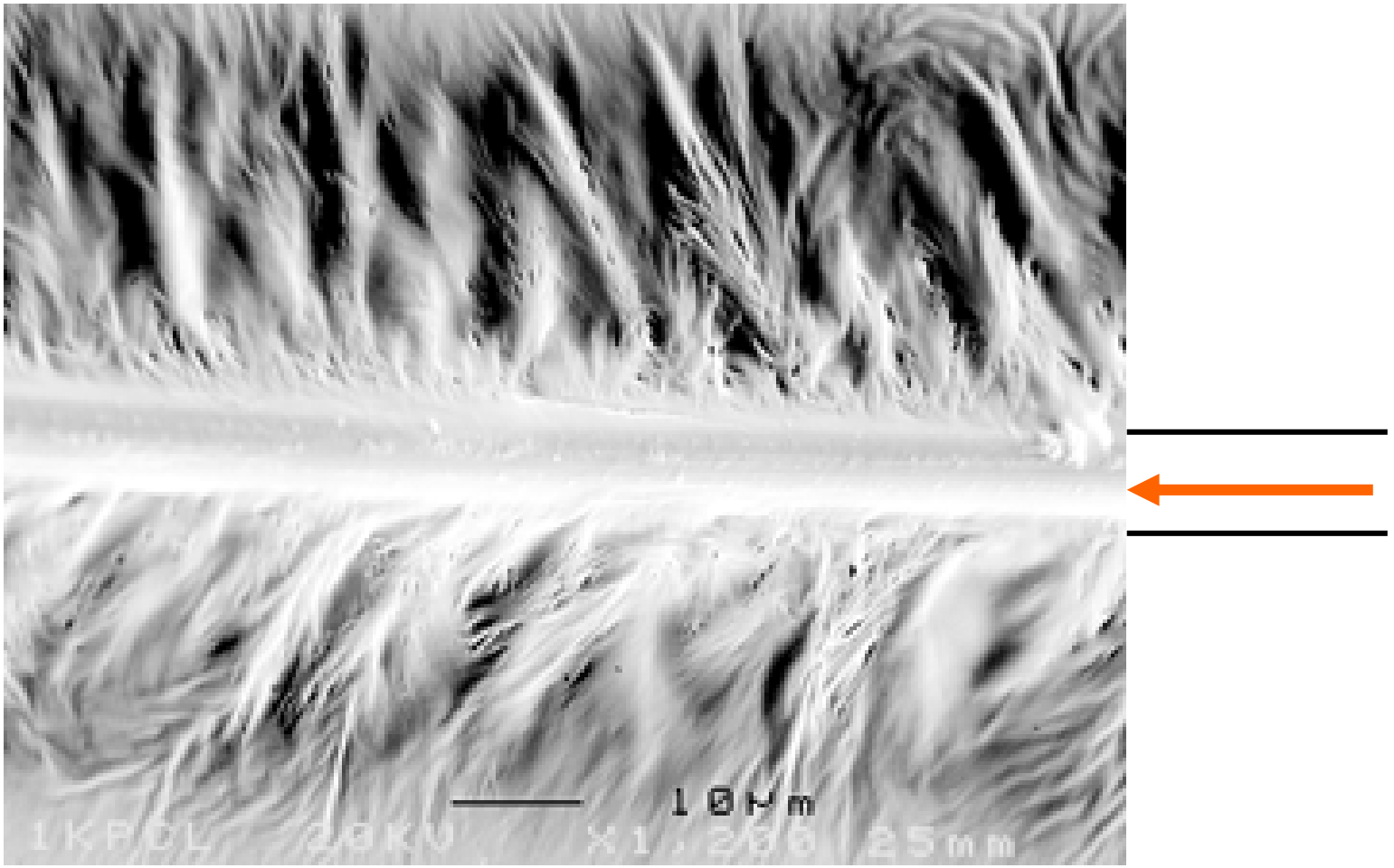
But atactic styrene has no such order. The phenyl groups come on any which side of the chain they please. With no order, the chains can't pack very well. So atactic polystyrene is very amorphous.

Other atactic polymers like poly(methyl methacrylate) and poly(vinyl chloride) are also amorphous. And as you might expect, stereoregular polymers like isotactic polypropylene and polytetrafluoroethylene are highly crystalline.

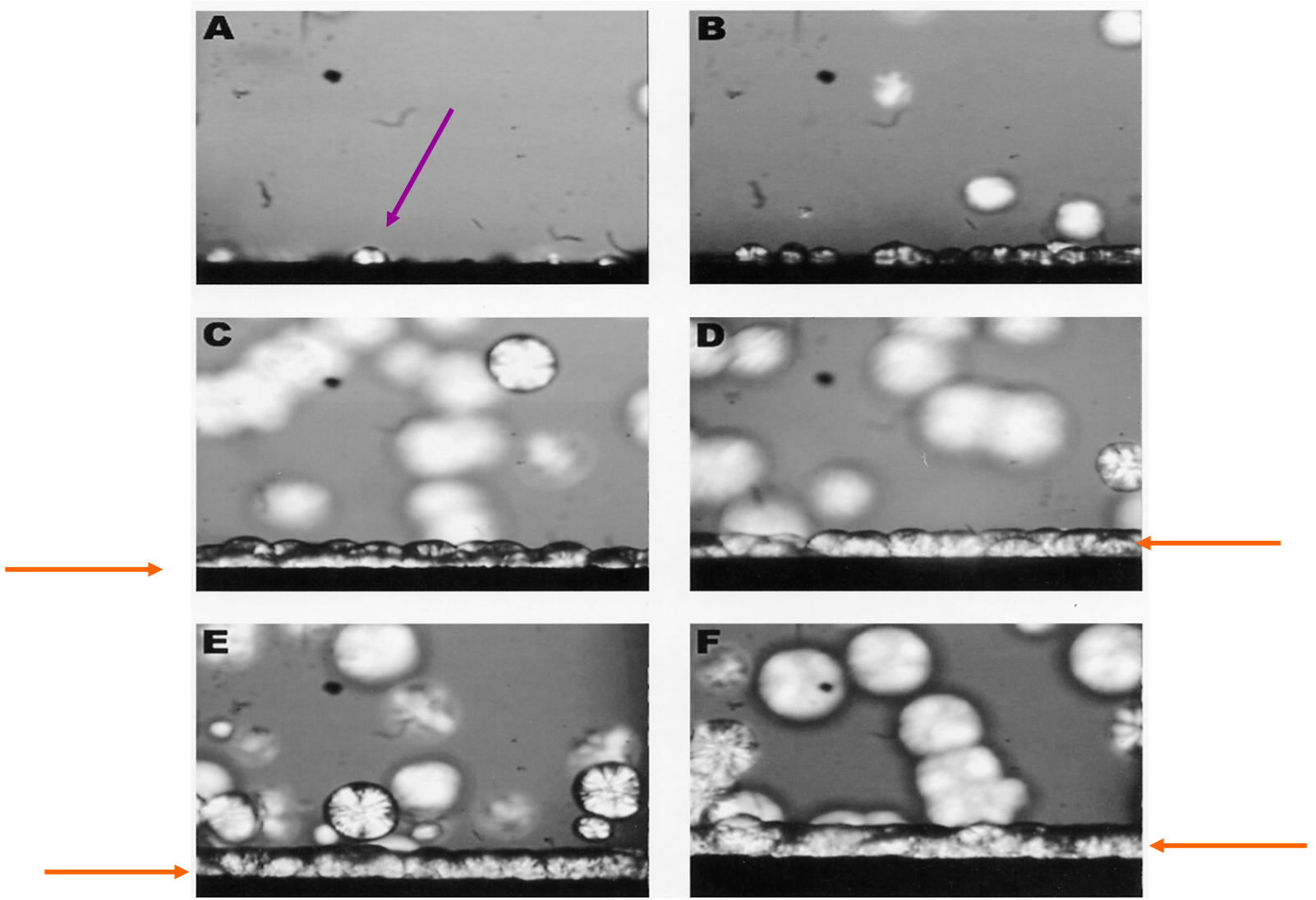
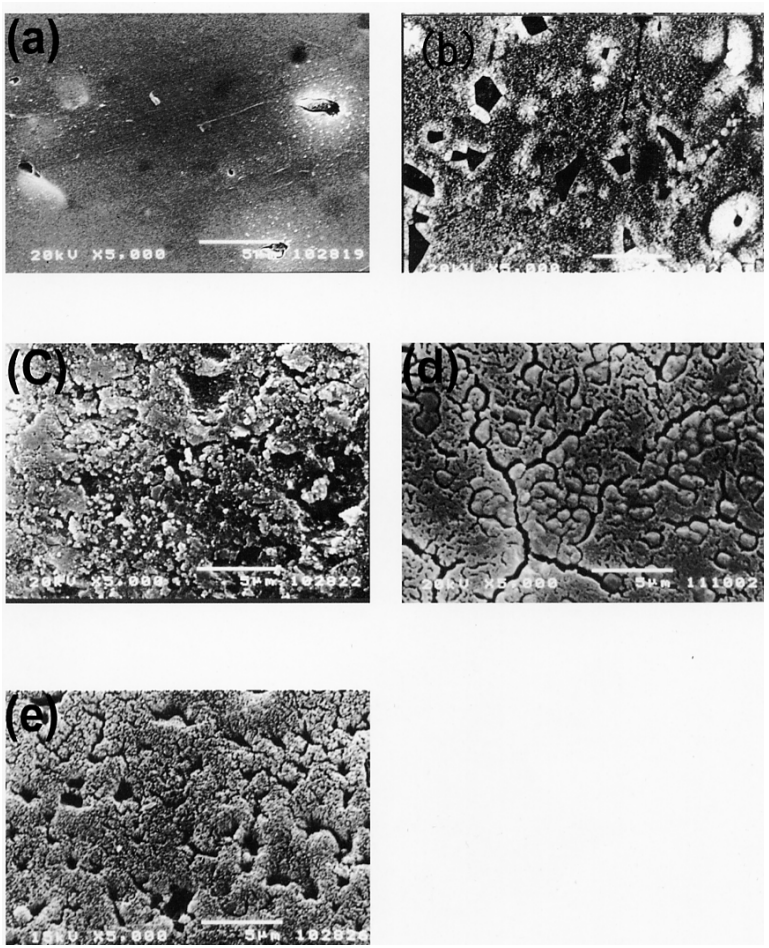
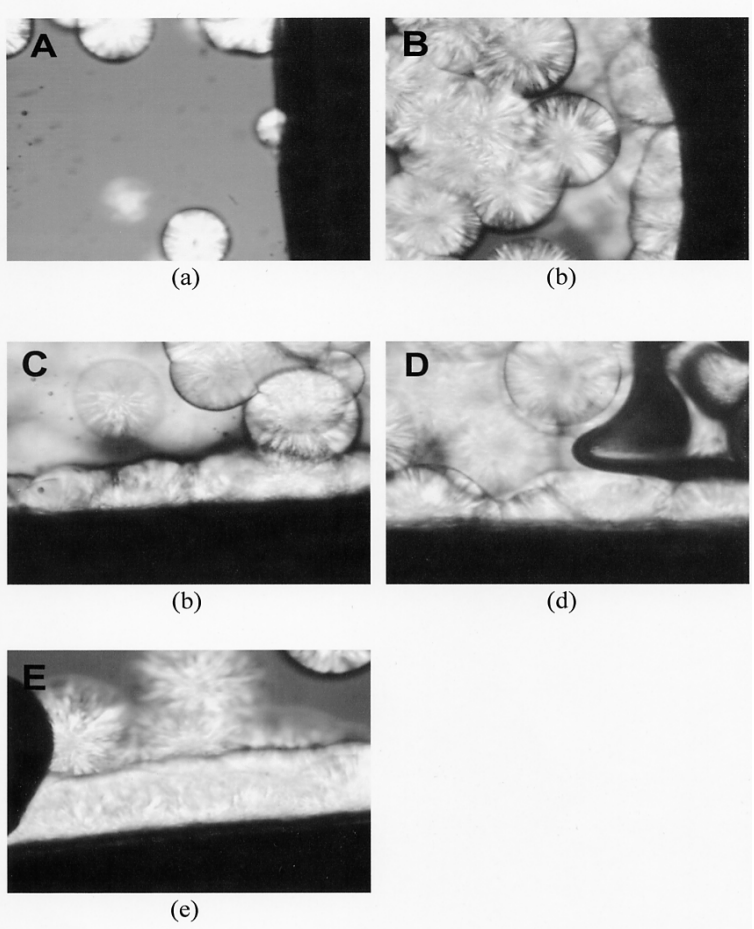
Transcrystallization of iPP on Pitch-based HM Carbon Fiber



SEM of iPP on Pitch based HM carbon Fiber



Transcrystallization of iPP on PTFE substrate



Transcrystallization of iPP on anodized Al substrate