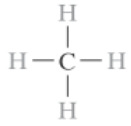
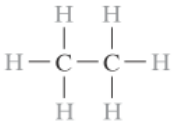
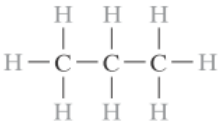
CH14 高分子結構

未飽和→含雙或三鍵

飽和→全單鍵

Paraffin Compounds: C_nH_{2n+2}

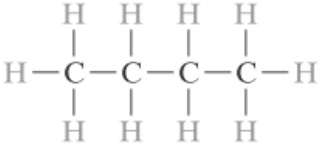
Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

尾巴ane!

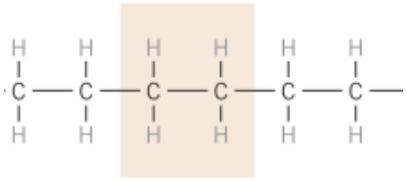
for butane; normal butane has the structure

沸點:-0.5

較高!



isomerism!

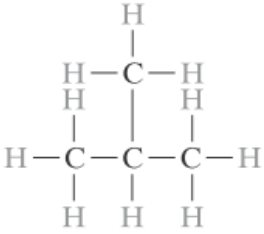


Repeat unit

whereas a molecule of isobutane is represented as follows:

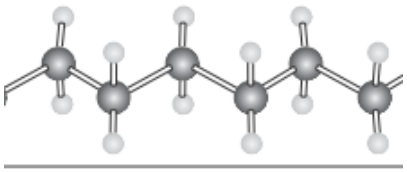
沸點:-12.3

較低!



(a)

109° C-C 0.154nm



Homopolymer→所有單體同

Copolymer→有不同單體

Functionality→一個 monomer 可以形成幾個 bond

Bifunctional→2 bond→2-D chain-like

Trifunctional→3bond→3-D network

分子量→測量黏度、osmotic pressure

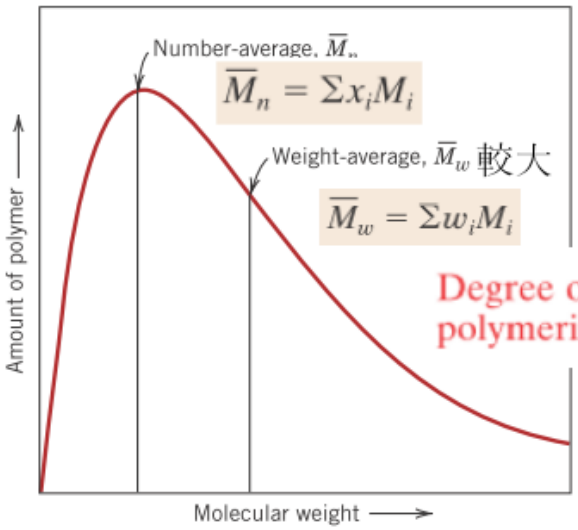
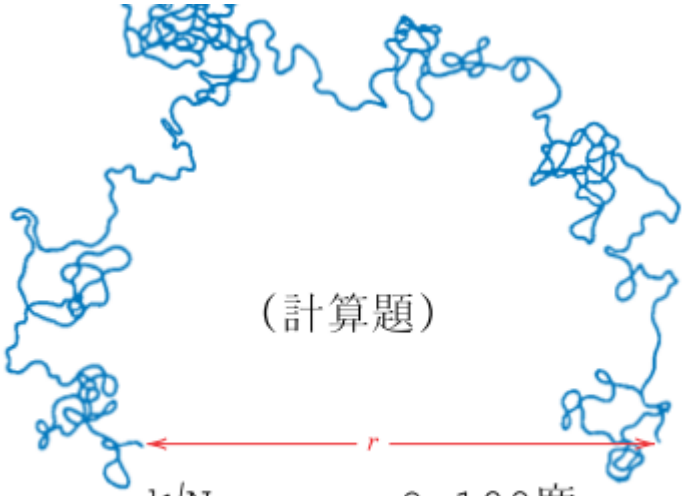


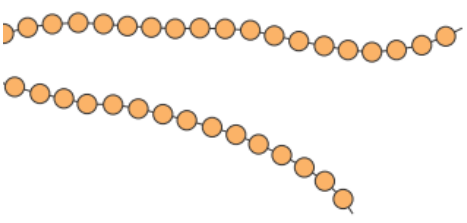
Figure 14.4 Distribution of molecular weights for a typical polymer.

Degree of polymerization— $DP = \frac{\overline{M}_n}{m}$ 單體分子量



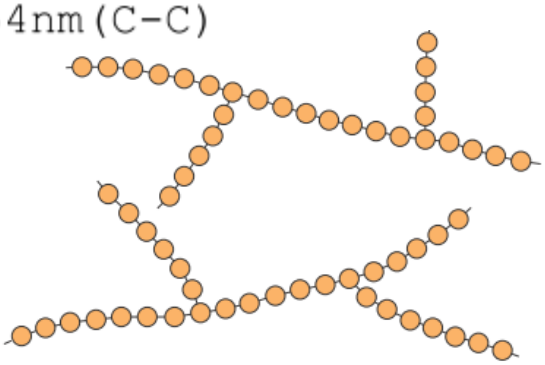
r=d√N　　θ=109度

L=Ndsin(θ/2)　d=0.154nm(C-C)



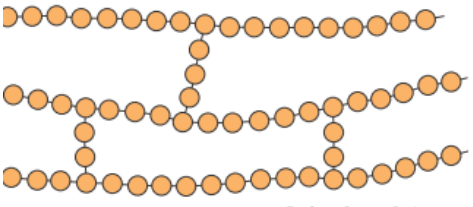
(a)

linear->鏈間大量凡德瓦



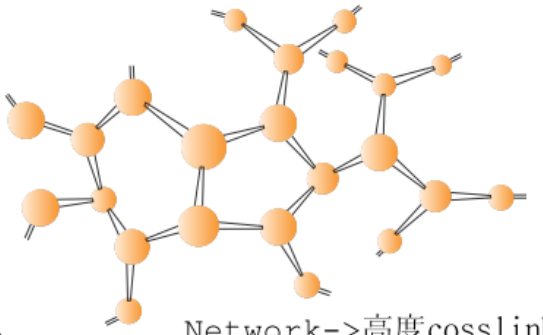
(b)

Branched->側支使密度下降



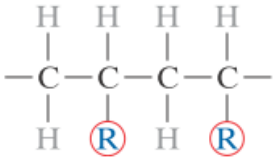
crosslinked(EX.硫化)

(c)

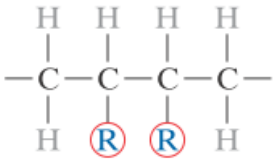


Network->高度cosslinked or三官能基

(d)



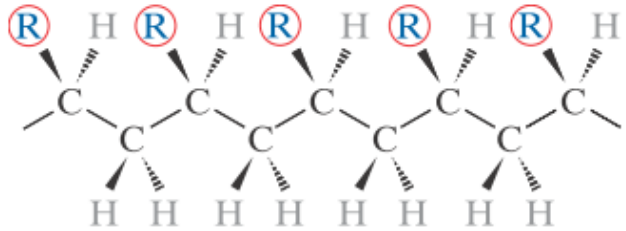
head-to-tail configuration
(主要)



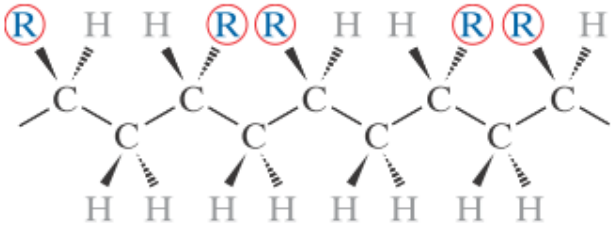
the head-to-head configuration
(R和R排斥)

[7] The term *configuration* is used in reference to arrangements of units along the axis of the chain, or atom positions that are not alterable except by the breaking and then reforming of primary bonds.

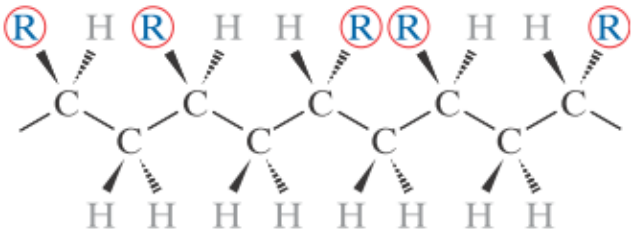
Stereoisomerism→原子以一樣的方式連結(頭對頭)，但有不同的 spatial arrangement



isotactic configuration
(same side)

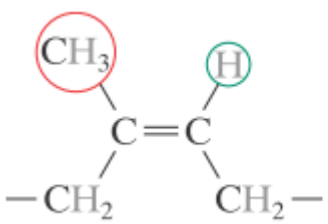


syndiotactic configuration
(alternate)

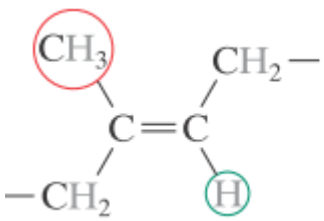


atactic configuration
(random)

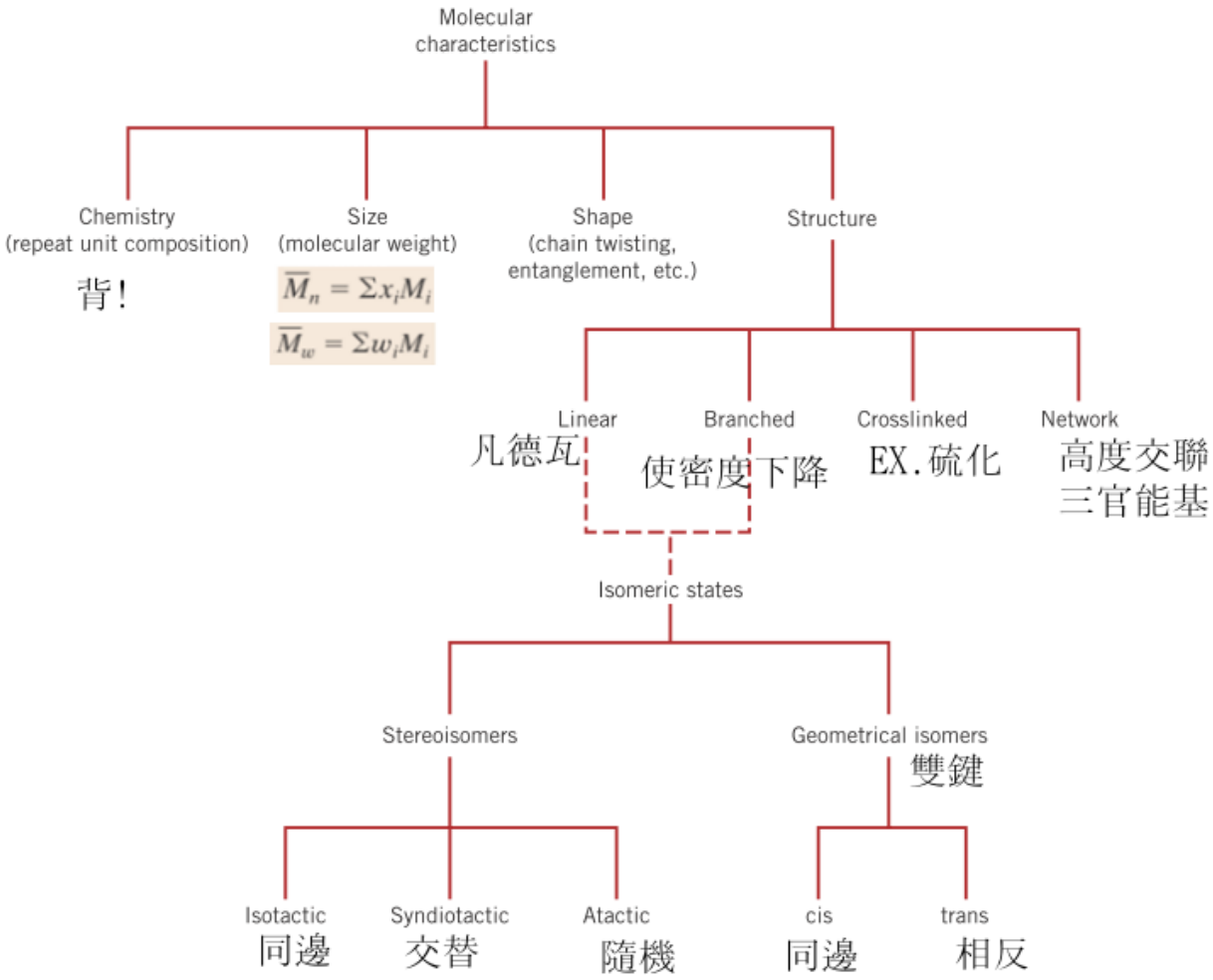
※不可能僅靠旋轉就轉換 configuration
※一般不會只有一種，主要組態取決於 synthesis 的方法
Geometrical Isomerism→單體有雙鍵



cis-polyisoprene
(same side)



Trans-polyisoprene
(opposite side)



※What is the difference between configuration and conformation in relation to polymer chains?

Conformation→鏈分子的 outline 和形狀

Configuration→原子的排列位置，且是無法改變的，除非打斷然後 reforming primary bonds.

Thermoplastics	加熱軟化(最後 liquefy)，冷卻硬化→reversible 加熱→分子運動加劇→二極鍵結力消失 當溫度加過高→會產生不可逆的 degradation 通常 linear、branched、soft
Thermosetting	永久硬化 Network、共價 crosslinked Crosslink usually extensive→10~50% crosslinked 但溫度非常高還是會 degradation EX. vulcanized rubbers, epoxies, and phenolics, polyester resins

Copolymer

Random→SBR(Styrene–butadiene rubber)、NBR(Nitrile rubber，acrylonitrile and butadiene)

Alternating

Block→ Impact modified polystyrene→ alternating blocks of styrene and butadiene

graft

polymer crystallinity→ the packing of molecular chains to produce an ordered atomic array

※比較:金屬幾乎都是結晶；陶瓷不是全結晶就是全非晶；高分子則從非晶到約95%結晶都有可能

結晶度越高，密度越高→**結晶度可以由密度測量**

$$\%\,\text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

※想成→[ρ(式樣)/ρ(全結晶)]*(結晶度) = ρ(式樣-非晶)/ρ(全結晶-非晶)

Factor

1.冷卻速度→越快越非晶

2.鏈組態→越複雜越非晶

結晶度越高→通常越能抵抗熱的分解和軟化

Polymer crystal

1.fringe-micelle model→半結晶分子包含許多小結晶區域(crystallites)

2.chain-folded model→稀薄溶液成長的單晶

3.spherulite

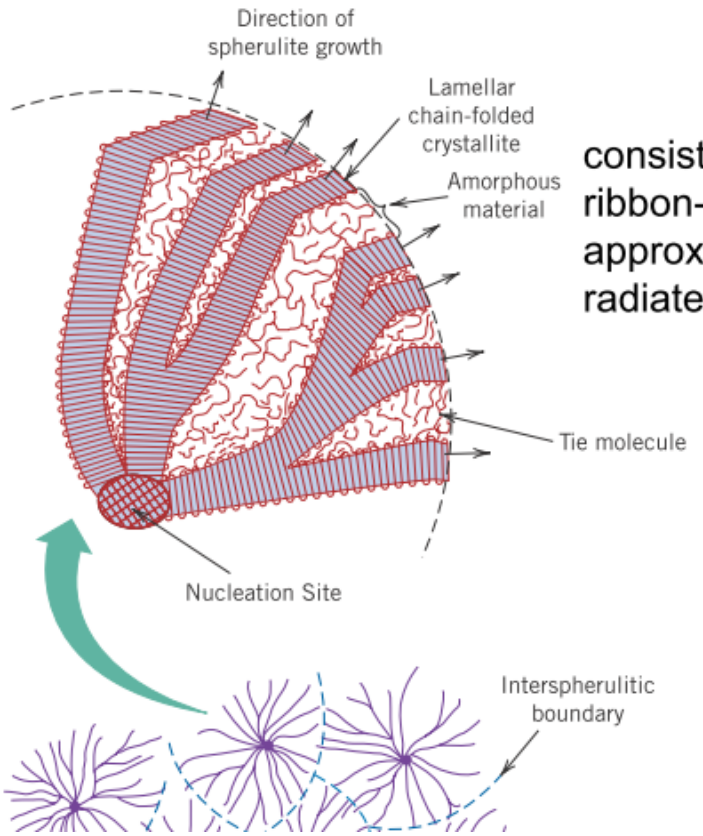
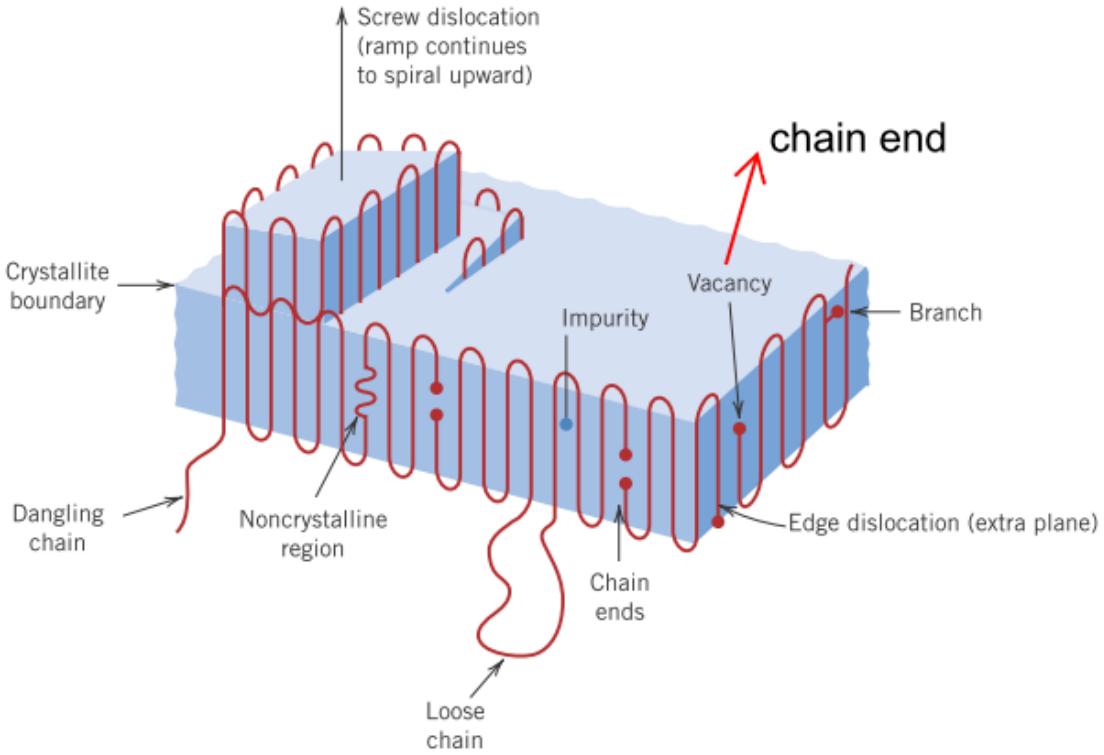


Figure 14.13 Schematic representation of the detailed structure of a spherulite.

consists of an aggregate of
ribbon-like chain-folded crystallites(lamellae)
approximately 10 nm thick
radiate outward from a single nucleation site

Defect



高分子的擴散

小的 foreign molecules (O_2、H_2O、CO_2、CH_4)

$$J = P_M \frac{\Delta P}{\Delta x} \xrightarrow{\text{近似}} P_M = DS$$

D：擴散系數

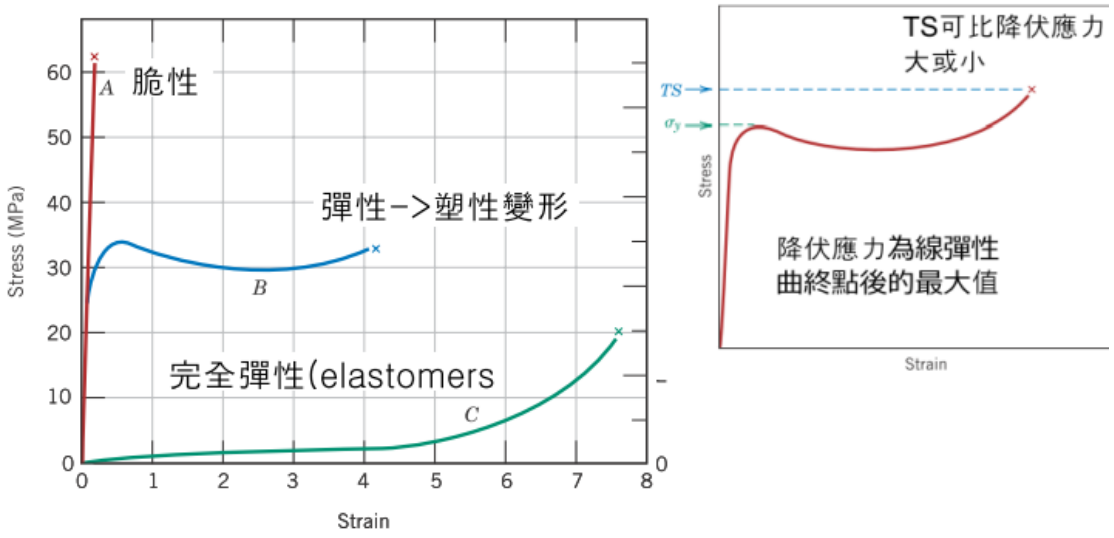
S：擴散物種的溶解度

小分子in nonglassy polymers

permeability coefficient

the units for the permeability coefficient are (cm^3 STP)(cm)/(cm^2-s-Pa).

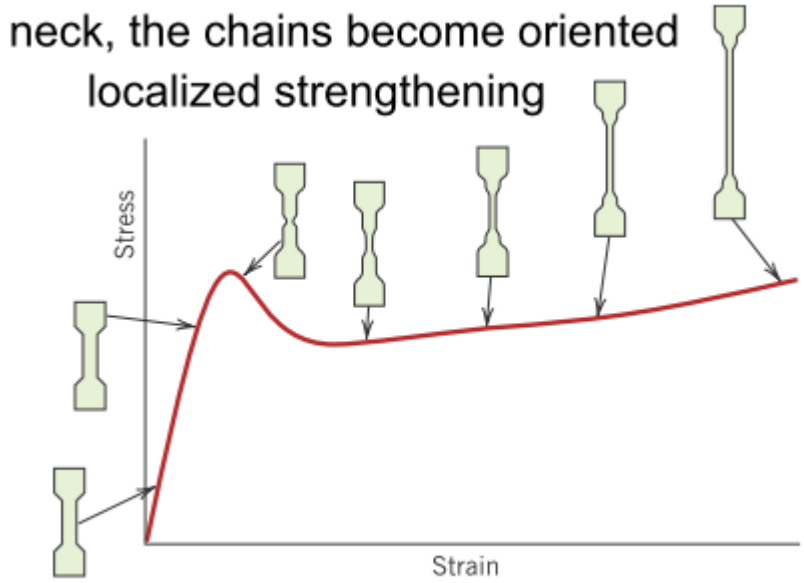
CH15 分析應用製程



※金屬的 TS 可到 4100MPa；高分子最高到 100MPa

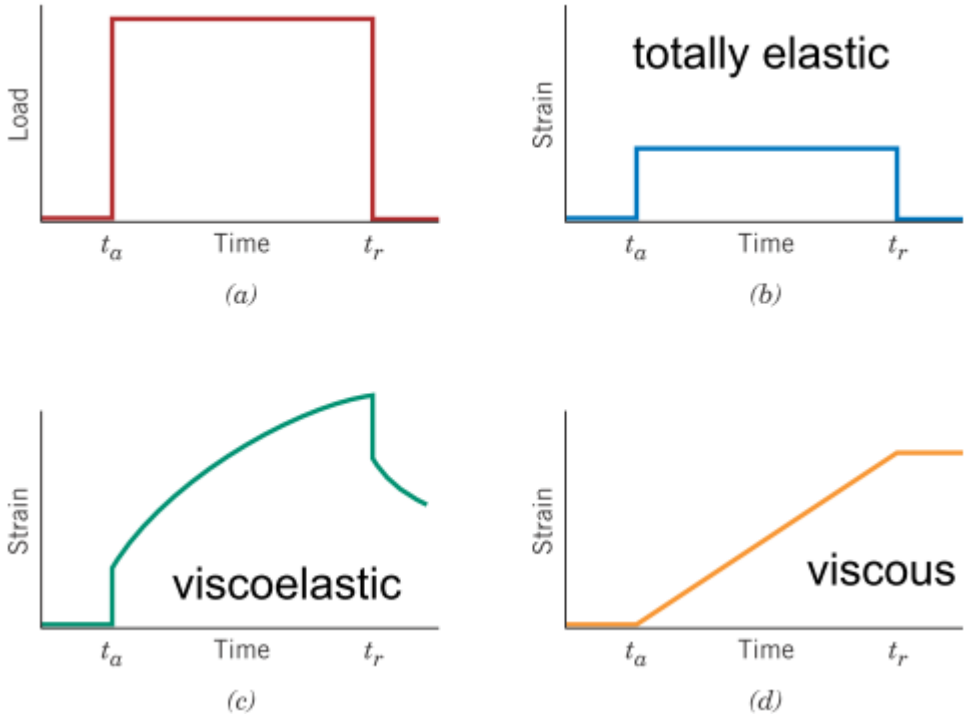
金屬的塑性伸長很少超過 100%；高分子卻可到 1000%

※factor→溫度增加和 strain rate 的降低，效果是一樣的→更延



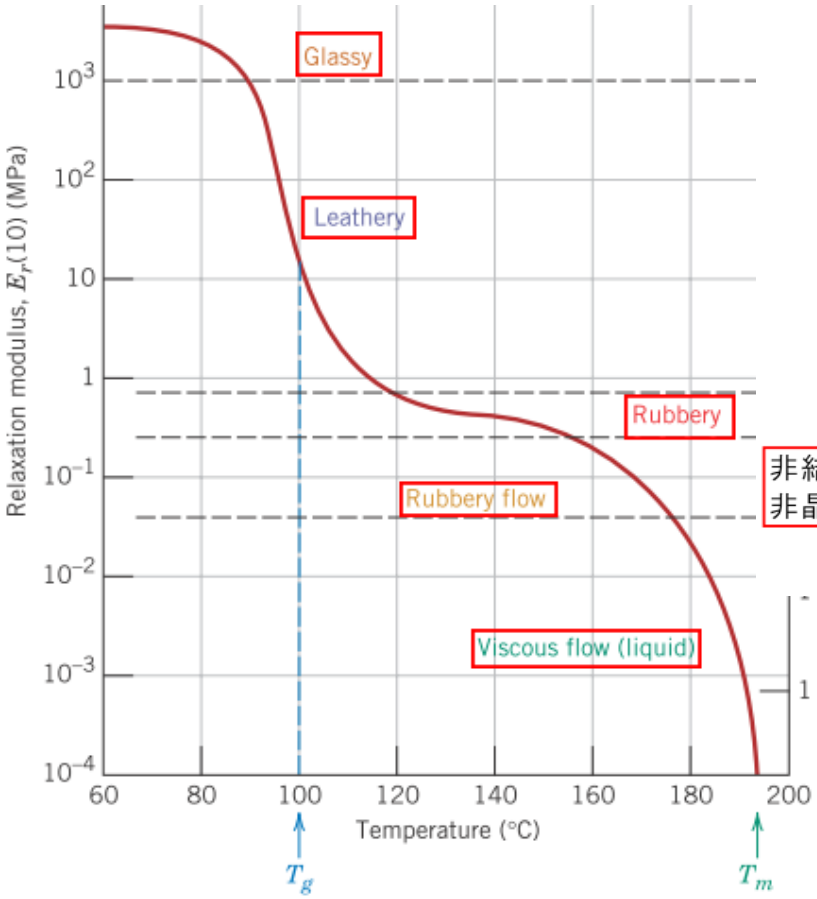
※此現象與金屬相反

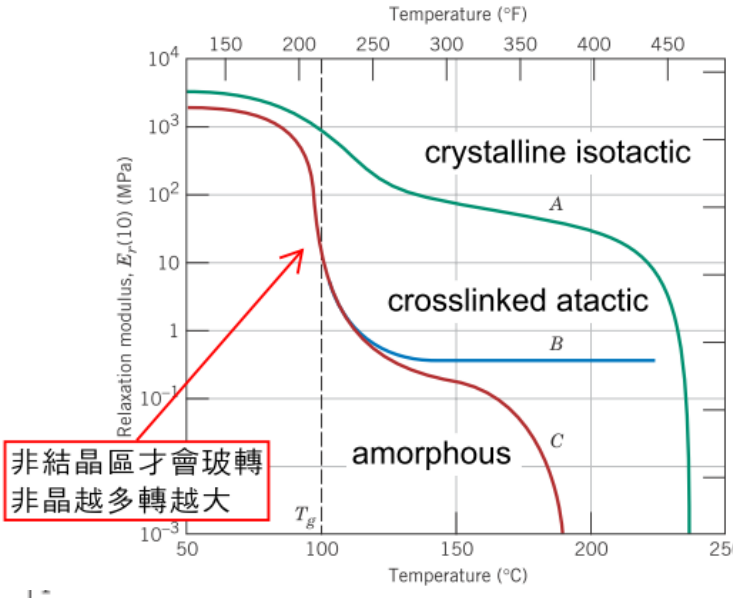
VISCOELASTIC DEFORMATION



Relaxation modulus $E_r(t) = \dfrac{\sigma(t)}{\epsilon_0}$ 固定應變

溫度越大其值越小



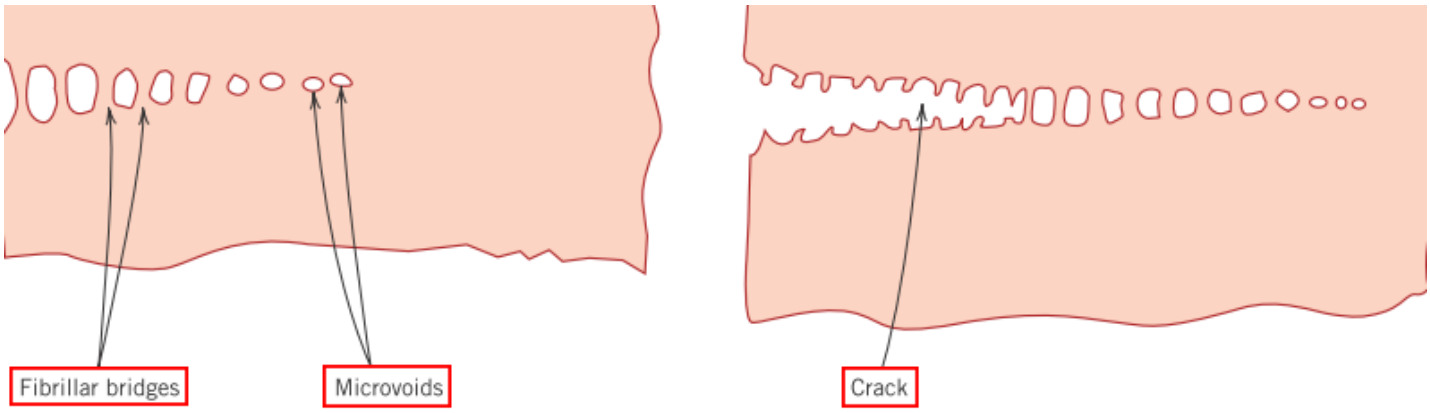


Viscoelastic Creep

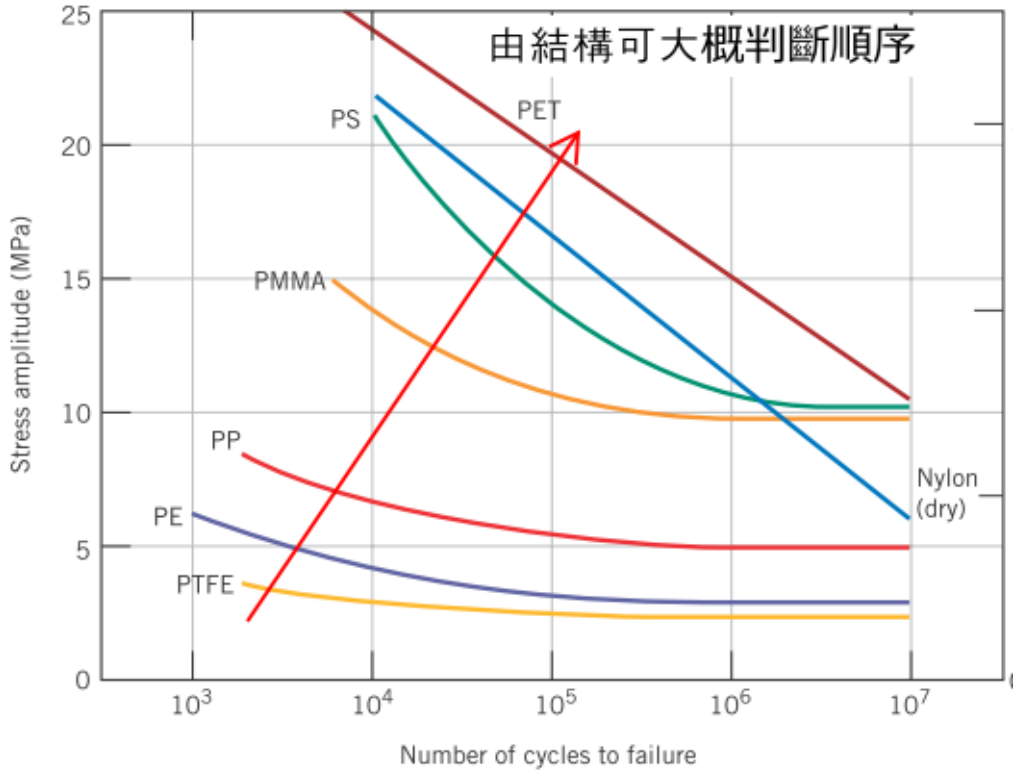
$$E_c(t) = \frac{\sigma_0}{\epsilon(t)}$$ 固定應力

溫度↑→Ec↓→creep↑
結晶度↑→ Ec↑→應變↓

FRACTURE



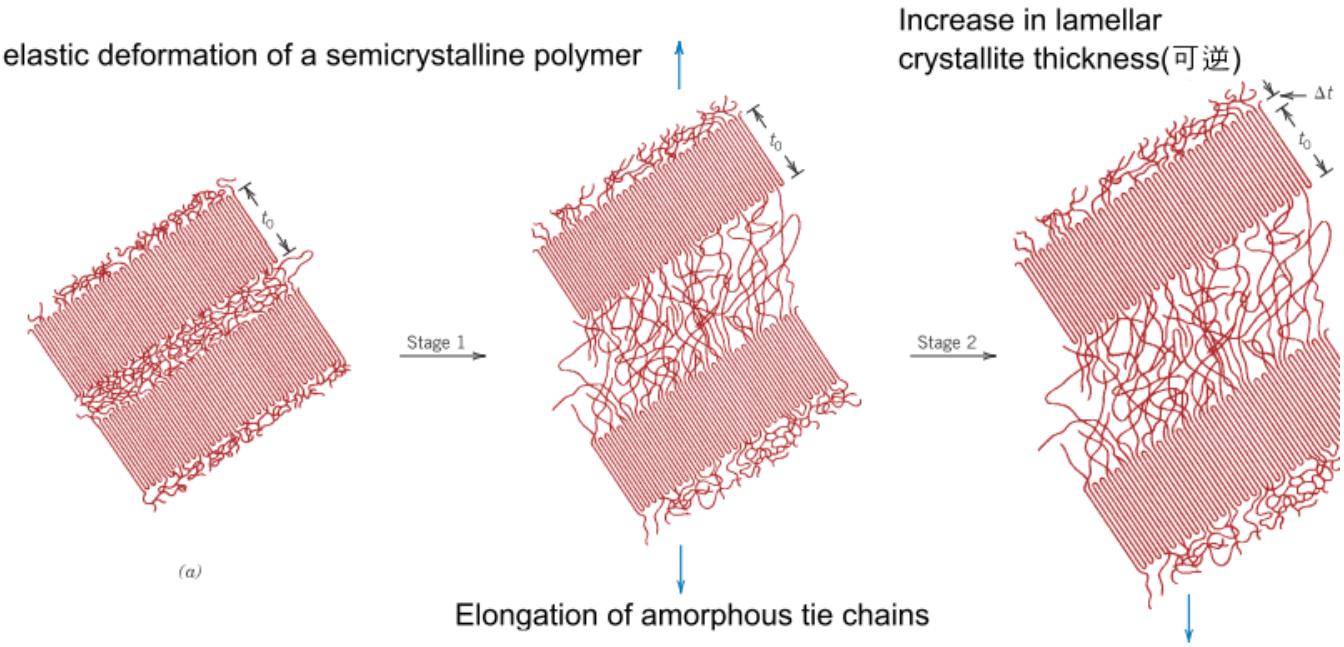
crazing(熱塑材料)
craze-->非常局部的塑性變形->產生 small and interconnected microvoids
Fibrillar bridges在microvoid間形成
當負載夠大->microvoids grow and coalesce->crack
craze吸收fracture energy.增加fracture toughness

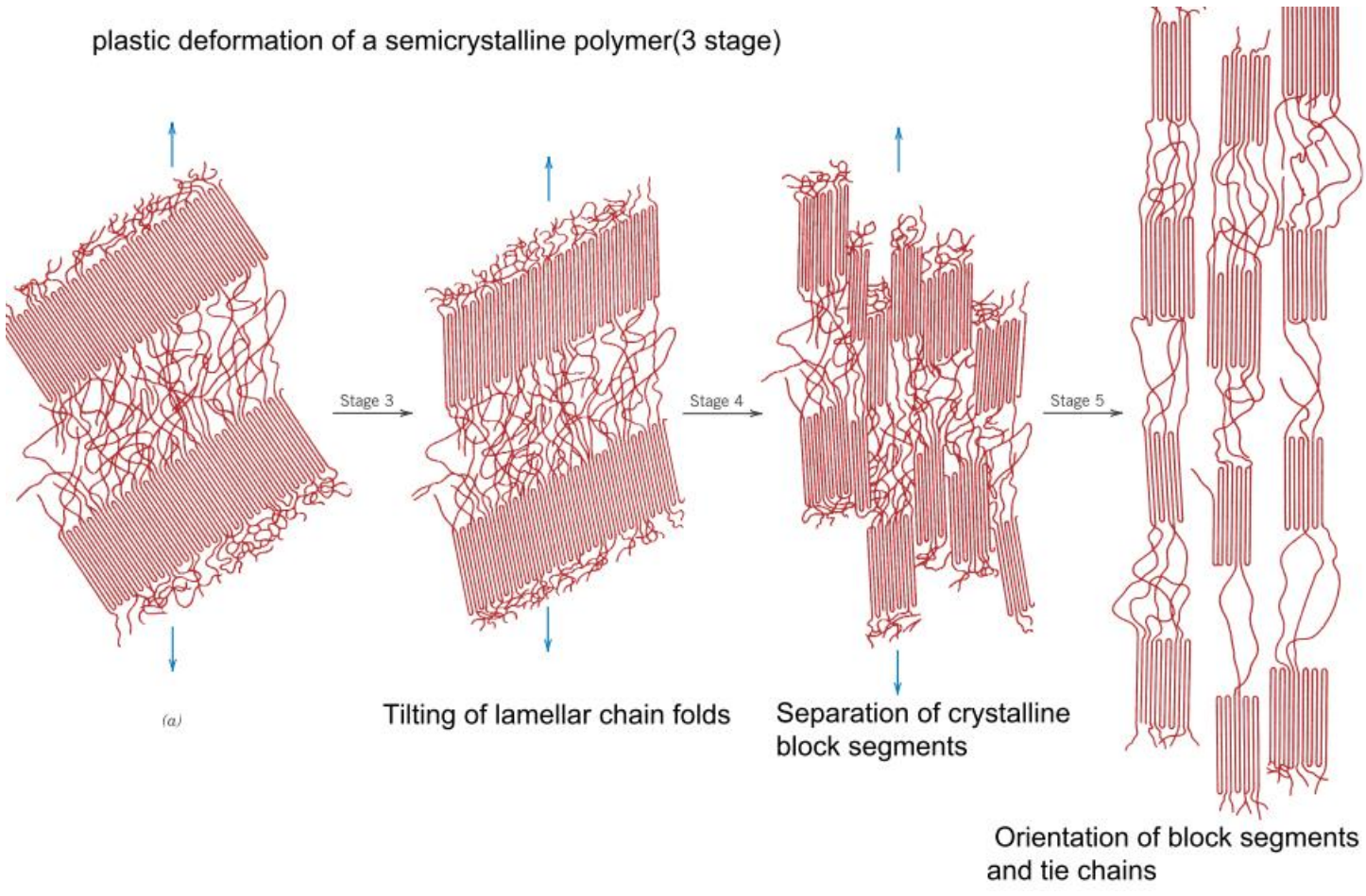


Impact strength→一樣用 Izod、Charpy
Fatigue→比金屬低很多
Tear strength→撕開標準幾何物所需能量
Hardness→較 metal、ceramic 軟

強化變形機構

半結晶
彎曲和拉伸共價鍵.分子鏈及次級鍵結，彈性模數視為結晶、非晶相複合





半結晶機械性質 factor

1.分子量→不直接影響 tensile modulus；但直接影響 tensile strength

$$TS = TS_{\infty} - \frac{A}{\overline{M}_n}$$ 分子量越大 chain entanglement 增加

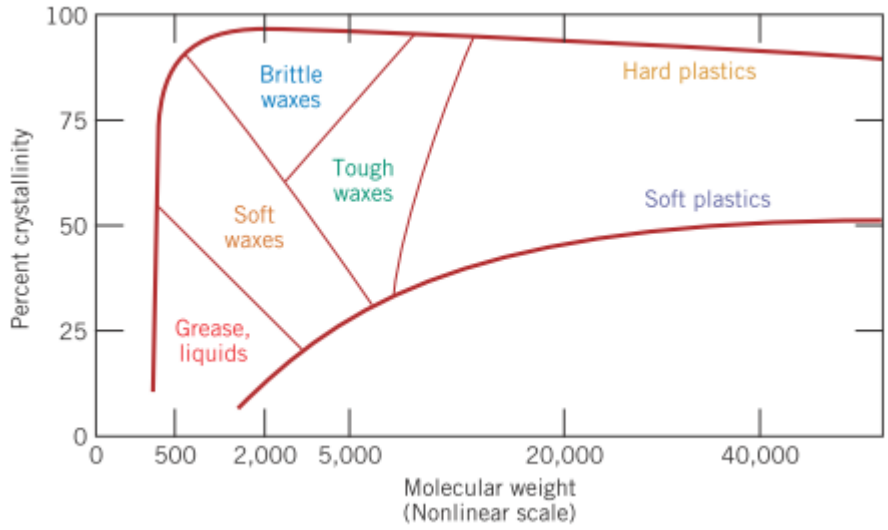
2.結晶度↑→次級鍵影響↑→TS↑→brittle

3. Predeformation by Drawing→類似應變硬化，高度非等向性的鏈取向，次級鍵影響也增加→強化

4.熱處理

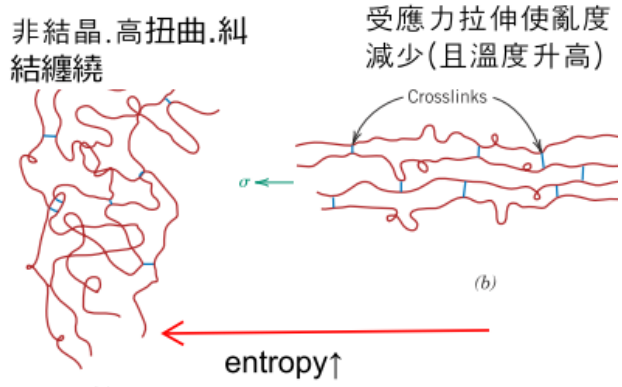
若已拉伸→熱處理使鏈取向消失→TS↓、延性↑(同金屬)

未拉伸→TS↑、yield strength↑、延性↓(與金屬相反)



大概記位置

Elastomer



彈性體的條件(熱固 in nature)

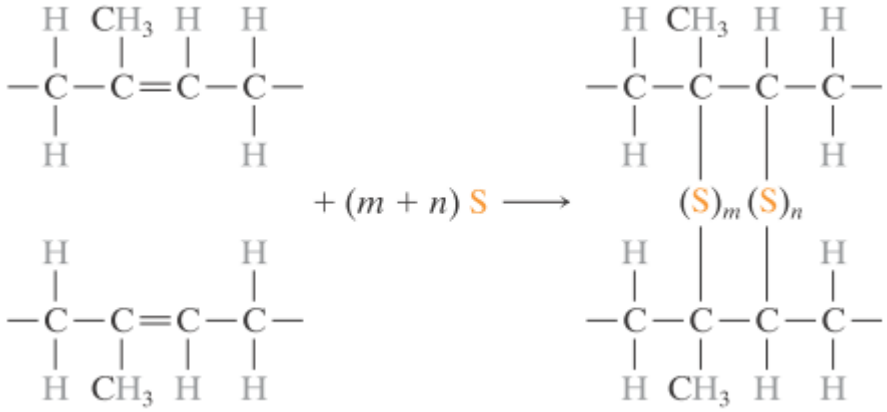
1.必須非晶，且自然盤旋糾結

2.鏈鍵結的旋轉相對自由

3.塑性變形需延遲→靠 crosslink→利用 Vulcanization

4.必須超過玻轉溫度

Vulcanization(不可逆化學反應)



主要的 crosslinked 位置在雙鍵 C，使 E ↑ TS ↑ 抗 degration ↑

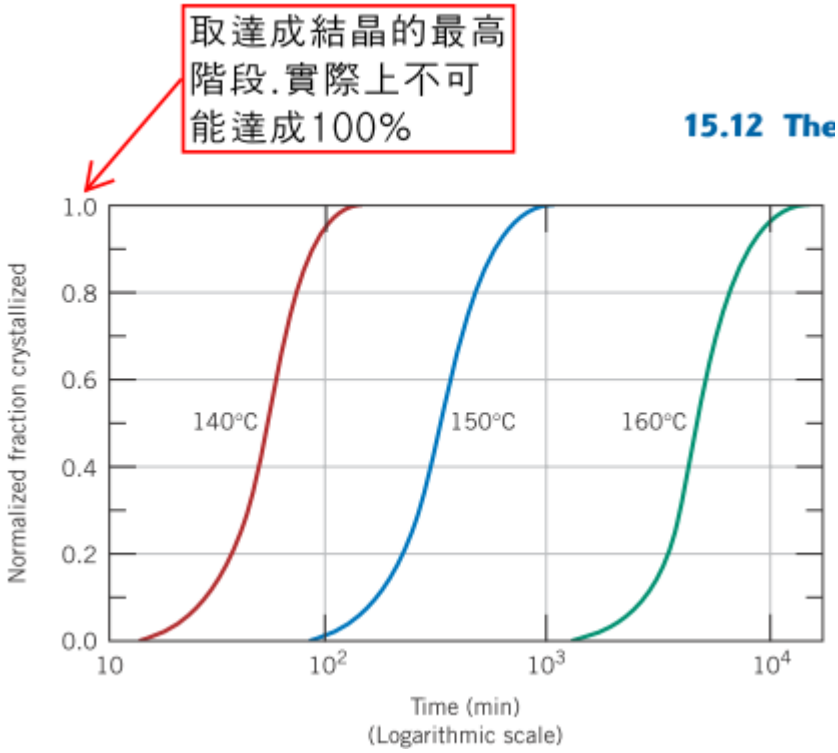
※硫化要在 forming operation 之後，因為一但硫化，就很難再塑性變形了

結晶化

對許多固態轉換，都是以

Avrami equation $y = 1 - \exp(-kt^n)$ (sigmoidal-shaped curve)

結晶分率也是以此式表



溫度越高速率越低；分子量越高速率越低

速率也可以 50%結晶時間的倒數來特性化

※Melting

高分子熔化是發生在一溫度範圍!取決於式樣的經歷

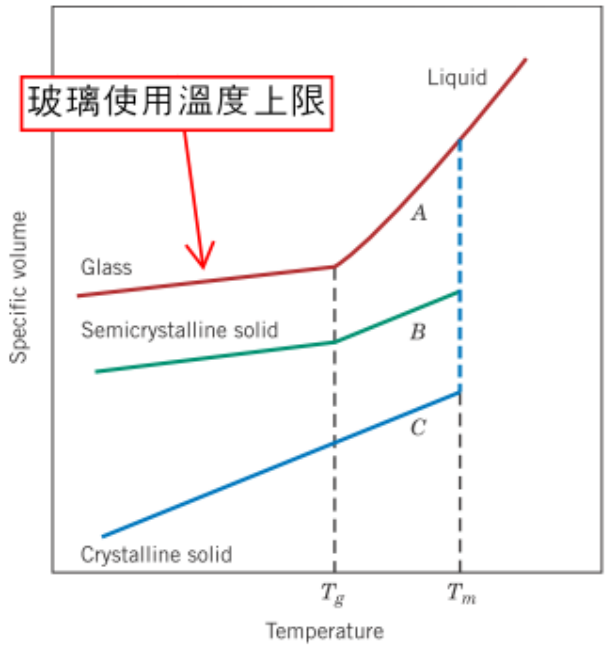
Lamellae 越厚→熔點越高

雜質或缺陷→降低熔點

為加熱速率的函數→速率越高→熔點越高

退火→使 lamellae 變厚，且減少 vacancy 等缺陷→熔點升高

Glass transition



※T_g 值大概落在 0.5~0.8T_m 之間

※影響熔點和玻轉溫度的 factor

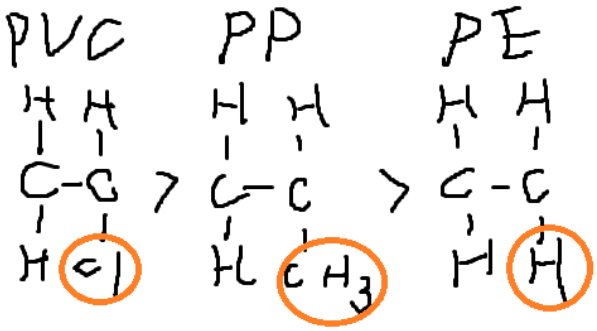
1.雙鍵、芳香族↑

2.側枝↑

3.極性側枝或原子團↑

4.分子量↑

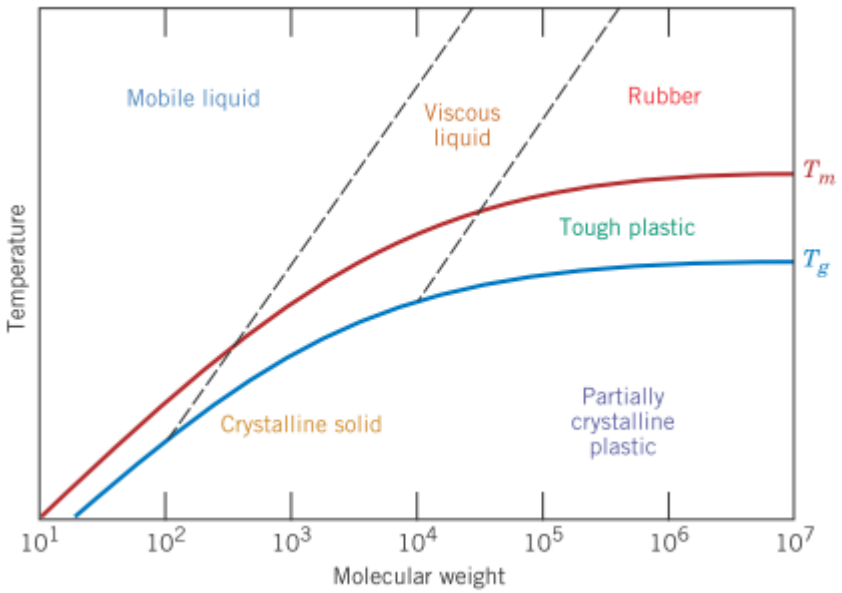
都會使 T_g、T_m 上升



※crosslink↑→T_g↑ &E↑→玻轉溫度和彈性模數為正相關!!

※有空看一下下面各材料的結構與熔點的關聯性

Material	*Glass Transition Temperature [°C (°F)]*	*Melting Temperature [°C (°F)]*
Polyethylene (low density)	−110 (−165)	115 (240)
Polytetrafluoroethylene	−97 (−140)	327 (620)
Polyethylene (high density)	−90 (−130)	137 (279)
Polypropylene	−18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)



Polymer types

*Table15.3 考試前喵一眼 知到有哪些塑膠&功能 有印象就好

Elastomer(都 crosslinked)

性質取決於硫化程度、或是否使用任何強化

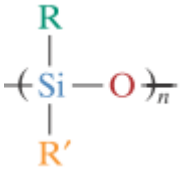
最重要的 synthetic elastomer→SBR→automobile tires，並利用 carbon black 強化

NBR→非常抗 degradation & swelling，應用跟汽油、化學管有關

NR→天然橡膠→應用跟 SBR 同

CR

VMQ，silicone(矽力康!)→他的 backbone 是 O 和 Si 交替!!



低溫高彈性，穩定溫度高(250°C)，抗 weathering、lubricants，生物相容性→blood tubing(醫療應用)，有些還可在室溫硫化!!(EX. RTV rubbers)

*Table15.4 考前看

fibers

至少 100:1 的長度直徑比

高分子量、chain 組態結構→高自由度

Texture industry

要有很高的 TS→結晶度要高→linear and unbranched chains

Polar group 也可以提高結晶度和鏈分子間作用力

thermal properties→熔點和玻轉溫度→影響清洗和保持

化學穩定性、環境抵抗力、不可燃、快乾

各種應用

Coating

1.保護

2.外觀

3.電絕緣

分類→ paint, varnish, enamel, lacquer, and shellac

很常見的→**latex**→他有較低的 volatile organic compound(VOC)emissions

(VOC 和大氣會產生煙，使用 latex 使達到環境標準)

Adhesives

An adhesive is a substance used to bond together the surfaces of two solid materials (termed "adherends")

兩種 bonding 機構→mechanical & chemical

Mechanical→ actual penetration of the adhesive into surface pores and crevices

Chemical→ intermolecular forces(共價鍵或凡德瓦力) between the adhesive and adherend,極性側基會增加凡德瓦力。

Natural adhesive→animal glue, casein, starch,rosin

New adhesive→ synthetic polymers

joining technologies→ riveting, bolting, and welding

主要缺點為溫度限制!

Films

0.025 and 0.125 mm

polyethylene, polypropylene, cellophane, and cellulose acetate

應用上重要特性

1.低密度 2.高 flexibility 3.高 TS、tear strength 4.抗潮濕和化學攻擊 5.低氣體 permeability

Foams

熱固和熱塑都有

Gas bubbles are generated throughout the now-fluid mass, which remain in the solid upon cooling and give rise to a sponge-like structure

Advance polymeric materials

Ultrahigh Molecular Weight Polyethylene (UHMWPE)

分子量大概 $4*10^6$ g/mol

1. An extremely high impact resistance
2. Outstanding resistance to wear and abrasion
3. A very low coefficient of friction
4. A self-lubricating and nonstick surface
5. Very good chemical resistance to normally encountered solvents
6. Excellent low-temperature properties
7. Outstanding sound damping and energy absorption characteristics
8. Electrically insulating and excellent dielectric properties

應用

This unusual combination of properties leads to numerous and diverse applications for this material, including bullet-proof vests, composite military helmets, fishing line, ski-bottom surfaces, golf ball cores, bowling alley and ice skating rink surfaces, biomedical prostheses (Section 22.12), blood filters, marking pen nibs, bulk material handling equipment (for coal, grain, cement, gravel, etc.), bushings, pump impellers, and valve gaskets.

Liquid Crystal Polymers (LCPs)

LCPs are composed of extended, rod-shaped, and rigid molecules.

可考慮為液體結晶狀態，即非結晶且非液體

依據排列的方向、位置可分為 smectic(層列型)、nematic(向列型)、chilesteric(膽固醇型)

主要應用→ liquid crystal displays (LCDs)→ cholesteric types of LCPs

顯示器是由兩片玻璃中間以三明治方式包著液晶材料，外塗導電薄膜，當施加電壓，使 LCP 分子的取向化中斷，使 LCP 材料變暗，而產生可見字元。

(台大有考過液晶的解釋和顯示器的應用原理，但考過了應該就不會在出了，稍微記一下，考出來至少掰一點東西)

Some of the nematic type of liquid crystal polymers are rigid solids at room Temperature→熱穩定性、化學惰性→因為極高的分子間交互作用

Thermoplastic Elastomers (TPEs or TEs)

Styrenic block copolymers

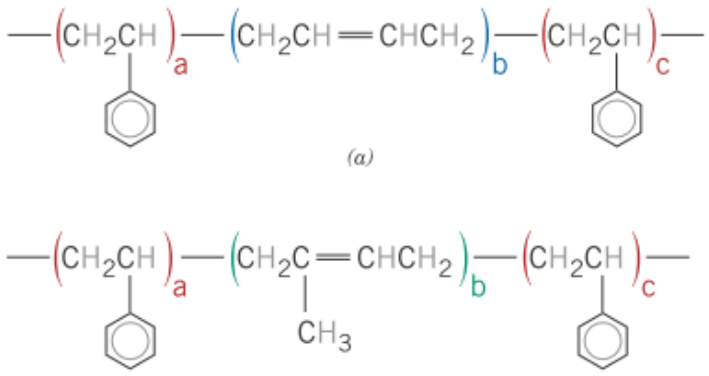
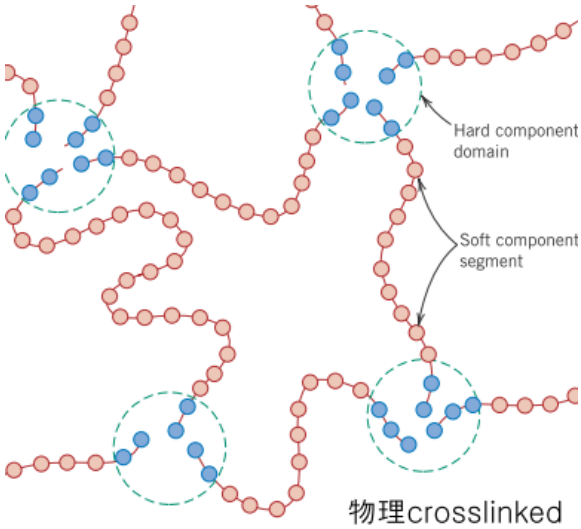


Figure 15.21 Representations of the chain chemistries for (*a*) styrene-butadiene-styrene (S-B-S), and (*b*) styrene-isoprene-styrene (S-I-S) thermoplastic elastomers.



加熱超過熔點，物理交連消失，容易使用各種成型技術，溶解-固化為可逆!!

*比較:一般的彈性體→熱固型!!化學 crosslinked、不可逆

後面的合成和製程不想看

考試前把所有有機畫過一便!!