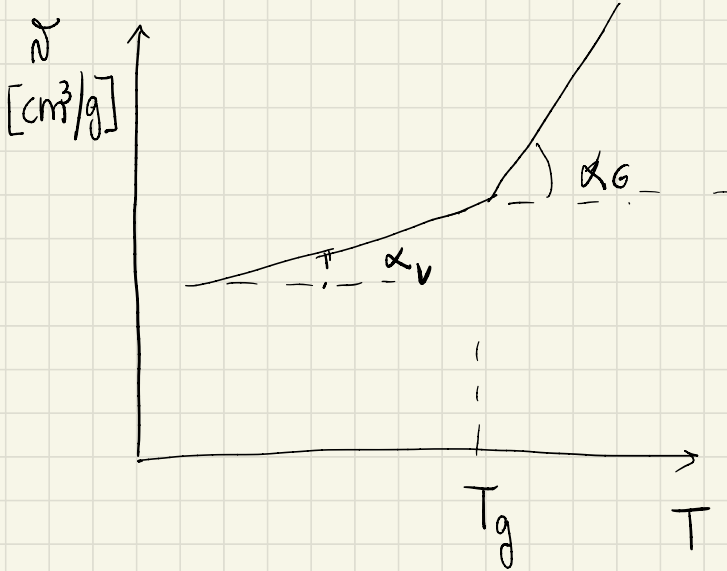


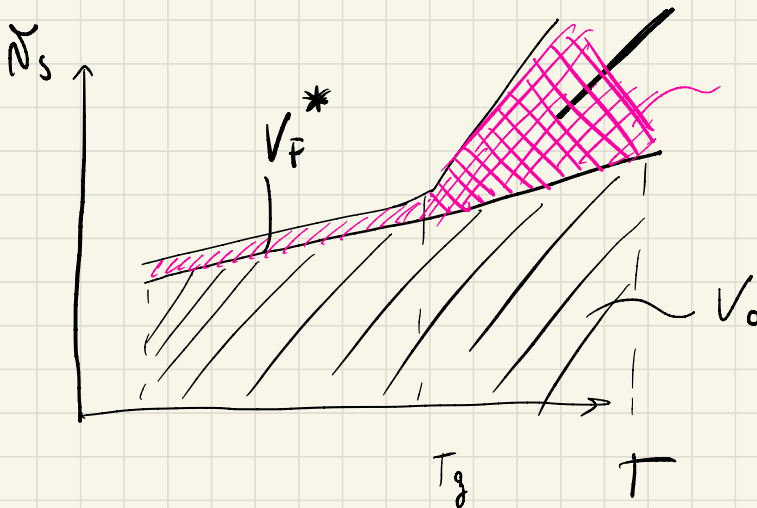
# LEZIONE 9

18.10.2022

POLIMERO AMORFO



$$\alpha_v = \frac{1}{V} \frac{\partial V}{\partial T}$$



VOLUME  
LIBERO  
 $V_F$

IL VOLUME  
REALMENTE  
OCCUPATO  
dagli atomi

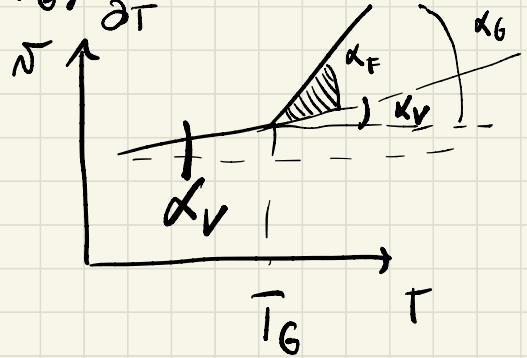
$$V_F = V_F^* + (T - T_G) \frac{\partial V}{\partial T}$$

$$\alpha_F = \alpha_G - \alpha_V$$

$$f_F = \frac{V_F}{V}$$

$$f_F^* = \frac{V_F^*}{V}$$

$$\alpha_F \approx \frac{1}{V} \frac{\partial V}{\partial T}$$



$$F_F = f_F^* + (T - T_G) \alpha_F$$

Per  $T \leq T_G$   $F_F = f_F^*$

$T > T_G$   
 $F_F = f_F$

$$f_F^* = 2.5\%$$

Eq. ne di William - Landell - Ferry WLF

$(AB)_m$

$$f_V^A = f_g^A + (T - T_g^A) a_f^A$$

(16.11)

COPOLIMERI

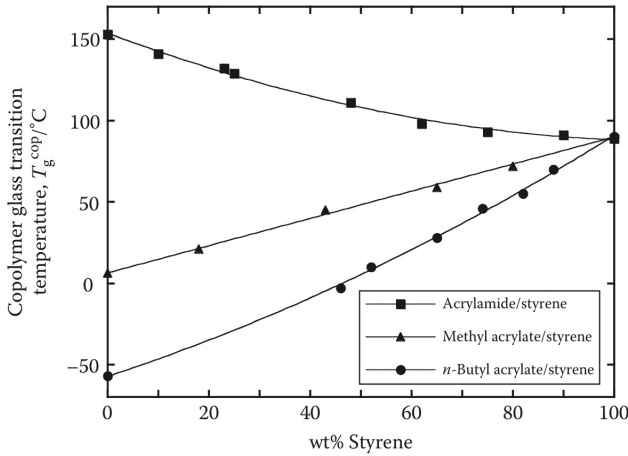


FIGURE 16.5 Variation of copolymer glass transition temperature with the weight fraction of styrene for various styrene-based statistical copolymers. (Data taken from Illers, K.H., *Kolloid-Zeitschrift.*, 190, 16, 1963.)

$$F_V^A = F_g^A + (T - T_g^A) \alpha_F^A$$

$$F_V^B = F_g^B + (T - T_g^B) \alpha_F^B$$

$$F_V^{\text{cop}} = F_g^{\text{cop}} + (T - T_g^{\text{cop}}) \alpha_F^{\text{cop}}$$

$$\alpha^{\text{cop}} = W_A \alpha_F^A + W_B \alpha_F^B$$

$(AB)_m$

$$W_A = \frac{M_A}{M_{\text{TOT}}}$$

$$W_B = \frac{M_B}{M_{\text{TOT}}}$$

$$\frac{1}{T_g^{\text{cop}}} \approx \frac{W_A}{T_g^A} + \frac{W_B}{T_g^B}$$

$T_g^{\text{cop}} \approx \alpha^{\text{cop}}$  dipendono dalle frazioni ponderali

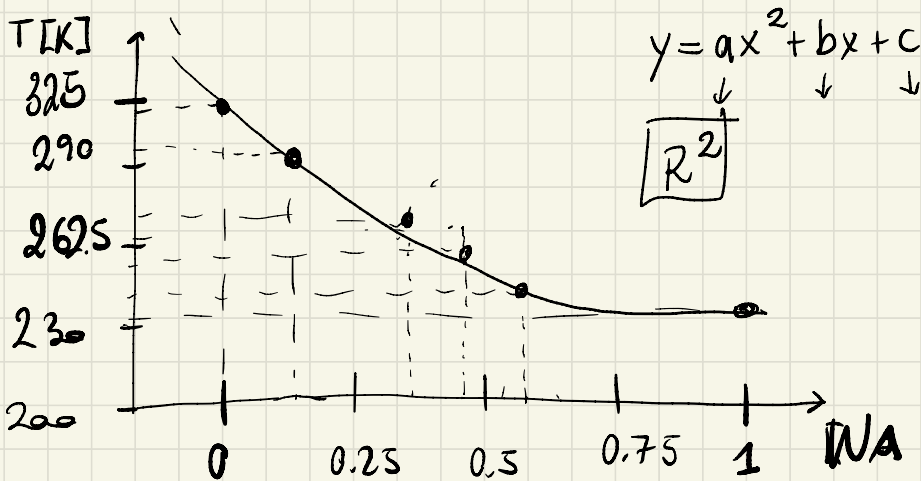


RANDOM COIL

16.4 The following data were obtained for the values of glass transition temperature  $T_g$  of poly[(vinylidene fluoride)-*co*-chlorotrifluoroethylene] as a function of the weight fraction  $w_A$  of vinylidene fluoride. By fitting these data to a suitable curve estimate, the value of  $T_g$  for a copolymer with  $w_A = 0.75$ .

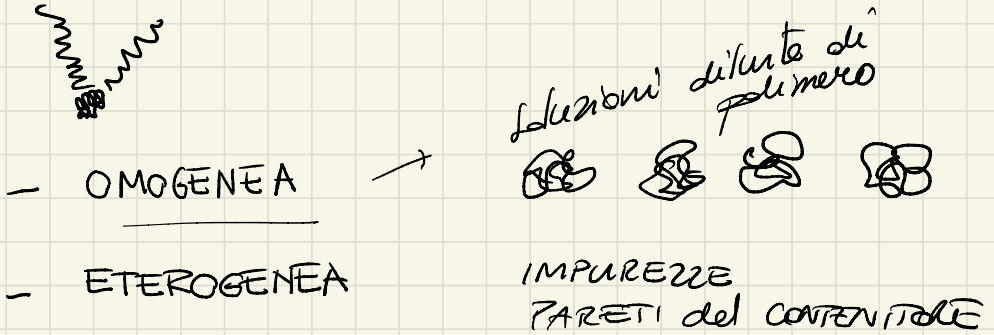
$w_A$	0	0.14	0.35	0.4	0.54	1.0
$T_g/K$	319	292	270	265	258	235

$$0^\circ\text{C} = -273.15\text{K}$$



# Cristallizzazione e fusione

↳ NUCLEAZIONE e ACCRESCIMENTO



→ PROCESSO TERMODINAMICAMENTE FAVORITO

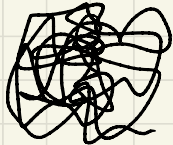
$$G = H - TS \rightarrow \begin{matrix} \nearrow \text{temperatura} \\ \text{Entropia} \end{matrix}$$

↓ Entalpia (calore latente)

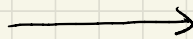
Energia libera di Gibbs

$\Delta G \rightarrow 0$  più il processo è favorito

FUSO POLIMERICO



Alta S



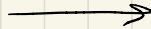
SOLIDO

AMORFO

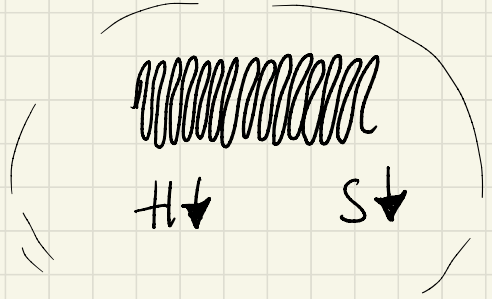


H = cost

S



SOLIDO CRISTALLINO



$$\Delta G = \Delta H - T\Delta S$$



CRISTALLINITA'  
del MATERIALE



FASE AMORFA

Viene favorita la cristallizzazione

In condizioni quasi-stazionarie

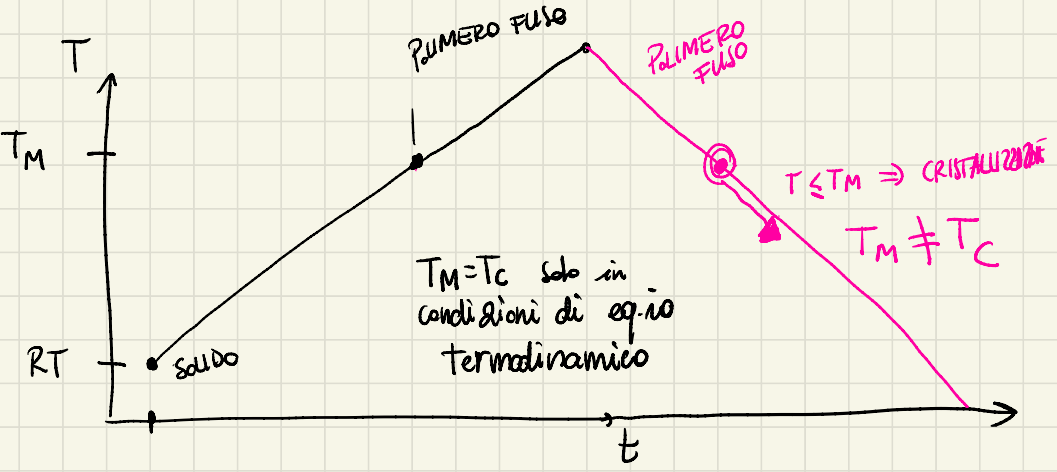
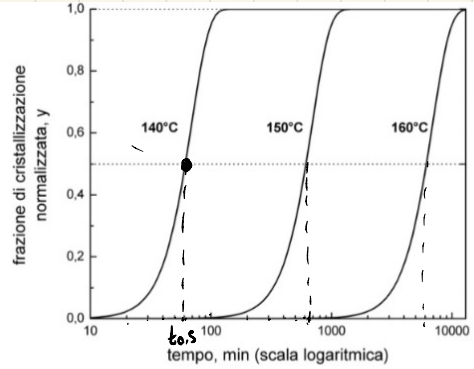
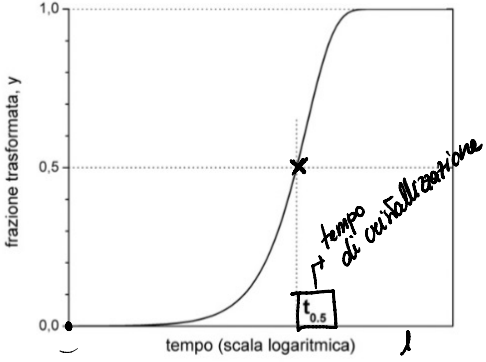
# Equazione di Avrami

FRIZIONE  
di MATERIALE  
CRISTALLIZZATO

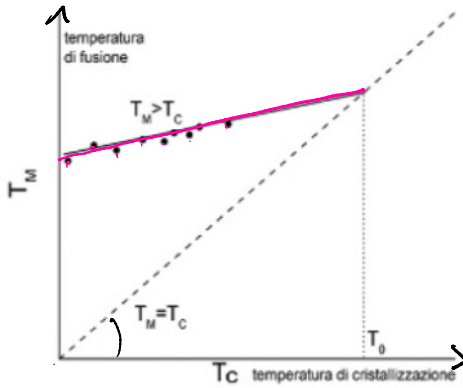
$$y = 1 - e^{-kt^m}$$

$K, m$   
costanti che dipendono  
dal materiale

Se  $T_M = 200^\circ\text{C}$



## 2. Temperatura di fusione e temperatura di cristallizzazione



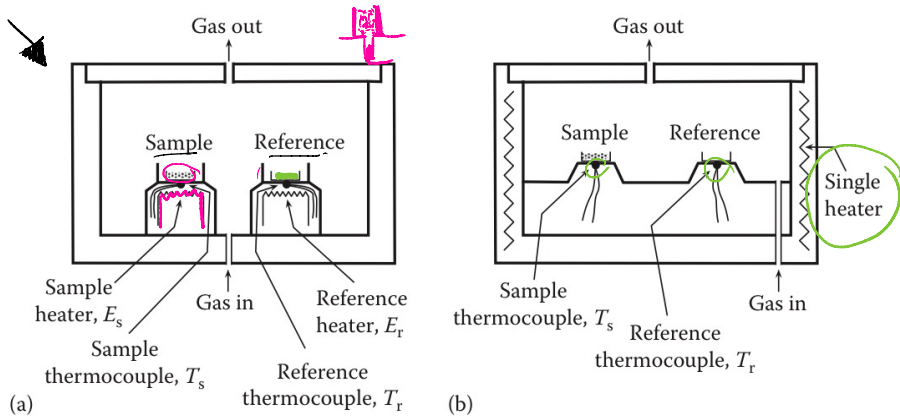
Se lavoro in condizioni di  
Eq. 10 TD  $\Rightarrow T_C = T_M$   
( $y = x$ )

Se non lavoro in condizioni  
di Eq. 10 TD  $\Rightarrow T_M > T_C$

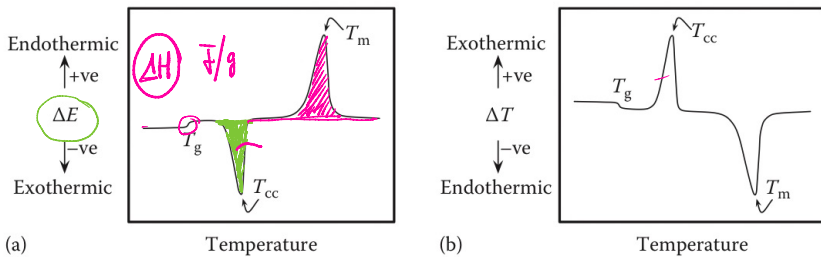
Fig. 6.4 - Determinazione della temperatura  $T_0$  di transizione solido-liquido per un cristallo polimerico perfetto e di dimensioni molto grandi (teoricamente infinite).



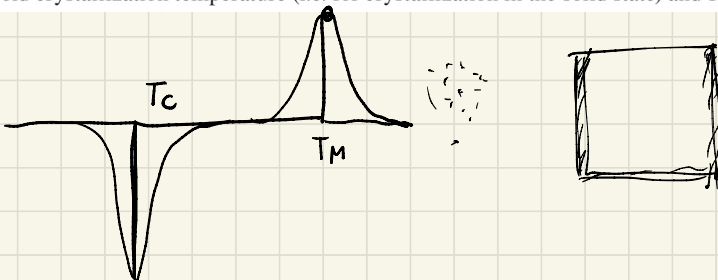
# DSC: Differential Scanning Calorimetry



**FIGURE 17.33** Schematic diagrams showing the key features of cell design for (a) power-compensation DSC and (b) heat-flux DSC. The sample is shown contained in an aluminium pan with an empty aluminium pan as the reference.  $T_s$  and  $T_r$  are, respectively, the temperatures of the sample and reference. In power-compensation DSC, the separate energy inputs to the sample and reference,  $E_s$  and  $E_r$  respectively, are adjusted such that  $T_s = T_r$  as both cells are heated or cooled. Heat-flux DSC employs a single heater and  $\Delta T (= T_s - T_r)$  is monitored as the cell is heated or cooled. The atmosphere can be controlled by flowing a gas through the cell enclosure.



**FIGURE 17.34** Schematic diagrams showing (a) power-compensation and (b) heat-flux DSC traces expected for an amorphous sample of a crystallizable polymer, where  $T_g$  is the glass transition temperature,  $T_{cc}$  is the cold crystallization temperature (i.e. for crystallization in the solid state) and  $T_m$  is the melting temperature.



**TABLE 17.4**

**Approximate Values of Melting Temperature,  $T_m$ , for Various Polymers**

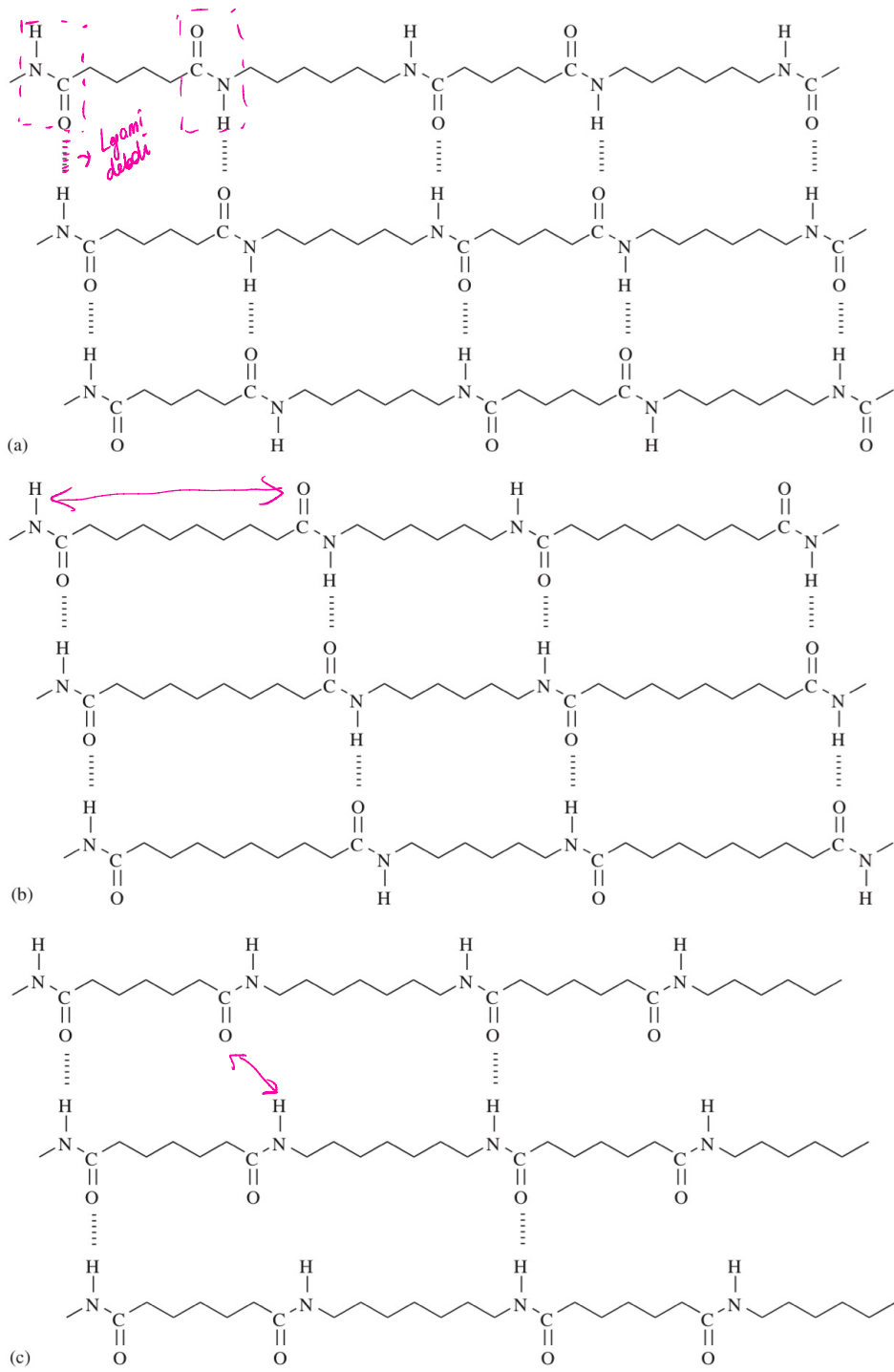
Repeat Unit	$T_m / ^\circ\text{C}$
$-\text{CH}_2-\text{CH}_2-$	137-146
$-\text{CH}_2-\text{CH}_2-\text{O}-$	67
$-\text{CH}_2-\text{CH}_2-\text{CO}-\text{O}-$	122
$-\text{H}_2\text{C}-\text{C}_6\text{H}_4-\text{CH}_2-$	397
$-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$	330
$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$	260
$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{NH}-$	258
<b>Side group (X)</b>	
$-\text{CH}_2-\text{CHX}-$	
$-\text{CH}_3$	187
$-\text{CH}_2-\text{CH}_3$	125
$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	78
$-\text{CH}_2-\text{CH}(\text{CH}_3)_2$	235
$-\text{C}_6\text{H}_5$	240

*Handwritten notes:*  
 - "grasso AMMIDICO" written next to the amide repeat units.  
 - A skeletal structure of a branched alkane is drawn below the side groups.  
 - A benzene ring with a dashed circle and arrow is labeled "PS".

**TABLE 16.1**

**Approximate Values of Glass Transition Temperature,  $T_g$ , for Various Polymers**

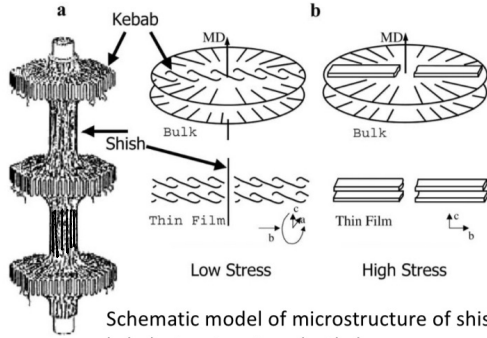
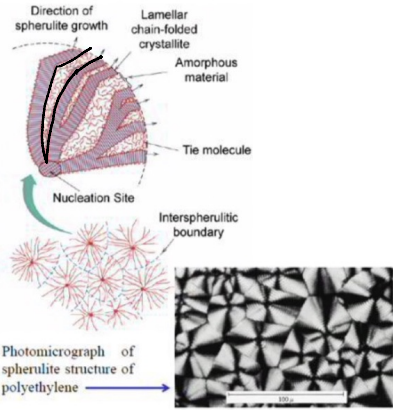
Repeat Unit	Polymer Name	$T_g / ^\circ\text{C}$
$-\text{CH}_2-\text{CH}_2-$	Polyethylene	-130 to -10
$-\text{CH}_2-\text{CH}_2-\text{O}-$	poly(ethylene oxide)	-67
$-\text{H}_2\text{C}-\text{C}_6\text{H}_4-\text{CH}_2-$	poly( <i>p</i> -xylylene)	80
<b>Vinyl polymers</b>		
$-\text{CH}_2-\text{CHX}-$	Side group (X)	
	$-\text{CH}_3$	-23
	$-\text{CH}_2-\text{CH}_3$	-24
	$-\text{CH}_2-\text{CH}_2-\text{CH}_3$	-40
	$-\text{CH}_2-\text{CH}(\text{CH}_3)_2$	30
	$-\text{C}_6\text{H}_5$	100
	$-\text{Cl}$	81
	$-\text{OH}$	85
	$-\text{CN}$	97



**FIGURE 17.37** Differences in patterns of hydrogen bonding in crystals of various nylon polymers: (a) nylon 6.6,  $T_m = 265^\circ\text{C}$ ; (b) nylon 6.10,  $T_m = 222^\circ\text{C}$ ; (c) nylon 7.7,  $T_m = 210^\circ\text{C}$ .

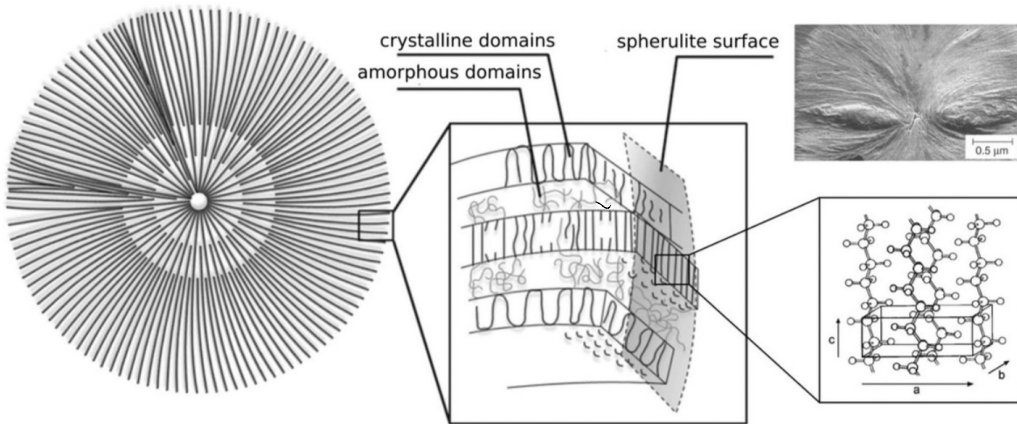
## Struttura cristalline

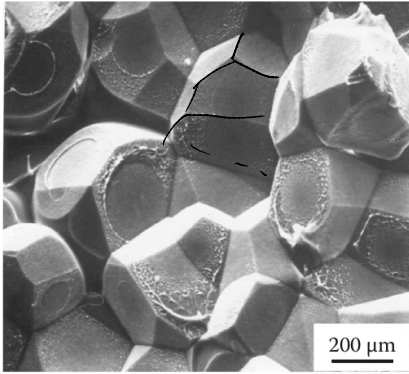
**Spherulites:** Aggregates of lamellar crystallites ~ 10 nm thick, separated by amorphous material. Aggregates are formed upon solidification from a melted state and are approximately spherical in shape.



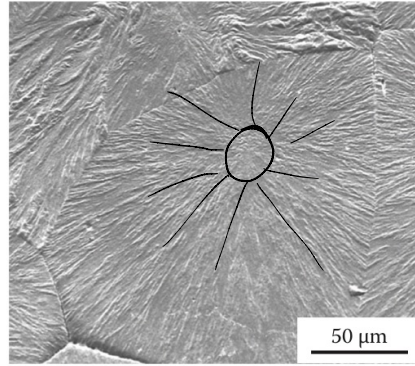
Schematic model of microstructure of shish-kebab structure in polyethylene. Note the example of lamellar or kebab twisting in low stress conditions. [From Processing of Polymers, edited by H.E.H. Meijer, 1997;18:189. Copyright (1997) VCH, New York].

## Struttura cristalline





(a)



(b)

**FIGURE 17.14** Scanning electron micrographs of polypropylene spherulites. (a) Fracture surfaces of a brittle sample of low molar mass polymer showing interspherulitic fracture. (Courtesy of K. Friedrich, University of Kaiserslautern, Kaiserslautern, Germany.) (b) An etched surface of polypropylene crystallized at 128°C showing the structure of the individual spherulites and the spherulite boundaries. (Courtesy of M. Burke, University of Manchester, Manchester, U.K.)