

# POLIMERI

Concetto “giovane”, sviluppatosi a partire dagli anni 20-30 dal concetto di “Macromolecole” (Pickles, 1927), inizialmente osteggiato dai chimici dell’epoca, abituati a sostanze a basso PM e punti di fusione definiti. Nell’ottocento (Graham, 1861) erano stati definiti

**cristalloidi** (diffondono bene in soluzione) e

**colloidi** (non diffondono, viscosi, glue-like, non cristallizzano).

La definizione fu accettata ammettendo l’esistenza di aggregati di piccole molecole, ma non quella di macromolecole.

## POLIMERI NATURALI

proteine, amido, cellulosa,  
DNA, collagene, gomma, seta, ...

## POLIMERI ARTIFICIALI

PP, PE, PET, PTFE,  
PVC, PDMS, PU, PEEK, ...

stato di aggregazione  $\neq$  cristallino, liquido

PM INDEFINITO  $\rightarrow$  distribuzione PM  $\bar{\rightarrow}$  M

M ELEVATO,  $10^3 \div 10^8$  u.m.a.

$T_f, T_{eb}$  INDEFINITI



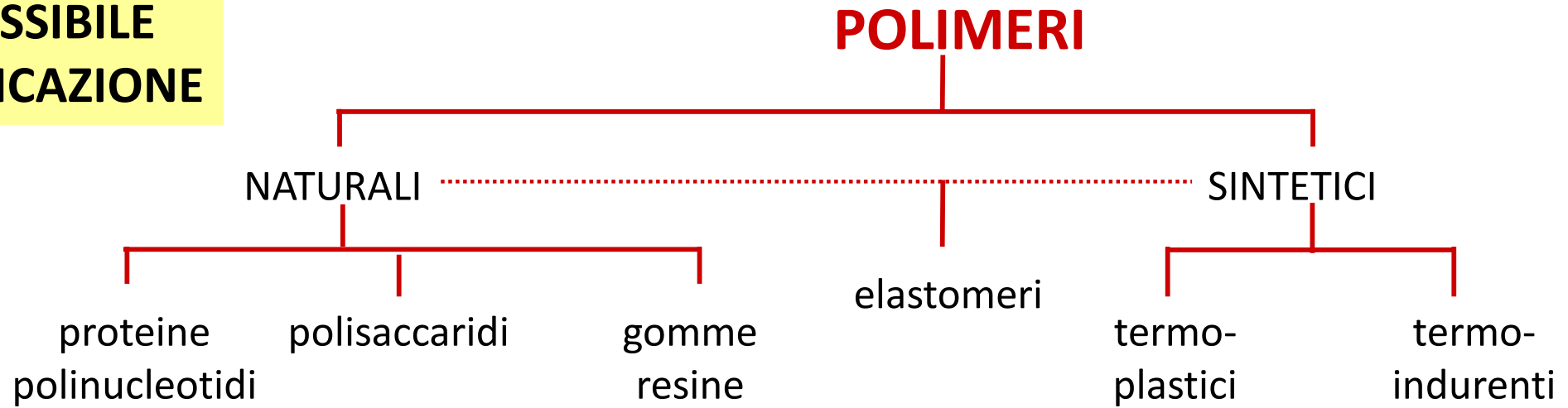
Hermann Staudinger 1881 – 1965

Nobel Laureate  
in Chemistry  
1953

*for his discoveries in the field  
of macromolecular chemistry*

Partendo dal lavoro di Pickles, Staudinger, sviluppò il concetto di **MACROMOLECOLA**, composta da piccole unità ripetitive, di dimensioni e PM vicine ai composti convenzionali.

## UNA POSSIBILE CLASSIFICAZIONE



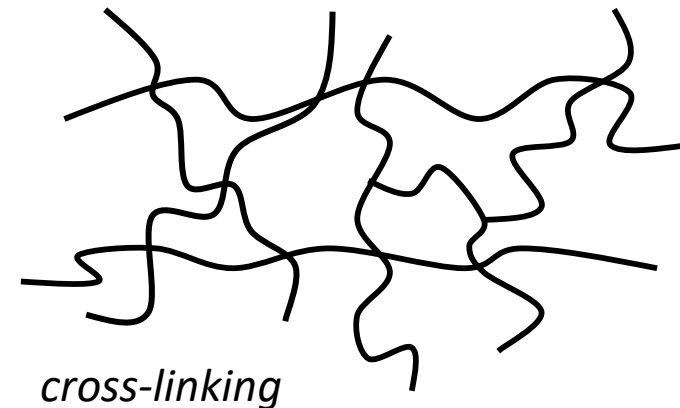
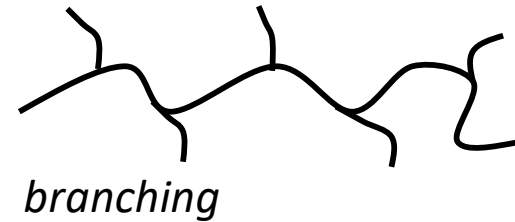
**MONOMERO → POLIMERO = (residuo)<sub>n</sub>**

**MON. BIFUNZIONALI → POL. LINEARI**

$\text{CH}_2=\text{CH}_2$ ,  $\text{CH}_2=\text{CHCl}$ ,  $\text{HO-R-COOH}$

**MON. POLIFUNZIONALI → POL. RAMIFICATI**

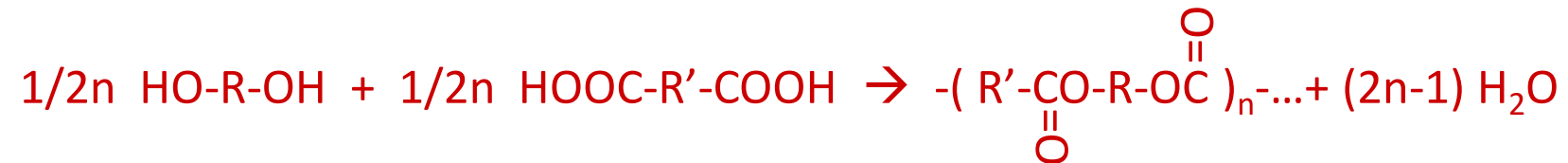
$\text{HOCH}_2\text{-CHOH-CH}_2\text{OH}$



# REAZIONI DI POLIMERIZZAZIONE

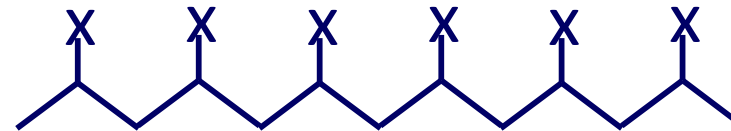
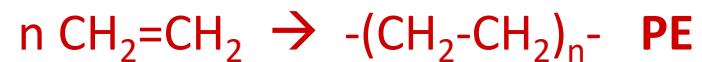
## CRESCITA A STADI (Step growth) – poliesteri, poliamidi,...

prevedono una sequenza di reazioni di condensazione, spesso catalizzate,  
Tra due molecole di monomero, con eliminazione di molecole leggere, tipo H<sub>2</sub>O, HCl, etc.



## ADDIZIONE – poliolefine,...

Reazioni a catena di tipo radicalico o ionica, spesso catalizzate.  
Il polimero ha la stessa composizione del monomero



**CO-POLIMERI  
DA MONOMERI  
BIFUNZIONALI**

A → A-A-A-A-A-A-A-A-A-A-A-A-A omopolimero



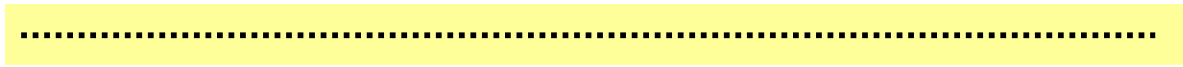
B-A-A-B-B-A-B-B-A-A-A-B-B-A statistico

A + B → A-B-A-B-A-B-A-B-A-B-A-B-A-B- alternato

A-A-A-A-B-B-B-B-A-A-A-B-B-B- a blocchi

ad innesto (graft)

A-A-A-A-A-A-A-A-A-A-A-A-A  
-B-B-B-B  
-B-B-B-B



A + B + C → Ter-polimeri



Karl Ziegler 1898 – 1973

Nobel  
Laureates  
in Chemistry  
1963



Giulio Natta 1903 – 1979

*for their discoveries in the field of the  
chemistry and technology of high polymers*




# MOPLLEN®

## casalinghi inconfondibili

Per la cucina, per il bagno, per la vita di ogni giorno. Tanti, tantissimi oggetti, diversi nella forma, nelle dimensioni, nel colore, fabbricati da tante industrie di trasformazione. Difficile la scelta. No. Un riferimento c'è: preciso, sicuro, inconfondibile. E' l'etichetta gialla di MOPLLEN. Vuol dire resistenza, indeformabilità, robustezza. Solo con l'etichetta avete la certezza che è MOPLLEN.



1.67 Capolinea

MONTECATINI EDISON S.p.A.  Divisione Petrochimica e Resine - Milano



### Un carico prezioso

Prezioso, sì, ma non fragile. E neppure pesante. E neppure costoso. Perché prezioso allora? Perché è di Moplen. Moplen è veramente un materiale prodigioso per la vita moderna. Così leggero, economico, robusto. Gli acidi non lo corrodono; neppure l'acqua bollente lo può danneggiare. Per trasportare, contenere, conservare ogni cosa, l'ideale è Moplen. In casa o sul luogo di lavoro, oggi c'è Moplen. Dalla vasca più grossa sino al più piccolo imbuto ogni oggetto di Moplen deve portare questa etichetta. Solo così sarete certi che l'oggetto è di Moplen. *Attenzione all'etichetta!*

## Moplen®

MONTESHELL PETROCHIMICA S.p.A. Largo G. Donegani 1/2, Milano



I polimeri atattici, in genere, non cristallizzano; gli altri si se le condizioni lo permettono.

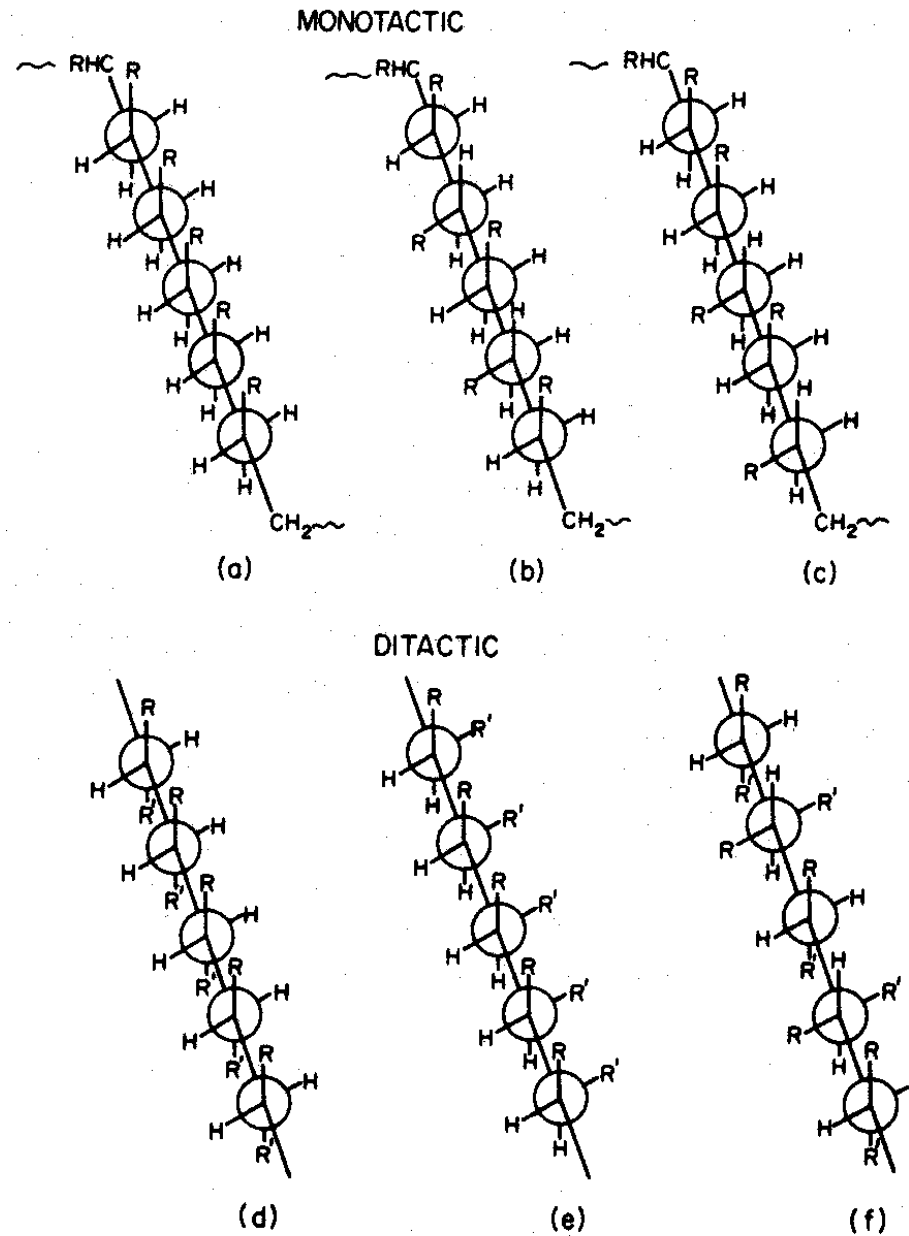


FIGURE 6.1. Newman projections of various stereoregular forms, (a) Isotactic, (b) Syndiotactic, (c) Atactic, (d) Erythro-di-isotactic, (e) Threo-di-isotactic, and (f) Di-syndiotactic.



TABLE 1.4. Thermoplastics

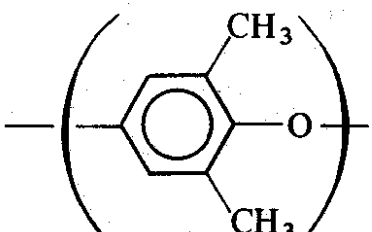
Polymer	Repeat unit	Density (g cm <sup>-3</sup> )	Uses
Polyethylene (High Density) (Low Density)	—(CH <sub>2</sub> CH <sub>2</sub> )—	0.94 to 0.96 0.92	Household products, insulators, pipes, toys, bottles
Polypropylene	—(CH <sub>2</sub> CH(CH <sub>3</sub> ))—	0.90	Waterpipes, integral hinges, sterilizable hospital equipment
Poly(4-methylpentene-1) (TPX)	$\begin{array}{c} \text{---(CH}_2\text{CH)---} \\   \\ \text{CH}_2 \\   \\ \text{CH} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	0.83	Hospital and laboratory ware
Poly(tetrafluoroethylene) (PTFE)	—(CF <sub>2</sub> CF <sub>2</sub> )—	2.20	Non-stick surfaces, insulation, gaskets
Poly(vinyl chloride) (PVC)	—(CH <sub>2</sub> CHCl)—	1.35 to 1.45	Records, bottles, house siding and eaves
Polystyrene	—(CH <sub>2</sub> CH(C <sub>6</sub> H <sub>5</sub> ))—	1.04 to 1.06	Lighting panels, lenses, wall tiles, flower pots
Poly(methylmethacrylate) (PMMA)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{---(CH}_2\text{---C---)} \\   \\ \text{COOCH}_3 \end{array}$	1.17 to 1.20	Bathroom fixtures, knobs, combs, illuminated signs
Polycarbonates	—(R.O.COO →)	1.20	Cooling fans, marine propellers, safety helmets
Poly(2,6-dimethylphenylene oxide)		1.06	Hot water fittings, sterilizable, medical, and surgical equipment

TABLE 1.5. Some common elastomers and their uses

Polymer	Formula	Uses
Natural rubber (polyisoprene- <i>cis</i> )	$\left( \text{CH}_2 - \underset{\text{CH}_3}{\text{C}} = \text{CH} - \text{CH}_2 \right)_n$	General purposes
Polybutadiene	$\left( \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right)_n$	Tyre treads
Butyl	$\left( \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} \right)_n$	Inner tubes, cable sheathing, roofing, tank liners
SBR	$\left( \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right)_n$	Tyres, general purposes
ABS	$\left( \text{CH}_2 - \underset{\text{CN}}{\text{CH}} - \text{CH}_2 - \underset{\text{CH} - \text{CH} = \text{CH} - \text{CH}_2}{\text{CH}} - \text{C}_6\text{H}_5 \right)_n$	Oil hoses, gaskets, flexible fuel tanks
Polychloroprene	$\left( \text{CH}_2 - \underset{\text{Cl}}{\text{C}} = \text{CH} - \text{CH}_2 \right)_n$	Used when oil resistance, good weathering, and inflammability characteristics are needed
Silicones	$\left( \text{O} - \underset{\text{R}}{\overset{\text{R}}{\text{Si}}} \right)_n$	Gaskets, door seals, medical application flexible moulds
Polyurethanes	$\left( \text{R}_1 - \text{NHCOOR}_2\text{OCHN} \right)_n$	Printing rollers, sealing and jointing
EPR	$\sim \left( \text{CH}_2 - \text{CH}_2 \right)_m \left( \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right)_p \sim$	Window strips and channelling

**TABLE 1.6. Room temperature curing adhesives and sealants**

<i>Type</i>	<i>General description</i>	<i>Particular advantages</i>	<i>Limitations (general operating temp. range)</i>
Moisture curing polyurethanes (PUs)	Sealants (rather than adhesives) which cure by an isocyanate reaction to atmospheric H <sub>2</sub> O	Adhesive/sealing effect to a wide range of substrates	Slow curing Usually low modulus (- 80°C to + 120°C)
RTV (room temp. vulcanising) silicones	Sealants (rather than adhesives) which cure on exposure to atmospheric moisture by a condensation mechanism that results in release of side products such as acetic acid, alcohols or amines	Excellent thermal, oxidative and hydrolytic stability	Unpleasant side products Limited adhesion (- 80°C to + 200°C)
Anaerobic adhesives and sealants	Fluids which cure in the absence air and the presence of metals, heat of UV light by the free radical mechanism	Very good adhesion to metals and ceramics Resistant to organic solvents	Relatively brittle when cured Curing is sensitive to substrate and to joint geometry (- 50°C to + 150°C)
Cyanoacrylate adhesives	Relatively low viscosity which cure anionically in response to substrate-borne atmospheric moisture	Excellent adhesion to a wide range of substrates Very effective on rubber and on most plastics	Brittle when cured Limited thermal and hydrolytic stability (- 50°C to + 80°C)
Acrylics	Methacrylic adhesives which cure free radically in response to substrates treated with a primer/hardener. The adhesives usually contain rubber toughener	Forms durable adhesive joints to metallic substrates High peel strenght	Inhibited by atmospheric oxygen Limit cure-through-gap (- 50°C to + 100°C)

poli + CRU

poli + monomero

Name	Structure	Trivial name
poly(methylene)	$-(CH_2CH_2)_n-$	polyethylene <b>PE</b>
poly(propylene)	$-(CH(CH_3)-CH_2)_n-$	polypropylene <b>PP</b>
poly(1,1-dimethylethylene)	$-(C(CH_3)_2-CH_2)_n-$	polyisobutylene
poly(1-methyl-1-butenylene)	$-(C(CH_3)=CHCH_2CH_2)_n-$	polyisoprene
poly(1-butenylene)	$-(CH=CHCH_2CH_2)_n-$	polybutadiene
poly(1-phenylethylene)	$-(CH(CH_6)-CH_2)_n-$	polystyrene <b>PS</b>
poly(1-cyanoethylene)	$-(CH(CN)-CH_2)_n-$	polyacrylonitrile <b>PAN</b>
poly(1-hydroxyethylene)	$-(CH(OH)-CH_2)_n-$	poly(vinylalcohol) <b>PVA</b>
poly(1-chloroethylene)	$-(CH(Cl)-CH_2)_n-$	poly(vinylchloride) <b>PVC</b>
poly(1-acetoxyethylene)	$-(CH(OOCCH_3)-CH_2)_n-$	poly(vinylacetate)
poly(1,1-difluoroethylene)	$-(C(F)_2-CH_2)_n-$	poly(vinylidene fluoride) <b>PVdF</b>

Name	Structure	Trivial name
poly(1-(methoxycarbonyl)ethylene)	$-(CH(COOCH_3)-CH_2)_n-$	poly(methylacrylate)
poly(1-(methoxycarbonyl)-1-methyl-ethylene)	$-(C(CH_3)(COOCH_3)-CH_2)_n-$	<b>PMMA</b> poly(methylmethacrylate)
poly(oxymethylene)	$-(OCH_2)_n-$	polyformaldehyde
poly(oxyethylene)	$-(OCH_2CH_2)_n-$	<b>PEO</b> poly(ethylene oxide) <b>PEG</b> (sometimes called polyethylene glycol)
poly(oxyphenylene)	$-(O-C_6H_4)_n-$	poly(phenyleneoxide)
poly(oxyethylene-oxyterephthaloyl)	$-(OCH_2CH_2OOC-C_6H_4-CO)_n-$	<b>PET</b> poly(ethylene terephthalate)
poly(iminohexamethyleneiminoadipoyl)	$-(NH(CH_2)_6NHCO(CH_2)_4CO)_n-$	poly(hexamethylene adipamide)
poly(difluoromethylene)	$-(C(F)_2)_n-$	<b>PTFE</b> poly(tetrafluoroethylene)
poly((2-propyl-1,3-dioxane-4,6-diyl)methylene)	$-(C_6H_{10}(C_3H_7)-CH_2)_n-$	poly(vinylbutyryl)

inoltre esistono i "trademark"  
es. GORE-TEX®, TEFLON®

**Polimeri** non hanno PM ben definito, piuttosto si parla di una distribuzione di PM

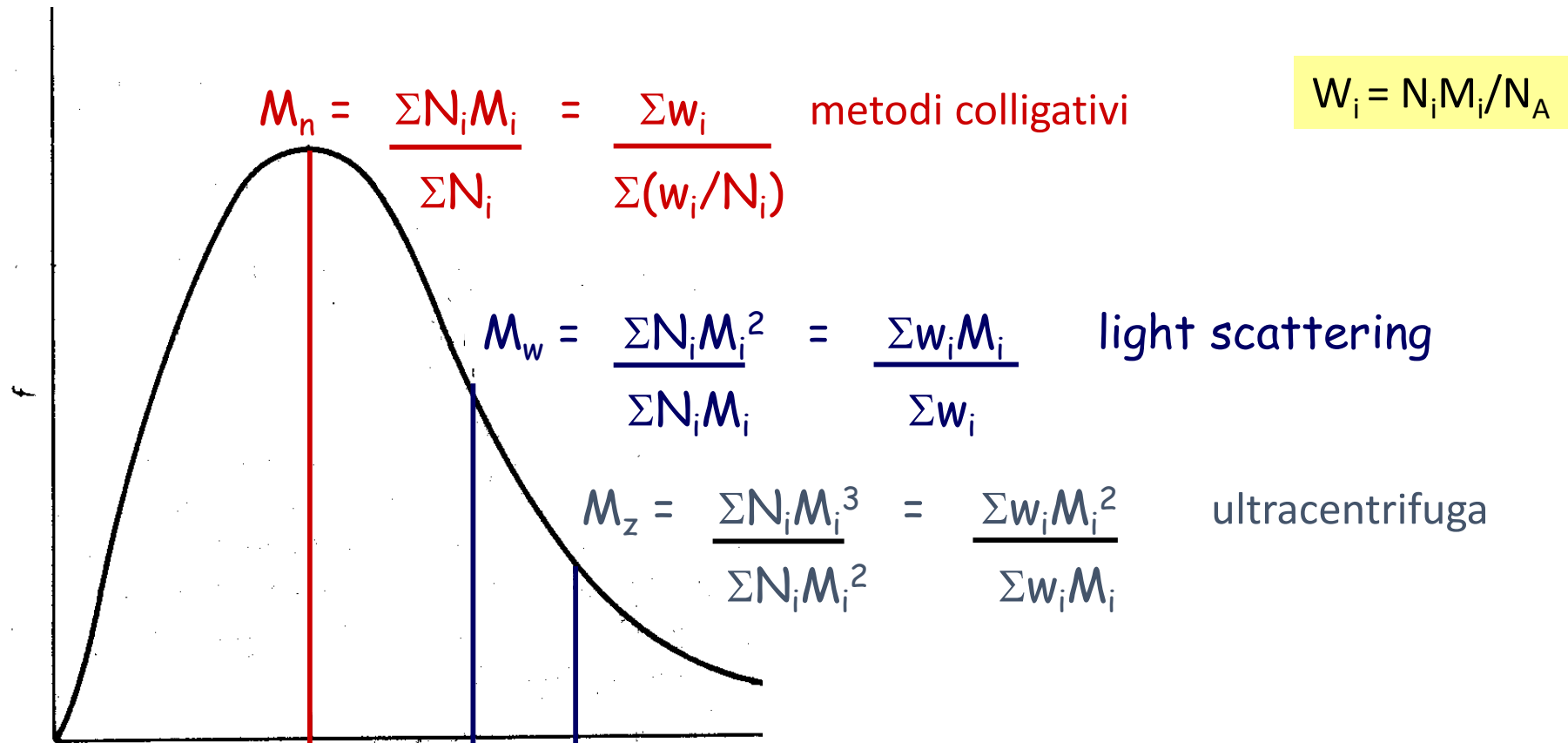


FIGURE 1.1. Typical distribution of molar masses for a synthetic polymer sample, where  $f$  is the fraction of polymer in each interval of  $M$  considered.

La distribuzione della lunghezza della catena, formatasi per eventi casuali, determina la distribuzione dei pesi molecolari.

$M_n$  = media numerica → numero di molecole con  $M_i$

$M_w$  = media pesata → peso (forma) delle molecole

# DETERMINAZIONE DEL PESO MOLECOLARE

Gel Permeation  
Chromatography

Size exclusion

Pressione osmotica

$$\lim_{c \rightarrow 0} p/c = RT/M_n$$

Fino a  $M_n \cong 40.000$  u.a

Ebullioscopia  
Crioscopia

Light scattering  
(tecniche laser)

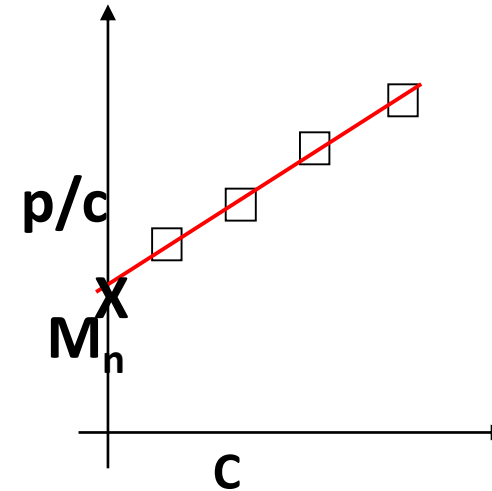
$$R_{\Theta} = i_0 r^2 / I_0 \quad 1/R_{\Theta} \propto 1/M_w + K_1 c + \dots K_n c^n$$

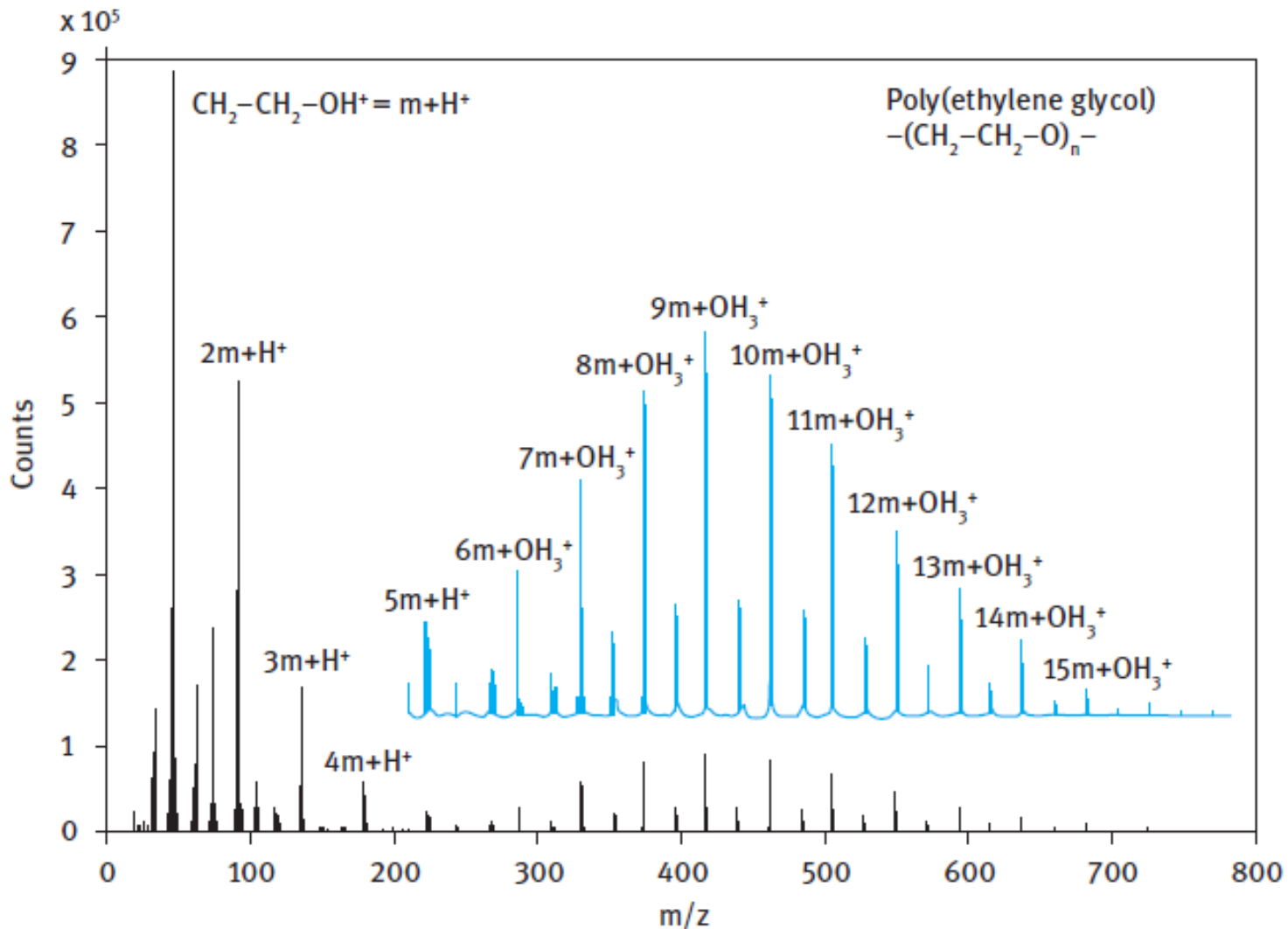
$I_0$  = intensità luminosa diffusa

$R$  = distanza di osservazione

$\Theta$  = angolo del raggio incidente

$R_{\Theta}$  = Rayleigh ratio





**Fig. 2.5:** Positive-ion TOF-SIMS spectrum of PEG obtained after bombardment with an 8-keV Cs<sup>+</sup> primary ion beam. The sample was prepared as thin film deposited from a 1-mg/ml ethanol solution. With permission from Keller BA, Hug P, *Anal Chim Acta* 393, 201–12, 1999. Copyright 1999, Elsevier [53].

## INDICE DI ETEROGENEITÀ

$M_w/M_n$  generalmente vicino a 2  
 misura la larghezza della distribuzione (1.5 - 50)

## GRADO MEDIO DI POLIMERIZZAZIONE

indica il numero di unità, in media, per catena

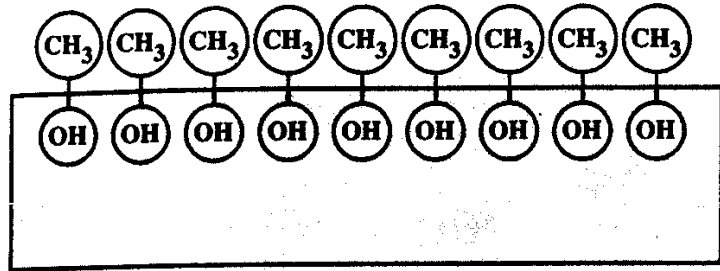
polimero

$$X_{n(w)} = \frac{M_{n(w)}}{M_0}$$

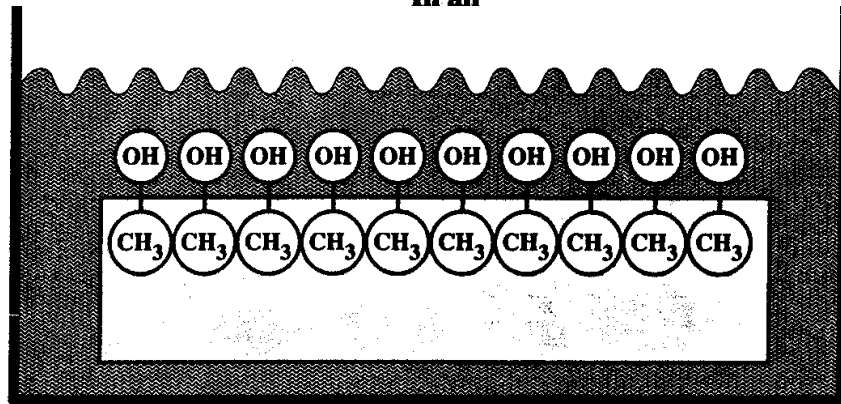
monomero



# CHAIN MOBILITY



In air



Under water

many materials can undergo a reversal of surface when transferred from air into a water environment (e.g. hydroxylated polymer)

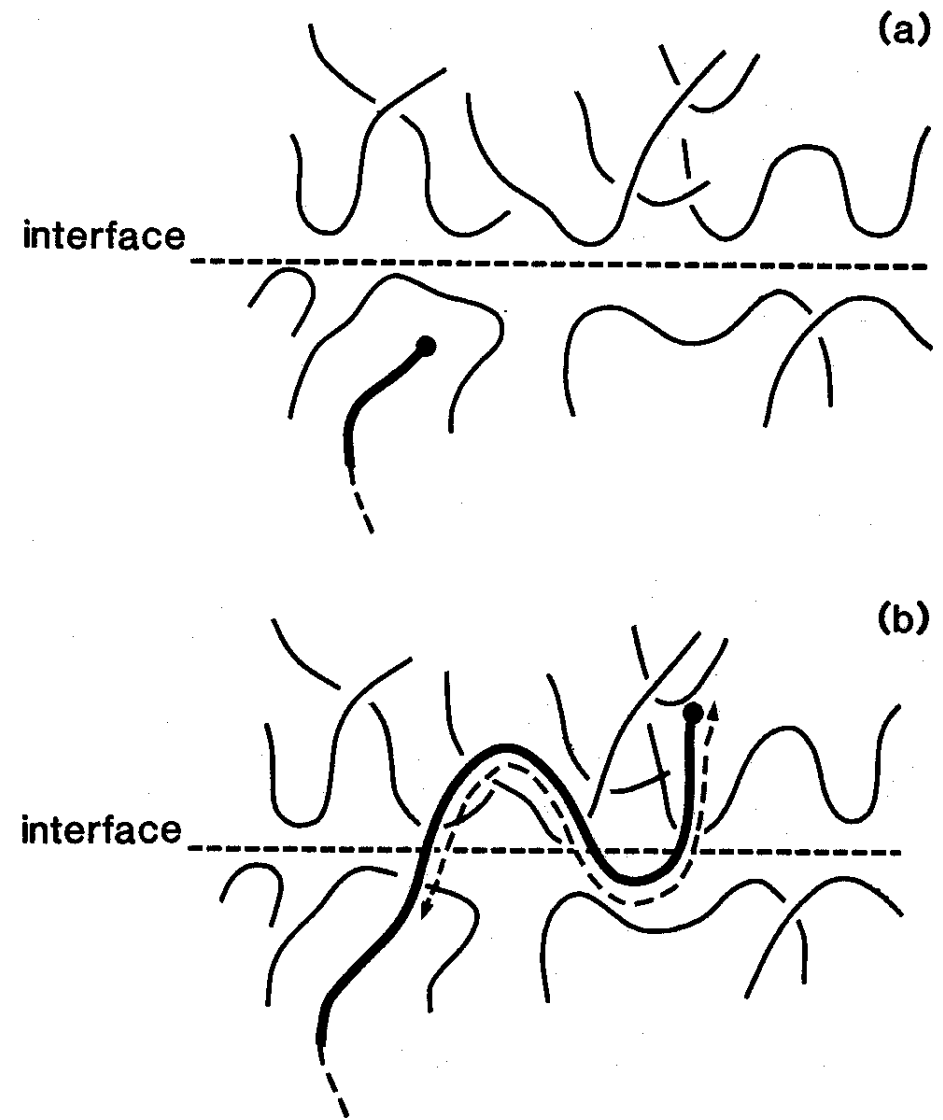


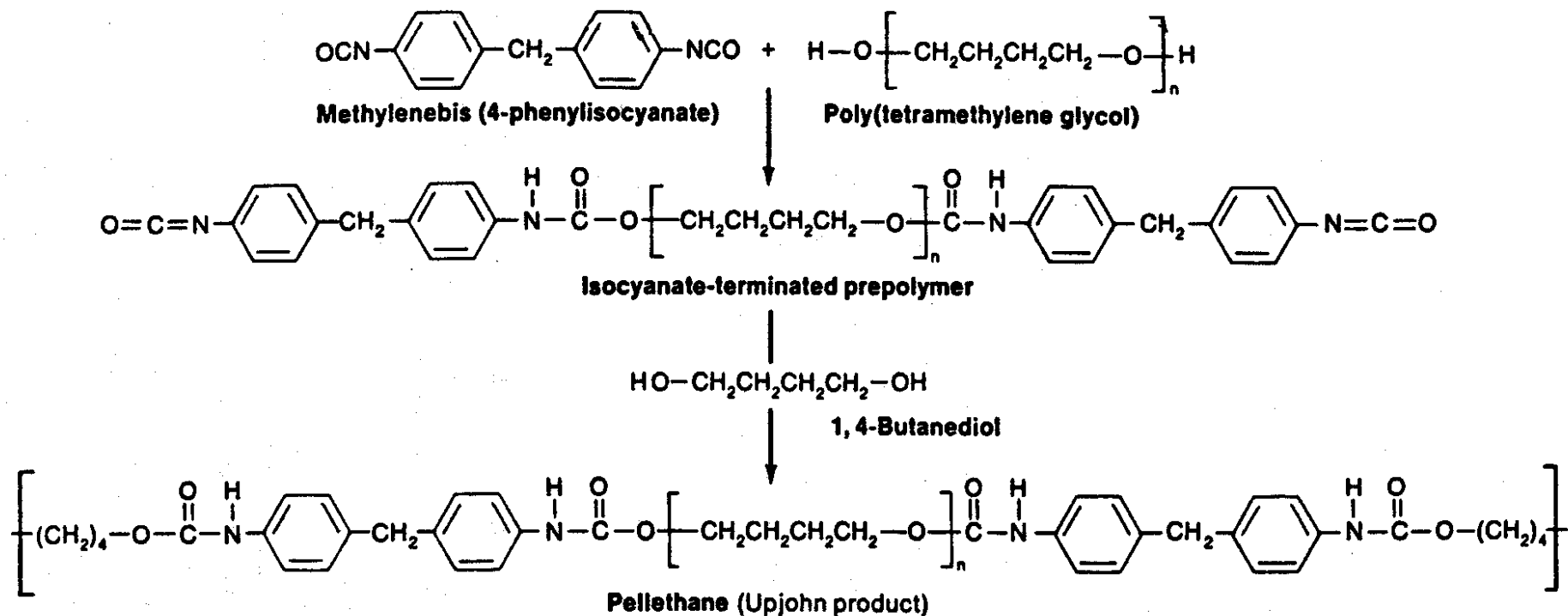
FIGURE 12.6. Schematic of chain movement across an interface: (a) first contact and (b) after having been in contact for some time, with a chain from one surface having *reptated* across into the interface of the adjoining polymer block.

Healing phenomena

# Poliuretani

TABLE 2.4. Formation of (a) aromatic polyurethane, Pellethane, (b) aromatic polyurethane Biomer, and (c) aliphatic polyurethane Tecoflex

(a)

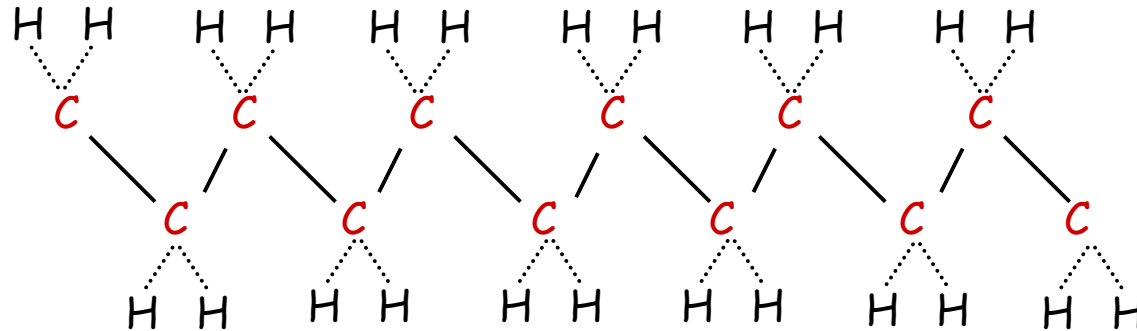


**HARD  
SEGMENT  
IDROFILO  
(POLARE)**

**SOFT  
SEGMENT  
IDROFOBO  
(APOLARE)**

**FORMA E GRANDEZZA** delle catene dipendono dalla **CONFORMAZIONE** degli atomi di carbonio nelle catene.

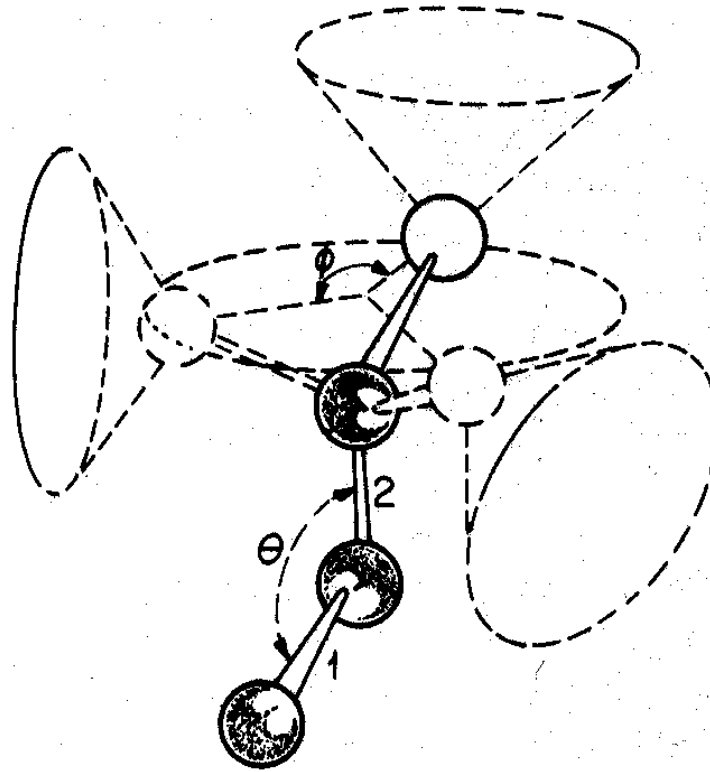
**GRANDEZZA, FORMA E PESO MOLECOLARE** delle catene caratterizzano il polimero e le sue proprietà, annesse al grado di **CRISTALLINITÀ**.



Immaginiamo il polietilene, es a  $PM \cong 1.6 \cdot 10^5$ . Angolo  $109^\circ$ .

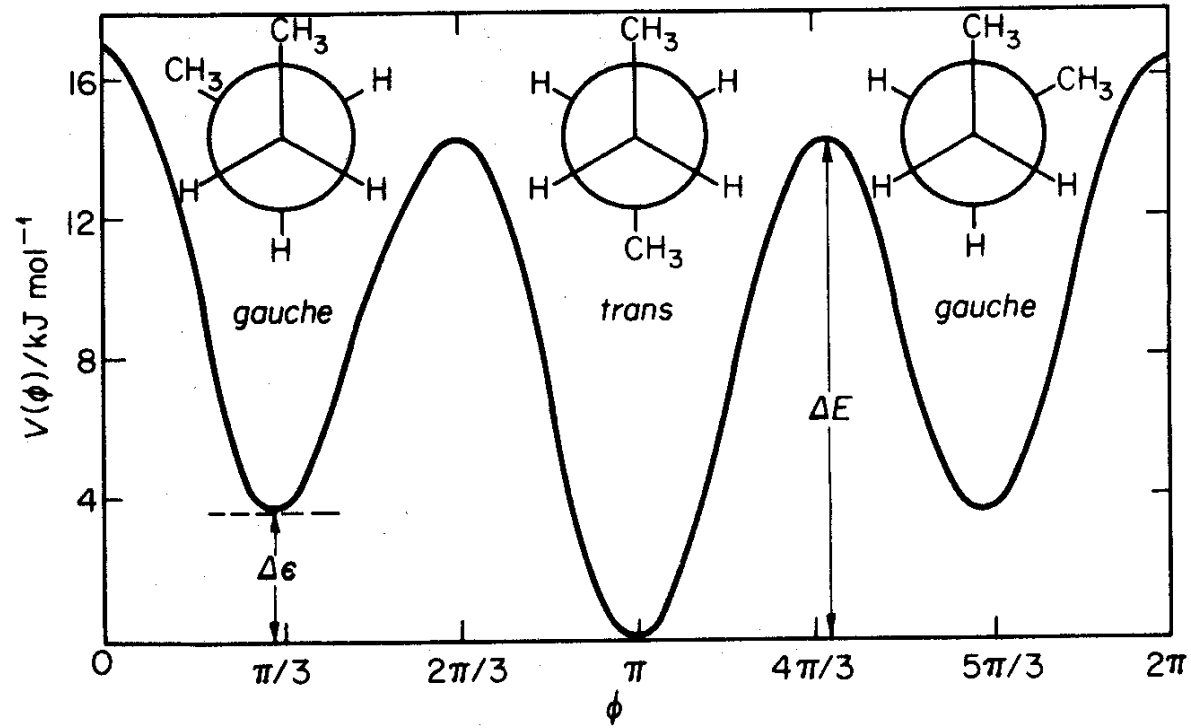
Assumendo una catena sempre a zig-zag e una lunghezza di legame C-C di  $1.5 \text{ \AA}$ , si hanno 10.000 atomi C per catena, una lunghezza  $1.25 \mu$  e un diametro di  $3 \text{ \AA}$  (un filo)

**è realistico pensare che sia tutto "Trans" ?**



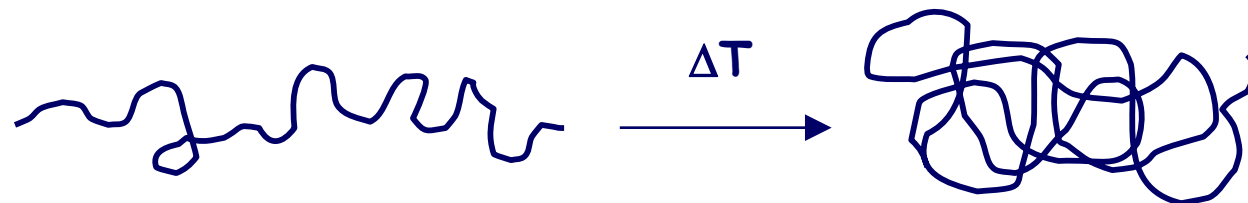
**FIGURE 1.4.** Diagrammatic representation of the cones of revolution available to the third and fourth bonds of a simple carbon chain with a fixed bond angle  $\theta$ .

Dato che ogni gruppo di 4 atomi C dei  $10^4$  della catena può scegliere tra 3 possibili stati rotazionali stabili per la catena, sono possibili un totale di  $3^{10.000}$  forme, benché l'unica "tutta trans" sia la più stabile. La catena sarà quindi "aggrovigliata" in modo casuale, e sarà tanto più mobile quanto maggiore è la temperatura.



La distribuzione di stati *trans* e *gauche* dipende anche dalla temperatura, secondo la legge di Boltzmann: la molecola si aggroviglia sempre più all'aumentare della temperatura

$$N_g/N_t = 2 e^{-\Delta\epsilon/kT}$$



solido rigido  $\xrightarrow{T_g}$  liquido viscoso

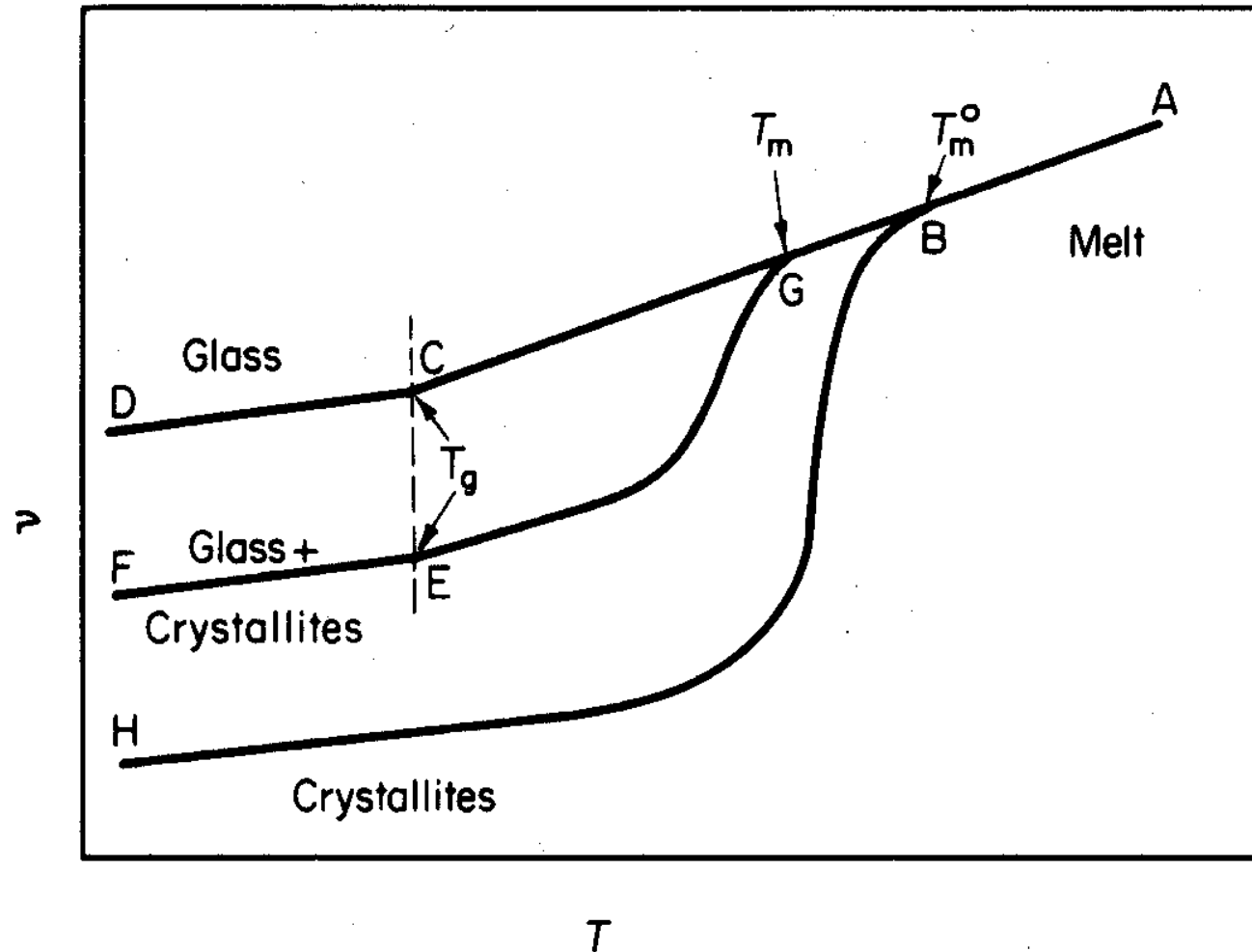
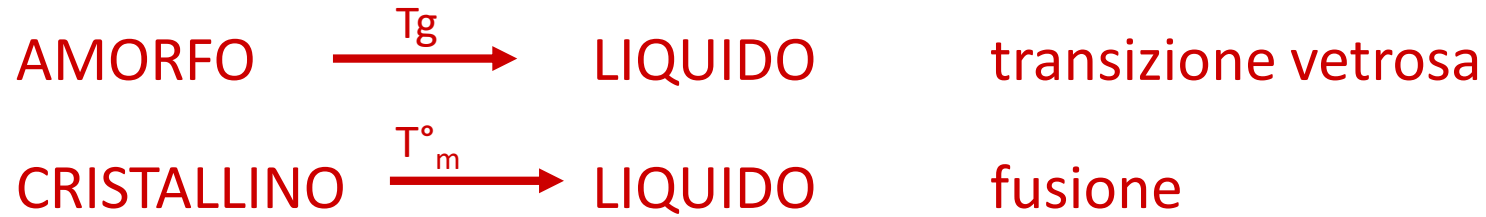


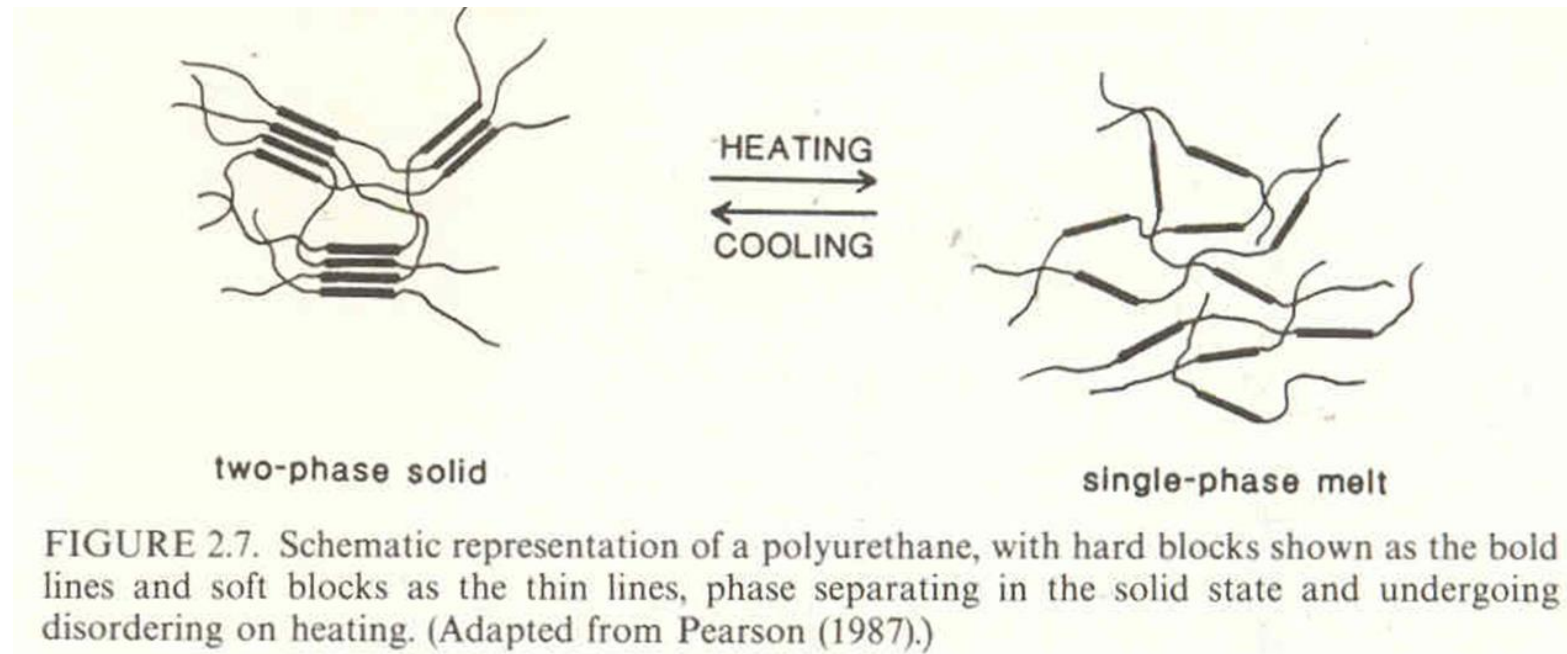
FIGURE 1.6. Schematic representation of the change of specific volume  $v$  of a polymer with temperature  $T$  for (i) a completely amorphous sample (A-C-D), (ii) a semi-crystalline sample (A-G-F), and (iii) a perfectly crystalline material (A-B-H).

All'aumentare di T il polimero raggiunge l'energia termica (cinetica) sufficiente, per cui le catene possono muoversi liberamente, come in un liquido viscoso.



In realtà i polimeri mostrano spesso una percentuale di cristallizzazione, caratteristica di zone amorphe alternate a zone cristalline, per cui si misura sempre una  $T_g$  e si registra l'intervallo  $T_m^\circ - T_m$  di rammollimento.

$T_m < T_m^\circ$ , caratteristica del polimero con il 100% di cristallinità, a causa della distribuzione di forma dei cristalli e di lunghezza delle catene





# CRISTALLINITA'

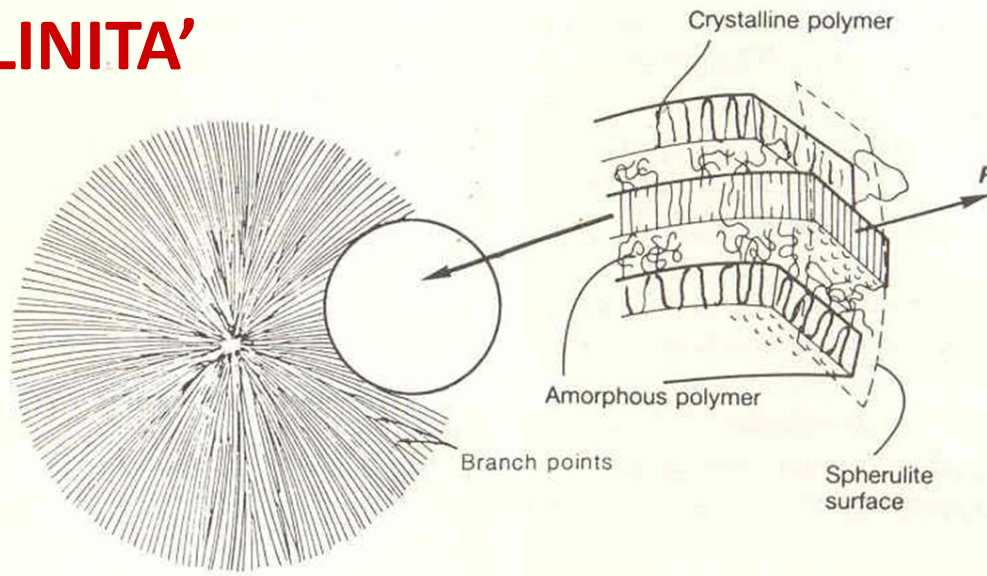


FIGURE 11.8. Fully-developed spherulite grown from the melt, comprising chain folded lamellae (magnified section) and branching points which help to impart a spherical shape to the structure. Most rapid growth occurs in the direction of the spherulite radius  $R$ . (Adapted from McCrum *et al.* (1988) with permission from Oxford University Press.)

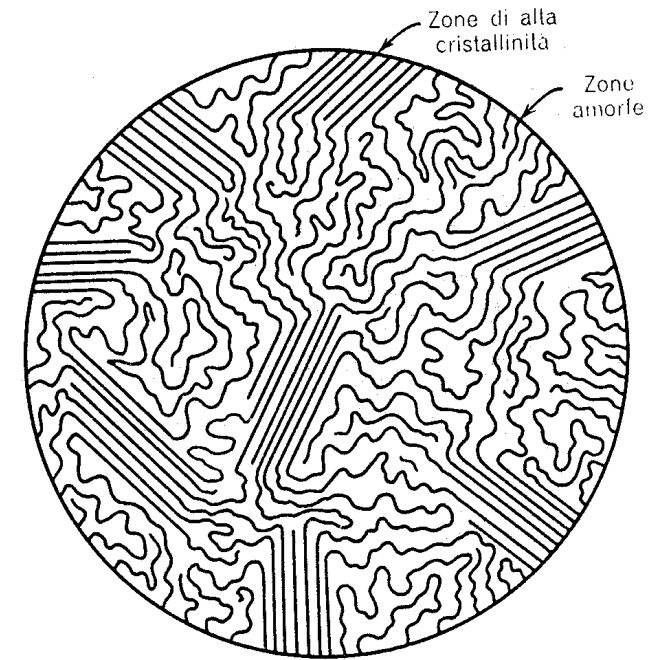


Fig. 10.3 Modello delle « micelle a frange » dei cristalliti nei polimeri.

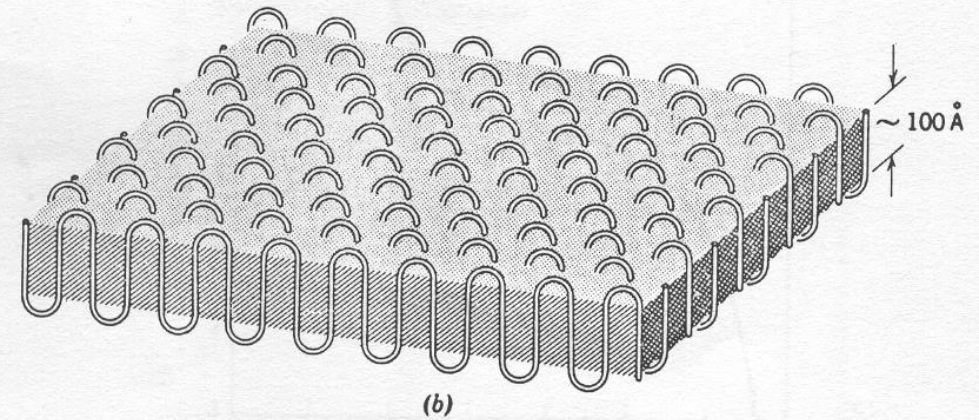
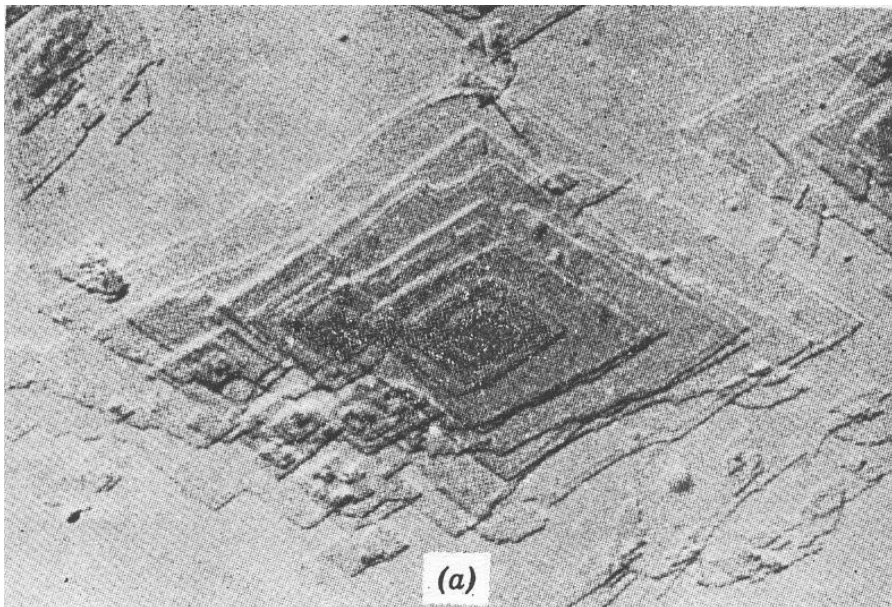
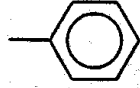
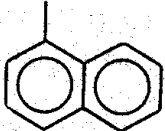
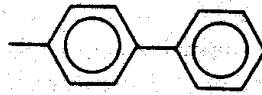


Fig. 10.4 (a) Micrografia elettronica di un monocristallo di polietilene (da A. Keller, R. H. Doremus, B. W. Roberts, e D. Turnbull (eds.) *Growth and Perfection of Crystals*. John Wiley & Sons, N. Y., 1958, p. 499); (b) struttura molecolare del polietilene cristallino.

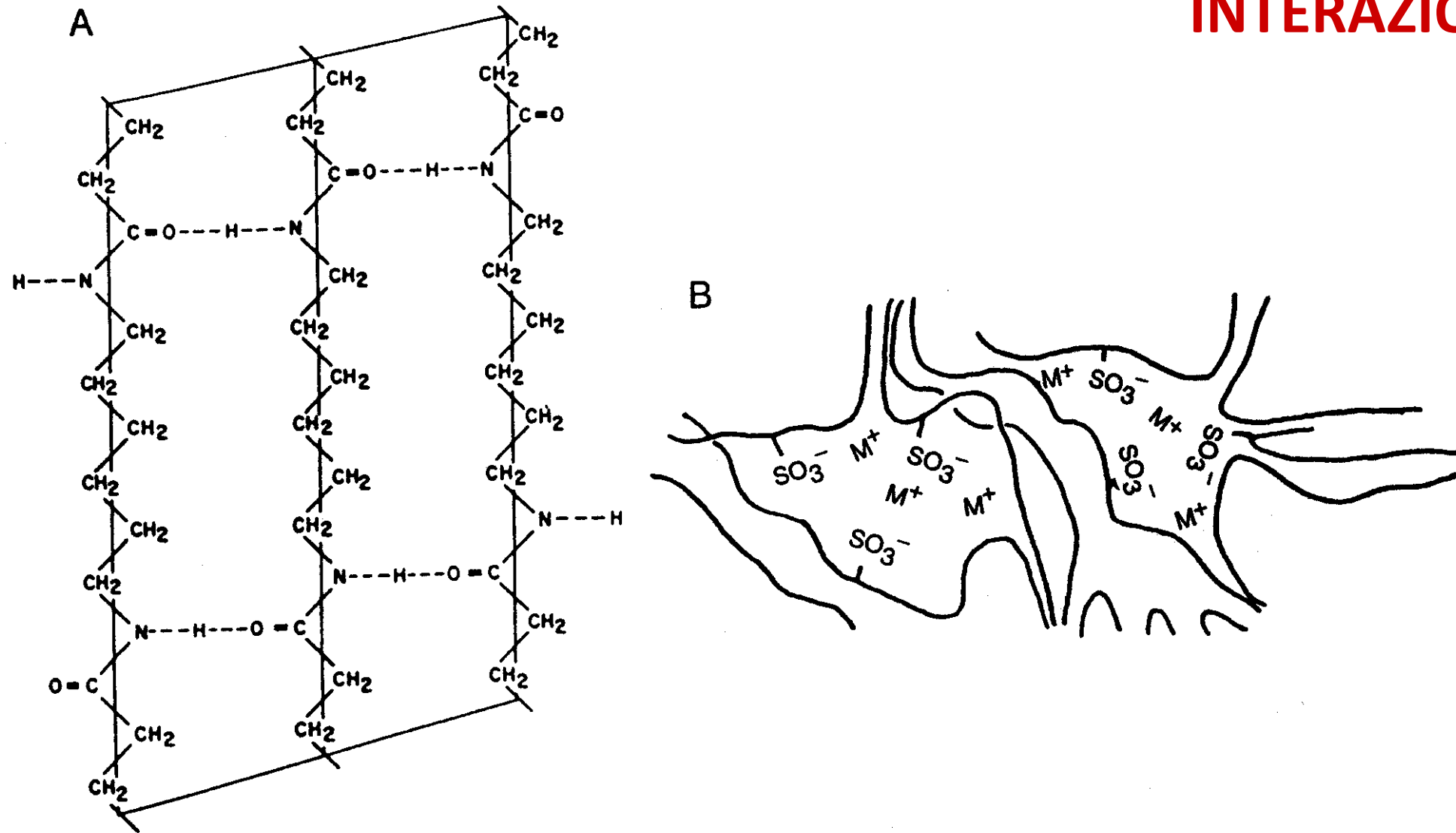
$$T_g = f(M, V_x, \dots)$$

TABLE 12.2. Glass transition temperatures for atactic polymers of the general type  $\text{-(CH}_2\text{-CXY)-}_n$

Polymer	$T_g/\text{K}$	$V_x/\text{cm}^3 \text{mol}^{-1}\dagger$	Group X
<i>Type <math>\text{-(CH}_2\text{CHX)-}_n</math></i>			
polyethylene	188	3.7	—H
polypropylene	253	25.9	—CH <sub>3</sub>
poly(but-1-ene)	249	48.1	—C <sub>2</sub> H <sub>5</sub>
poly(pent-1-ene)	233	70.3	—C <sub>3</sub> H <sub>7</sub>
poly(hex-1-ene)	223	92.5	—C <sub>4</sub> H <sub>9</sub>
poly(4-methyl pent-1-ene)	302	92.5	—CH <sub>2</sub> —CH(CH <sub>3</sub> ) <sub>2</sub>
poly(vinyl alcohol)	358	11.1	—OH
poly(vinyl chloride)	354	22.1	—Cl
polyacrylonitrile	378	30.0	—CN
poly(vinyl acetate)	301	60.1	—O—C—CH <sub>3</sub>    O
poly(methyl acrylate)	279	60.1	—C—O—CH <sub>3</sub>    O
poly(ethyl acrylate)	249	82.3	—COOC <sub>2</sub> H <sub>5</sub>
poly(propyl acrylate)	225	104.5	—COOC <sub>3</sub> H <sub>7</sub>
poly(butyl acrylate)	218	126.7	—COOC <sub>4</sub> H <sub>9</sub>
polystyrene	373	92.3	
poly( $\alpha$ -vinyl naphthalene)	408	143.9	
poly(vinyl biphenyl)	418	184.0	
<i>Type <math>\text{-(CH}_2\text{C(CH}_3\text{)X)-}_n</math></i>			
	$T_g/\text{K}$	$V(X+Y)\text{cm}^3 \text{mol}^{-1}\dagger$	
poly(methyl methacrylate)	378	86.0	
poly(ethyl methacrylate)	338	108.2	
poly(propyl methacrylate)	308	130.4	
polymethacrylonitrile	393	55.9	
poly( $\alpha$ -methylstyrene)	445	118.2	

<sup>†</sup>Calculated using LeBas volume equivalents. (See Glasstone "Textbook of Physical Chemistry" Macmillan, 1951, Chapter 8.)

# INTERAZIONI



**FIG. 4.** (A) Hydrogen bonding in nylon 6,6 molecules in a triclinic unit cell:  $\sigma$ -form. (From L. Mandelkern, *An Introduction to Macromolecules*, Springer-Verlag, 1983, p. 43, with permission.) (B) Ionic aggregation giving rise to physical cross-links in ionomers.



**Tg dipende anche da fattori cinetici  
es. velocità di raffreddamento**

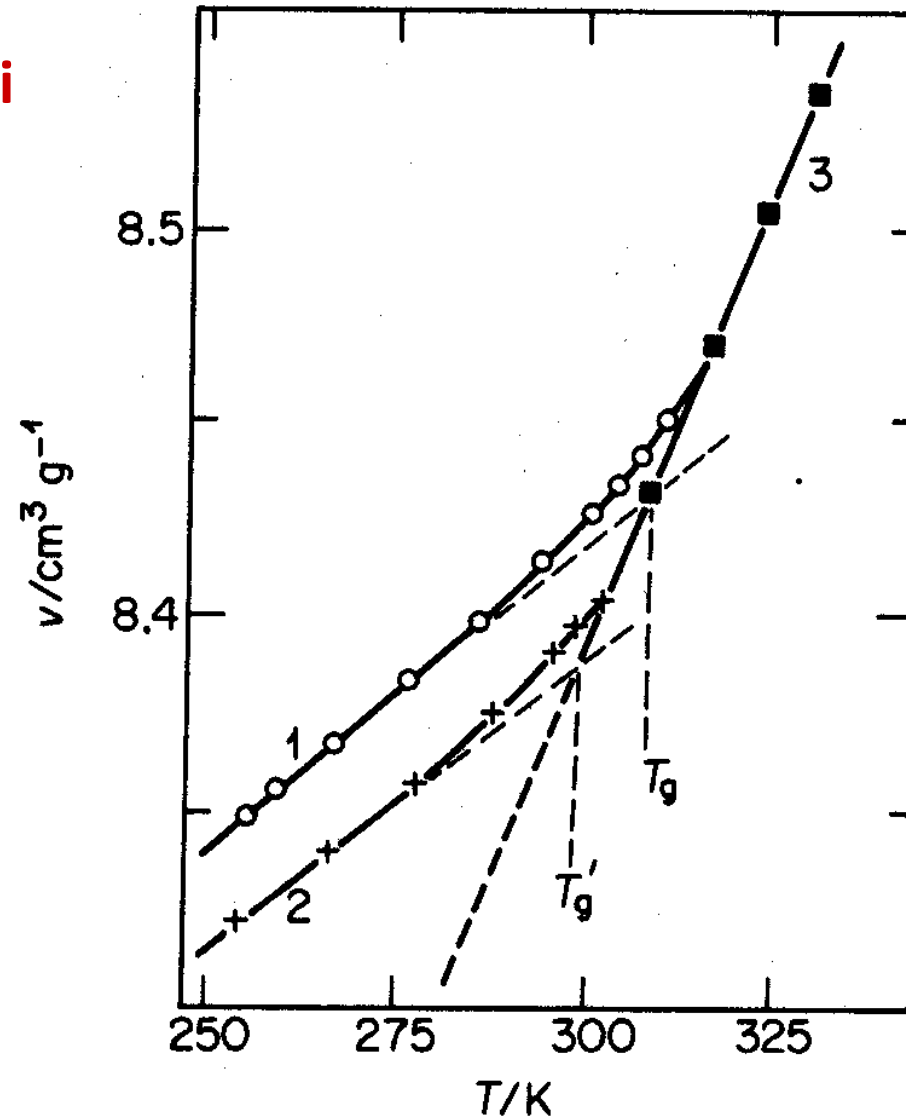


FIGURE 12.8. Specific volume  $v$  plotted against temperature for poly(vinyl acetate) measured after rapid cooling from above the  $T_g$ ; 1, measured 0.02 hour after cooling; 2, measured 100 hours after cooling;  $T_g$  and  $T'_g$  are the glass transition temperatures measured for the different equilibration times. (After Kovacs, 1958.)

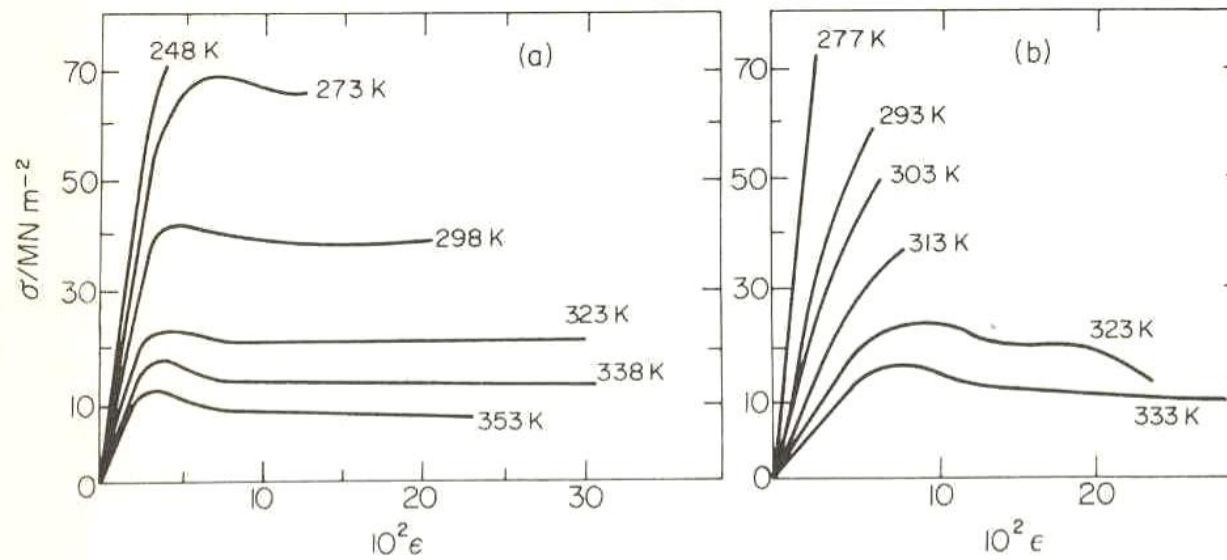


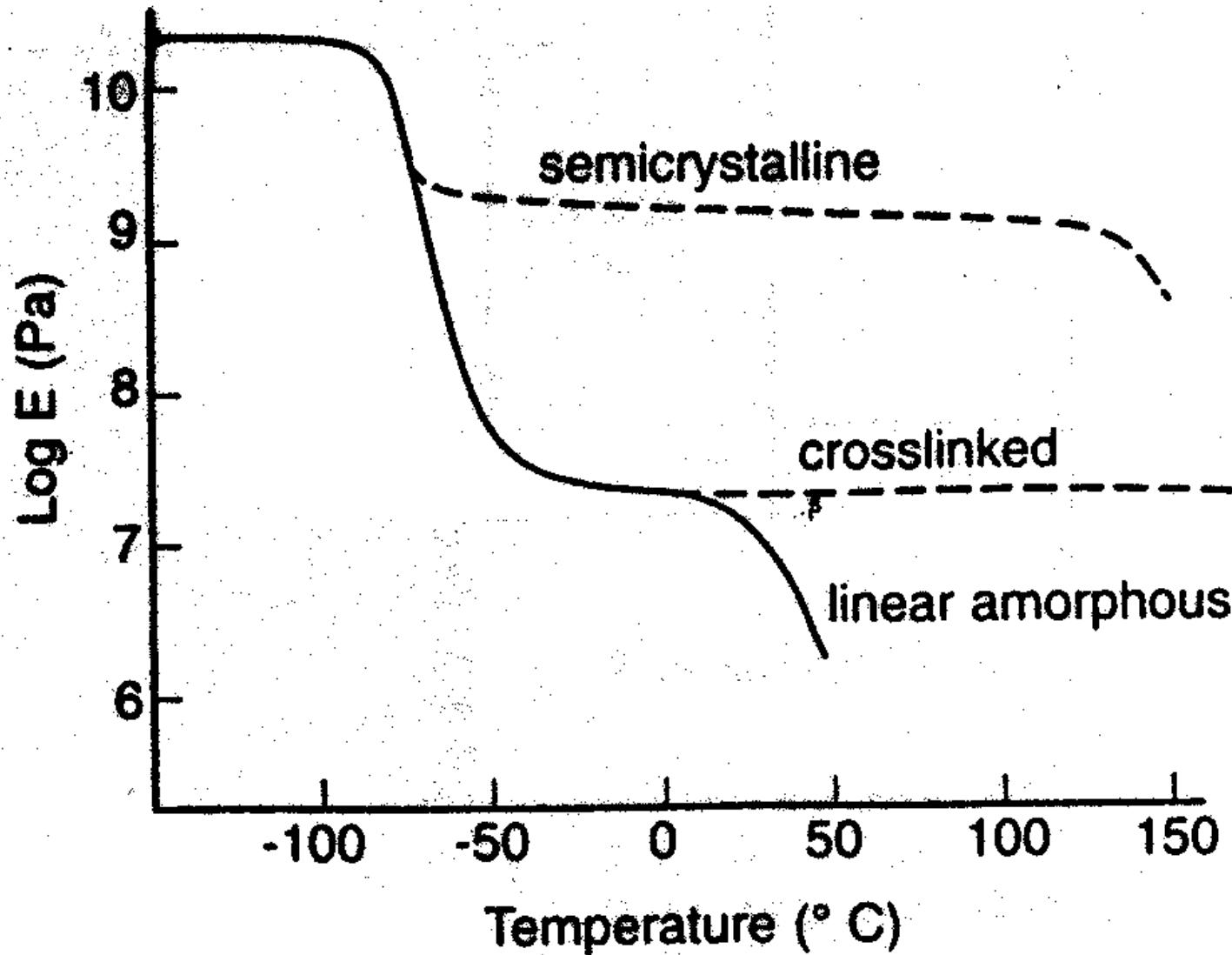
FIGURE 13.7. Influence of temperature on the stress-strain response of (a) cellulose acetate and (b) poly(methyl methacrylate). (From data by Carswell and Nason.)

#### EFFECT OF TEMPERATURE ON STRESS-STRAIN RESPONSE

Polymers such as polystyrene and poly(methyl methacrylate) with a high  $E$  at ambient temperatures fall into the category of hard brittle materials which break before point Y is reached. Hard tough polymers can be typified by cellulose acetate and several curves measured at different temperatures are shown in figure 13.7(a). Stress-strain curves for poly(methyl methacrylate) are also shown for comparison (figure 13.7(b)).

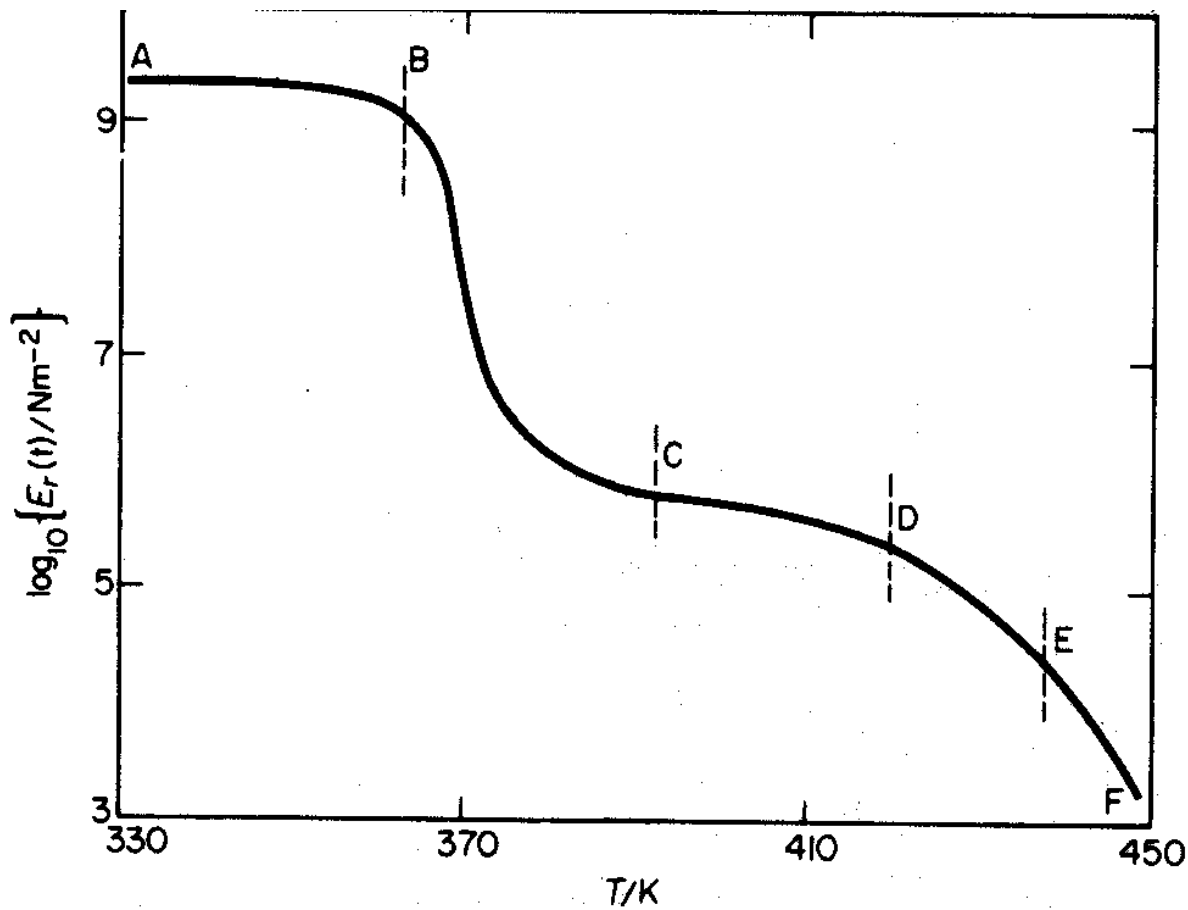
It can be seen that the effect of temperature on the characteristic shape of the curve is significant. As the temperature increases both the rigidity and the yield strength decrease while the elongation generally increases. For cellulose acetate there is a transformation from a hard brittle state below 273 K to a softer but tougher type of polymer at temperatures above 273 K. For poly(methyl methacrylate) the hard brittle characteristics are retained to a much higher temperature, but it eventually reaches a soft tough state at about 320 K. Thus if the requirements of high rigidity and toughness are to be met, the temperature is important. Cellulose acetate meets these requirements if used at 298 K more satisfactorily than when used at 350 K where the modulus is smaller and the ability to absorb energy, represented by the area under the curve, is also lower.

## Comportamento in funzione della temperatura



IL PLATEAU, NEL CASO DEI POLIMERI CRISTALLINI, È MOLTO PIÙ LARGO E AD ALTO MODULO, PER L'AZIONE DI RINFORZO DEI CRISTALLITI

**FIG. 8.** Dynamic mechanical behavior of polymers.



PS, amorfo

FIGURE 12.1. Five regions of viscoelasticity, illustrated using a polystyrene sample. Also shown are the strain–time curves for stress applied at  $x$  and removed at  $y$ : (a) glassy region; (b) leathery state; (c) rubbery state; and (d) viscous state.

stato vetroso (amorfo)

leathery

rubbery

rubbery flow (liquido viscoso)

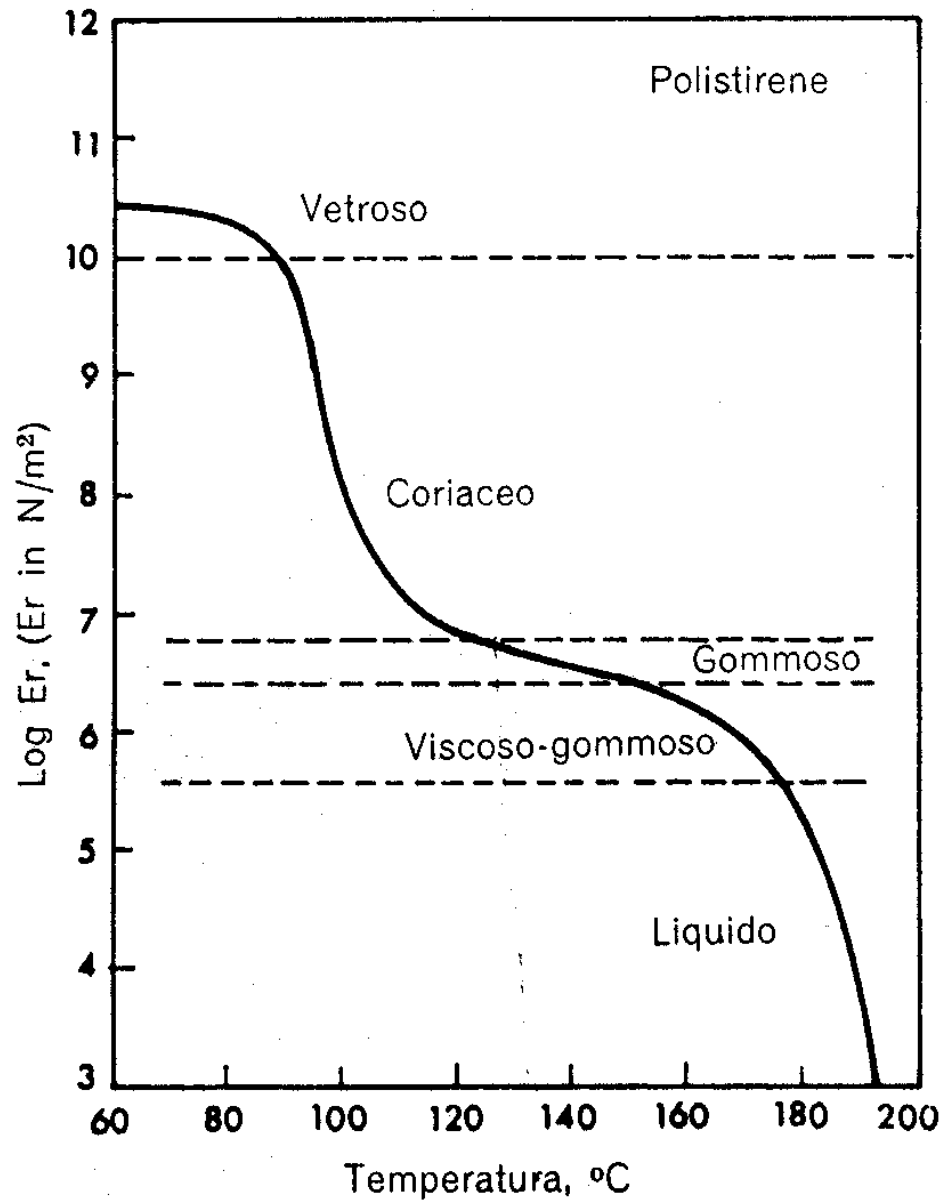
(A-B) le catene sono “congelate”, il materiale non si deforma e ha comportamento elastico

(B-C) le catene hanno abbastanza energia per iniziare a muoversi.  $T_g$  è in questo intervallo

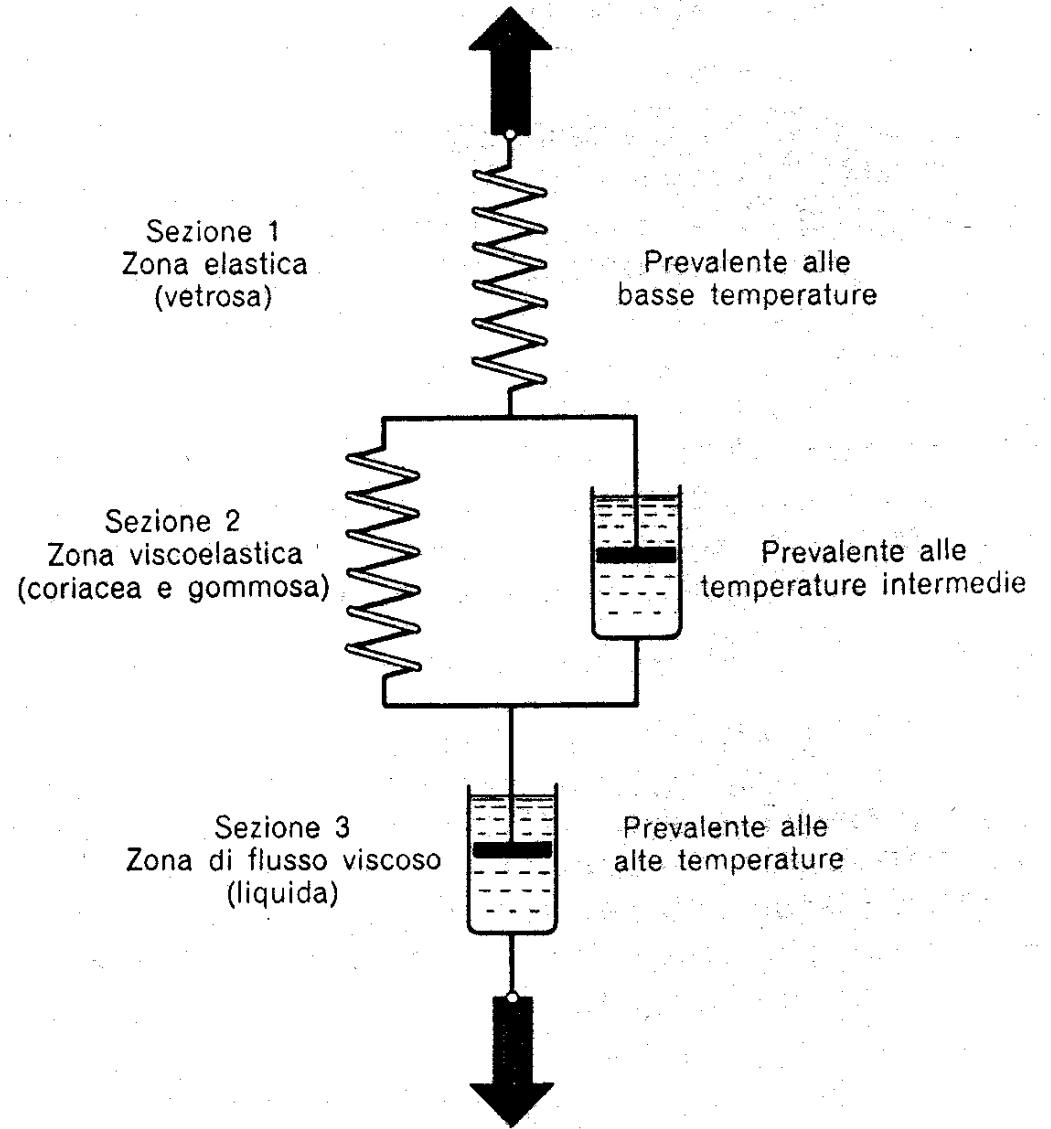
(C-D-E) il modulo  $f(T)$  va a plateau

(E-F) regime di flusso





modulo elastico  $E_f(T)$ , e le cinque zone di comportamento viscoelastico



analogia meccanica del comportamento viscoelastico dei polimeri

# **ANALISI TERMICA**

**DTA    Differential Thermal Analysis**

**DSC    Differential Scanning Calorimetry**

**TGA    Thermal Gravimetric Analysis**

**TMA    Thermal Mechanical Analysis**

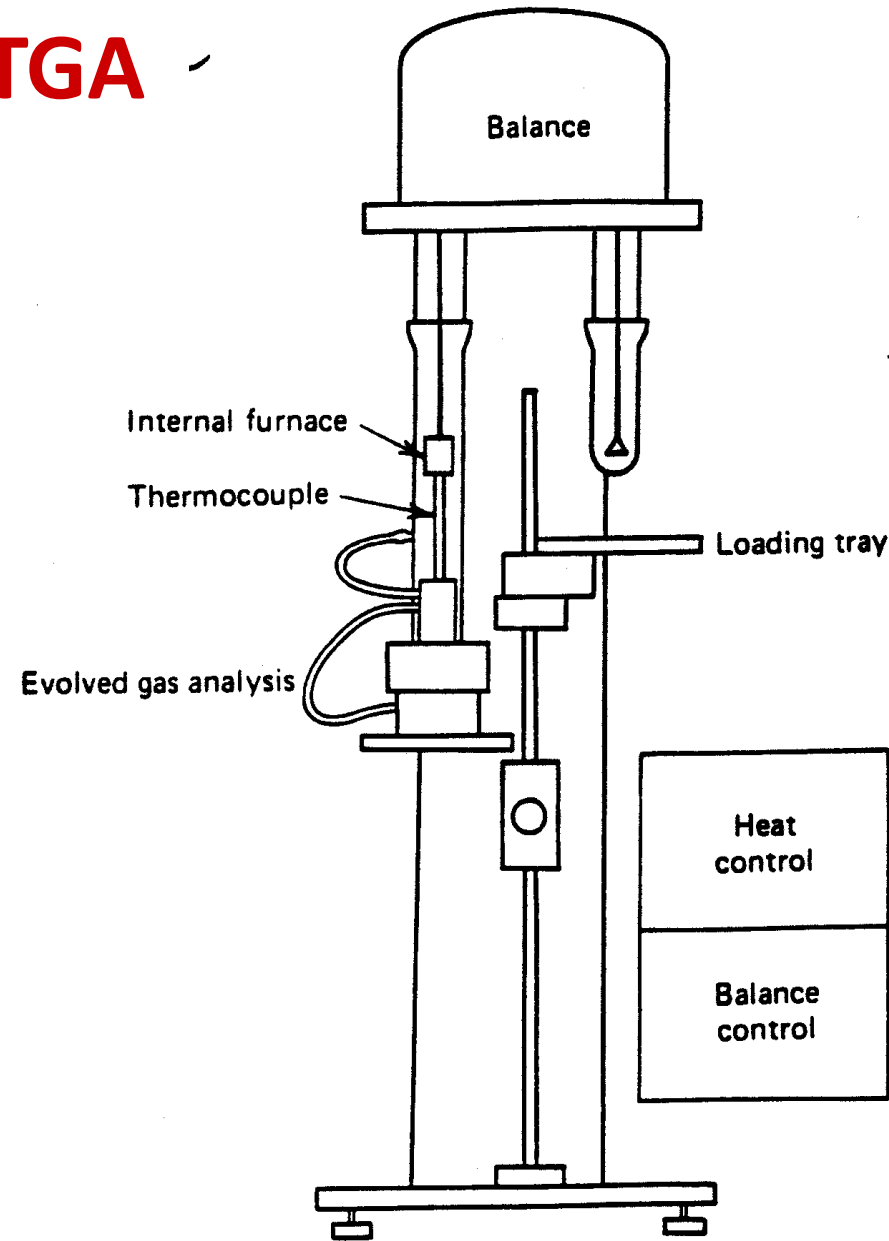
**TEA    Thermal Evolution Analysis**

**TOA    Thermal Optical Analysis**

**TBA    Torsional Braid Analysis**

**GC,MS applicate ai prodotti di decomposizione termica**

**TGA**



**Figure 5.20** Thermogravimetric analyzer, Perkin-Elmer TGS-2.

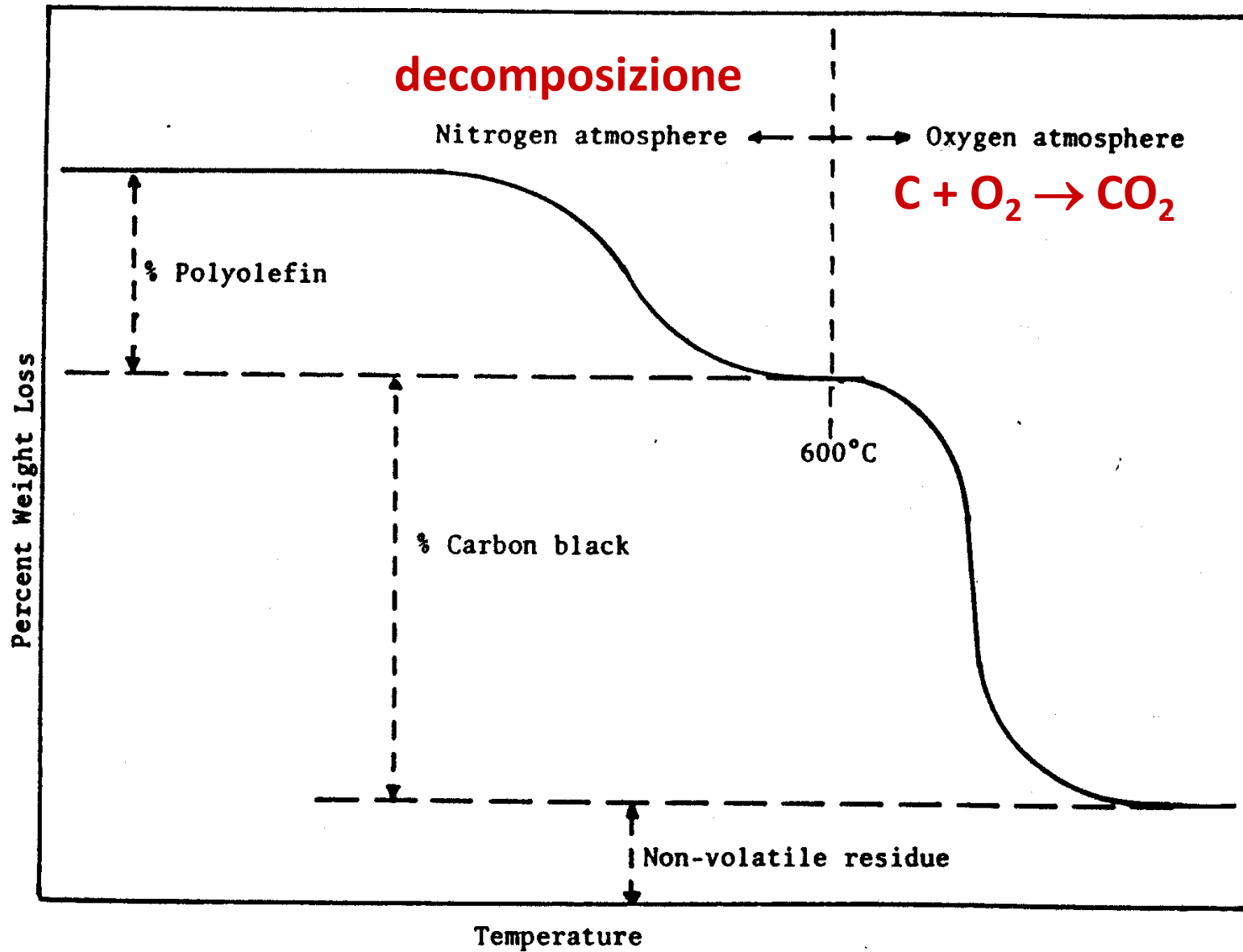
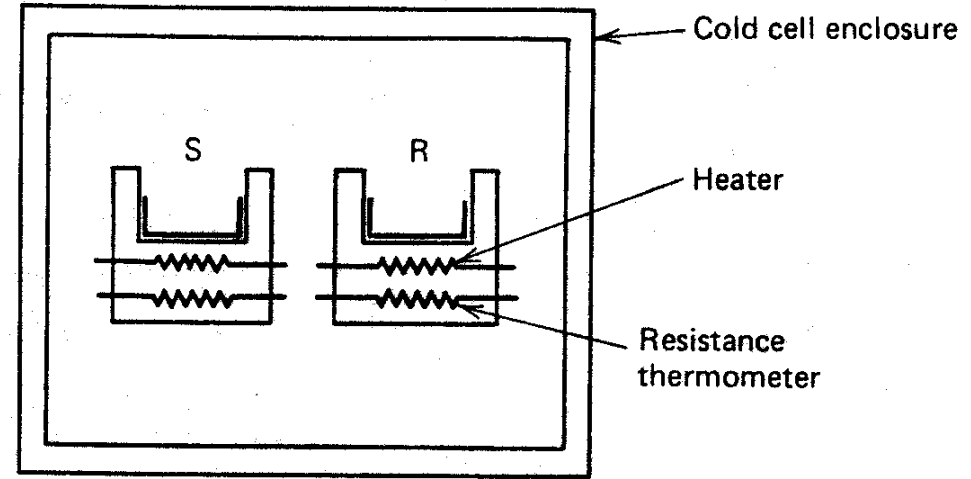


Figure 5.13 Thermogravimetric curve of carbon-filled polyolefin.

**Thermal analysis** When a substance undergoes a physical or chemical change, a corresponding change in enthalpy  $\Delta H$  is observed. In Differential Thermal Analysis, DTA, the change is detected by measuring the enthalpy difference between the material under study and an inert standard. The sample is placed in a heating block and warmed at a uniform rate. The sample temperature  $T_s$  is monitored and compared with that of an inert reference (e.g., alumina powder or an empty sample pan)  $T_r$ , subjected to the same linear heating program. As the temperature of the block raises at constant rate (5-20 K/min)  $T_s$  and  $T_r$  will keep pace until a change in the sample occurs. **If the change is exothermic  $T_s$  exceeds  $T_r$  for a short time, if endothermic  $T_s$  temporarily lags behind.**  $\Delta T$  is recorded, changes due to melting or crystallization appear as peaks. Since the heat capacities of sample and reference are different,  $\Delta T$  is never actually zero, and a change in heat capacity, such as that due to a glass transition, cause a shift in the baseline. Changes for decomposition, crosslinking, and existence of polymorphic forms can also be detected. As  $\Delta T$  is a function of the thermal conductivity and bulk density of the sample, DTA is non quantitative and relatively uninformative. To overcome these drawbacks Differential Scanning Calorimetry (DSC) is used; instead of measuring  $\Delta T$ , in DSC during a change a servo-system immediately increases the energy input to sample or reference to maintain both at the same  $T$ . Thermograms obtained are similar to DTA, but actually represent the amount of electrical energy supplied to the system, so the areas under the peaks are proportional to the occurred  $\Delta H$ . Calibration allow the heat capacity of a sample to be calculated quantitatively. This information is additional to that gained on crystallization, melting, glass transitions, and decompositions.

# DSC

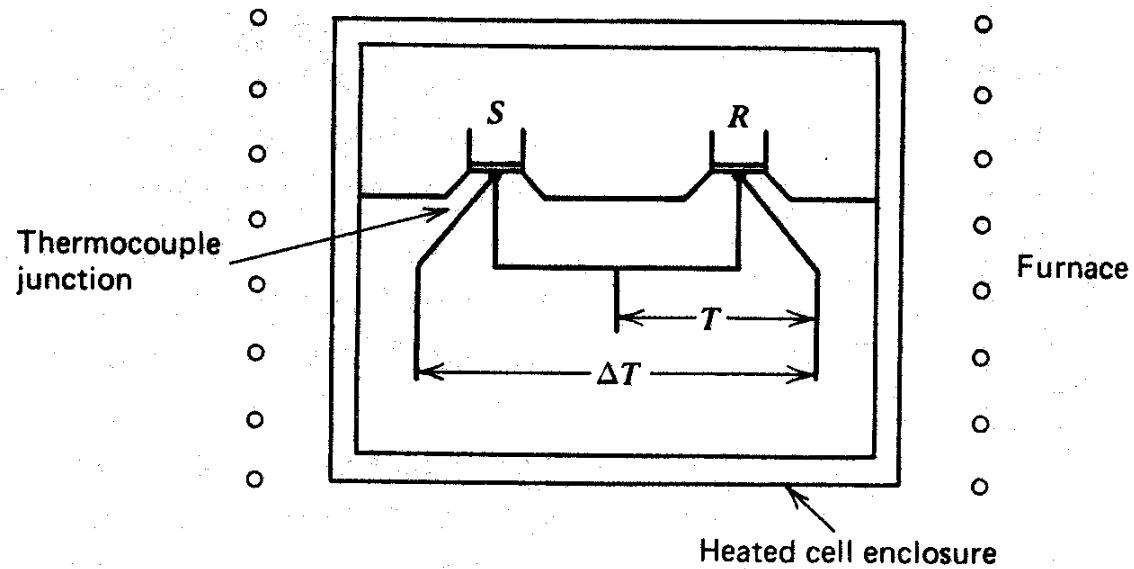
Lavora compensando elettronicamente le variazioni di calore nel campione rispetto ad un riferimento. Entrambi sono mantenuti alla stessa  $T$ .



(a)

# DTA

Misura la differenza di temperatura tra il campione ed un riferimento inerte (calorimetria)



(b)

Figure 5.19 Design of DSC and calorimetric DTA cells. (a) DSC cell; (b) calorimetric DTA cell.

$\Delta H < 0$

$\Delta H > 0$

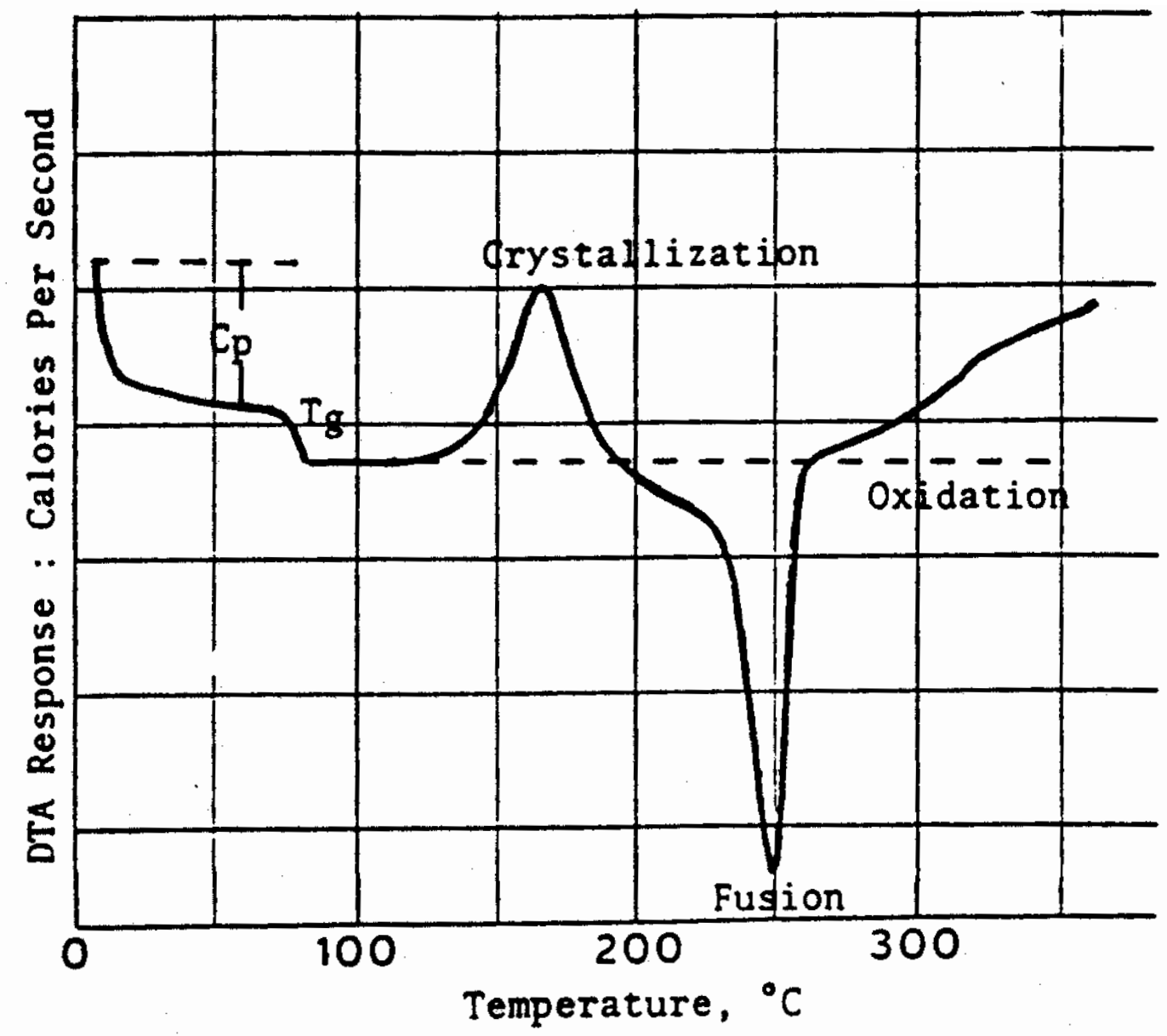
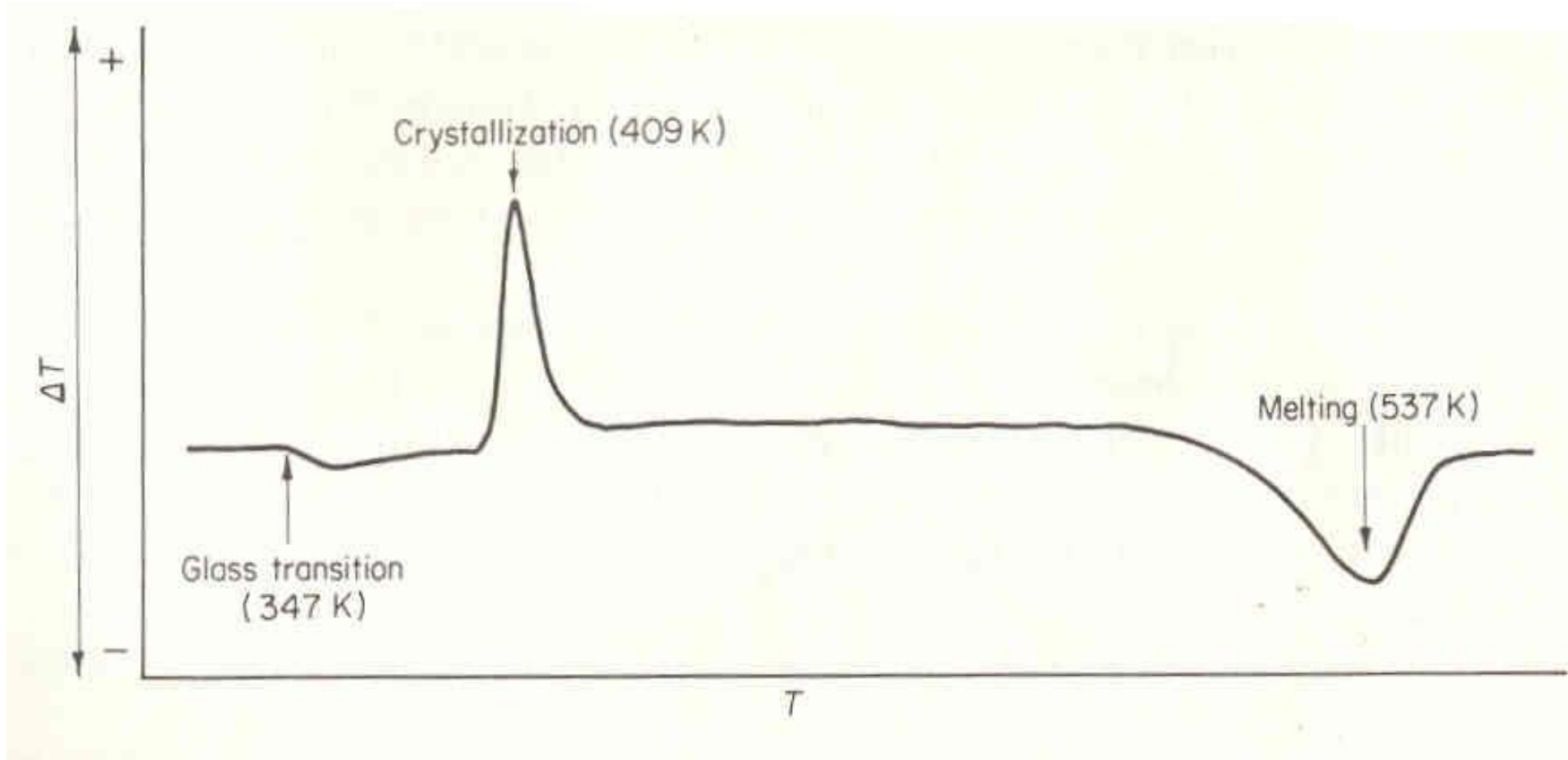
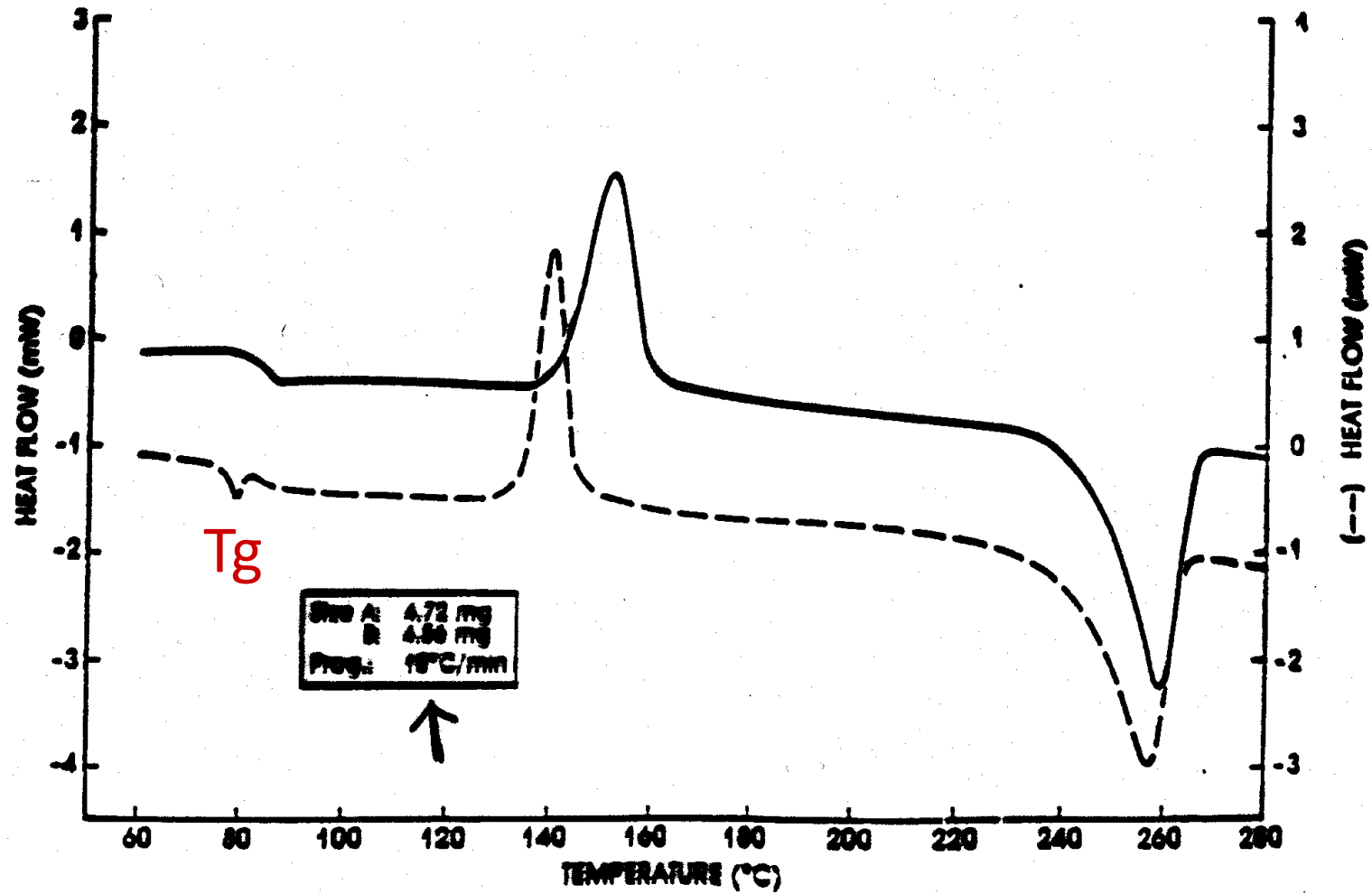


Figure 5.18 DTA curve of quenched poly (ethylene terephthalate).



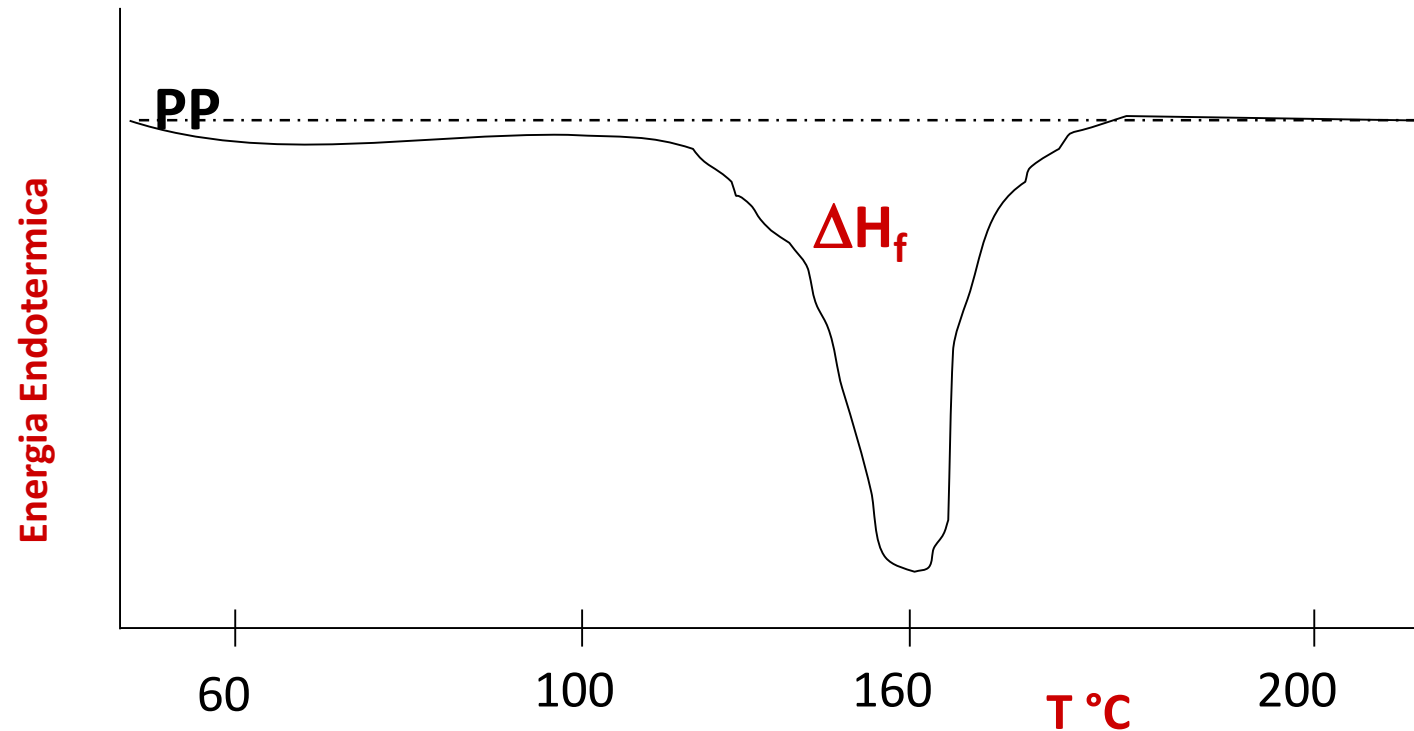
A DTA curve for quenched terylene showing the glass transition, melting endotherm, and a crystallization exotherm peak





Dual sample DSC used to study the influence of thermal history on transitions in aged/unaged amorphous PET

## GRADO DI CRISTALLINITÀ

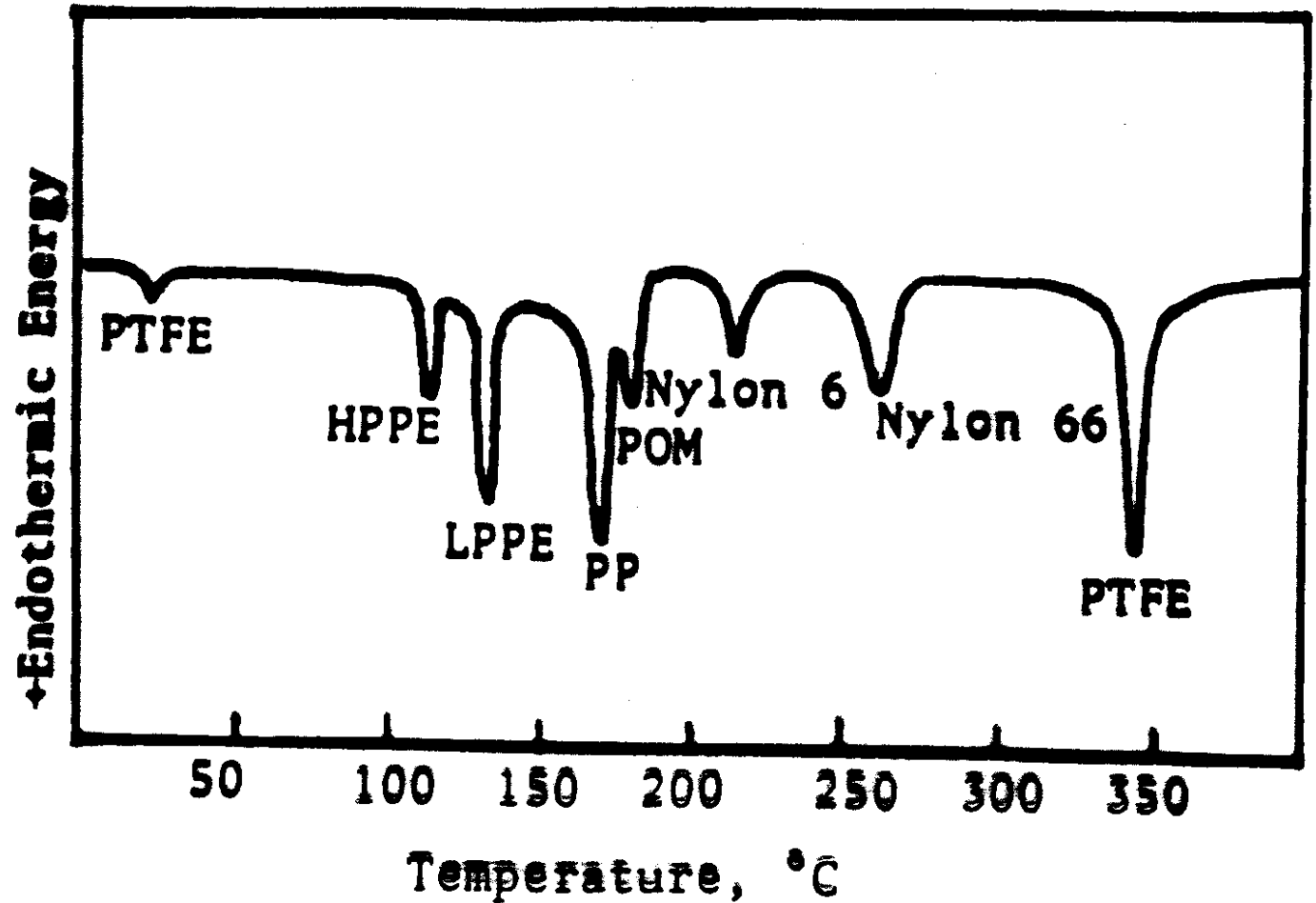


la scansione in temperatura (DSC ) viene effettuata lungo l'intervallo di fusione. L'area del picco endotermico di fusione è approssimativamente pari al  $\Delta H_f$ .

La % di cristallinità si ottiene per confronto con i dati ottenuti su un polimero cristallino al 100%

$$\% \text{ cristallinità} = \frac{\Delta H_f}{\Delta H_{\mu}} \times 100$$

## Analisi DTA qualitativa di una miscela di polimeri



DTA melt curve of polymer mixture:

High-pressure polyethylene (HPPE); Low-pressure polyethylene (LPPE)

Polypropylene (PP); Polyoxymethylene (POM)

Nylon 6; Nylon 66; Polytetrafluoroethylene (PTFE)

# DIFFRAZIONE

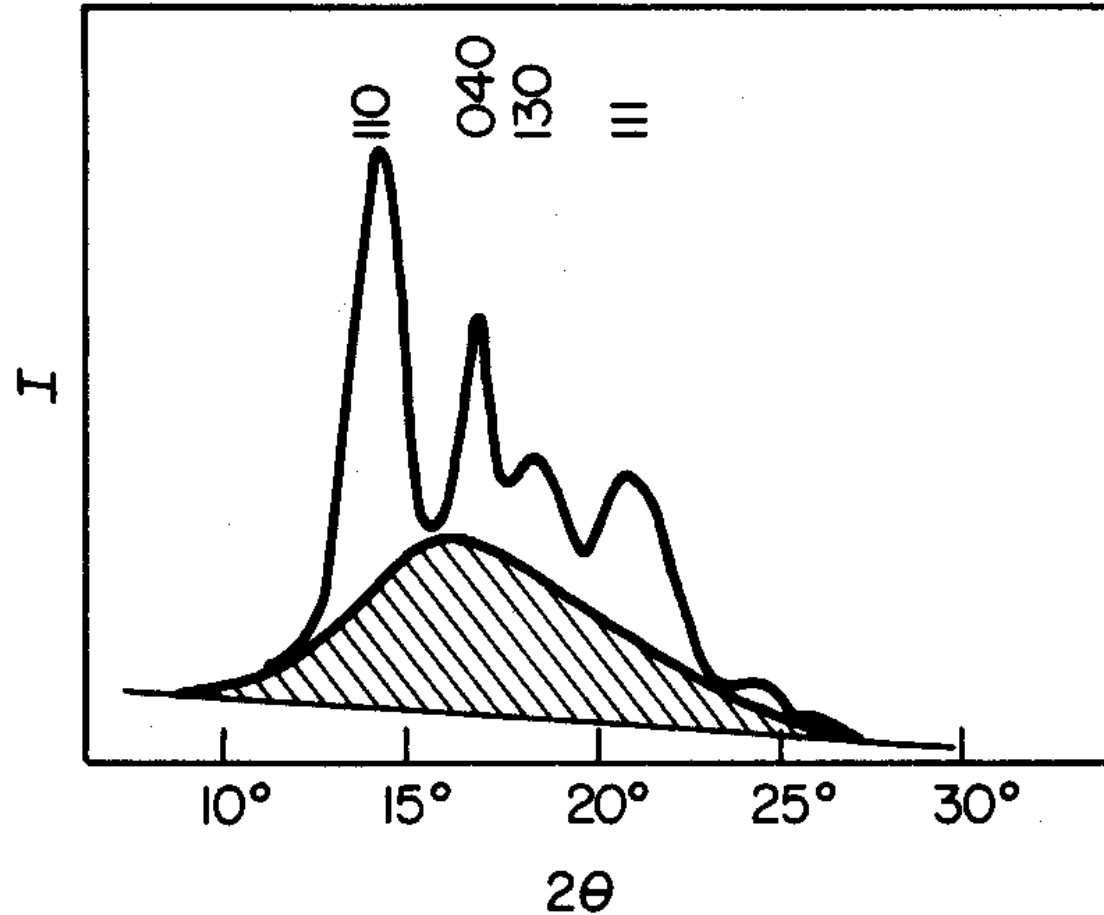
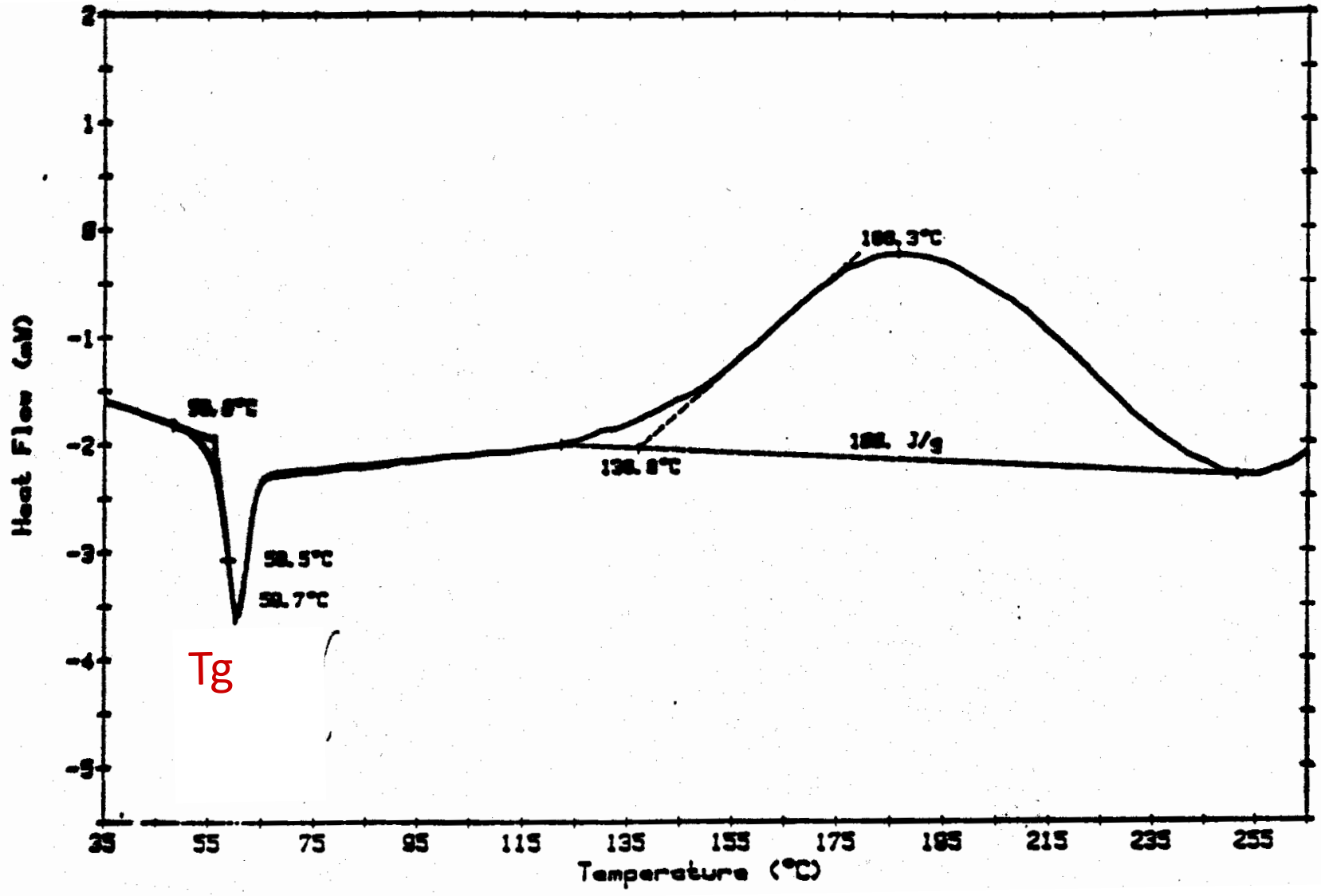


FIGURE 10.6. X-ray diffraction curves; the intensity  $I$  as a function of angle for totally amorphous polypropylene (shaded area), and for a sample with a 50 per cent crystalline content.



DSC data from an epoxy thermosetting resin illustrating cure profile

I polimeri cristallini modificano il piano della luce polarizzata a causa dell'anisotropia dell'indice di rifrazione rispetto all'asse del cristallo. I passaggi di stato possono essere studiati con il variare della luce polarizzata.

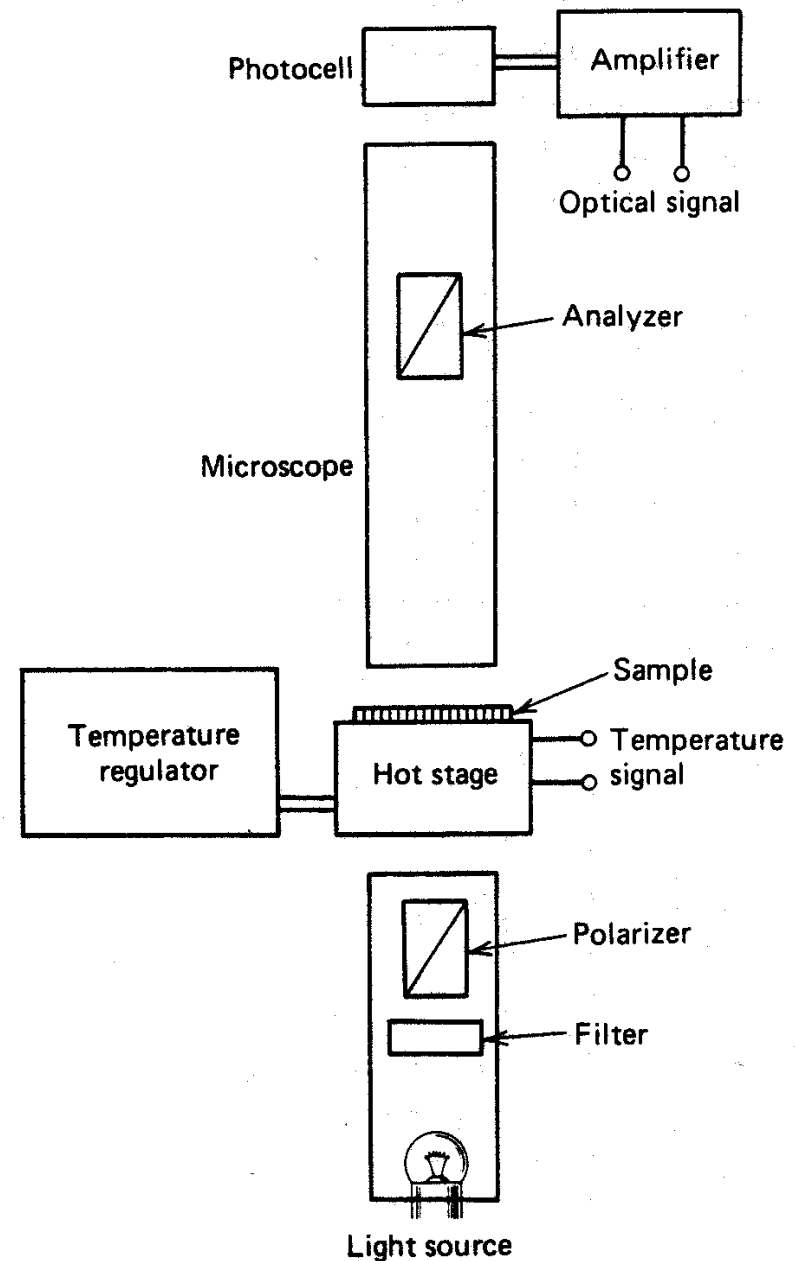


Figure 5.23 Apparatus for thermal optical analysis.