

# Polymers in solid state

## 1. The amorphous state

# Amorphous state

1. Glass transition
2. Equilibrium and glassy state: physical aging
3. Glass transition theories
4. Effect of molecular parameters on the glass transition temperature,  $T_g$ .
5. Modification of  $T_g$ .
6. Methods to determine  $T_g$ .

# Polymer classification

- Physical state
  - *(semi)crystalline*
  - *amorphous*
- Reaction to environment
  - *Thermoplastic*
  - *Thermoset/termoedurecíveis (PTFE, bakelite)*
- Industrial polymers
  - *Plastics*
  - *Fibers*
  - *Rubbers (elastomers)*
  - *Adhesives (tintas e vernizes)*
  - *Coatings/revestimentos*

# Specific volume low MW materials

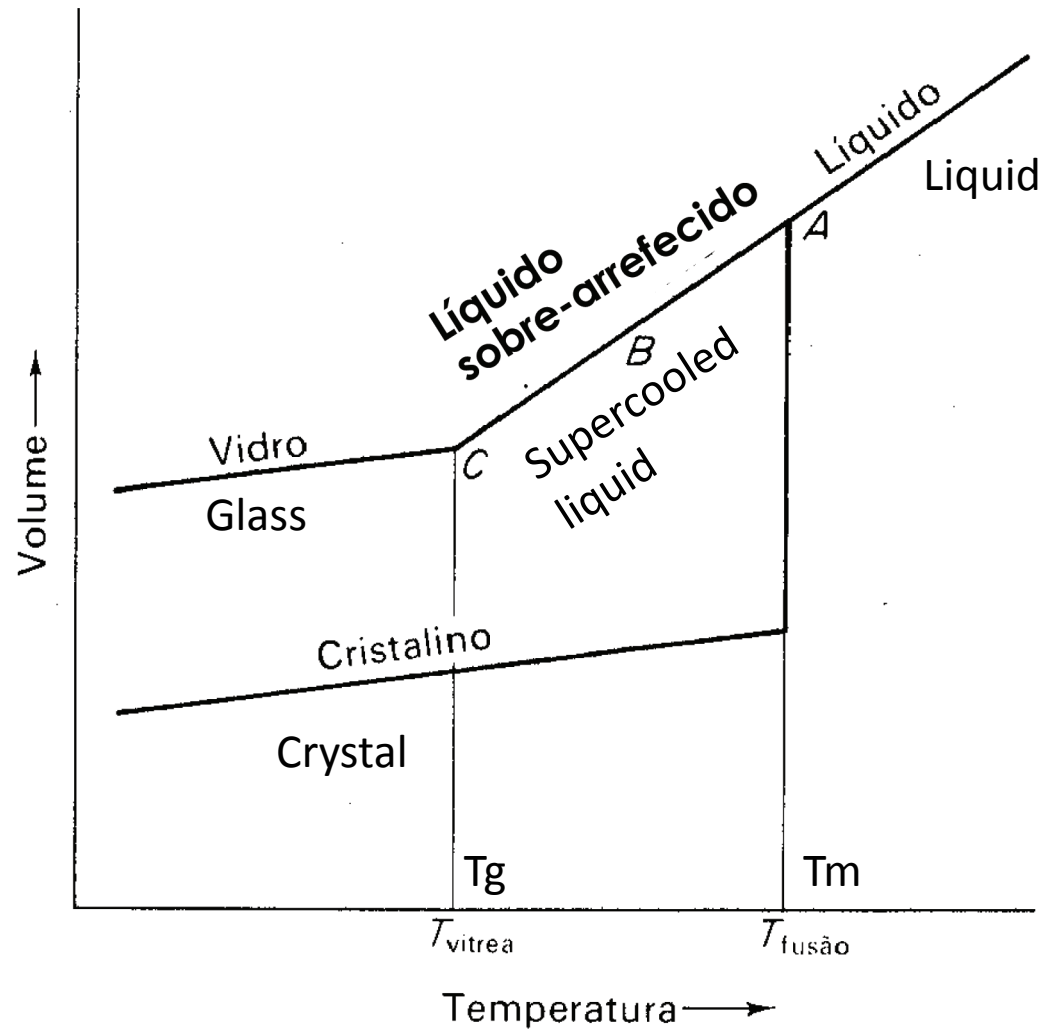


Fig. 1.5-1. Curvas volume-temperatura para glicerina (esquemáticos).

# Specific volume\_polymers

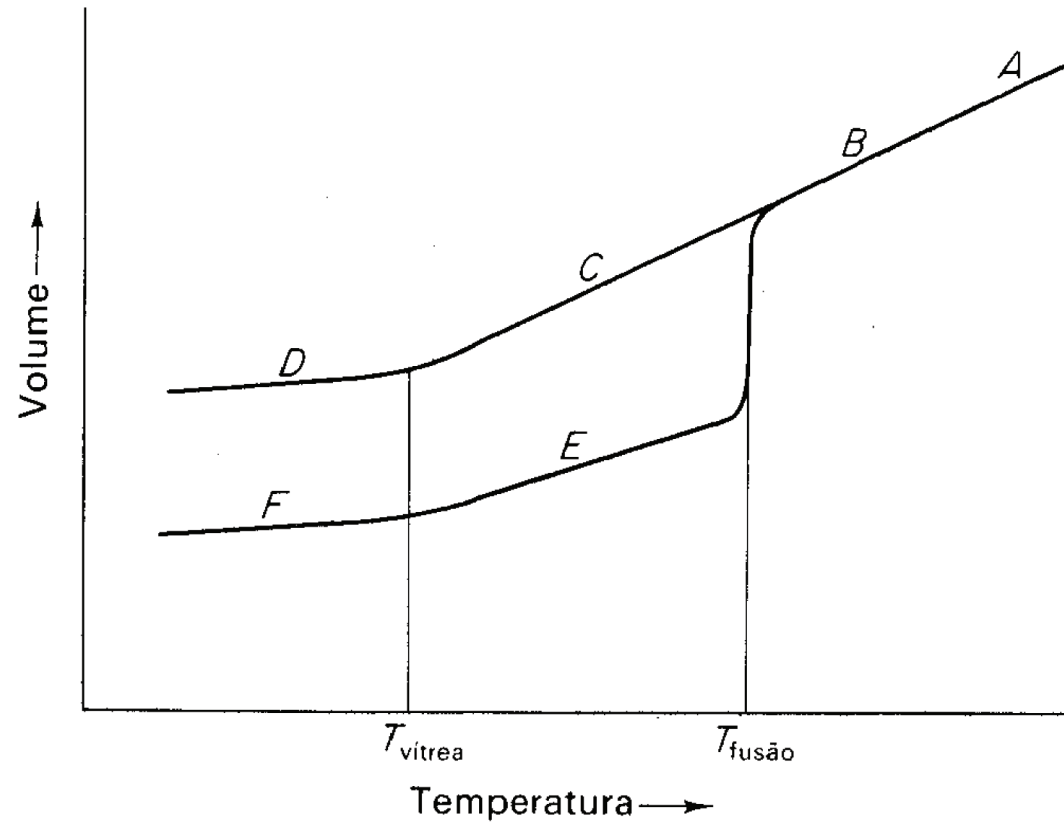
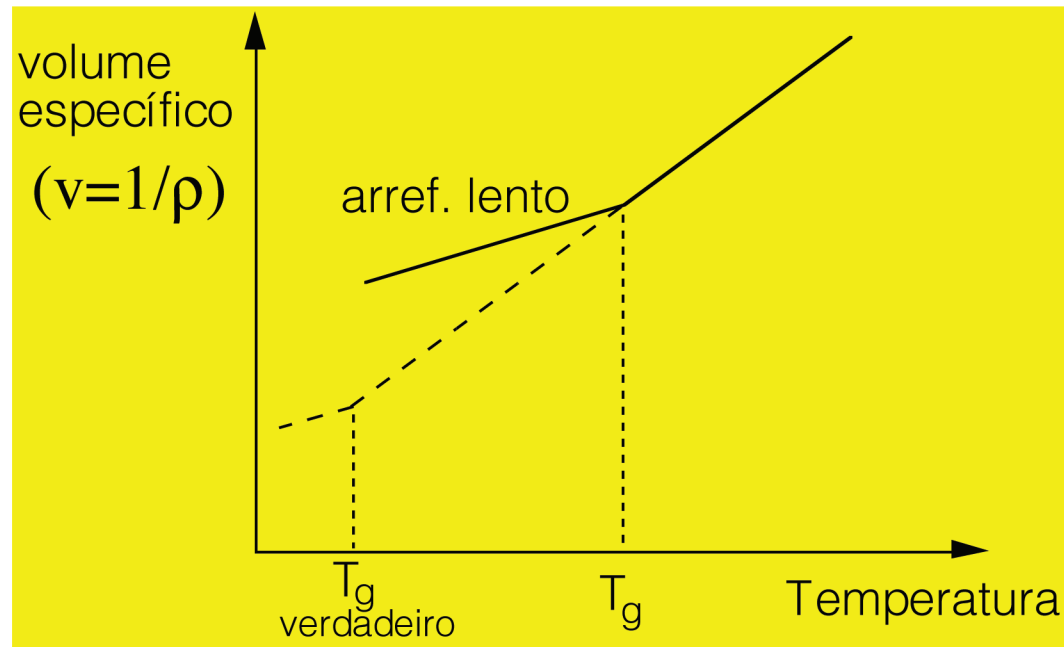


Fig. 1.5-2. Curvas volume-temperatura para um polímero cristalino. (A) Região de líquido. (B) Líquidos com alguma resposta elástica. (C) Região de materiais elastoméricos. (D) Região vítrea. (E) Cristalitos em uma matriz de características de borracha. (F) Cristalitos em uma matriz vítrea.

Cooling from the melt → glassy solid:

.Fast cooling (quenching)

.Unable to crystallize



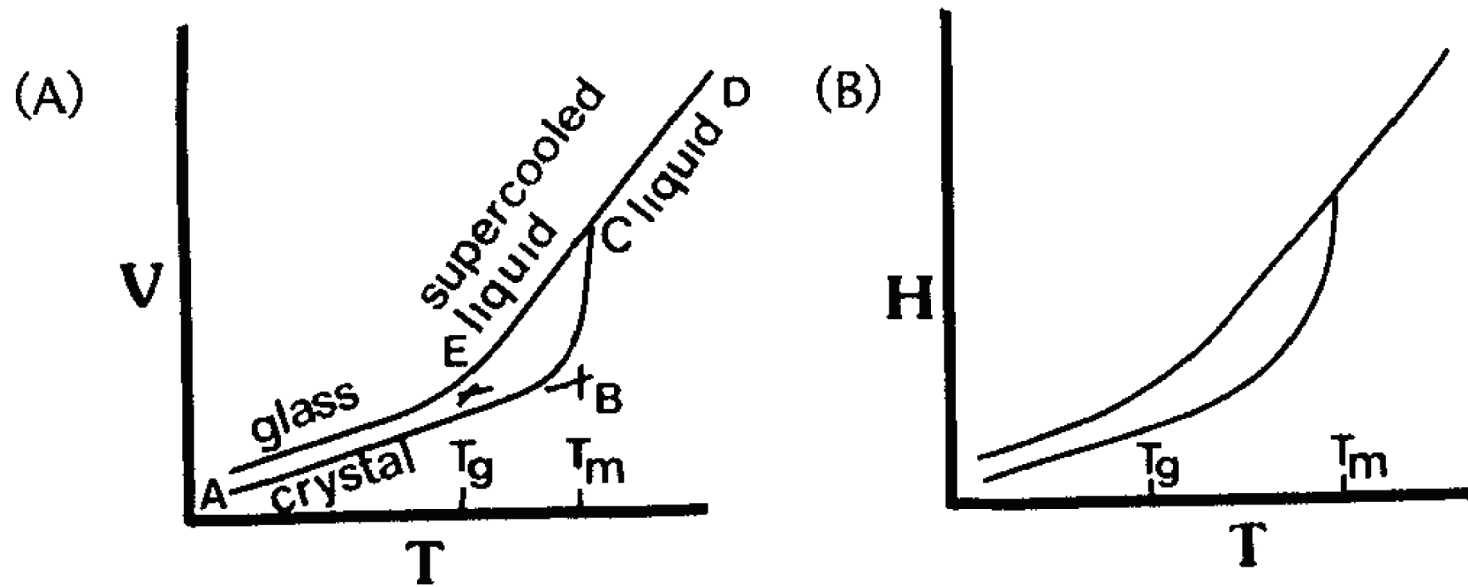
*$\Delta T_g \approx 3^\circ C$  por  
ordem de  
grandeza da  
variação da  
velocidade de  
arrefecimento*

*Por arrefecimento - perda e por fim impedimento das rotações em torno das ligações simples.*

*Moléculas retidas num estado desordenado - **vidro***

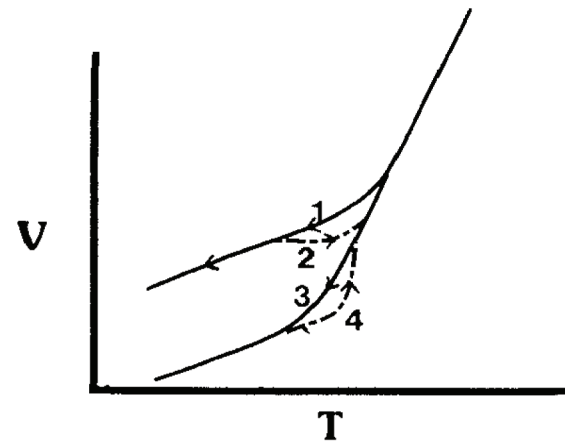
# Changes of thermodynamic properties at the glass transition

## Volume and enthalpy



# Changes of thermodynamic properties at the glass transition

## Hysteresis effects



Heating/cooling  
rates  
**velocidades de  
aquec/arref:**

$$v_1 > v_2$$

$$v_3 \ll v_1$$

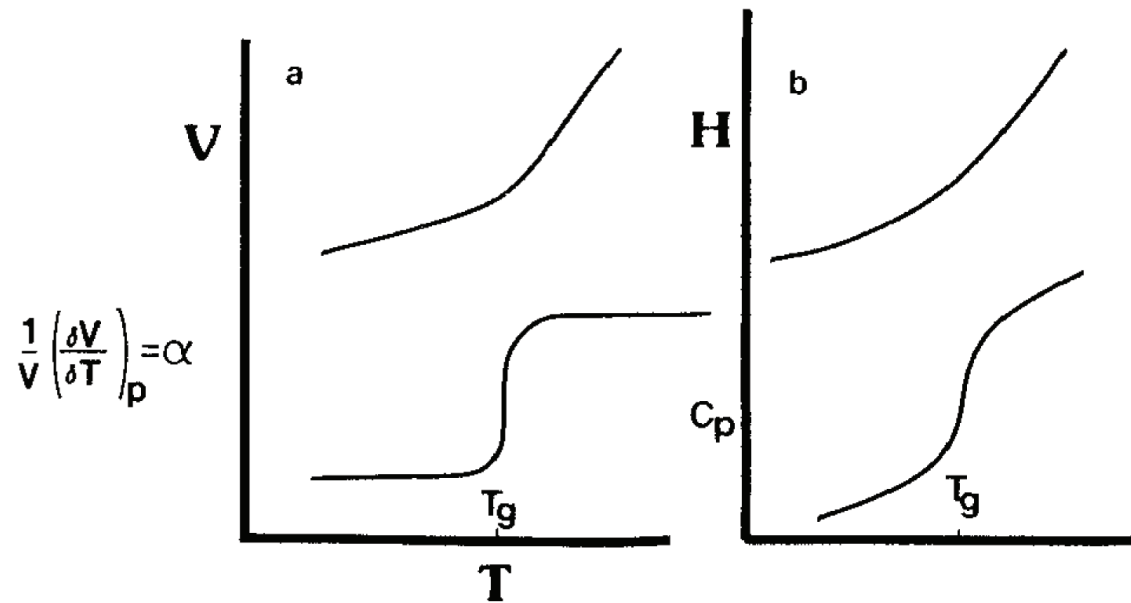
$$v_3 < v_4$$

**FIGURE 4.** Hysteresis effects in volume–temperature plots near  $T_g$ . (Adapted from reference 19.)



# Changes of thermodynamic properties at the glass transition

## Expansion coefficient and heat capacity



**FIGURE 5.** Temperature dependence of (a) volume and expansion coefficient ( $\alpha$ ) and (b) enthalpy and heat capacity ( $C_p$ ) near  $T_g$ .

# Equilibrium and glassy state\_physical aging

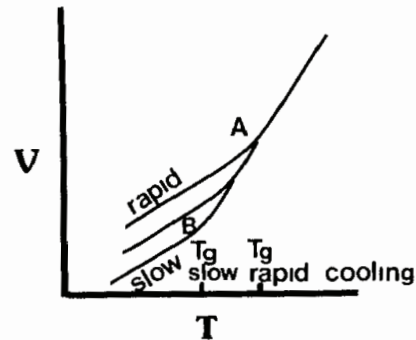


FIGURE 2. Volume-temperature behavior as a function of cooling rate.

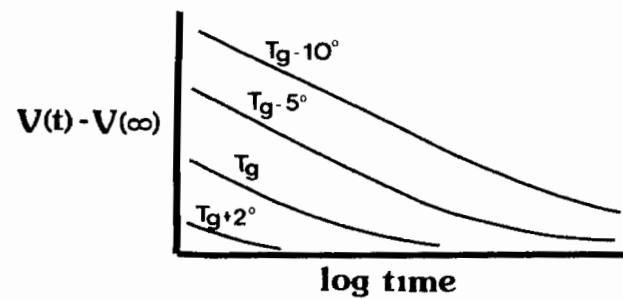


FIGURE 3. Isothermal volume contraction near the glass transition temperature. (Adapted from reference 5.)

Volume reduction over time: physical aging

# Changes of mechanical properties at the glass transition

## Viscosity

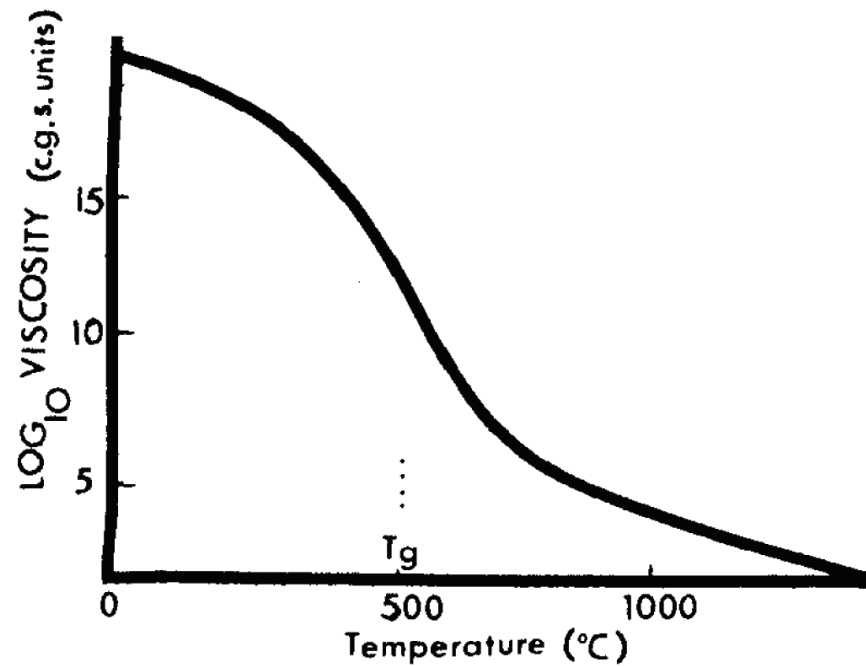
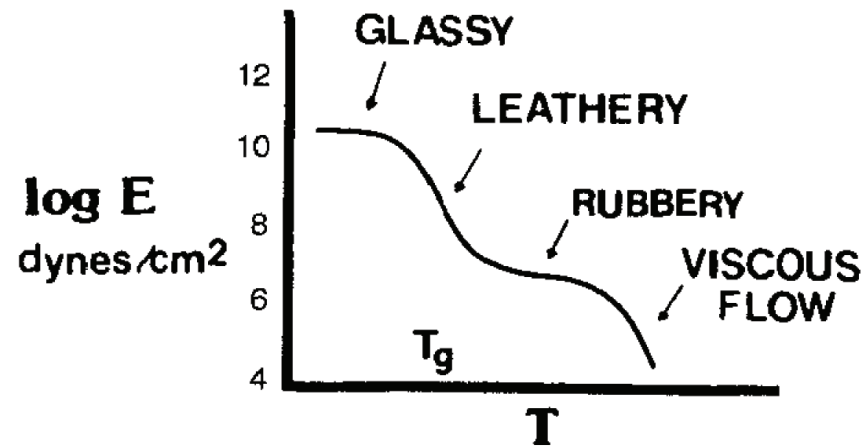


FIGURE 6. Viscosity–temperature plot for a soda–lime–silica glass. (Reproduced with permission from reference 19. Copyright 1956 Methuen.)

Viscosity at T<sub>g</sub> (for many non-crystalline materials) is  $\approx 10^{13}$  poise

# Changes of mechanical properties at the glass transition

## Modulus



**FIGURE 7.** Modulus–temperature plot for a typical linear polymer. (Adapted from reference 20.)

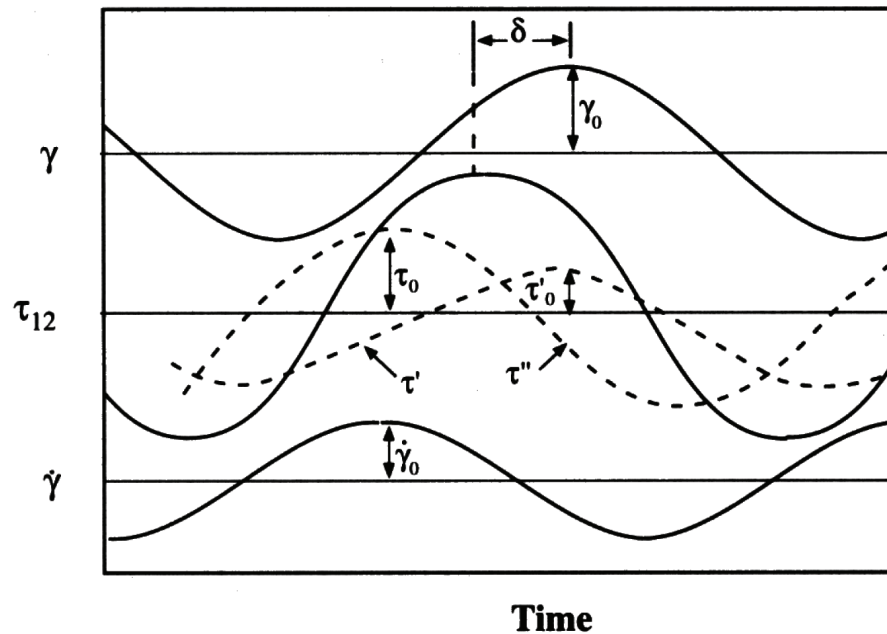
Between  $T_g - 20^\circ\text{C}$  and  $T_g + 30^\circ\text{C}$ , the modulus decreases by three orders of magnitude. For organic polymers without or with low density of cross-links,  $E(T_g) \approx 10^9$  dynes/cm<sup>2</sup>.

# Changes of mechanical properties at the glass transition

## Loss tangent (energy dissipation)

Deformação oscilatória sinusoidal:  $\varepsilon = \gamma = \gamma_0 \text{sen}(\omega t)$  strain

Tensão desfasada de  $\delta$ :  $\sigma = \sigma_0 \text{sen}(\omega t + \delta)$  stress



# Changes of mechanical properties at the glass transition

Expressing  $\sigma$  as a “in phase” ( $\sigma'$ ) plus an “out of phase” ( $\sigma''$ ) components

$$\sigma = \sigma' + \sigma'' = \sigma'_0 \sin(\omega t) + \sigma''_0 \cos(\omega t)$$

$$\tan \delta = \sigma''_0 / \sigma'_0$$

$$E' = \sigma'_0 / \gamma_0; \quad E'' = \sigma''_0 / \gamma_0$$

$E'(\omega)$  módulo de armazenamento ( em fase), módulo elástico  
storage modulus (in phase), elastic modulus

$E''(\omega)$  módulo de perda ( desfasado), módulo viscoso  
loss modulus (out of phase), viscous modulus

$$\tan \delta = \frac{E''}{E'} \quad \text{Loss tangent}$$

# Changes of mechanical properties at the glass transition

## Loss tangent

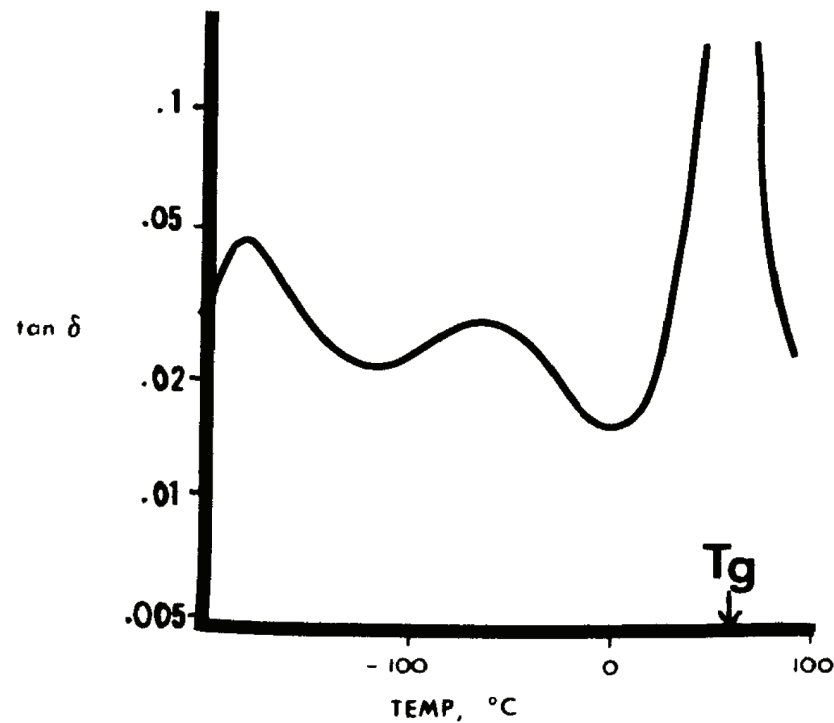


FIGURE 8. Loss tangent versus temperature at ca. 1 Hz for poly[2-methyl-6-(2-octyl)phenylene oxide]. (Adapted from reference 21.)

The position of the  $\tan \delta$  peak depends on the frequency.

# Theories of the glass transition

## 1. Free volume theory

Partindo da equação de Doolittle:  $\log \eta = A + B \frac{V_0}{V_f}$  Doolittle equation

tomando a fracção de volume livre:  $f = \frac{V_f}{V_0 + V_f} \approx \frac{V_f}{V_0}$  Fractional free volume

então  $\log \eta = A + B \frac{1}{f}$

Acima de  $T_g$   $f_T = f_g + \alpha_f (T - T_g)$  (above  $T_g$ )

$\alpha_f$  is the difference of the expansion coefficient above and below  $T_g$  ( $\approx 4.8 \times 10^{-4} \text{ K}^{-1}$ )



# Theories of the glass transition

## 1. Free volume theory

Combining the two equations above, one gets

$$\log \frac{\eta_T}{\eta_g} = \log a_T = B \left( \frac{1}{f_T} - \frac{1}{f_g} \right)$$

which, by comparing with the WLF equation

$$\log a_T = \frac{-17.4(T - T_g)}{51.6 + T - T_g}$$

leads to

$$f_g = 2.5\%$$

This relation is valid for a range of materials, but not for all forming glasses

# Theories of the glass transition

## 2. Thermodynamic theory

Gibbs Di Marzio theory- based on the analysis of the configurational entropy of a polymer as function of the temperature: if the configurational entropy approaches 0 at a given temperature above 0K, then there must be a glass transition, named  $T_2$ .

The theory predictions on the effect of several factors, such as density of cross-links, plasticizer content, molecular weight,.., are in good agreement with experiment.

Sillinger – suggests that such “ideal” glass transition  $T_2$  cannot occur for substances with unlimited molecular weight.

# Theories of the glass transition

## 3. Kinetic theories

Based on the the rate of volume contraction

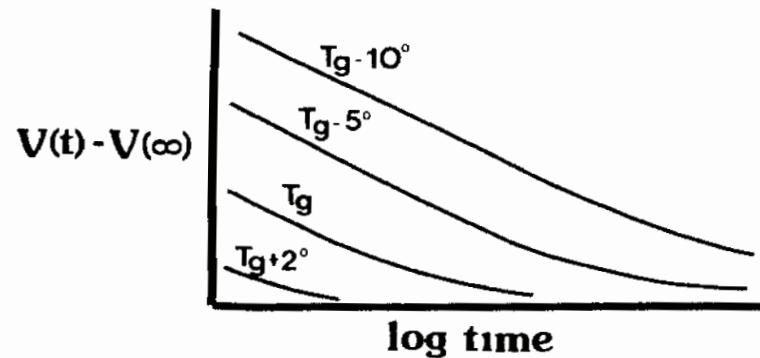


FIGURE 3. Isothermal volume contraction near the glass transition temperature. (Adapted from reference 5.)

Simple assumption: first-order process

$$-\frac{dV}{dt} = k_v (V_t - V_\infty) = \frac{1}{\tau_v} (V_t - V_\infty)$$

The more excess free volume there is, the faster it will shrink.

This is not very accurate, as  $\tau_v$  (volume relaxation time) depends on time.

# Theories of the glass transition

## 3. Kinetic theories

A better approximation:

$$-\frac{dV}{dt} = \frac{1}{b + a\tau_v} (V_t - V_\infty) \quad \Leftrightarrow \quad k_v = \frac{1}{b + a\tau_v} = f(t)$$

$\tau_v$  - tempo de relaxação de volume: corresponde ao tempo ao fim do qual 1/2.72 (ou 1/e) do volume livre em excesso foi excluído

Polystyrene sample:  $T_g \approx 90^\circ \text{C}$  (1 °C/min)

**Table II. Volume Relaxation Times at Various Temperatures**

Temperature (°C)	$\tau_v$
100	0.01 s
95	1 s
91	40 s
90	2 min
89	5 min
88	18 min
85	5 h
79	60 h
77	1 year

Observed  $T_g$  corresponds to  $\tau_v \approx 1-5$  min

# Effect of molecular parameters on the glass transition temperature

❖ Rotation of a chain segment with about 10 bonds (or 20-50 atoms)

## **Factors:**

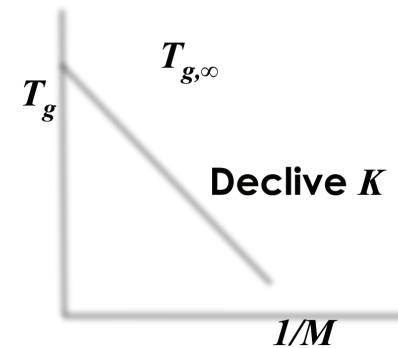
1. Molecular weight
2. Chain stiffness
3. Intermolecular forces
4. Side chains: length and volume
5. Stereochemistry

# Effect of molecular parameters on Tg

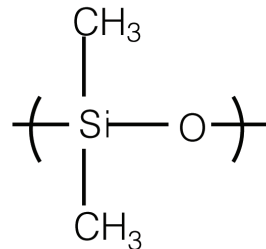
## 1. Effect of the molecular weight

Increase of the molecular weight → reduction of the number of chain ends → reduction of the free volume → Tg increases

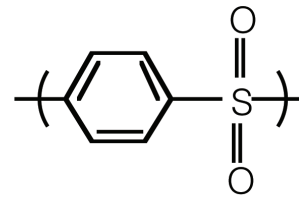
$$\text{Empirical relation: } T_g = T_{g,\infty} - \frac{K_g}{M_n}$$



## 2. Effect of main chain stiffness



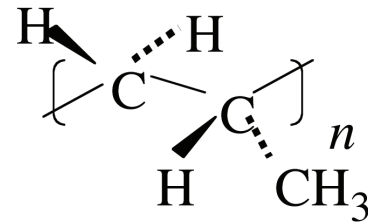
polidimetilsiloxano,  
Tg = -127 °C



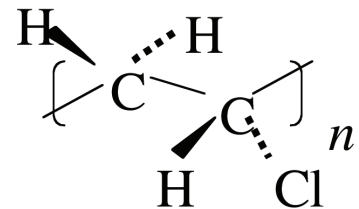
polifenilenossulfona,  
Tg > 500 °C

# Effect of molecular parameters on Tg

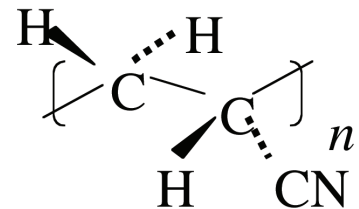
## 3. Effect of intermolecular forces e.g. side groups polarity



*Polipropileno*  
 $T_g = -14 \text{ }^\circ\text{C}$



*Poli(cloreto de vinilo), PVC*  
 $T_g = +87 \text{ }^\circ\text{C}$



*Poliacrilonitrilo*  
 $T_g = +103 \text{ }^\circ\text{C}$

# Effect of molecular parameters on Tg

## Cohesive energy density (CED)

$$DEC = \frac{\Delta H_v - RT}{V_m} \quad \begin{array}{l} \text{Energia molar de vaporização} \\ \text{Volume molar} \end{array}$$

Hildebrandt solubility parameter ( $\delta$ )

$$\delta = \sqrt{DEC}$$

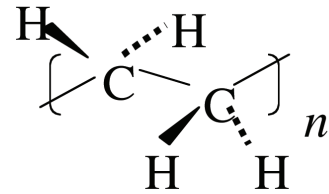
$$DEC = 0.5 m R T_g - 25 m$$

→ intermolecular forces increase Tg

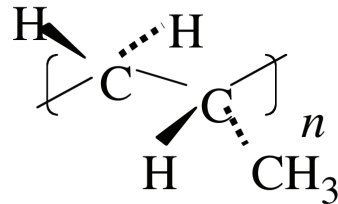


# Effect of molecular parameters on Tg

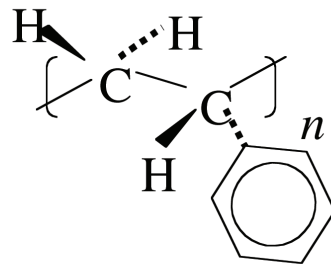
## 4.1. Effect of the volume of the side groups



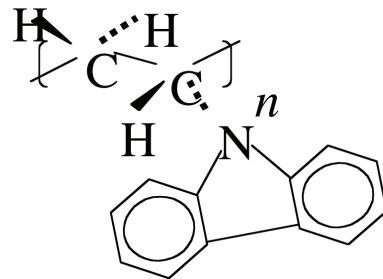
*Polietileno*  
 $T_g = -120^\circ\text{C}$



*Polipropileno*  
 $T_g = -14^\circ\text{C}$



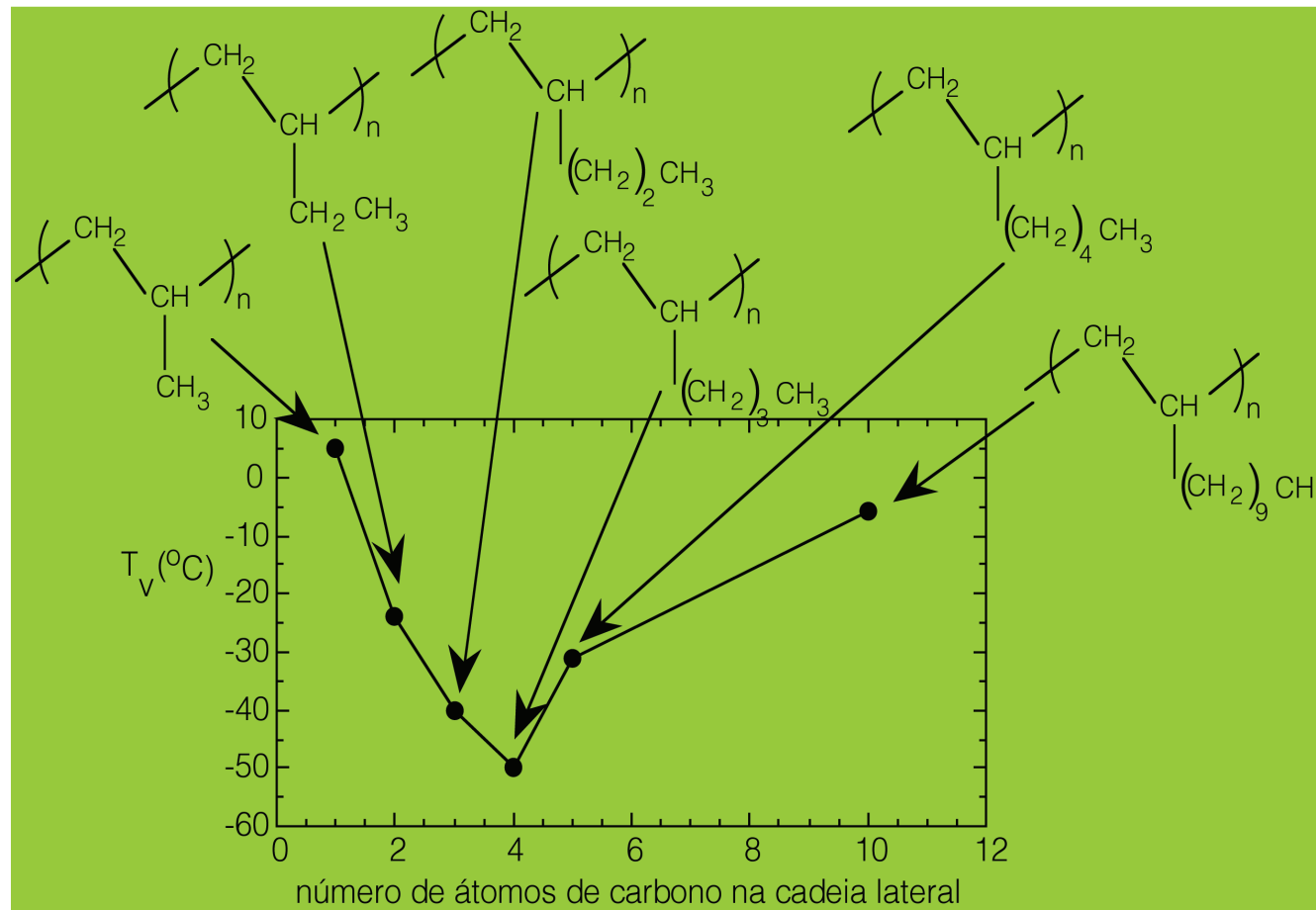
*Poliestireno*  
 $T_g = +100^\circ\text{C}$



*Poli(vinilcarbazole)*  
 $T_g = +280^\circ\text{C}$

# Effect of molecular parameters on Tg

## 4.2. Effect of the length of the side groups



$$T_g(\text{polietileno}) = -120 \text{ } ^\circ\text{C}$$

# Effect of molecular parameters on Tg

## 5. Effect of tacticity

<i>Polímero</i>	<i>Tg(°C)</i>		
	<i>Sindiotáctico</i>	<i>Atáctico</i>	<i>Isotáctico</i>
<i>Poli(metacrilato de metilo)</i>	105	105	38
<i>Polipropileno</i>	-4	-6	-18
<i>Poliestireno</i>	100		99

# Modification of Tg

1. Crystallinity

2. Cross-links

3. Copolymerisation

Empirical relations (weight fractions of each monomer and Tg of the homopolymers)

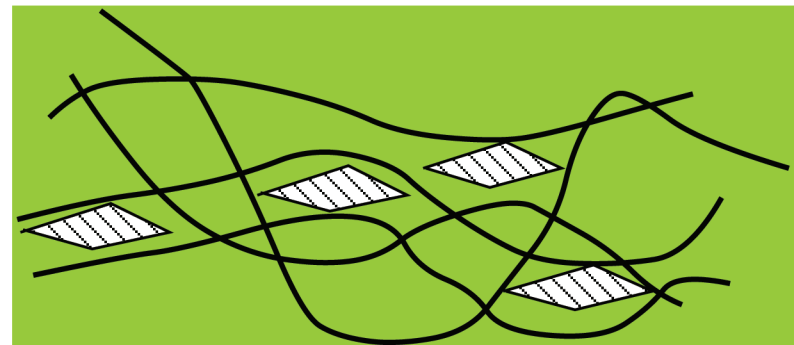
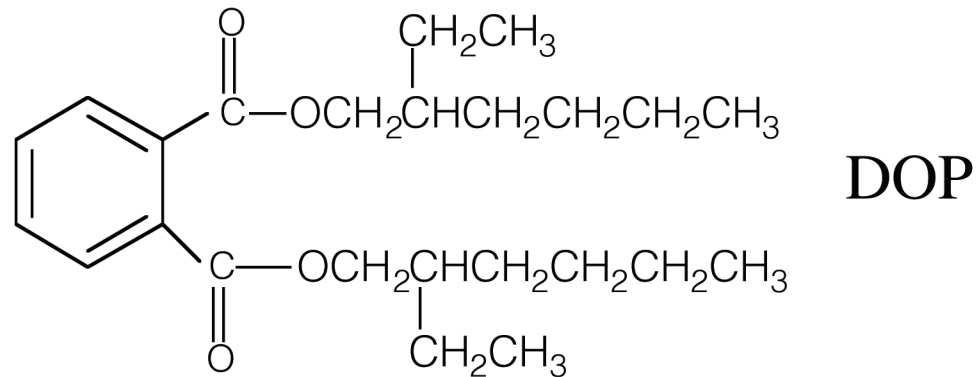
$$\text{i) } T_g(\text{copol}) = w_1 T_g(1) + w_2 T_g(2)$$

$$\text{ii) } \frac{1}{T_g(\text{copol})} = \frac{w_1}{T_g(1)} + \frac{w_2}{T_g(2)}$$

# Modification of Tg

## 4. Plasticizers (non volatile solvents, to reduce Tg

About 80% of total production used in PVC



Some additives increase Tg instead!

# Methods to determine T<sub>g</sub>

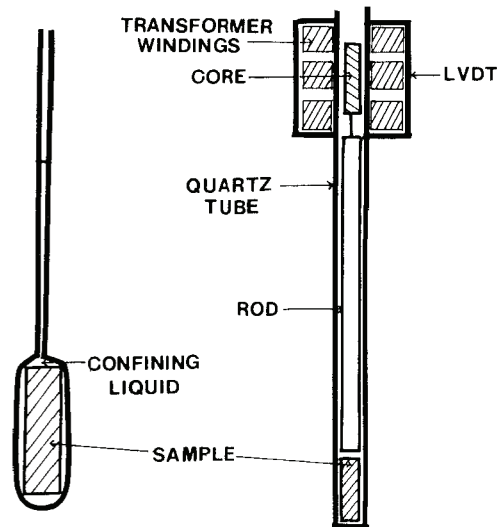
## i) Methods based on volume changes (dilatometry)

Volume dilatometer

Linear dilatometer



$$\text{Volume} = f(T)$$

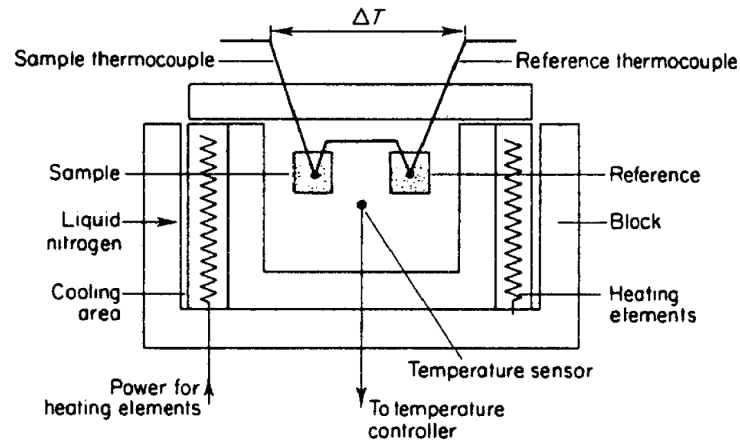


LVDT- "linear variable differential transformer"

$$\text{Voltage} = f(T)$$

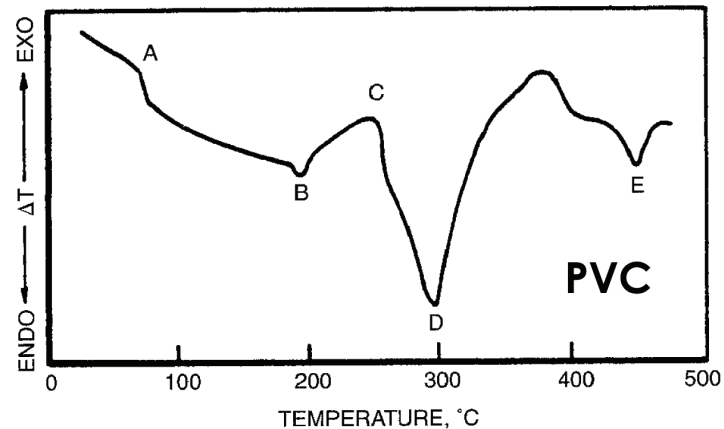
# Methods to determine T<sub>g</sub>

## ii) Methods based on specific heat changes

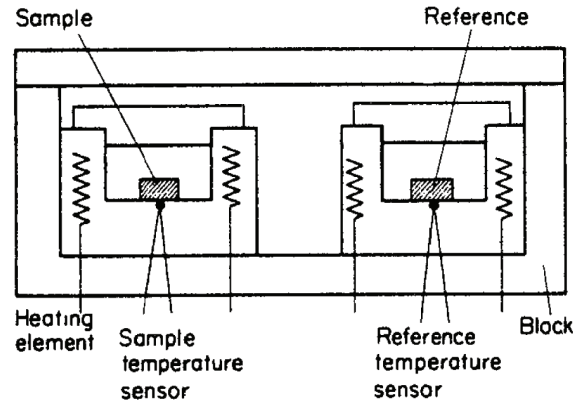


DTA

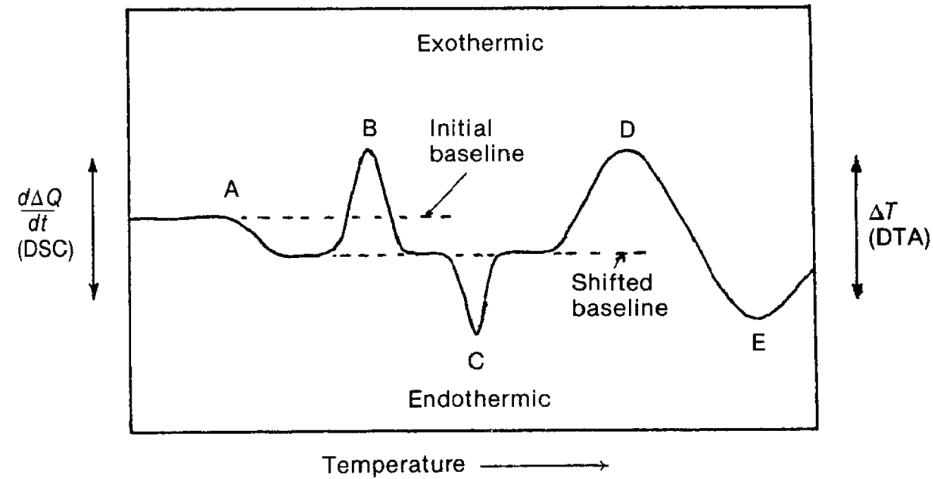
**FIGURE 5.17.** Differential thermal analysis (DTA) thermogram of poly(vinyl chloride): (A) glass transition,  $T_g$ ; (B) melting point; (C) oxidative attack; (D) dehydrochlorination; and (E) probable depolymerization. [From Matlack and Metzger,<sup>79</sup> copyright 1966. Reprinted by permission of John Wiley & Sons, Inc.]



# Methods to determine T<sub>g</sub>



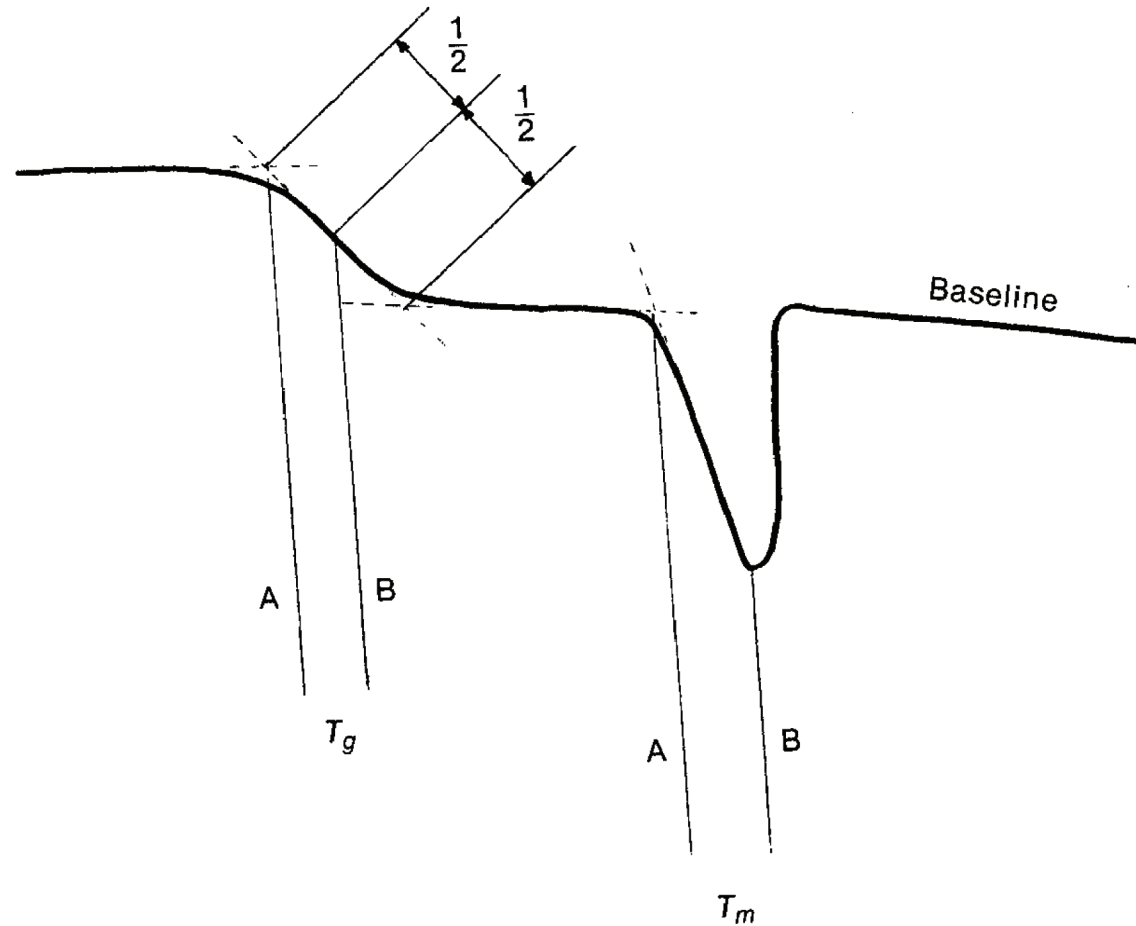
DSC



**FIGURE 5.16.** Idealized differential scanning calorimetry (DSC) or differential thermal analysis (DTA) thermogram: (A) temperature of glass transition,  $T_g$ ; (B) crystallization; (C) crystalline melting point,  $T_m$ ; (D) crosslinking; and (E) vaporization.  $d\Delta Q/dt$  = electrical power difference between sample and reference;  $\Delta T$  = difference in temperature between sample and reference.



# Methods to determine Tg



**FIGURE 5.18.** Methods of reporting transition temperatures: (A) at the onset, and (B) at the inflection point or maximum,  $T_g$  = glass transition temperature;  $T_m$  = crystalline melting point.

# References

- “Principles of Polymer Systems”, 2ed., F. Rodriguez, McGraw-Hill-Int. Student Ed., 1983
- “Introduction to Macromolecular Science”, P. Munk, John Wiley & Sons, 1989
- “Physical Properties of Polymers”, James E. Mark *et al.*, 2ed, Am. Chem. Soc., Washington, 1993.
- “Polymer Chemistry- An Introduction”, M.P. Stevens, 3ed.