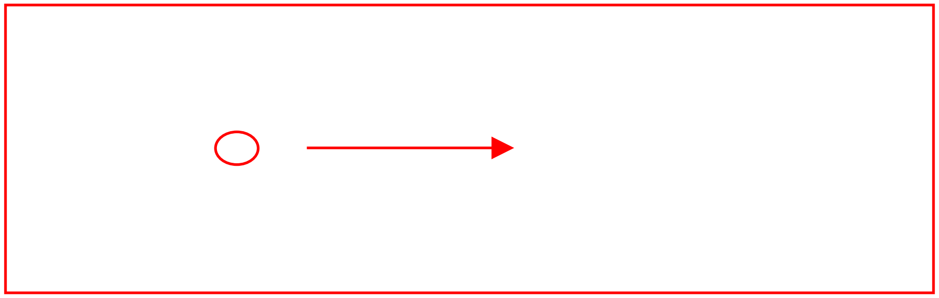
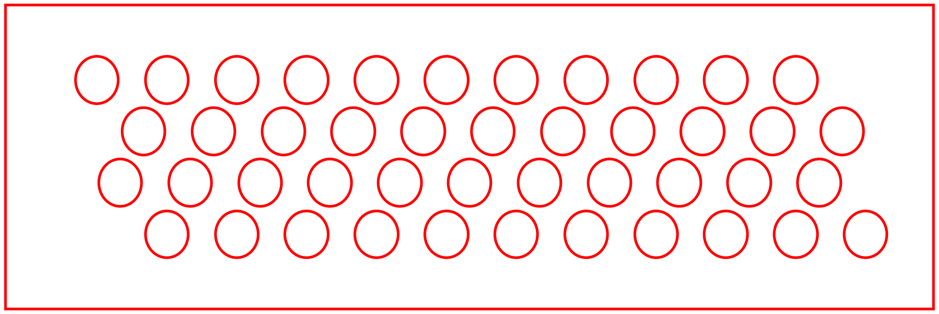
# MOTION

**The easy stuff;**

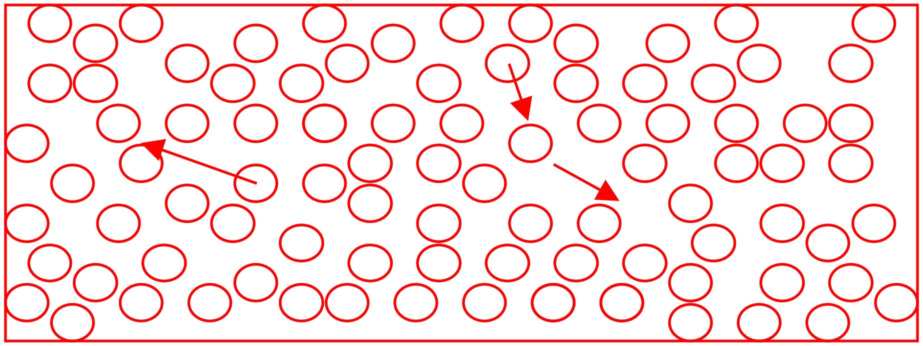


**The gaseous state - Translational motion**



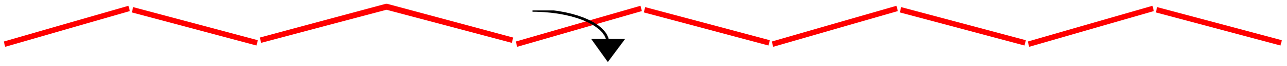
**The crystalline state - Oscillations about a Mean position**

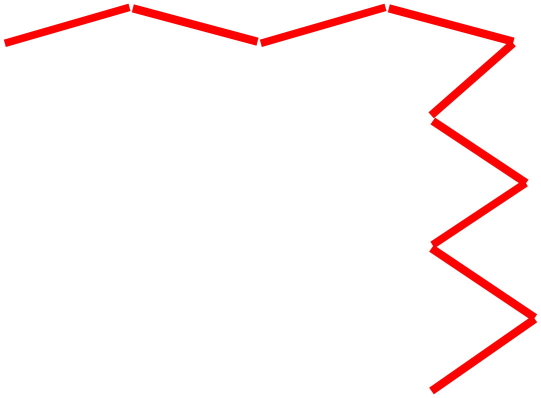
**The hard stuff;**



**The liquid state - Coupled motions**

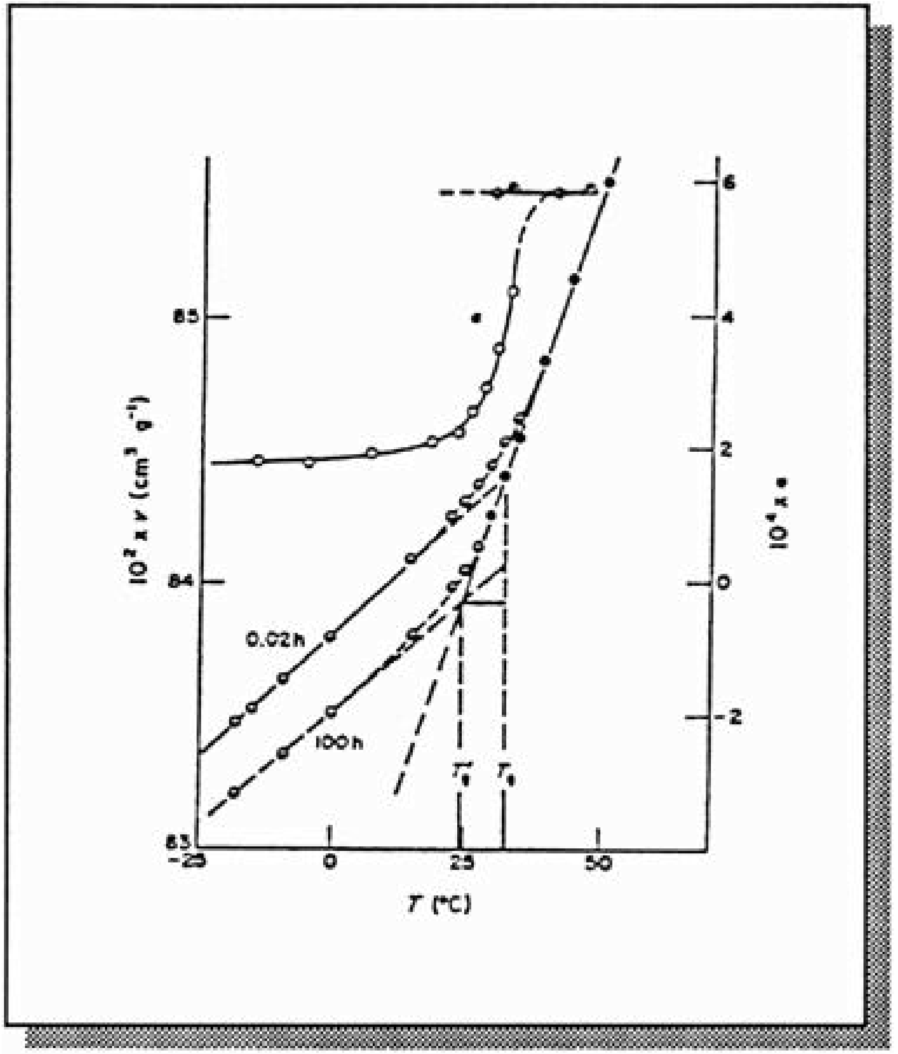
# MOTION IN POLYMERS





**LARGE SCALE MOTION PREVENTED BY RANDOM CLOSE PACKING IN THE MELT**

# THE NATURE OF THE GLASS TRANSITION



*Reproduced with permission from*
*A. J. Kovacs,* J. Polym. Sci.*, **30**, 131 (1958).*

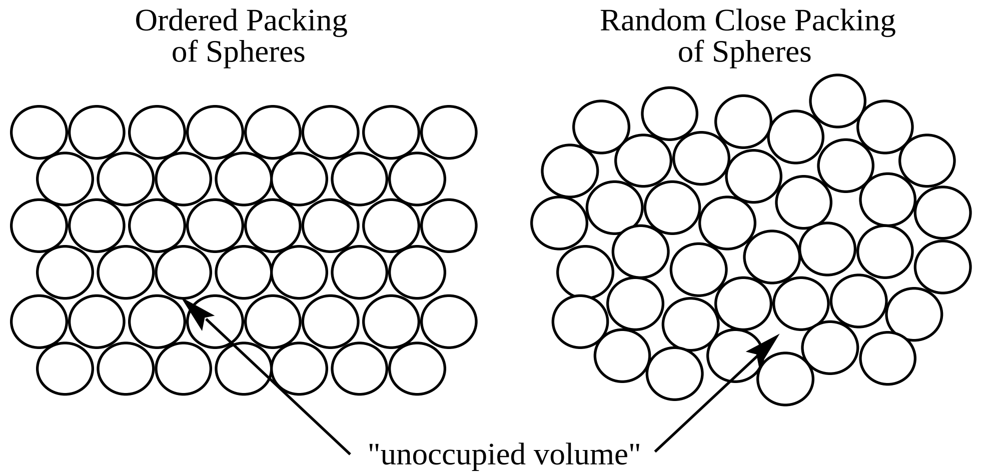
Tg - a thermodynamic Transition or a kinetic Phenomenon ?

The observed Tg depends Upon the rate of heating Or cooling ~ therefore Kinetic. But is there an Underlying thermodynamic Transition ?

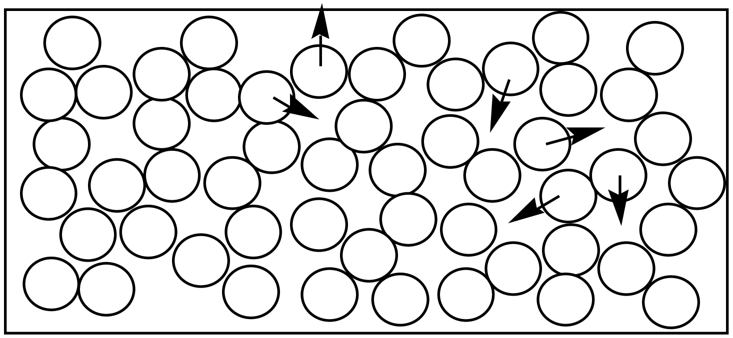
# THE CONCEPT OF FREE VOLUME

Free volume is not the same as "unoccupied" or empty volume.

Molecules have thermal motion. For a material in the glassy state we can think of the motion as the balls oscillating in a cage of their neighbors. These oscillations create some "free volume" over and above the empty space characteristic of random close packing.



Two dimensional representation of the packing of spheres.



For polymers, motion of chain segments, and not the entire polymer molecule, is important.

# THE CONCEPT OF FREE VOLUME

- Free volume is not the same as "unoccupied" or empty volume.

- Molecules have thermal motion. For a material in the glassy state we can think of the motion as the balls oscillating in a cage of their neighbors. These oscillations create some "free volume" over and above the empty space characteristic of random close packing.

- Free volume increases with temperature as the amplitude of the oscillations increases.

- Free volume is not equally shared between all the molecules, but fluctuates. At some instant of time one molecule might be trapped in a local close-packed cage of its neighbors, while another has Sufficient "free volume" available to it that it bounces into a new position.

- The idea that the Tg corresponds to the point where the free volume falls below a critical value was suggested by Fox and Flory.

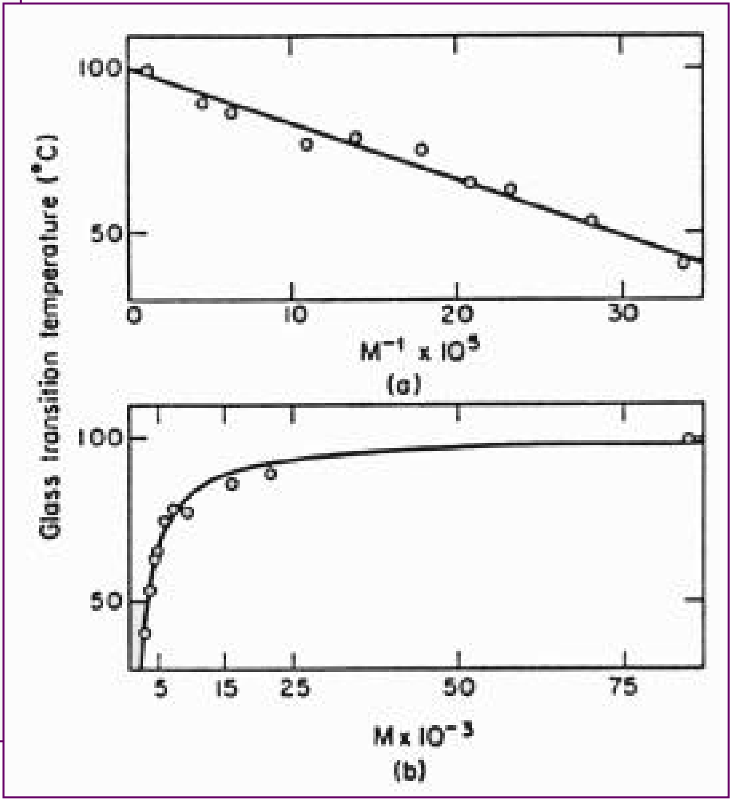
# THE EFFECT OF MOLECULAR WEIGHT

The ends of a chain have more freedom of motion than the segments in the center of a chain and, crudely, can be thought of as having "more free volume".

Low molecular weight chains have more ends per unit volume than long chains,
hence a higher free volume, hence a lower Tg.

Fox and Flory used such simple free volume arguments to obtain the following equation:

$$T_g = T_g^{\infty} - \frac{K}{\overline{M}_n}$$



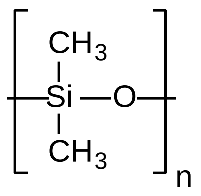
Glass transitions of polystyrene fractions plotted as a function of molecular weight, M (bottom) and 1/M (top).

From T. G. Fox and P. J. Flory, J. Appl. Phys., 21, 581 (1950).

# THE EFFECT OF CHAIN STIFFNESS

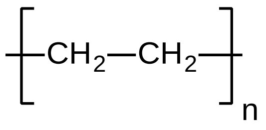
- Chain stiffness affects chain mobility.

- If there are bulky groups, such as benzene rings, in the backbone of the polymer chain, there is a high energy barrier to rotations, which then only occur at higher temperatures.



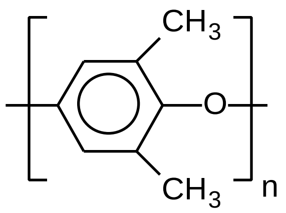
Poly(dimethyl siloxane)

**$T_g$ - 120°C**



Polyethylene

**$T_g$ - 80°C**



Poly(phenylene oxide)

**$T_g$ + 200°C**

**Increasing Chain Stiffness**

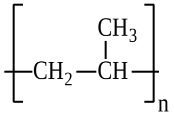
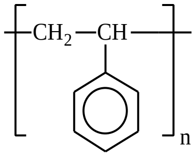
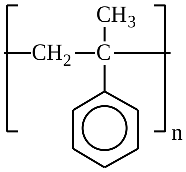
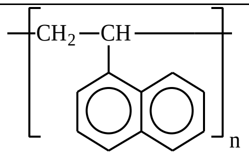
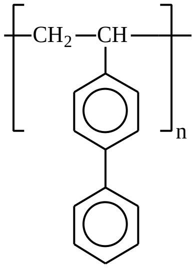
# THE EFFECT OF BULKY SIDE GROUPS

The presence of bulky pendant groups attached to the polymer backbone raises the Tg, through steric hindrance to bond rotations.

As the pendant group gets larger, the Tg increases. However, as at some point the attached groups no longer get in the way of bond rotations as they get further and further away from the chain.

The effect of attaching a methyl group to the main chain of PS, to give poly(_-methyl styrene), is greater than increasing the size of the aromatic unit, because the close proximity of this group to the polymer backbone introduces a higher degree of steric hindrance.

Compare PaMS, PVN and PVBP.

| Polymer | Chemical Structure | $T_g$ |
|---|---|---|
| Polyethylene | $-\!\!\left[CH_2-CH_2\right]_n\!\!-$ | ≈ - 80°C * |
| Atactic Polypropylene |  $-\!\!\left[CH_2-\underset{}{\overset{CH_3}{CH}}\right]_n\!\!-$ | ≈ - 10°C |
| Atactic Polystyrene |  | ≈ 100°C |
| Atactic Poly(α-methyl styrene) |  | ≈ 175°C |
| Atactic Poly(1-vinyl naphthalene) |  | ≈ 135°C |
| Atactic Poly(vinyl biphenyl) |  | ≈ 145°C |

# THE EFFECT OF FLEXIBLE SIDE GROUPS

Tg decreases with increasing side-chain length.

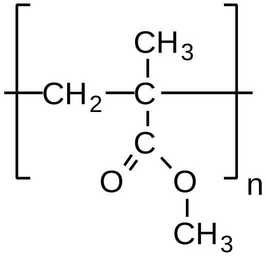
Substituents closest to the chain, the methyl and ester group, provide the bulk of the steric hindrance.

The rest of the attached side chain can "get out of the way" of motions of the main chain through rotations around side-chain bonds.

Because these side chains increase the free volume through their effect on the packing of the chains, the Tg is lowered.

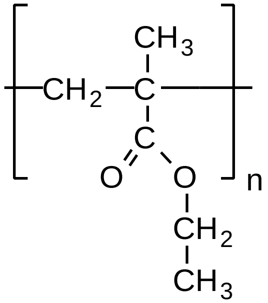
Increasing Length of Flexible Side Group

Poly(methyl methacrylate)



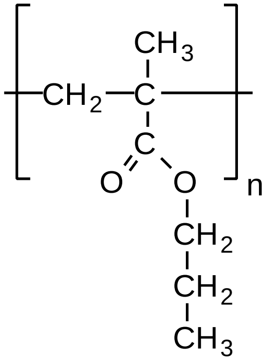
**$T_g$ 105°C**

Poly(ethyl methacrylate)



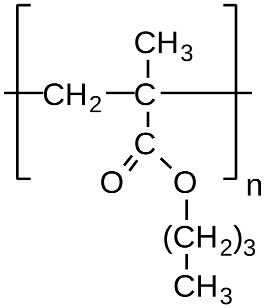
**$T_g$ 65°C**

Poly(propyl methacrylate)



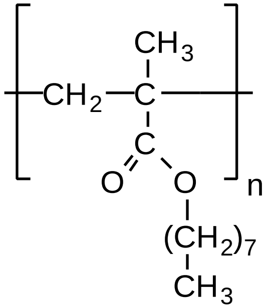
**$T_g$ 38°C**

Poly(butyl methacrylate)



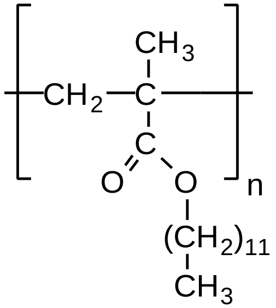
**$T_g$ - 2°C**

Poly(octyl methacrylate)



**$T_g$ - 42°C**

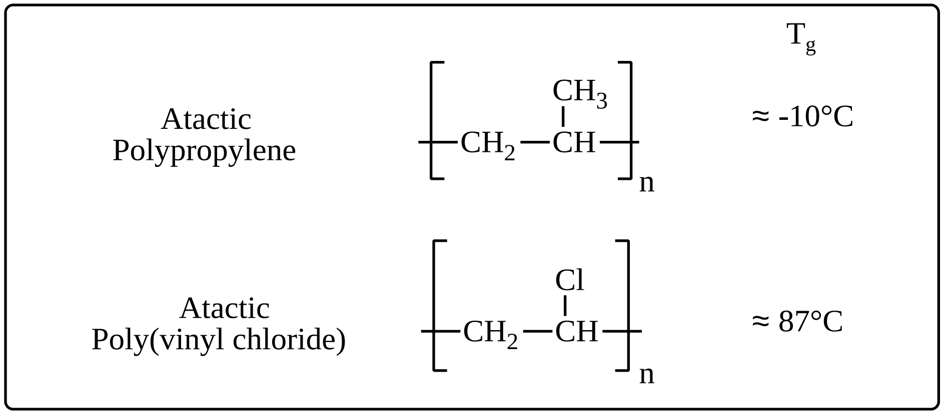
Poly(dodecyl methacrylate)



**$T_g$ - 62°C**

# THE EFFECT OF INTERMOLECULAR ATTRACTIONS AND CROSSLINKING

Strong intermolecular attractions also act so as to raise the Tg.



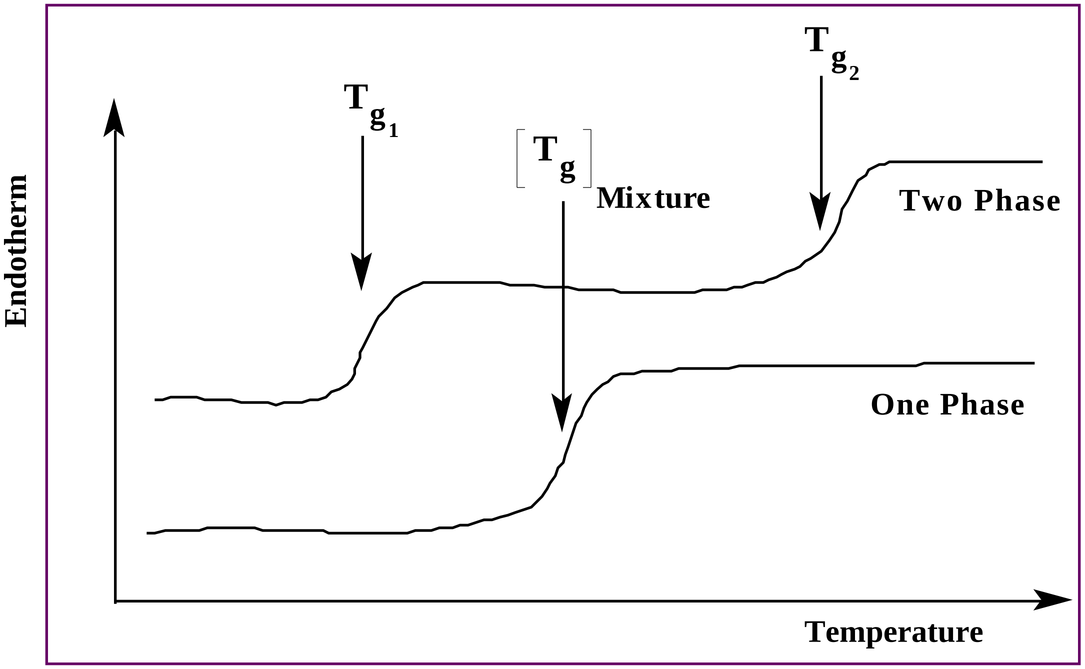
| | | $T_g$ |
|---|---|---|
| Atactic Polypropylene | $\left[ -CH_2-\overset{CH_3}{\overset{\vert}{C}H}- \right]_n$ | ≈ -10°C |
| Atactic Poly(vinyl chloride) | $\left[ -CH_2-\overset{Cl}{\overset{\vert}{C}H}- \right]_n$ | ≈ 87°C |

- The chlorine atom and methyl group have approximately the same effect on bond rotations.
- The polar character of the Cl atom leads to stronger forces of attraction between chains, however, so that on average these groups are closer.
- The free volume is less and the Tg is higher (reality is probably a bit more complicated than this
- Similarly, cross-linking decreases free volume, because parts of the chain
- Are tied more closely together, hence Tg increases.

# THE EFFECT OF DILUENTS AND COPOLYMERIZATION

Schematic diagram depicting the intermediate Tg observed in a miscible mixture, relative to one that is phase separated

Q: what would you expect for a random copolymer vs. a block copolymer ?

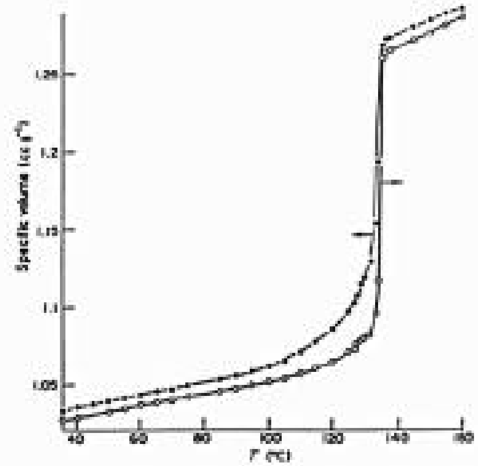


The Tg of a mixture can be simply rationalized on the basis of free volume arguments to give the Fox equation

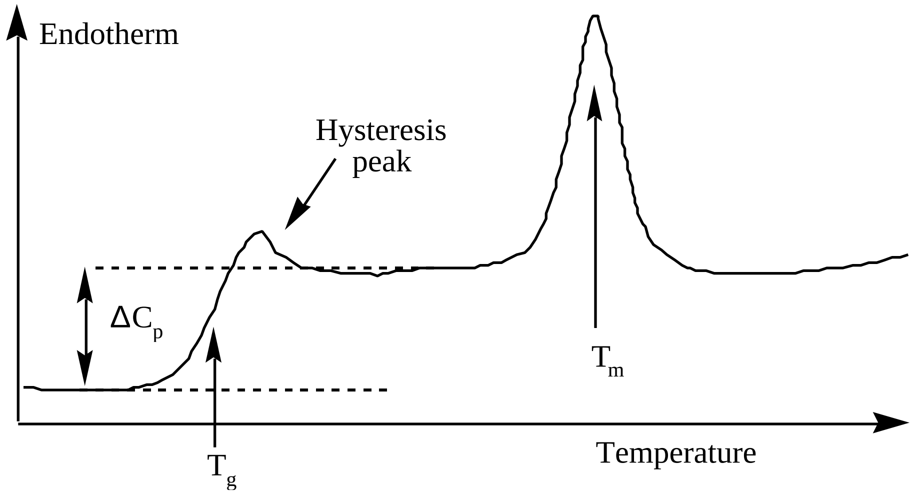
$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}}$$

# CHARACTERISTICS OF THE CRYSTALLINE MELTING POINT

When we use the word "melting" we will mean the transition from an ordered crystalline phase to a disordered liquid phase, usually at a well-defined temperature.



A plot of specific volume as a function of temperature for linear polyethylene samples. From R. Chiang and P. J. Flory, *JACS*, 83, 2857 (1961).



A DSC plot showing a change in the specific heat (ΔCp) at the glass transition temperature (Tg) and an endothermic peak at the melting temperature (Tm).

# MELTING - EQUILIBRIUM CONSIDERATIONS

$$\Delta G_f = \Delta H_f - T\Delta S_f$$

**AT EQUILIBRIUM** $\Delta G_f = 0$

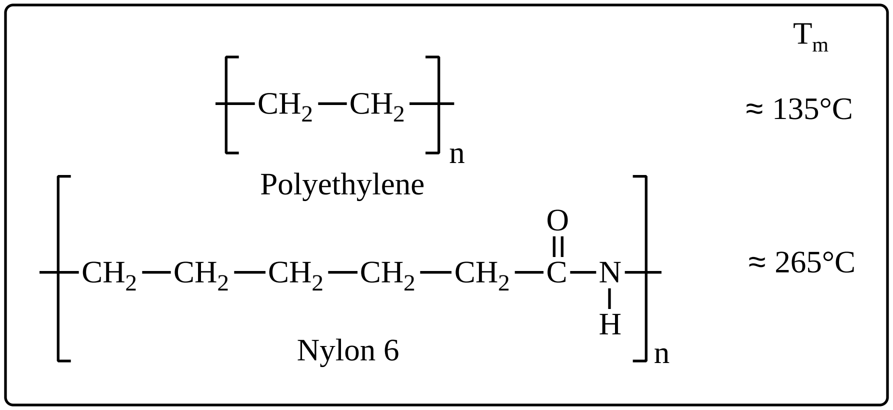
**HENCE** $T_m = \dfrac{\Delta H_f}{\Delta S_f}$

**THE TRICK IS TO RELATE THESE QUANTITIES TO MOLECULAR PROPERTIES. WE SHALL SIMPLY USE QUALITATIVE ARGUMENTS**

# THE EFFECT OF CHEMICAL STRUCTURE —ENTHALPY CONSIDERATIONS

Assumption: enthalpy is simply related to the force of attraction between the chains.

$\Delta H_m$ must be related to the difference in the forces of attraction between polymers packed in a regular array in the crystalline domains and the forces between those same chains when randomly intertwined in the melt.

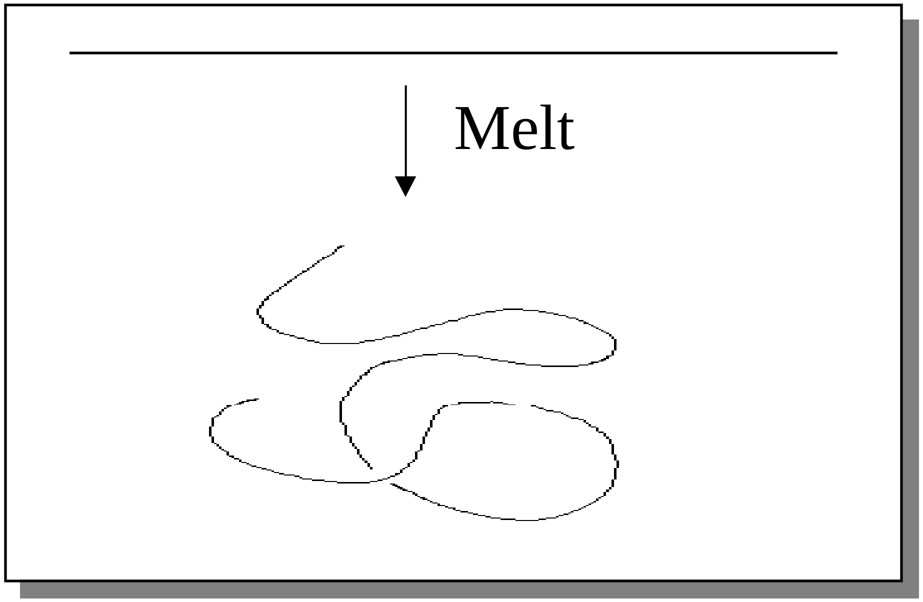


$$T_m = \frac{\Delta H_f}{\Delta S_f}$$

The forces of attraction between the simple hydrocarbon segments found in polyethylene are weak dispersion forces (≈ 0.2 kcal/mole). In contrast, nylon 6 contains the amide group, which forms hydrogen bonds that are an order of magnitude stronger (≈ 5 kcal/mole).

# THE EFFECT OF CHEMICAL STRUCTURE —ENTROPY CONSIDERATIONS

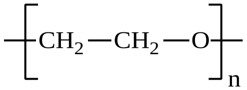
In the crystalline state a polymer chain is in a single ordered conformation. Upon melting the chain escapes the cage of the crystalline lattice and now has the freedom to sample all the conformations available to it.



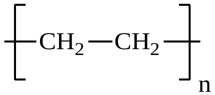
$$\boxed{\Delta S_f = k(\ln \Omega_{melt} - \ln \Omega_{cryst})}$$

# ENTROPY CONSIDERATIOS - CHAIN STIFFNESS (SIMILAR INTERACTIONS)

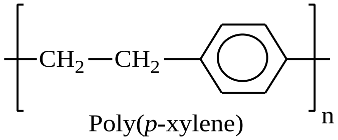
$T_m$


Poly(ethylene oxide)

≈ 65°C

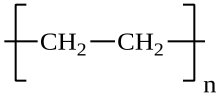

Polyethylene

≈ 135°C

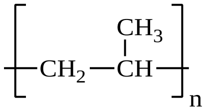

Poly(*p*-xylene)

≈ 400°C

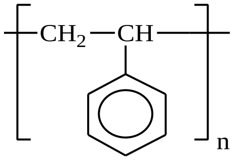
$T_m$


Polyethylene

≈ 135°C


Isotactic Polypropylene

≈ 170°C


Isotactic Polystyrene

≈ 225°C

$$T_m = \frac{\Delta H_f}{\Delta S_f}$$

Bond rotations are inhibited by steric hindrance and the number of configurations available to the chain becomes limited.