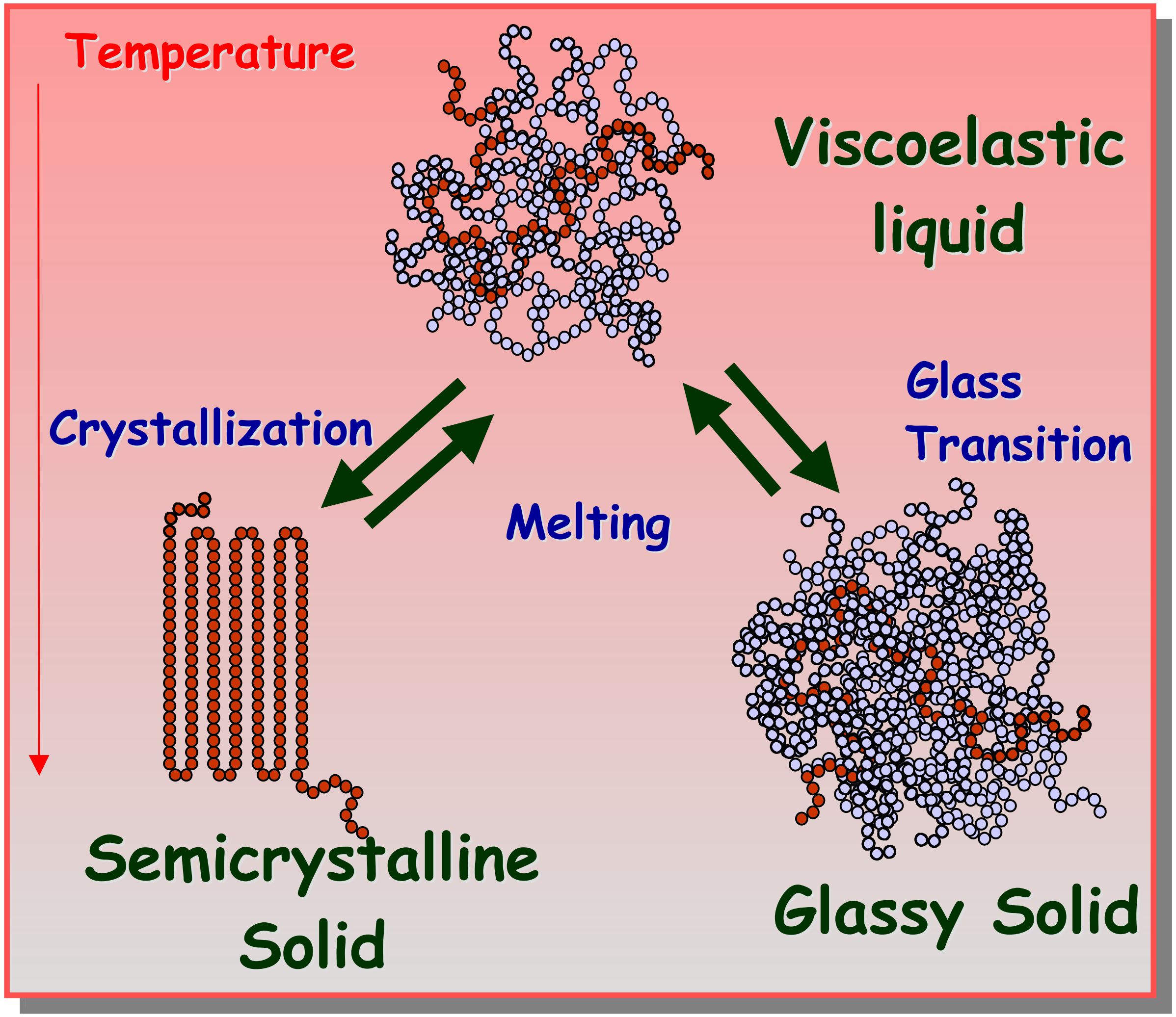
Thermal Transitions: Crystallization, Melting and the Glass Transition

Today:

- *Glassy polymers and the nature of the glass transition*
- *The factors that affect Tg*
- *Plasticizers*

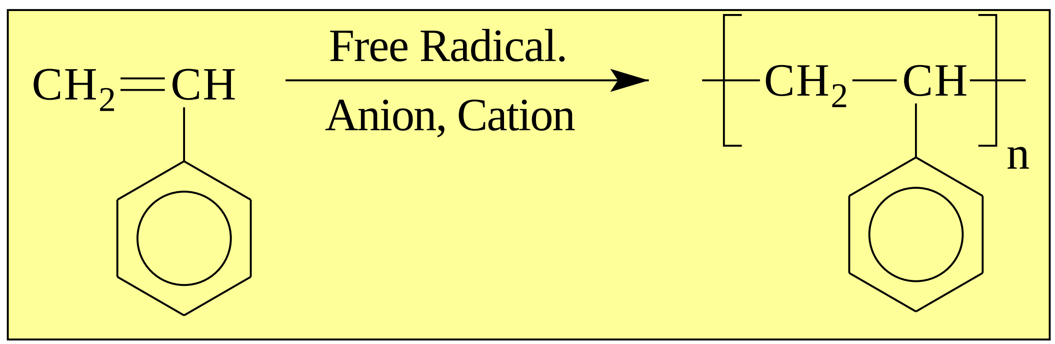
Chapter 8 in CD (Polymer Science and Engineering)

Glassy Solids and the Glass Transition



Polystyrene

Clear polystyrene articles

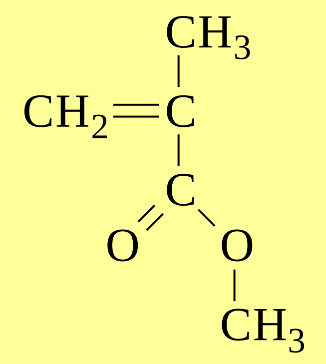


Foamed polystyrene articles

Poly(methyl methacrylate)

1873

Methyl acrylate, a close relative of methyl methacrylate (MMA), was first prepared in 1873 by Caspery and Tollens, and first polymerized in 1880 by Kahlbaum.



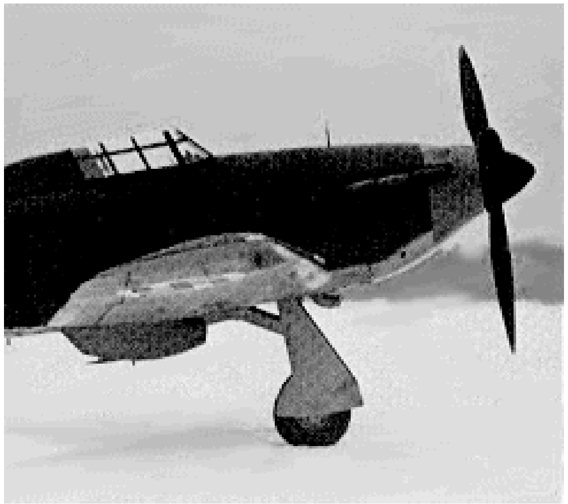
Methyl methacrylate

1901

Otto Röhm, who was a cofounder of the famous Röhm and Haas company, obtained his doctorate in Germany. His thesis was on acrylate polymers. In general, these materials were elastomeric in nature and they were pursued to some degree as possible substitutes for rubber.

1930's

W. Bauer (Germany) and R. Hill (UK) studied esters of methacrylic acid and found that MMA produced an beautifully clear glassy material, poly(methyl methacrylate) (PMMA). With war clouds on the horizon, scientists and engineers of both countries recognized that 'Plexiglas' or 'Perspex', as PMMA was called, had potential as cockpit canopies for military aircraft. Commercial production of PMMA was started at ICI (UK) in 1934 and throughout the war years most of the PMMA produced went for aircraft applications.



A Hawker "Hurricane" with Perspex canopy

Poly(methyl methacrylate)

Polycarbonate

1898

Polycarbonates were evidently described at the beginning of the 20th century by Einhorn and, a little later, by Bischoff and von Hedenstrom. There were, however, intractable solids and received no commercial attention.

1930's

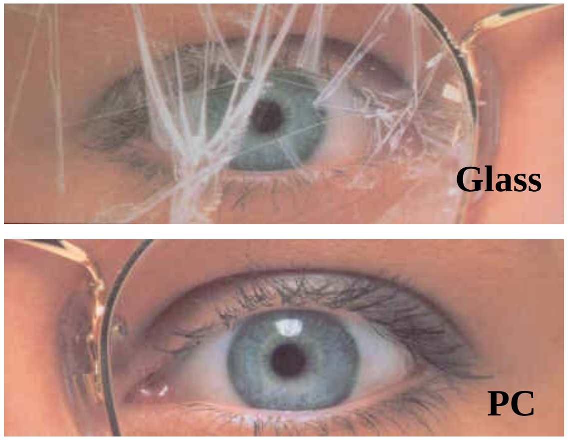
Some 30 years later, a number of aliphatic polycarbonates were prepared in Wallace Carothers' laboratory at DuPont (see Case Study IV). But, they were found to have low melting points and were highly susceptible to hydrolysis. They were not pursued commercially.

Polycarbonate windows

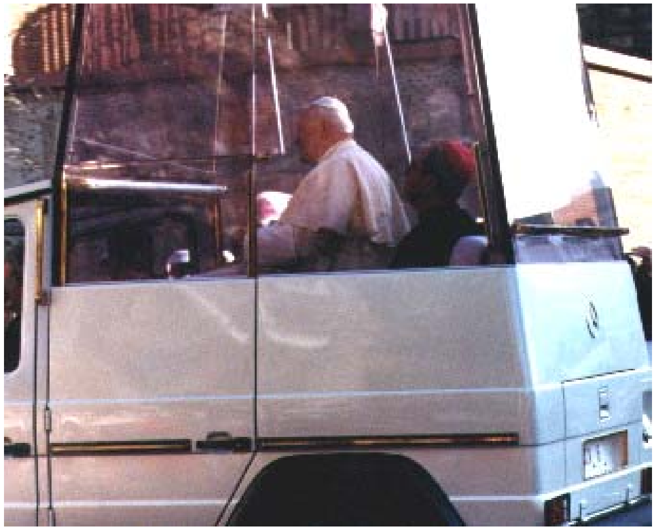
1950's

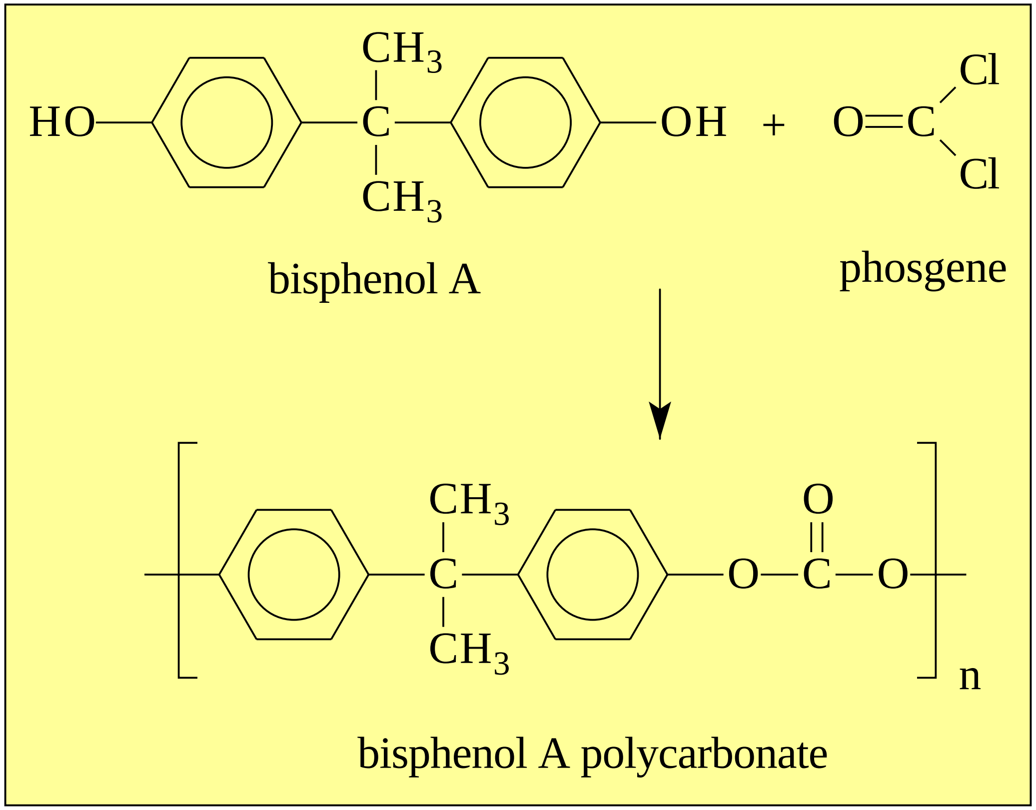
Herman Schnell, working at the Bayer A. G. company in Germany, discovered that reaction of phosgene with bisphenol A (a compound that was available and already used for epoxy resins) produced an aromatic polycarbonate that had superb physical and mechanical properties. Schnell, a protégé of Otto Bayer (see Case Study VII), was well familiar with the reactions of phosgene, and obtained a patent in the Fall of 1953. Unbeknownst to either company, in the same time period General Electric in the US was also developing aromatic polycarbonates and applying for patents. Guess what, it took some 10 years to settle the ensuing dispute and before cross-licensing negotiations were agreed to (sound familiar?)

Polycarbonate

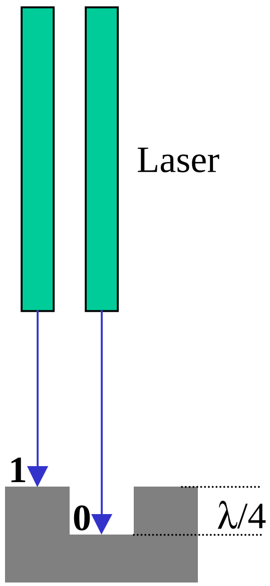


Tough Stuff!





Polycarbonate



Schematic of hole in disc

Good definition

Poor definition

Polycarbonate CD's.

PVC – Hazardous Material?

From "The Poison Plastic" published by Greenpeace (www.greenpeace.org):

"Most common plastics pose serious threats to human health and the environment. The problems of plastics include extreme pollution from production, toxic chemical exposure during use, hazards from fires, and their contribution to the world's growing waste crisis. But one plastic stands alone; PVC, throughout its lifetime, is the most environmentally damaging of all plastics."

Source: Exxon.

No Need to Apologize!

"From packaging materials, through fibers, foams and surface coatings, to continuous extrusions and large scale moldings, plastics have transformed almost every aspect of life. Without them much of modern medicine would be impossible and the consumer electronics and computer industries would disappear. Plastic sewage and water pipes alone have made an immeasurable contribution to public health worldwide."

Getting Flexible – PVC

PVC pipe & fixtures

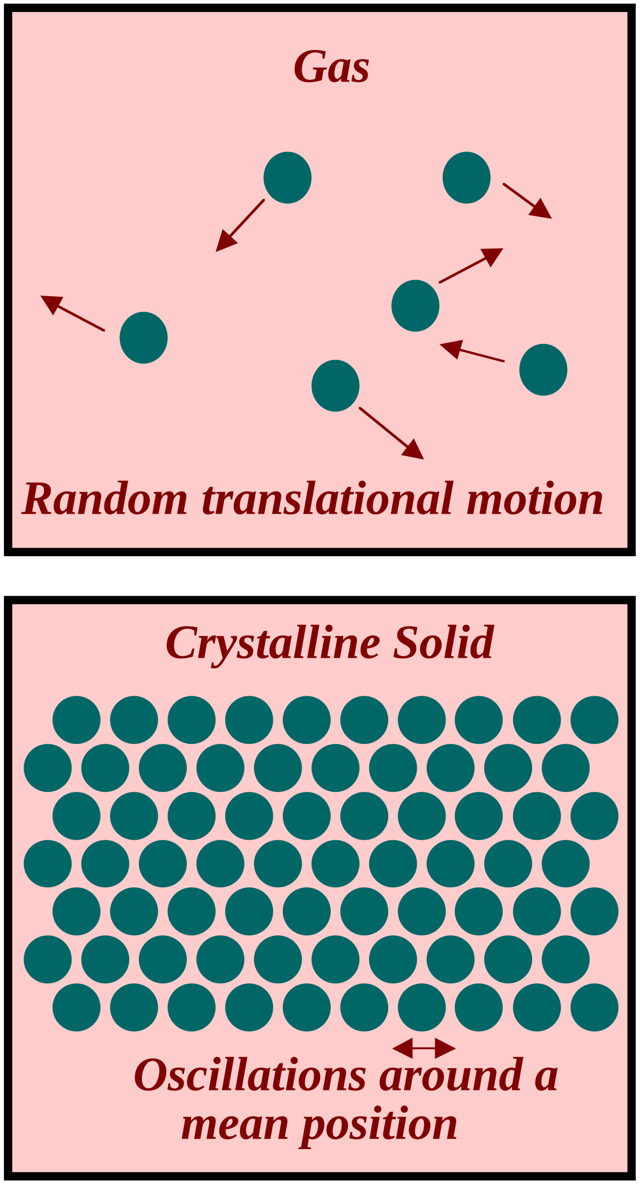
PVC siding

PVC roofing material

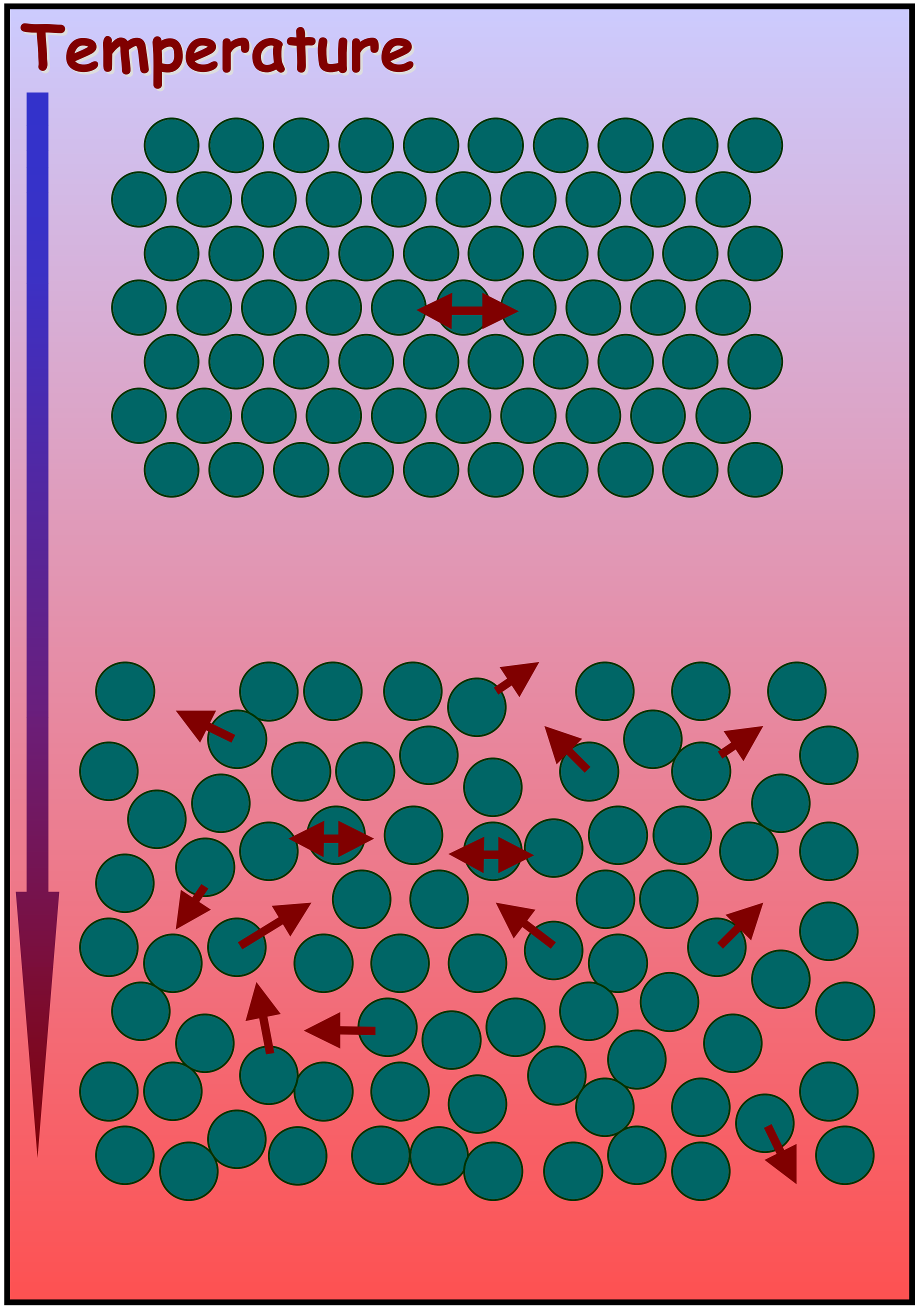
PVC door and frame

PVC window

Motion



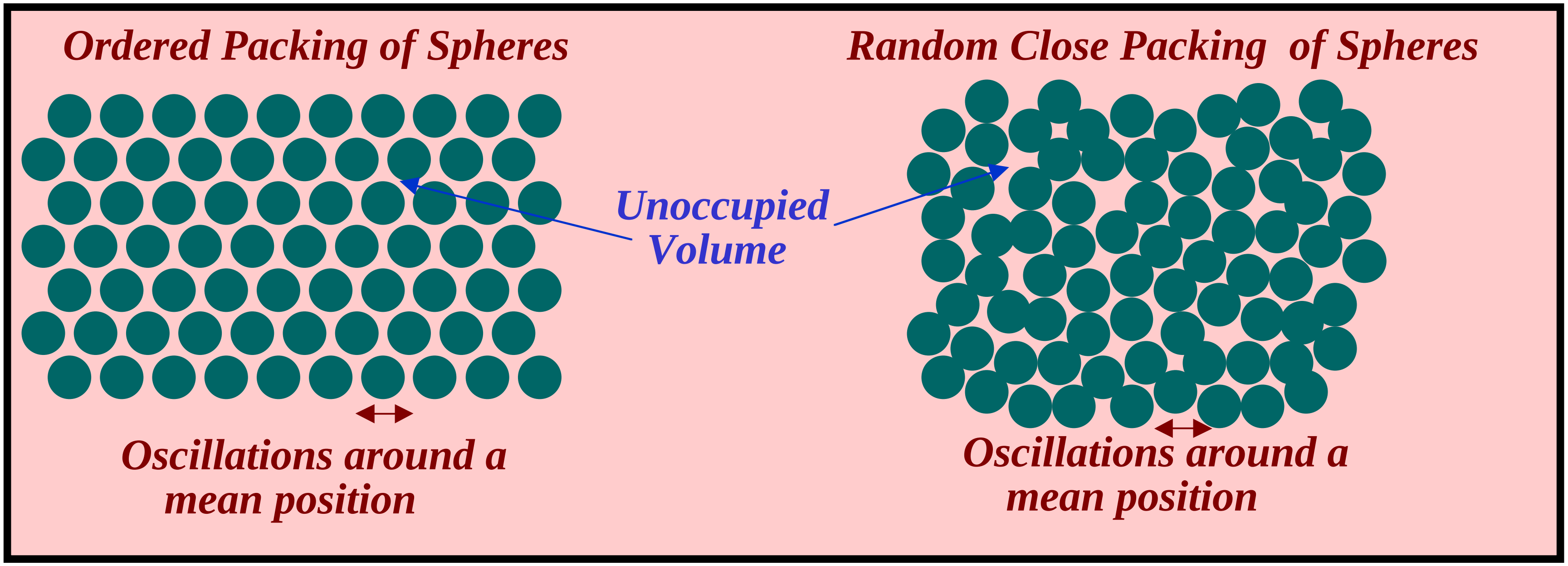
These types of motion are readily described (eg in quantum mechanics you no doubt considered a particle in a box and the harmonic oscillator).



Liquids

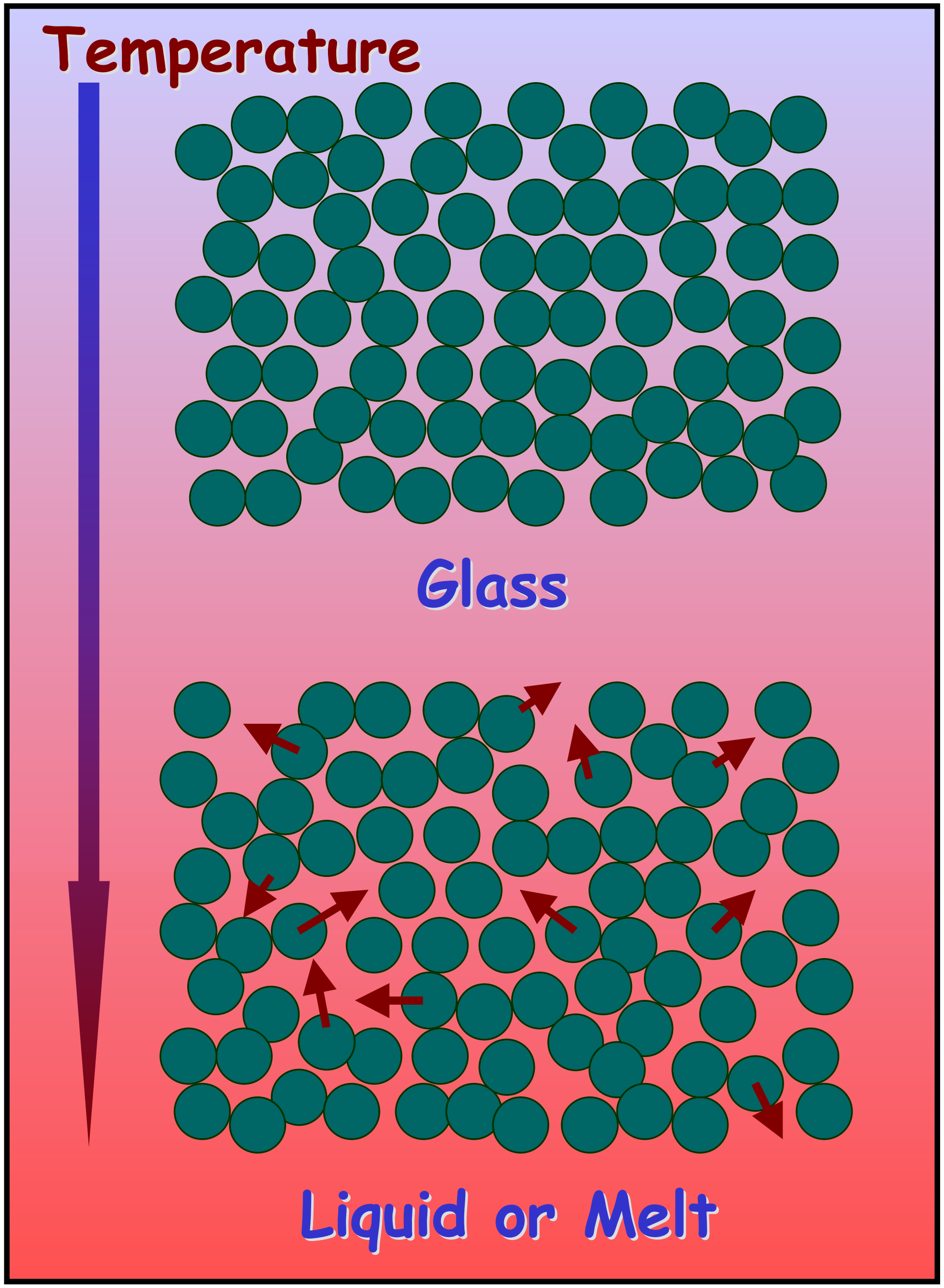
In the liquid state the motion is a complex coupling of vibrational oscillations and translational movement, as "holes" open up as a result of random displacements of neighbors. Not as easily described, but there has to be enough "empty space" in the material as a whole for this to occur.

Free Volume

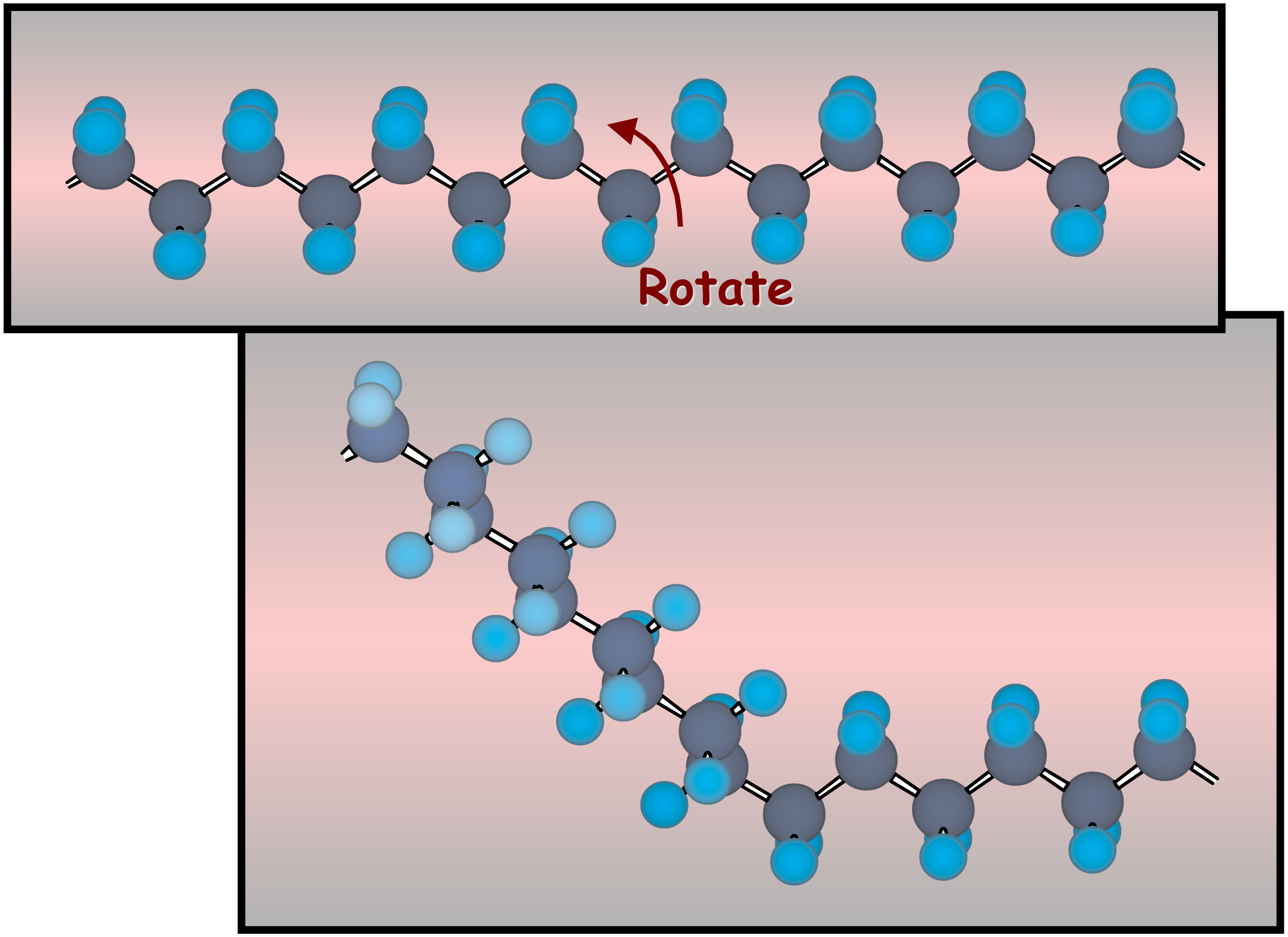


Ordered Packing of Spheres
Random Close Packing of Spheres
Unoccupied Volume
Oscillations around a mean position
Oscillations around a mean position

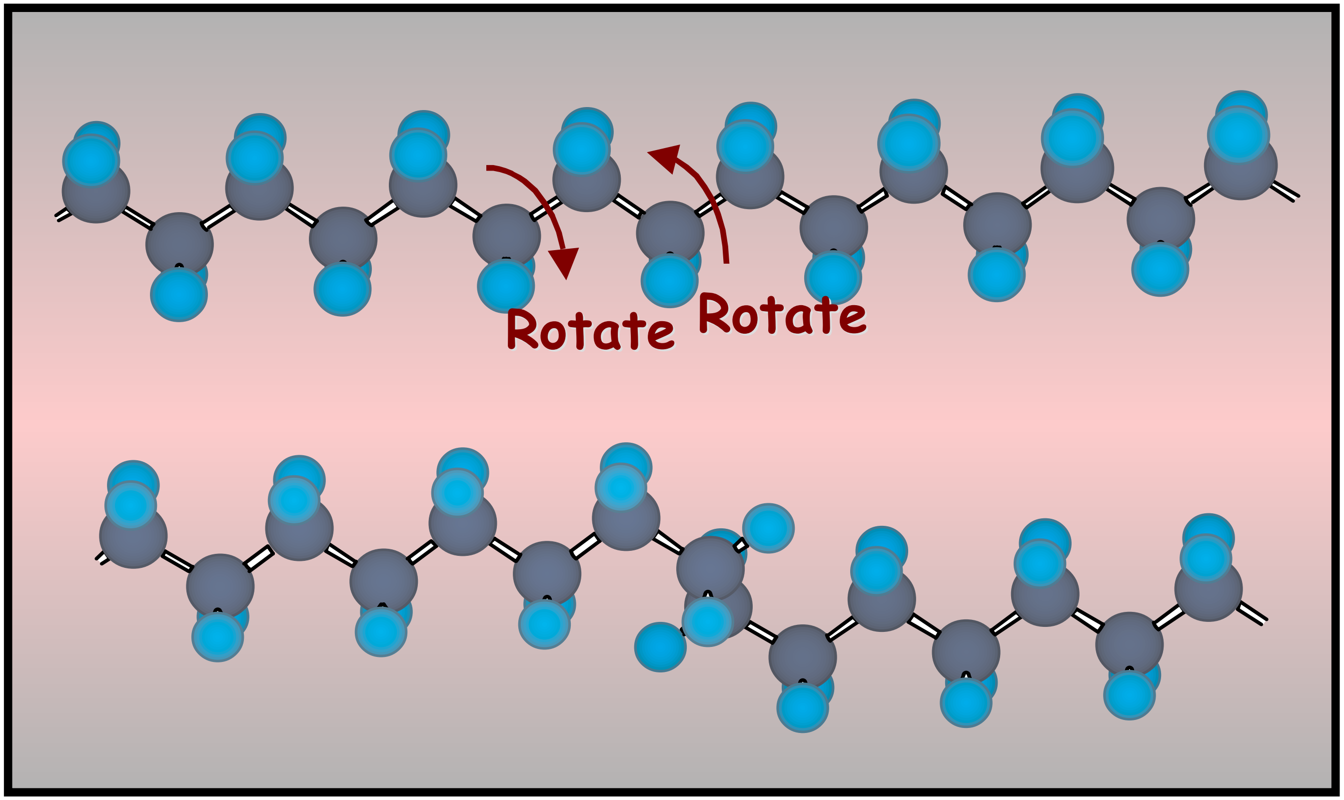
Free Volume



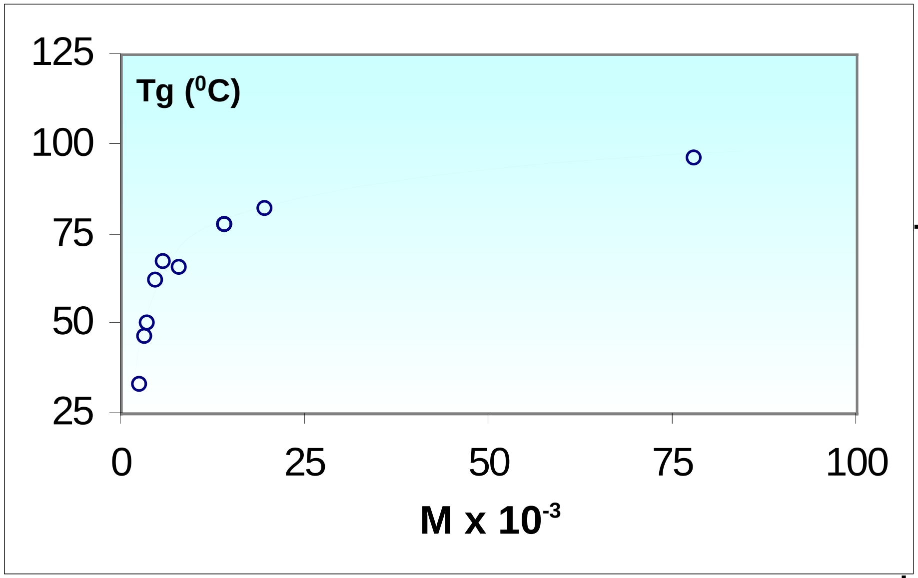
Motion in Polymers - The Dynamics of Polymer Chains



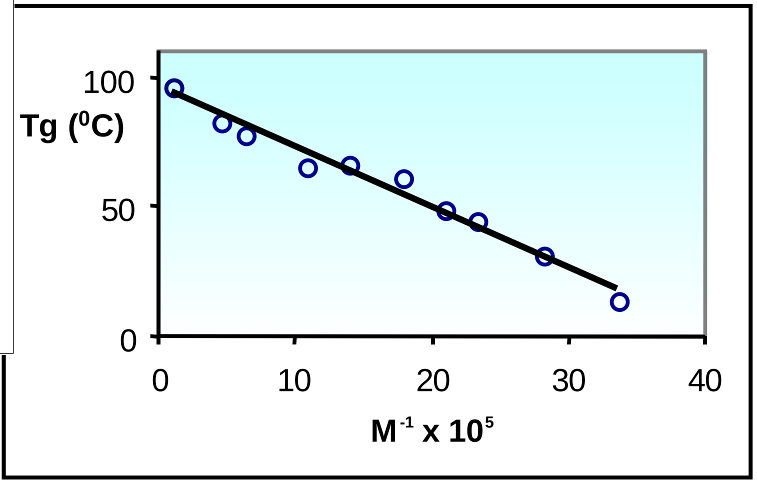
Motion in Polymers - The Dynamics of Polymer Chains



Factors that Affect the Tg
Molecular Weight



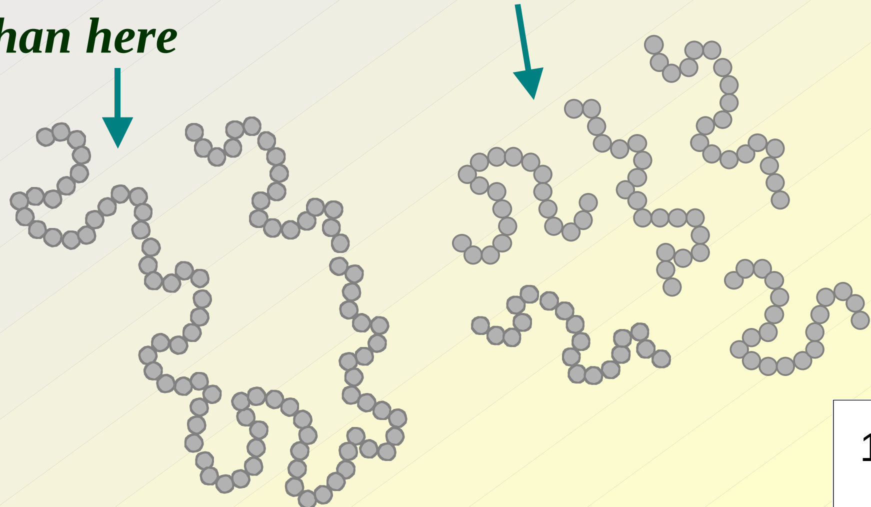
$$T_g = T_g^{\infty} - \frac{K}{\overline{M}_n}$$

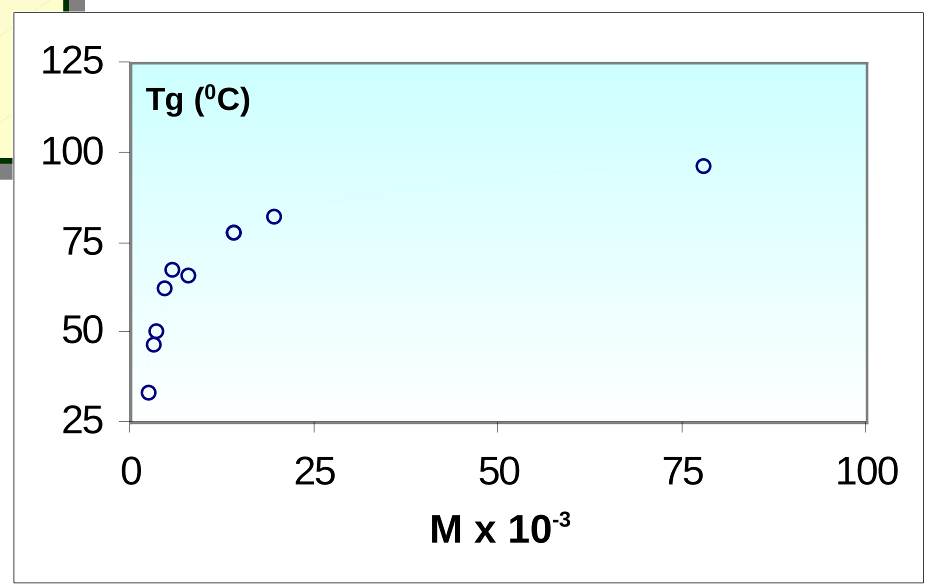


Redrawn from the data of T.G. Fox and P.J. Flory,
J.Appl. Phys., 1950, 21, 581

Factors that Affect the Tg
Molecular Weight

Same total number of beads, but there are more ends here than here





Factors that Affect the Tg
Chemical Structure

$- CH_2 - CH -$
$\quad\quad\quad\;\; | $
$\quad\quad\quad CH_3$

Atactic Polypropylene

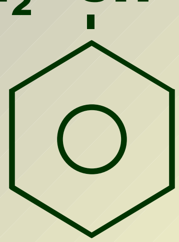
$T_g \sim ?$

$- CH_2 - CH_2 -$

Polyethylene

$T_g \sim ?$

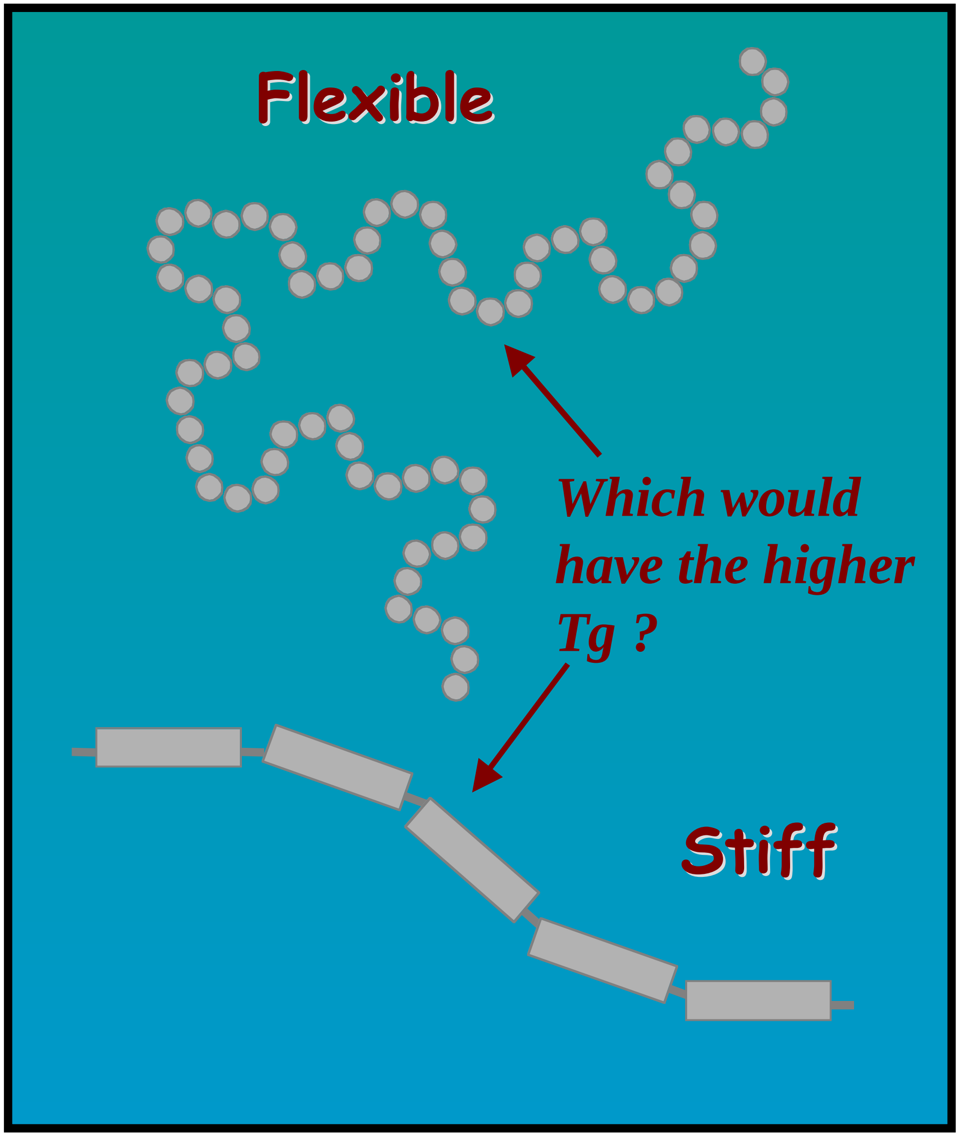
$- CH_2 - CH -$



Atactic Polystyrene

$T_g \sim ?$

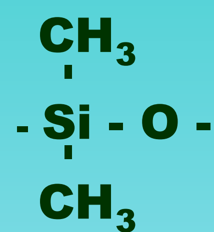
Factors that Affect the Tg
Chain Stiffness



Chain Stiffness

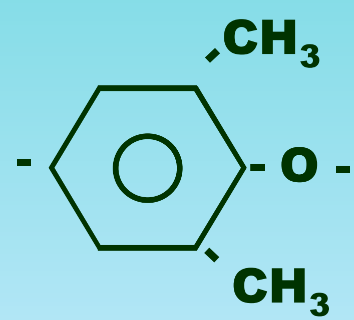
$- CH_2 - CH_2 -$ $T_g \sim -80^0C$

Polyethylene



$T_g \sim -120^0C$

Poly (dimethyl siloxane)



$T_g \sim 200^0C$

Poly (phenylene oxide)

Bulky Substituents

$-CH_2-CH_2-$

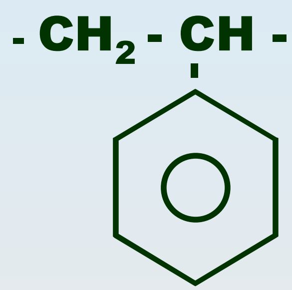
Polyethylene

$T_g \sim -80^0C$

$-CH_2-CH-$ (with CH_3 on CH)

Atactic Polypropylene

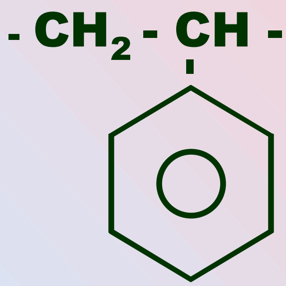
$T_g \sim -10^0C$



Atactic Polystyrene

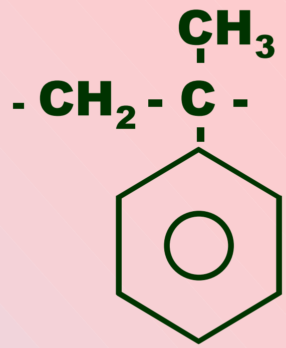
$T_g \sim 100^0C$

Bulky Substituents



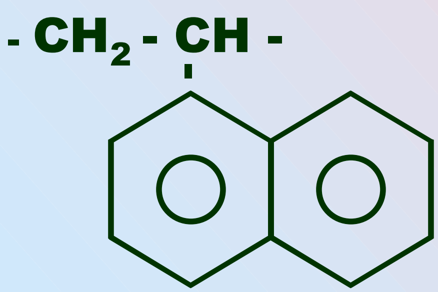
T_g ~ 100^0C

Atactic Polystyrene



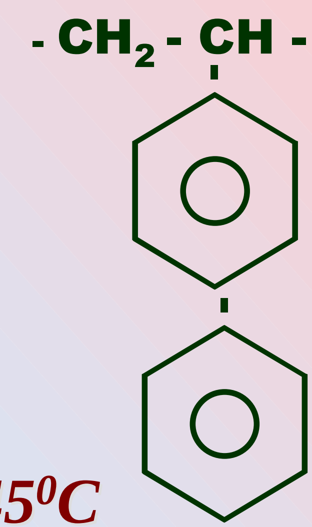
T_g ~ 175^0C

Atactic
Poly(α-methyl styrene)



T_g ~ 135^0C

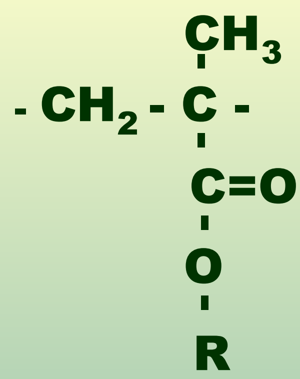
Atactic
Poly(1-vinyl naphthalene)



T_g ~ 145^0C

Atactic Poly(vinyl biphenyl)

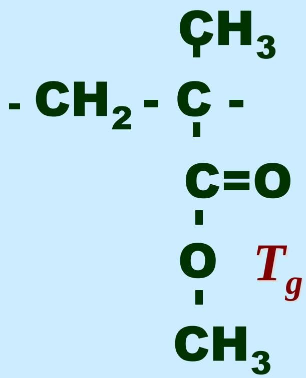
Flexible Substituents



R = Methyl - CH_3
R = Ethyl - CH_2 - CH_3
R = Propyl - CH_2 - CH_2 - CH_3
R = Butyl - CH_2 - CH_2 - CH_2 - CH_3
etc.

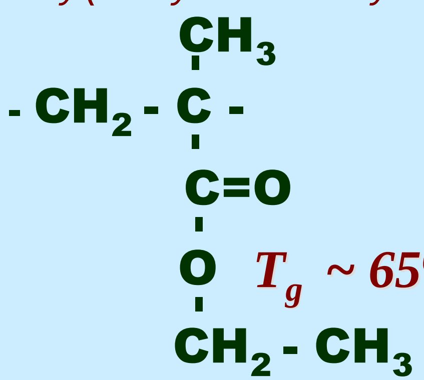
Flexible Substituents

Poly(methyl methacrylate)



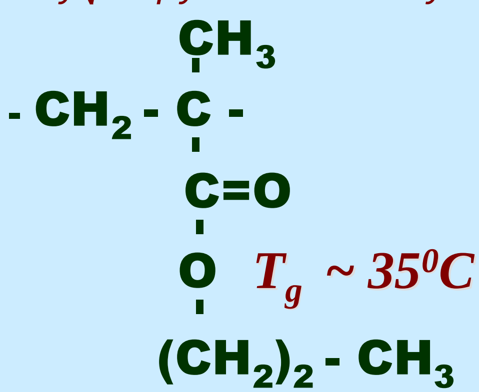
$T_g \sim 105^0C$

Poly(ethyl methacrylate)



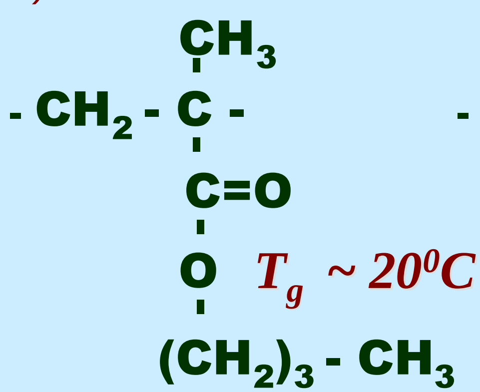
$T_g \sim 65^0C$

Poly(propyl methacrylate)



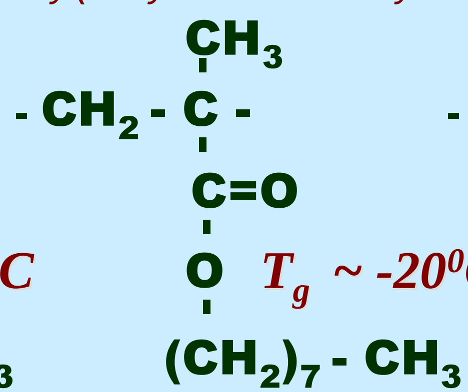
$T_g \sim 35^0C$

Poly(butyl methacrylate)



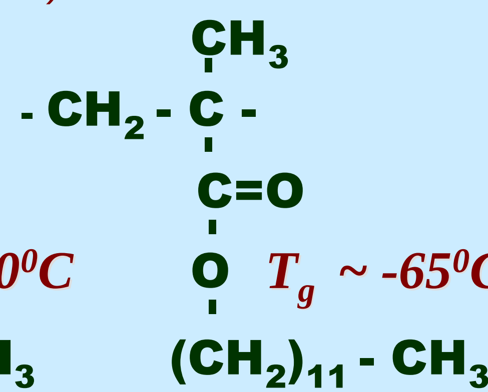
$T_g \sim 20^0C$

Poly(octyl methacrylate)



$T_g \sim -20^0C$

Poly(dodecyl methacrylate)



$T_g \sim -65^0C$

The Effect of Intermolecular Interactions

$- CH_2 - \underset{|}{C}H -$
$\quad\quad\quad CH_3$

Atactic Polypropylene

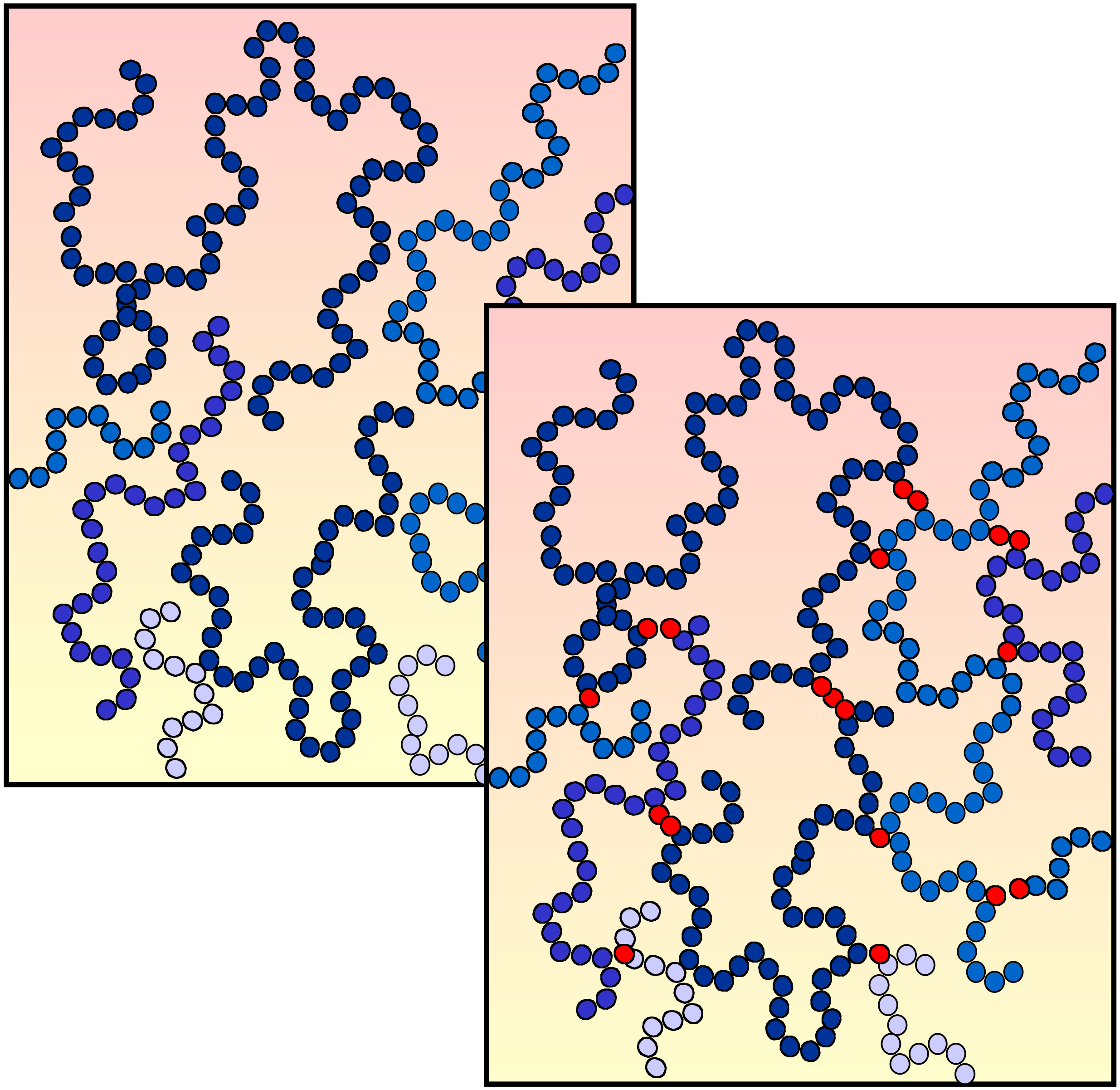
$T_g \sim -10^0C$

$- CH_2 - \underset{|}{C}H -$
$\quad\quad\quad Cl$

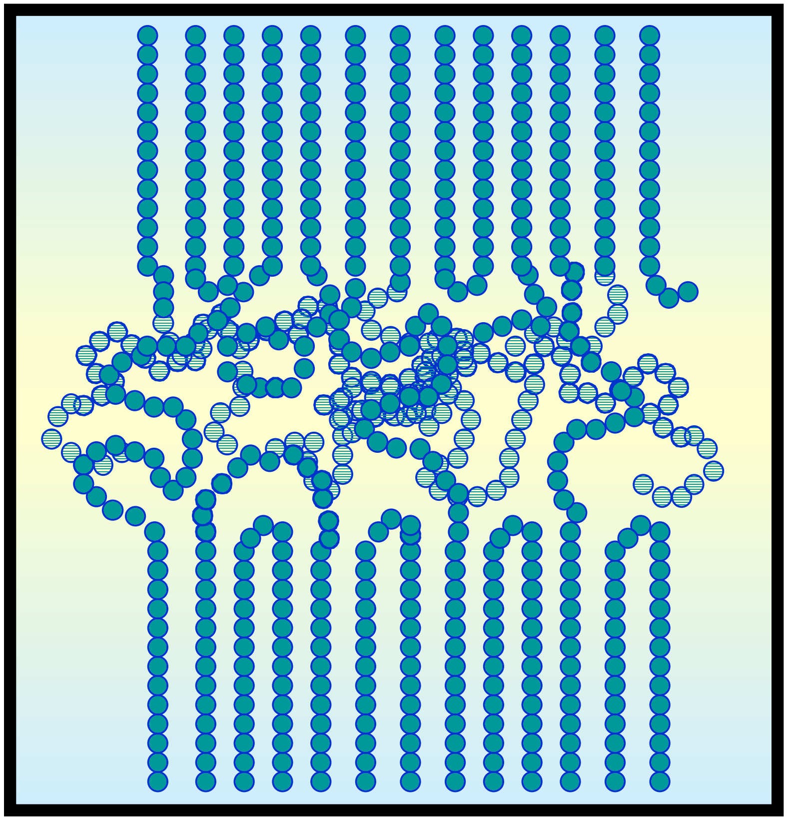
PVC

$T_g \sim +87^0C$

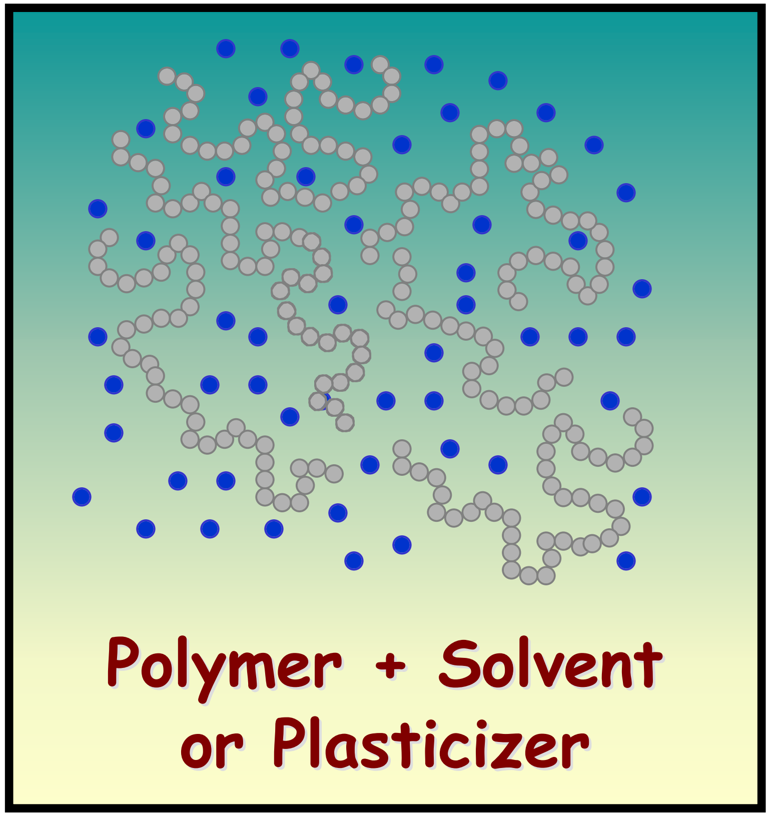
The Effect of Cross - Linking



The Effect of Crystallization



The Effect of Diluents



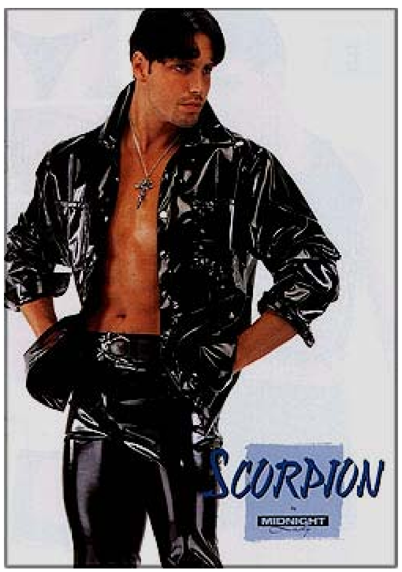
Plasticized PVC

Cable sheathing.

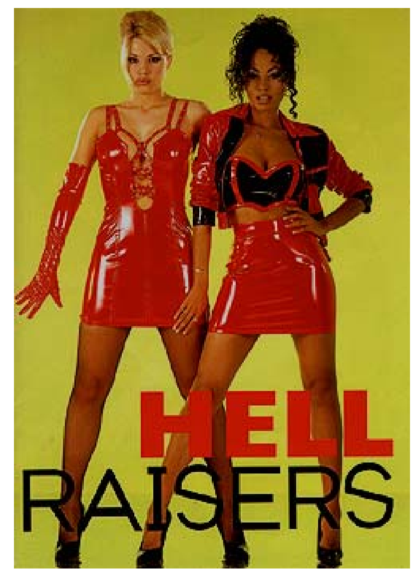
PVC bottles.

PVC “leather”.

Cling wrap.



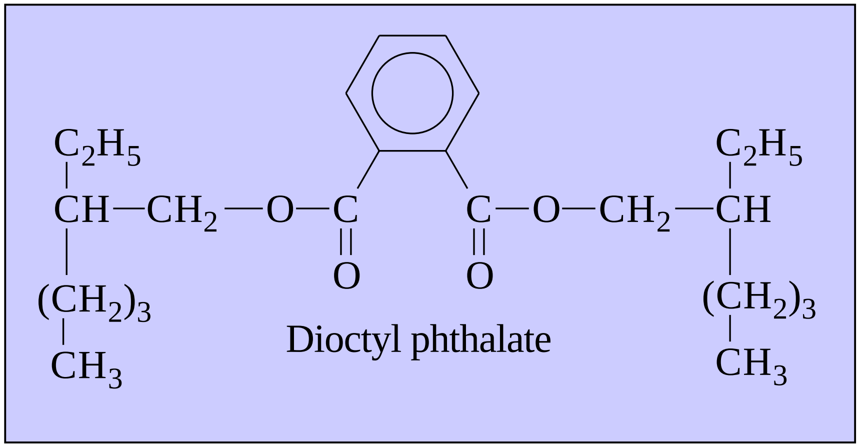
PVC apparel.



PVC apparel.

Plasticized PVC

Soft plasticized PVC toys



Dioctyl phthalate

A water filled plasticized PVC teething ring.

PVC – "The Poison Plastic"?

Some pigmented PVC compounds

If Greenpeace and similar organizations had their druthers PVC (and ultimately, chlorine) would be banned! Why you may ask? To quote a "fact sheet" entitled *"The Poison Plastic"* published by Greenpeace (www.greenpeace.org):

"Most common plastics pose serious threats to human health and the environment. The problems of plastics include extreme pollution from production, toxic chemical exposure during use, hazards from fires, and their contribution to the world's growing waste crisis. But one plastic stands alone; PVC, throughout its lifetime, is the most environmentally damaging of all plastics."

Of course, it is not difficult to find an authoritative opinion that takes the opposite view. For example, in a chapter on PVC in his 1994 book, *"The Consumer's Good Chemical Guide"*, John Emsley, Science Writer in Residence, Department of Chemistry at Cambridge University, states, *"As far as I am aware, no member of the public has ever been harmed by PVC, and many people owe their lives to it. It is time we learned to live in peace with a rather wonderful plastic."* The Commonwealth Scientific and Industrial Research Organization of Australia concluded in 1998, "- - - *the balance of evidence suggests that there is no alternative material to PVC in its major product applications that has less overall effect on the environment."*