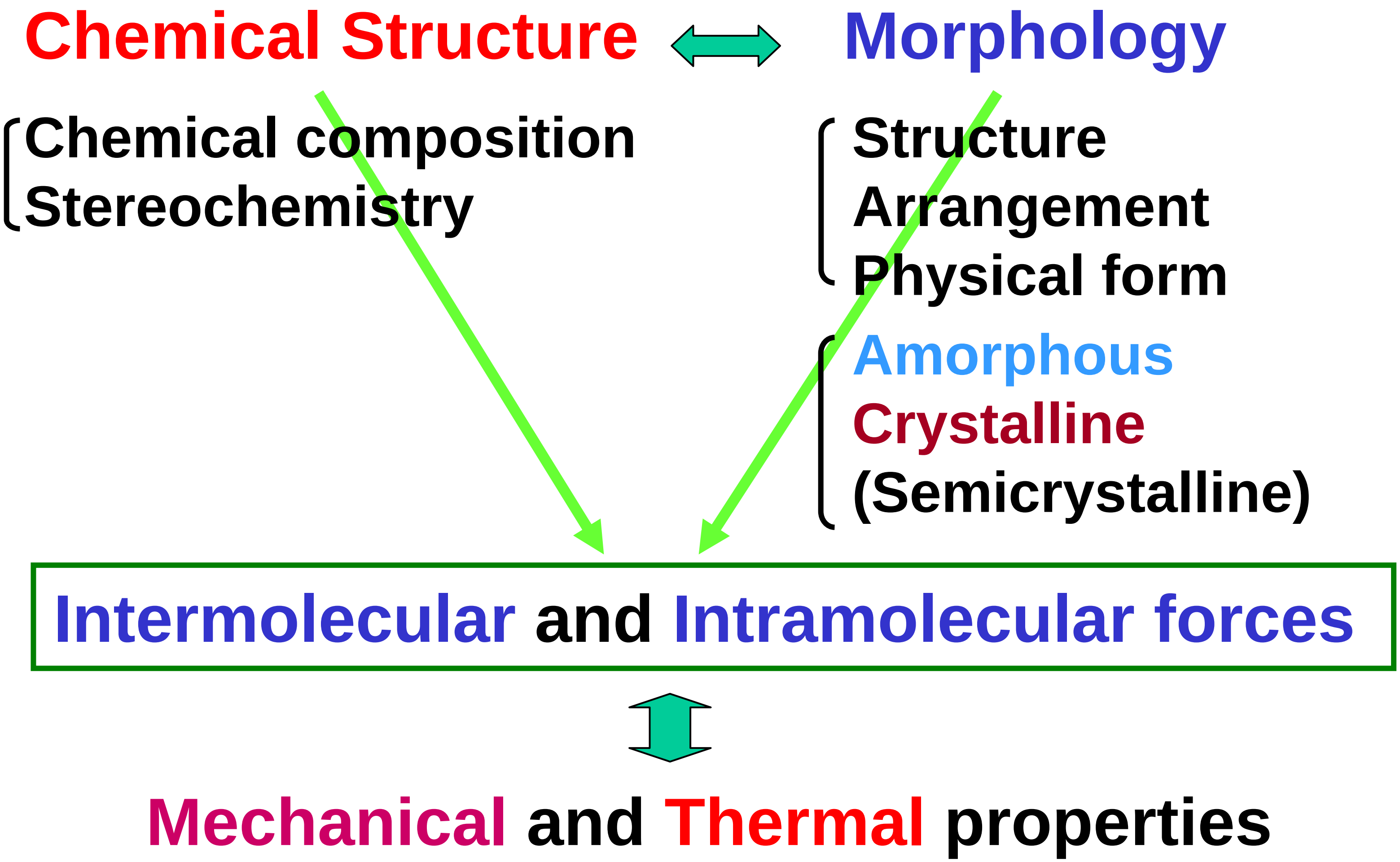
Chapter 4. Chemical Structure and Polymer Properties



Chemical Structure ⟷ **Morphology**

Chemical Structure:
- Chemical composition
- Stereochemistry

Morphology:
- Structure
- Arrangement
- Physical form
  - Amorphous
  - Crystalline
  - (Semicrystalline)

Intermolecular and Intramolecular forces

↕

Mechanical and Thermal properties

4.2. Fabrication Methods

Molding, extrusion, casting: Three basic techniques

A) Compression molding (Fig 4.1)

1) Thermosetting polymers

2) In situ crosslinking in the mold cavity

3) Partially cured (B-stage) $\xrightarrow[\Delta]{}$ Fully cured (C-stage)

↓

Flow under pressure

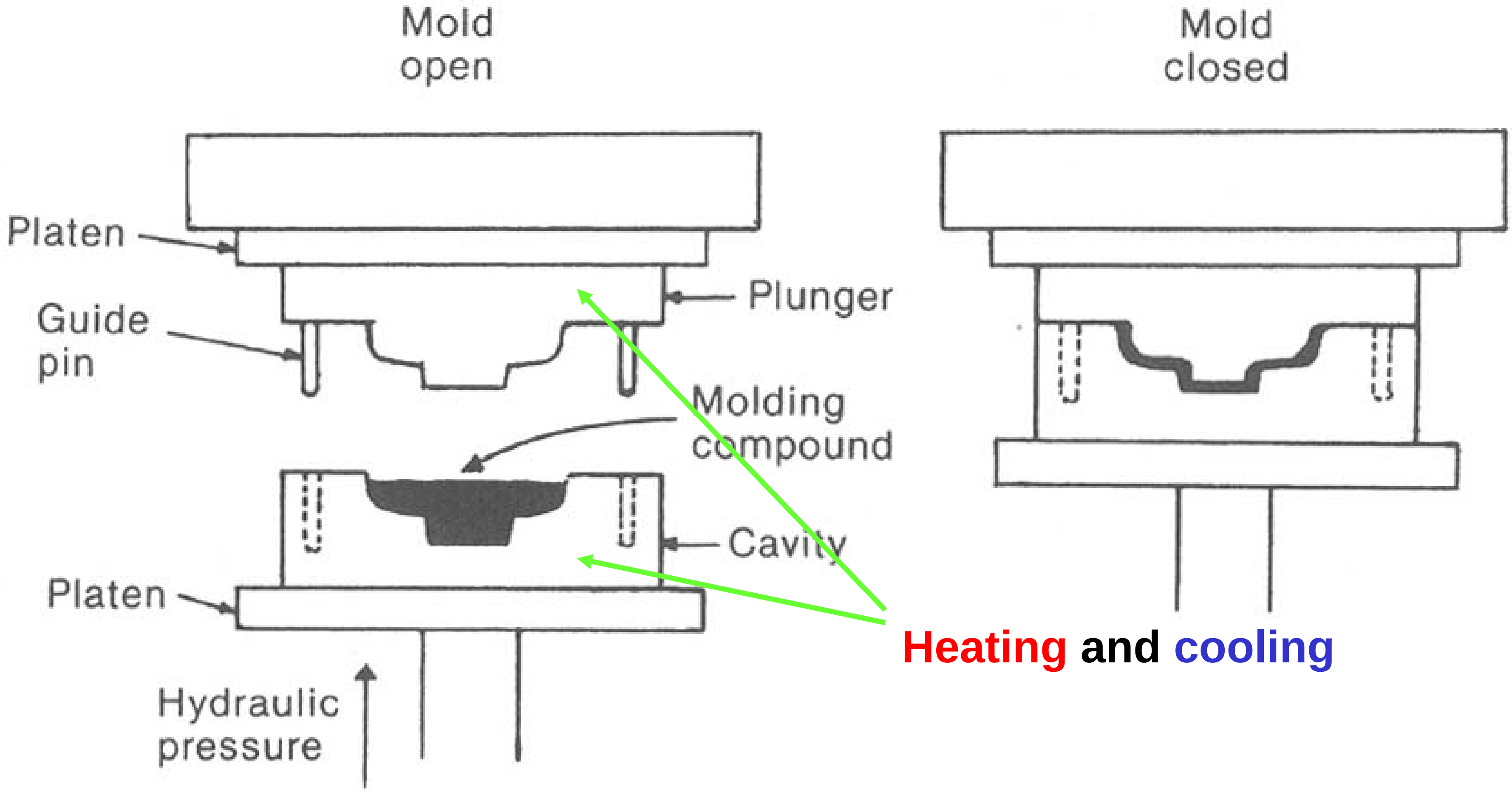
4) Preform = Prepreg ← Polymeric binder + Reinforcing material (glass fiber)

+

Liquid polymer

→ FRP (Fiber-Reinforced Plastic)

Fig 4.1 Compression molding



Heating and cooling

B) Injection molding (Fig 4.2)

1) Thermoplastics

2) Screw is used to feed the polymer to the mold

3) Injection molding is faster than compression molding

C) Reaction injection molding (RIM) (Fig 4.3)

1) Themosetting polymers

2) Monomer or low-M.-W. polymeric precursor are mixed and injected into the mold

3) Reaction rates must be synchronized with the molding process

4) Advantages : Polymerization prior to molding eliminated. Energy requirements for handling of the monomers are much lower than those for viscous polymers.

D) Reinforced reaction injection molding (RRIM)

Reinforced fillers

Fig 4.2 Injection molding

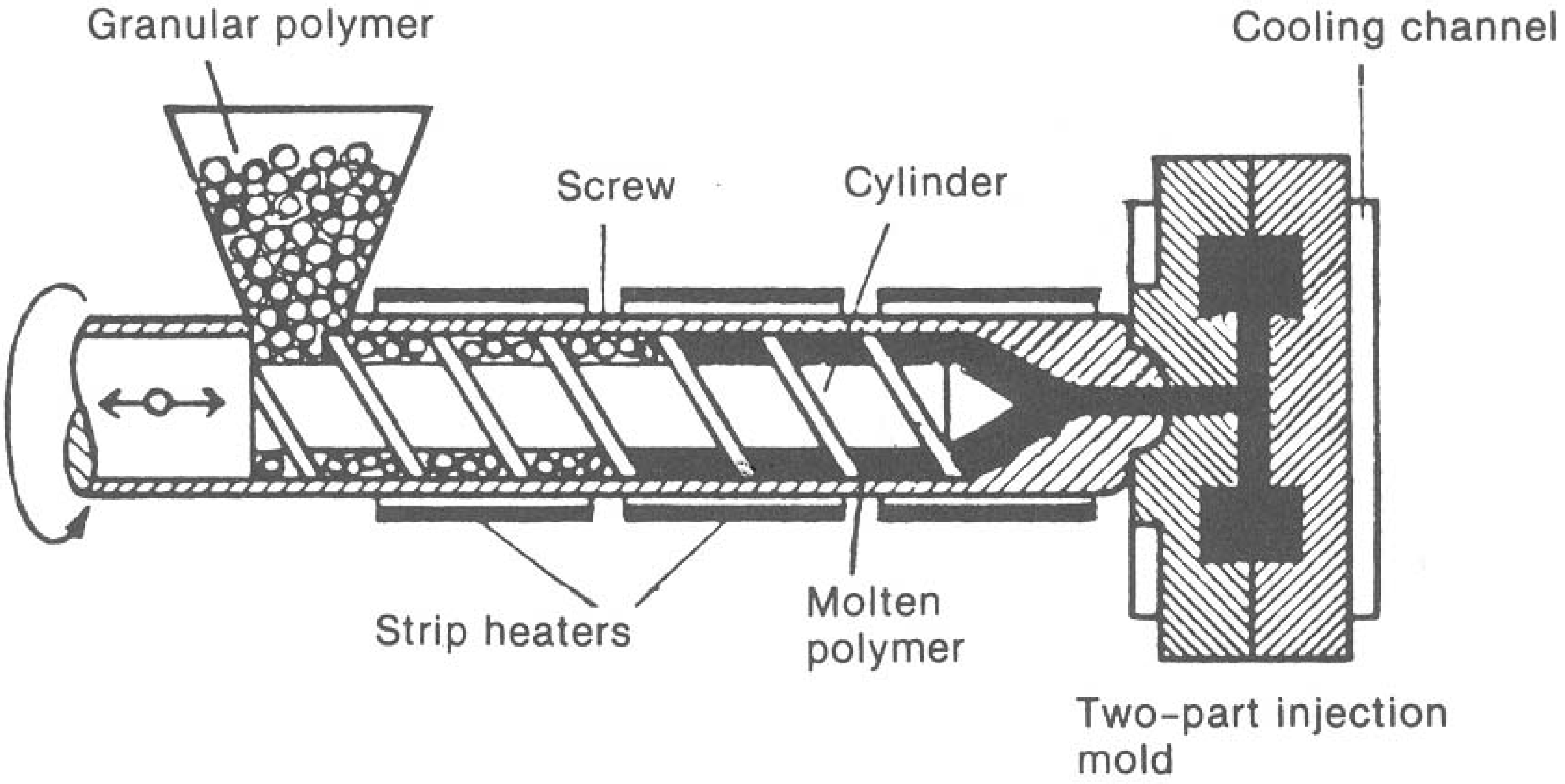
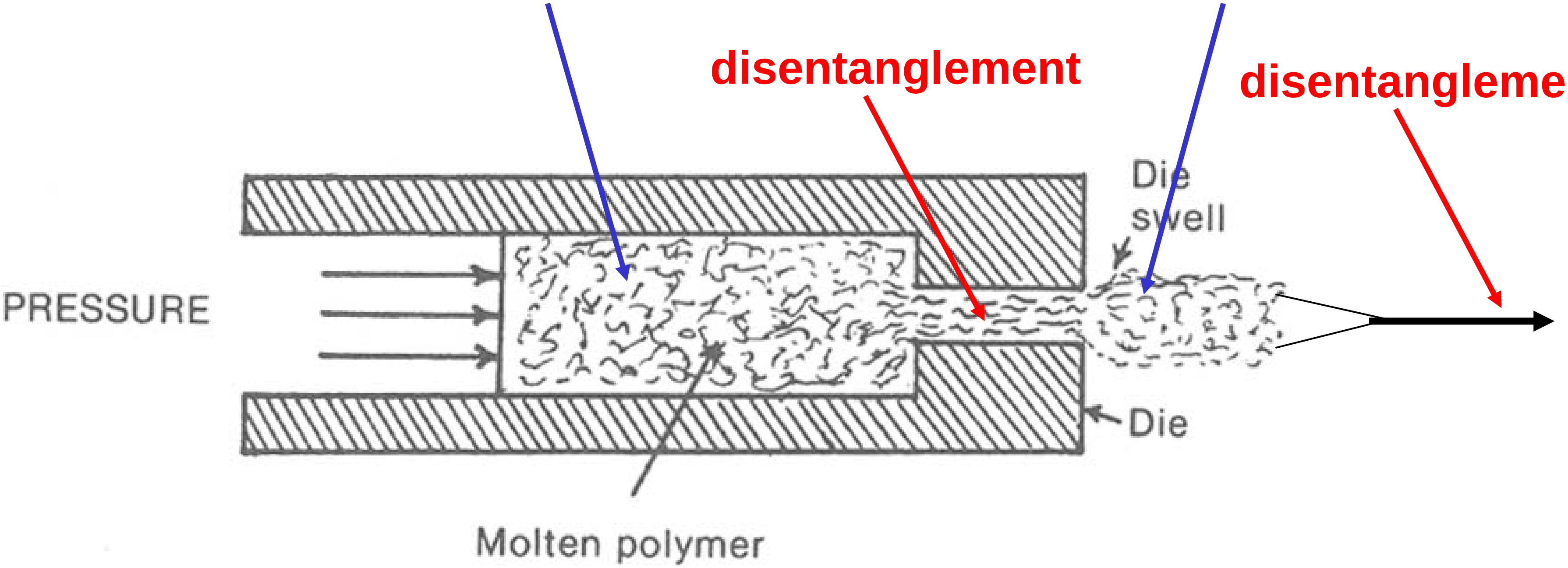


Fig 3.2 Polymer flow through a die orifice



elastic

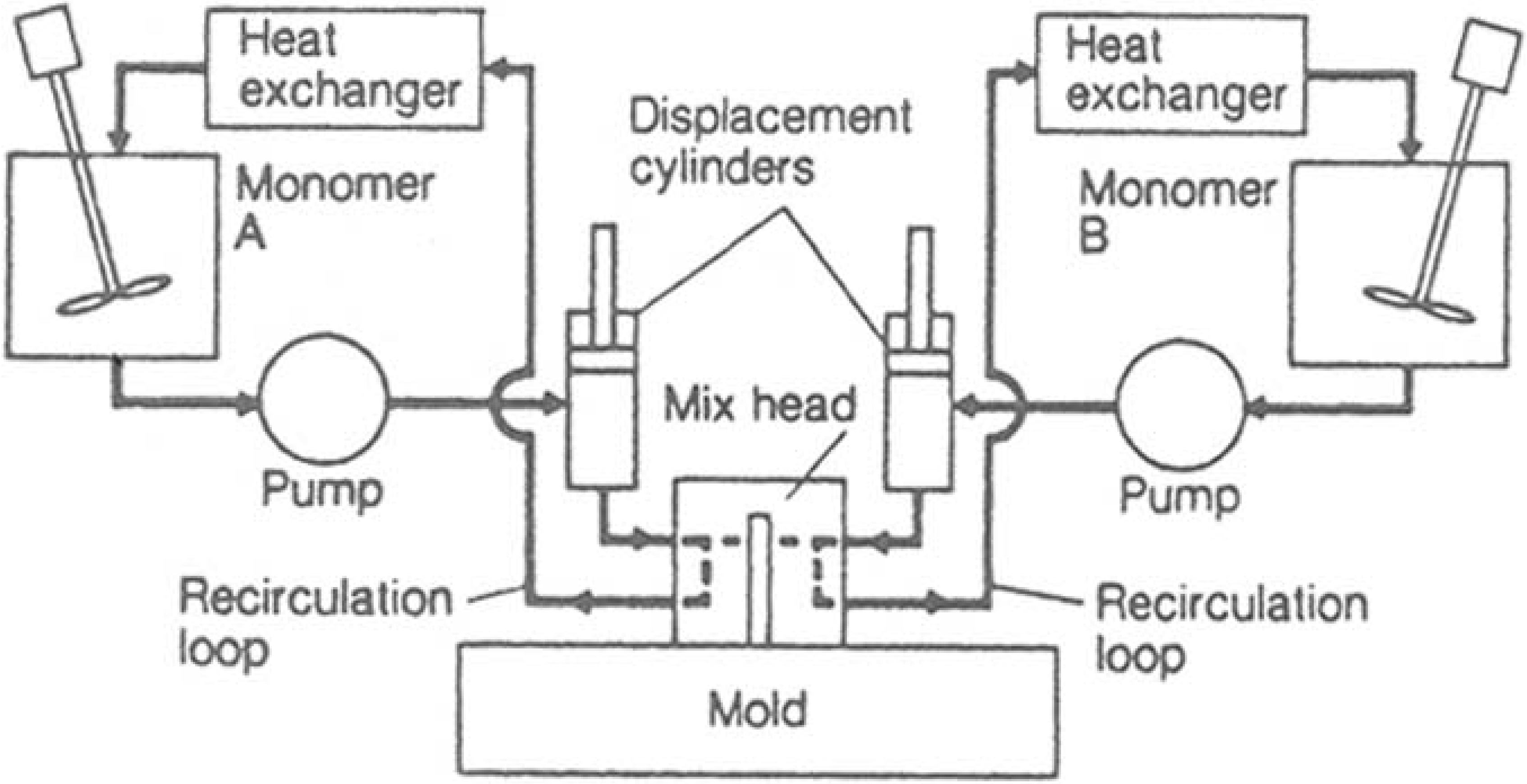
entanglement

reentanglement

disentanglement

disentanglement

Fig 4.3 Reaction injection molding (RIM)



E) Blow molding (Fig 4.4)

Manufacturing bottles

Polymer tubing (parison) is blown by compressed air or drawn by vacuum into the shape of the mold.

F) Casting

Pouring molten polymer into a mold and allowing the product to cool

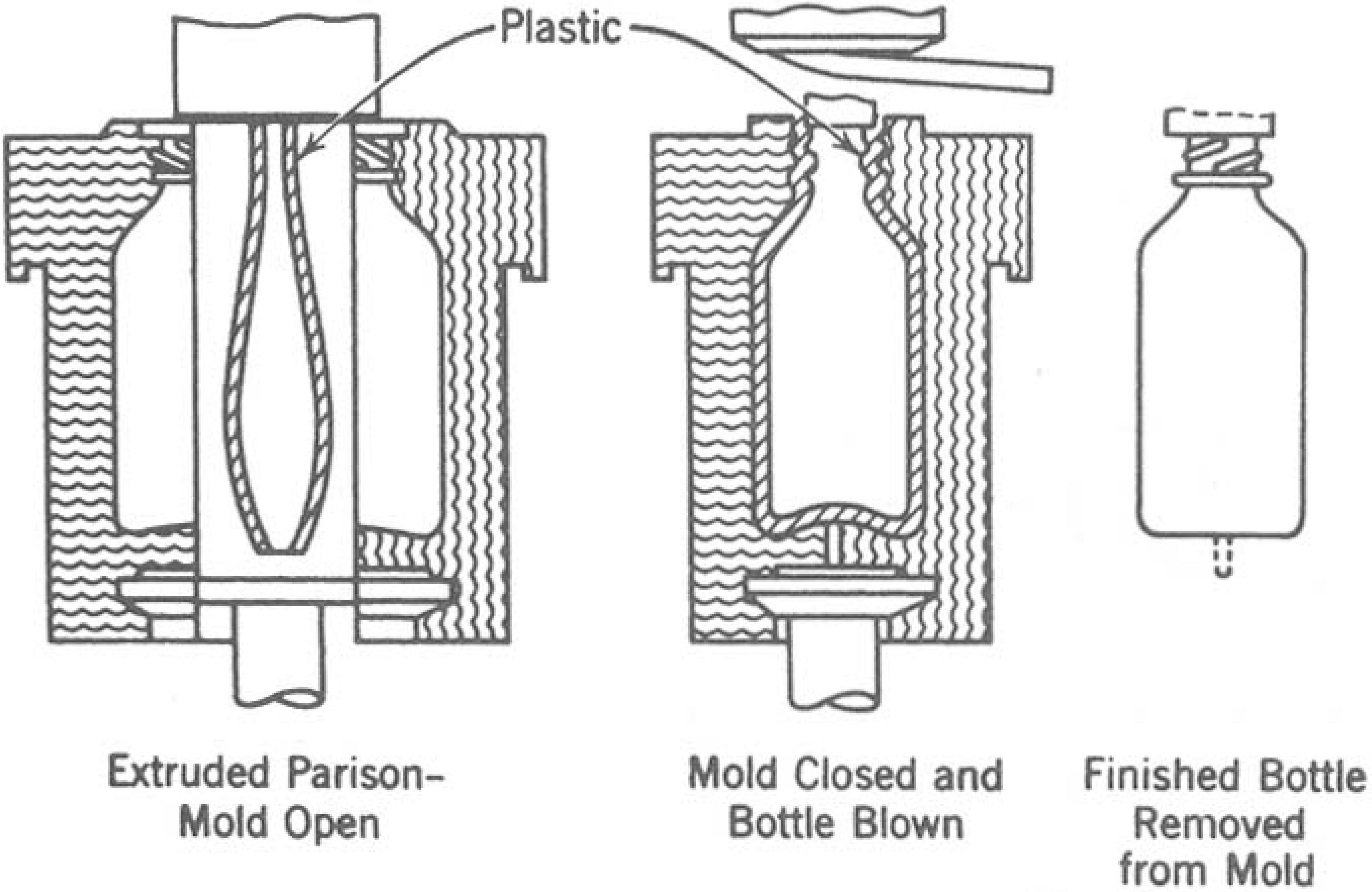
G) Extrusion

Forcing compacted, molted polymer through a die shaped to give the desired object

Extruder resembles the injection molding apparatus (Fig 4.2) except that the mold cavity is replaced with a die (Fig 3.2)

Useful for making elongated objects such as rods or pipes.

Fig 4.4 Blow molding



H) Polymer Films

By casting from solution

By passing polymer under high pressure between hot rollers (calendering)

By extrusion through a slit die or through a ring-shaped die

I) Fibers by spinning

Polymer is forced under pressure through a perforated plate (spinneret) (Fig 4.5)

Melt spinning: polymer melt

The melt is cooled by cold air

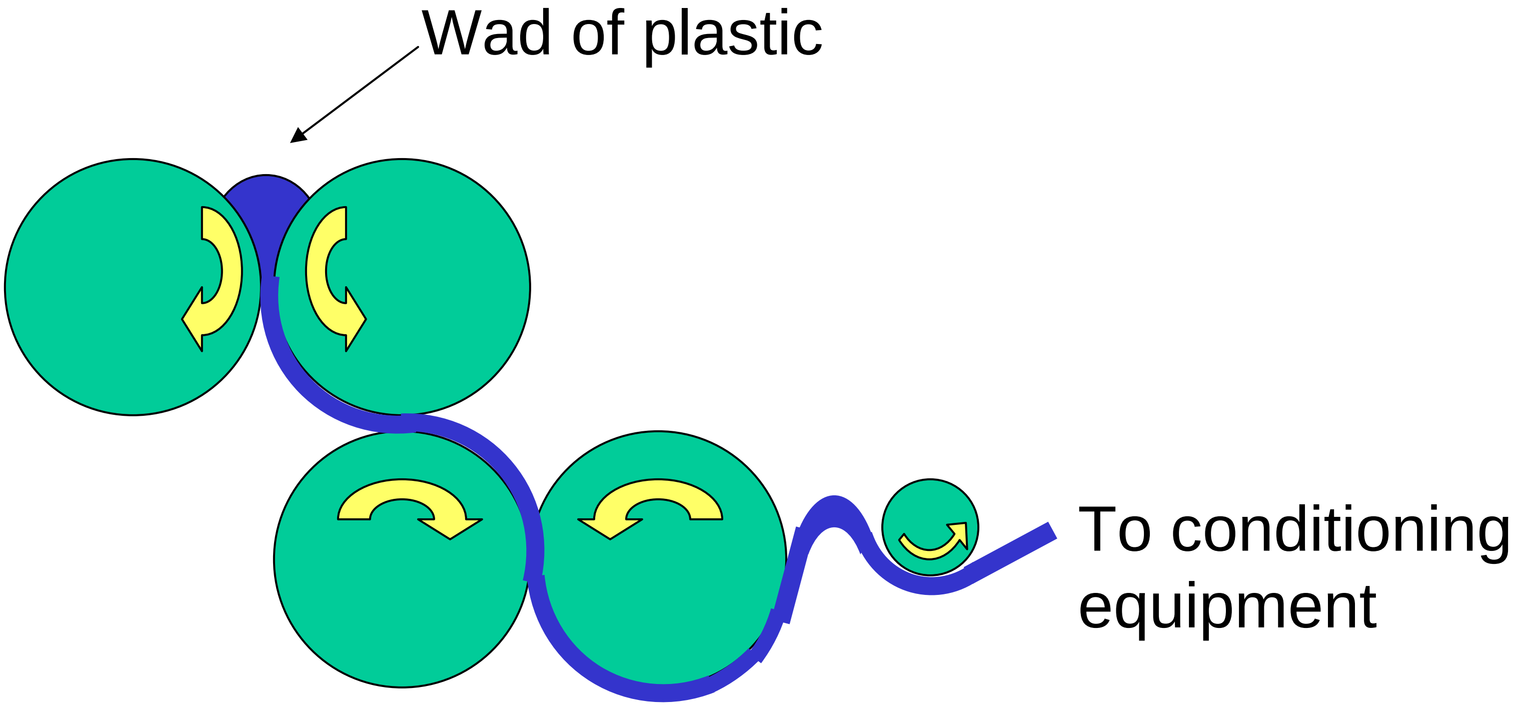
Dry spinning: polymer solution

The solvent is removed by evaporation with heat

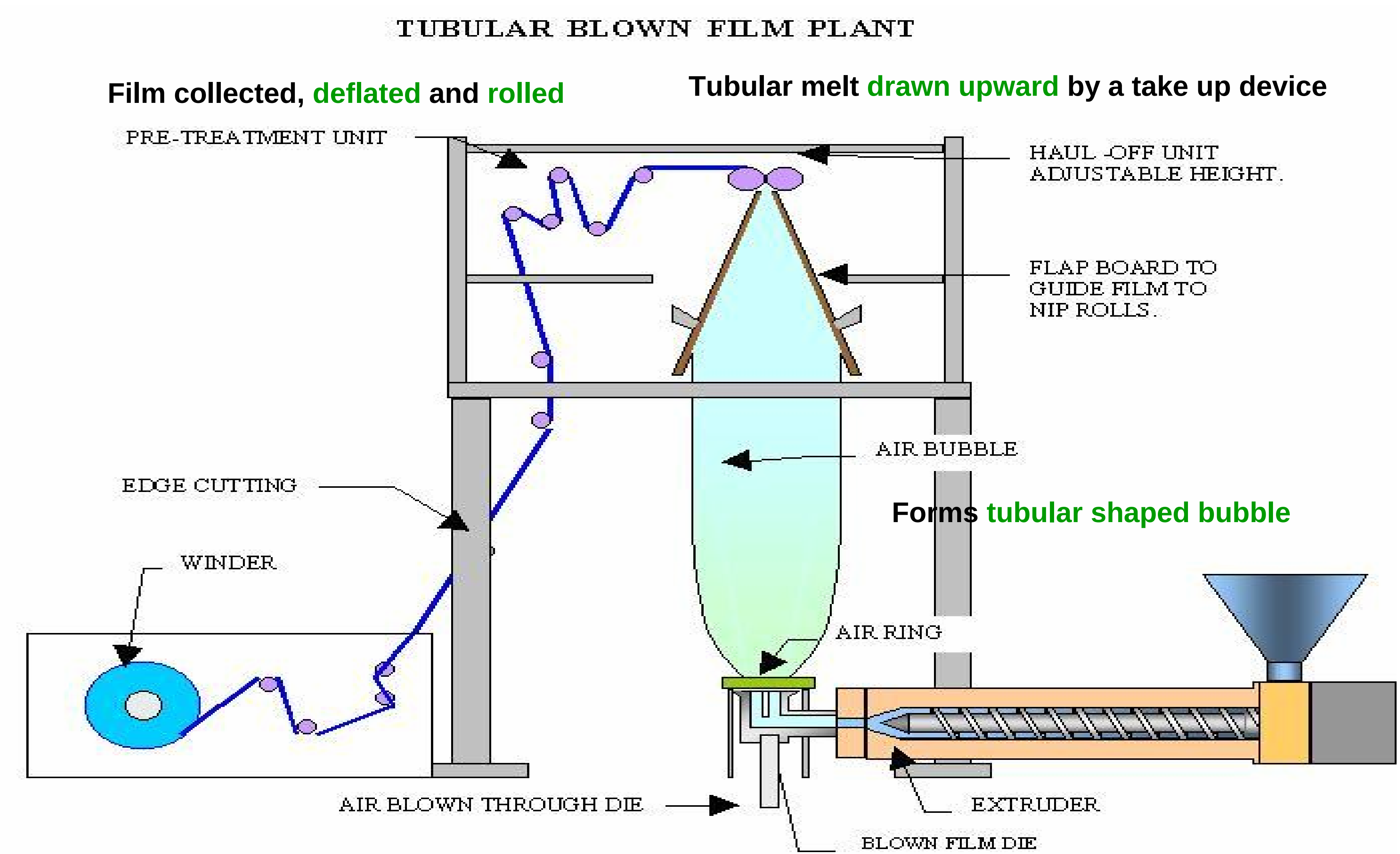
Wet spinning : polymer solution

The solvent is removed by leaching with another solvent

Four-roll calender



Blown film molding process



Film collected, deflated and rolled

Tubular melt drawn upward by a take up device

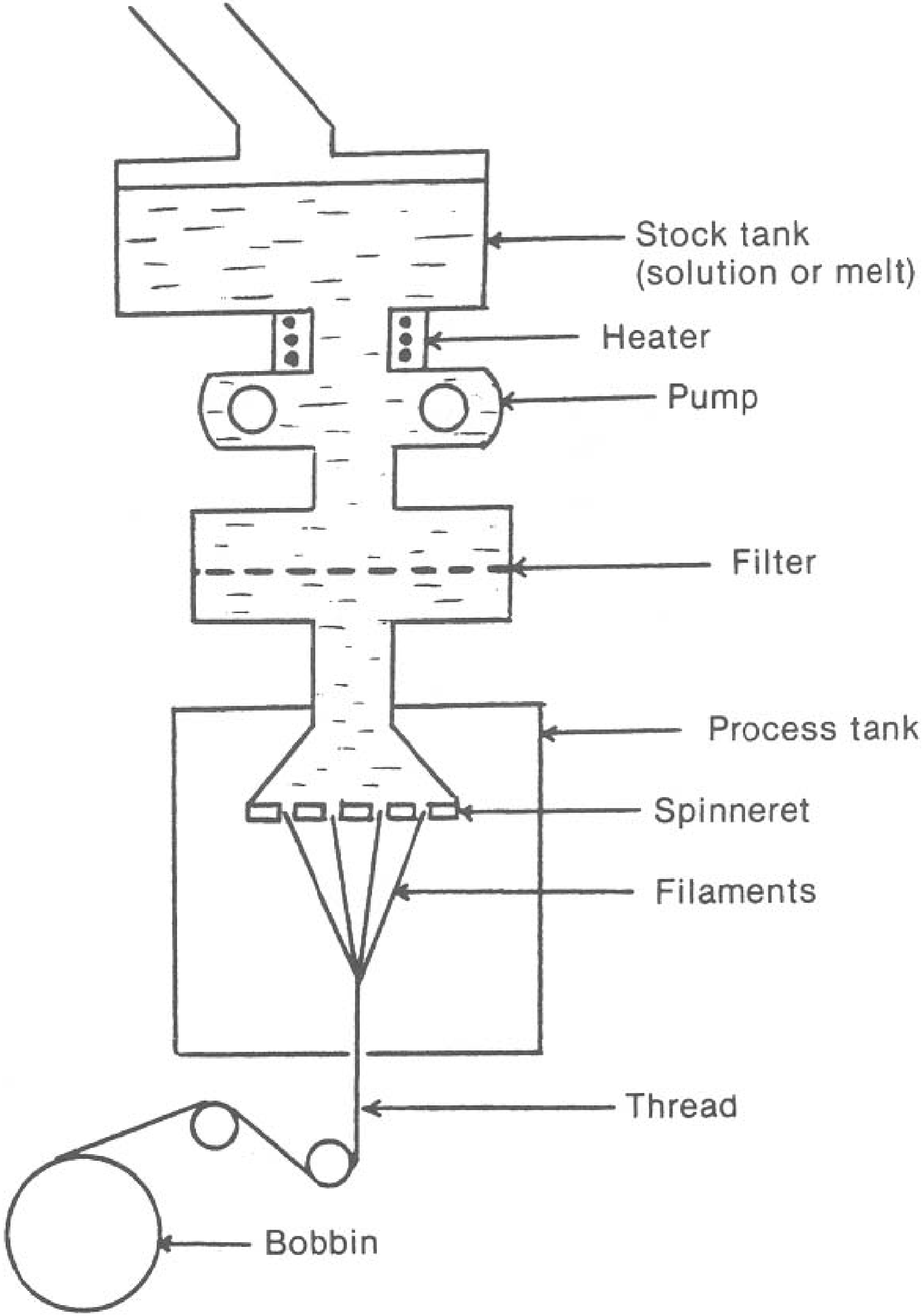
Forms tubular shaped bubble

Air at the center of die used for inflation of bubble and for cooling

Polymer melt extruded through an annular slit die

Fig 4.5 Fibers by spinning

Polymer is forced under pressure through a perforated plate (spinneret)



J) Polymeric foams : by incorporation a blowing agent into the polymer

Physical blowing agents :

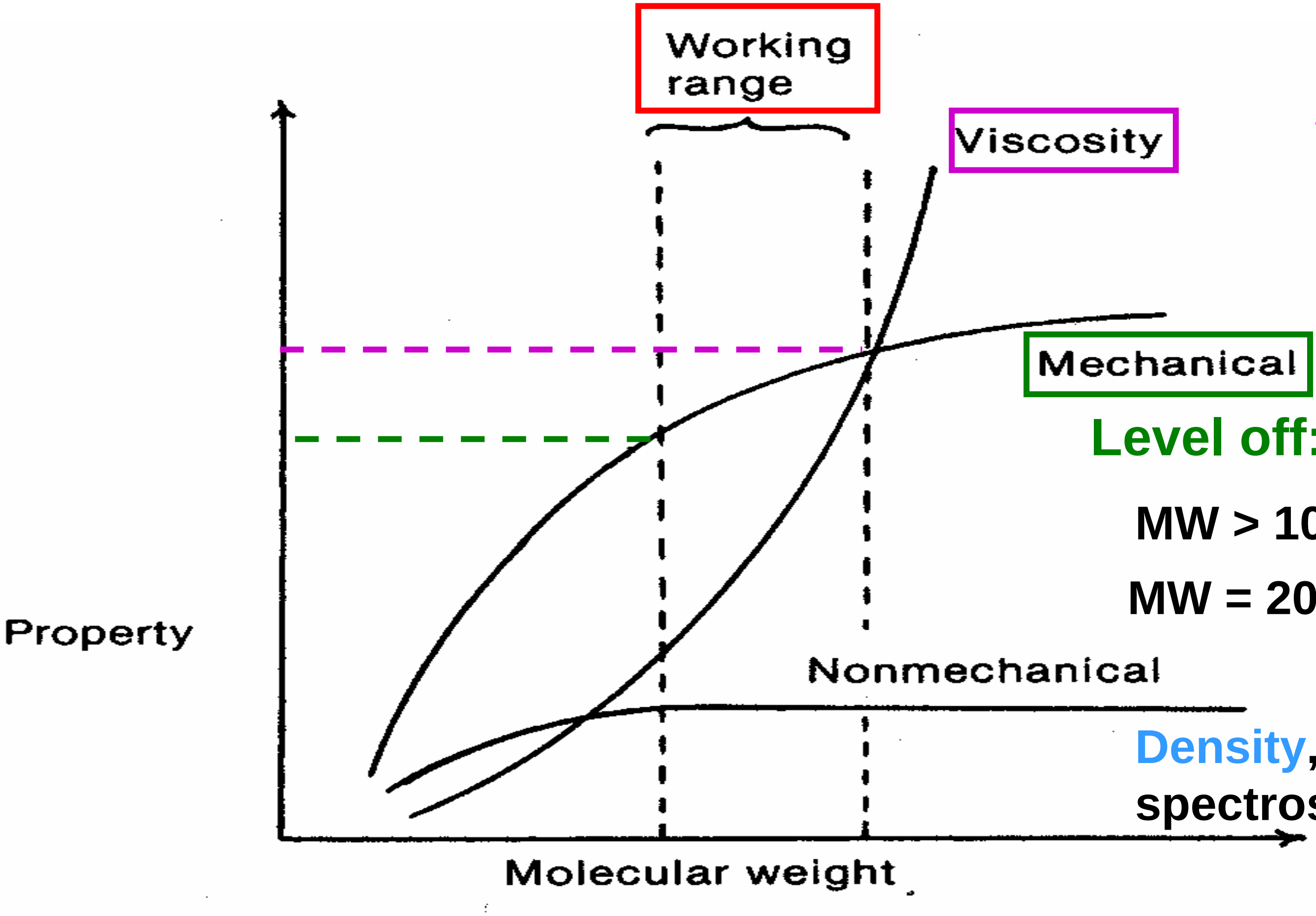
- Gases (air, nitrogen, carbon dioxide) dissolved in the molted polymer under pressure
- Low-boiling liquids (pentane) that vaporize on heating or under reduced pressure.
- Chlorofluorocarbon, once the blowing agents of choice, were discontinued after being linked to stratospheric ozone depletion

Chemical blowing agents :

Compounds that decompose on heating and give off nitrogen

4.3. Mechanical Properties

Fig 4.6. Dependence of **properties** on **M.W.**



$\eta \propto M^{3.4}$

Level off:

MW > 10^5 PE

MW = 20,000 – 50,000 polyamide

Density, refractive index, spectroscopic absorption

Tensile strength : Resistance to stretching

Compressive strength : Resistance to compression

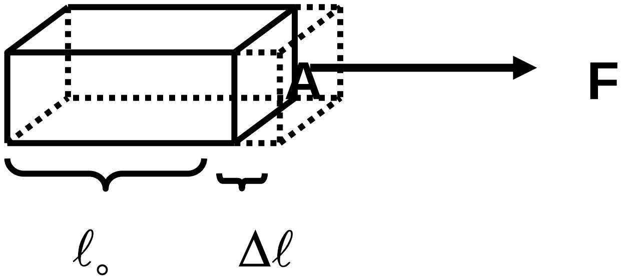
Flexural strength : Resistance to bending (flexing)

Impact strength : Resistance to sudden stress, like a hammer blow

Fatigue : Resistance to repeated applications of tensile, flexural, or compressive stress

Tensile stress (σ)

$$\sigma = \frac{F}{A}$$



where
- F = force applied
- A = cross-sectional area

Tensile strain (ε)

$$\varepsilon = \frac{\Delta\ell}{\ell_o}$$

where
- ℓ_o = original length
- $\Delta\ell$ = change in sample length

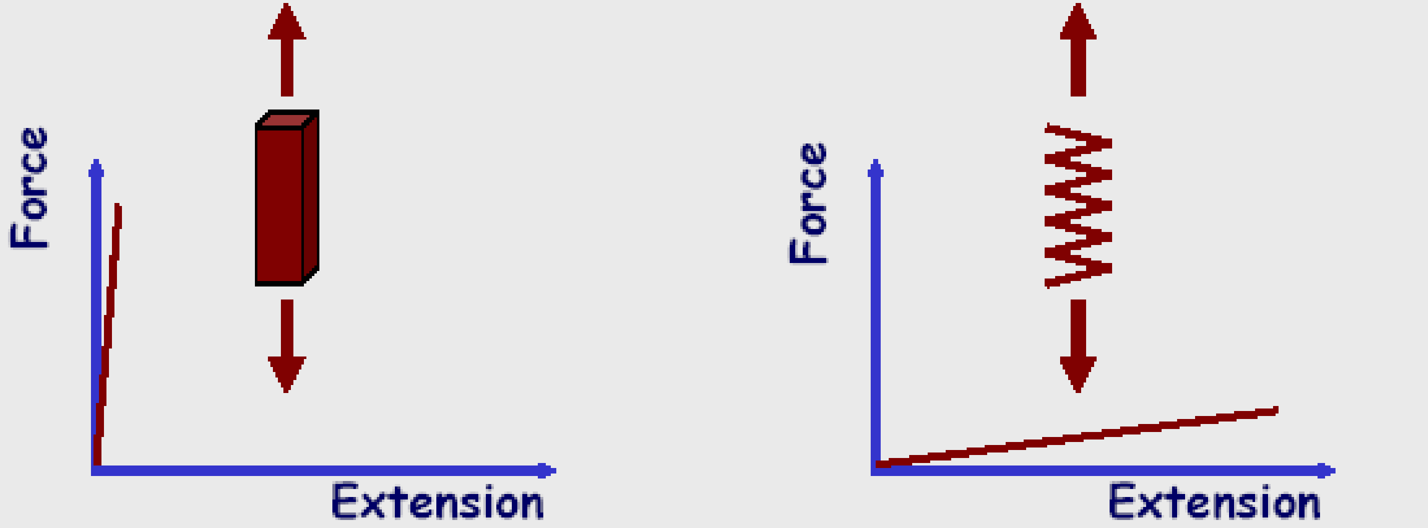
Tensile modulus (E) : resistance to tensile stress

$$E = \frac{\sigma}{\varepsilon}$$

Hooke's Law

$$\sigma = \mathbf{E}\varepsilon$$

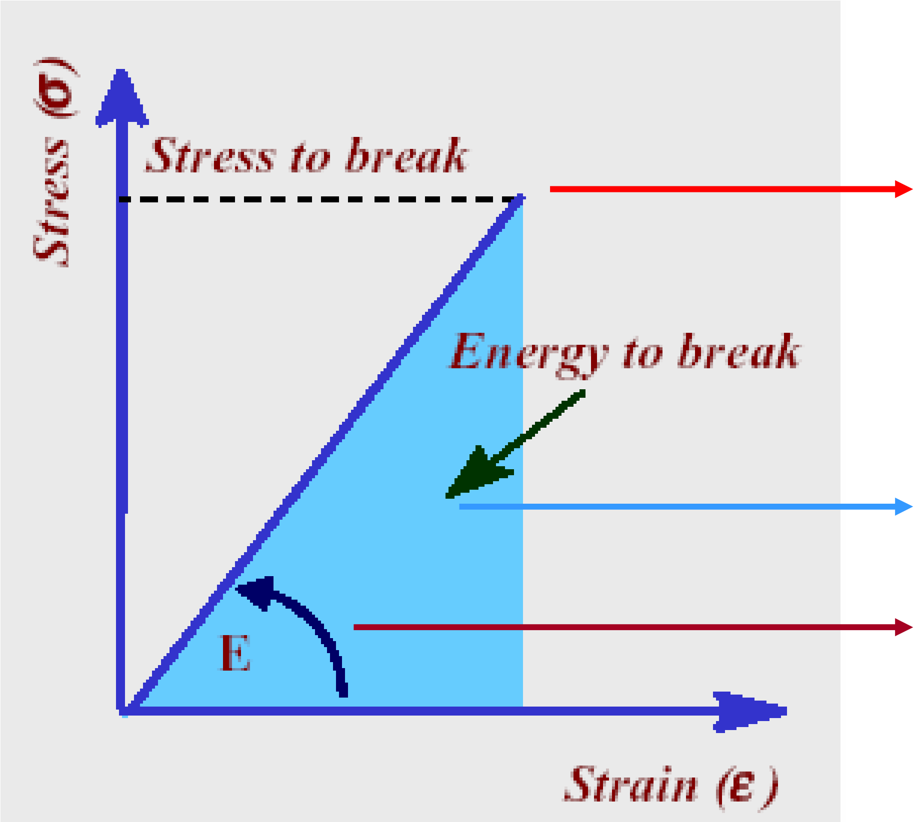
E = Young’s modulus



Questions : slope depends upon shape as well as the material being stretched - can we obtain a material property -stiffness ?

how linear is the response of real materials ?

Elastic Properties of Materials



Strength

Toughness

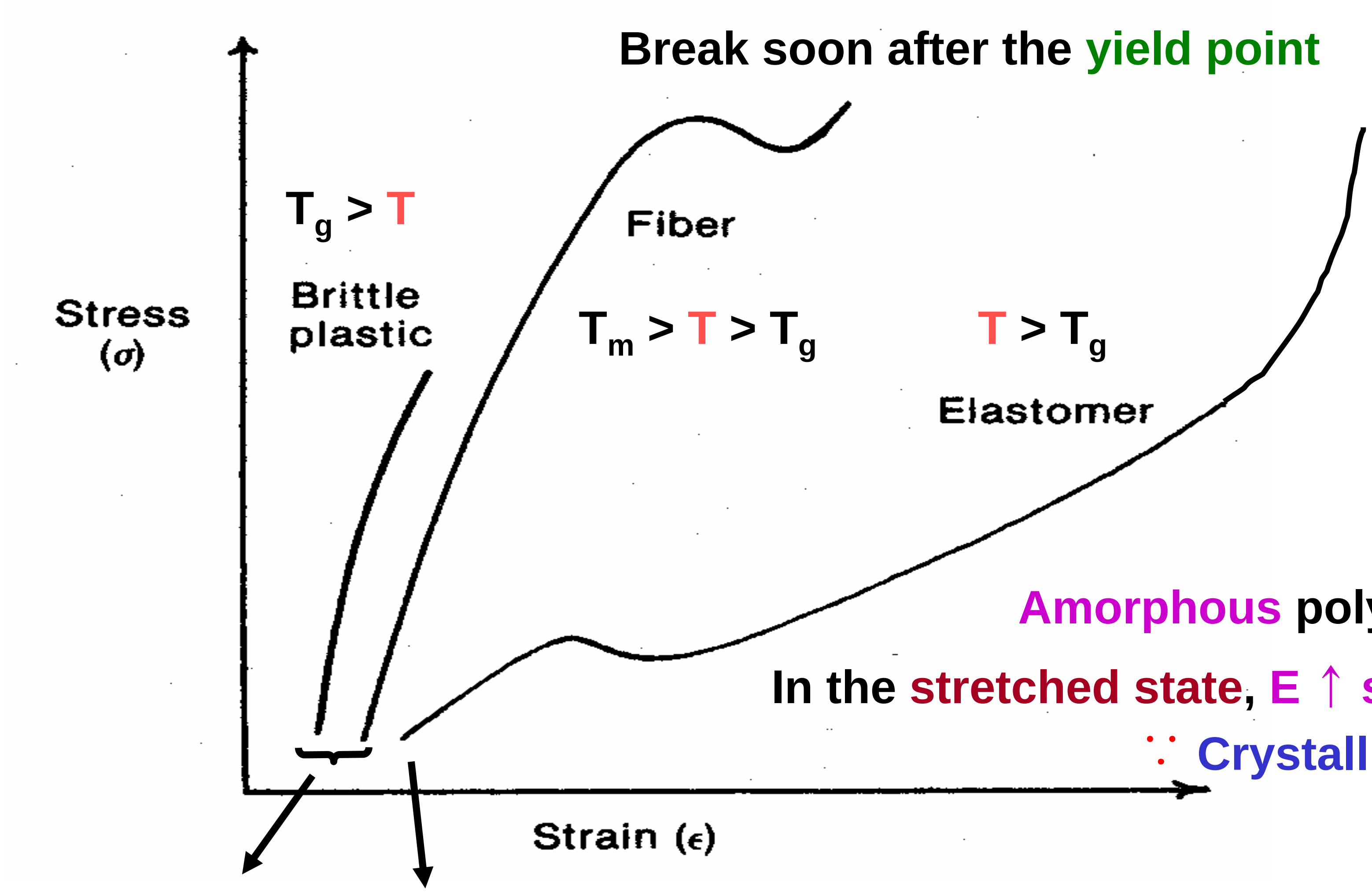
Stiffness

Fig 4.7. Tensile stress-strain behavior

Crystalline polymer

Greater stress and strain at break

Break soon after the yield point



Amorphous polymer

In the stretched state, E ↑ sharply

∵ Crystallinity ↑

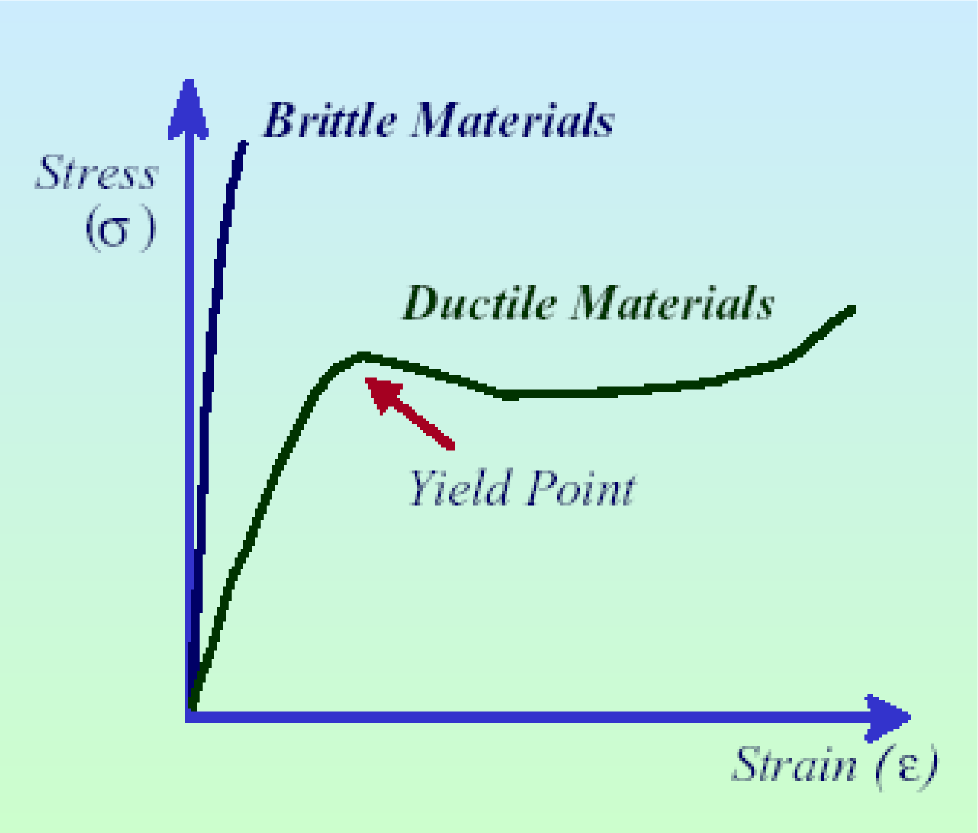
High E

Low E

Elastic and Plastic Deformation

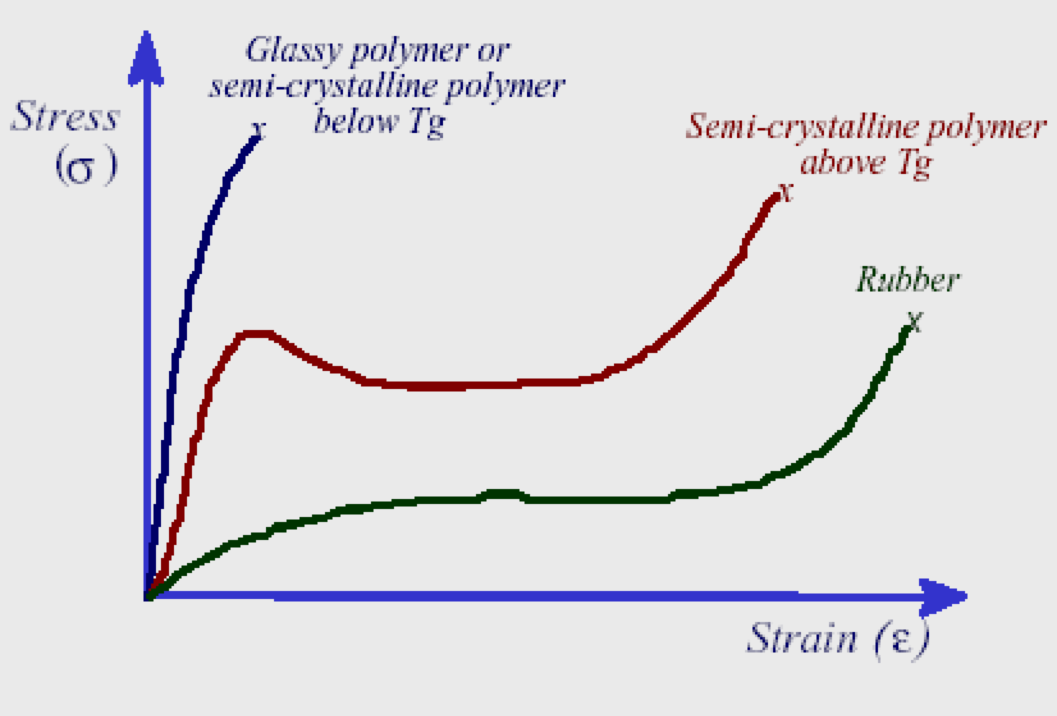
REAL MATERIALS

**Some brittle* materials, like ceramics, at first glance appear to be almost ideal in their behavior.
But, these materials are usually nowhere near as strong as they should be.**



Even more drastic deviations from ideal behavior are observed in ductile materials (e.g. many metals), where a yield point occurs well before fracture.

Stress/Strain of Polymers



For glassy and semi-crystalline polymers we see this type of brittle and ductile behavior.

For elastomers, however, elastic but non-linear behavior is often observed up to strains of 500%!

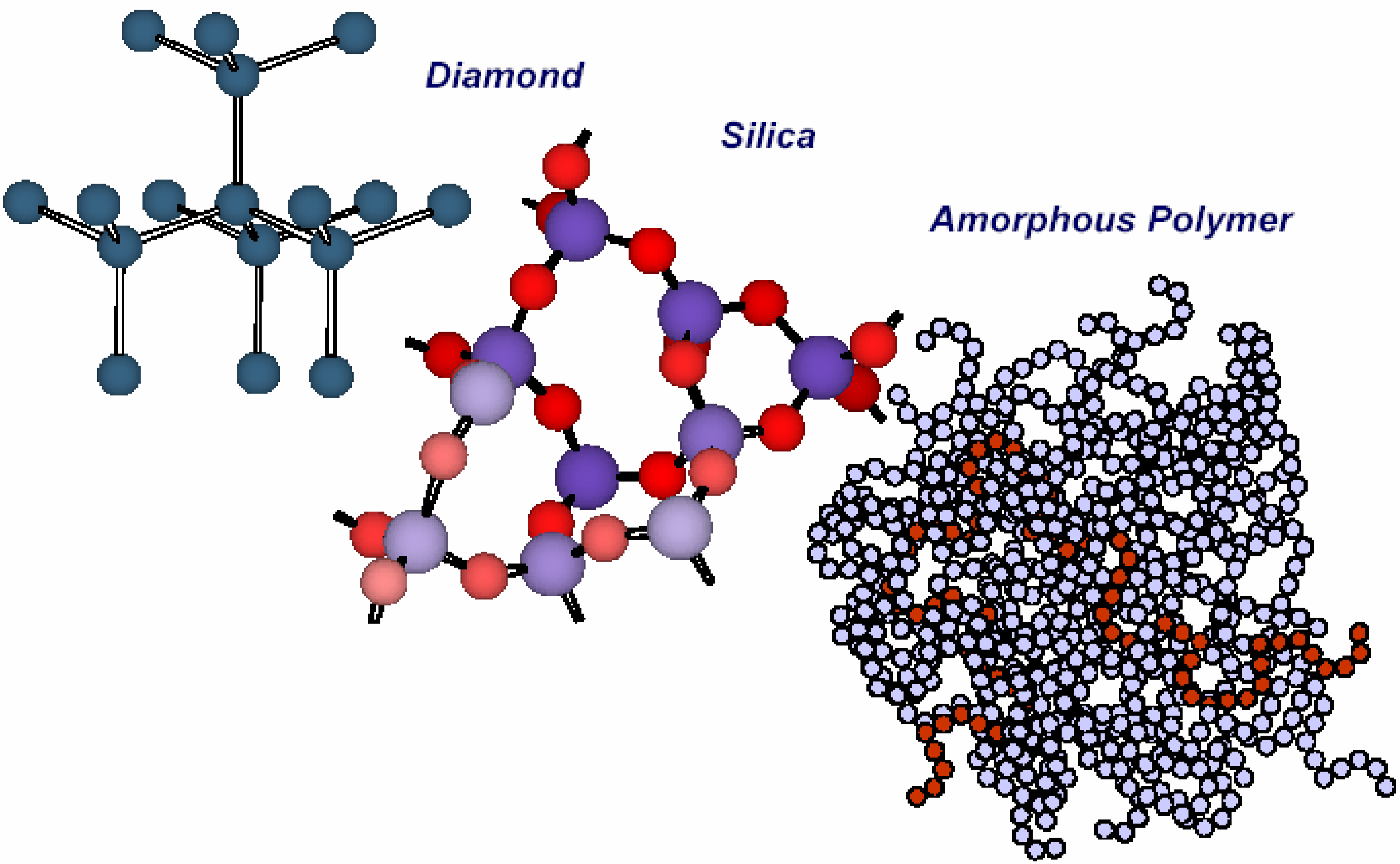
Furthermore, even in the initial apparently Hookean regions of the stress/strain behavior of polymers an elastic (time dependent) responses are usually observed!

Stiffness

Material	E (lbs/sq. inch)	E (MPa)
Rubber	0.001×10^6	7
Polyethylene	0.2×10^6	150
Wood	2.0×10^6	14,000
Concrete	2.5×10^6	17,000
Glass	10.0×10^6	70,000
Steel	30.0×10^6	210,000
Diamond	170.0×10^6	1,200,000

Polymers aren’t very stiff!

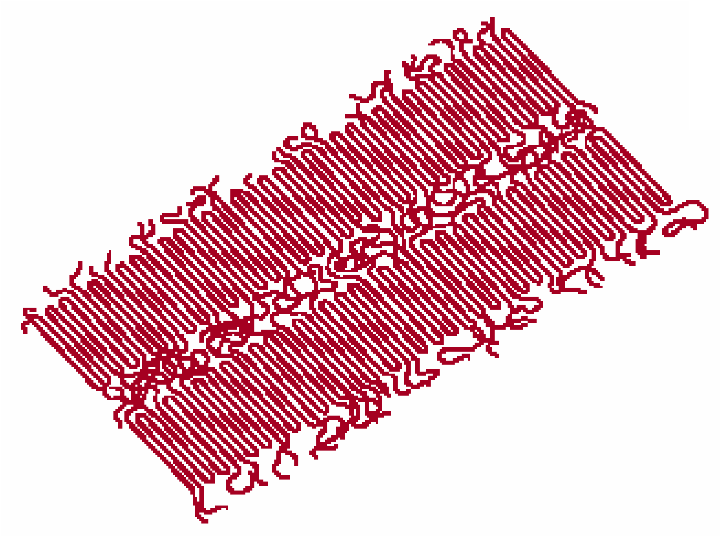
Stiffness and Structure



Stiffness of Polymers

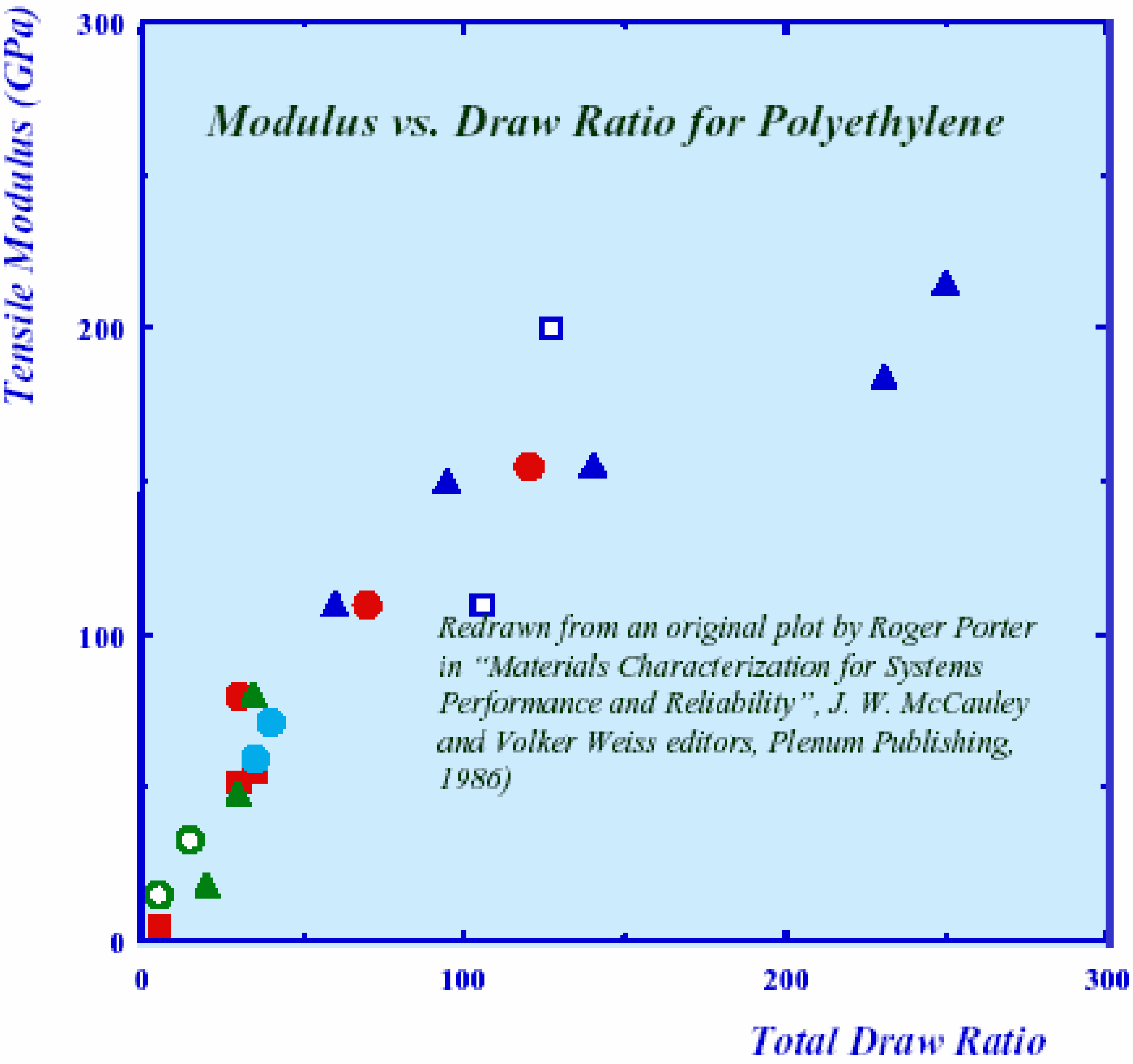
FACTORS:

- Crystallinity
- Cross-Linking
- Tg

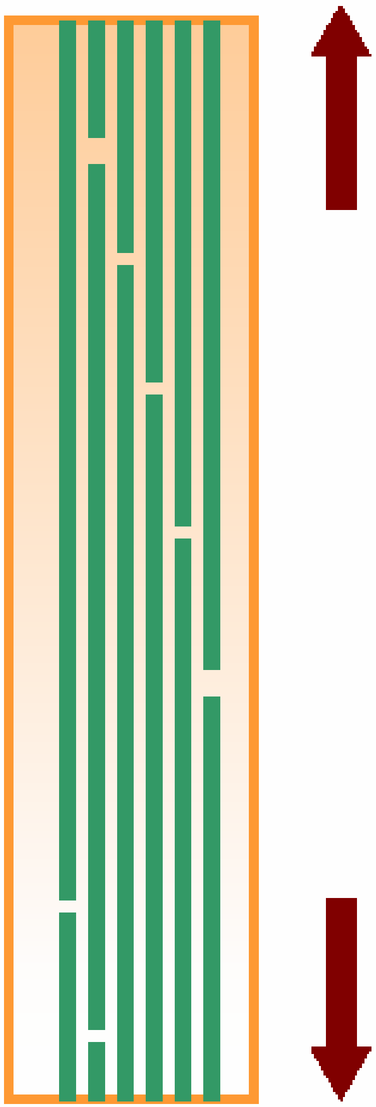


Polymer	E (MPa)
Rubber	7
Polyethylene	
High Density	830
Low Density	170
Poly(styrene)	3100
Poly(methyl methacrylate) (Plexiglas)	4650
Phenolic Resins (Bakelite)	6900

Fibers



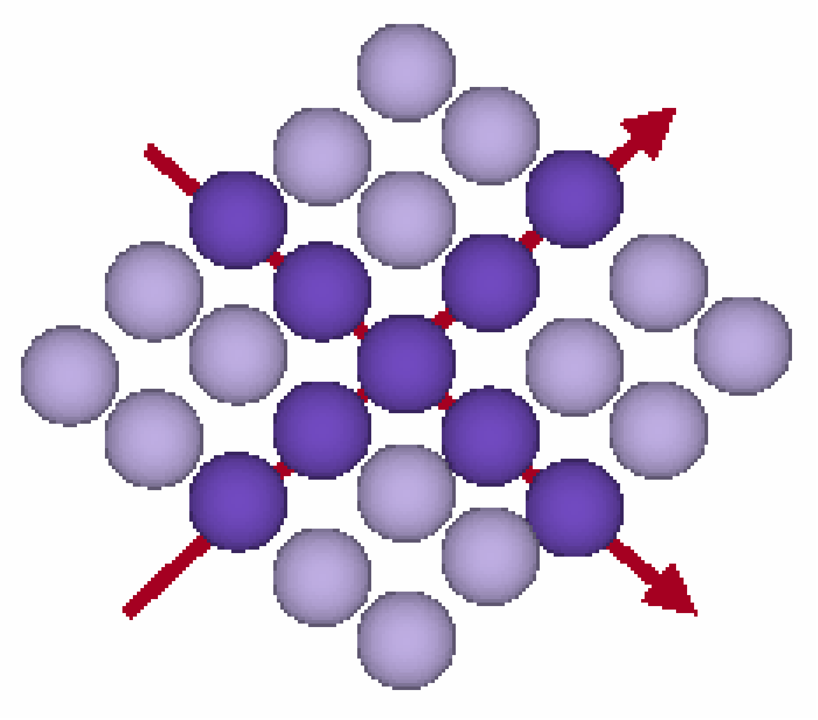
Redrawn from an original plot by Roger Porter in "Materials Characterization for Systems Performance and Reliability", J. W. McCauley and Volker Weiss editors, Plenum Publishing, 1986)

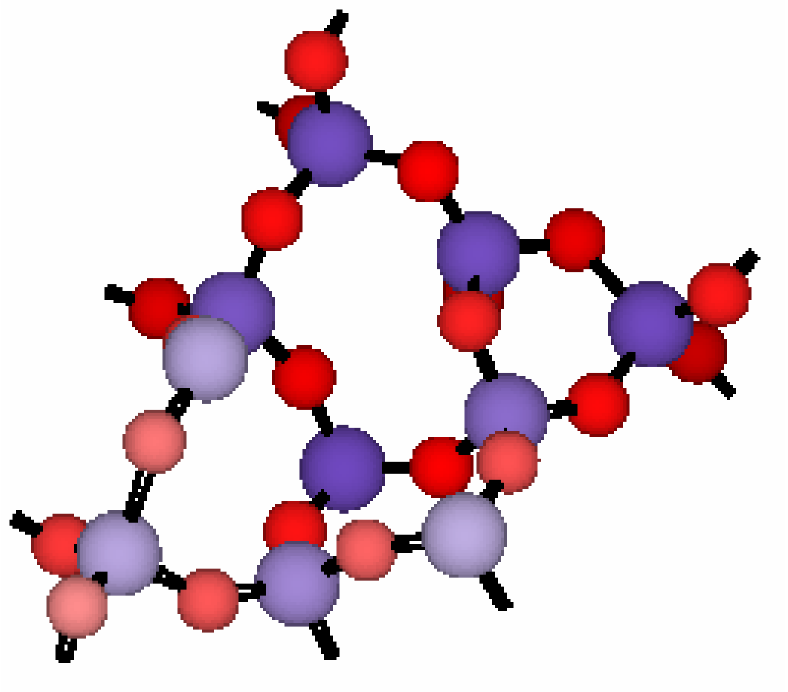


Tensile Strength

Material	TS (psi)	TS (MPa)
Steel piano wire	450,000	3,000
High - tensile steel	225,000	1,500
Aluminium alloys	20,000 - 80,000	140 - 550
Titanium alloys	100,000 - 200,000	700 - 1,400
Wood (spruce),along grain	15,000	100
Wood (spruce),across grain	500	7
Ordinary glass	5,000 - 25,000	30 - 170
Ordinary brick	800	5
Ordinary cement	600	4
Nylon fiber	140,000	950
Kevlar 29 fiber	400,000	2,800

Brittle vs Ductile Materials





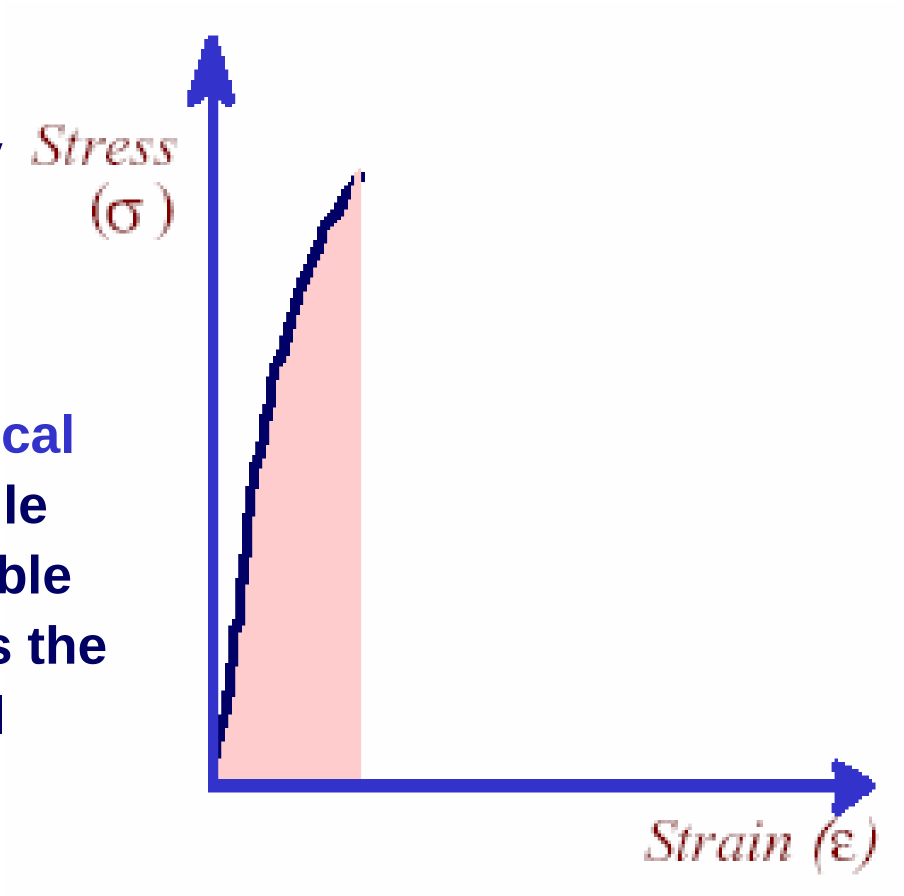
I can slip this way

or that, but you

can’t!

Strength and Toughness

- In window glass the molecular structure is perturbed to a relatively shallow depth during fracture and W is about 6G.



- Under any significant load the critical crack length is very short. The tensile strength of glass might be appreciable under a static load, but under stress the glass is in a fragile state, the critical crack length is small and slight perturbations can lead to crack propagation and failure.

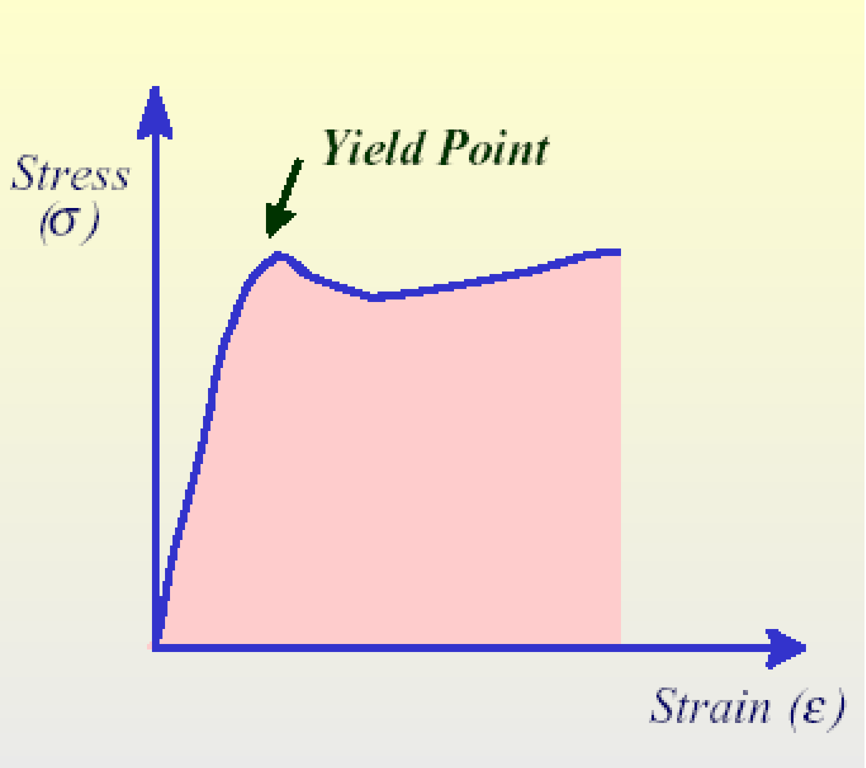
- Brittle materials in general have a low work of fracture or energy to break, as reflected in the area under the stress strain curve.

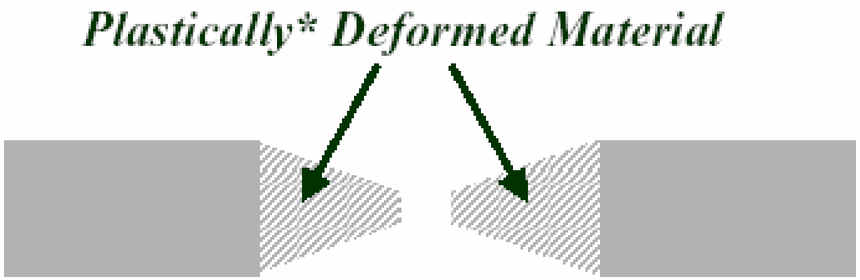
Strength and Toughness

- Mild steel and other ductile metals have an enormous work of fracture; W is of the order of 10^4 - 10^6 G and the critical crack length is very long.

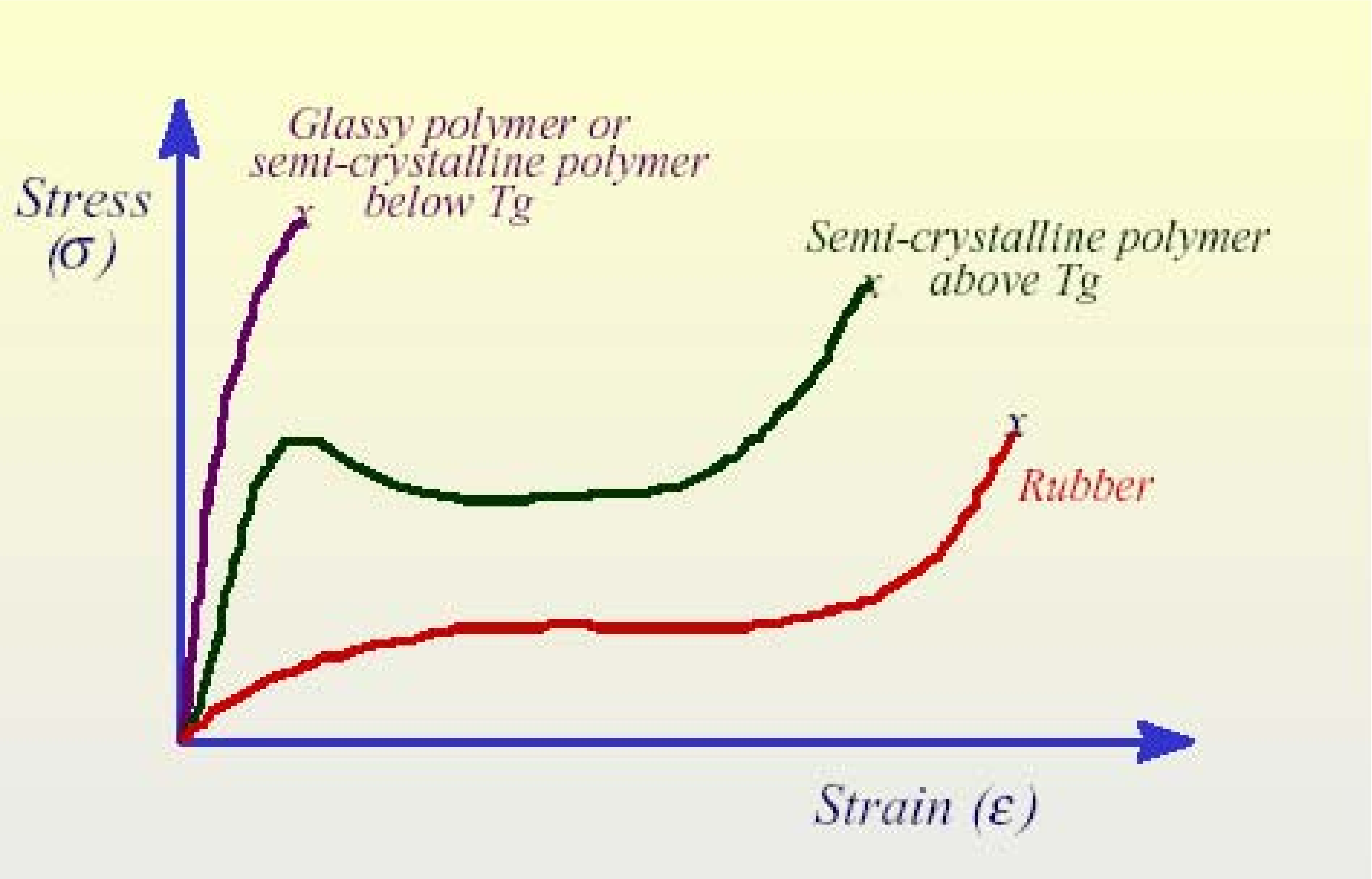
- The structure of these materials is perturbed to a significant depth below the fracture surface, hence the high work of fracture.

- The stress strain plots of such a material display a yield point, where a neck forms and the material deforms plastically.



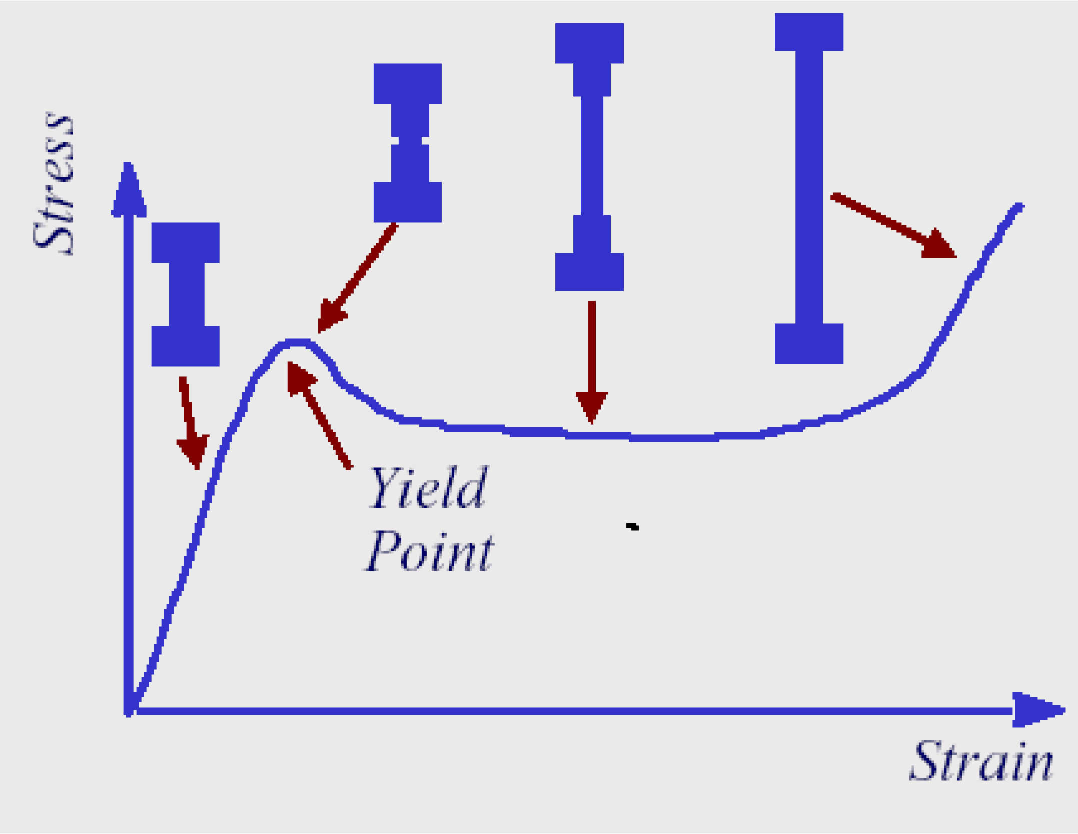


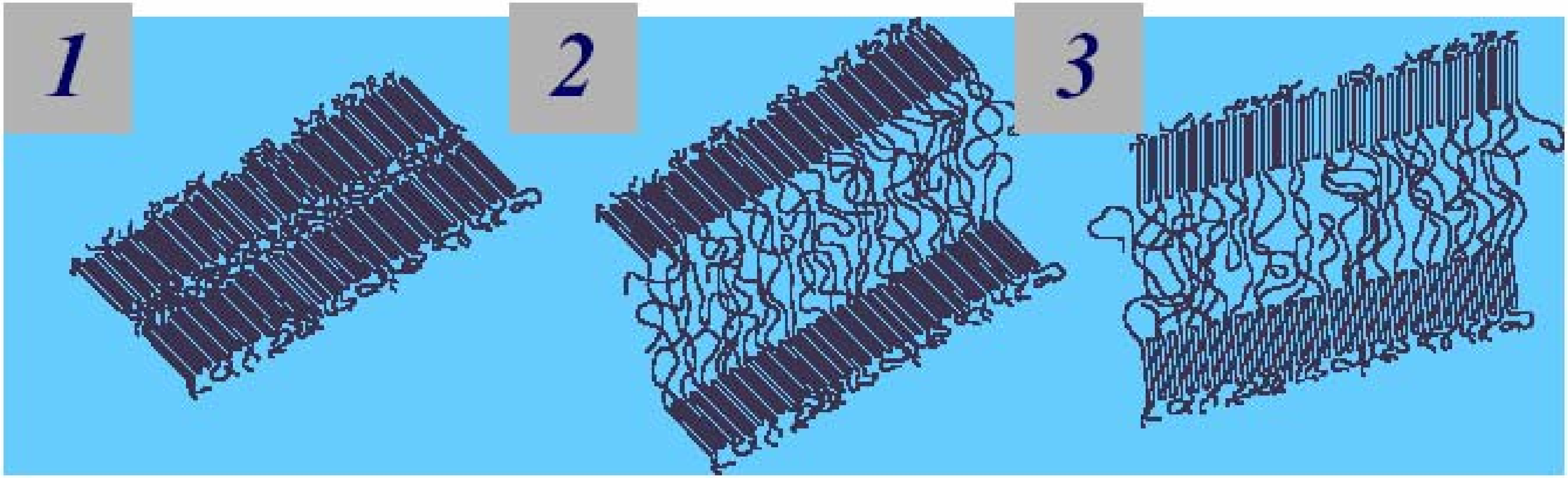
Stress / Strain



Yielding in Flexible Semi-Crystalline Polymers

Flexible semi-crystalline polymers such as polyethylene (where the T_g of the amorphous domains is below room temperature) usually display a considerable amount of yielding or "cold-drawing", as long as they are not stretched too quickly.

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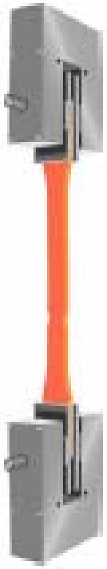

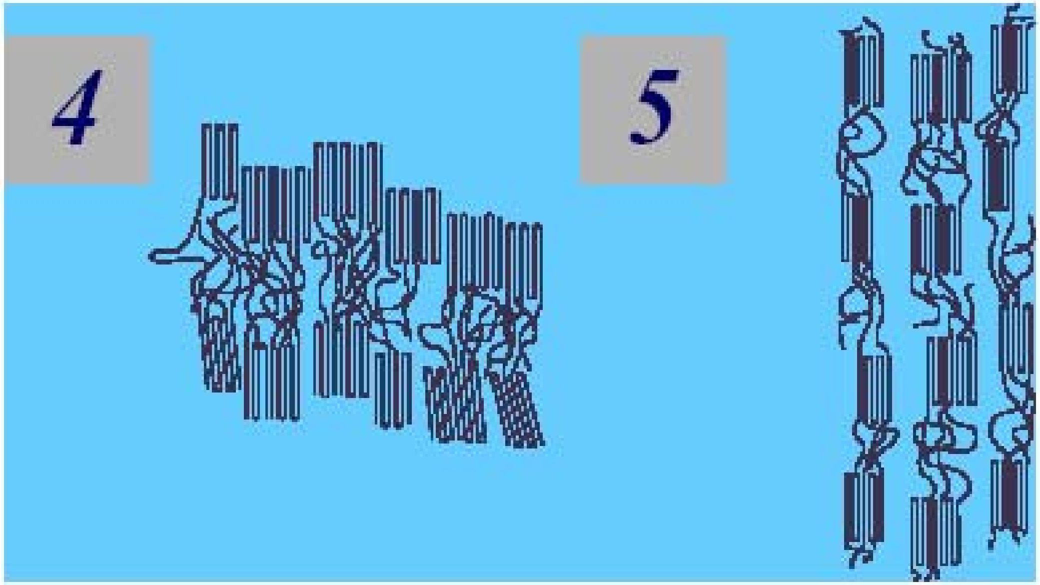
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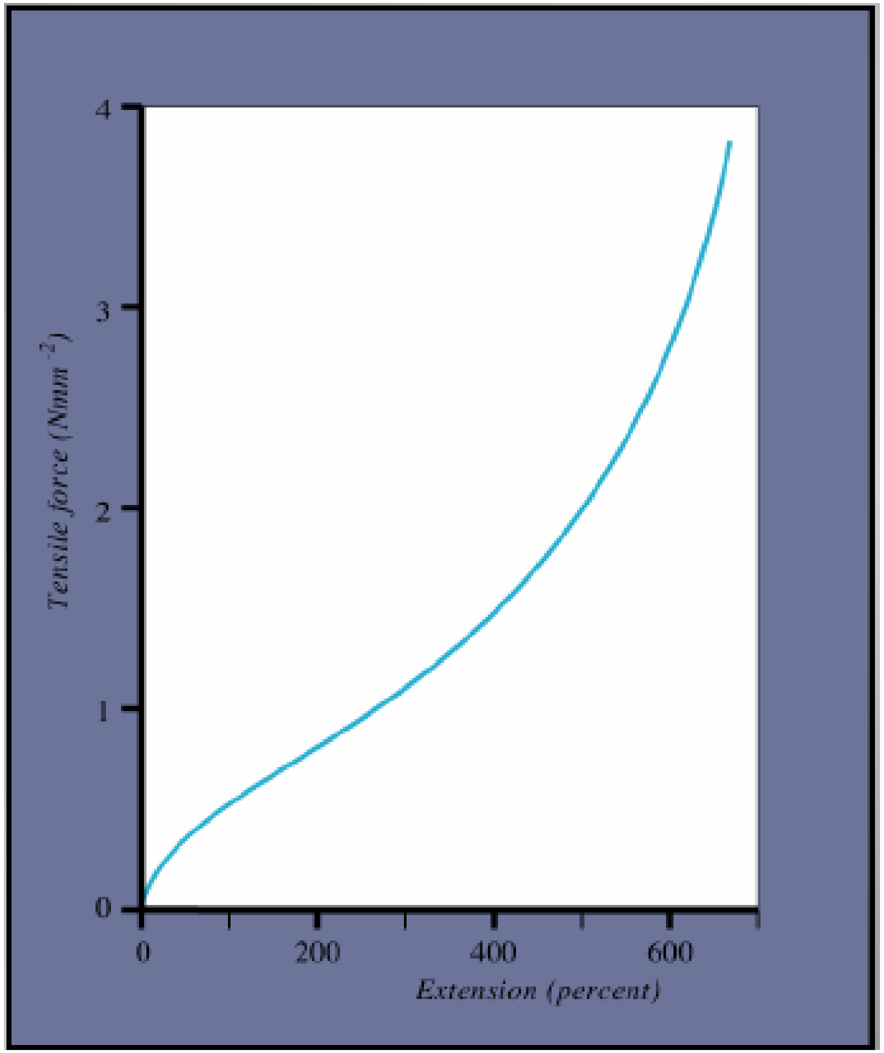
Rubber Elasticity

Linear and Non-Linear Behavior

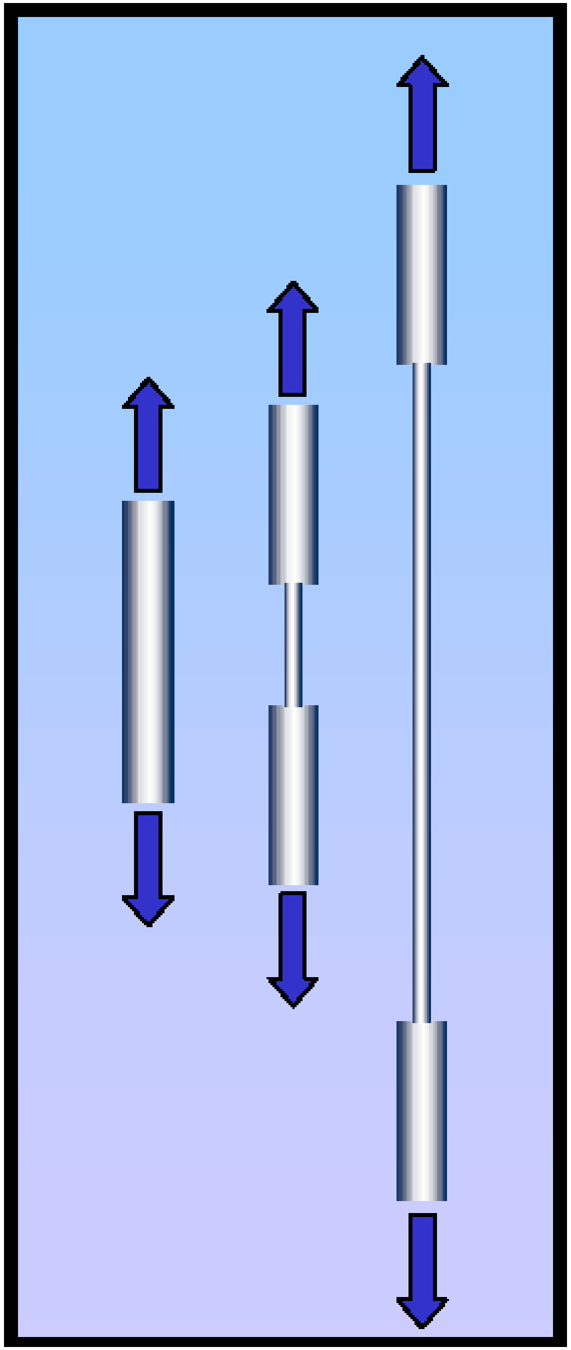
Rubbers also have strong stiff (covalent) bonds, but they are capable of stretching more than 500% elastically.

Instead of just minor deviations from Hooke's law we see behavior that is markedly nonlinear.

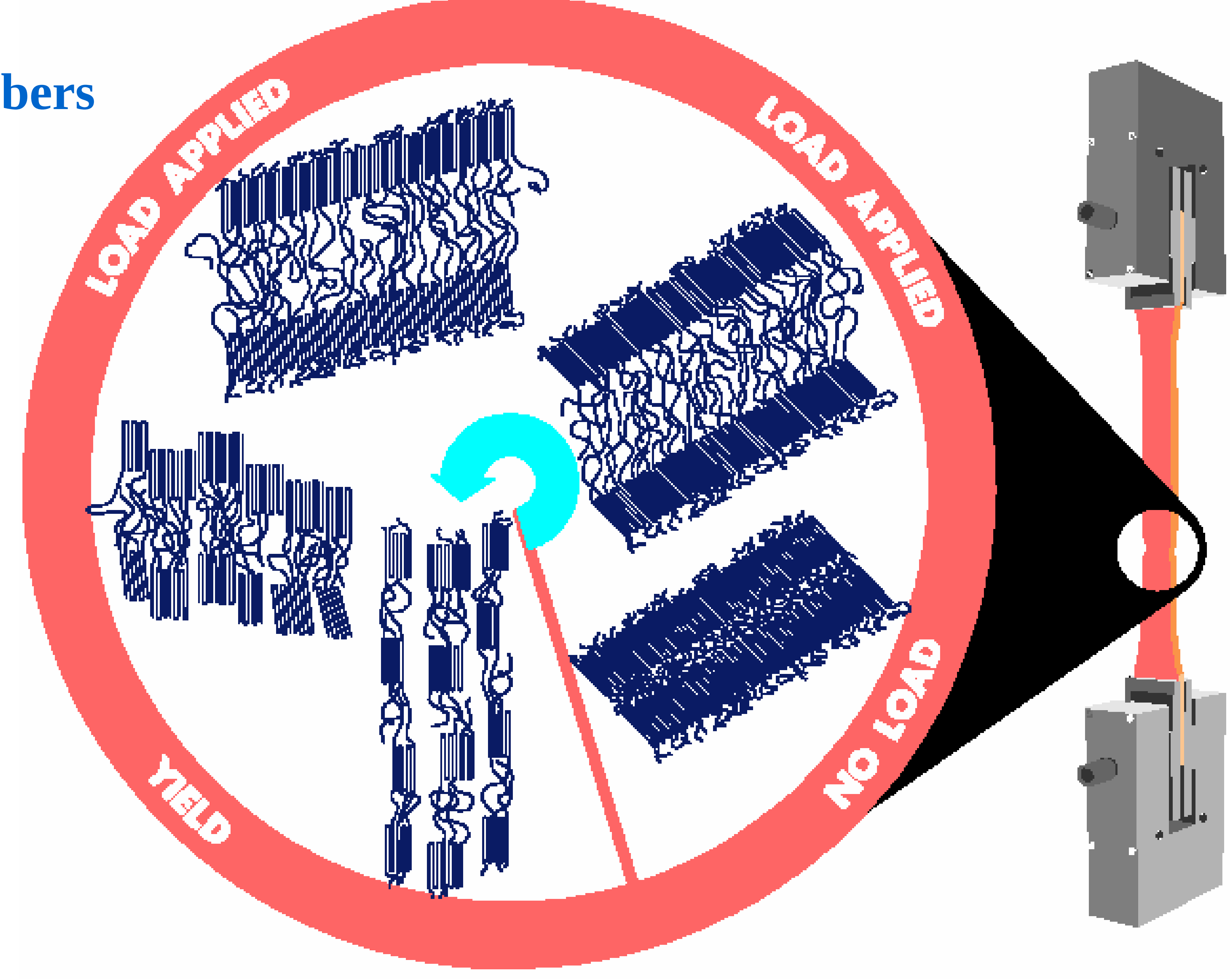
The bonds in these materials cannot be stretching this much, so what's going on.



Fibers

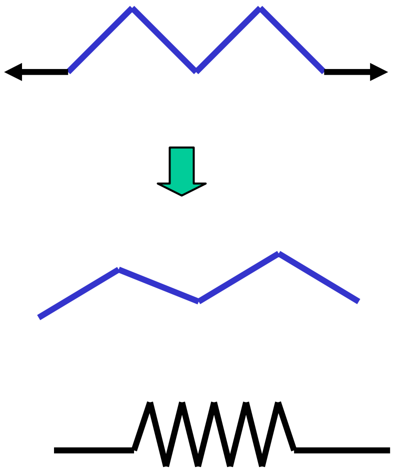


Fibers



Molecular Analogies of Viscoelasticity in Plastic Materials

A) Elasticity



Spring

$T < T_g$

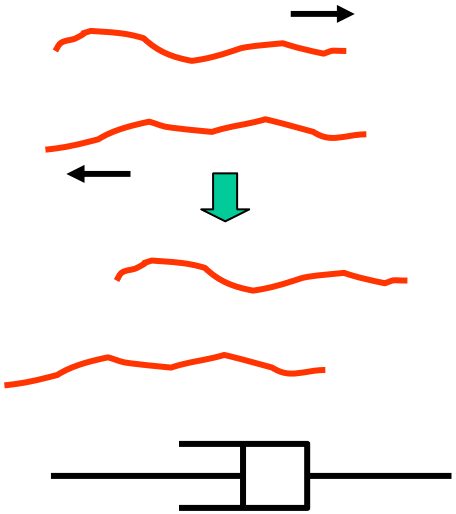
Low ε

High E

Deformation of bond angle and bond length

Reversible

B) Viscous flow



Dashpot

$T > T_g$

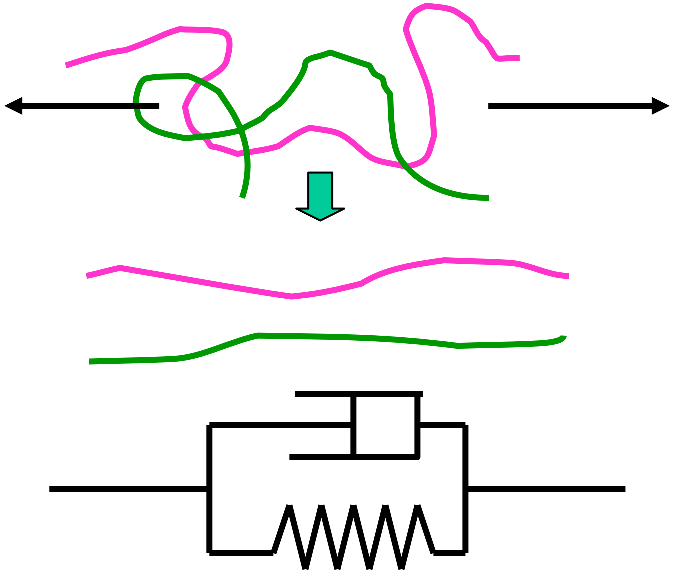
Sliding motion

Energy of deformation is dissipated as heat

Contributes to creep and stress relaxation

Irreversible

C) Chain uncoiling



Spring and dashpot

$T \approx T_g$

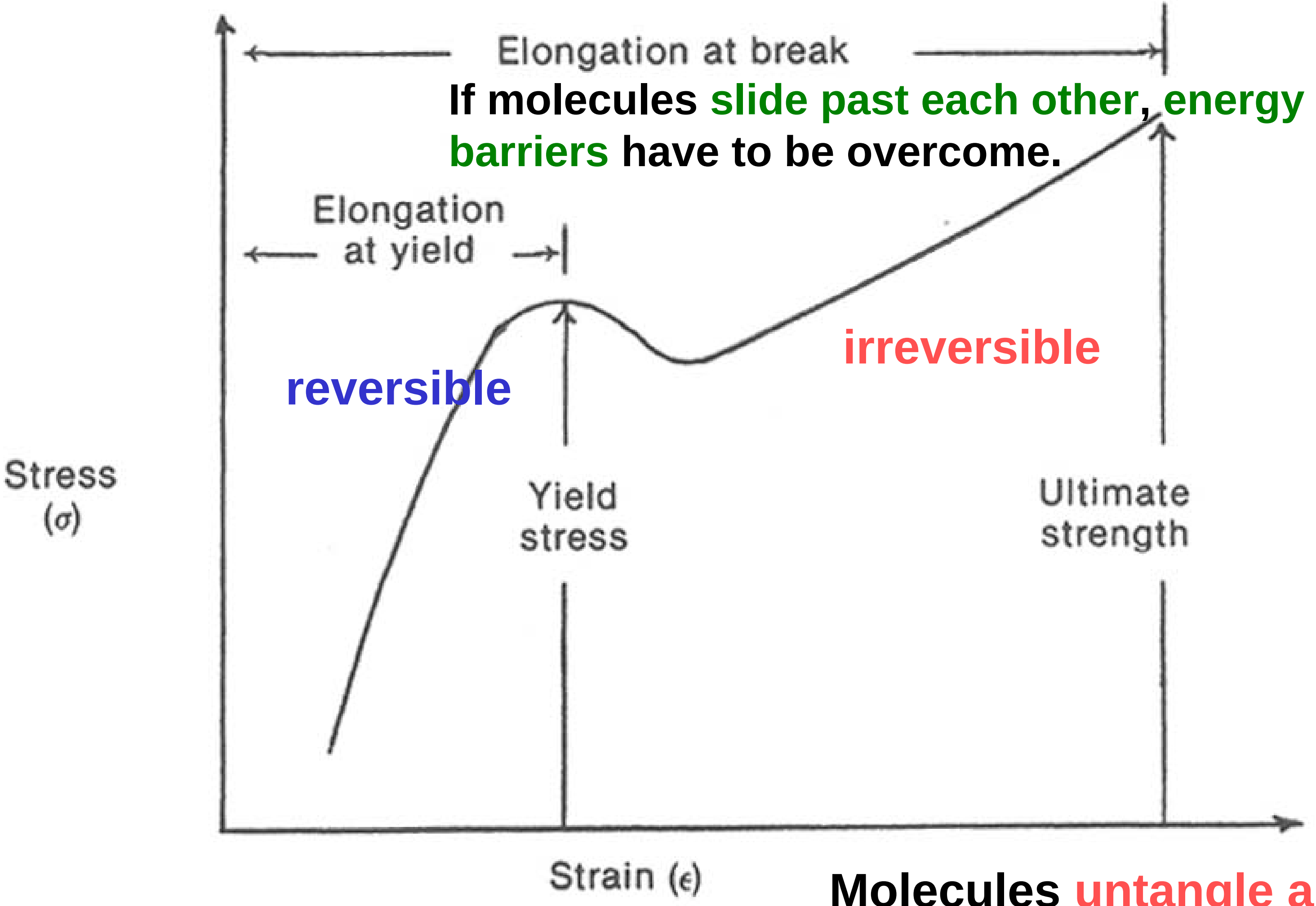
High ε

Low E

Bond rotation and segmental motion

Reversible (delayed)

Fig 4.8. General Tensile Stress-Strain Curve for a Typical Thermoplastic



If molecules slide past each other, energy barriers have to be overcome.

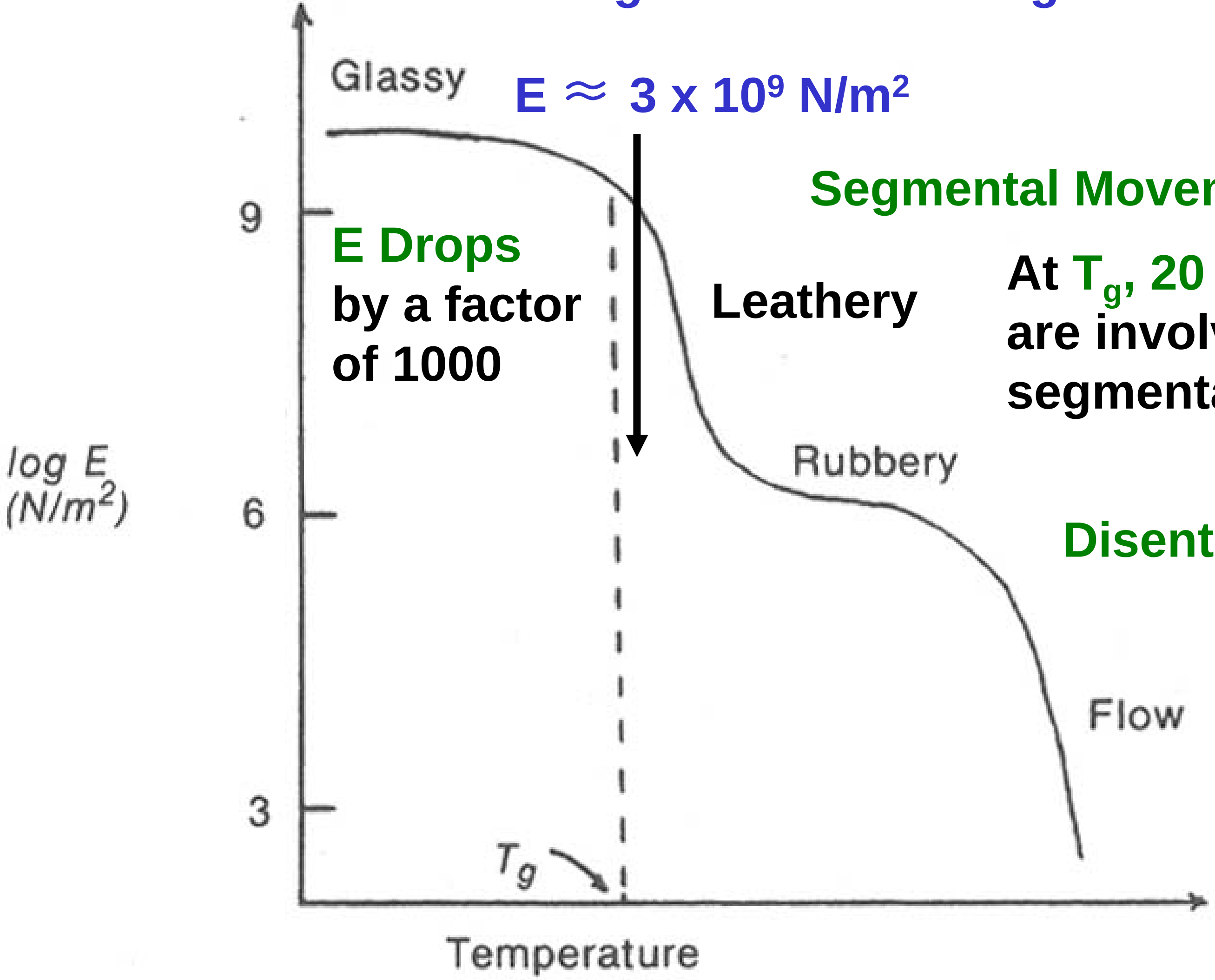
reversible

irreversible

Initial E: high

Molecules untangle and flow over one another

Fig 4.9. Effect of T on E of an Amorphous Thermoplastic



Deformation due to stretching
of Bond Angle and Bond Length

$E \approx 3 \times 10^9$ N/m²

Segmental Movement

E Drops
by a factor
of 1000

Leathery

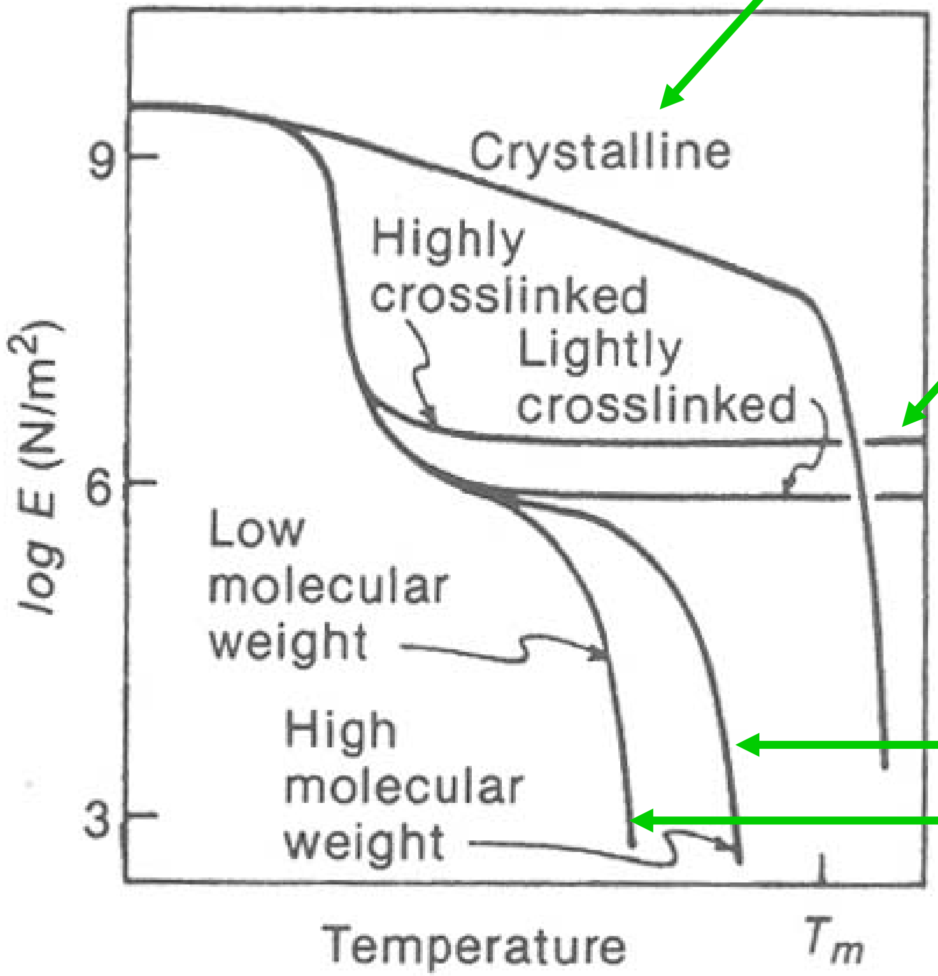
At T_g, 20 – 50 Chain Atoms
are involved in the
segmental movement.

Disentanglement

Sliding Motions
of Molecules

Fig 4.10. Effects of T on E of various polymers

Below T_m, Crystallites act as Crosslinks



No flow region

∵ Crosslinks prevent sliding motion

The higher the Crosslink Density, the greater will be the Modulus.

More Chain Entanglements

Few Chain Entanglements

The Higher the M.W., the Higher the Temp necessary to overcome the increased Molecular Entanglements.

MECHANICAL PROPERTIES OF SOLIDS

RHEOLOGICAL PROPERTIES OF FLUIDS

POLYMERS TREATED AS SOLIDS	**Strength** **Stiffness** **Toughness**
POLYMERS TREATED AS FLUIDS	**Viscosity of polymer melts** **Elastic properties of polymer melts**
VISCOELASTIC PROPERTIES	**Creep** **Stress Relaxation**

Time Dependent Properties: Creep (Cold Flow), Stress Relaxation

- Characteristic of Viscoelastic materials
- Arise from the Slippage of polymer molecules

Creep: Increase in strain when a polymer sample is subjected to a constant stress

Stress Relaxation:

Decrease in stress when a sample is elongated rapidly to constant strain

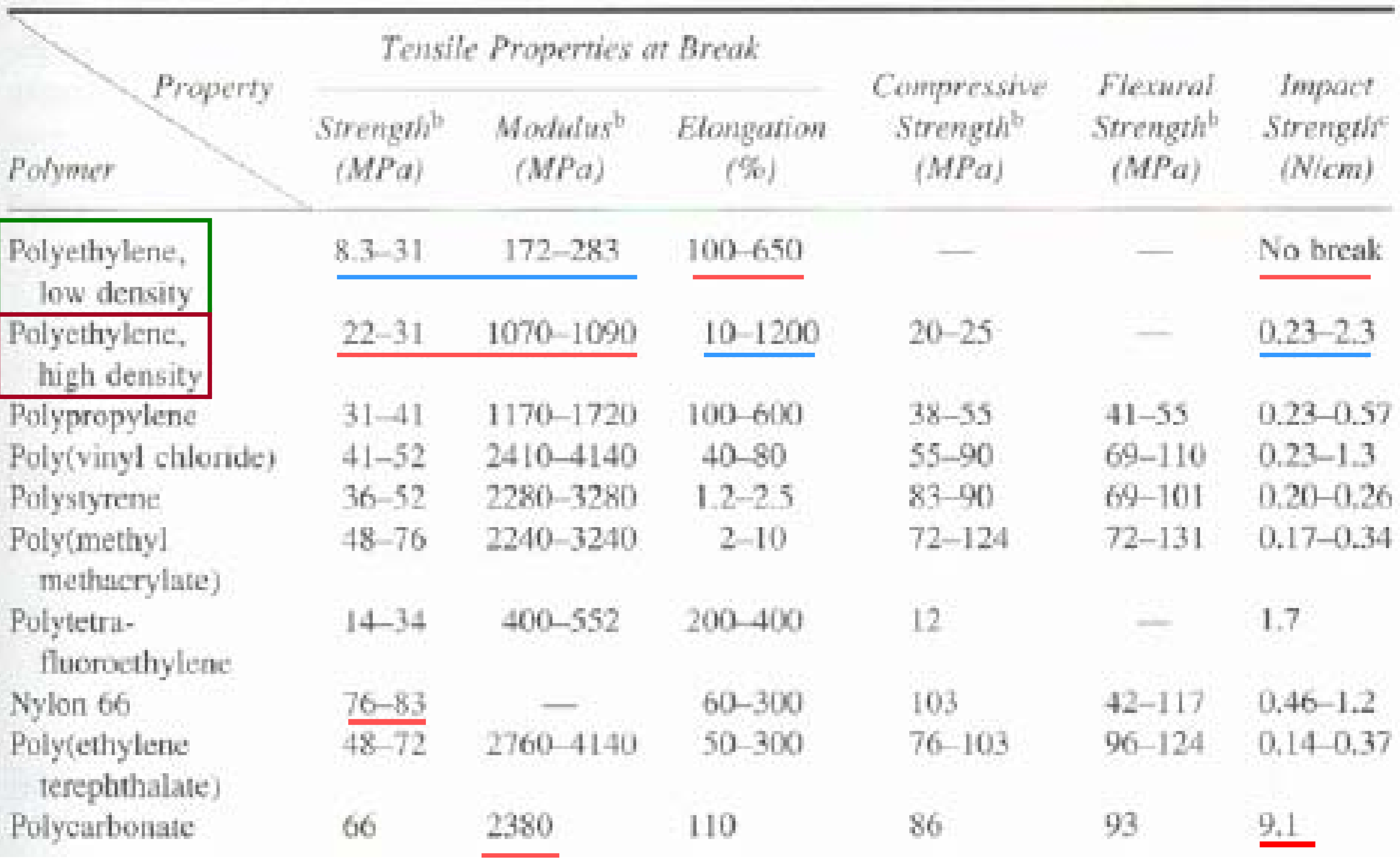
Chain Stiffening

(**Bulky Side Groups**, **Cyclic Units**, **Crosslinking**, **Crystallinity**)

➡ Tensile Strength ↑
Flexural Strength ↑
Compressive Strength ↑

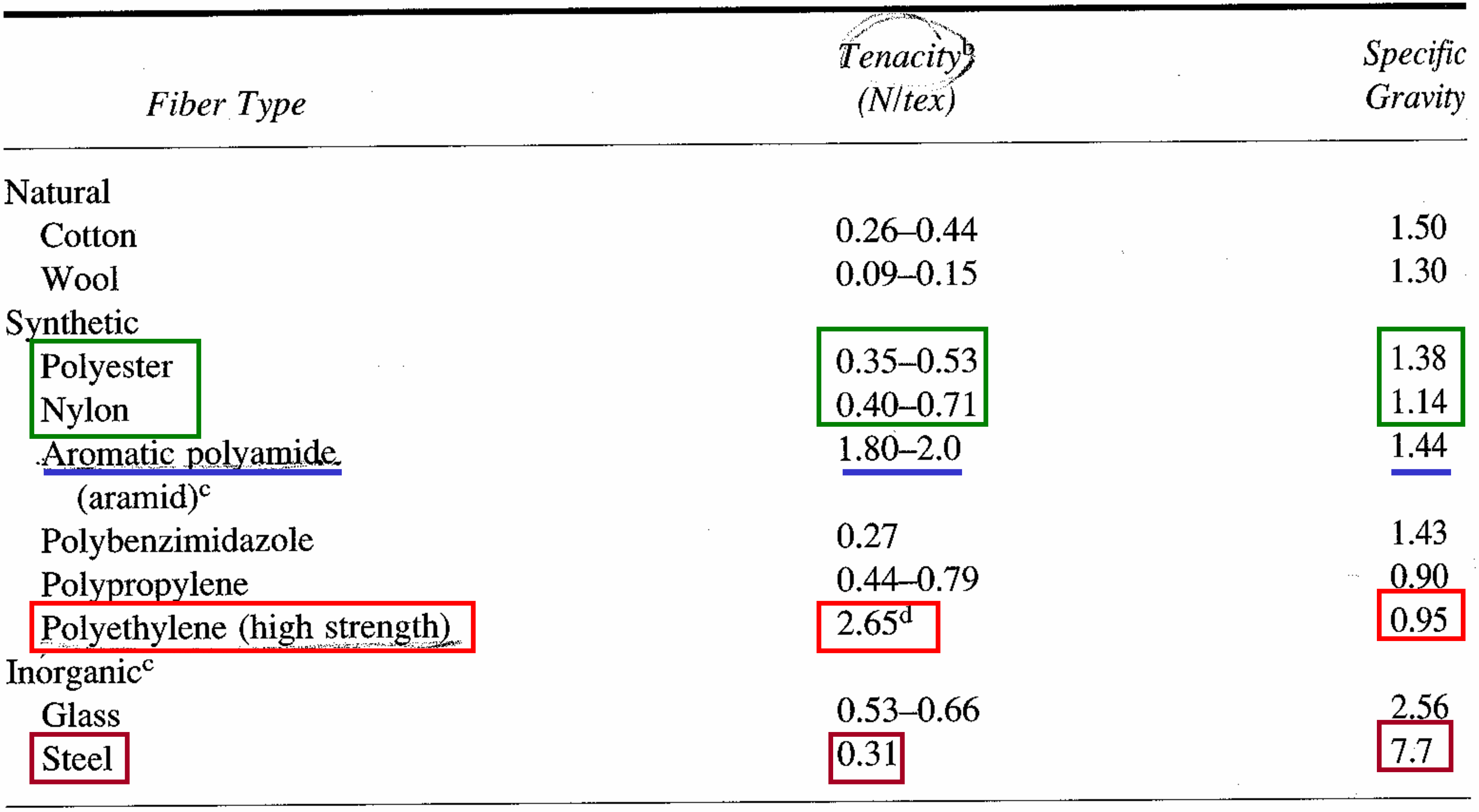
Tensile Elongation ↓
Impact Strength ↓

Table 4.1 Mechanical Properties of Common Homopolymers



Property / Polymer	Tensile Properties at Break			Compressive Strength[b] (MPa)	Flexural Strength[b] (MPa)	Impact Strength[c] (N/cm)
	Strength[b] (MPa)	Modulus[b] (MPa)	Elongation (%)			
Polyethylene, low density	8.3–31	172–283	100–650	—	—	No break
Polyethylene, high density	22–31	1070–1090	10–1200	20–25	—	0.23–2.3
Polypropylene	31–41	1170–1720	100–600	38–55	41–55	0.23–0.57
Poly(vinyl chloride)	41–52	2410–4140	40–80	55–90	69–110	0.23–1.3
Polystyrene	36–52	2280–3280	1.2–2.5	83–90	69–101	0.20–0.26
Poly(methyl methacrylate)	48–76	2240–3240	2–10	72–124	72–131	0.17–0.34
Polytetrafluoroethylene	14–34	400–552	200–400	12	—	1.7
Nylon 66	76–83	—	60–300	103	42–117	0.46–1.2
Poly(ethylene terephthalate)	48–72	2760–4140	50–300	76–103	96–124	0.14–0.37
Polycarbonate	66	2380	110	86	93	9.1

Table 4.2. Fiber Properties



Fiber Type	*Tenacity*[b] *(N/tex)*	*Specific Gravity*
Natural		
Cotton	0.26–0.44	1.50
Wool	0.09–0.15	1.30
Synthetic		
Polyester	0.35–0.53	1.38
Nylon	0.40–0.71	1.14
Aromatic polyamide (aramid)[c]	1.80–2.0	1.44
Polybenzimidazole	0.27	1.43
Polypropylene	0.44–0.79	0.90
Polyethylene (high strength)	2.65[d]	0.95
Inorganic[c]		
Glass	0.53–0.66	2.56
Steel	0.31	7.7

tex: weight in grams of 1000 m of fiber

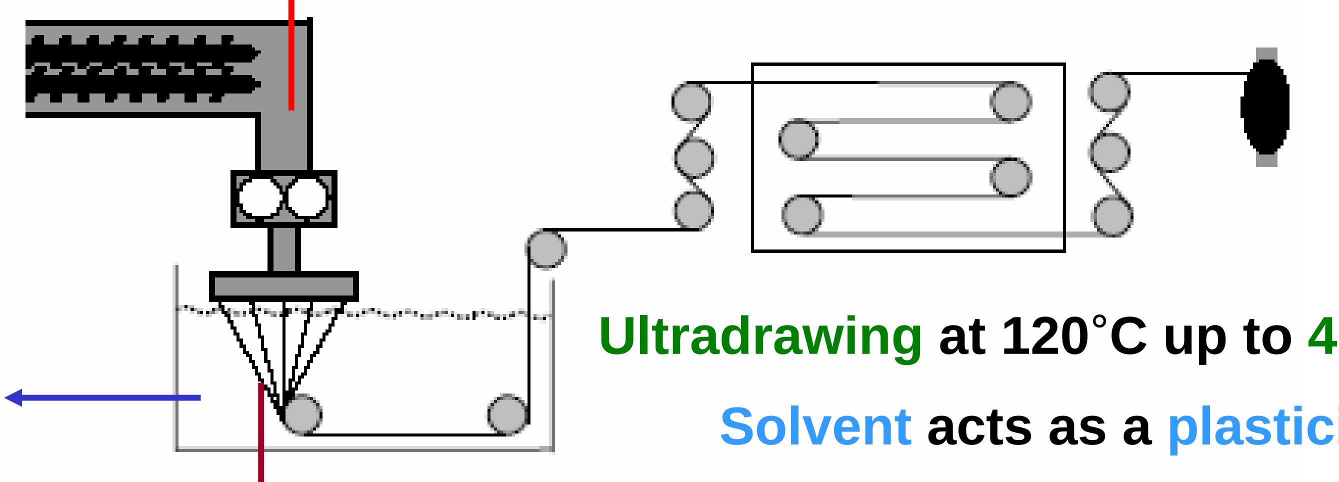
denier: weight in grams of 9000 m of fiber

Gel-Spinning

Convert ultra-high-M.W. (10^6) linear PE to a Gel with Solvent

→ **Spinning and Drawing**

1-2 % UHMW-PE in a hot solvent (xylene)



Ultradrawing at 120°C up to 40-100 x

Solvent acts as a plasticizer

Water

Crystallization

Evaporation of solvent

Gelly filament (containing a large amount of Solvent)

Applications for High-Strength PE Fibers

- Cut-resistant industrial gloves
- Protective glove liners for health care workers
- Bulletproof vests
- Crash helmets



Viscoelasticity

If we stretch a crystalline solid, the energy is stored in the chemical bonds

If we apply a shear stress to a fluid, energy is dissipated in flow

VISCOELASTIC

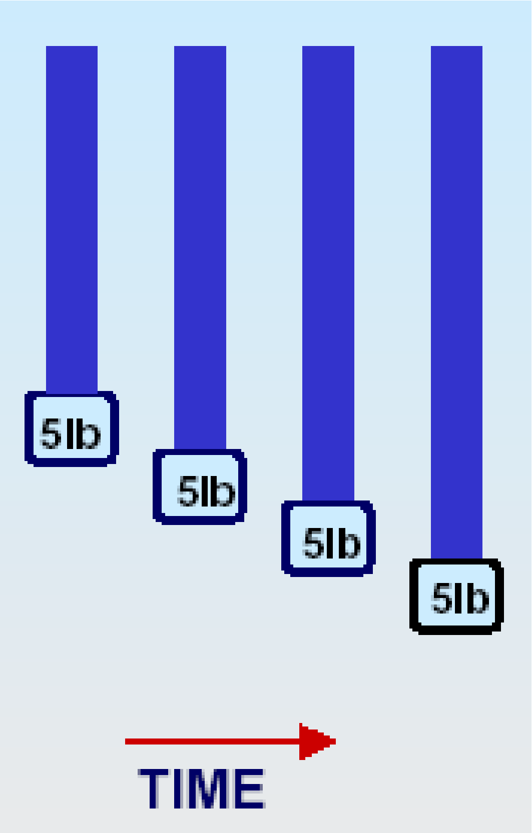
Ideally elastic behaviour

Ideally viscous behaviour

Experimental Observations

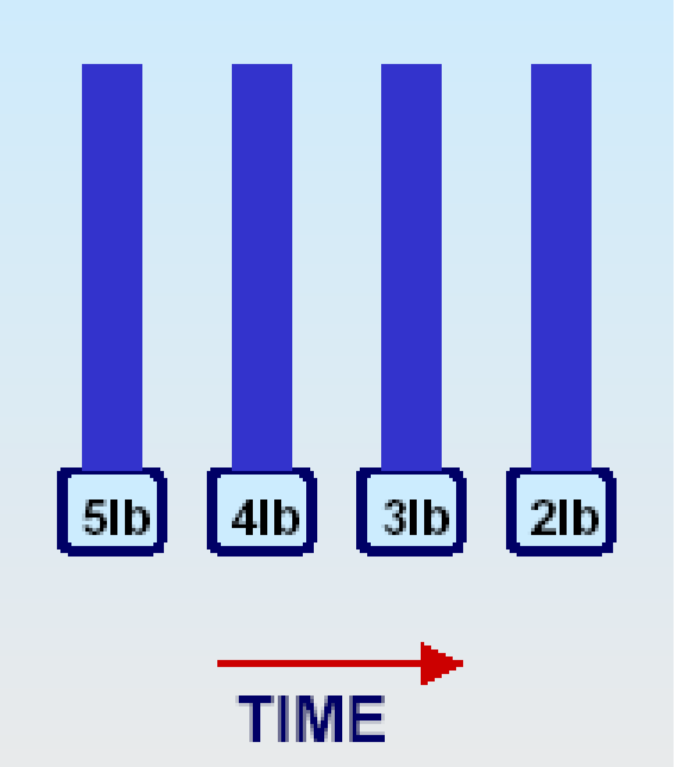
- **Creep**
- **Stress Relaxation**

Creep and Stress Relaxation

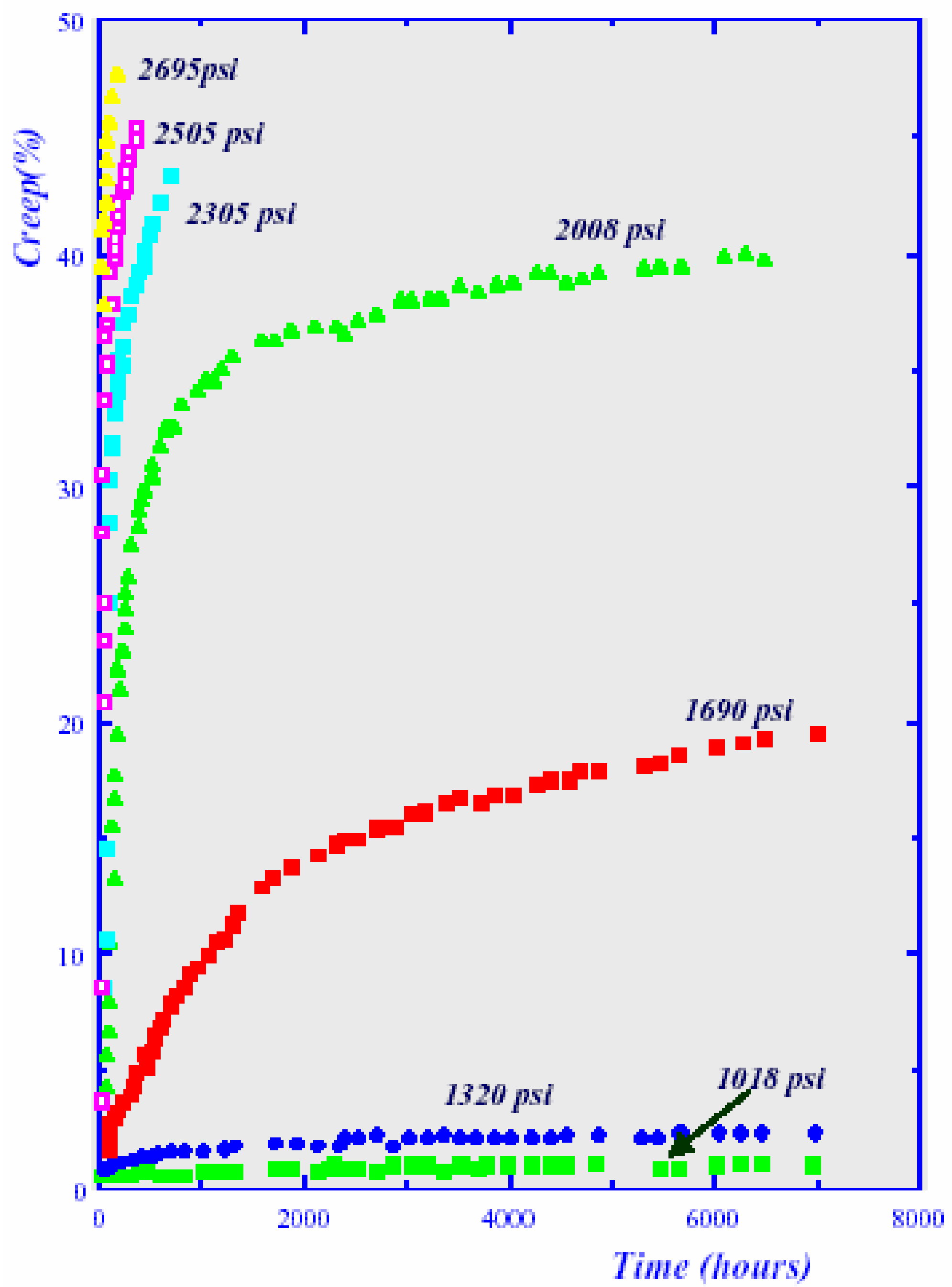


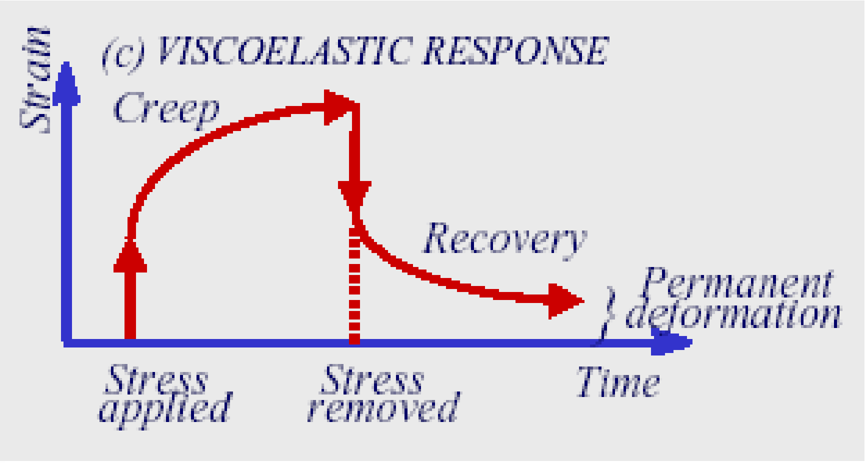
Creep - deformation under a **constant load** as a function of time

Stress Relaxation - **constant deformation** experiment

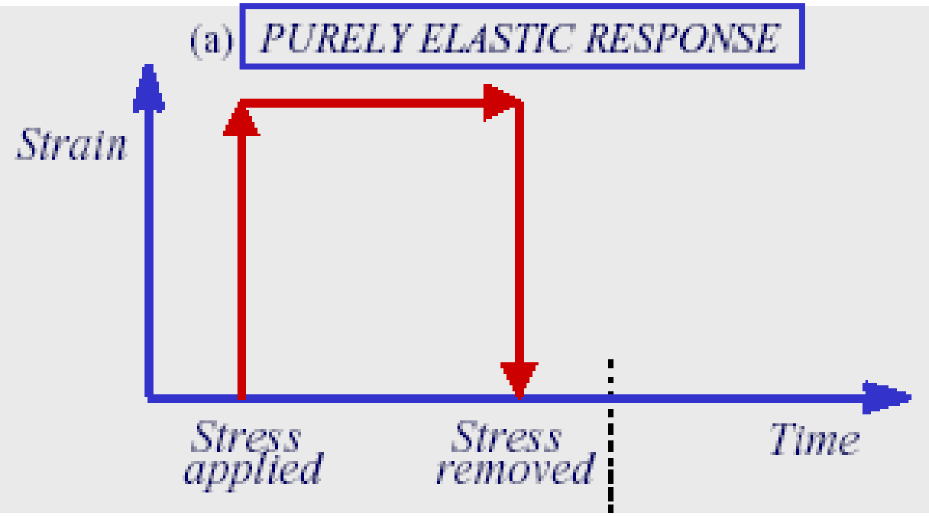


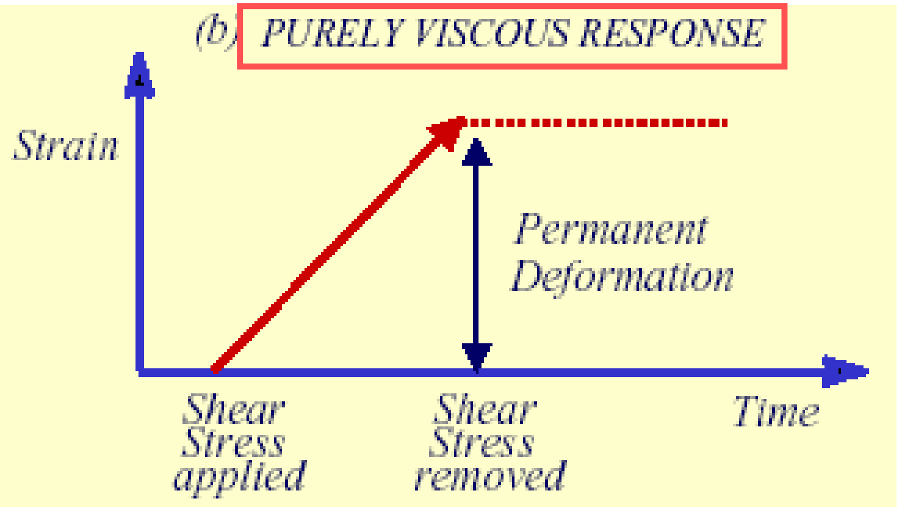
Creep and Recovery

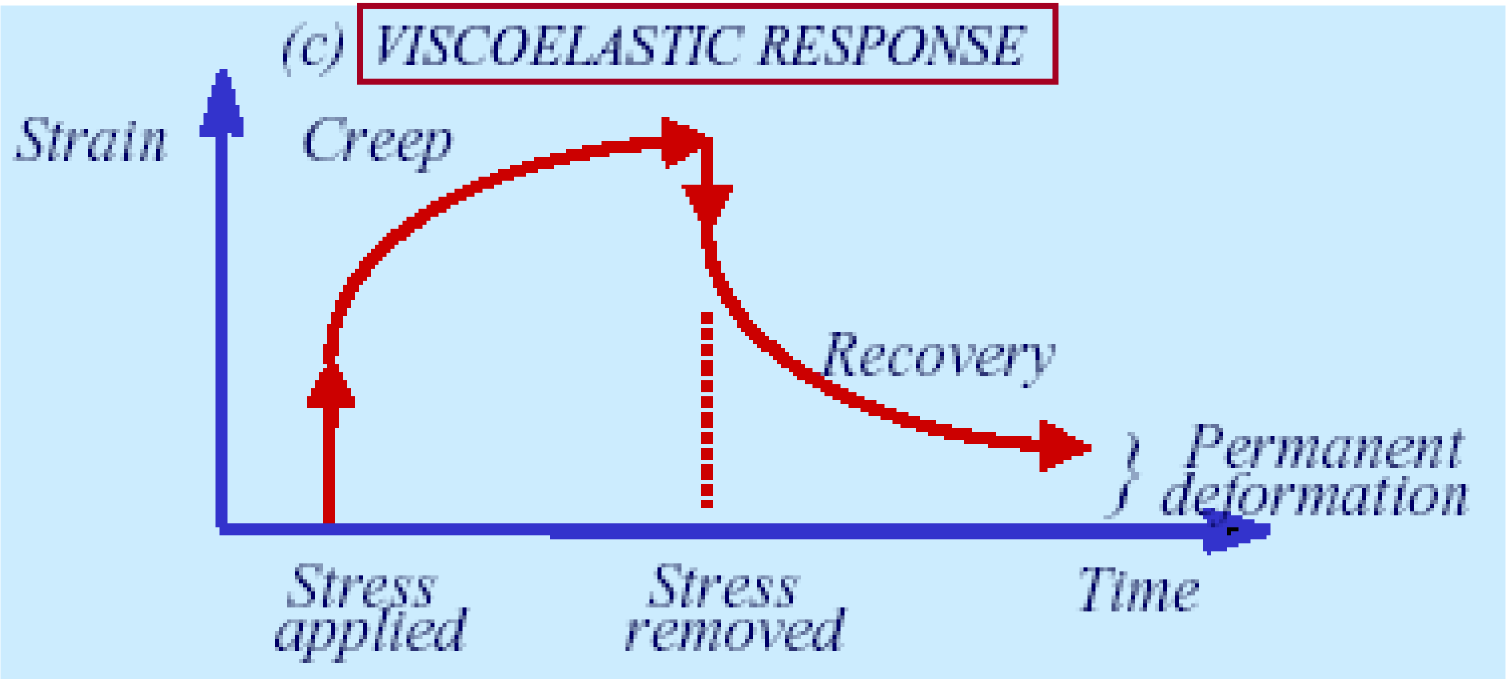




Strain vs. Time Plots - Creep



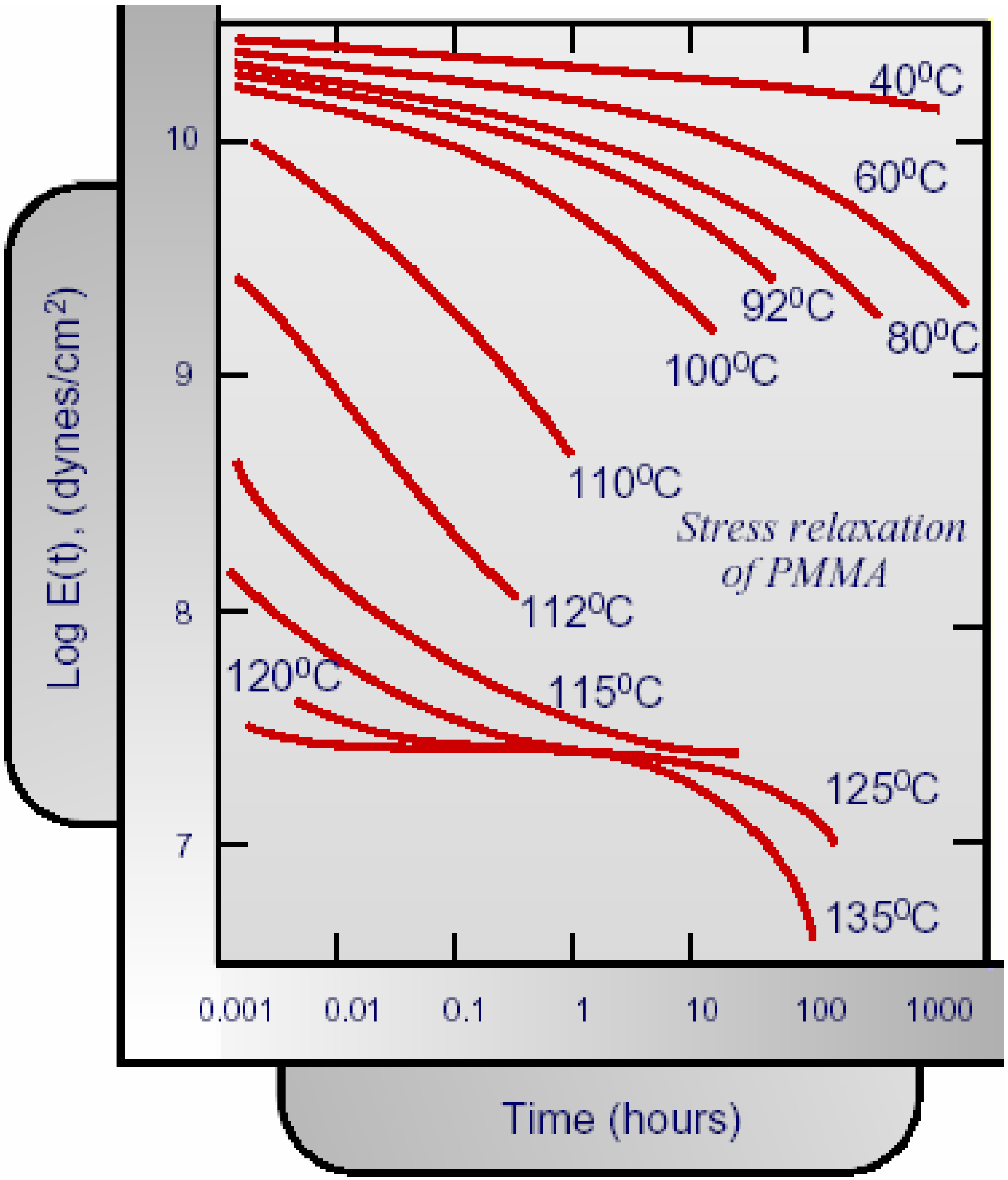




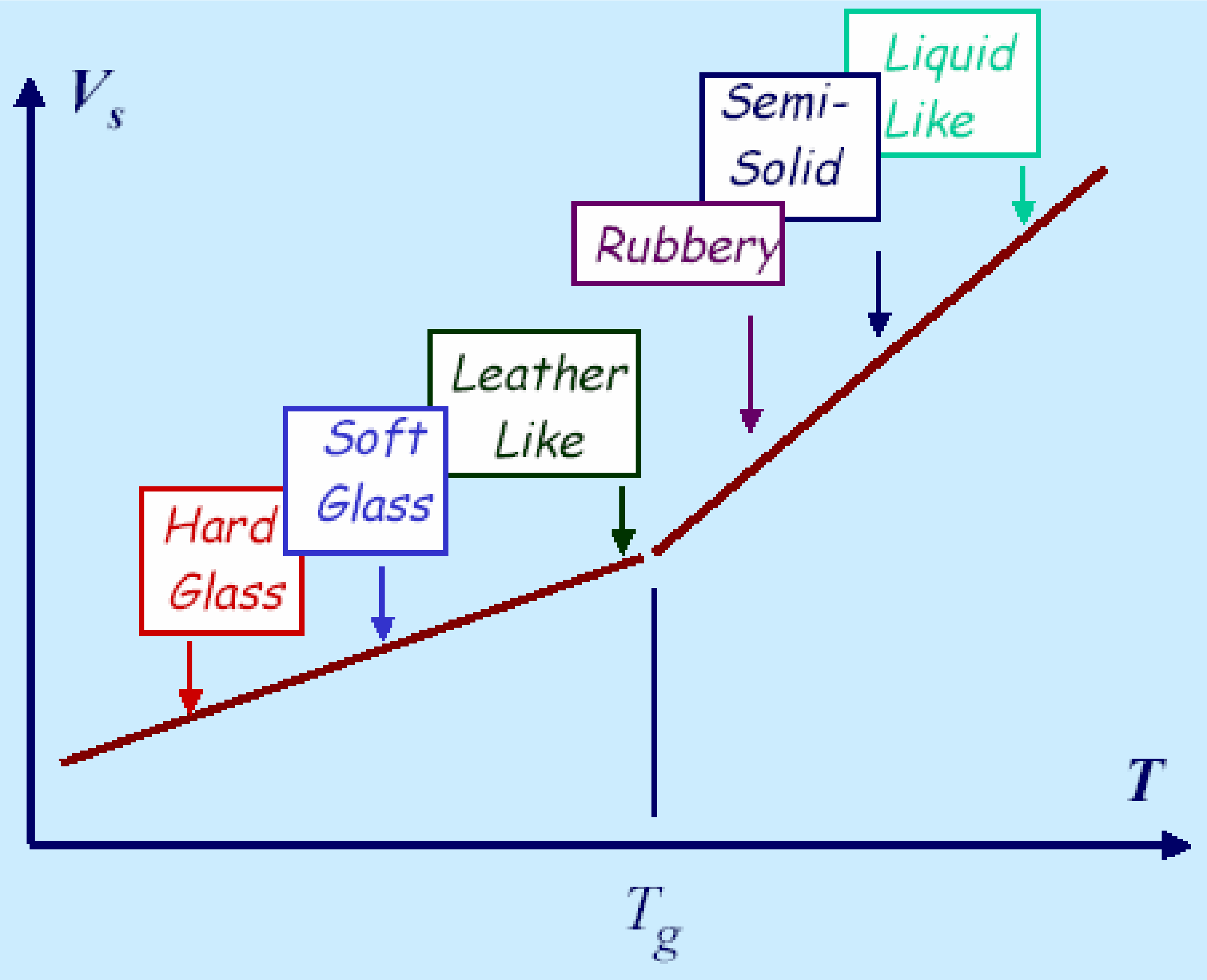
Stress Relaxation

The data are not usually reported as a stress/time plot, but as a modulus/time plot. This time dependent modulus, called the relaxation modulus, is simply the time dependent stress divided by the (constant) strain.

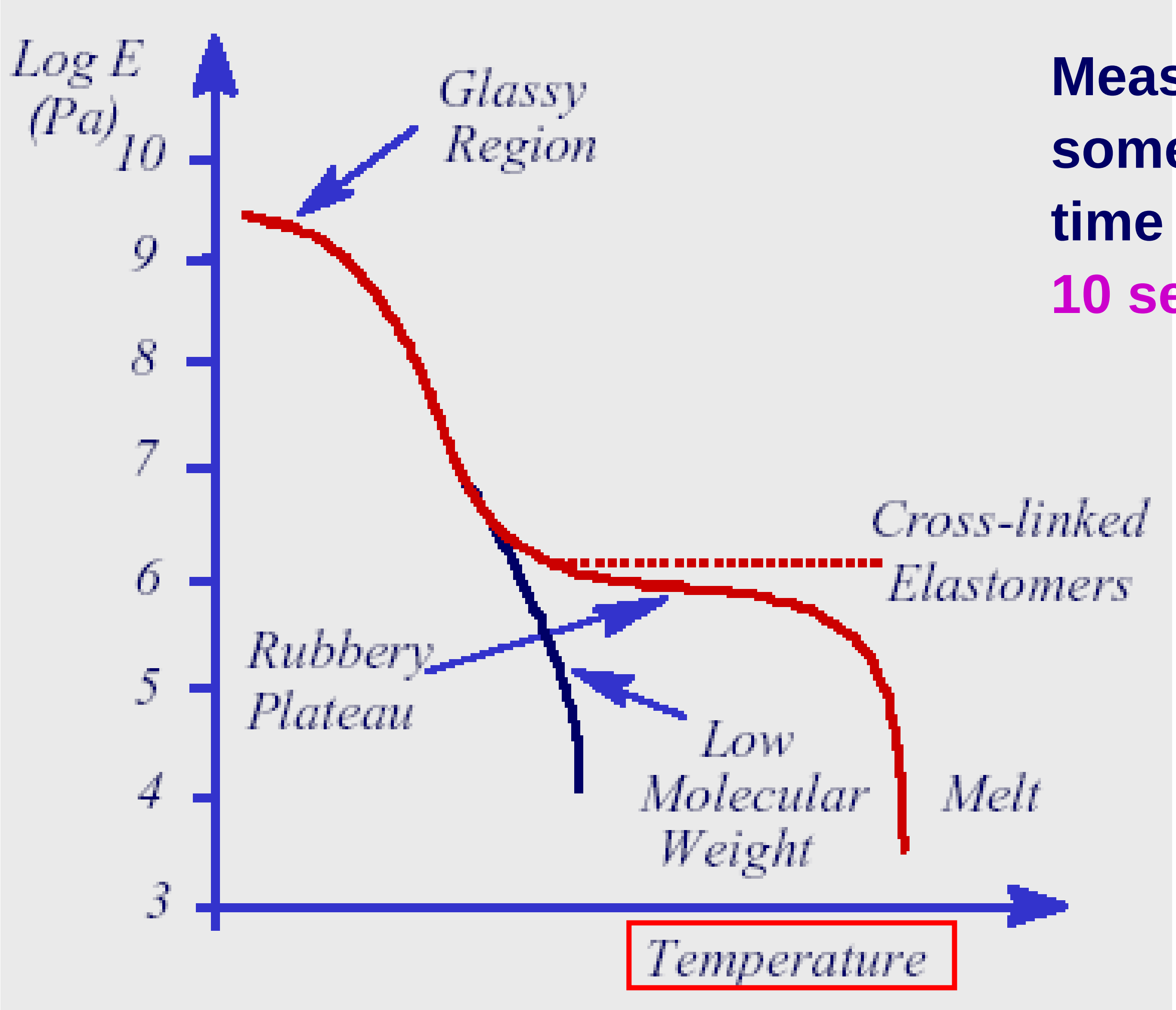
$$\boxed{E(t) = \frac{\sigma(t)}{\varepsilon_0}}$$



Amorphous Polymers – Range of Viscoelastic Behaviour



Viscoelastic Properties of Amorphous Polymers

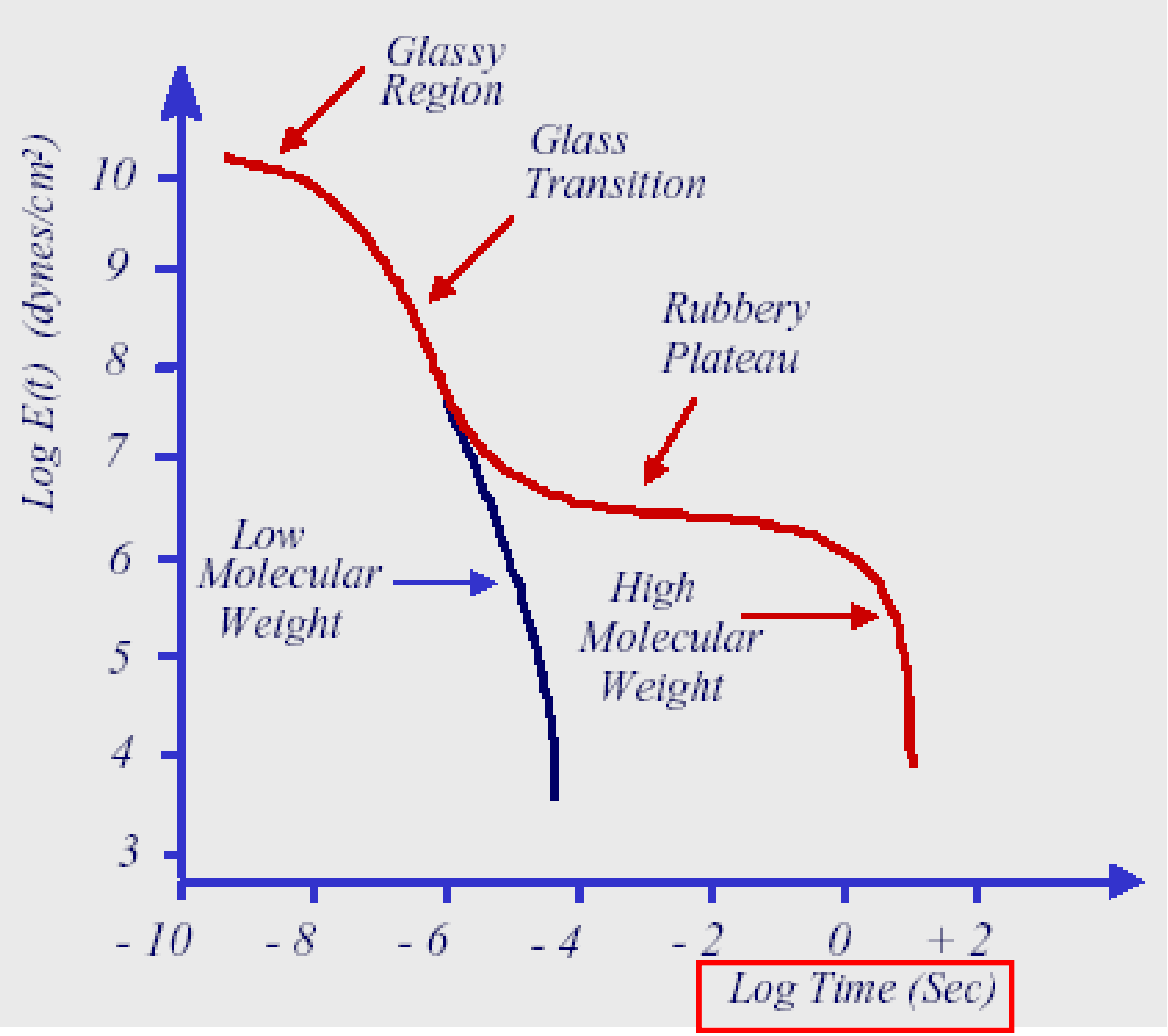


Measured over some arbitrary time period - say 10 secs

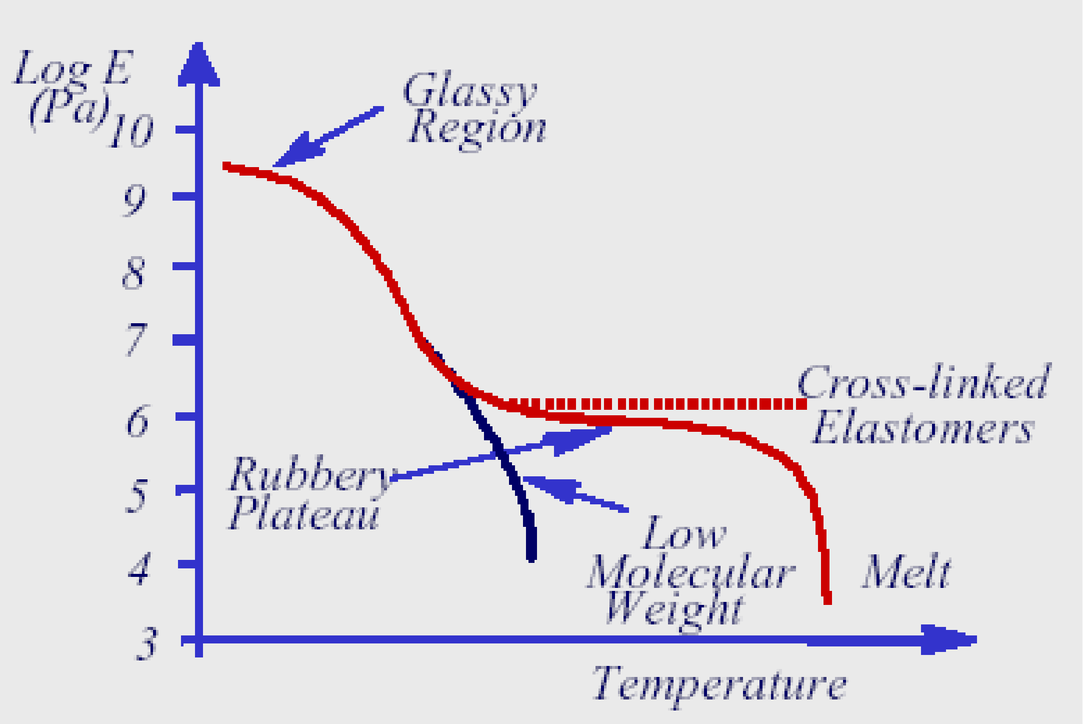
Viscoelastic Properties of Amorphous Polymers

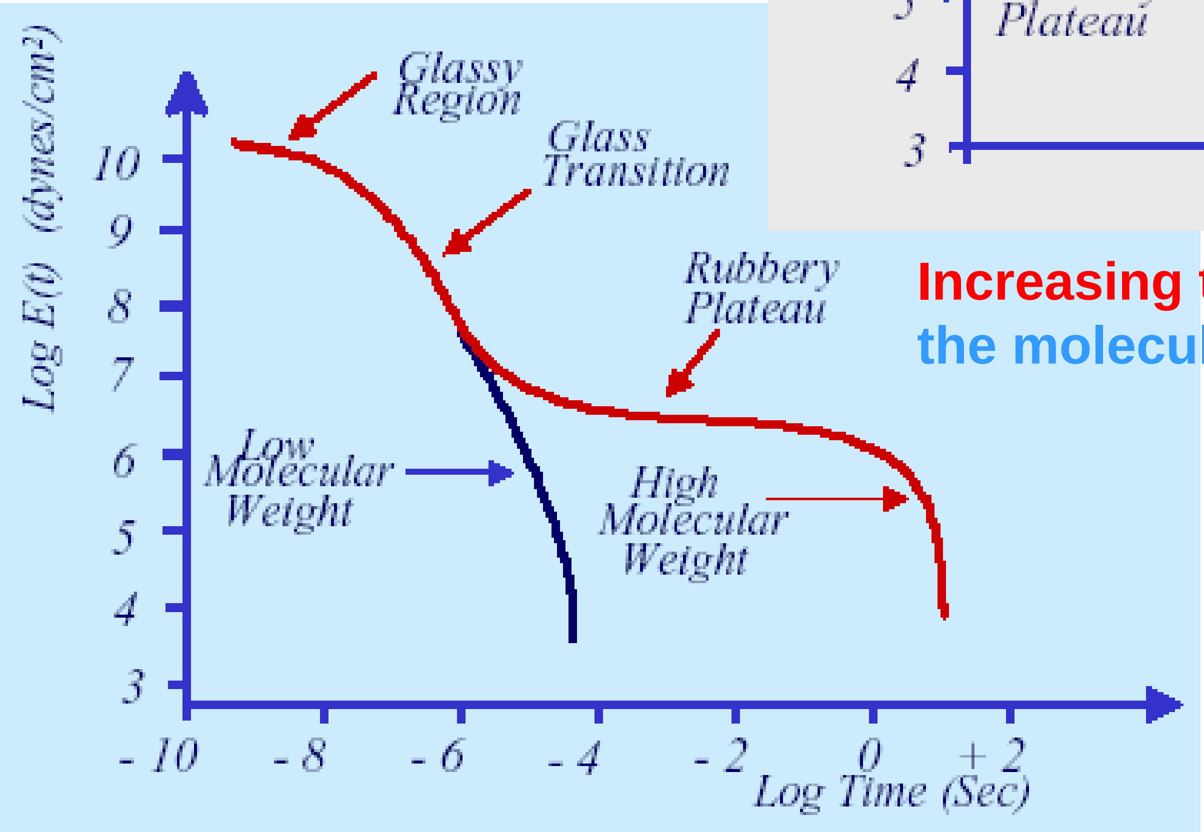
Stretch sample an arbitrary amount, measure the stress required to maintain this strain.

Then E(t) = σ(t)/ε



Time
Temperature
Equivalence

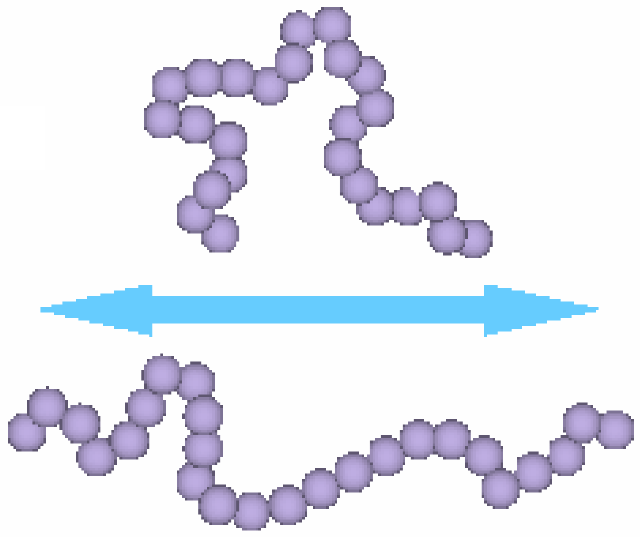




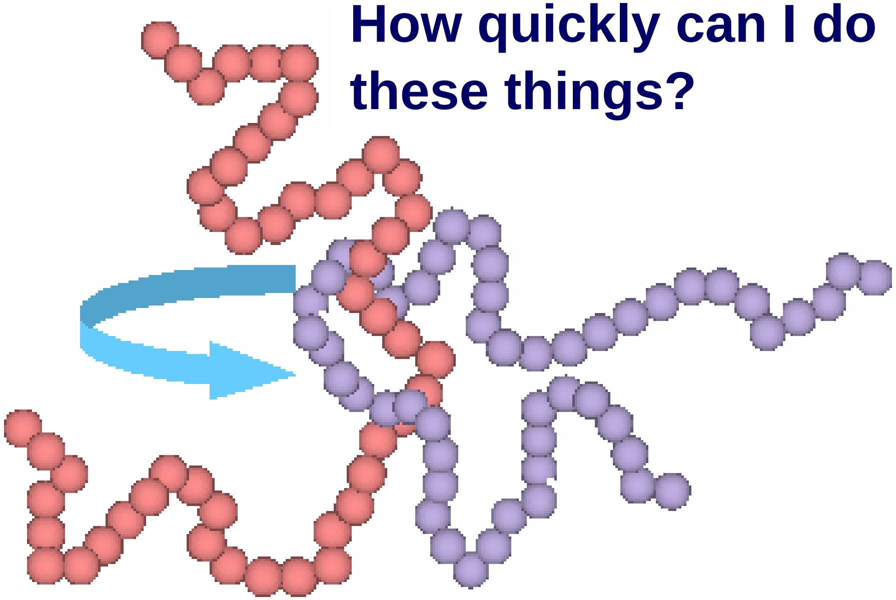
Increasing temperature speeds up the molecular disentanglement.

Relaxation in Polymers

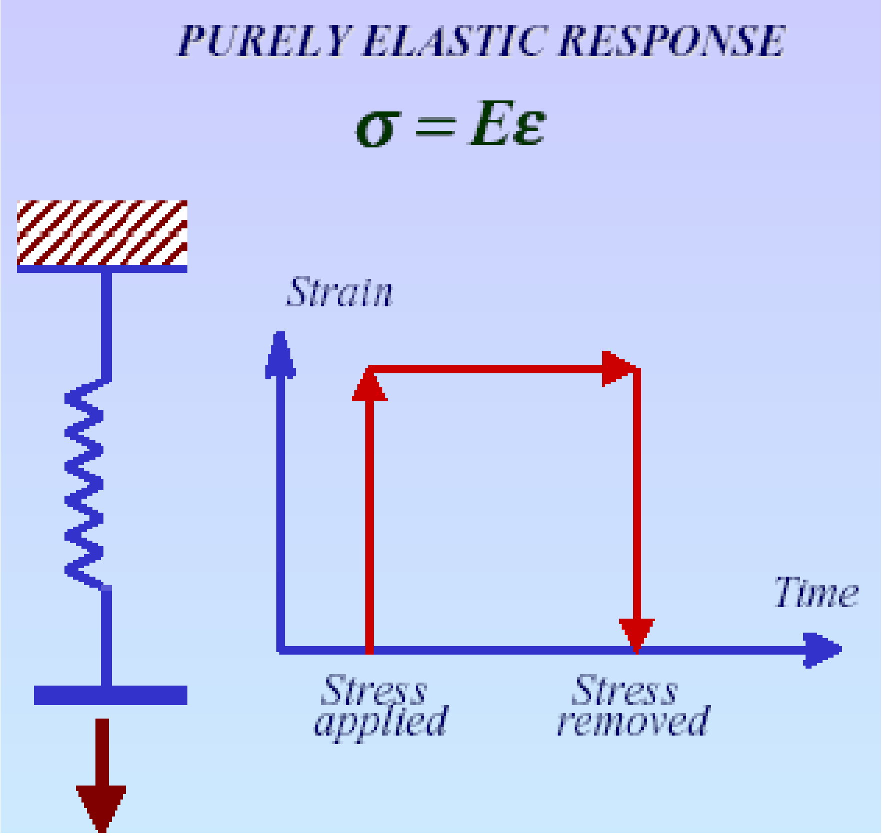
First consider a hypothetical isolated chain in space, then imagine stretching this chain instantaneously so that there is a new end - to - end distance. The distribution of bond angles (trans, gauche, etc) changes to accommodate the conformations that are allowed by the new constraints on the ends. Because it takes time for bond rotations to occur, particularly when we also add in the viscous forces due to neighbors, we say the chain RELAXES to the new state and the relaxation is described by a characteristic time τ.

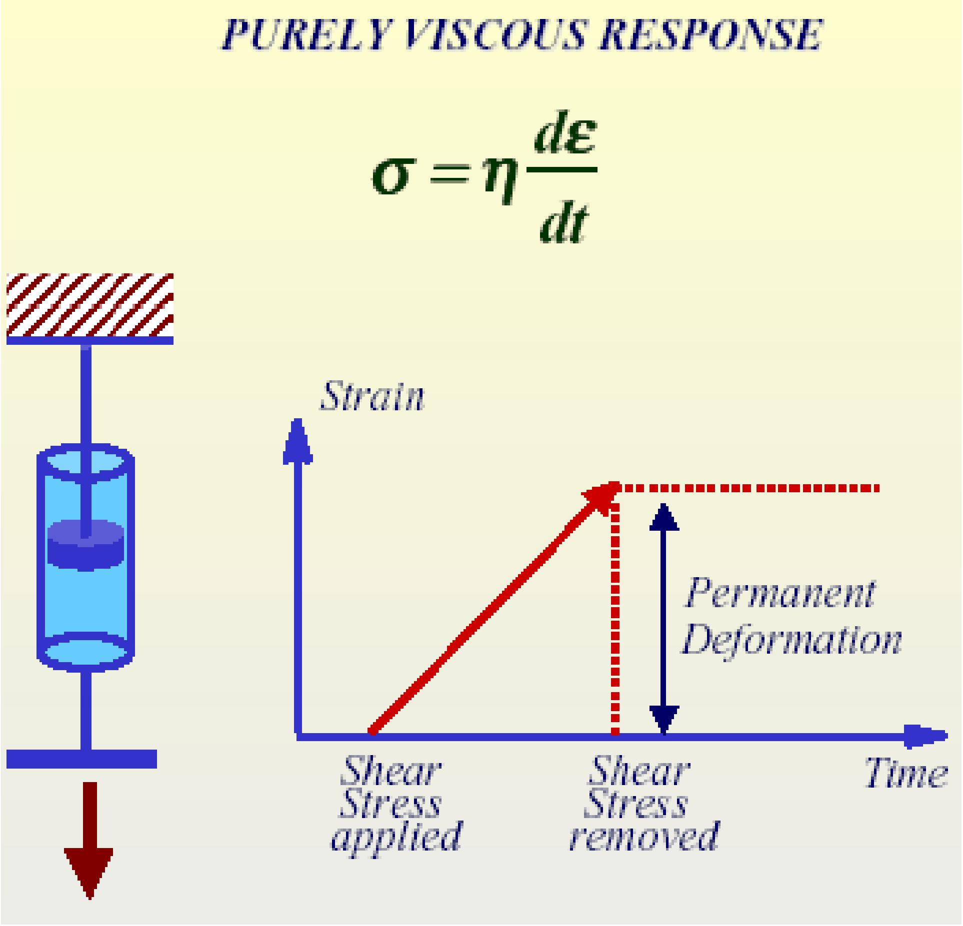


How quickly can I do these things?



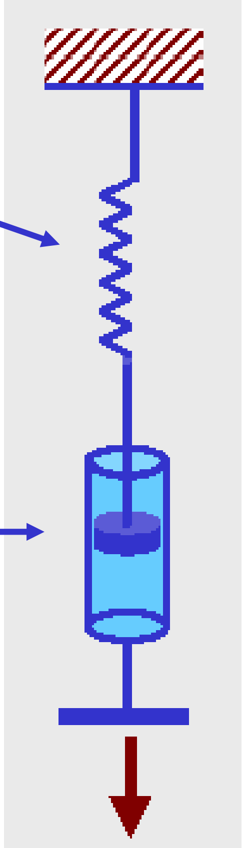
Strain vs. Time for Simple Models





Maxwell Model

Maxwell was interested in creep and stress relaxation and developed a differential equation to describe these properties



Maxwell started with Hooke's law

$$\sigma = E\varepsilon$$

Then allowed σ to vary with time

$$\frac{d\sigma}{dt} = E\frac{d\varepsilon}{dt}$$

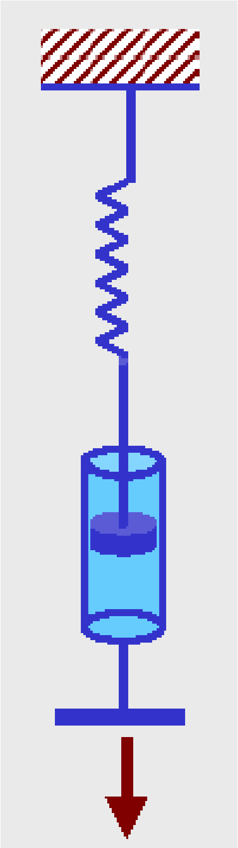
Writing for a Newtonian fluid

$$\sigma = \eta\frac{d\varepsilon}{dt}$$

Then assuming that the rate of is simply a sum of these two contributions

$$\boxed{\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E}\frac{d\sigma}{dt}}$$

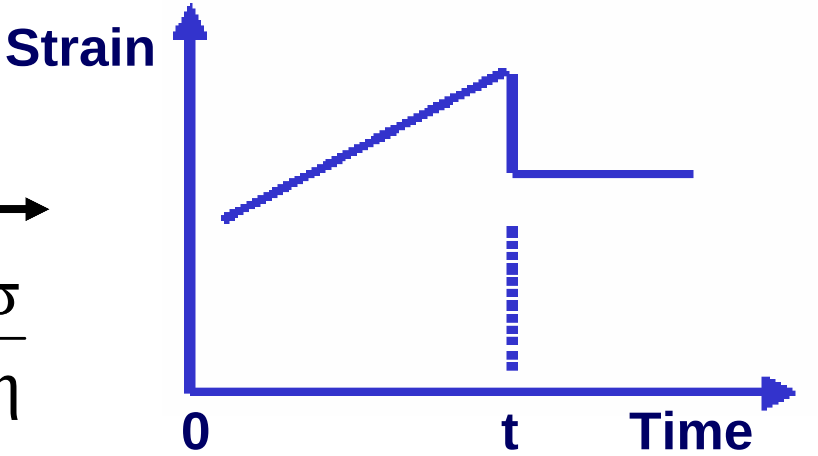
MAXWELL MODEL – Creep and Recovery



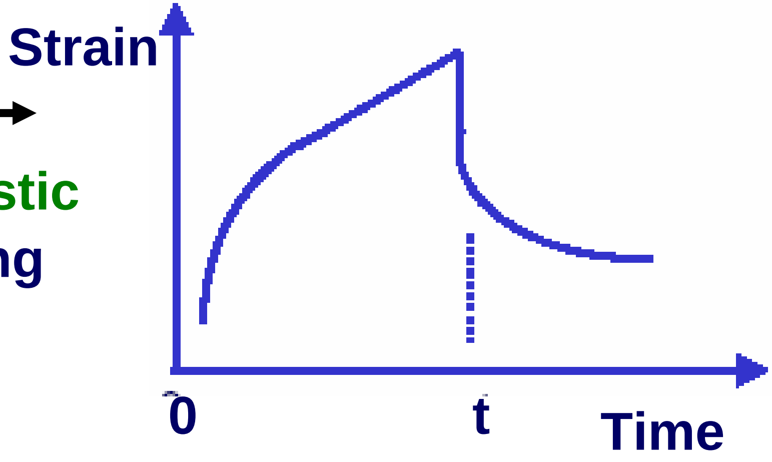
A picture representation of Maxwell's equation

Creep and recovery

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E}\cancelto{0}{\frac{d\sigma}{dt}} \Rightarrow \frac{d\varepsilon}{dt} = \frac{\sigma}{\eta}$$



Recall that real viscoelastic behavior looks something like this



Maxwell Model – Stress Relaxation

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{E}\frac{d\sigma}{dt}$$

In a stress relaxation experiment

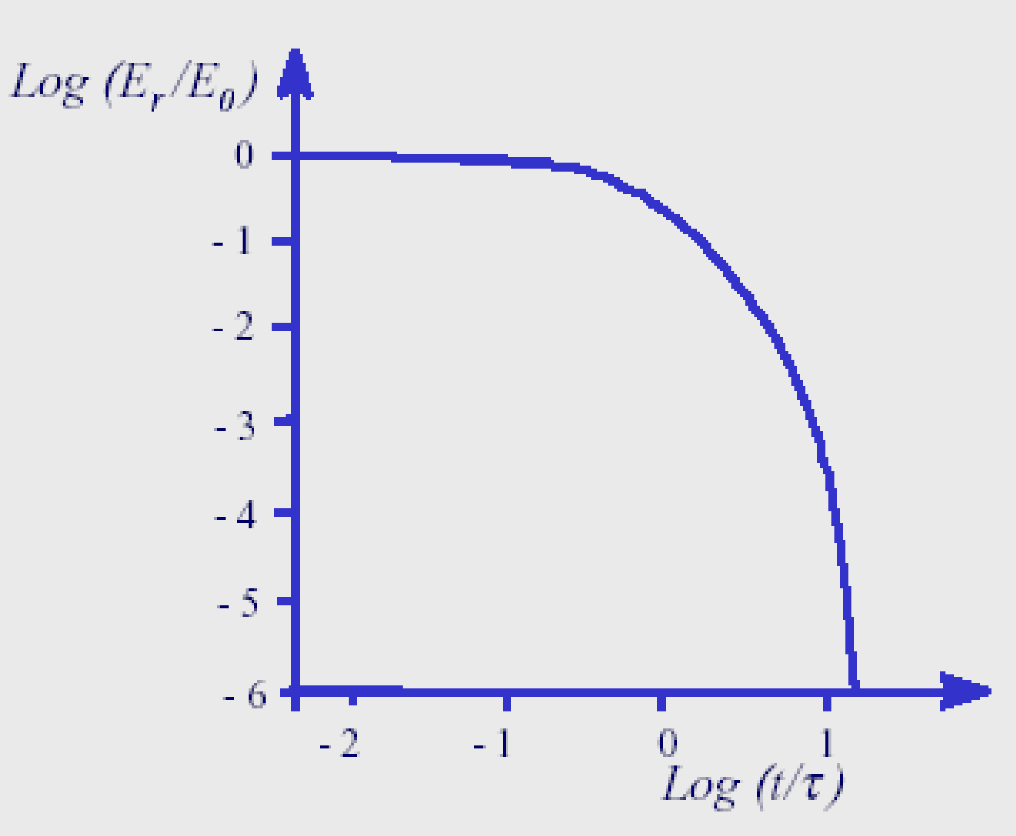
$$\frac{d\varepsilon}{dt} = 0$$

Hence $$\frac{d\sigma}{\sigma} = -\frac{E}{\eta}\,dt$$

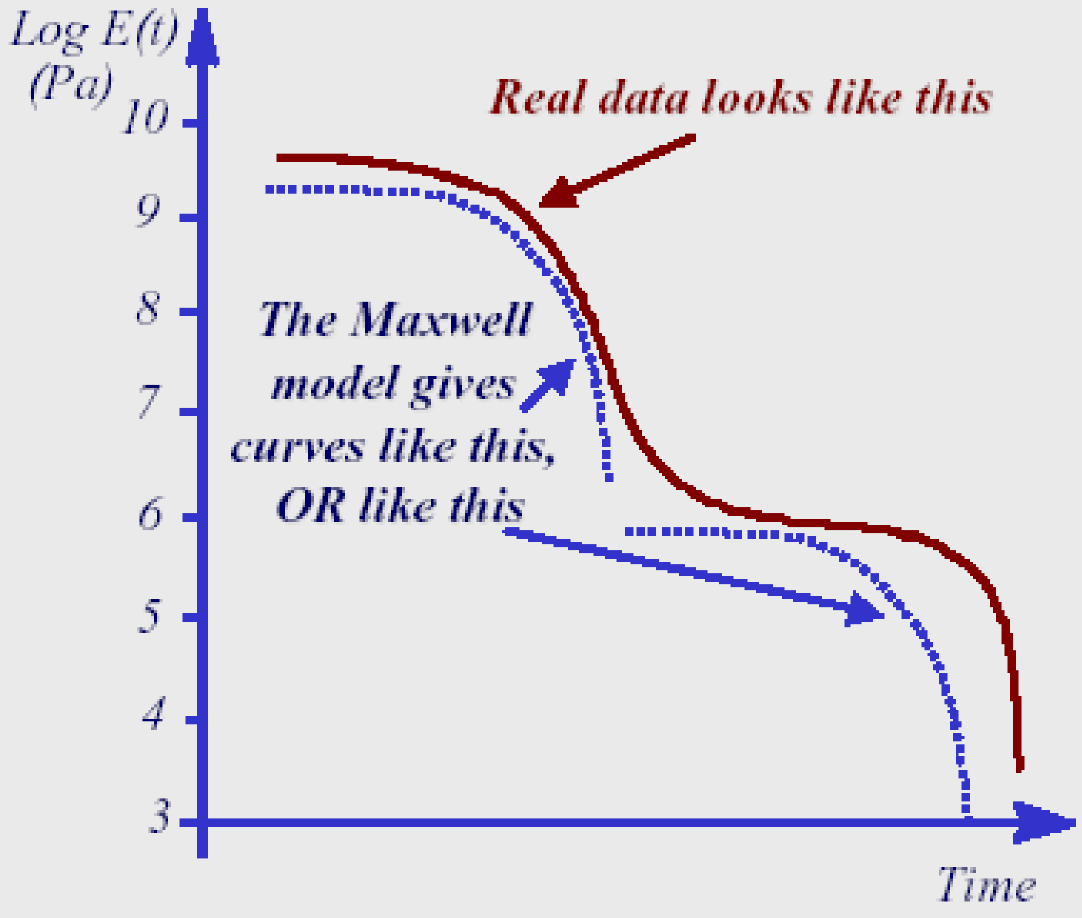
$$\boxed{\sigma = \sigma_0 \exp[-t/\tau_t]}$$

Where $$\tau_t = \frac{\eta}{E}$$

Relaxation time



Maxwell Model – Stress Relaxation



MAXWELL MODEL

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} = \frac{\sigma_0}{\varepsilon_0} \exp\left[-\frac{t}{\tau_t}\right]$$

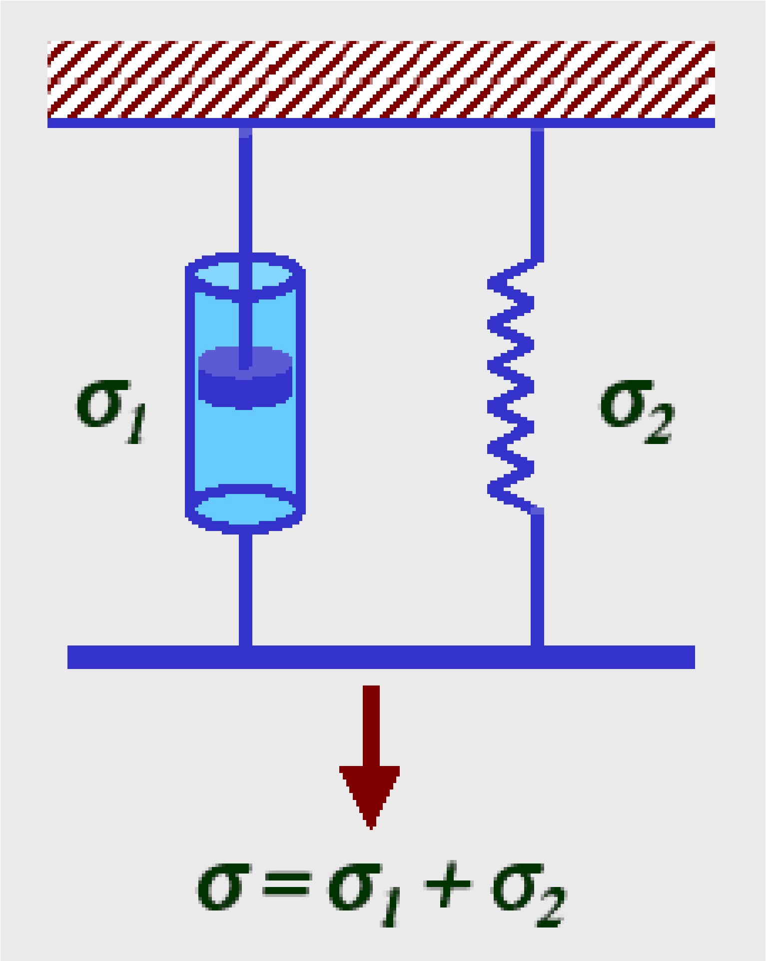
Voigt Model

Maxwell model essentially assumes a uniform distribution of stress. Now assume uniform distribution of strain - VOIGT MODEL

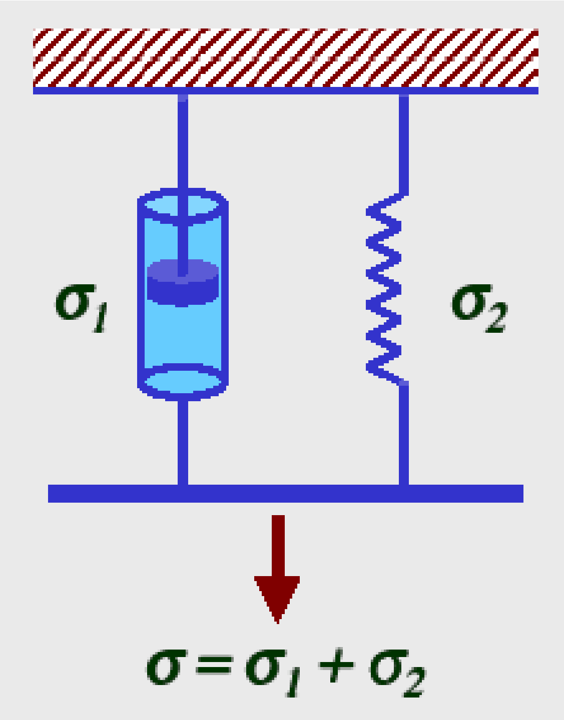
Equation

$$\sigma(t) = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt}$$

(Strain in both elements of the model is the same and the total stress is the sum of the two contributions)



Voigt Model – Creep and Stress Relaxation



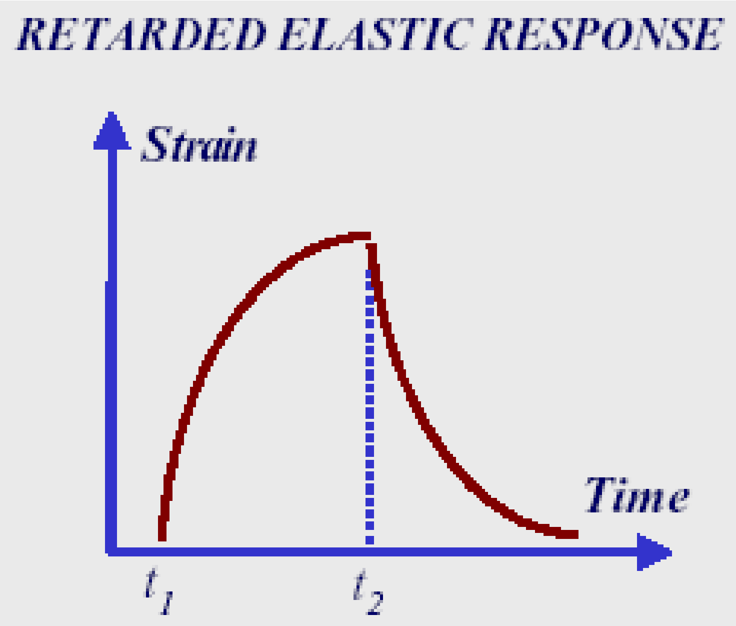
Gives a retarded elastic response but does not allow for “ideal” stress relaxation, in that the model cannot be “instantaneously” deformed to a given strain.

But in CREEP σ = constant, σ_0

$$\sigma(t) = \sigma_o = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt}$$

$$\boxed{\varepsilon(t) = \frac{\sigma_o}{E}\left(1 - \exp\left(-\frac{t}{\tau_t}\right)\right)}$$

τ_t = retardation time $= \dfrac{\eta}{E}$



Creep

Constant Stress, σ_o

$$\sigma(t) = \sigma_o = E\varepsilon(t) + \eta\frac{d\varepsilon(t)}{dt}$$

$$\sigma_o - E\varepsilon(t) = \eta\frac{d\varepsilon(t)}{dt}$$

$$\frac{\sigma_o}{E} - \varepsilon(t) = \frac{\eta}{E}\frac{d\varepsilon(t)}{dt}$$

$$\frac{d\varepsilon}{\frac{\sigma_0}{E} - \varepsilon(t)} = \frac{dt}{\tau_t}$$

$$-\ln\left(\frac{\sigma_0}{E} - \varepsilon(t)\right) + \ln\frac{\sigma_o}{E} = \frac{t}{\tau_t}$$

$$1 - \frac{\varepsilon(t)E}{\sigma_o} = \exp\left(-\frac{t}{\tau_t}\right)$$

$$\boxed{\varepsilon(t) = \frac{\sigma_o}{E}\left(1 - \exp\left(-\frac{t}{\tau_t}\right)\right)}$$

Recovery

$\sigma = 0$ $$\sigma(t) = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt} = 0$$

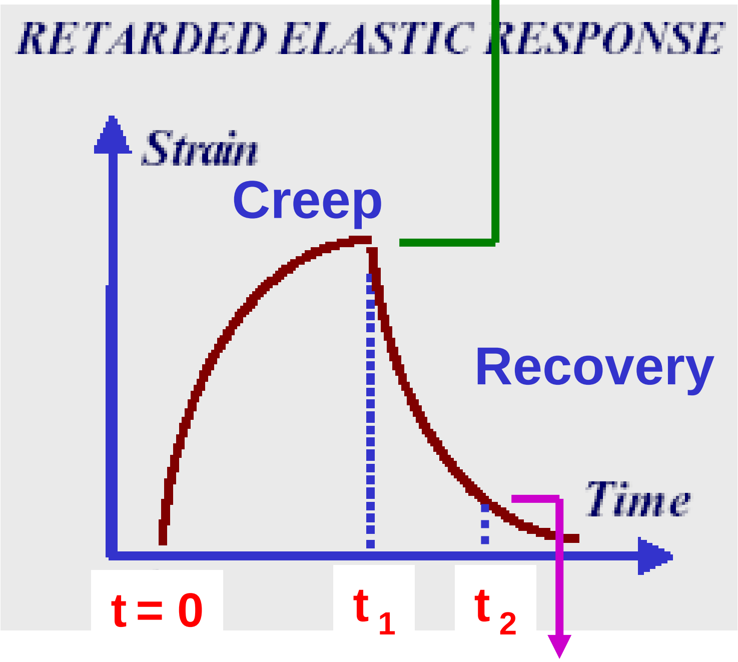
⇨ $$\varepsilon(t) = -\tau_t \frac{d\varepsilon(t)}{dt}$$

$$\frac{d\varepsilon(t)}{\varepsilon(t)} = -\frac{dt}{\tau_t}$$

$$\ln \frac{\varepsilon(t)}{\varepsilon(0)} = -\frac{t}{\tau_t}$$

$$\boxed{\varepsilon(t) = \varepsilon(0)\exp\left(-\frac{t}{\tau_t}\right)}$$

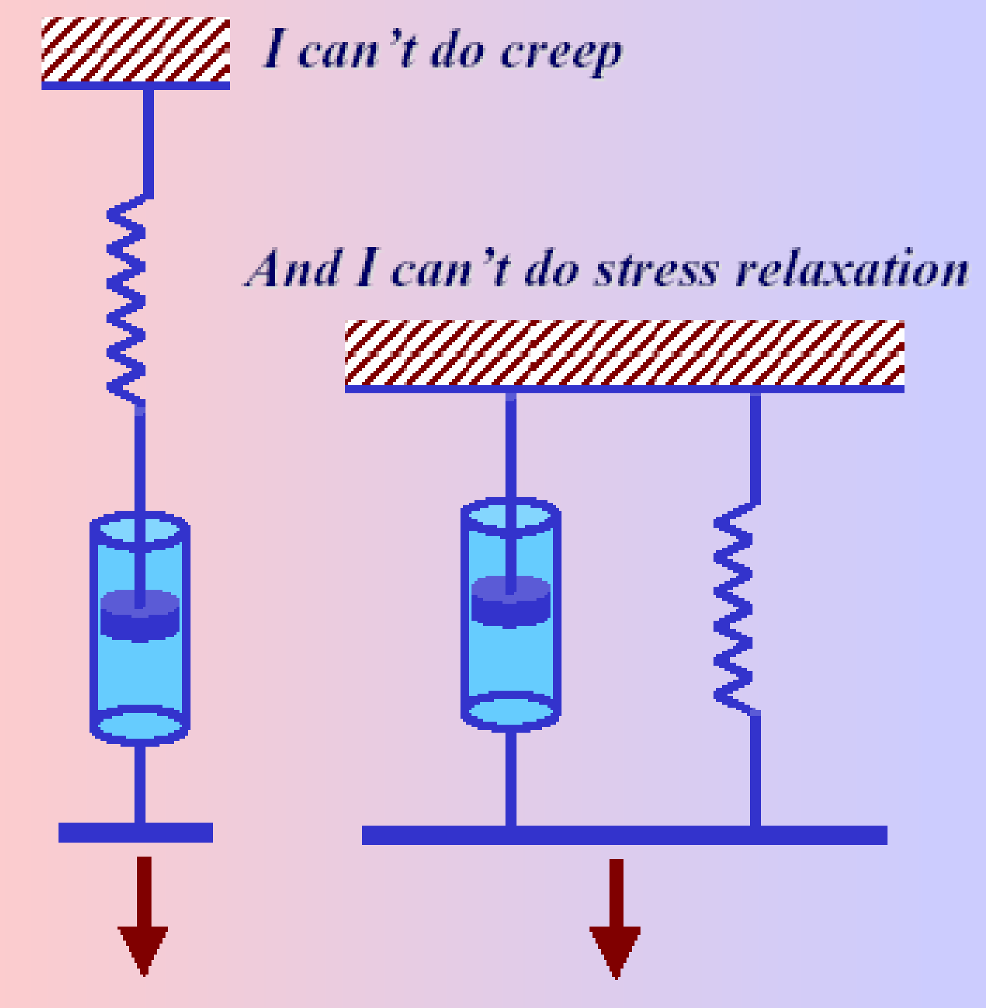
$$\boxed{\varepsilon(t_1) = \frac{\sigma_o}{E}\left(1 - \exp\left(-\frac{t_1}{\tau_t}\right)\right)}$$



$$\varepsilon(t_2) = \varepsilon(t_1)\exp\left(-\frac{t_2 - t_1}{\tau_t}\right)$$

$$= \frac{\sigma_o}{E}\left(1 - \exp\left(-\frac{t_1}{\tau_t}\right)\right)\exp\left(-\frac{t_2 - t_1}{\tau_t}\right)$$

Problems with Simple Models



- The Maxwell model cannot account for a retarded elastic response

- The Voigt model does not describe stress relaxation

- Both models are characterized by single relaxation times - a spectrum of relaxation times would provide a better description

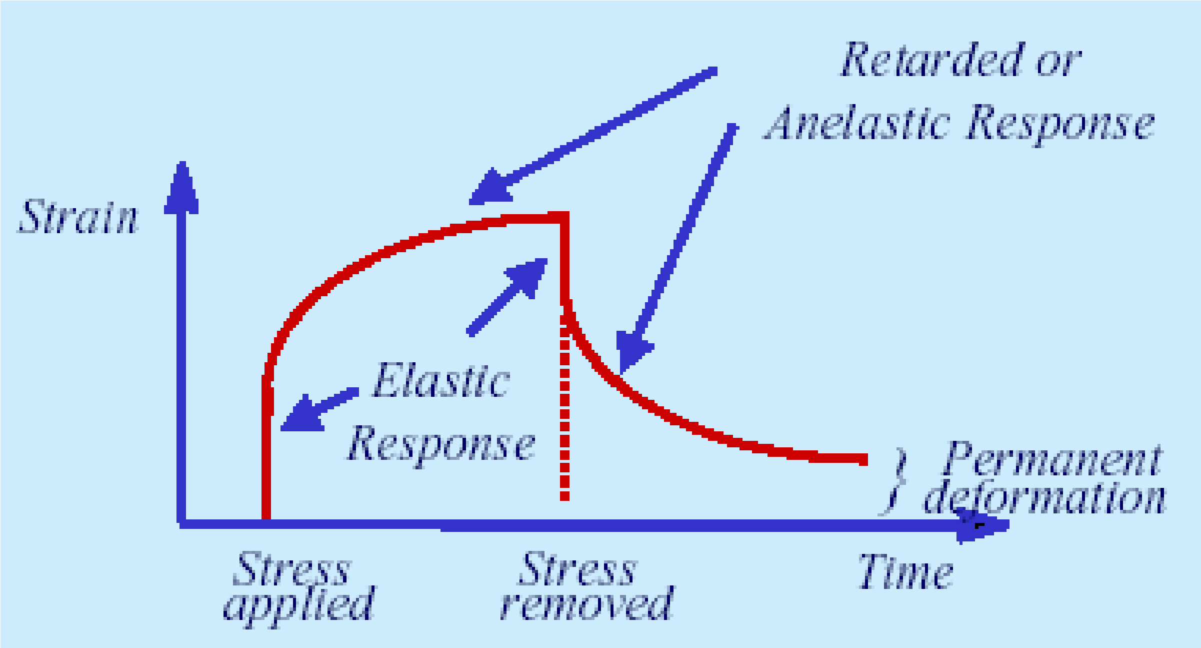
NEXT - CONSIDER THE FIRST TWO PROBLEMS THEN -THE PROBLEM OF A SPECTRUM OF RELAXATION TIMES

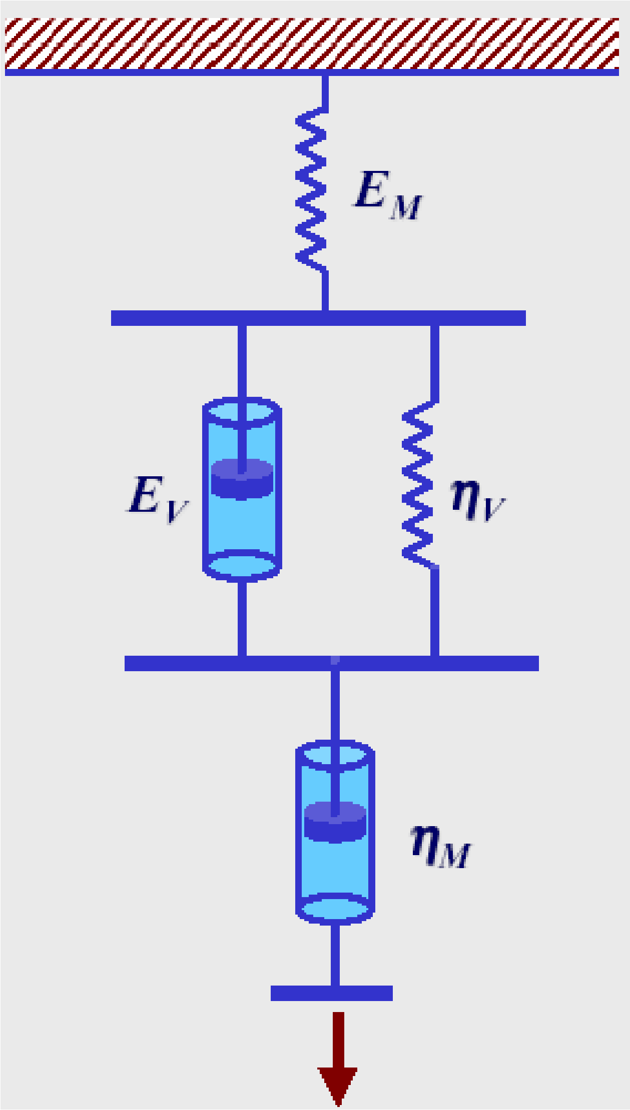
Four – Parameter Model

Elastic + viscous flow + retarded elastic

(e.g. CREEP)

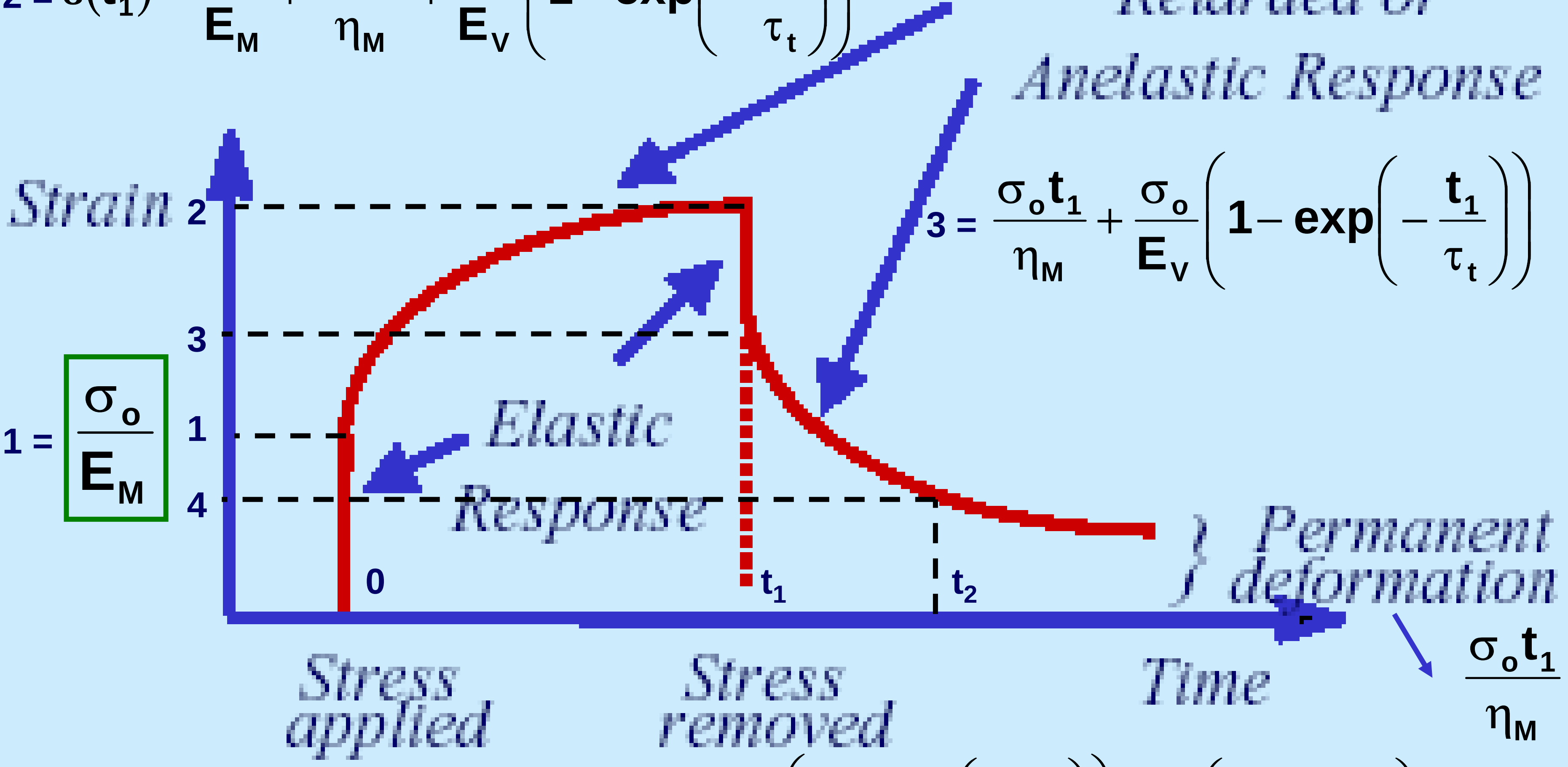
$$\varepsilon(t) = \boxed{\frac{\sigma_o}{E_M}} + \boxed{\frac{\sigma_o t}{\eta_M}} + \boxed{\frac{\sigma_o}{E_V}\left(1 - \exp\left(-\frac{t}{\tau_t}\right)\right)}$$





$$\varepsilon(t) = \boxed{\frac{\sigma_o}{E_M}} + \boxed{\frac{\sigma_o t}{\eta_M}} + \boxed{\frac{\sigma_o}{E_V}\left(1-\exp\left(-\frac{t}{\tau_t}\right)\right)}$$

$$2 = \varepsilon(t_1) = \frac{\sigma_o}{E_M} + \frac{\sigma_o t_1}{\eta_M} + \frac{\sigma_o}{E_V}\left(1-\exp\left(-\frac{t_1}{\tau_t}\right)\right)$$



$$3 = \frac{\sigma_o t_1}{\eta_M} + \frac{\sigma_o}{E_V}\left(1-\exp\left(-\frac{t_1}{\tau_t}\right)\right)$$

$$1 = \boxed{\frac{\sigma_o}{E_M}}$$

$$\frac{\sigma_o t_1}{\eta_M}$$

$$4 = \frac{\sigma_o t_1}{\eta_M} + \frac{\sigma_o}{E_V}\left(1-\exp\left(-\frac{t_1}{\tau_t}\right)\right)\exp\left(-\frac{t_2-t_1}{\tau_t}\right)$$

4.4 Thermal Stability

A) Origins of Decomposition

1) Bond breakage

$\left\{ \begin{array}{l} \text{Decreased materials properties} \\ \text{Depolymerization with many polymers} \end{array} \right.$

This is especially true with vinyl polymers

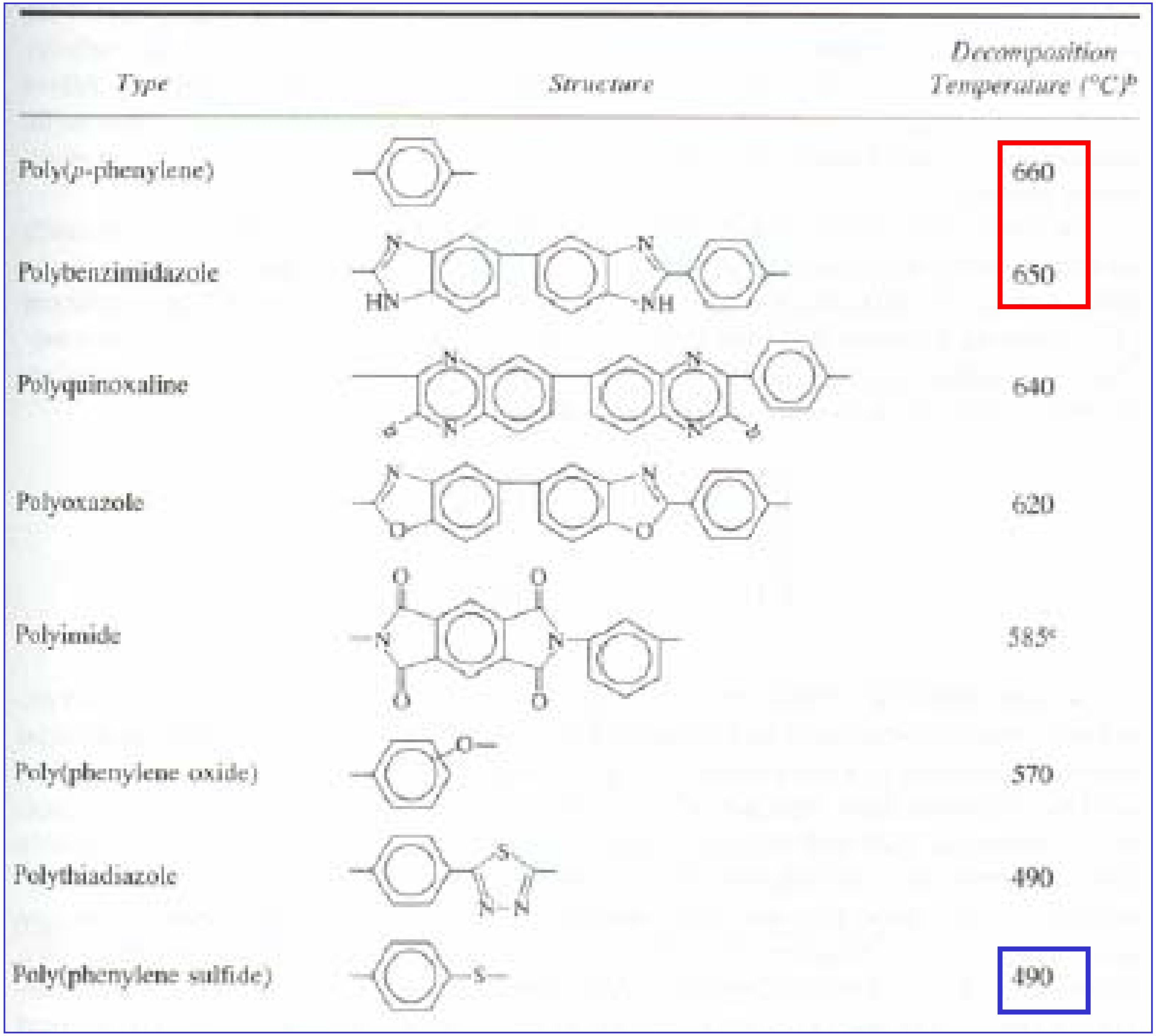
2) Aromatization upon heating

3) Thermal Stability Criterion

$T_d \geq 400\ ^\circ C$

B) Thermally Stable Polymers

TABLE 4.3 Representative Thermally Stable Polymers



Type	*Structure*	*Decomposition Temperature (°C)*[b]
Poly(*p*-phenylene)		660
Polybenzimidazole		650
Polyquinoxaline		640
Polyoxazole		620
Polyimide		585[c]
Poly(phenylene oxide)		570
Polythiadiazole		490
Poly(phenylene sulfide)		490

1) Primarily a function of Bond Energy

a) T↑ ⇒ Bond vibration ↑ ⇒ Bond rupture

b) Cyclic repeating units:

Breaking of one bond in a ring does not lead to a decrease in M.W. and the probability of two bonds breaking within one ring is low

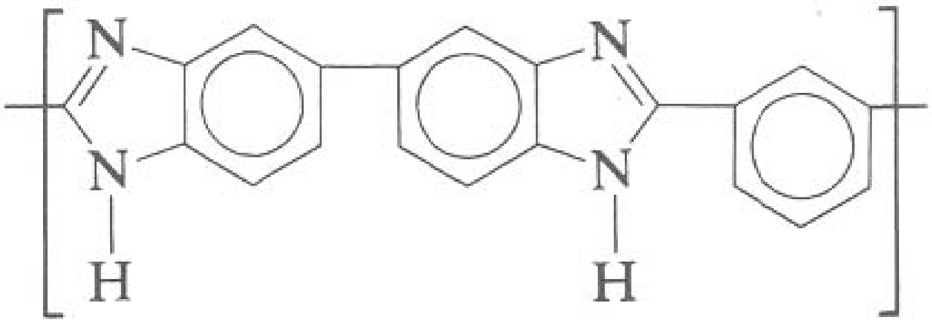
c) Ladder or semiladder polymers : Higher thermal stability than open-chain polymers

2) Thermooxidative Stability Values

a) Initial onset may be lower than those in inert atmospheres

b) Initial decomposition is still via bond rupture then new mechanism involving oxidation may come into play

Polybenzimidazole (Hoechst Celanese, trade name PBI)



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Uses : Astronauts’ space suits and Firefighters’ protective clothing

- Rigid aromatic polymers :

High T_g, High melt viscosity, Low solubility ∴ Intractable

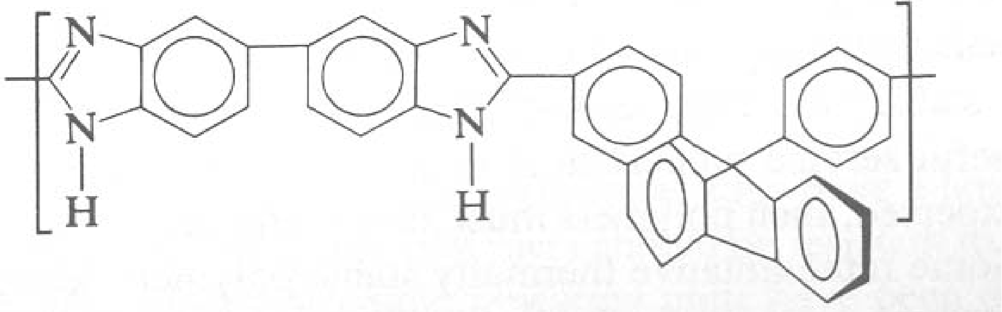
<Solution 1>

Incorporation of “Flexibilizing groups” such as ether or sulfone into the backbone

⇨ Greater solubility and lower viscosity but thermal stability suffers

<Solution 2>

Introduction of cyclic aromatic groups that lie perpendicular to the planar aromatic backbone



Cardo polymers (from Lartin cardo : loop)

⇨ Improved solubility
No sacrifice of thermal properties

<Solution 3>

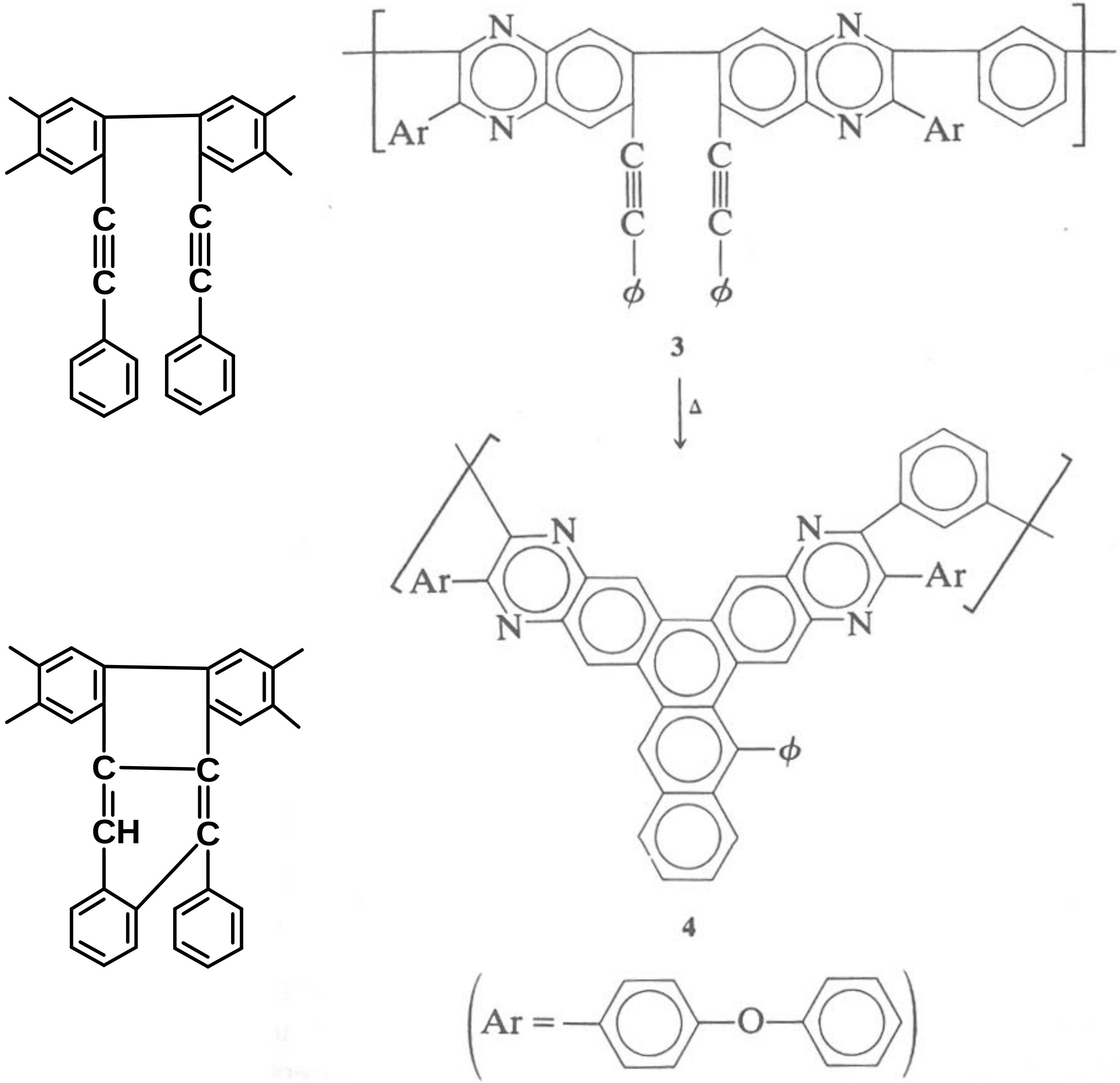
Incorporation of reactive groups into the polymer backbone that undergo intramolecular cycloaddition on heating

(Scheme 4.1)

⇨ **Improved processability**

∵ Longer flow times are possible because little or no crosslinking takes place.

T_g ↑ because of chain stiffening



$T_g = 215°C$

$T_g = 265°C$

Scheme 4.1 Increasing T_g of a polyquinoxaline by intramolecular cycloaddition

<Solution 4>

Aromatic oligomers or prepolymers capped with reactive end groups

➡ End-capped oligomers melt at relatively low temp. and are soluble in a variety of solvents.

On heating, they are converted to thermally stable network polymers

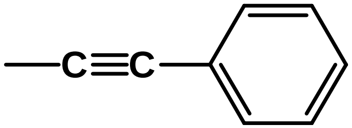
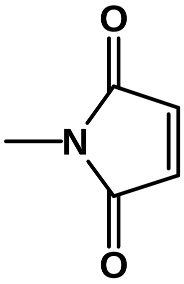
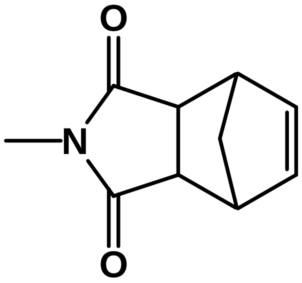
Table 4.4 Reactive End Groups for converting oligomers to network polymers

Phenylethynyl-terminated oligomers for aerospace applications

Chemistry of network polymer formation :

Cycloaddition or addition polymerization reactions of the end groups

Table 4.4 Reactive End Groups for Converting Oligomers to Network Polymers

Type	Structure	Cure Temp (^{o}C)
Cyanate	$-O-C\equiv N$	170
Ethynyl	$-C\equiv CH$	200
Phenylethynyl		350
Maleimide		200
Nadimide		300

Common name for 5-norbornene-2,3-dicarboximide

4.5. Flammability and Flame Resistance

Because synthetic polymers are used increasingly in construction and transportation, considerable efforts has been expended to develop nonflammable polymers.

Inherently nonflammable : Poly(vinyl chloride)

Polymers having a high halogen contents

Self-extinguishing : Polycarbonate

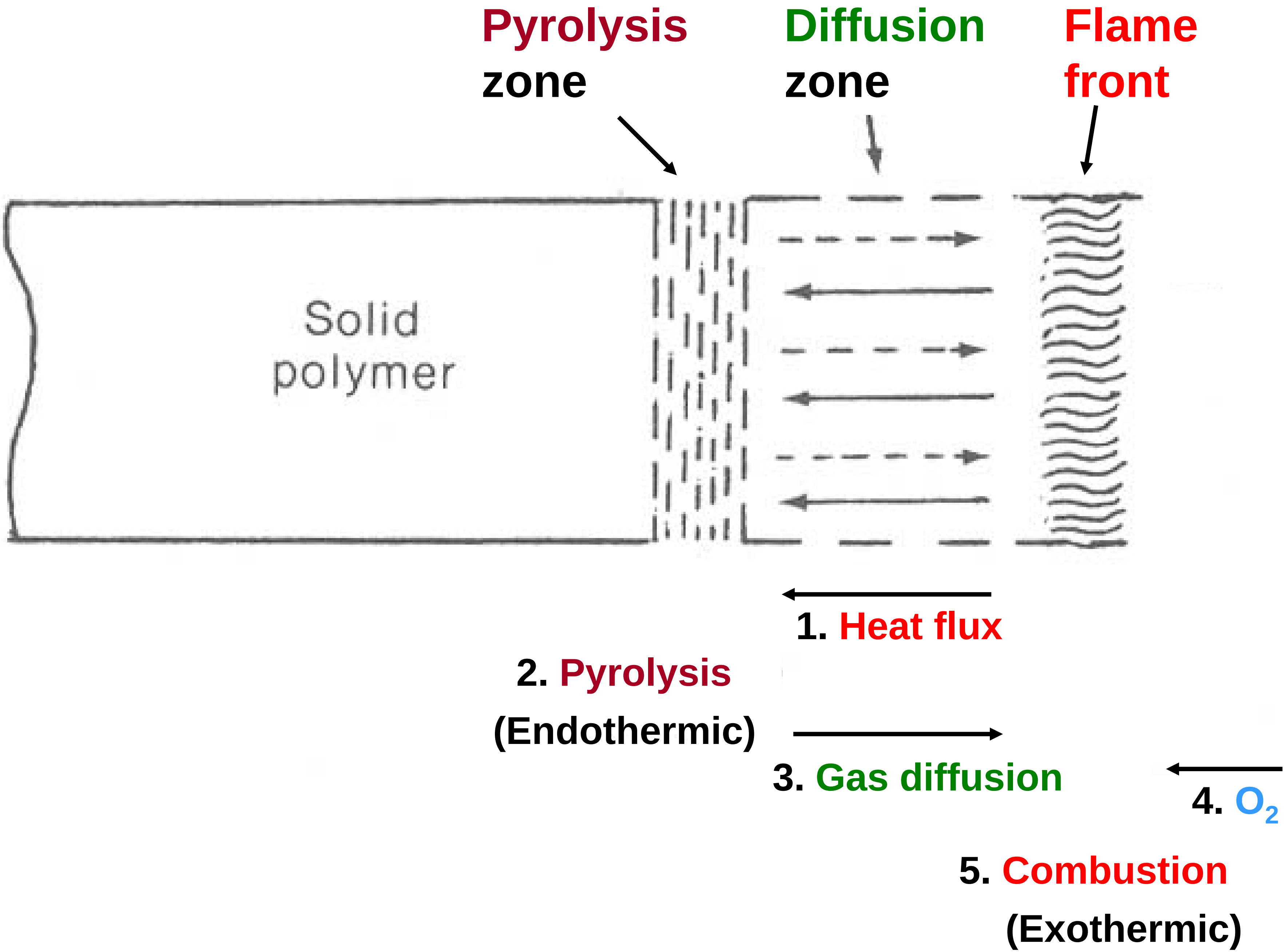
Burn as long as a source of flame is present,
but stop burning when the flame is removed.

Flammable : Most polymers

- **Burning Steps**

1. An external heat source increases the polymer temp to a point where it begins to decompose and release combustible gases.

2. Once the gases ignite, the temp increases until the release of combustibles is rapid enough for combustion to be self-sustaining so long as sufficient oxygen is available to support the combustion process.



Pyrolysis zone

Diffusion zone

Flame front

1. **Heat flux**

2. **Pyrolysis**

(Endothermic)

3. **Gas diffusion**

4. O_2

5. **Combustion**

(Exothermic)

○ Flame Chemistry

Flame contain atoms, free radicals, and ions

Dominant free radicals: H•, HO•, and •O•, and hydrocarbon species

* Hydrogen combustion

● Branching reactions

$H\bullet + O_2 \rightarrow HO\bullet + \bullet O\bullet$

$\bullet O\bullet + H_2 \rightarrow HO\bullet + H\bullet$

● Chain or propagation reactions

$HO\bullet + H_2 \rightarrow H_2O + H\bullet$

● Recombination reactions

$H\bullet + HO\bullet \rightarrow H_2O$

$H\bullet + H\bullet \rightarrow H_2$

* Methane combustion

$$CH_4 \xrightarrow[- H\bullet]{H\bullet,\ HO\bullet,\ \bullet O\bullet} CH_3\bullet$$

$$CH_3\bullet \xrightarrow[- H\bullet]{+\ \bullet O\bullet} CH_2O$$

$$CH_2O \xrightarrow[- H\bullet]{H\bullet,\ HO\bullet,\ \bullet O\bullet} CHO\bullet$$

$$CHO\bullet \xrightarrow[- H\bullet]{H\bullet,\ HO\bullet,\ \bullet O\bullet} CO$$

$$CO \xrightarrow[- H\bullet]{+\ HO\bullet} CO_2$$

Polystyrene, poly(methyl methacrylate) :

Combustible gases

High in monomer ∵ Thermally induced depolymerization

Monomer breaks down further to lower M.W. combustible products, including hydrogen, as it diffuses toward the flame.

Where depolymerization dose not occur, surface oxidation plays a role in generation of combustible gases.

Approaches to flame resistance

1. **Retarding the combustion process in the vapor phase**
2. **Causing "char formation" in the pyrolysis zone**
3. **Adding materials that decompose either to give nonflammable gases or endothermically to cool the pyrolysis zone**

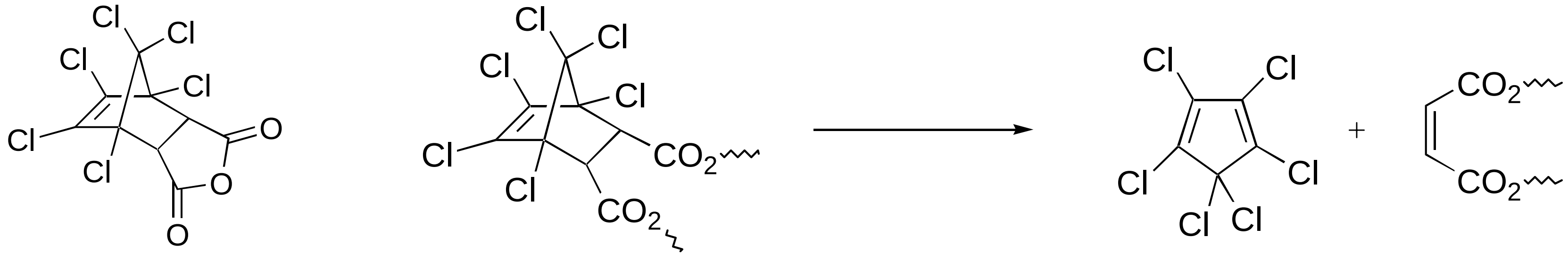
1. Combustion occurs by a series of free radical propagation and radical transfer reactions

Reduce the concentration of radicals in the vapor by incorporating radical traps into the polymer

e.g. Halogenated compounds

Hydrogen halide that is released reacts with free radicals to form less reactive halogen atoms.

Polyesters prepared with 5 decompose on heating by the retrograde Diels-Alder reaction, and the resultant hexachlorocyclopentadiene, 6, suppresses radical formation in the vapor phase and inhibits free radical depolymerization in the pyrolysis zone.



5 **6**

Antimony oxides are often used in combination with halogen compounds

∵ Synergistic effects arising from formation of antimony halides

Disadvantage of halogen compounds : Toxicity of hydrogen halide formed during burning.

Halogen in Sb-X FR system interrupts the high-energy hydrogen-oxygen branching and chain reactions by competing for hydrogen atoms and hydroxyl radicals

$$H\bullet + HBr \rightarrow H_2 + Br\bullet$$

$$HO\bullet + HBr \rightarrow H_2O + Br\bullet$$

$$Br\bullet + H\bullet \rightarrow HBr$$

Sb_2O_3 + Chlorinated organic compounds

$$Sb_2O_3 + 2\ HCl \rightarrow 2\ SbOCl + H_2O$$

$$5\ SbOCl \rightarrow SbCl_3 + Sb_4O_5Cl_2\ (170 – 280\ ^oC)$$

$$3\ Sb_4O_5Cl_2 \rightarrow 2\ SbCl_3 + 5\ Sb_2O_3\ (320 – 700\ ^oC)$$

Antimony-Halogen Synergism

$$SbX_3 + H\bullet \rightarrow HX + SbX_2$$

$$SbX_2 + H\bullet \rightarrow HX + SbX$$

$$SbX + H\bullet \rightarrow HX + Sb$$

$$Sb + \bullet O\bullet \rightarrow SbO$$

2. Char formation at the surface of polymer

Acts as a barrier to inhibit gaseous products from diffusing to the flame, and to shield the polymer surface from the heat flux.

Aromatic polymers have a natural tendency toward char formation, which accounts for their generally low flammability.

Crosslinking increases char formation

Introduction of chloromethyl groups onto polystyrene

∵ Crosslinking during pyrolysis

Phosphorus-containing compounds: Effective in reducing the flammablility of cellulose by promoting dehydration to yield unsaturated compounds that subsequently polymerize to a crosslinked char.

Intumescent flame retardants: Flame retardants that promote formation of a carbonaceous char.

3. Hydrated alumina, $Al_2O_3 \cdot 3H_2O$

Evolve water endothermically to cool the pyrolysis zone

Sodium bicarbonate decomposes to form carbon dioxide, which in turn dilutes the combustible gases.

Toxic decomposition products and smoke

HCN ← N-containing polymers such as polyamides and polyurethanes
HCl ← Poly(vinyl chloride)
CO ← Almost all polymers

Smoke arises from formation of acetylene and benzene, which condense to form soot particles.

Ironically, flame retardants that operate in the vapor phase probably promote smoke formation by removing radicals that might otherwise oxidize the soot-forming particles.

4.6 Chemical Resistance

One of the problems that oil companies face with their huge petroleum storage tanks: rusting away of the metal bottom from underneath.

<Remedy>

Spray-coating the inside floor of the tanks with glass fiber-reinforced unsaturated polyester

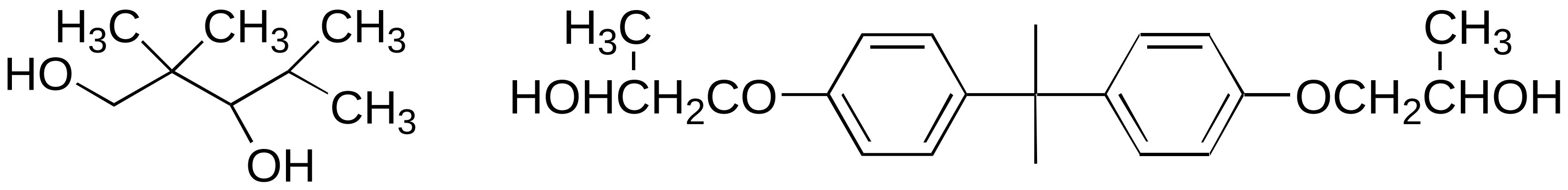
→ Lengthens the tank's lifetime significantly

→ Avoids the expense of having to replace the tank bottom with steel

Two general approaches to increase chemical resistance

1. **To increase the steric hindrance about the ester groups**
2. **To reduce the # of ester groups per unit chain length**

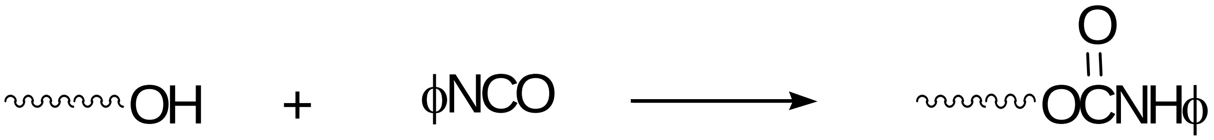
Both increase the hydrophobic nature of the polyesters



Another approach:

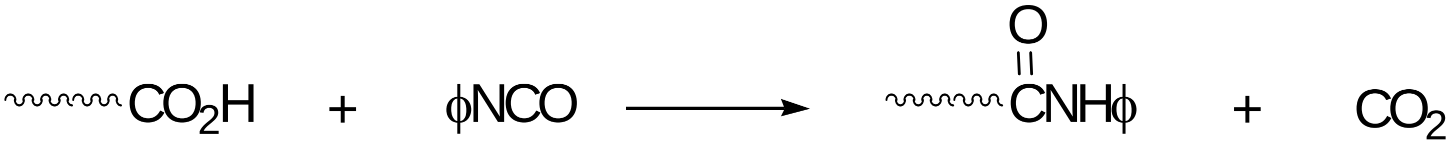
To reduce the hydrophilic nature of the end groups

Phenyl isocyanate converts hydroxyl groups of polyesters to urethanes,



$$\sim\sim\sim OH \quad + \quad \phi NCO \longrightarrow \sim\sim\sim O\overset{\overset{O}{\|}}{C}NH\phi$$

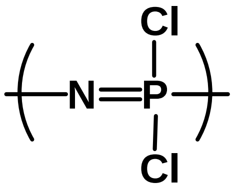
and carboxyl to amide



$$\sim\sim\sim CO_2H \quad + \quad \phi NCO \longrightarrow \sim\sim\sim \overset{\overset{O}{\|}}{C}NH\phi \quad + \quad CO_2$$

Fluorine:

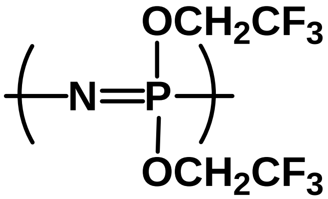
Element that imparts both water and solvent resistance to a variety of polymers



$$-\!\left(N=\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}}\right)\!-$$

Polyphosphazene:

Very unstable in the presence of moisture



$$-\!\left(N=\overset{\displaystyle OCH_2CF_3}{\underset{\displaystyle OCH_2CF_3}{P}}\right)\!-$$

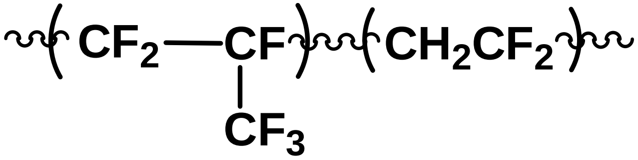
Highly moisture resistant

Ethylene-chlorotrifluoroethylene copolymer:

$-(CH_2CH_2)-(CClFCF_2)-$

A chemically resistant coating for underground cables.

$-(CF_2CF_2)-$ $-(CH_2CF_2)-$



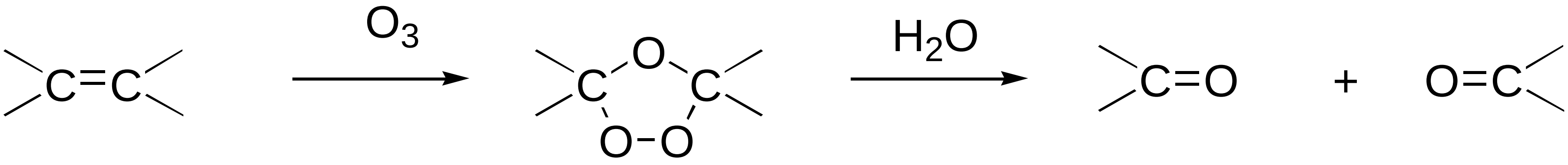
$$\sim\left(CF_2-\underset{\displaystyle CF_3}{CF}\right)\sim\left(CH_2CF_2\right)\sim$$

For gaskets, sealants, valves, and so on, where resistance to lubricating fluids is necessary

Ozone:

Formed by the action of ultraviolet light or electrical discharge on oxygen

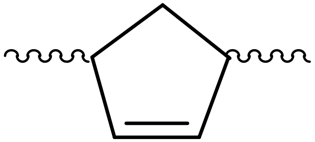
Degrades polymers containing double bonds in backbone by ozonolysis followed by hydrolysis



<Solution>

To replace the commonly used 1,3-butadiene or isoprene in the elastomer with a cyclic diene such as cyclopentadiene.

Ozonolysis may still occur, but the backbone remains intact.



Crystalline polymers: More resistant than amorphous counterparts

∵Close chain packing reduces permeability

Crosslinking increase solvent resistance

Particularly important in the microelctronics industry

Coating a substance with a polymer that crosslinks under the influence of light or ionizing radiation.

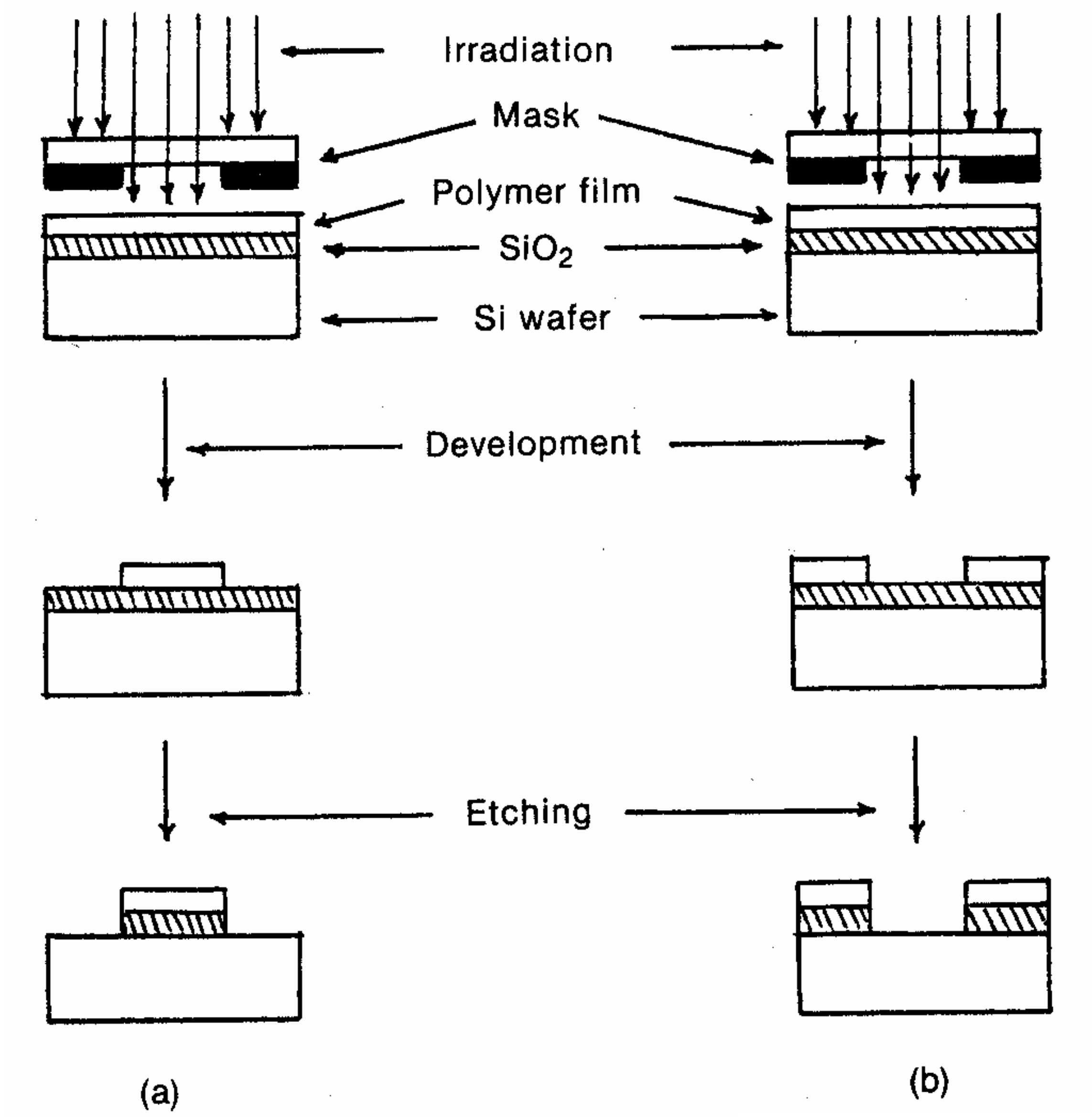
A mask carrying the pattern to the transferred to the substrate is placed over the coated surface is irradiated.

The pattern allows radiation through, and those portions of the polymer thus exposed undergo crosslinking.

When the mask is removed, the unexposed parts of the polymer are dissloved with solvents, leaving behind the desired pattern.

Negative resist: the exposed portions of the surface becomes resistant to solvent

Fig. 4.12 Lithographic procedure in manufacture of integrated circuits



Crosslinking
Polarity Change

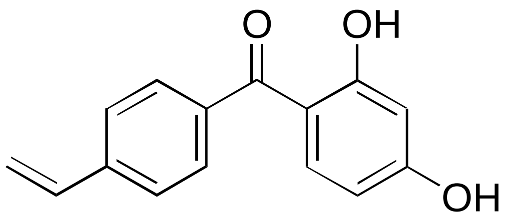
Degradation
Polarity Change

Negative resists

Positive resists

Sunlight brings about polymer degradation

Monomer containing ultraviolet-absorbing chromophores such as 2,4-dihydroxy-4’-vinylbenzophenone have been incorporated into vinyl polymers to improve light stability.



4.7 Degradability

Most polymers: very durable → Polymer waste products

Degradable by sunlight and soil microorganisms

↓ ↓

Photodegradable Biodegradable

New markets in agriculture, medicine, and microelectronics for polymers that degrade at a predictable rate.

A) Photochemically degradable = Photodegradable

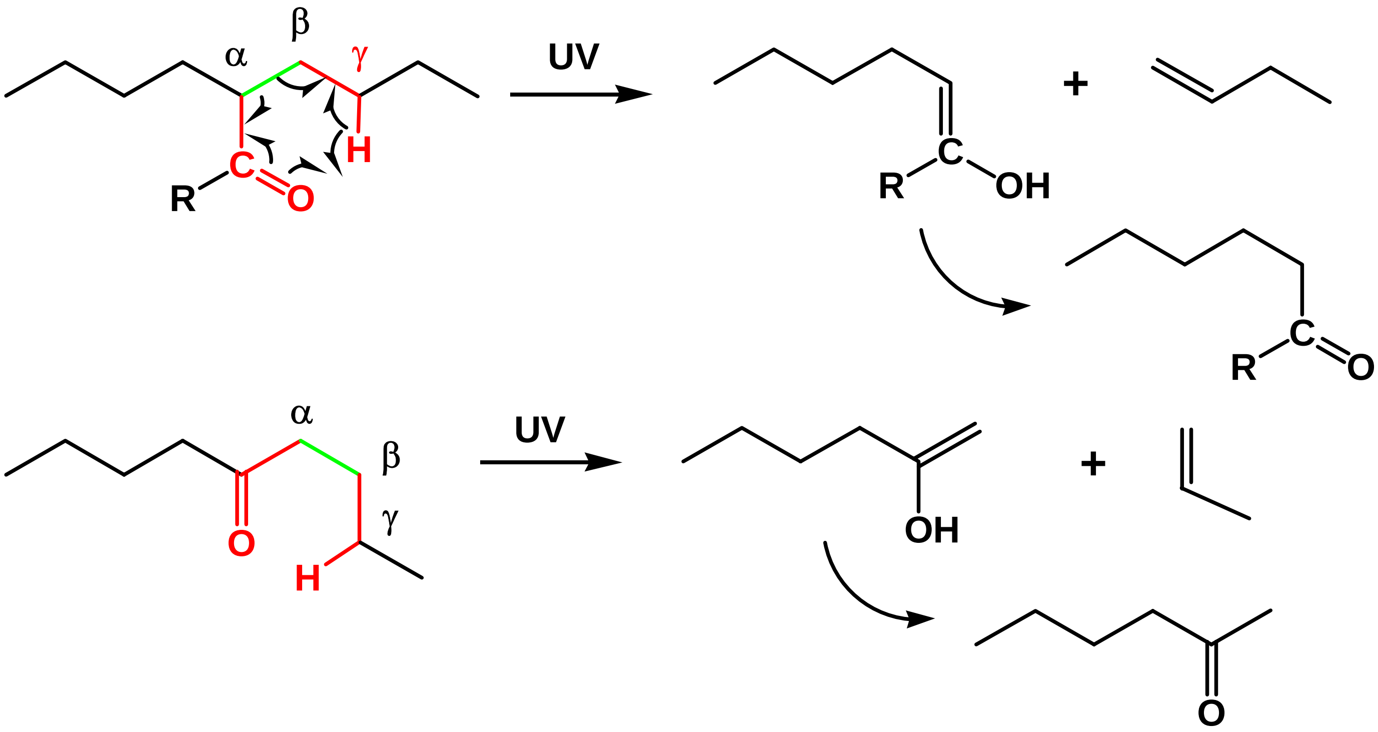
Incorporation of carbonyl groups

Absorb UV radiation to form excited states

↓

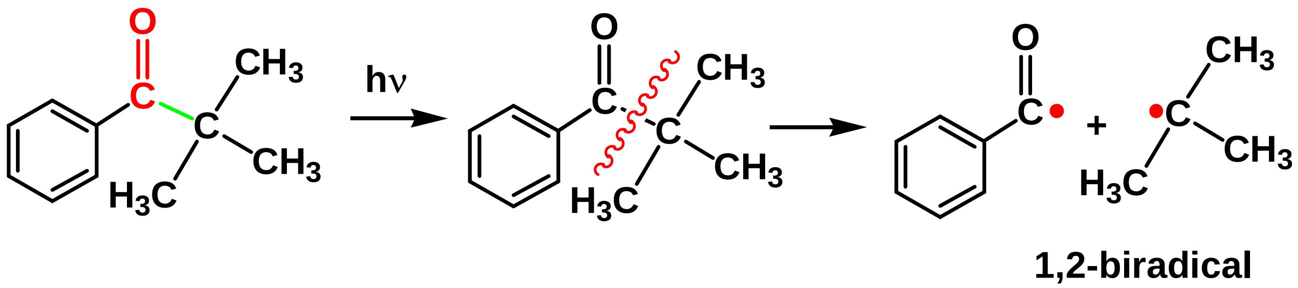
Bond cleavage

Norrish type II reaction

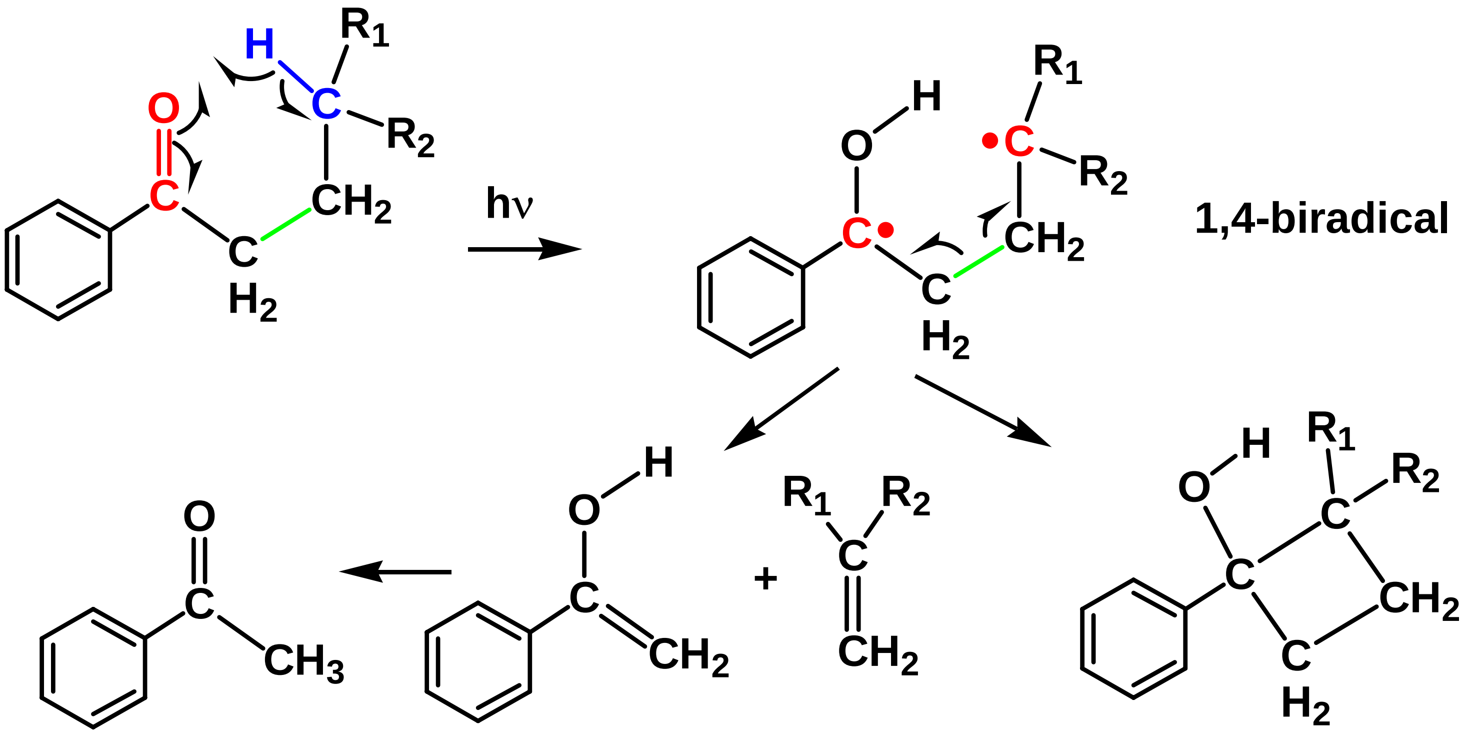


Commercially available photodegradable packing materials employ this technology

Norrish type I reation



Norrish type II reation



B) Biodegradable polymers

Microorganisms degrade polymers by catalyzing hydrolysis and oxidation.

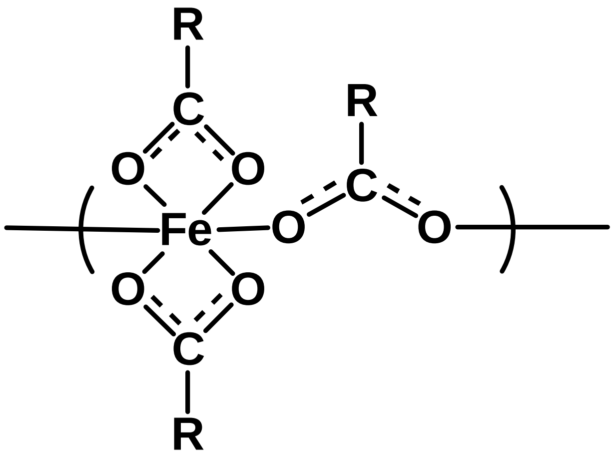
The lower the M.W., the more rapidly the polymer degrades.

C) Resist technology and controlled release applications.

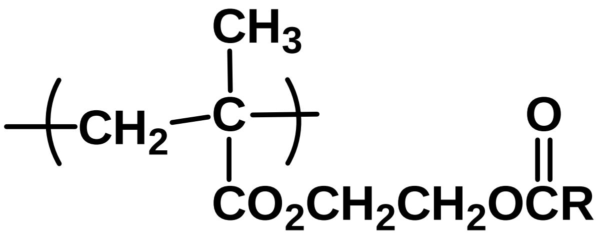
Degradable polymers are used for positive resists

Controlled release refers to the use of polymers containing agents of agricultural, medicinal, or pharmaceutical activity, which are released into the environment of interest at relatively constant rates over prolonged periods.

Herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) has been incorporated into polymers either as a chelate with iron (16) or as a hydrolyzable pendant ester group on a vinyl polymer (17).



(16)

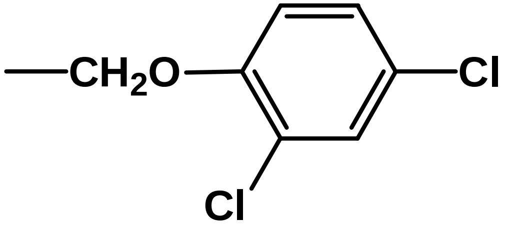


$$-\!\left(CH_2-\overset{CH_3}{\underset{CO_2CH_2CH_2O\overset{O}{\overset{\|}{C}}R}{C}}\right)\!-$$

(17)

where

R=

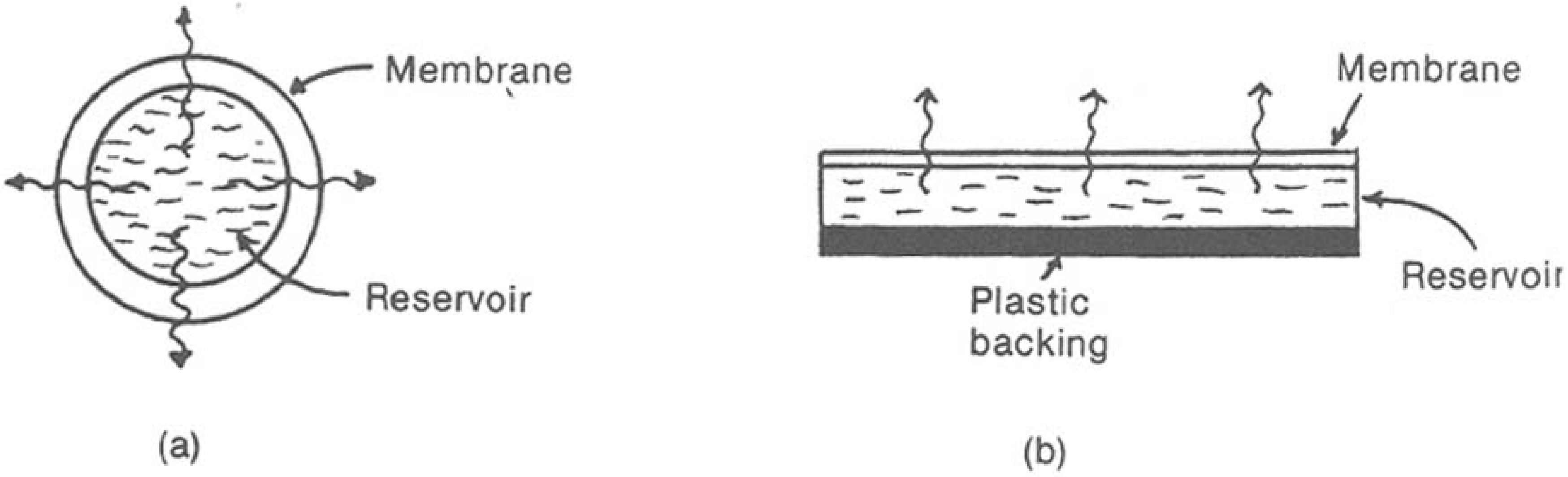


Controlled release based on polymer permeability to encapsulate the active reagent within a polymeric membrane or a strip.

Fig 4.13 Membrane-controlled release devices

(a) Microencapsulation

(b) Strip

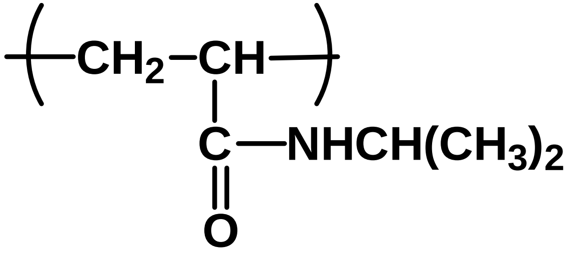


Transdermal patches: **release drugs through the skin**

Degradable polyesters: **used as disappearing surgical sutures.**

Smart polymers: **polymers that respond in a predictable way to change in temperature or polarity**

e.g. Poly(N-isopropylacrylamide),

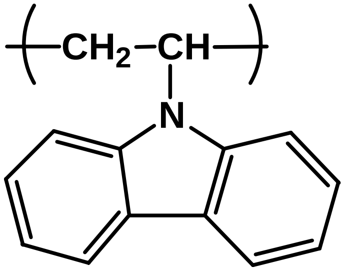


$$\left(CH_2-\underset{\underset{\displaystyle O}{\overset{\displaystyle \|}{C}}-NHCH(CH_3)_2}{\underset{|}{CH}} \right)$$

Shrinks reversibly in response to increase in temperature

4.8 Electrical conductivity

A) Poly(N-vinylcarbazole)



Photoconducting, conduct electricity a small degree under the influence of light

Used in the electrophotography (phtocopying) industry.

B) Poly(sulfur nitride) and polyacetylene:

Highly conducting in the presence of dopants

C) Structural features for conduction

1. Delocalization: an extended conjugated system is usually necessary for backbone conductivity

2. Doping

Dopants:

- Electron acceptors: e.g. AsF_5 or halogen
- Electron donors: e.g. alkali metals

Conductivity varies with dopant concentration

3. Morphology:

Conduction is influenced by configurational and conformational factors, as well as crystallinity.

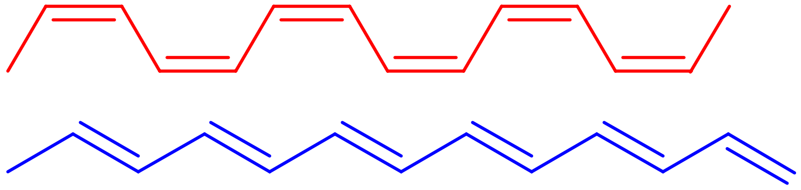
Conductivity of polyacetylene film in the direction of molecular alignment is increased significantly by stretching

Insulators: $\sigma < 10^{-8}$ **S/cm**
Semiconductors: $10^{-7} < \sigma < 10^{-1}$ **S/cm**
Conductors: $\sigma > 10^{2}$ **S/cm**

Poly(sulfur nitride): $\sigma = 100$ **S/cm**
Superconductivity at $T < 0.3$ **K**

Polyacetylene

Cis $\sigma = 1.7 \times 10^{-9}$ **S/cm**
Trans $\sigma = 4.4 \times 10^{-5}$ **S/cm**



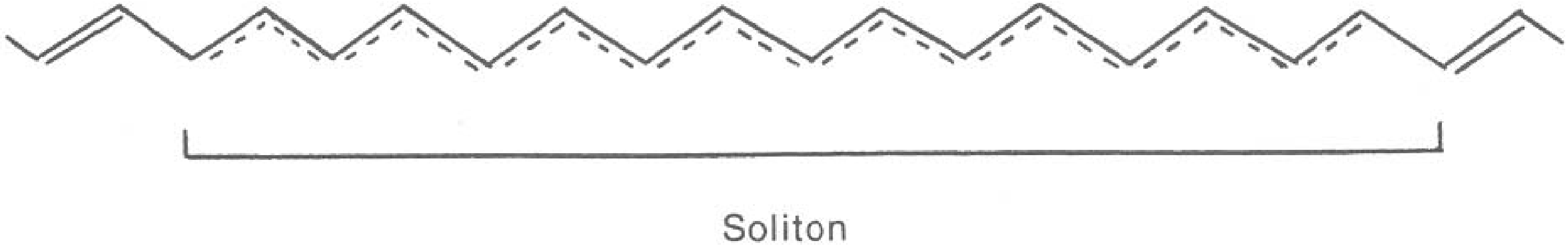
Doping apparently converts the red metallic-colored cis isomer to blue metallic trans.

Dopant forms a charge transfer complex with the polymer that give rise to highly delocalized cation radicals or anion radicals depending on whether the dopant is electron accepting or donating, respectively

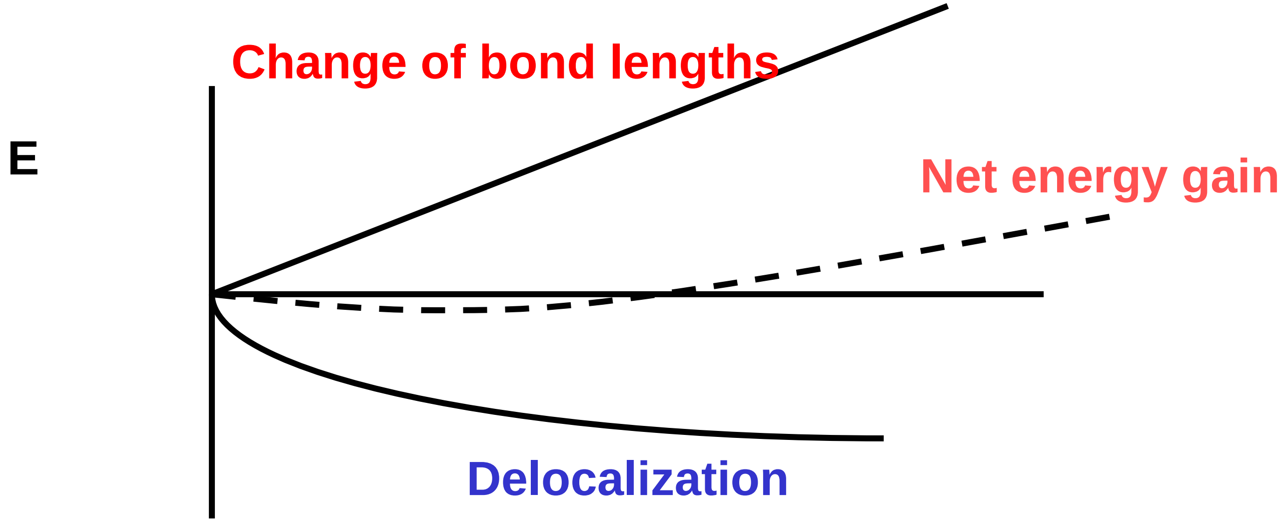
$$2\,\left(\!-CH{=}CH-\!\right) \;+\; 3I_2 \;\longrightarrow\; \left(\!-CH{=}CH-\!\right)^{\overset{+}{\cdot}} \;+\; 2I_3^{-}$$

$$\left(\!-CH{=}CH-\!\right) \;+\; Na \;\longrightarrow\; \left(\!-CH{=}CH-\!\right)^{\overset{-}{\cdot}} \;+\; Na^{+}$$

The delocalized regions, called solitons, extend about 15 bond lengths, at which point the energy gain arising from lengthening of double bonds and shortening of single bonds apparently outweighs stabilization arising from delocalization.



Soliton: neutral (radical), positive (carbocation), or negative(carboanion).



Conduction: **movement of electrons intramolecularly and intermolecularly via the positive or negative solitons.**

Intermolecular conduction is highly dependent on crystallinity, which accounts for the increase in polyacetylene's conductivity (to as much as 1.5×10^5 S/cm) when films of the polymer are properly oriented.

Polyacetylene: Instability to air and moisture

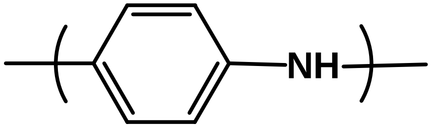
More stable conducting polymers: polyaniline, polypyrrole, polythiophene, poly(p-phenylene), poly(p-phenylenevinylene)

Typical dopants: AsF_5, $I_2 \xrightarrow{\text{reduced to}} AsF_6^-$ and I_3^-

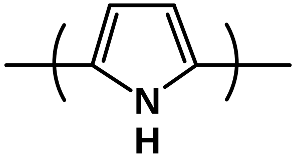
HCl for polyaniline

Conjugated Organics

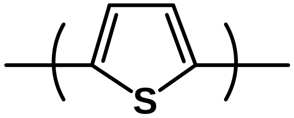
Polyaniline



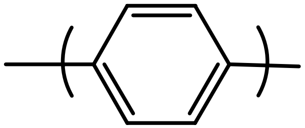
Polypyrrole



Polythiophene



Poly(*para*-phenylene)



Poly(*para*-phenylenevinylene)

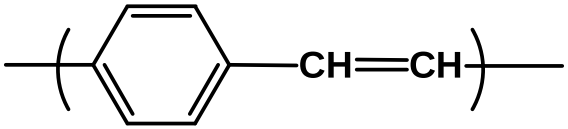
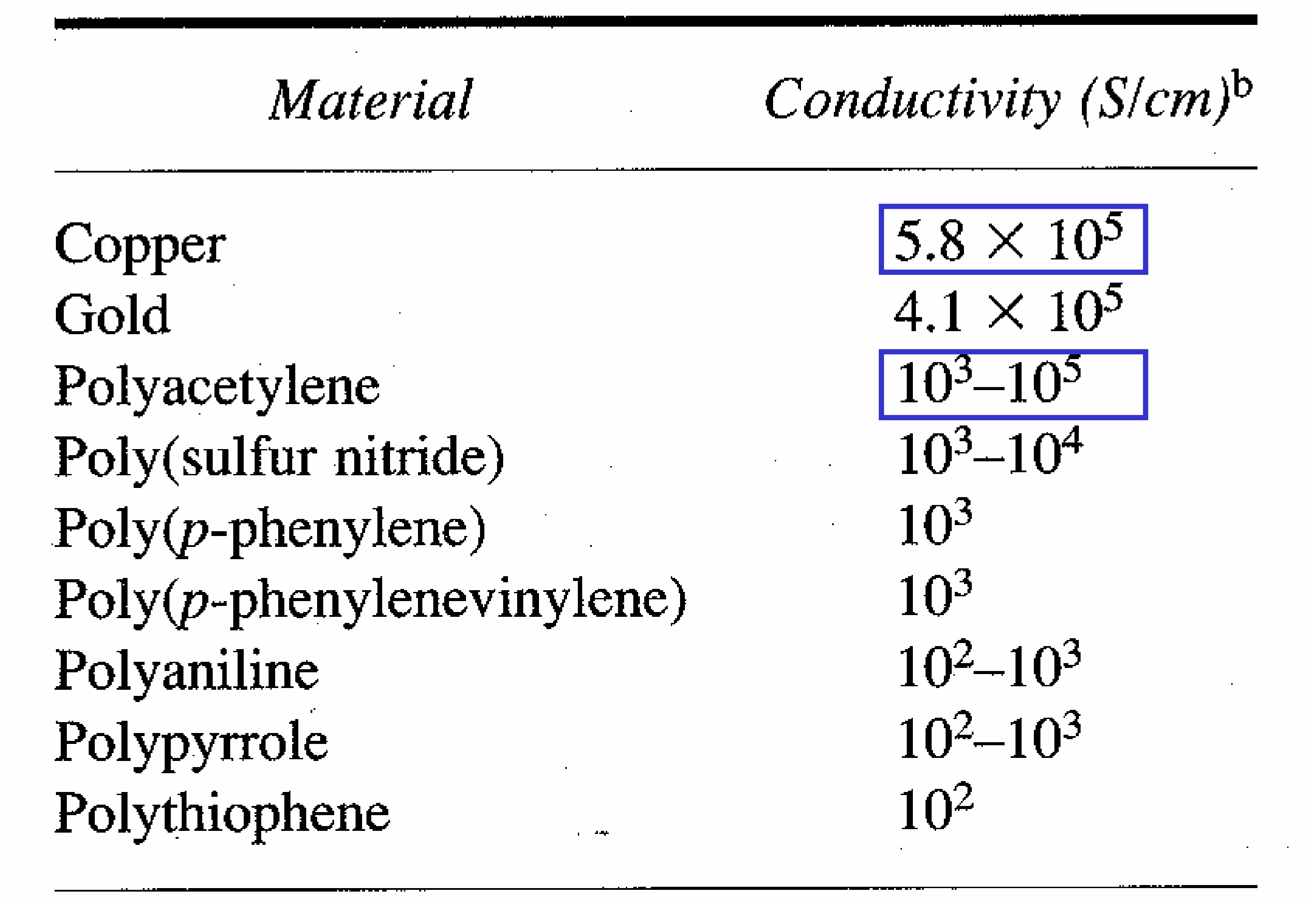


Table 4.5 Conductivities of Metals and Doped Polymers



Material	*Conductivity (S/cm)*[b]
Copper	5.8×10^5
Gold	4.1×10^5
Polyacetylene	10^3–10^5
Poly(sulfur nitride)	10^3–10^4
Poly(*p*-phenylene)	10^3
Poly(*p*-phenylenevinylene)	10^3
Polyaniline	10^2–10^3
Polypyrrole	10^2–10^3
Polythiophene	10^2

D) Typical applications:

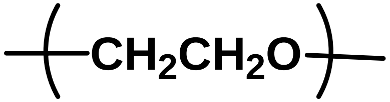
a) Light-weight batteries b) Thin-film transistors
c) Light-emitting diodes d) Antistatic materials
e) Molecular electronics

E) Ionic conductors / Polyelectrolytes:

Solid electrolytes, polyelectrolytes for solid battery applications generally consist of polymers such as poly(ethylene oxide) or polyphosphazene in combination with metal salts.

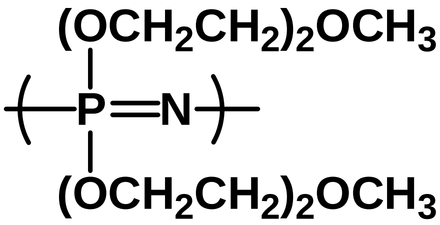
4:1 ratio of poly(ethylene oxide) to $NaBF_4$ is typical.
To function as an effective polyelectrolyte, the polymer should be highly amorphous and a low T_g to allow the freedom of molecular movement necessary for ion transport.

Poly(ethylene oxide)

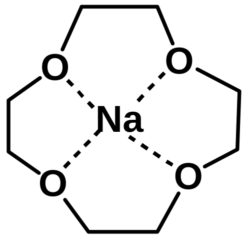


$$\left(CH_2CH_2O \right)$$

Polyphosphazene



$$\left(\begin{matrix} (OCH_2CH_2)_2OCH_3 \\ | \\ P{=}N \\ | \\ (OCH_2CH_2)_2OCH_3 \end{matrix} \right)$$



4.9 Nonlinear Optical Properties

Conjugated polymers: a key role in photonics

Photonics = the use of photons instead of electrons for information and image processing.

Photonic devices = operate at a much higher rate and to store information much more densely than electronic devices

Nonlinear Optical (NLO) property :

Reflective index change in response to a light – induced electric field

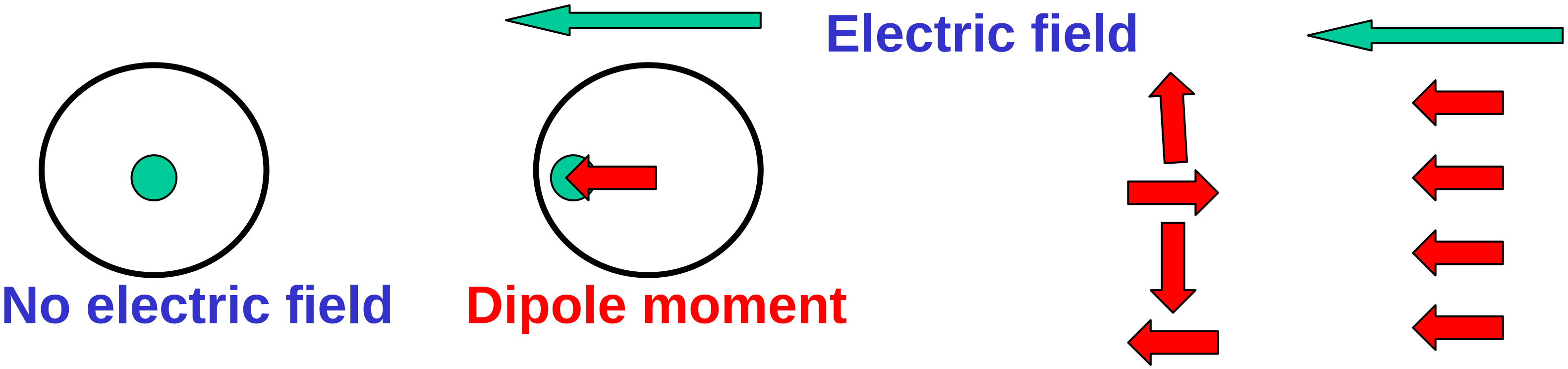
NLO Chromophores :

Dipole moieties containing electron–donating groups at one end and electron–attracting groups at the other

∴ A large change in dipole moment is induced upon excitation

For the polymer to exhibit NLO properties, the dipole moments must be aligned ⇒ Poled polymer

Heating above T_g, applying a strong electric field to bring about alignment , then cooling



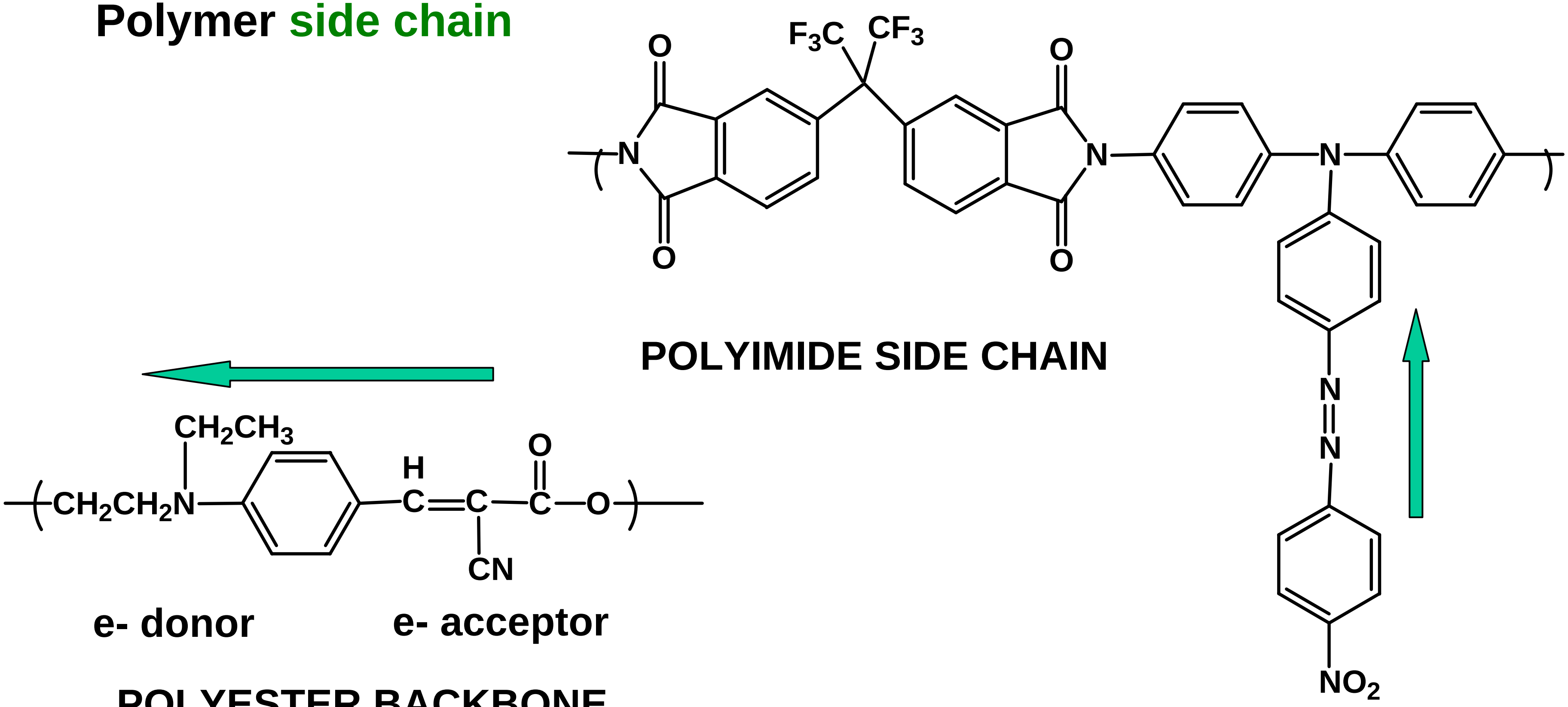
Electric field

No electric field

Dipole moment

Chromophores are incorporated into the polymer

- Low – mol – wt compound dissolved (host – guest systems)
- Polymer backbone
- Polymer side chain



POLYIMIDE SIDE CHAIN

e- donor

e- acceptor

POLYESTER BACKBONE

4. 10 Additives

Purpose

(1) To alter the properties of the polymer

(2) To enhance processability

Table 4.6 Polymer Addition