BASICS ON POLYMERIZATION

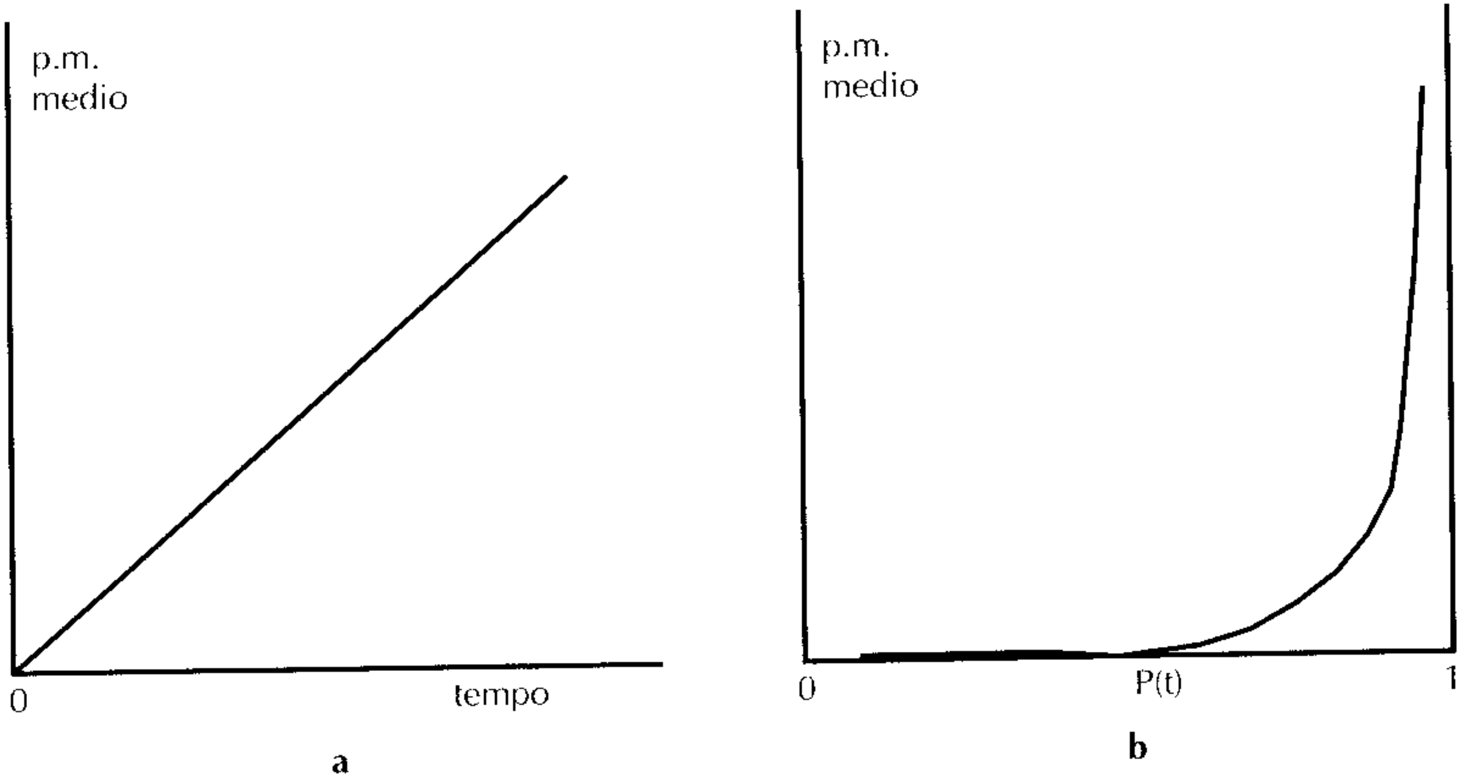
Step Polymerization vs. Chain Polymerization

Step Polymerization

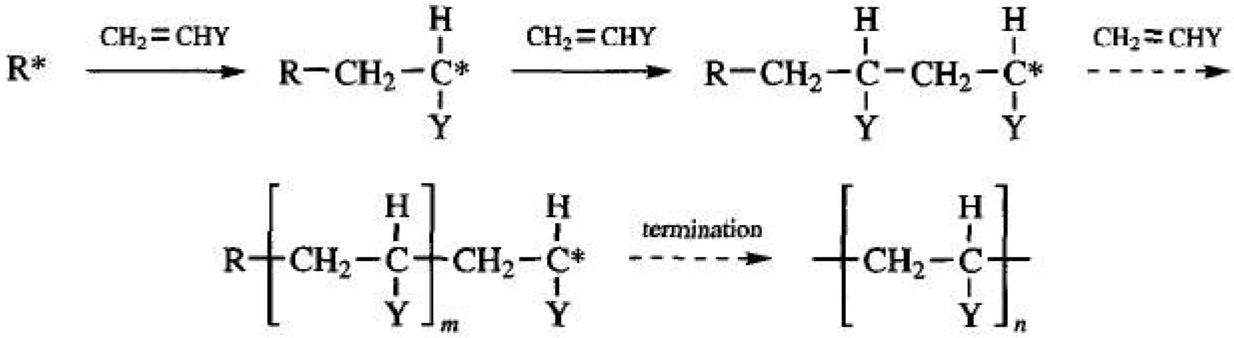
- Reaction occurs between any of the different sized species present in the reaction system
- Monomer disappears fast
- Molecular weight increases relatively slowly with conversion

Chain Polymerization

- Monomer only reacts with the reactive center
- Chain growth is very rapid, high molecular weight polymer is formed immediately
- Monomer concentration decreases throughout the polymerization, while the number of high molecular weight polymer molecules increases
- The molecular weight of the polymer is relatively independent on monomer conversion


p.m.
medio
0
tempo
a
p.m.
medio
0
P(t)
1
b

Chain Polymerization



R* can be a free radical, cation or anion

- Monomer only reacts with the reactive center
- Chain growth is very rapid
- Monomer concentration decreases throughout the polymerization, while the number of high molecular weight polymer molecules increases
- The molecular weight of the polymer is relatively independent on

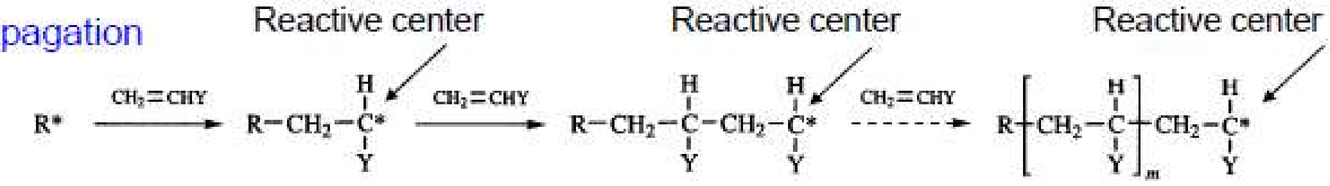
General Mechanism of Chain Polymerization

1. Initiation

Reactive center

$$I \longrightarrow R^*$$

2. Propagation



Reactive center

Reactive center

Reactive center

$$R^* \xrightarrow{CH_2=CHY} R-CH_2-\overset{H}{\underset{Y}{C^*}} \xrightarrow{CH_2=CHY} R-CH_2-\overset{H}{\underset{Y}{C}}-CH_2-\overset{H}{\underset{Y}{C^*}} \xrightarrow{CH_2=CHY} R\left[CH_2-\overset{H}{\underset{Y}{C}}\right]_m CH_2-\overset{H}{\underset{Y}{C^*}}$$

3. Termination

The active species can be a:

Free radical → Radical chain polymerization
Anion → Anionic polymerization
Cation → Cationic polymerization

The choice of polymerization method does not only depend on the **structure of the monomer**, but also on the desired **molecular weight**, **molecular weight distribution**, etc.

General Considerations of Polymerizability

Polymerizability of vinyl monomers: $n\ CH_2{=}CHY \longrightarrow -[CH_2-CHY]_n-$

1. Thermodynamic feasibility: $\Delta G < 0$

   For a wide range of monomers, $\Delta G < 0$

2. Kinetic feasibility:

   Does the reaction proceed at a reasonable rate under a particular set of conditions?

   This depends on:

   (i) Type of propagating center (+, -, or •)

   (ii) Substituent effects (i.e. the nature of Y)
   - Inductive effects
   - Resonance effects

General Considerations of Polymerizability

The ability to carry out a thermodynamically feasible polymerization depends on its kinetic feasibility

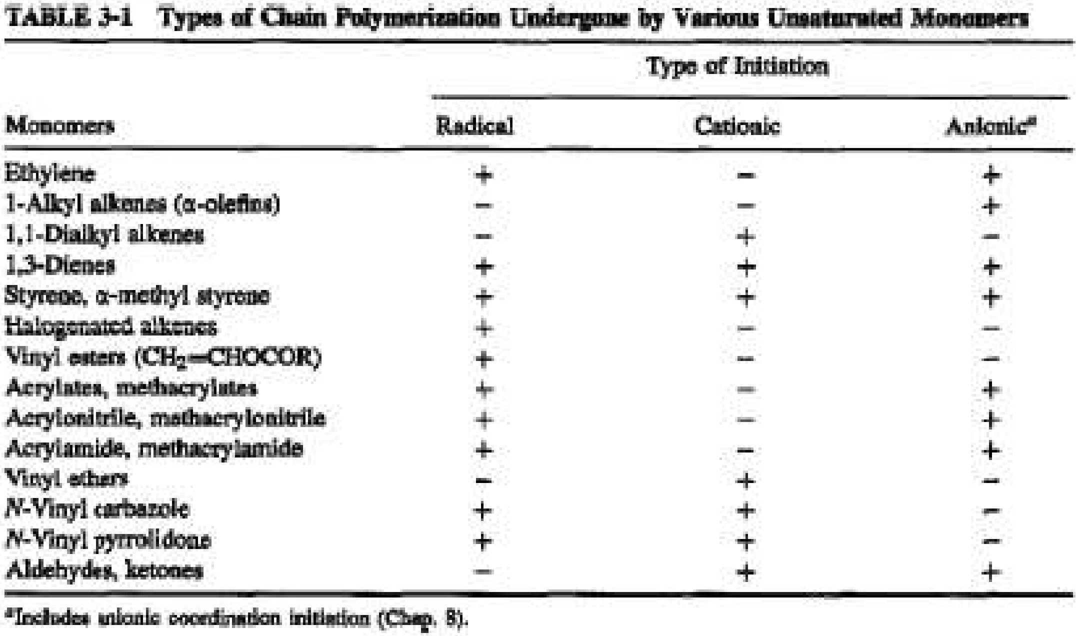
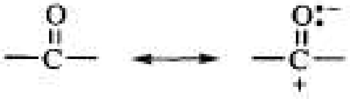


TABLE 3-1 Types of Chain Polymerization Undergone by Various Unsaturated Monomers

Monomers	Type of Initiation: Radical	Cationic	Anionic[a]
Ethylene	+	−	+
1-Alkyl alkenes (α-olefins)	−	−	+
1,1-Dialkyl alkenes	−	+	−
1,3-Dienes	+	+	+
Styrene, α-methyl styrene	+	+	+
Halogenated alkenes	+	−	−
Vinyl esters ($CH_2{=}CHOCOR$)	+	−	−
Acrylates, methacrylates	+	−	+
Acrylonitrile, methacrylonitrile	+	−	+
Acrylamide, methacrylamide	+	−	+
Vinyl ethers	−	+	−
N-Vinyl carbazole	+	+	−
N-Vinyl pyrrolidone	+	+	−
Aldehydes, ketones	−	+	+

[a] Includes anionic coordination initiation (Chap. 8).

The carbonyl bond is not prone to radical polymerization due to its polarized nature



Radical Chain Polymerization

1. Initiation

$$I \xrightarrow{k_d} 2R\cdot$$

$$R\cdot + M \xrightarrow{k_i} M_1\cdot$$

R· = initiator radical / primary radical
$M_1\cdot$ = chain-initiating species
k_d = rate constant for initiator decomposition
k_i = rate constant for the initiation step

2. Propagation

$$M_1\cdot + M \xrightarrow{k_p} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{k_p} M_3\cdot$$

$$M_3\cdot + M \xrightarrow{k_p} M_4\cdot$$

etc., etc.

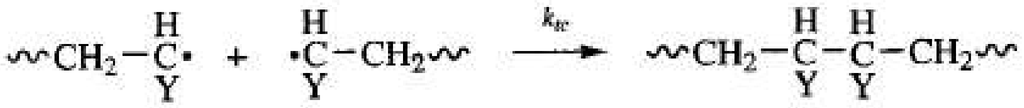
k_p = rate constant for propagation
(10^2-10^4 $L.mol^{-1}.s^{-1}$)

or in general terms

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot$$

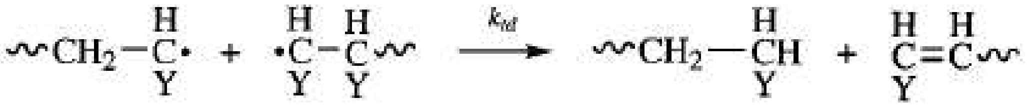
[concept of equal reactivity of functional groups]

3. Termination



$$\sim CH_2-\underset{Y}{\overset{H}{C}}\cdot + \cdot\underset{Y}{\overset{H}{C}}-CH_2\sim \xrightarrow{k_{tc}} \sim CH_2-\underset{Y}{\overset{H}{C}}-\underset{Y}{\overset{H}{C}}-CH_2\sim$$

Combination (coupling)



$$\sim CH_2-\underset{Y}{\overset{H}{C}}\cdot + \cdot\underset{Y}{\overset{H}{C}}-\underset{Y}{\overset{H}{C}}\sim \xrightarrow{k_{td}} \sim CH_2-\underset{Y}{\overset{H}{C}}H + \underset{Y}{\overset{H}{C}}=\overset{H}{C}\sim$$

Disproportionation

$$M_n\cdot + M_m\cdot \xrightarrow{k_{tc}} M_{n+m}$$

$$M_n\cdot + M_m\cdot \xrightarrow{k_{td}} M_n + M_m$$

or:

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} \text{dead polymer}$$

k_{tc} = rate constant for termination by coupling
k_{td} = rate constant for termination by disproportionation

with: $k_t = ak_{tc} + (1-a)k_{td}$

- k_t = rate constant for termination (10^6-10^8 $L.mol^{-1}.s^{-1}$)
- a and (1-a) the fractions of termination by coupling and disproportionation, respectively

Rate of Polymerization

Assumption: k_p and k_t independent of the size of the radical (concept of equal reactivity of functional groups)

$$\frac{-d[\mathrm{M}]}{dt} = R_i + R_p \quad \Longrightarrow \quad \frac{-d[\mathrm{M}]}{dt} = R_p \qquad\qquad R_p = k_p[\mathrm{M}\cdot][\mathrm{M}] \quad (1)$$

The number of monomer molecules reacting in the initiation step can be neglected compared to the polymerization step

Steady-state assumption:

$$R_i = R_t = 2k_t[\mathrm{M}\cdot]^2 \qquad\qquad [\mathrm{M}\cdot] = \left(\frac{R_i}{2k_t}\right)^{1/2} \quad (2)$$

Combine (1) and (2):

$$R_p = k_p[\mathrm{M}]\left(\frac{R_i}{2k_t}\right)^{1/2}$$

Thermal Initiation

- Thermal homolytic dissociation:
  - Dissociation energy 100-170 kJ/mol
  - O-O, S-S, N-O compounds

- Examples:

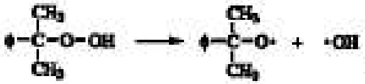
Acyl peroxides


Acetyl peroxide

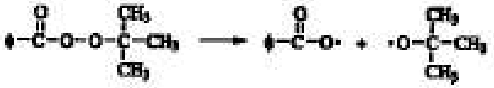

Benzoyl peroxide

Hydroperoxides

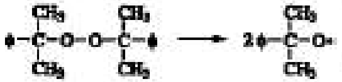

t-Butyl hydroperoxide

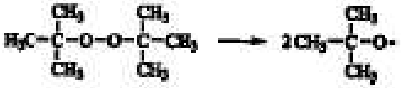

Cumyl hydroperoxide

Peresters


t-Butyl perbenzoate

Alkyl peroxides


Cumyl peroxide


t-Butyl peroxide

Azo compounds

(C-N bond dissociation energy is high, but homolysis is driven by the formation of the highly stable N_2 molecule)

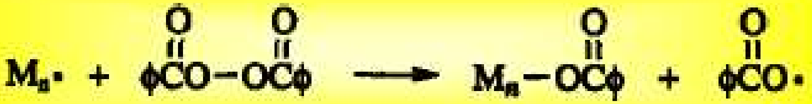

2,2'-Azobisisobutyronitrile (AIBN)

Initiator Efficiency

Initiator efficiency (f) = fraction of radicals formed in the primary step of initiator decomposition, which are successful in initiating polymerization

Initiator is wasted due to:

1) Induced decomposition of initiator (= chain transfer to initiator)



$$M_n\cdot + \phi\overset{O}{\overset{\parallel}{C}}O-O\overset{O}{\overset{\parallel}{C}}\phi \longrightarrow M_n-O\overset{O}{\overset{\parallel}{C}}\phi + \phi\overset{O}{\overset{\parallel}{C}}O\cdot$$

2) Side reactions of radicals formed in the primary decomposition step

$$\phi\overset{O}{\overset{\parallel}{C}}O-O\overset{O}{\overset{\parallel}{C}}\phi \longrightarrow 2\,\phi COO\cdot \longrightarrow$$

Decomposition of the primary radicals into non-active species

Often (1) is neglected when values of f are discussed

f: ~ 0.3-0.8

The Cage Effect

The cage effect describes lowering of f due to reactions of radicals entrapped in a solvent cage

(the brackets indicate the presence of a solvent cage)

$$\phi COO{-}OOC\phi \rightleftharpoons [2\phi COO\cdot]$$

$$[2\phi COO\cdot] \longrightarrow [\phi COO\phi + \phi CO_2]$$

$$[2\phi COO\cdot] + M \longrightarrow \phi CO_2\cdot + \phi COOM\cdot$$

$$[2\phi COO\cdot] \longrightarrow 2\phi COO\cdot$$

$$\phi COO\cdot + M \longrightarrow \phi COOM\cdot$$

$$\phi COO\cdot \longrightarrow \phi\cdot + CO_2$$

$$\phi\cdot + M \longrightarrow \phi M\cdot$$

$$\phi\cdot + \phi COO\cdot \longrightarrow \phi COO\phi$$

$$2\phi\cdot \longrightarrow \phi{-}\phi$$

$$[2\phi COO\cdot] \longrightarrow [\phi COO\cdot + CO_2 + \phi\cdot]$$

$$[\phi COO\cdot + CO_2 + \phi\cdot] \longrightarrow [CO_2 + \phi COO\phi]$$

$$[\phi COO\cdot + CO_2 + \phi\cdot] \longrightarrow \phi COO\cdot + CO_2 + \phi\cdot$$

$$[2\phi COO\cdot] \longrightarrow [2CO_2 + 2\phi\cdot]$$

$$[2CO_2 + 2\phi\cdot] \longrightarrow [2CO_2 + \phi{-}\phi]$$

$$[2CO_2 + 2\phi\cdot] \longrightarrow 2CO_2 + 2\phi\cdot$$

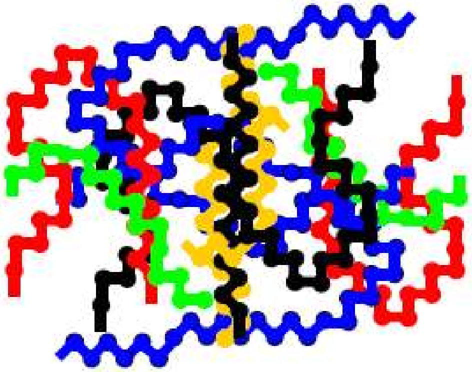
WHAT IS A NETWORK POLYMER?

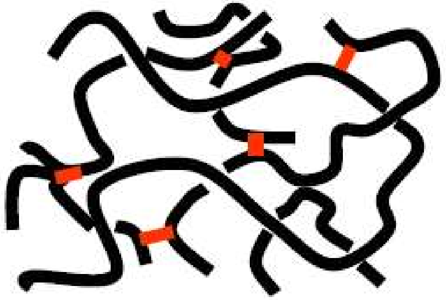
Thermoplastic polymers

- linear (or lightly branched polymer chain)
- one-dimensional connectivity
- finite molecular weight
- amorphous or crystalline
- flows as a melt when heated
- soluble in solvents

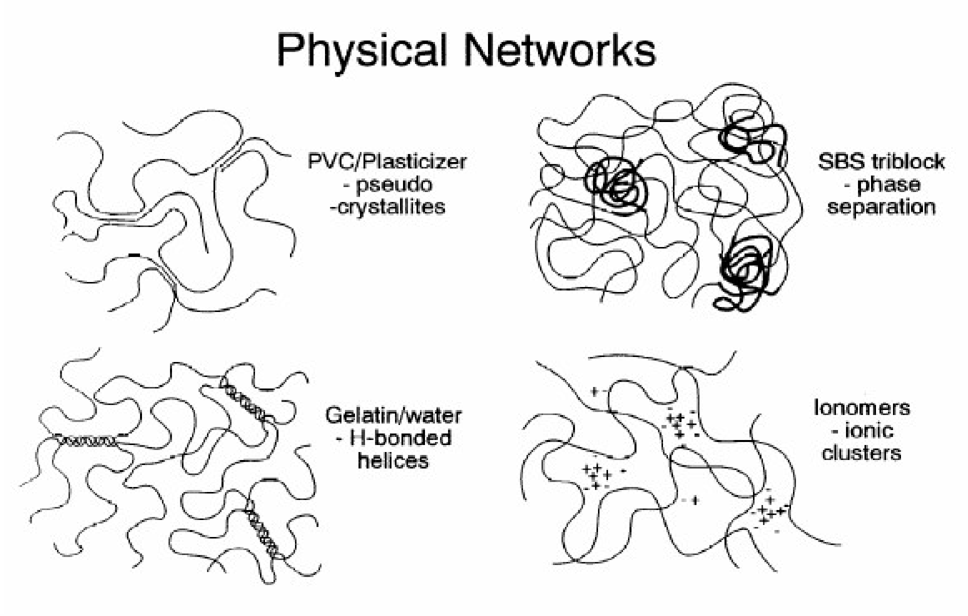
Crosslinked polymer

- hyper-branched chain
- three dimensional connectivity
- infinite molecular weight
- amorphous
- rubber-like at high temperatures
- insoluble (but swells) in solvents

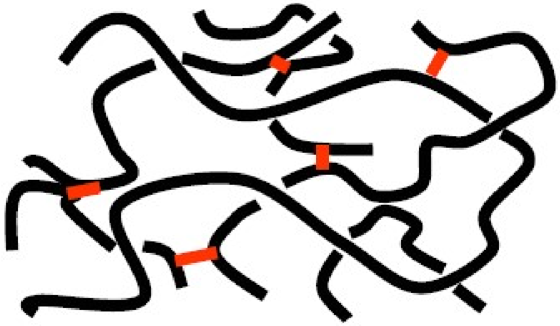




Physical networks and crosslinked networks



Chains held together by:
- crystals
- dispersed block copolymer phase
- H-bonds
- ions



Chains held together by chemical linkages formed by:
- chain growth polymerization
- step growth polymerization
- chain linking

TS are networks formed by the chemical reaction of monomers, at least one of which has a functionality higher than 2.

The synthesis starts from a mixture of reactive molecules, the TS precursors.

IN the course of the polymer network formation 2 principal structural transformations may occur: **Gelation** and **Vitrification**

At a particular reaction extent gelation takes place meaning that a giant macromolecule percolates through the sample.

Before Gelation

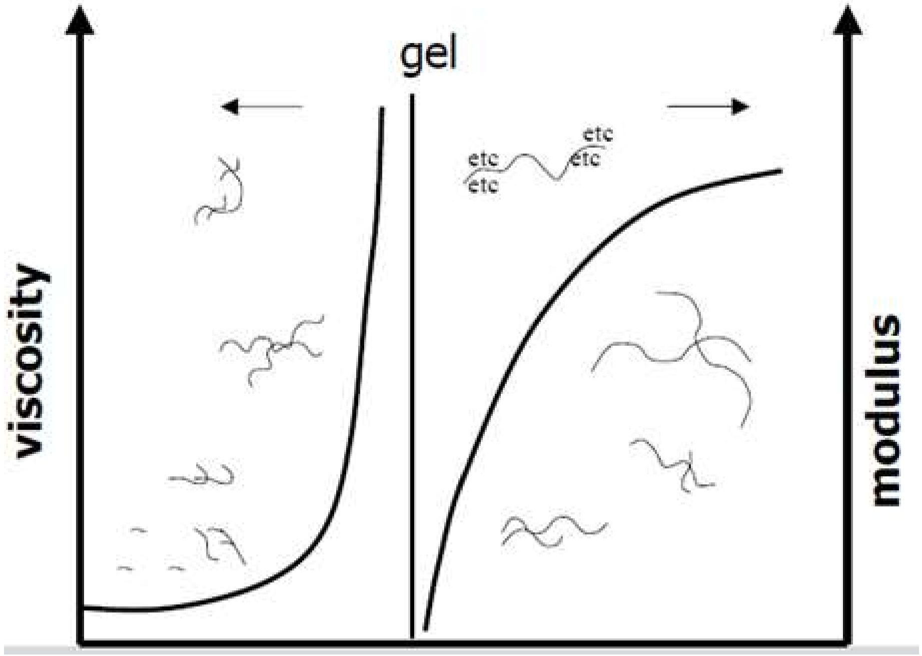
The material is a sol with a finite value of viscosity

At Gelation

Viscosity increase to infinte

After Gelation

An insoluble fraction (the gel fraction,
Is present in the system



- **Free Radical**
- ***Advantages:***
- Wider Applications
- Availability of wide range of photoinitiators
- ***Disadvantages:***
- Oxygen inhibition

- **Cationic**

Advantages

- Rapid
- No oxygen inhibition
- ***Disadvantages***
- Inhibited by bases
- Cured products may contain acids and counter anion impurities

- **Anionic**
- ***Advantages***
- Rapid
- ***Disadvantages***
- Inhibited by Protics
- Limited initiators

A radical polymerization :

$$M \quad \overset{h\nu}{\rightsquigarrow} \quad M^{\bullet} \quad \rightsquigarrow \quad (M)_n^{\bullet} \quad \rightsquigarrow \quad P$$

or a cationic polymerization :

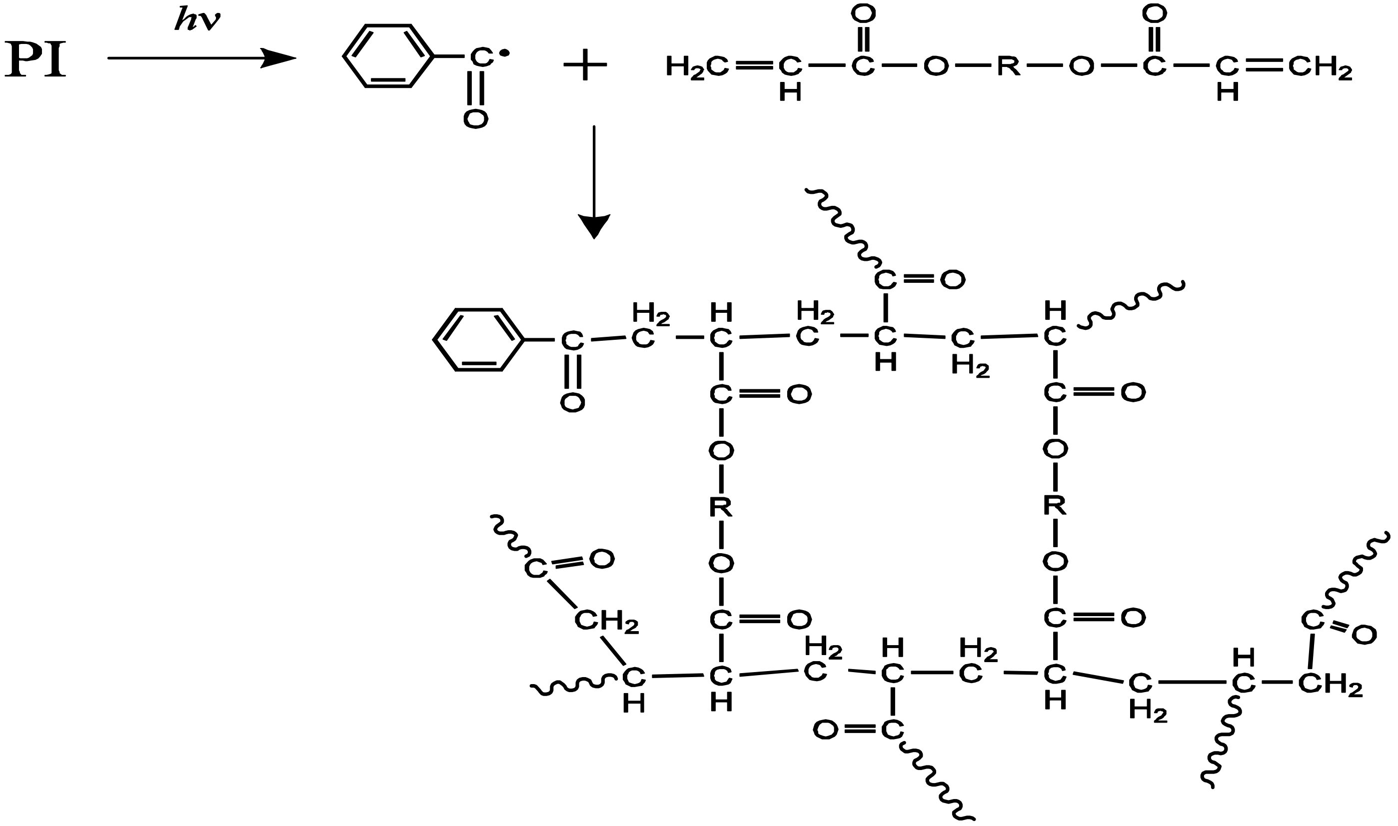
$$M \quad \overset{h\nu}{\rightsquigarrow} \quad M^{+} \quad \rightsquigarrow \quad (M)_n^{+} \quad \rightsquigarrow \quad P$$

or an anionic polymerization :

$$M \quad \overset{h\nu}{\rightsquigarrow} \quad M^{-} \quad \rightsquigarrow \quad (M)_n^{-} \quad \rightsquigarrow \quad P$$

Property	**Radical**	**Cationic**
Polymerization rate	High	Moderate/High
Oxygen sensitivity	Substantial	Absent
Volume change on cure	Large	Negligible
Adhesion	Moderate/Good	Good
Postcure	Absent	Strong
Chemical resistance	Moderate/Good	Good
Irritant properties of the monomers	High	Absent

RADICAL PHOTOPOLYMERIZATION



CATIONIC PHOTOPOLYMERIZATION

$$\mathrm{PhI}^{\dot{+}}\mathrm{X}^{-} + \mathrm{R{-}H} \longrightarrow \mathrm{PhI} + \mathrm{H}^{+}\,\mathrm{X}^{-} + \mathrm{R}\cdot$$