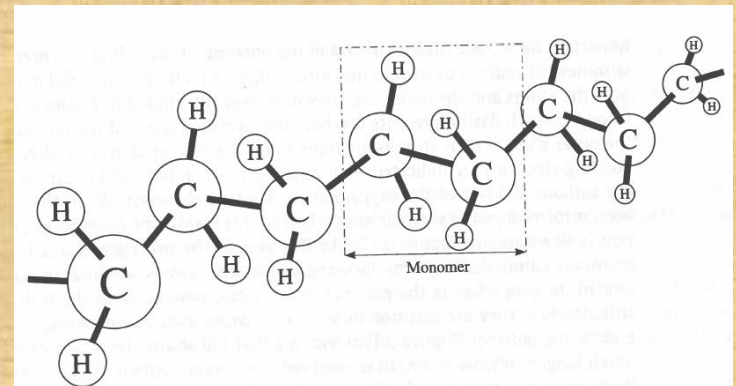


Structure and Properties of Engineering Polymers

Lecture: **Polymerization Reactions and Techniques**

Nikolai V. Priezjev



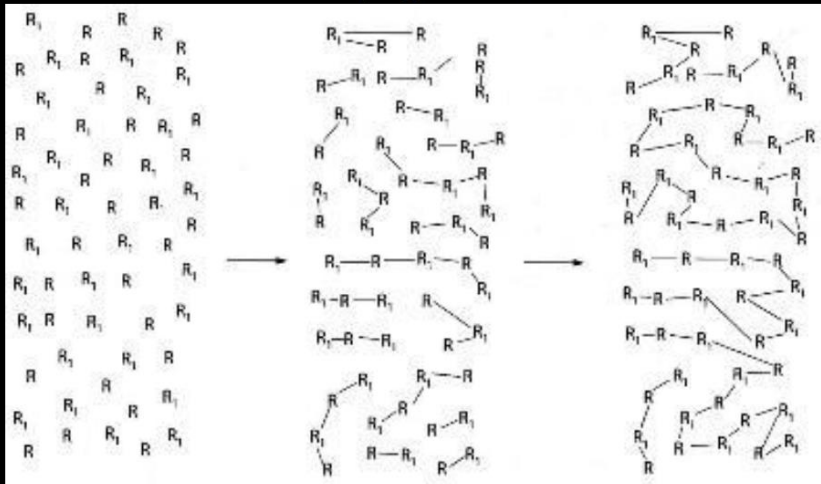
Textbook: *Plastics: Materials and Processing* (Third Edition), by A. Brent Young (Pearson, NJ, 2006).

Polymerization Reactions and Techniques

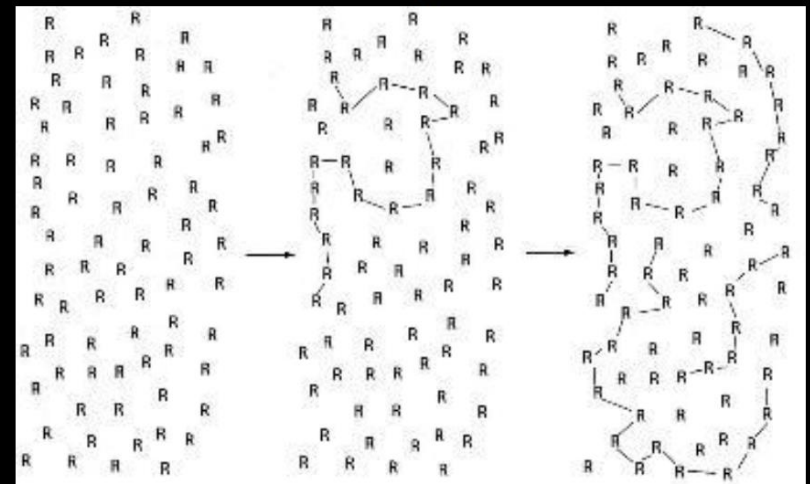
Step-growth polymerization or condensation polymerization

Chain-growth polymerization or addition polymerization

Step-growth



Chain-growth



Step-Growth Polymerization



Wallace Carothers

- Father of polymerizations
- Worked at Dupont
- Inventor of Nylon
- Killed himself when 41

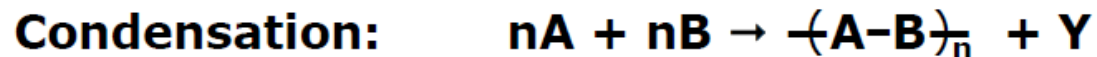
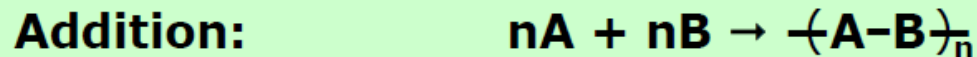
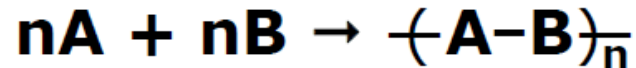
$$DP = \frac{1}{1-p}, PDI = 1+p$$

p = monomer conversion
DP = Degree of polymerization
(DP=5 of polymer has 5 monomer in it)

- Formerly: Condensation polymerization (Carothers, 1931)
- Monomers are **difunctional** — each has *two* reactive functional groups
- Chain growth occurs through coupling (condensation, addition) reactions
- [Monomer] decreases rapidly before any high-MW polymer is formed
- Rate of polymerization is highest at outset, decreases as chain ends are consumed => long reaction times

Step-Growth Polymerization (cont.)

Schematic:



The number average **degree of polymerization** (X_n) is

$$DP = X_n = \frac{N_0}{N} = \frac{\text{Number of molecules at start}}{\text{Number of molecules at end}}$$

The ratio [A]:[B] strongly influences chain length

Step-Growth Polymerization (cont.)

Example:

	$\frac{N_0}{N}$	\bar{X}_n
A B A B A B A B A B A B	12/12	1
A-B A B A B A B A B A B	12/11	1.1
A-B A B A B A B-A B A B	12/10	1.2
A-B A B A B A-B-A B A B	12/9	1.3
A-B A B A B A-B-A B-A B	12/8	1.5
A-B-A B A B A-B-A B-A B	12/7	1.7
A-B-A B A B-A-B-A B-A B	12/6	2
A-B-A B-A B-A-B-A A-A B	12/5	2.4
A-B-A B-A B-A-B-A B-A-B	12/4	3
A-B-A-B-A B-A-B-A B-A-B	12/3	4
A-B-A-B-A B-A-B-A-B-A-B	12/2	6
A-B-A-B-A-B-A-B-A-B-A-B	12/1	12

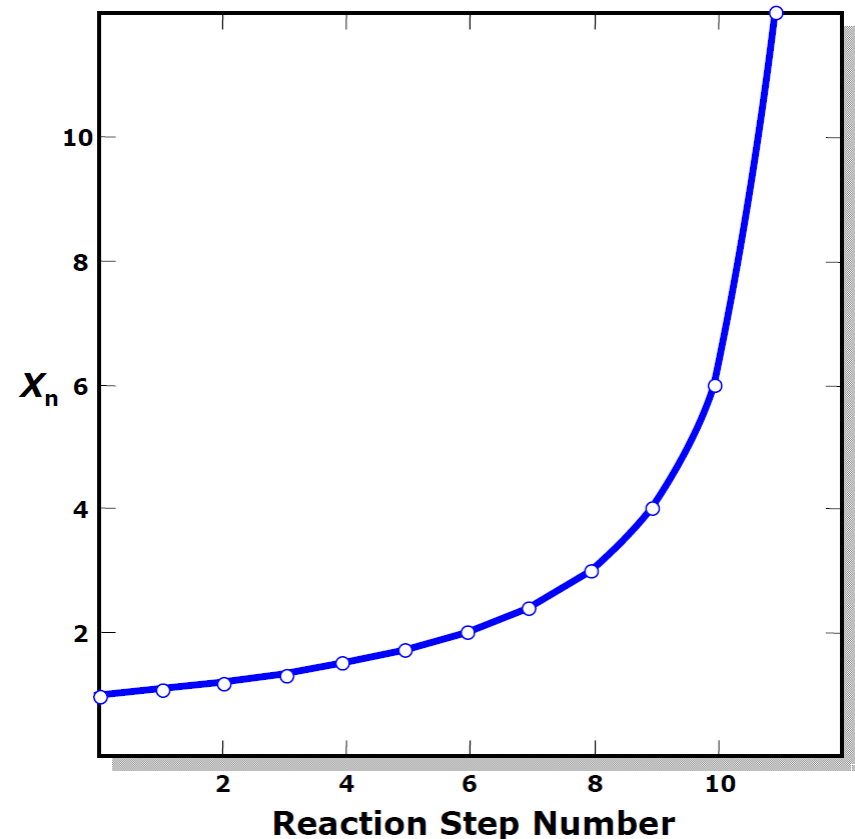
Step-Growth Polymerization (cont.)

Degree of Polymerization:

The number average **degree of polymerization** (X_n) is

$$DP = X_n = \frac{N_0}{N} = \frac{\text{Number of molecules at start}}{\text{Number of molecules at end}}$$

	N_0/N	X_n
A B A B A B A B A B A B	12/12	1
A-B A B A B A B A B A B	12/11	1.1
A-B A B A B A B-A B A B	12/10	1.2
A-B A B A B A-B-A B A B	12/9	1.3
A-B A B A B A-B-A B-A B	12/8	1.5
A-B-A B A B A-B-A B-A B	12/7	1.7
A-B-A B A B-A-B-A B-A B	12/6	2
A-B-A B-A B-A-B-A A-A B	12/5	2.4
A-B-A B-A B-A-B-A B-A-B	12/4	3
A-B-A-B-A B-A-B-A B-A-B	12/3	4
A-B-A-B-A B-A-B-A-B-A-B	12/2	6
A-B-A-B-A-B-A-B-A-B-A-B	12/1	12

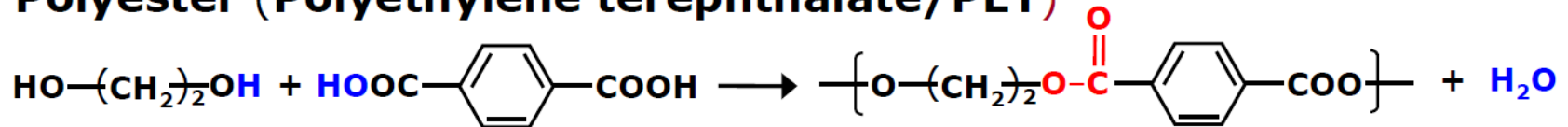


X_n = average number of monomers per chain

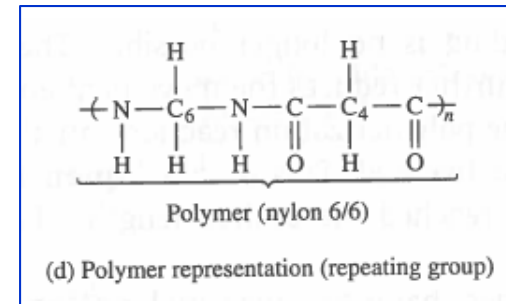
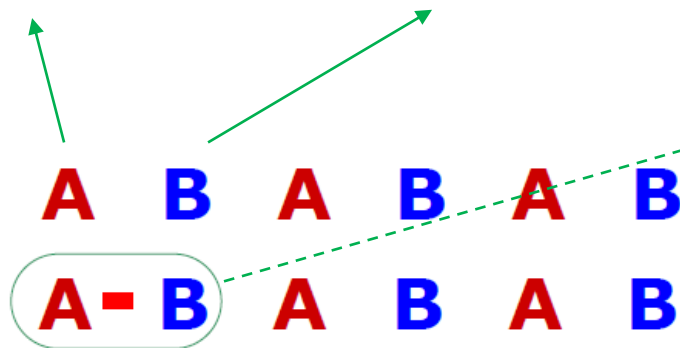
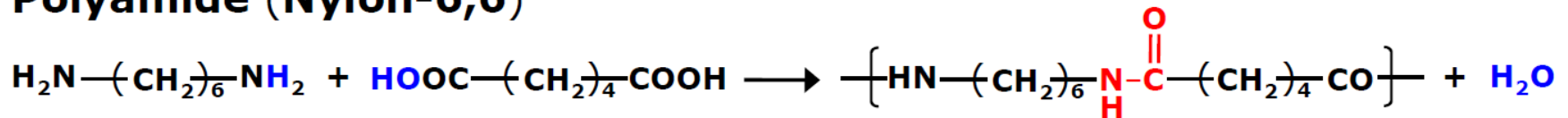
Representative Step-Growth Reactions

Condensation Reactions

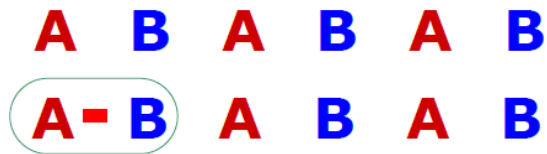
Polyester (Polyethylene terephthalate/PET)



Polyamide (Nylon-6,6)



Predicting Molar Mass in Step-Growth Polymerization



The number average **degree of polymerization** (X_n) is

$$DP = X_n = \frac{N_0}{N} = \frac{\text{Number of molecules at start}}{\text{Number of molecules at end}}$$

The **extent of reaction** (p) is

$$p = \frac{\text{Number of *functional groups* reacted}}{\text{Initial number of *functional groups*}}$$

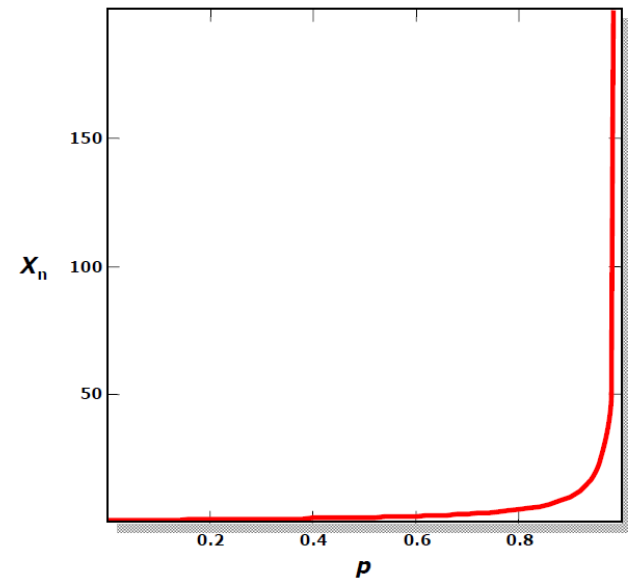
X_n = average number of monomers per chain

Since the total number of molecules (N) decreases by 1 for each condensation step,

$$p = \frac{N_0 - N}{N_0} \quad \text{or} \quad \frac{N_0}{N} = \frac{1}{1-p}$$

$$X_n = \frac{1}{1-p}$$

Carothers equation



Step-Growth Reactions: MW Distribution

MW=Molecular Weight

$$X_n = \frac{N_0}{N} = \frac{1}{1-p}$$

The corresponding weight-average degree of polymerization is

$$X_w = \frac{1+p}{1-p}$$

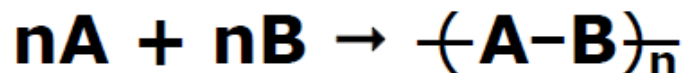
The molecular weight distribution (polydispersity) is therefore

$$\frac{X_w}{X_n} = 1 + p$$

⇒ as $p \rightarrow 1$, **MWD** → **2** for any linear step-growth pzn

MWD=Molecular Weight Distribution

Step-Growth Reactions: Molecular Weight Control

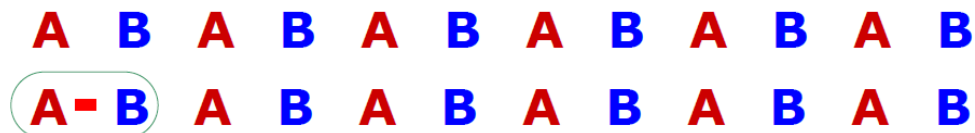


- Lowering the temperature before the reaction is complete can reduce product MW.

Result: a thermally unstable product.

- Alternative: use a non-stoichiometric reactant ratio ($[A] < [B]$). The less abundant reactant is consumed completely. In terms of *functional* groups ($N_A < N_B$), the reactant ratio is

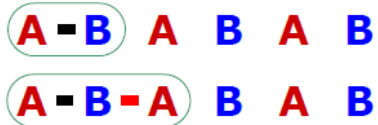
$$r = \frac{N_A}{N_B} < 1$$



Substituting gives the general Carothers equation:

$$X_n = \frac{1 + r}{1 + r - 2rp}$$

Step-Growth Reactions: Molecular Weight Control



$$X_n = \frac{1 + r}{1 + r - 2rp}$$

$$r = \frac{N_A}{N_B}$$

r	X_n			
	$p = 0.900$	$p = 0.950$	$p = 0.990$	$p = 0.999$
1.000	10.0	20.0	100.0	1000.0
0.999	10.0	19.8	95.3	666.8
0.990	9.6	18.3	66.8	166.1
0.950	8.1	13.4	28.3	37.6
0.900	6.8	10.0	16.1	18.7

The number average **degree of polymerization** (X_n) is

$$\text{DP} = X_n = \frac{N_0}{N} = \frac{\text{Number of molecules at start}}{\text{Number of molecules at end}}$$

The **extent of reaction** (p) is

$$p = \frac{\text{Number of functional groups reacted}}{\text{Initial number of functional groups}}$$

Step-Growth Reactions: Molecular Weight Control



Producing high-MW step-growth polymers requires

- High conversions ($p > 0.98$)
- Stoichiometric ratios of functional groups
- High-purity monomers
- No side reactions

$$r = \frac{N_A}{N_B}$$

The number average **degree of polymerization** (X_n) is

$$DP = X_n = \frac{N_0}{N} = \frac{\text{Number of molecules at start}}{\text{Number of molecules at end}}$$

The **extent of reaction** (p) is

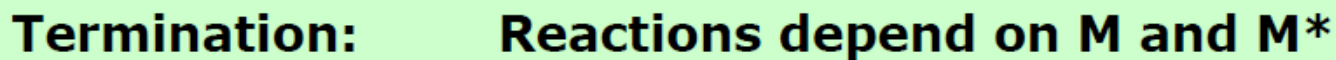
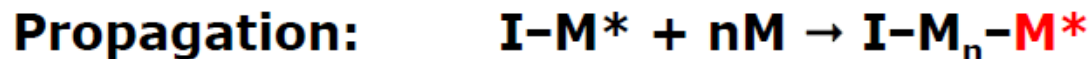
$$p = \frac{\text{Number of functional groups reacted}}{\text{Initial number of functional groups}}$$

Chain-Growth Polymerization

- Formerly: Addition polymerization (Carothers, 1931)
- Polymerization requires an **initiator**, a substance that starts the reaction
- Chain growth occurs by addition of monomer to a relatively small number of initiation sites (free radicals, anions, cations, transition metal complexes)
- Reaction mixture contains monomer and a low concentration of growing chains
- [Monomer] decreases steadily as polymer is formed

Chain-Growth Polymerization (cont.)

Schematic:



$$DP = X_n = \frac{\text{Moles of monomer consumed}}{\text{Moles of chains produced}}$$

The ratio [initiator]:[monomer] strongly influences chain length

$$DP = X_n = \frac{\text{Moles of monomer consumed}}{\text{Moles of chains produced}}$$
[illegible]

Mol_{cons}	X_n
	0
1	1
2	2
3	3
4	4
5	5
6	6
7	7
8	8
9	9
10	10
11	11
12	12

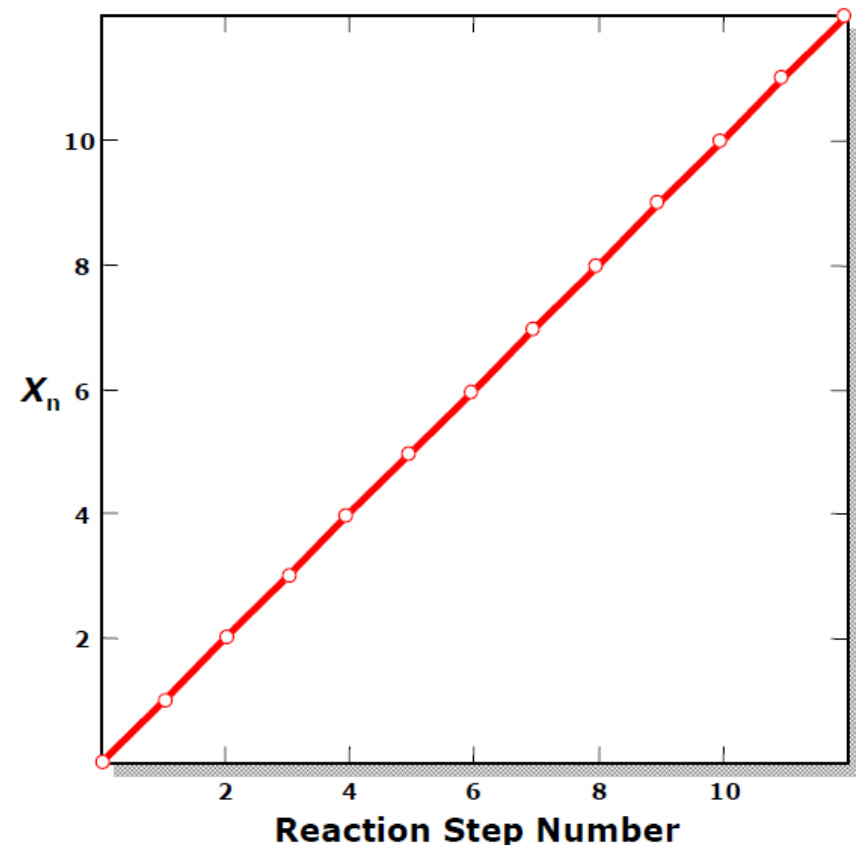
Chain-Growth Polymerization (cont.)

Degree of Polymerization:

$$DP = X_n = \frac{\text{Moles of monomer consumed}}{\text{Moles of chains produced}}$$



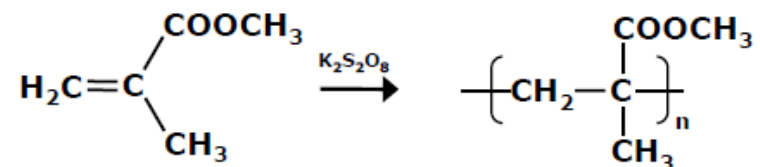
<u>Mol_{cons}</u>	<u>X_n</u>
	0
1	1
2	2
3	3
4	4
5	5
6	6
7	7
8	8
9	9
10	10
11	11
12	12



Representative Chain-Growth Reactions

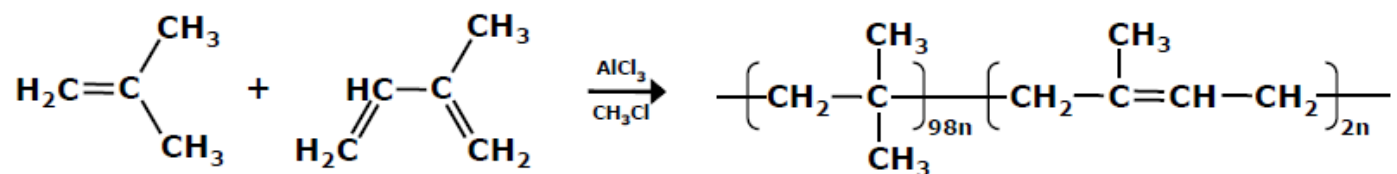
Free-Radical Vinyl

Poly(methyl methacrylate)



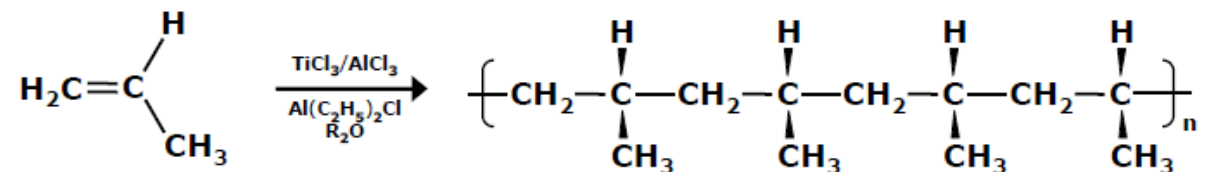
Carbocationic/Anionic

Butyl Rubber (IIR)



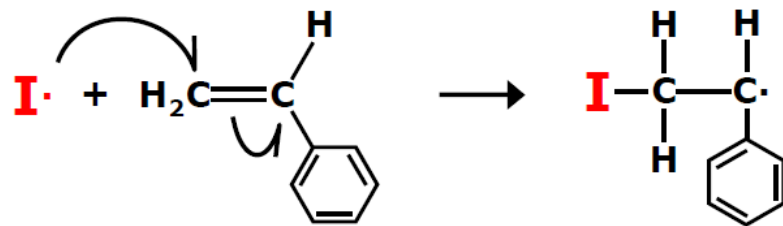
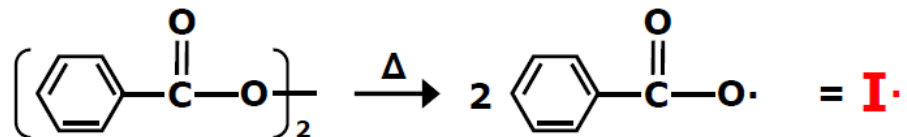
Coordination

Polypropylene

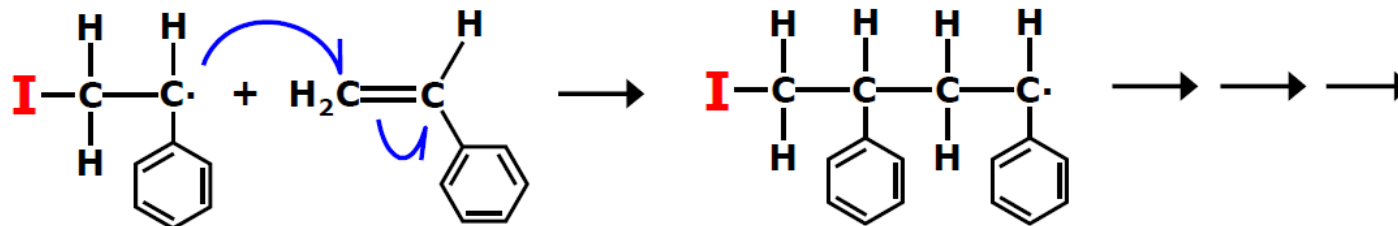


Chain-Growth Polymerization (cont.)

Initiation

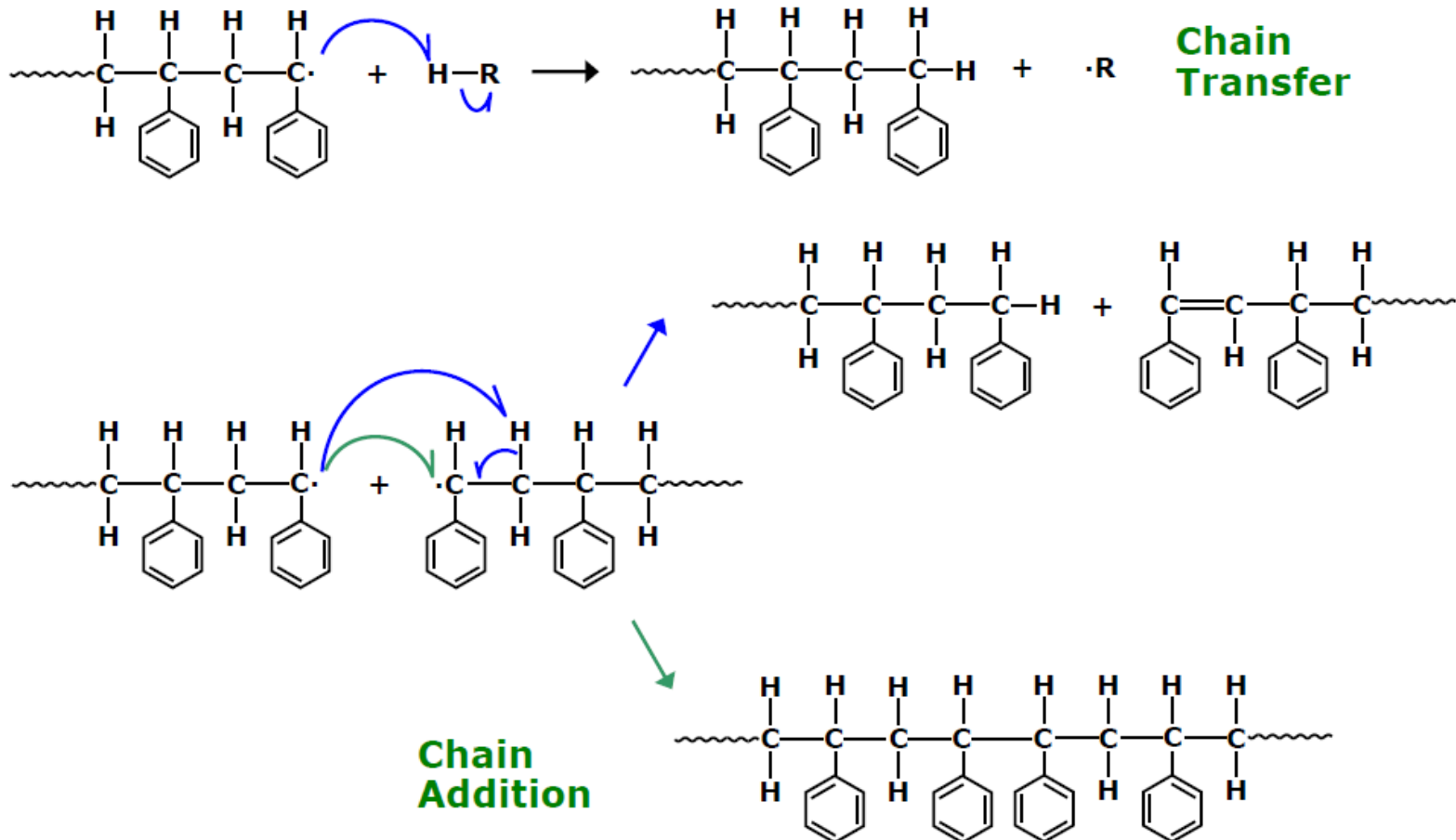


Propagation



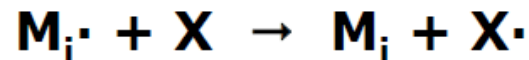
Chain-Growth Polymerization (cont.)

Termination



Chain-Growth Reactions: Molecular Weight Control

- Most monomer is (or should be) consumed by polymer chain growth, not initiation.
- **Termination** involves reactions that stop polymerization.
- **Chain transfer** to monomer, solvent, or initiator kills the polymer chain but continues the kinetic chain (new chains can be initiated):



- Chain length is proportional to $[M]$ and $1/[I]^{1/2}$:

$$X_n = K \frac{[M]}{[I]^{1/2}}$$

- To maximize DP, increase $[M]:[I]$ in the reaction mixture or increase K by the choice of monomer.



Molecular Weight Control (cont.)

If chain transfer processes to both monomer (M) and solvent (S) are important:

$$\frac{1}{X_n} = \frac{1}{X_{n0}} + C_M + C_S \frac{[S]}{[M]}$$

Mayo (Mayo-Walling) eqn

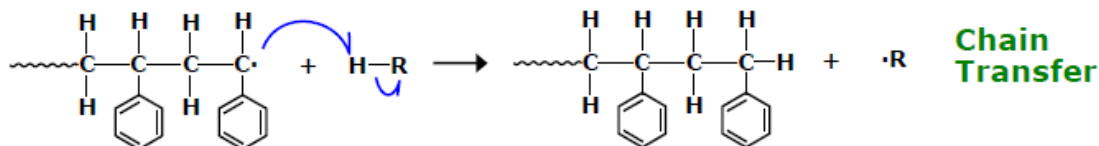
where X_{n0} is the DP you get with no chain transfer.

If transfer to monomer is not important, then

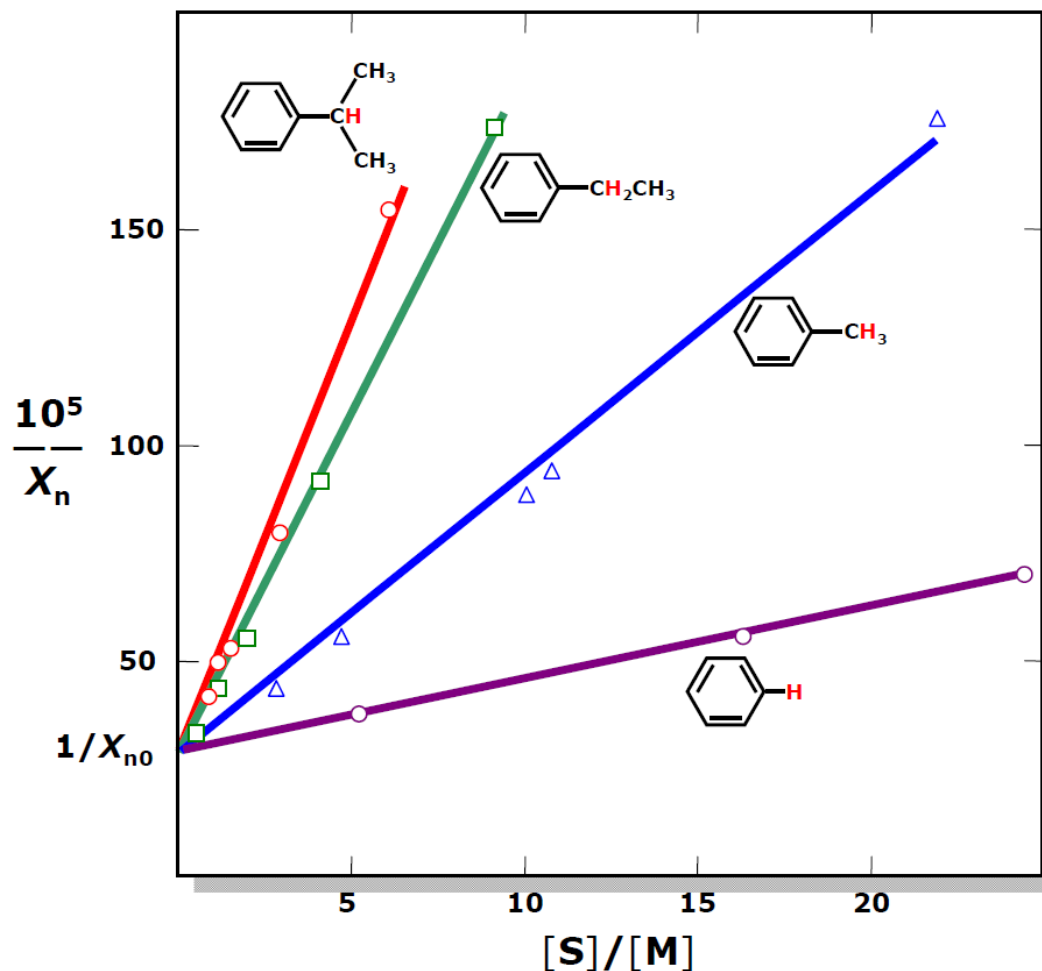
$$\frac{1}{X_n} = \frac{1}{X_{n0}} + C_S \frac{[S]}{[M]}$$

Simplified Mayo eqn

The reciprocal of DP should be a linear function of the ratio of [S] to [M]. The slope would be a function of the rate of chain transfer to solvent.



Styrene Polymerization: Chain Transfer to Solvent



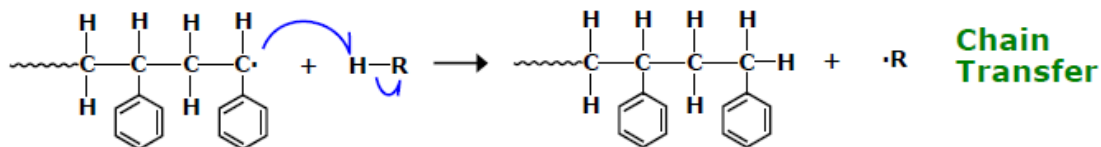
$$\frac{1}{X_n} = \frac{1}{X_{n0}} + C_s \frac{[S]}{[M]}$$

The number average **degree of polymerization** (X_n) is

$$DP = X_n = \frac{N_0}{N} = \frac{\text{Number of molecules at start}}{\text{Number of molecules at end}}$$



Adapted from R.A. Gregg & F.R. Mayo,
1947 *Disc. Faraday Soc.*, 2, 328-337



Chain-Growth vs Step-Growth Reactions

Step-Growth

All molecules present (monomer, oligomer, polymer) can react with any other molecule.

Monomers exist throughout the reaction, but **large quantities of monomers are consumed early in the reaction.**

There is **no termination step** and the end groups of the oligomers and polymers are reactive throughout the polymerization process.

The reaction proceeds rapidly at the beginning but the molecular weight increases only slowly and high MW's are only attained at the end of the process by long oligomers reacting with each-other.

Long reaction times are needed for the synthesis of long (high molecular weight) polymers.

Molecular species of any length (oligomers) exist throughout the reaction, with the length distribution broadening and shifting to higher MW with increasing reaction time.

Chain-Growth

During propagation, only monomers react to the "active site" at the end of the growing chain.

Monomers exist throughout the reaction; its concentration decreases steadily with time.

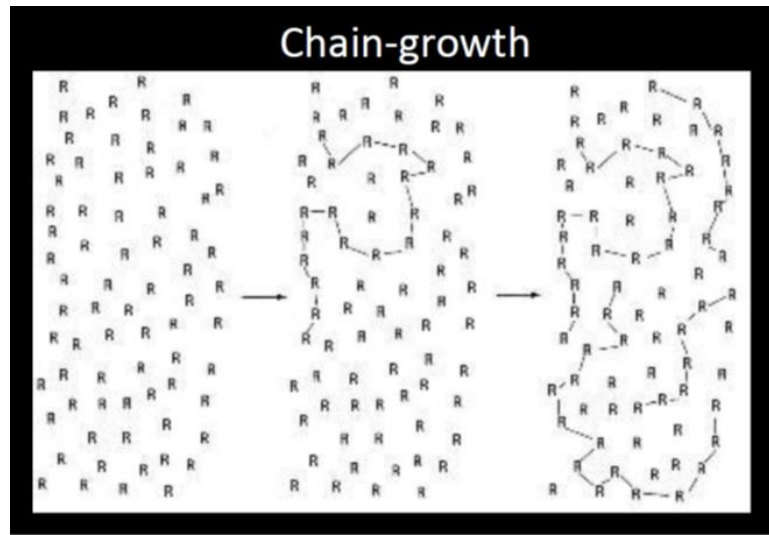
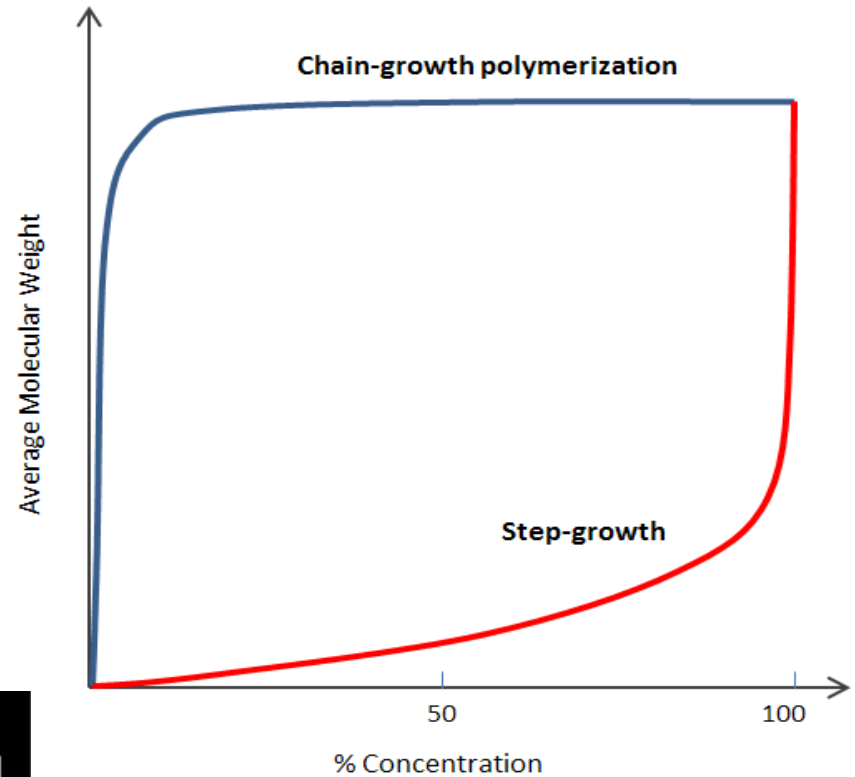
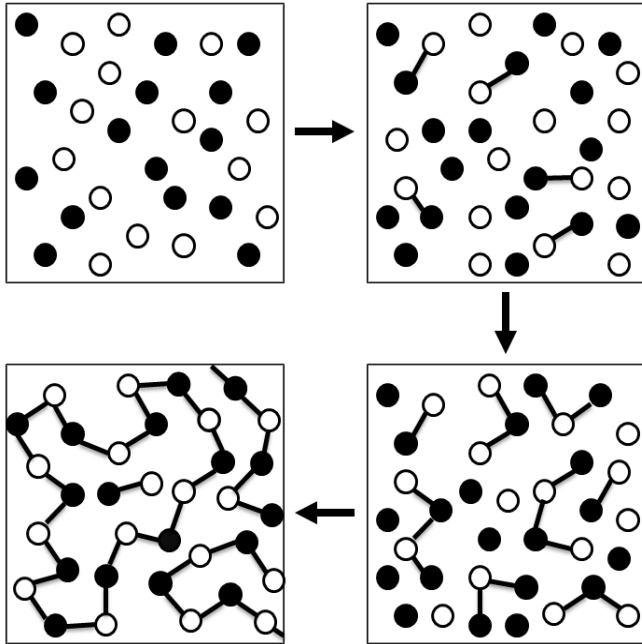
There are two distinctive mechanisms during polymerization; these are **initiation and propagation**. In most cases there is also a termination step.

The reaction speed depends on the concentration of initiator (and co-initiator) and high-molecular weight polymers form throughout the duration of the reaction.

Long reaction times have high degrees of conversion but do not affect (much) the (average) molecular weight.

The mixture contains primarily monomers and polymers, and only small amounts of growing polymer chains;

Chain-Growth vs Step-Growth Reactions



Copolymerization

- Simultaneous polymerization of two or more monomers yields **copolymers** with unique properties unlike those of **homopolymers** from each monomer.
- Copolymers with irregular (random) monomer sequences can have rubber-like properties because of reduced crystallinity.
- Appropriate reaction conditions can provide a range of tailored structures:
 - Random (statistical) **-ABBABAABBAABAB-**
 - Alternating **-ABABABABABABAB-**
 - Block **-AAAABBBBAAAABBBB-**
 - Graft **-AAAAAAAAAAAAAAAA-**
 BBBB BBBB



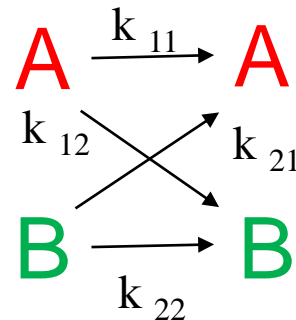
Copolymerization: Composition Control

- Monomers differ in their ability to copolymerize.
- The relative rates of monomer reaction are a function of the monomer concentrations ($[A]$, $[B]$) and the monomer **reactivity ratios** (r_n):

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

where k_{ij} is the rate constant for the reaction of monomer i with monomer j .

- Reactivity ratios determine copolymer composition and structure.**



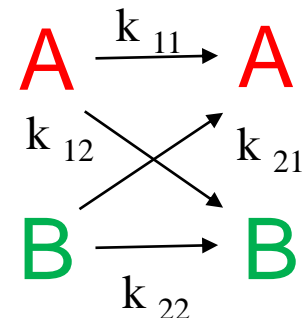
Copolymerization: Reactant Ratios

B B B B B B B A

Monomer 1	r_1	Monomer 2	r_2	T, °C
Ethylene	0	Acrylonitrile	7	20
	0.79	Vinyl acetate	1.4	130
	0.58	1,3-Butadiene	1.4	50
Styrene	0.29	Acrylonitrile	0.020	60
	55	Vinyl acetate	0.01	60
	0.78	1,3-Butadiene	1.4	5
Me acrylate	0.84	Acrylonitrile	1.5	50
	6.4	Vinyl acetate	0.03	60

monomer reactivity ratios (r_n):

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$



Copolymerization: Composition Control

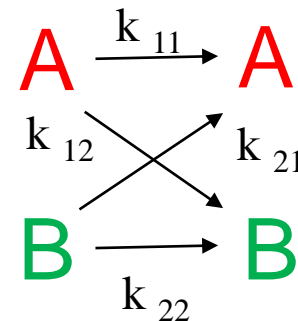
B A B A B A B A

Limiting (or idealized) reactivity ratios:

- $r_1 = r_2 = 0$ Neither chains end adds its own monomer. Results: 1. a perfectly **alternating copolymer** and 2. an **azeotropic copolymer** composition (the ratio of monomers in the feed = the ratio of monomer units in the copolymer).
- $r_1 = r_2 = \infty$ Each chain adds only its own monomer. Result: a mixture of **homopolymers**.
- $r_1 r_2 = 1$ or $r_1 = r_2 = 1$ All chain ends add either monomer with equal probability in an **ideal copolymerization**. Result: a **random copolymer**.

monomer **reactivity ratios** (r_n):

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$



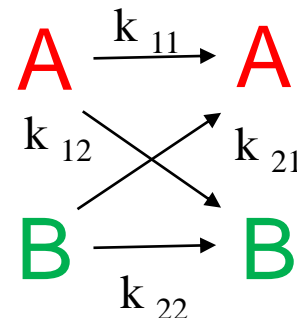
Copolymerization: Composition Control (cont.)

- In most cases r_i is not exactly 0, 1, or ∞ ; polymers tend toward a particular composition and type of structure.
- Comonomer sequences can be inferred from $r_1 r_2$ values:
 - $r_1 r_2 < 1$ Tendency toward alternating structure
 - $r_1 r_2 > 1$ Tendency toward block structure
 - $r_1 r_2 \gg 1$ Tendency toward homopolymer structure
- When $r_1 \gg 1 \gg r_2$ there is copolymer **composition drift**.
 - At low conversions, the copolymer is enriched in the more reactive monomer.
 - At high conversions, the copolymer is enriched in the less reactive monomer that remains.
- Composition drift can be reduced by delayed or (semi-batch) continuous addition of the more reactive monomer.

monomer **reactivity ratios** (r_n):

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$



Copolymerization: Composition Control (cont.)

In terms of the mole fraction (f) of each monomer in the co-monomer mixture,

$$f_1 = \frac{[A]}{[A] + [B]} \quad f_2 = 1 - f_1 = \frac{[B]}{[A] + [B]}$$

the copolymer equation, expressed as the mole fraction (F) of each monomer unit in the copolymer chain, is:

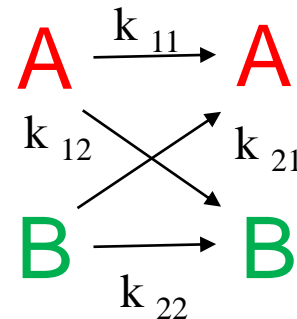
$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

$$F_2 = 1 - F_1$$

These equations can be used to calculate the relationship of reactant feed composition to instantaneous polymer composition for various reactant ratios.

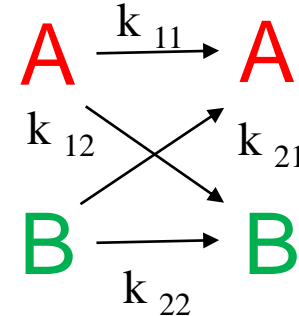
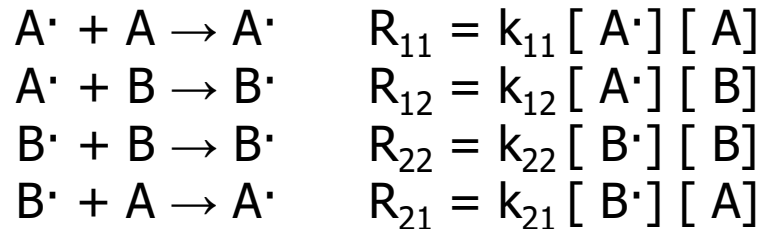
monomer reactivity ratios (r_n):

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$



Copolymerization: Composition Control (cont.)

Blending two monomers results in four simultaneously occurring propagation reactions with different rate equations:



Symmetry: $k_{21} [B^\cdot] [A] = k_{12} [A^\cdot] [B]$

The rates of monomer consumption are given:

$$d[A]/dt = k_{11} [A^\cdot] [A] + k_{21} [B^\cdot] [A]$$

$$d[B]/dt = k_{22} [B^\cdot] [B] + k_{12} [A^\cdot] [B]$$

Monomer reactivity ratios:
 $r_1 = k_{11} / k_{12}$
 $r_2 = k_{22} / k_{21}$

Divide the first equation by the second equation, we obtain the Mayo-Lewis equation:

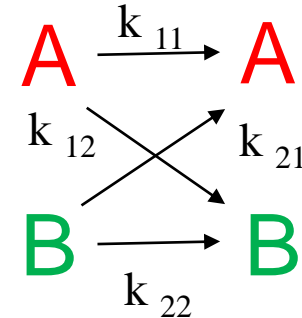
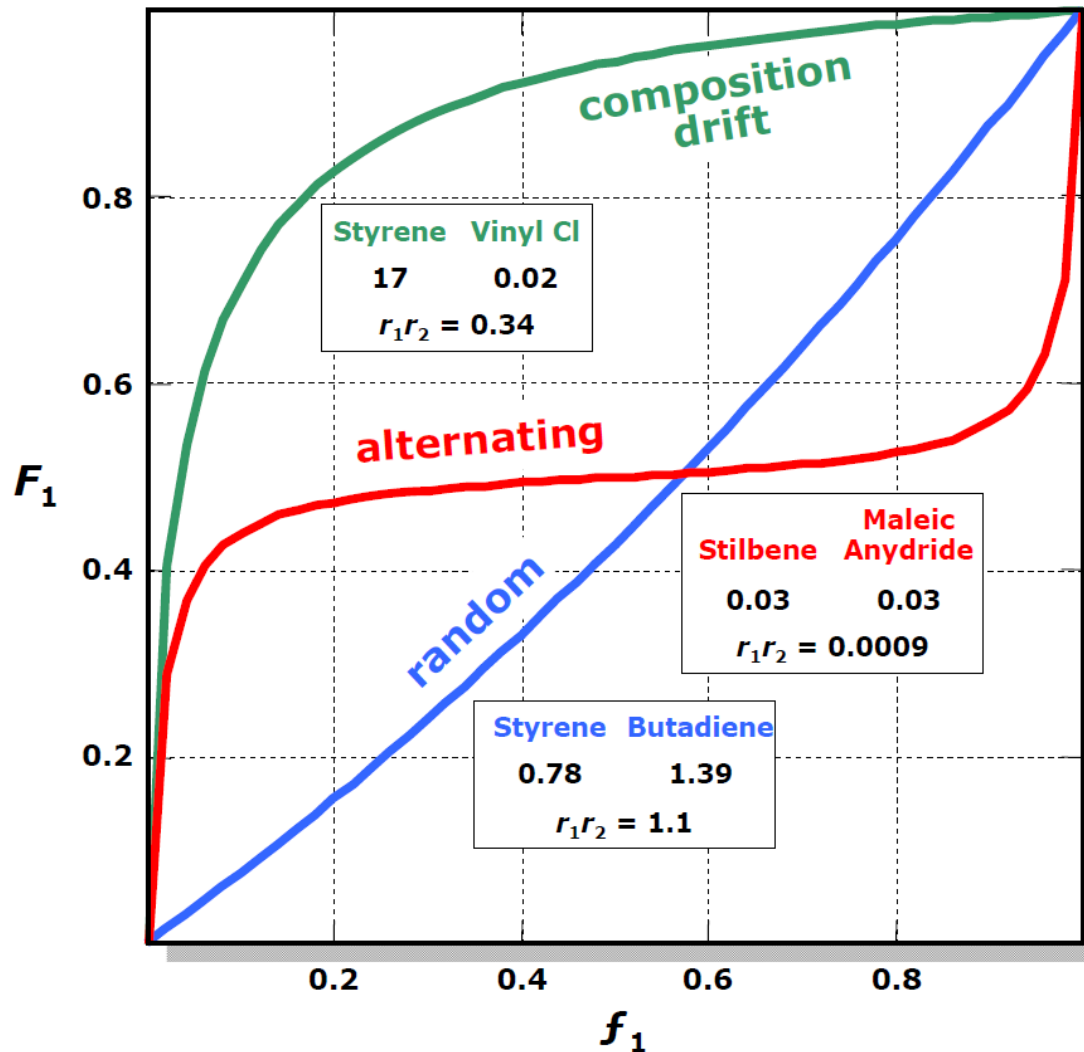
$$d[A]/d[B] = ([A]/[B]) \cdot (r_1[A]/[B] + 1) / ([A]/[B] + r_2)$$

The mole fraction of unreacted monomer f_1 (in the feed/reactor) and the mole fraction in an increment of copolymer F_1 formed at a given stage in the polymerization process:

$$f_1 = [A] / ([A] + [B]) = 1 - f_2$$

$$F_1 = d[A]/d([A]+[B]) = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2) = 1 - F_2$$

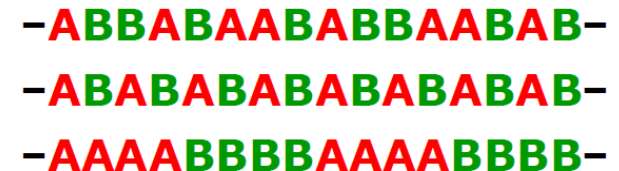
Copolymer Composition: Impact of $r_1 r_2$



Monomer reactivity ratios

$$r_1 = k_{11} / k_{12}$$

$$r_2 = k_{22} / k_{21}$$



$$f_1 = [A] / ([A] + [B]) = 1 - f_2$$

Incremental Polymer Composition (F_1) as a Function of Monomer Composition (f_1) for Different Reactivity Ratios

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)$$

Copolymer Composition

Exercise:

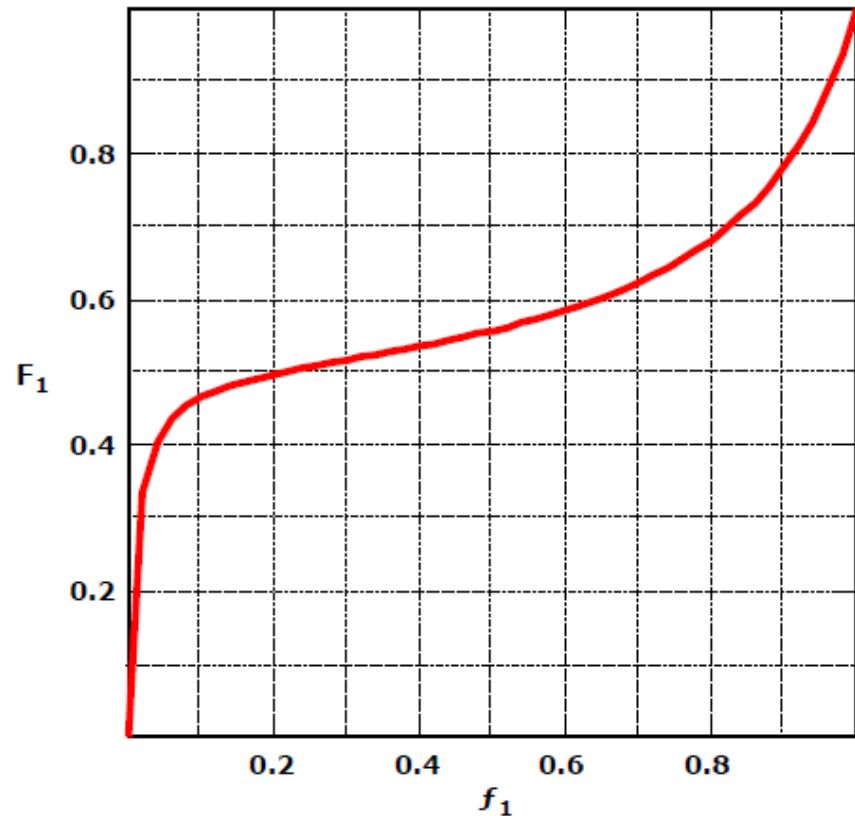
The graph shows the feed and product compositions for the free-radical reaction of styrene (monomer 1) and acrylonitrile (monomer 2).

What feed composition do you need to get a copolymer that is 50% styrene?

- a) About 55% styrene
- b) About 55% acrylonitrile
- c) About 25% styrene

What *kind* of copolymer will you get?

- a) One that tends to have an alternating structure.
- b) One that is enriched in styrene.
- c) One that tends to be a mixture of copolymers.

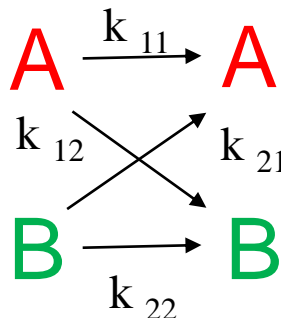


Incremental Polymer Composition (F_1) as a Function of Monomer Composition (f_1)

-**A****B****B****A****B****A****A****B****A****B****B****A****A****B****A****B**-
 -**A****B****A****B****A****B****A****B****A****B****A****B****A****B****A****B**-
 -**A****A****A****B****B****B****A****A****A****B****B****B****B****B****B**-

$$r_1 = k_{11} / k_{12}$$

$$r_2 = k_{22} / k_{21}$$



$$f_1 = [A] / ([A] + [B]) = 1 - f_2$$

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)$$

Polymerization Reactions

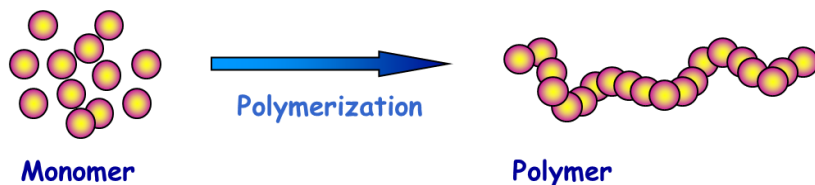
Step-growth polymerization or condensation polymerization

Chain-growth polymerization or addition polymerization

Polymerization Techniques

Condensation polymerization

- Melt polycondensation
- Solution polycondensation

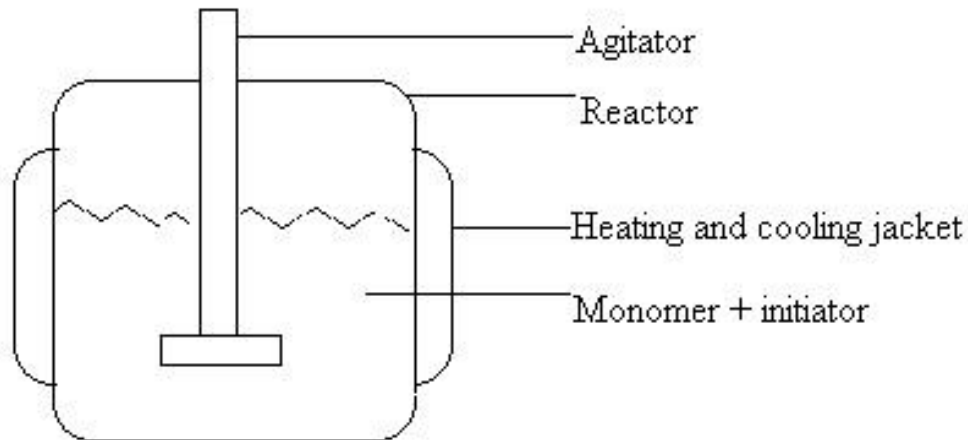


Addition polymerization

- Bulk polymerization
- Solution polymerization
- Suspension polymerization
- Emulsion polymerization

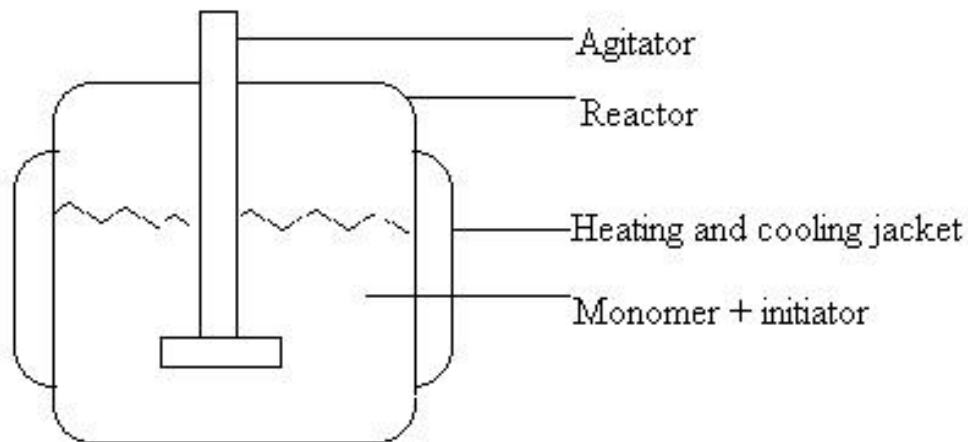
Bulk Polymerization

- Mass or block polymerization: Polymerization of the **undiluted** monomer.
- Carried out by adding a soluble initiator to pure monomer (**in liquid state**).
- The mixture is constantly agitated & heated to polymerization temperature.
- Once the reaction starts, heating is stopped as the reaction is exothermic.



Bulk Polymerization

- The heat generated is dissipated by circulating water jacket.
- Viscosity increases dramatically during conversion.
- The method is used for the polymerization of liquid state monomers.
- It is usually adopted to produce polystyrene, polyvinyl chloride, polymethyl methacrylate and low density polyethylene.



Autoacceleration: Trommsdorff or "gel" effect

In general, rate of polymerization depends on the rate constants of initiation, propagation and termination.

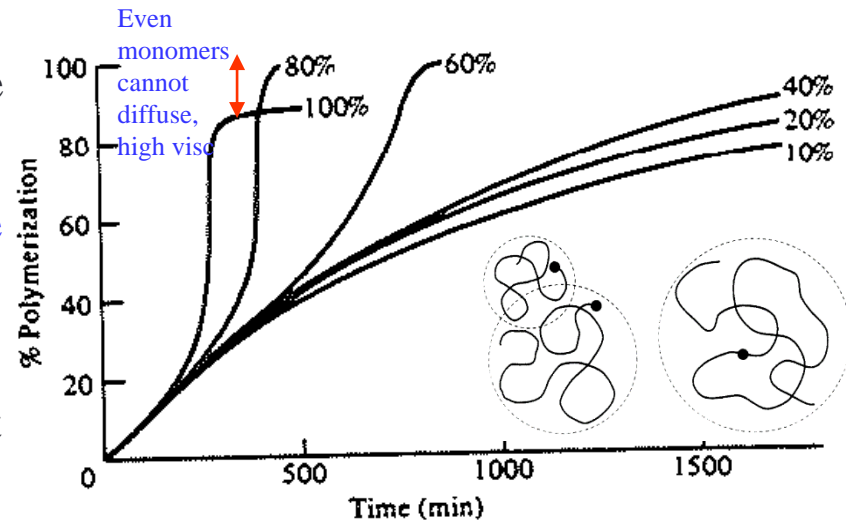
Considerable increase in both the polymerization rate and the molecular weight which is known as the gel or Trommsdorff effect.

Autoacceleration is independent of the initiator and it results in a noticeable *increase in temperature*.

Drastic increase in the rate of polymerization and the simultaneous increase in the average molecular weight is caused by a noticeable decrease in the termination rate (diffusion controlled).

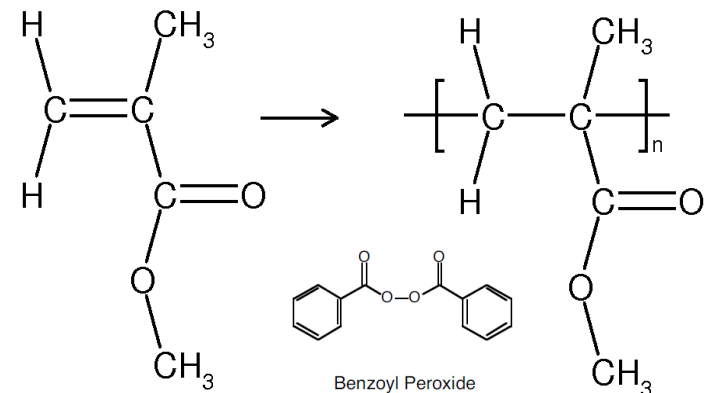
The net rate of termination in the autoacceleration regime (high viscosity) will dramatically decrease, whereas the reactivity of the monomers will not change much due to the small size of the monomers.

The reaction rate between two polymers of very different length will be entirely determined by the *shorter chain*.



Polymerization of poly methyl methacrylate PMMA at 50°C in the presence of benzoyl peroxide initiator at various concentrations of monomer in benzene (inert solvent).

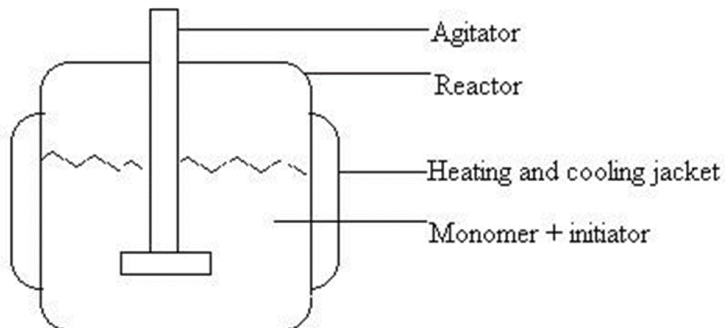
Bulk free radical polymerization of MMA to PMMA



Bulk Polymerization

Advantages

- The system is simple and requires thermal insulation.
- The polymer is obtained pure.
- Large castings may be prepared directly.
- Molecular weight distribution can be easily changed with the use of a chain transfer agent.



Disadvantages

- Heat transfer and mixing become difficult as the viscosity of reaction mass increases.
- Highly exothermic.
- The polymerization is obtained with a broad molecular weight distribution due to the high viscosity and lack of good heat transfer.
- Very low molecular weights are obtained.
- Hard to remove all unreacted monomers: food contact!!!

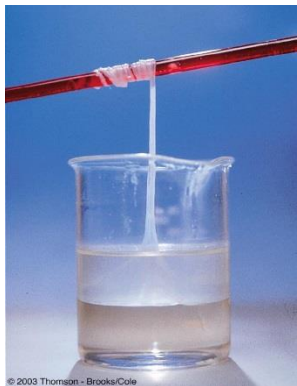
Solution Polymerization

- Some disadvantages of bulk polymerization are eliminated in solution polymerization.
- Monomer along with initiator dissolved in solvent, formed polymer stays dissolved.
- The mixture is kept at polymerization temperature and constantly agitated.
- Depending on concentration of monomer the viscosity of solution does not increase.
- After the reaction is over, the polymer is used as such in the form of polymer solution or the polymer is isolated by evaporating the solvent.
- Polymer so formed can be used for surface coating.
- It is used for the production of Polyacrylonitrile, PVC, Polyacrylic acid, Polyacrylamide, Polyvinyl alcohol, PMMA, Polybutadiene, etc

Solution Polymerization

Advantages

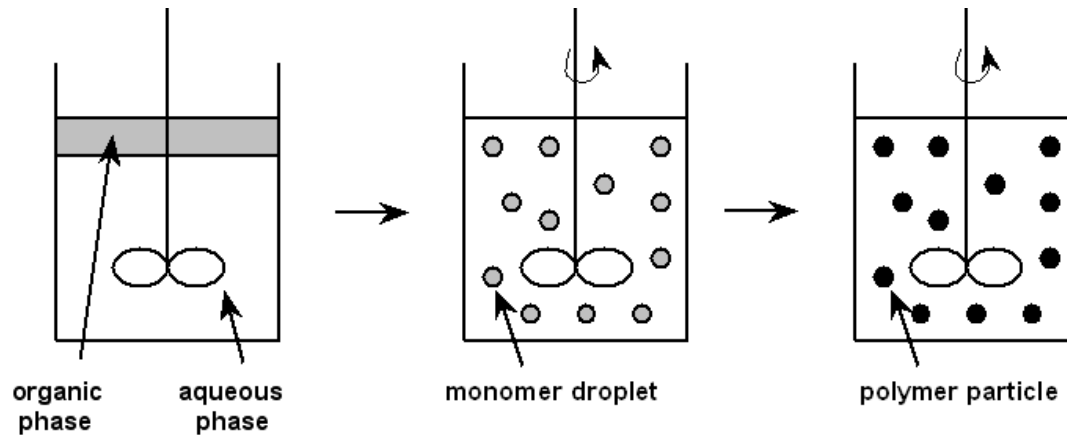
- The solvent acts as a diluent and helps in facilitating continuous transfer of heat of polymerization. Therefore **temperature control is easy**.
- The solvent allows easy stirring as it **decreases the viscosity of reaction mixture**.
- Solvent also facilitates the ease of removal of polymer from the reactor.
- Viscosity build up is negligible.



Disadvantages

- To get pure polymer, evaporation of solvent is required *additional technology*, so it is essential to separate & recover the solvent.
- The method is more expensive since it uses costly solvents.
- High molecular weight polymers cannot be formed as the solvent molecules may act as chain terminators.
- The technique gives a smaller yield of polymer per reactor volume, as the solvent waste the reactor space.
- The purity of product is also not as high as that of bulk polymerization. Removal of last traces of solvent is difficult.

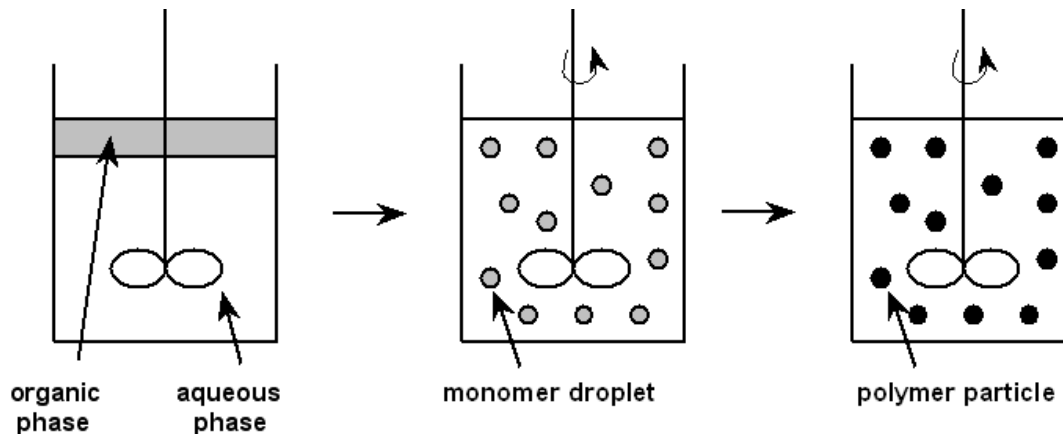
Suspension Polymerization



- Dissolved *monomers suspended in liquid phase* (like water) in form of droplets.
- ***Initiators used are monomer soluble***, e.g., dibenzoyl peroxide.
- The size of monomer droplets is ***50-200 μm*** in diameter.
- The dispersion is maintained by continuous agitation and ***the droplets are prevented to coalesce*** (unite or merge) by ***adding small quantity of stabilizers***.
- The stabilizers used are PVA, gelatin, cellulose along with inorganic stabilizers such as kaolin, magnesium silicate, aluminum hydroxide, calcium/magnesium phosphate, etc if necessary.
- Each droplet is a tiny bulk reactor. The polymerization takes place inside the droplet and product formed being insoluble in water.

Suspension Polymerization

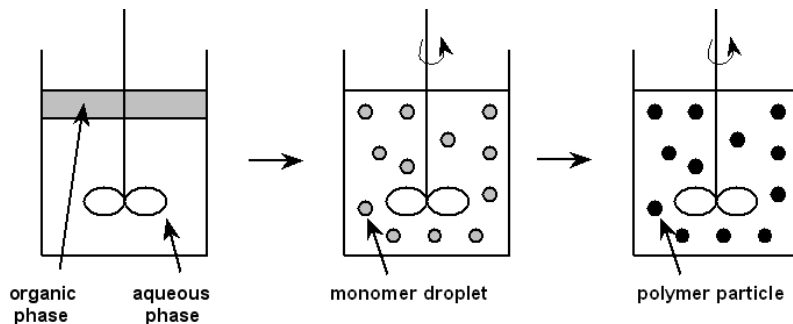
- The product separated out in the form of spherical pearls or beads of polymer.
- Hence the technique is also known as **Pearl polymerization** / **Granular polymerization** / **Bead polymerization**.
- The products are small uniform spheres. They can be used directly for some applications as precursors of ion exchange resins otherwise they can be extruded & chopped to form larger, easily molded pellets.
- They can be dissolved in a suitable medium for use as adhesives and coatings.
- This technique is used to form PVC, Polyvinyl acetate, Polystyrene, Styrene-divinyl benzene copolymer beads (used for ion exchange) etc.



Suspension Polymerization

Advantages

- The process is comparatively cheap as it involves only water instead of solvents.
- Viscosity increase is negligible.
- Agitation and temperature control is easy.
- Product isolation is easy since the product is insoluble in water.



Disadvantages

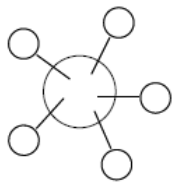
- The method can be adopted *only* for water insoluble monomers.
- It is difficult to control polymer size.
- **Polymer purity is low** due to the presence of suspending and stabilizing additives that are difficult to remove completely.
- Suspension polymerization reaction is highly agitation sensitive.
- Larger volume of reactor is taken up by water. **Low yield per reactor volume.**

Emulsion Polymerization

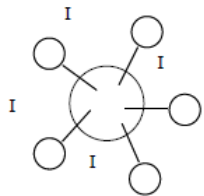
In emulsion polymerization there are some key “ingredients”:

- The monomer must be insoluble in water and polymerizable by free radicals
- Water-soluble initiator
- Water
- Surfactant

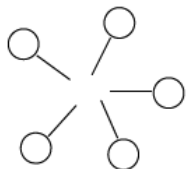
Add monomer and disperse as droplets:



large monomer drops (~mm)



micelle with monomer (1Å to 0.1µm) and initiator (I)

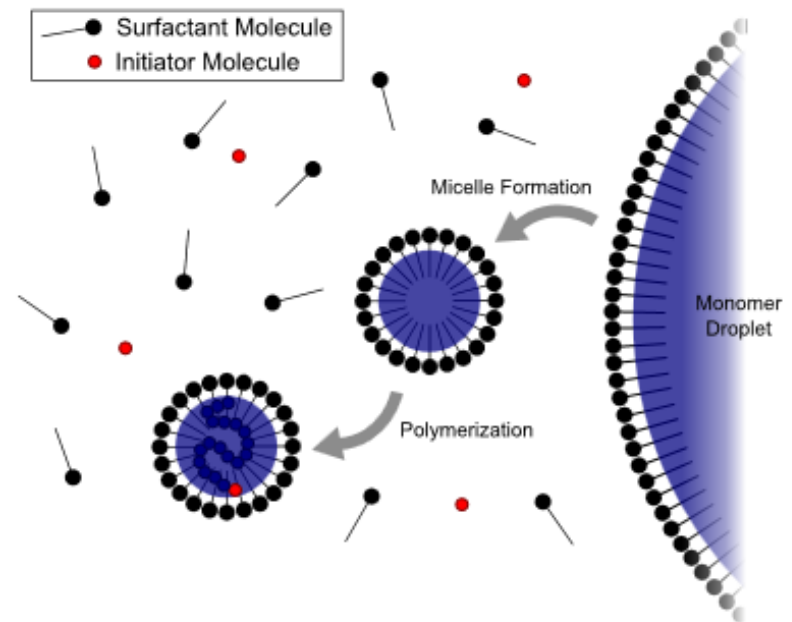


Excess surfactant creates empty micelles in the water.

The initiator (I) can diffuse into the micelle particle and polymerize the monomer

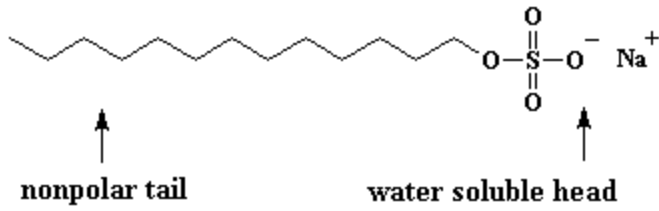
More monomer from the droplet diffuses over and polymerizes

Thus the particle size increases

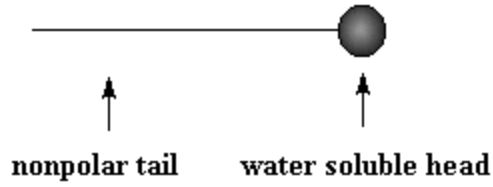


How Soap Works?

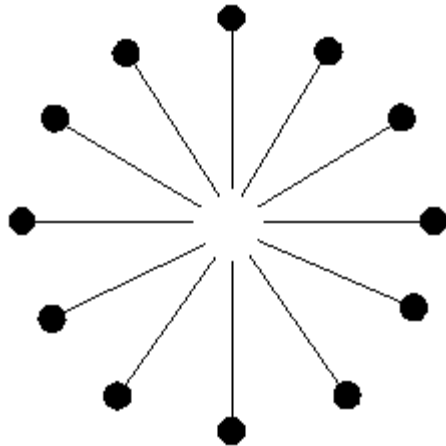
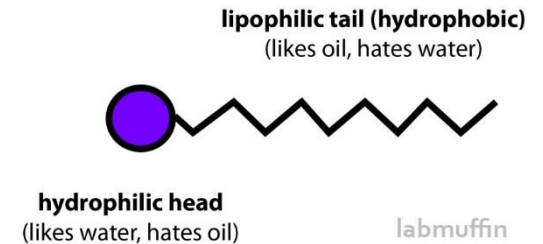
Surfactant molecule



Sod

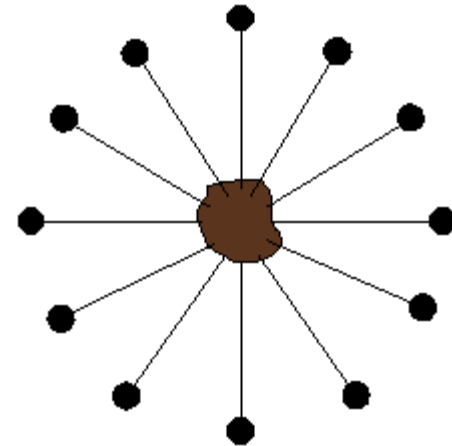


SURFACTANT MOLECULE



Dirt

=



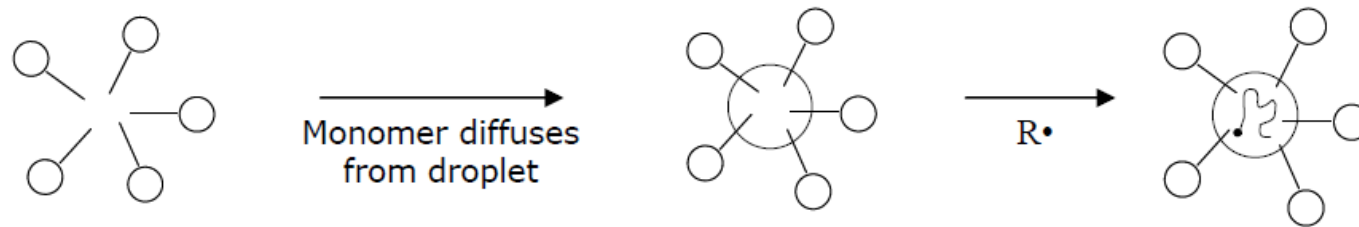
Surfactant molecules
congregate and form micelles

Dirt is dissolved in the micelle, the micelle is
dissolved in water and can be wash out

Emulsion Polymerization

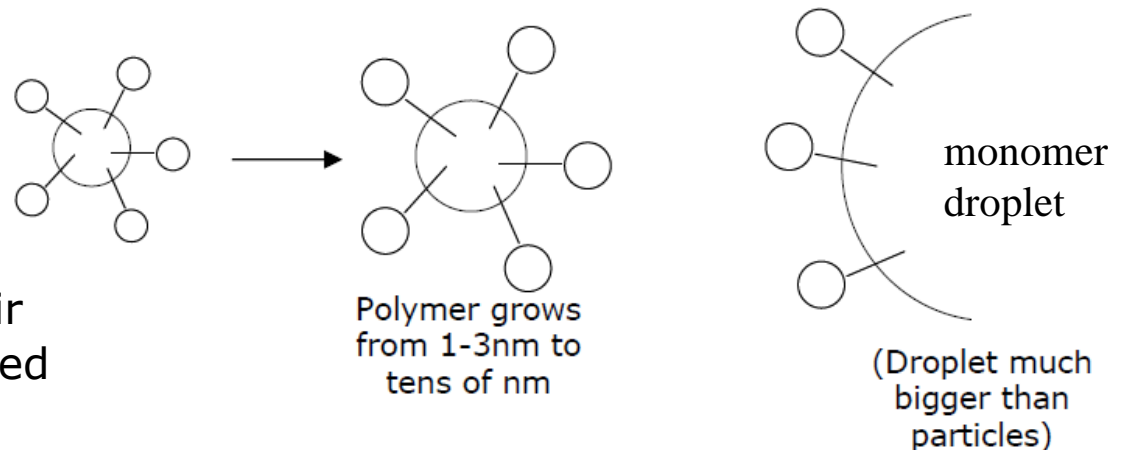
Stage I:

- The monomer diffuses to the empty micelle from droplet
- Polymerization initiated in micelles to become polymer particles
- New particles are generated as micelles are consumed
- This stage lasts for conversion $\sim 0-15\%$



Stage II:

- No more surfactant available to generate new particles
- Monomer diffuses into now a constant number of particles to maintain some equilibrium $[M]$ with the particle

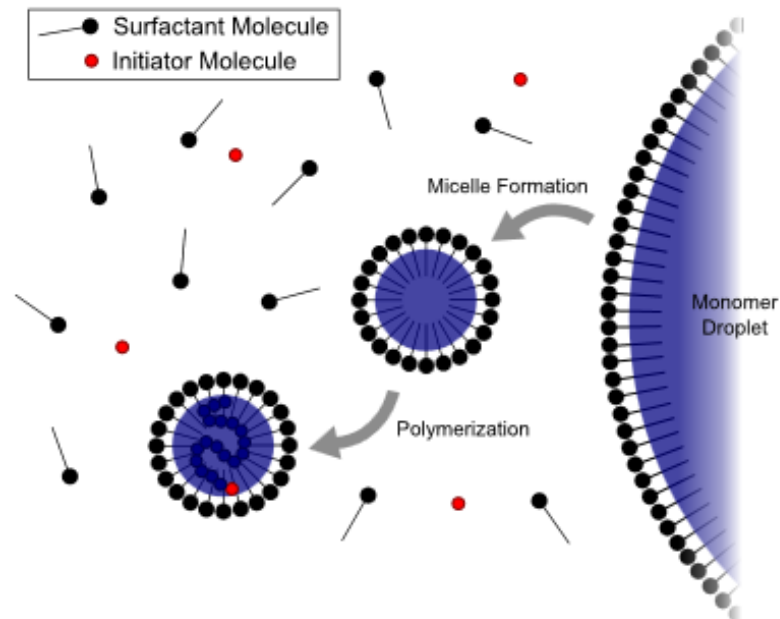


- The monomer reservoir drops get slowly consumed

Emulsion Polymerization

Stage III:

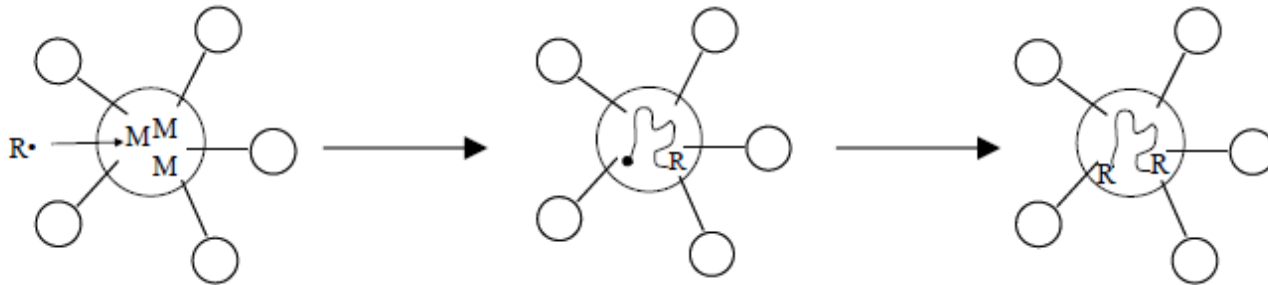
- This stage occurs when conversion $\sim 40-60\%$
- All the monomers exist in particles
- The monomer droplets are exhausted
- $[M]$ in particles continually decreasing as conversion increases
- Particle size is constant
- Conversion rate can reach up to 80-100%



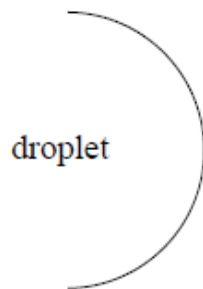
Emulsion Polymerization

Smith-Ewart Model

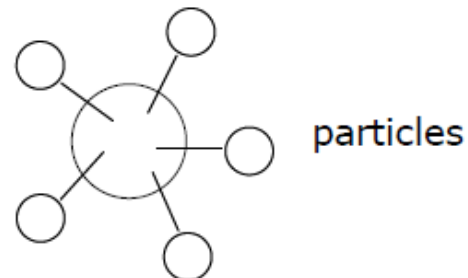
- The Smith-Ewart model states that one radical diffuses into a particle at a time and termination occurs when another radical R^\bullet diffuses in:



- There is 1-100 seconds between radical entry events



Vs



- The total surface area of the micelles is much greater than the total surface area of the fewer, larger monomer droplets; therefore the initiator typically reacts in the micelle and not the monomer droplet.

Emulsion Polymerization

Advantages

- High molecular weight polymers.
- Fast polymerization rates.
- Allows removal of heat from the system.
- Viscosity remains close to that of water and is not dependent on molecular weight. Easy to control.
- The final product can be used as such, does not need to be altered or processed.

Disadvantages

- Surfactants and polymerization adjuvants - difficult to remove.
- For dry (isolated) polymers, water removal is an energy-intensive process.
- Designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer.