



## Plastics Topics – Polymer chemistry

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# Plastics Topics – Polymer chemistry

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## 1. General classification of polymer products

Carothers (1929) suggested the classification of polymers into two groups, condensation and addition polymers. According to this classification:

- Condensation polymers were those in which the repeat unit of the chain lacked some of the atoms present in the monomer, e.g., in many cases H<sub>2</sub>O is eliminated during the reaction.
- Addition polymers those in which the sub-group loss does not take place.

Flory (1953) amended this classification and placed the emphasis on the mechanism of formation, i.e., condensation polymers are formed by stepwise intermolecular condensation of reactive groups and addition polymers result from a chain reaction around an active centre.

This removes the emphasis of the classification on the loss of the small molecule and allows a more consistent terminology e.g., polyurethane would be classed as addition because it does not lose any atoms but the reaction is kinetically of the step reaction (condensation) type.

The distinguishing features of chain and step mechanisms are set out in Table 1.

Chain Polymerisation	Step Polymerisation
<ul style="list-style-type: none"><li>• Only growth reaction adds repeating units one at a time.</li><li>• Monomer concentration decreases steadily during reaction.</li><li>• High polymer formed at once: polymer molecular weight changes little during the reaction.</li><li>• Longer time gives higher yields but little change in molecular weight.</li></ul>	<ul style="list-style-type: none"><li>• Any two molecular species present can react.</li><li>• Monomer disappears early in the reaction: At a Degree of Polymerisation of 10 &lt; than 1% monomer remains.</li><li>• Polymer molecular weight rises steadily during reaction.</li><li>• Need long times for high molecular weights.</li></ul>

Table 1 - The Chain and Step Methods

## 2. Step reaction (Condensation) Polymerisation

The type of product formed in a condensation reaction is determined by the 'functionality' of the monomers i.e., by the average number of reactive groups per monomer molecule. Mono-functional monomers give only low molecular weight compounds e.g., a mono-basic acid and a monohydric alcohol, both mono-functional react to form a monoester of zero functionality (ethanol + propionic acid => ethyl propionate).

Bi-functional monomers give linear polymers, i.e., terephthalic acid + ethylene glycol react to give another bi-functional molecule, a polyester (terylene).

Poly-functional monomers (more than 2 functional groups per molecule) give branched or cross-linked polymers.

Polycondensation can thus lead to either thermoplastic or thermosetting products, dependent on the functionality of the reactants. Typical examples of these are nylons (polyamides), polyesters, alkyds, phenol-formaldehyde resins etc. In general, there are two monomers present and the product is a co-polymer.

### Bi-functional Monomers

In addition to linear polymer formation, bi-functional monomers can react to give a cyclic product. The type of product is governed by the size of the ring. If less than 5 atoms or greater than 7 are present then a linear polymer is usually formed. If a ring of 5 can form then this will occur to the exclusion of a linear polymer. For six and seven a mixture may be formed. The governing characteristic is the strain involved in forming the valence angles of the ring atoms.

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The degree of polymerisation of a condensation polymer can be controlled by varying the time of reaction or by adjusting the temperature. Chilling the polymerising material at the required degree of polymerisation stops the reaction but subsequent heating may lead to an unstable product. In general, the reaction is stopped by adjusting the composition of the reaction mixture away from stoichiometric equivalence by adding a slight excess of one bi-functional reactant or by adding a small amount of a mono-functional reagent, i.e., stabilisation of nylon by acetic acid. This is in fact a problem because great care must be taken to get high degrees of polymerisation since the loss of one ingredient, side reactions or the presence of mono-functional impurities may severely limit the degree of polymerisation achieved.

It is possible to polymerise a bi-functional monomer of the type A-B with a small amount of monomer of functionality  $f$  of the type R-A $_f$ . If the reaction is carried to completion, the resulting polymer consists of  $f$  chains growing out from a central unit R. Network structures cannot occur and as  $f$  increases the molecular weight distribution becomes more concentrated.

### Polyfunctional monomers

The use of a polyfunctional monomer allows the formation of a 3-D network from chained branching and cross-linking. The cross-linked polymers have a greater rigidity and when a high degree of cross-linking takes place the product is rigid and insoluble in most solvents. The point at which this occurs is the "gel point" and divides the mixture into two parts:

- The 'gel', which is an infinitely large polymer network insoluble in most non-degrading solvents.
- The 'sol', which remains soluble and can be extracted from the gel.

As the reaction proceeds the sol is converted to gel and the mixture is rapidly converted to an elastic material of infinite viscosity. The extent of reaction at which gelation will occur has been theoretically predicted by Carothers.

In many cases a tri-functional unit is introduced in controlled quantities to a bi-functional mix to promote some cross-linking. Careful control of the quantities of the reactants is necessary to give an end product of the required properties.

## 3. Chain (Addition) Polymerisation

The polymers formed in this way are always thermoplastics because of the essentially linear nature of the reaction. The monomers always contain a double bond and, with the exception of fluorinated compounds, always contain the methylene group, CH<sub>2</sub>. The basic monomer is thus of the form:

**CH<sub>2</sub>=C.R<sub>1</sub>.R<sub>2</sub> where R<sub>1</sub> and R<sub>2</sub> are additional groups**

or for fluorine:

**CF<sub>2</sub>=CF<sub>2</sub> or CF<sub>2</sub>=CCIF**

In this reaction there is generally an active centre associated with a single polymer molecule which is responsible for the addition to, and growth of, the chain. Polymer molecules are formed straight away and no species of molecular weight between the monomer and high molecular weight polymer are found. The active centre can be one of the three types: cation, anion and free radical.

### Radical Chain Polymerisation

In this type of chain polymerisation, a free radical mechanism is involved in the splitting of the double bond to allow chain building to begin.

The free radical has an odd number of electrons and thus an unpaired electron. These can be produced by a variety of methods such as:

1. Thermal decomposition of organic peroxides or hydroxide e.g., benzoyl peroxide at greater than 70°C decomposes to give benzoate radicals.  
Azo- or diazo compounds, e.g., azobisisbutyronitrile, also decompose in this manner.
2. Photolytic decomposition of covalently bonded compounds (photoinitiation), e.g., azobisisbutyronitrile decomposes under UV light in the 3600Å region. This takes place at temperatures low enough that thermal decomposition does not occur and allows a very controlled source of free radicals.

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3. Radiation dissociation of covalent bonds.
4. Redox initiation in aqueous solutions.

The stability and reactivity of free radicals varies widely with primary being more reactive than secondary.

### Initiation

When free radicals are generated in the presence of the double bond the radical adds to the double bond and regenerates another radical.

**i.e.,  $R-R \Rightarrow 2R^\bullet$**

**$R^\bullet + CH_2=CHX \Rightarrow RCH_2\dot{C}$**

The isolation of the free radical fragments from polymers and the use of heavy atoms or radioactive atoms confirms this mechanism.

The efficiency of the initiator radical can be estimated by comparison of the number of chains formed versus the number of radicals decomposed.

### Propagation

As the polymer radical increases in length, it retains its activity at the growing end and successive monomers are added to propagate the chain.

Individual chains are formed in short bursts of activity and not as a continuous process. The process of growth is, however, very rapid - in some cases explosively so.

### Termination

Propagation would continue until the monomer was exhausted were it not for the tendency of radicals to react in pairs and thus lose their reactivity. This is somewhat countered by the relatively low concentration of radicals compared with that of the monomer. Termination can occur by:

- Combination or coupling.
- Disproportionation - when this occurs a mix of saturated and unsaturated terminal groups is formed, e.g., PMMA at  $>60^\circ\text{C}$
- Transfer agents - these are able to use up the free radical to prevent further chain growth, e.g., benzoquinone is often added to monomer solutions to prevent spontaneous polymerisation and then removed prior to polymerisation.

### Other factors

- Inhibition or retardation - substances similar to transfer agents but of a lower reactivity.
- Configuration - The addition can occur in either head-to-tail or head-to-head or tail-to-tail configurations.
- A random structure containing both arrangements is the normal form.

### Ionic Chain Polymerisation

In this type of polymerisation an ionic catalyst is used and this may be either a cation or an anion. In general, the three stages of initiation, propagation and termination are present although the mechanisms are much different e.g., the rate of polymerisation is independent of temperature since no energy is needed for initiation, termination cannot occur by disproportionation (like ions repel) and the degree of polymerisation is inversely proportional to temperature (since the termination reaction requires energy whereas the propagation reaction does not).

Initiation of ionic polymerisation usually involves the transfer of an ion or an electron to or from the monomer, with the formation of an ion pair. It is thought that the counter-ion of this pair stays closely bound to the ion. Ionic polymerisation is usually carried out in an inert non-aqueous media (e.g., toluene) and the catalyst supplies both an ion and a counter-ion. Termination never involves two growing chains but involves a uni-molecular reaction of a chain with its counter-ion or a transfer reaction leaving a species too weak to propagate.

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Monomers with electron donating groups, which supply a high electron density at the double bond, favour polymerisation by electron accepting initiators i.e., cations. Typical catalysts for this are proton donors such as Lewis acids and Friedel-Crafts catalysts e.g.,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ ,  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{SnCl}_4$ .

Monomers with electron abstracting groups, e.g., vinyl and vinylidene chloride, respond best to electron donors. Typical catalysts include alkali metals, alkoxides, alkyls, aryls, hydroxides and cyanides.

### Co-ordination Chain Polymerisation

This technique is sometimes called "stereo-specific" specific or "stereo-regular" polymerisation but the term "co-ordination polymerisation" is used to suggest the existence of a force which governs the orientation with which a monomer approaches the growing end. The mechanism involved may be free radicals or ionic.

In 1953 Zeigler used an organo-metallic catalyst to polymerise ethylene (normally requiring high pressure and temperature) at ordinary pressures and temperatures. The resulting polyethylene proved to be less branched and thus more crystalline and denser than usual. This also gave a higher melting point. Natta discovered that polymers, such as polypropylene, made using Ziegler catalysts, are different from normal polymers. Instead of the random atactic (Greek: without order) structure normally found, the groups attached to the carbon backbone were oriented to form a regular pattern. In one type the side groups were all on the same side of the chain (isotactic = Greek: same order) and in the other type there was a regular alternation of direction (syndiotactic = Greek: contrasting order). The tactic polymer forms are denser and the syndiotactic polymers have a tough cohesive structure because of interlocking of the side chains above and below the backbone.

The Ziegler catalyst consists of a combination of a metal halide and an organo-metallic compound used in an inert solvent such as hexane, e.g., Titanium tetrachloride ( $\text{TiCl}_4$ ) complexed with trialkyl aluminium ( $\text{Al}[\text{C}_2\text{H}_5]_3$ ) which is used for industrial polyethylene production.

Other catalysts having Zeigler type properties are the Phillips and Standard Oil catalysts. The Phillips catalysts are chromium oxide supported on a base of alumina-silica and the Standard catalysts are either molybdenum oxide on alumina or nickel on activated carbon. In some instances, it is possible to obtain stereospecificity from a soluble catalyst, e.g., isoprene or lithium butyl in a non-polar solvent.

Ethylene is polymerised to a highly linear chain, polypropylene can be made in isotactic or syndiotactic forms, but higher alpha-olefins give only isotactic chains. PMMA can be produced in either isotactic or syndiotactic forms by an anionic mechanism using toluene or other complexes respectively.

Monomer	Radical	Cationic	Anionic	Coordination
+ = high polymer		- = no reaction or oligomers only		
Acrylonitrile	+	-	+	+
Dienes	+	-	-	-
Ethylene	+	+	-	+
Isobutylene	-	+	-	-
Propylene	-	-	-	+
Styrene	+	+	+	+



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Vinyl Chloride	+	-	-	+
Vinyl Fluoride	+	-	-	-
Tetrafluoroethylene	+	-	-	+
Vinyl ethers	-	+	-	+
Vinyl esters	+	-	-	-

**Table 2 - Types of Chain Polymerisation for Monomers**

### 4. Copolymerisation

This type of polymerisation occurs when two suitable monomers are polymerised together. The resulting polymer chain contains a mixture of monomer units and the proportions are different from those of a mixture of the two equivalent homopolymers. Many monomers are known which will not polymerise with themselves, even under extreme conditions, but which will copolymerise with other compounds, e.g., Maleic acid anhydride will copolymerise with SO<sub>2</sub>.

A copolymer contains mixed repeat units and in radical addition copolymerisation the structure of the product depends on the relative polarizability or monomer reactivity ratios. A monomer reactivity ratio of less than 1 means that the monomer favours addition to the opposite kind of radical, and if both monomers do this exclusively the result is a regular alternating copolymer. If the chain end has no influence on the addition i.e. A monomer adds equally well to its own or the opposite kind of radical (product of ratios =1) the result is a random copolymer. If the ratio is greater than 1, the monomer favours addition to its own kind and if this happens exclusively then two homopolymers are formed simultaneously. This reactivity depends on the monomer structure, if they have double bonds adjacent to phenyl or methyl groups the activity is increased. Other groups vary in that some attract electrons away from the double bond and some direct them to it. This results in the double bond being polarised and the distribution of monomer units is affected by this polarisation. Monomers with similar bond polarities are random and those with different polarities form alternating polymers.

In condensation copolymerisation there is usually no selective reactivity and the repeat units are randomly distributed in the same proportion as in the initial monomer mixture.

Block copolymerisation yields runs of one unit alternating with runs of another as in,

**AAAAAAAAABBBBBBBBBBAAAAAAAAAABBBBBBBB.**

These are produced by:

1. The use an initiator which decomposes in stages.
2. The production of polymer radicals by irradiation of a monomer with UV light.
3. The addition of a different monomer to a system in which the first monomer has been exhausted but polymer ions are still "living". The polymer then begins to grow again.
4. Condensation polymerisation of mixed and suitably prior condensed homopolymers of low molecular weight.

Graft copolymerisation yields a backbone of units of one type onto which are grafted units of a different type. Thus, if a monomer B is addition polymerised in the presence of preformed polymer A, which may be in solution or dispersed, some of B becomes grafted to A. The active centres for this can also be created by irradiation of the stock polymer.

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## 5. Conditions and Reactions

### Bulk

This is used for condensation production where the reaction is only slightly exothermic and most of the reaction occurs while the viscosity of the mixture is low enough to allow ready mixing, heat transfer and bubble elimination.

Bulk polymerisation is not used for vinyl monomers because these are highly exothermic. As the reaction rate is temperature dependent the low viscosity can lead to "hot-spots" and "runaways". This method is mainly used for PMMA but sometimes also for PS.

### Solution

The monomer and the catalyst are dissolved in an inert solvent with the resultant solution being stirred and heated. Large quantities of solvent are needed and this has to be recovered and separated. The heat of polymerisation can be absorbed by the solvent and good control can be obtained. There is however a serious problem with solvent removal as the solvent can become part of the finished molecule and removal of the last traces of solvent is difficult and expensive. For this reason, the process is used mainly for products where the polymer is required as a solution, i.e., coating and impregnation.

### Suspension (pearl)

The monomer in this process is suspended in the carrier medium, usually H<sub>2</sub>O together with a monomer soluble catalyst. When the mixture is stirred, the monomer is broken into small droplets, each of which will contain a little of the catalyst. A stabiliser, such as talc or methyl cellulose, is also included to keep the particles separate from each other during the reaction. The heat of the reaction is absorbed by the aqueous medium and the reaction is easily controlled. The stabiliser is removed from the polymer by washing or flotation, leaving the polymer in the form of small beads or pearls which are dried before use. The process can be looked upon as a large number of tiny bulk polymerisations.

### Emulsion

This relies on the emulsification of the monomer with water using an anionic soap as an emulsifying agent. The initiator is dissolved in the aqueous phase from which it diffuses into the soap micelles coating the monomer. The resultant polymer is insoluble in the medium and is precipitated as it is formed or coagulated using Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> or used directly as an emulsion e.g., paints. Some traces of the emulsifying agent remain after washing but the process does produce the highest molecular weight product.

The role of the soap is such that at the beginning of the reaction, polymer is formed in the soap micelles which are a good environment for the free radicals formed in the aqueous phase. When the polymer particles are bigger than the micelles almost all the soap is absorbed and unactivated micelles disappear. Growth and polymerisation then occur only within the polymer particles already formed.

The various polymerisation systems are shown in Table 3

Type	Advantages	Disadvantages
<b>Homogeneous</b>		
Bulk (batch)	Minimum contamination. Simple equipment.	Strongly exothermic, large molecular weight distribution at high yield.
Bulk (continuous)	Lower conversion gives better heat control and narrower molecular weight distribution.	Requires agitation, materials transfer, separation and recycling.



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Solution	<p>Good control of heat of polymerisation.</p> <p>The solution may be directly usable.</p>	<p>Not for dry polymer because complete solvent removal is difficult.</p>
<b>Heterogeneous</b>		
Suspension	<p>Good control of heat of polymerisation.</p> <p>Suspension or resulting granular polymer may be directly usable.</p>	<p>Continuous agitation required. Contamination by stabiliser is possible.</p> <p>Washing, drying and compacting required.</p>
Emulsion	<p>Rapid polymerisation to high molecular weight with narrow distribution.</p> <p>Good heat control and may be directly usable.</p>	<p>Contamination with emulsifier is inevitable giving poor colour and colour stability.</p> <p>Washing drying and compacting may be required.</p>

**Table 3 - Polymerisation Systems**