

COURSE CODE: CHM 301  
COURSE TITLE: POLYMER CHEMISTRY AND RUBBER TECHNOLOGY  
NUMBER OF UNITS: 2 Units  
COURSE DURATION: 2 hours per week

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### **COURSE DETAILS:**

Course Coordinator: Dr. Akinola Kehinde AKINLABI  
Email: [akakinlabi@unaab.edu.ng](mailto:akakinlabi@unaab.edu.ng)  
Office Location: Room B102, COLNAS  
Other Lecturers: Prof. I. C. Eromosele, Dr. T. A. Afolabi

### **COURSE CONTENT:**

The nature of polymer, nomenclature, outline of sources of raw material for polymers: polymerization process, condensation and chain polymerization. Solubility and solution properties, polymer structure and properties. Fibre forming polymers. Introduction to rubber chemistry. Properties of commercial polymer- hydrocarbon plastic and elastomer.

### **COURSE REQUIREMENTS:**

This is a compulsory course for all 300 level chemistry students in the University. In view of this, students are expected to participate in all course activities and have minimum of 75% attendance to be able to write the final examination.

### **READING LIST:**

1. Young R. J. and Lovell P. A. (1997). Introduction to polymers. Chapman & Hall, London.
2. Billmeyer F. W. (1984). Textbook of polymer science, 3<sup>rd</sup> edn., Wiley Interscience, New York.
3. Cowie J.M.G. (1973). Polymers: Chemistry and Physics of Modern Materials, International Textbook Company, Aylesbury, UK.
4. Elias H.G. (1987). Mega Molecules, Springer-Verlag, Berlin.
5. Jenkins A.D. and Loening K.L. (1989). Nomenclature in Comprehensive Polymer Science, Pergamon Press, Oxford.
6. Morawetz H (1985). Polymers – The origins and Growth of a Science, John Wiley, New York.

### **LECTURE NOTES**

Nature of polymers.

Nomenclature

Raw-materials for polymers

Condensation & chain reaction with 2 or more bonds

Solubility & solution

Polymer structures & properties

Rubber chemistry

Polymers have existed in natural form since life began and those such as DNA, RNA, protein and polysaccharides play crucial roles in plant & animal life. From the earliest time man has exploited naturally occurring polymers as materials for providing clothing, decoration, shelter, tools, weapons, writing materials etc. The origin of the modern polymer industry, as commonly accepted, has been in the 19<sup>th</sup> century when important discoveries were made concerning the synthesis of certain natural monomers.

In 1820, Thomas Hancock discovered that when masticated natural rubbers, it becomes fluid making it easier to blend with additives and to mold. Some years later in 1839, Charles Goodyear found that the elastic properties of natural rubber could be improved and its tackiness eliminated by heating with sulphur.

New patents for these discoveries were issued in 1844 to Charles Goodyear. In 1851, Charles Goodyear (Charles Goodyear's brother) patented the vulcanization of natural rubber with a large amount of sulphur to produce a hard material commonly known as hard rubber or ebonite.

Cellulose nitrate also known as nitro-cellulose/gum cotton became prominent after Christian Schönbein prepared it in 1846. He was quickly to recognize the commercial value of the material as an explosive and within a year became widely manufactured.

More important about cellulose nitrate is that it is a hard elastic material which is soluble & could be moulded into different shapes via the application of heat & pressure.

In 1892, Charles Cross, Edward Bevan & Clayton Beadnell patented the viscous process for dissolving & then regenerating cellulose. The process was first used to produce viscous rayon textile fibres & subsequently for production of cellophane film (thin transparent material).

The polymeric materials described with far are semi-synthetic since they are produced from natural polymers. The first fully synthetic polymer was Leo Baekeland's bakelite phenol formaldehyde resin which was commercialized in 1910. The first synthetic rubber to be manufactured was known as methyl rubber and was produced from 2,3-dimethyl butadiene in January during World War I. As at this time the polymer industry was now firmly established. Its growth was restricted by the considerable lack of understanding of the nature of

polymers. For over a century, scientists have been reporting the usual nature of polymers and by 1920, the common belief was that they consisted of physical associations of small molecules. Few scientists give credence to the few points so passionately believed by Hermann Staudinger who also gave the field that polymers are composed of very high molecules containing long sequences of simple chemical units linked together by simple covalent bonds.

Staudinger introduced the word macromolecule to describe polymers. Thus by the early 1970's most scientists were convinced of the macromolecular structure of polymers. As the science of macromolecules emerged, a large number of synthetic polymers went into commercial production for the first time. These include; polystyrene, poly(methyl methacrylate), nylon 6,6, polyethylene, polyvinylchloride, styrene butadiene rubber, polytetrafluoro-ethylene as well as many others.

From the 1950's till date, regular advances too numerous to mention have continued to stimulate both synthetic and industrial polymeric processes while polymer science is now considered to be a matured subject its breath is ever increasing and these are many demanding changes awaiting scientists who venture into this multiple disciplinary science.

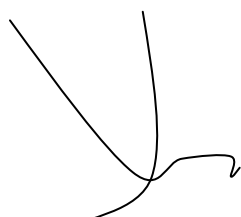
#### Basic definition & nomenclature

Several important terms and concepts must be understood in order to discuss the synthesis, characterization, structure and properties of polymer.

1. Polymer: is a substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary usually covalent bonds. The emphasis of substances in this definition is to highlight that although the word polymer and macromolecules are used interchangeably. The latter strictly define the molecules of which the former is composed.
2. Macromolecules: are formed by linking together monomer molecules through chemical reaction. The process by which this is achieved is known as polymerization

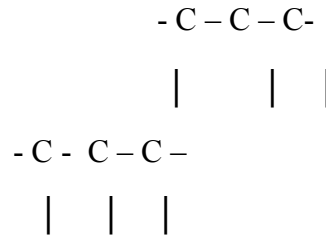
#### Skeletal structures

From the definition of macromolecules, it can be implied that they have a linear structure which may be represented by a chain with  $2n$ . There are also non-linear skeletal structures.





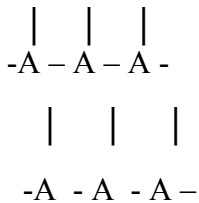
Linear



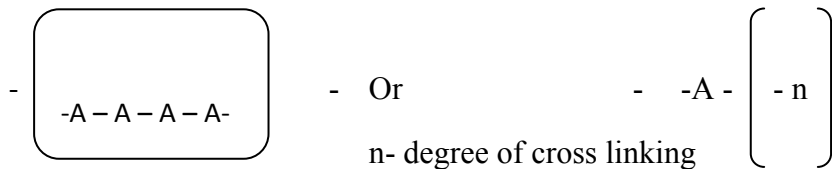
Branched

Network

1. Branched polymers have side chains or branches of significant length which are bonded to the main chain at branched point. The points are also known as junction points. Branched polymers are characterized in terms of the number and size of the branches.
2. Network polymer: they have 3-dimensional structures in which each chain is connected to each other by a sequence of junction points. Such polymers are said to be cross-linked and are characterized by their degree of cross-linking which is related directly to the number of junction points per unit volume.  
 Hint: the importance of cross-linking density is on vulcanization i.e. sulphur cross-linking of natural rubber. With low cross-linking density "low level of sulphur", the product will be a flexible elastomer whereas if a rigid material is desired, the cross-linking density needs to be high.
3. Homopolymer:





The former density of homopolymer is a polymer derived from 1 species of monomer. The word homopolymer is often used to describe polymers whose structure can be represented by multiple repetition of a single type of repeat units which may contain one or more species of monomer units. The chemical structure of a polymer is usually represented by that of a repeat unit enclosed by a bracket.



The hypothetical homopolymer can be represented by  $-(A)_n$  where n is the number of repeat units linked together to form a macromolecule.

Names, structure & uses of monomers & polymers

Monomer	Polymer	Uses / comments
1. Ethylene $\text{CH}_2=\text{CH}_2$	Polyethylene (PE) $-(\text{CH}_2-\text{CH}_2)-n$	Moulded objects, tubes, film, electrical insulation.
2. Propylene $\text{CH}_2=\text{C}_4\text{CH}_3$	polypropylene (PP) $-(\text{CH}_2-\text{CH})-n$	As a low density, it has similar uses as ethylene..
3. Tetrafluoroethylene	$\text{CH}_3$ Polytetrafluoro ethylene (PTFE) $-(\text{CF}_2 - \text{CF}_2)-n$	For moulding, film, coating. high temperature resistance, chemical inert, excellent Electrical insulation. It is expensive.
4. Styrene $\text{CH}_2 = \text{CH}$ 	polystyrene $-(\text{CH}_2 - \text{CH})-n$ 	Cheap moulded object modified with rubber to improve toughness.
5. Methyl methacrylate $\text{CH}_3$ $\text{CH}_2 = \text{C}$ $\text{C}=\text{O}$ $\text{O CH}_3$	polymethyl methacrylate $\text{CH}_3$ $-(\text{CH}_2-\text{C})-n$ $\text{C} = \text{O}$ $\text{O CH}_3$	It is transparent. Used in moulding & used in aeroplane windows. More expensive than polystyrene.
6. Vinyl chloride $\text{CH}_2 = \text{CH}$ $\text{Cl}$	polyvinyl chloride (PVC) $-(\text{CH}_3 - \text{CH})-n$ $\text{Cl}$	Used in H <sub>2</sub> O pipes & gutters, in bottles, gramophone records. used in plasticides to make PVC leather cloth. Used in rain coat, Flexible pipes, toys, electrical cable.
7. Vinyl acetate $\text{CH}_2 = \text{CH}$ $\text{O}$ $\text{C} = \text{O}$	polyvinyl acetate (PVA) $-(\text{CH}_2 = \text{CH})- n$ $\text{O}$ $\text{C}$	Used in surface coating, adhesives & chew gum.



## Copolymer

Copolymer was formerly define as a polymer derive from more than one specie of monomer. However, in accordance with the use of the world homopolymer, it is common practice to use a structure based definition thus the word copolymer more commonly is used to described polymers whole molecules contains 21 more different types of repeat unit. There are several categories of copolymer each being characterized by a particular form of arrangement of the repeat unit along the polymer chain. For simplicity, the representation of these categories will be illustrated by co-polymers containing only two different types of repeat unit (A &B).

### Statistical copolymer

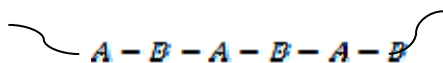
These are copolymer in which the sequential distribution of the repeat unit obeys no statistical laws e.g Markovian Law.

### Random copolymer

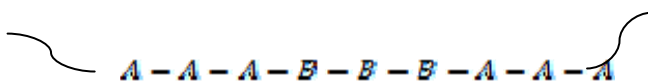
Are special type of statistical copolymer in which the distribution of repeat units is truly random.



### Alternating copolymer

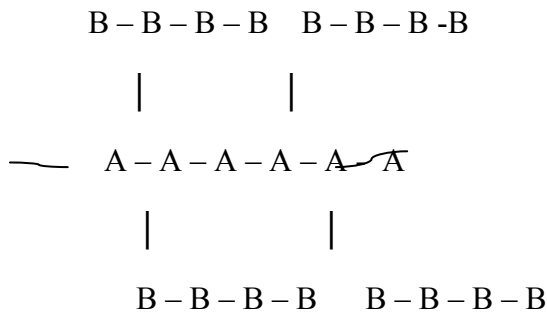


### Block copolymer



### Graft copolymer

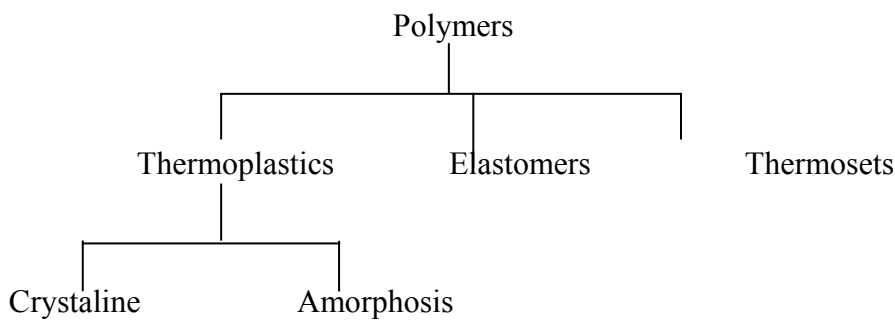
Are branched polymers in which the branches have a different chemical structure to that of the main chain. In their simplest form, they consist of a main Homopolymer chain with branches of a different homopolymer.



Block & graft copolymers usually show properties, characteristics of each of the constituents homopolymer. They also have some unique properties arising from the chemical linkages between the homopolymers sequences preventing them entirely from acting independently on each other.

Four synergism is a phenomenon in which combination of two different things may give more than of which is expected. e.g. 4+5 should be 9 but result to 20.

### Classification of polymers



The most common way of classifying polymers is shown above where are first separated into 3 groups: Thermoplastics, Elastomers & Thermosets.

Set : means cross linking

Crystrallines with well arranged form is called Annealing.

### Thermoplastics

Are often referred to just as plastics. They can be linear or branches polymer which can be melted upon the application of heat. Can be moulded or re- moulded into visually any shape using processing techniques such injection moulding & extrusion. They do not crystallize easily upon cooling to the solid state because it requires

considerable ordering of highly coiled and entangled micro molecules present in the liquid state. Those which do not crystallize invariably do not form perfect crystalline materials but instead are semi- crystalline with both crystalline and amorphous regions. The crystalline phases of such polymers are characterized by their melting temperature.

Many thermoplastic are however amorphous and incapable of crystallization and even upon annealing. Amorphous polymers are characterized by glass transition temperature “T<sub>g</sub>”. T<sub>g</sub> is the temperature at which materials transform from the glass state to the rubbery state (soft). This transform correspond to the concept of chain motion. Below T<sub>g</sub>, the polymer chains are unable to move and are frozen in position. Both T<sub>m</sub> and T<sub>g</sub> increase with increasing chain stiffness at increasing forces of intermolecular attraction.

### Elastomer

Are cross linked rubbery polymers that can be stretched easily to high extensions (e.g 3x → 10x their original dimension) and which rapidly recover their original dimension when applied stress is released. This property of elastomer is a reflection on their molecular structure in which the network is of low cross linked density. The rubbery polymer chain becomes extend upon deformation but are prevented by the permanent flow by the cross linked.

The word rubber often used in place of elastomer preferably should be used for describing rubbery polymers which are not cross linked.

### Thermosets

Are rigid materials and are network polymer in which chain motion is greatly restricted by a high degree of cross linking. As for elastomers, they are intractable once formed and degrade rather than melt upon the application of heat.

### Molar mass and degree of polymerization

Many properties of polymer shows a strong dependence upon the size of the polymers chain so that it is characterize by their dimensions. This normally is done by measuring the molar mass (m) of a polymer which is simply the mass of one mole of the polymer and usually is quoted in g/mol or kg/mol. The term molecule weight is still often used instead of molar mass but its not preferred because it can be somehow misleading. It is really a dimensionless quantity. Relative molecular mass is a very small quantity that can vary from (10<sup>-19</sup> – 10<sup>-18</sup>) for most polymer. Multiplying the numerical value of molar weight by specific unit g/mol will convert it into ≡ value of molar mass. For example, a molecular weight of 100000 is ≡ to a molar mass of 100000 g/mol which in turn is ≡ to molar mass of 100kg mol<sup>-1</sup>.

Molar mass of homopolymer is related to the degree of “polymerization” which is denoted with “X” is the number of repeat unit in the polymer chain and is given by simple relation;

$$M = XM_0$$



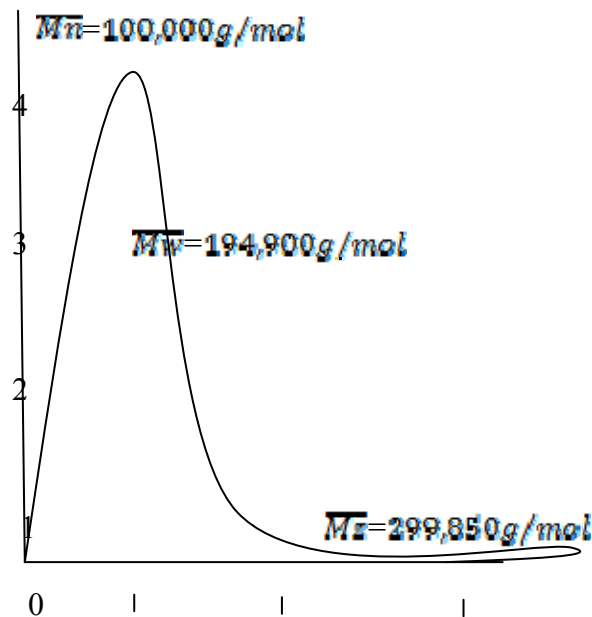
Where  $M_0 = \text{Molar mass of repeat unit}$

For copolymers, the sum of the product  $XM_0$  for each type of repeat unit is required to be found or to determine the molar mass.

### Molecular weight averages and molecular weight distribution

Synthetic polymers and many natural polymer will have a distribution of polymer chain length and hence molecular weight. Although some synthetic polymers have very narrow distribution and are referred to as “mono – disperse”. There are various techniques that can be used in measuring molecular weight averages. Most of the polymer molecule weight measurement techniques make use of some properties which is distributable to a particular molecular average since different properties are attributable to different averages, the molecular weight of a polymer can be expressed as a number of different averages. The mathematical definition of common averages and examples of techniques used in their measurement is as shown below:

	Averages	mathematical definition	techniques
1.	Number	$\overline{M}_n = \frac{\sum(N_i \cdot M_i)}{\sum N_i}$	osmometry
2.	Viscosity	$\overline{M}_v = \left( \frac{\sum(N_i \cdot M_i^{1+x})}{\sum(N_i \cdot M_i)} \right)^{1/x}$	solution viscosity
3.	Weight	$\overline{M}_w = \frac{\sum(N_i M_i^2)}{\sum(N_i M_i)}$	light scattering
4.	2- average	$\overline{M}_z = \frac{\sum(N_i M_i^3)}{\sum(N_i M_i^2)}$	sedimentation



200,000    500,000    800,000

Note: the techniques used for measure molecular weight averages have been in use for decades. This average do not give any form on the spread of the molecular weight distribution but it has been a common practice to quite the ratio of the weight average and number average as the polydispersity (D):

$$D = \frac{\bar{M}_w}{\bar{M}_n}$$

### Molar mass distribution

With very few exceptions, polymers consist of macro molecules have ranges of molar mass. The molar mass changes and the distribution of molar mass is discontinuous. The poly-dispersity is a useful indication of whether the polymer has a broad or narrow distribution. It gives no other information on the shape of the distribution. The distribution of GPC (Gel Permeation Chromatography). It is very possible to obtain data on the whole molecular weight distribution. Other instrument used is; SEC (size Exclusion chromatography).

### Number average molar mass

This is define as the sum of product of molar mass of each fraction multiplied by it mole fraction. It is often more convenient to use weight fractions rather than number of molecules.

### Weight fraction

This is define as mass of molecules of molar mass (m:) divided by the total mass of all molecules present.

Hint: a perfect mono-dispersed polymer will have poly-dispersity ratio of “1”.

For more complex component molar masses, measurement of Z-average and viscosity average are applied. The degree of polymerization averages are of more importance than molar mass averages.

### Techniques for measuring of specific molecular weight averages

1. Sedimentation: the measurement of z-average molecule weight by sedimentation requires the use of an ultra-centrifuge and is only undertaking by specialist laboratories. Z-average is not commonly quoted and the data is only required in specific situations.
2. Number average: it is obtained when coligative properties are measured. In the principle, the suppression of molecular point and elevation of b.point can be used. However, osmotic pressure measurement is the most frequenctly used. The two major types of osmotic pressure measurement is the most frequently used. The two major types of osmotic measurement are:
  1. Vapour phase osmemetry and (2) membrane.
3. weight average molecular weight measurement: this is normally measured by light scattering and it is possible to use either static or dynamic light scattering. The technique has been used for many years and the instrument depends upon conventional light sources such as Hg. In order to have measurable level of scattered light, it is necessary to operate with large volume of solution and at high scattering angles between 45<sup>0</sup> and

135°. The normal practice is to measure the scattered light at a range of scattered angle and for a range of solution concentration.

#### 4. viscosity average measurement:

The viscosity of a polymer in solution is normally directly related to its molecular weight. The measurement of solution viscosity is relatively simple and techniques do not require complex equipments and generally give good results between successive measurements.

The viscosity of average molecular weight is calculated from the intrinsic viscosity “ $\eta$ ” by applying the MARK HOUWINK equation.

$$M_v = K [\eta]^\alpha$$

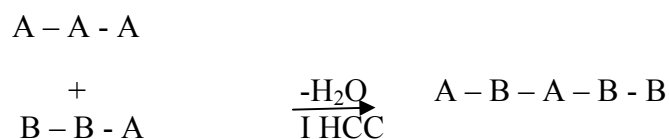
K and  $\alpha$  are parameters determined for polymers where absolute molecular weight data is available. There are large numbers of literature values of “K and  $\alpha$ ”. Depending on the types of polymer and nature of solvent.

#### Classification of polymerization reaction

Basic requirement for polymerization is that each molecule of monomer must be capable of being linked to two or more other molecules of monomer by chemical reaction i.e. monomer must have a functionality of two or more. Giving the simple relative requirements, there are multiple of reaction and associated monomer types that can be used to effect polymerization. The classification used in the formative years of polymer science was due to CAROTHERS. And is based upon comparison of the molecular formula of a polymer with that of a monomer / monomers from which it was formed.

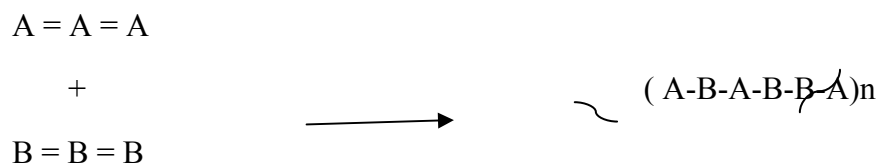
#### Condensation polymerization

They are polymerizations which yield polymers with repeat units having fewer atoms than present from monomers from which they formed. This usually arises from chemical reactions which involve the elimination of a small molecule e.g. H<sub>2</sub>O, HCl etc.



#### Addition polymerization

These are polymerizations which yield polymers with repeat units having identical formula to those of the monomers from which they are formed.



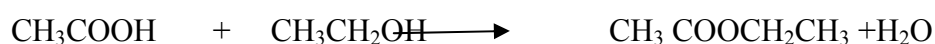
Carothers method of classification was found to be unsatisfactory because it was recognized that certain condensation polymerizations have the characteristic features of typical addition polymerization and that

some addition polymerization have characteristic feature of typical additional polymerization. A better basis for classification was provided in considering the underlined polymerization mechanism of which there are two general types.

1. Polymerization in which the polymer chain grow steowise by reaction that can occur between any two molecular species and this called STEP-GROWTH POLYMERIZATION.
2. Polymerization in which polymer chain grows only by reaction of monomers are a “reactive end-group” on the growing chain and is known as **chain growth polymerization**. This usually requires an initial reaction between the monomer and the initiator to start the growth of the chain. There has being effort to change the names to “step and chain polymerization” and this is what shall be adopt.

### Step polymerization

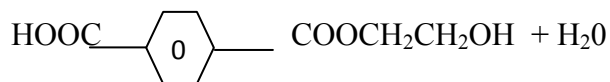
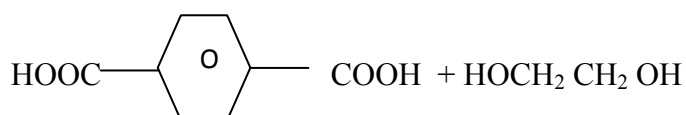
These involves successive reaction between pairs of mutually reactive functional groups which initially are provided by the monomers. The numbers of “functional group present on a molecule of monomers” of functionality is of crucial importanc and can be appreciated by considering the formation of ester linkages from the condensation reaction of carboxylic acids with hydroxyl group.



Acetic acid    ethyl alcohol

Acetic acid and ethyl alcohol are mono-functional compounds with upon reaction together yield ethyl acetate with elimination of water. The ethyl acetate formed is incapable of futher reaction hence, a polymer chain cannot form.

Let consider the reaction between Terephthalic acid and ethylene glycol:



The product of the above reaction is an ester which possesses one carboxylic end group and one hydroxyl end groups i.e. “ it is also difunctional” so far as there are different functional groups are present, there will be linear polymerization.

In step polymerization, the degree of polymerization occurs steadily throughout the reaction but the monomers is rapidly consumed during the early stages e.g.

When  $X_n = 10 \& \ll 1\%$

Contrary in chain polymerization high degree polymerization is of obtained at low monomer conversion. The monomers are being consumed steadily throughout schematic illustration of the fundamental differences in reaction mechanism between step and chain polymerization.

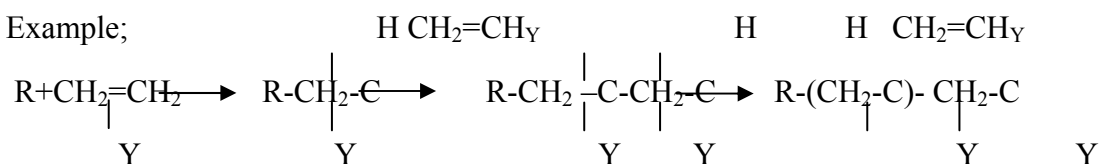
Formation	step polymerization	chain polymerization
1. Dimer	$0 + 0 \longrightarrow 0 - 0$	$I + 0 \longrightarrow I - 0$
2. Trimer	$0 - 0 + 0 \longrightarrow 0 - 0 - 0$	$I - 0 + 0 \longrightarrow I - 0 - 0$
3. Tetramer	$0 - 0 - 0 + 0 \longrightarrow 0 - 0 - 0 - 0$	$I - 0 - 0 + 0 \longrightarrow I - 0 - 0 - 0$
4. Pentamer	$0 - 0 + 0 - 0 \longrightarrow 0 - 0 - 0 - 0$	$I - 0 - 0 - 0 + 0 \longrightarrow I - 0 - 0 - 0 - 0$
5. Heptamer	$0 - 0 - 0 - 0 + 0 \longrightarrow 0 - 0 - 0 - 0 - 0$	$I - 0 - 0 - 0 - 0 + 0 \longrightarrow I - 0 - 0 - 0 - 0 - 0$

### DISTINGUISHABLE FEATURE BETWEEN STEP AND CHAIN POLYMERIZATION

CHAIN POLYMERIZATION	STEP POLYMERIZATION
1. Only growing chain reaction add repeating unit are at a time to the chain.	1. Any two molecular specie present can react.
2. Monomer concentration increases steadily throughout the reaction.	2. Monomers disappears early in the reaction.
3. Instantaneous formation of high molecular weight polymer with little change in molecular weight during the cause of reaction.	3. Steadily increase in molecular weight throughout the reaction i.e. both polymer size & amount of polymer depends on inversion.
4. Long reaction time leads to high yield with little effect on molecular weight.	4. Long reaction time is necessary to achieve high molecular weight polymer > 98% conversion.

Chain polymerization requires a catalyst which produces an initiator specie that can be denoted as "I" with a relative centre. The relative centre may either be a free radical, cation or anion. Polymerization proceeds by the propagation of the relative specie by the successive addition of a large number of monomer molecule in the chain reaction which takes place in a matter of few seconds. This type of reaction is most common with polymerization of vinyl monomers.

Example;



The chain grows for as long as there is availability of monomers.

### CAROTHERS THEORY

Carother developed a simple method of analysis for predicting the molar mass of polymer prepared by step polymerization. He recognized that the number average degree of polymerization with respect to monomer units is given by:

$$X_n = \frac{N_0}{N} \dots \dots \dots 1$$

Where  $N_0$  is number of molecules present initially & end if number of molecule remaining after a time + of molecule.

Assuming that there are equal number of functional group,  $X_n$  can be related to extent of reaction P at time t & P is given by:

$$P = \frac{\text{number of functional group that have reacted}}{\text{number of functional group present initially}}$$

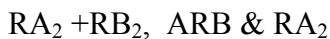
There is probability that any functional group present initially must have reacted since total number Q molecule increases by I for each reaction functional group then P becomes:

$$P = \frac{N_0 - N}{N_0} \text{ OR } \frac{N_0}{N} = \frac{I}{I - P} \dots \dots \dots 2$$

Combining (1) & (2)

$$X_n = \frac{I}{I - P} \dots \dots \dots 3$$

This equation is applicable to equation of the form;



In which there is an exact stiochiometric balance in the numbers of mutually reactive functional groups. The equation highlight the needs to attain very high extent of reaction in order to produce polymers with useful physical properties. Normally degree of polymerization of the order of 100 & above are required & hence, demanding values of P is either > 0.99. this clearly demonstrates the necessity of using monomers of high purity & reactions which are either highly effectively can be forced towards completion.

The number average molar mass ( $M_n$ ) is related to  $X_n$ ;

$$M_n = M_0 X_n$$



Where  $M_0$  is the main molar mass of the monomer units & is given by;

$$M_0 = \frac{\text{molar mass of repeat unit}}{\text{number of monomer units in the repeat unit}}$$

Slight stoichiometric in balance unit will limit the available value of  $M_n$ . Consider a reaction of  $RA_2 + RB_2$ , polymerization in which  $RB_2$  is present in excess, the ratio of the number of the different functional group present initially is known as reactant ratio denoted by “r”.

For a linear step polymerization, “r” is always defined so that it is < 1. thus, for the reaction under consideration I.e.  $RA_2 + RB_2$ ,

$$R = \frac{N_A}{N_B} \quad (4a)$$

Where  $N_A$  &  $N_B$  are respectively the numbers of A&B functional group present initially.

Since there are two functional groups present per molecule,

$$N_0 = \frac{N_A + N_B}{2} \quad (4b)$$

2

putting (4b) in (4a)

$$N_0 = \frac{N_A(1+r)}{2} \quad (5)$$

2

It is a common practise to define the extent of reaction P in terms of functional group present in minority. On this basis, we can have,

$$\begin{aligned} \text{Number of unreacted A group} &= N_A - PN_A = N_A(1-P) \\ &= rN_B(1-P) \end{aligned}$$

$$\begin{aligned} \text{Number of unreacted B group} &= N_B - PN_B = N_B(1-P) \\ &= N_B(1-rP) \end{aligned}$$

$$\text{From } N_0 = \frac{N_A + N_B}{2}$$

2

$$N_0 = \frac{rN_B(I - P) + NB(i - rP)}{2}$$

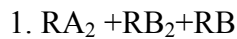
Put equation (5) and (6) into (1)  $x, y, z$

$$X_n = I + r \quad (7)$$

$$X_n = I + r(Z)$$

$$I + r - ZrP$$

(7) is applicable to reactions in which a mono-functional compound is included to control  $X_n$  e.g.;



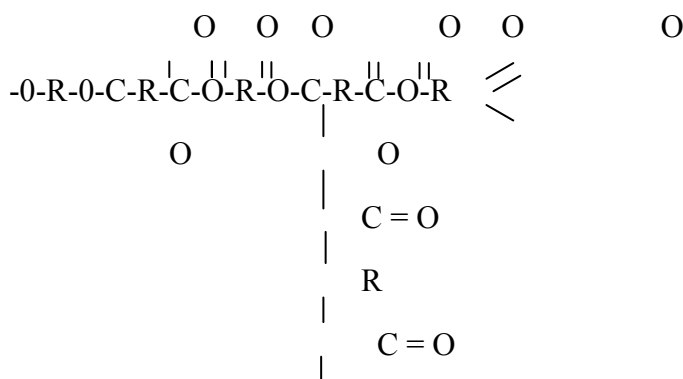
All that is required is to redefine R by putting;

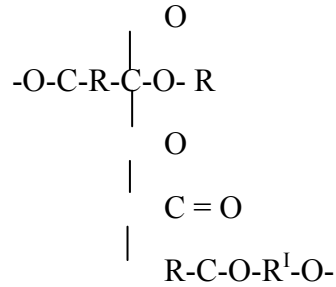
$$R = \frac{N_A}{N_B + 2NRB}$$

$N_B + 2NRB$  into (7)

The intrusion of a monomer with a functionality > 2 has a dramatic effect upon the structure & molar mass of the polymer formed. In the early stages of such reactions, the polymer has a branched structure & consequently increases in molar mass much more rapidly with the extent of reaction than for a linear step polymerization. As the reaction proceeds, further branching reaction leads ultimately to the formation of complex network structures which have properties that are quite different from those of a corresponding linear polymer.

For example, reaction of a dicarboxylic acid with a triol will lead to structure of this type.



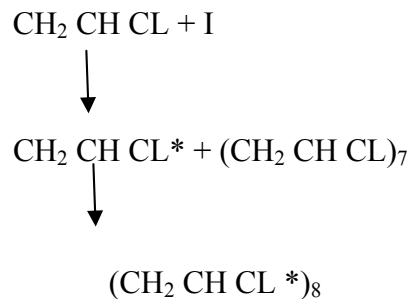


The point at which the first network molecule is formed is known as the GEL point because it is manifested by Gelation is an abrupt of the reacting mixture from the viscous liquid to a solid gel which show number tending to flow.

### Chain polymerization

#### Free radical polymerization:

Free radicals are independently existing specie which possesses an unpaired  $e^-$  & normally are highly ractive with short life time. Free radical polymerization are chain polymerization in which each polymer molecules grow by addition of monomer free to a terminal radical reactive site known as active centre. Consequent of every addition of monomer, the active center is transferred to the newly created chain end.



Free radical polymerization is the most widely practices method of chain polymerization & is used almost exclusively for the preparation of polymers from monomers of general structure:  $\text{CH}_2 = \text{CR}_1 \text{R}_2$ .

In common with other types of chain polymerization, the reaction can be divided into 3 distinct stages;

1. Initiation
2. Propagation
3. Termination

The general chemistry associated with each stage will be describe by considering for simplicity the polymerization of a general vinyl polymer ( $\text{CH}_2 = \text{CHX}$ )

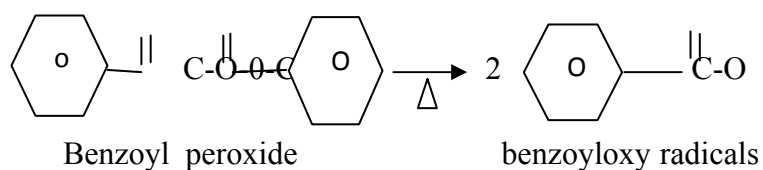
#### Initiation

thisstage involves creation of the free radical active centre & usually takes place in two steps. The first is the formation of free radical from an initiator & the second is the addition of one of the radicals to a molecule of monomer.

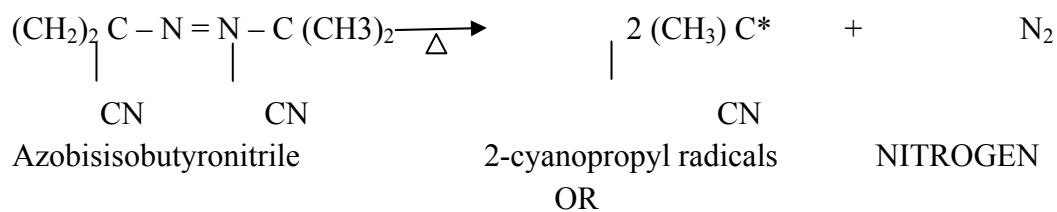
There are two principle ways in which free radicals can be formed;

1. Hemolytic ocission (homolysis) of a single bond
2. Single e<sup>-</sup> transfer to or from an ion or molecule (redox reaction)

1. Homolysis: can be effected by the application of heat & there are many compound in particular those containing peroxides with; o – o linkage and an azo with N = N linkage.

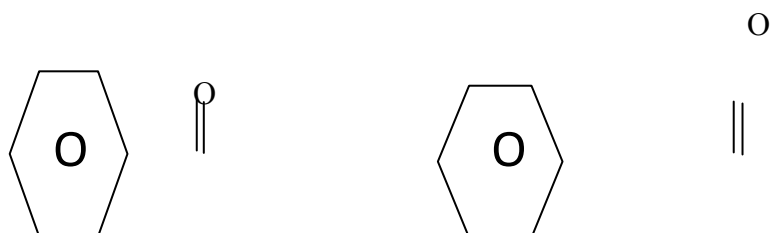


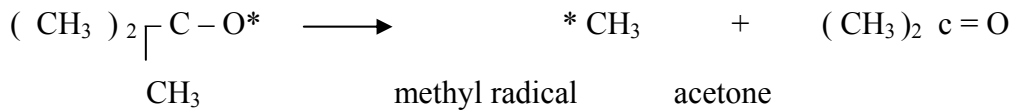
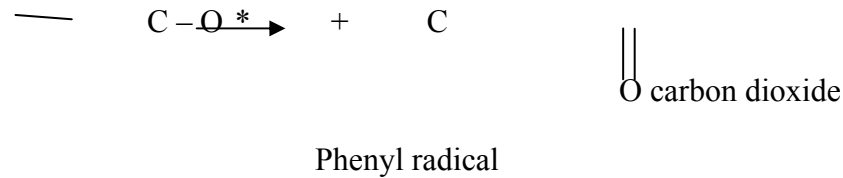
t - Butyl hydroperoxide                      t – butyl radical      hydroxyl radical



2,2 – Azobis (2 – cyanopropane)

Many of the radicals produced undergoes further breakdown before reacting with monomomers. For example there is β – scission such as;





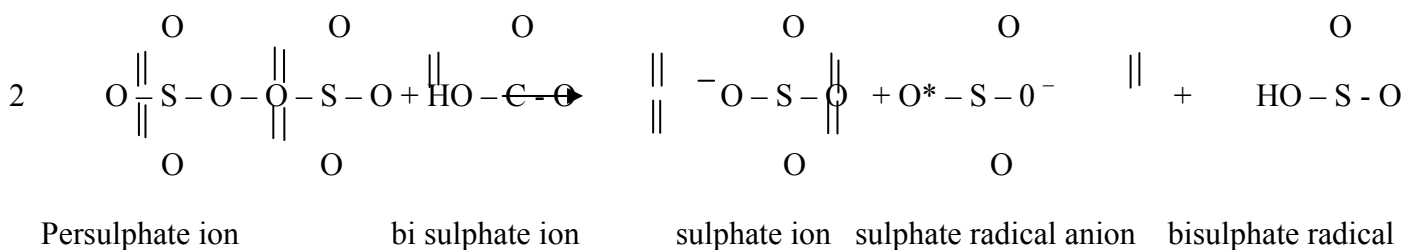
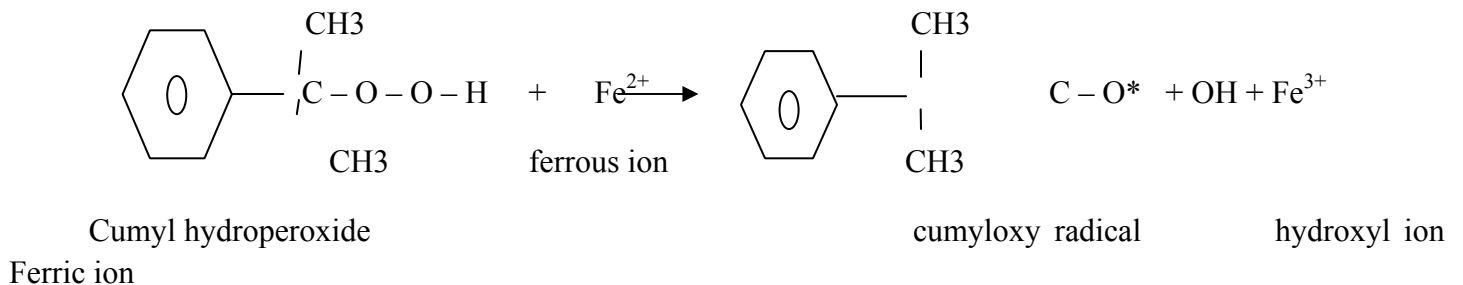
In each of this example, the asterisk indicates the side of the unpaired e<sup>-</sup>. Additionally, homolysis can be brought about by photolysis i.e. action of radiation usually UV. Example of this is the dissociation of azobisisobutyronitrile & the formation of free radicals from benzophenone & benoin.

An advantage of photolysis is that the formation of free radicals begins at the instant of exposure and ceases as soon as the light source is removed.

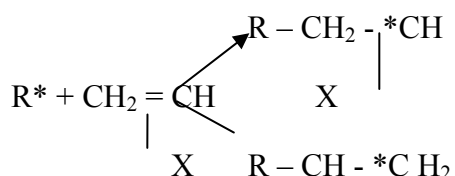
2. Single e<sup>-</sup> transfer:

Redox reaction are often used when it is necessary to perform polymerization at low temperature. Two examples are as given below:

1.



An active center is created when a free radical R\* generated from an initiator, attack, the  $\pi$  - bond of a molecule of monomer. There are two possibilities of this addition.

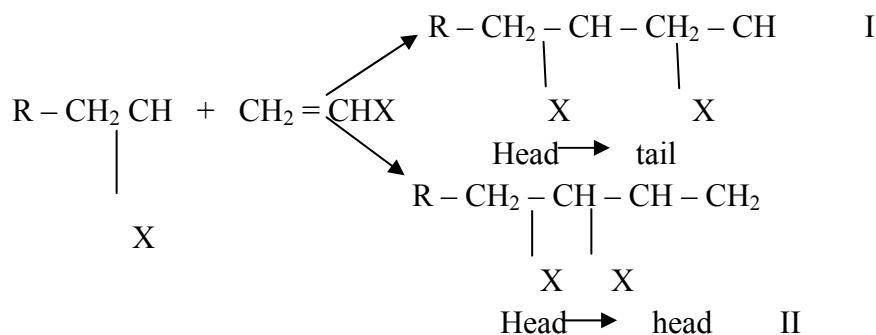


Mode I predominate because attack at the methylene carbon is less sterically hindered & yield a product free radical that is more stable because of the effect of adjacent X – group. Not all of the free radical formed from the initiator are destined to react with monomer. Some are lost in side reactions.

### Propagation

Involves growth of the polymer chain by rapid sequential addition of monomer to the active centre. As with the second step of initiation, there are two possible mode of propagation;

1. Head to tail addition
2. Head to head addition



Mode I predominate because attack at the methylene carbon is less sterically hindered & yields a product free radical that is more stable because of the effect of adjacent X – group. Thus, the polymer chain are principally of [ R – CH<sub>2</sub> CH<sub>x</sub> CH<sub>2</sub> CH<sub>x</sub> ].....

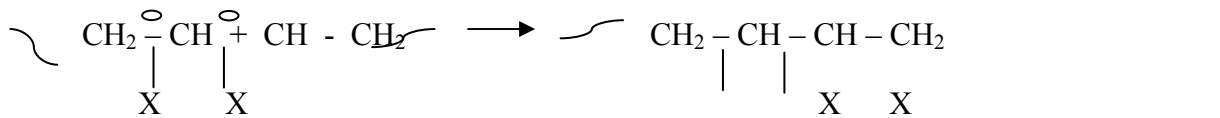
## TERMINATION

In this stage growth of polymer chain is terminated. The two most common mechanism of termination polymer chain. There can be two major ways

1. Combination
2. Disproportionation

### Combination

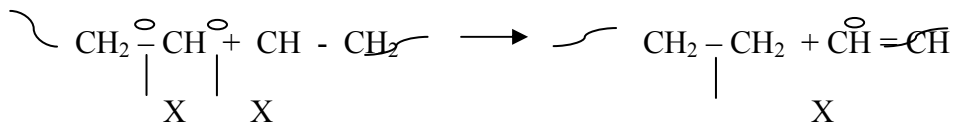
Involves coupling together of two growing chain to form a single polymer molecule.



NOTE: Result above is head to head linkage

### Disproportionation

Involves a hydrogen atom being abstracted from one growing chain by another & is as follows



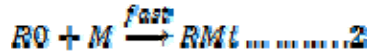
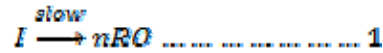
The two polymer molecules are formed one with a saturated end group & the other with an unsaturated end group. In general both types of termination reaction takes place but to different extent depending upon the monomer & the polymerization condition.

### Rate of polymerization

The general reaction scheme can be analysed to obtain equation that describes the kinetics of free radical polymerization.

### Kinetics of initiation

Initiation may be represented in two steps;

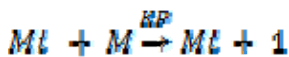


n is the number of free radicals “R” formed upon breakdown of one molecule of initiator I.

“n” can be 1 or 2 & M represent either a molecule of monomer or a monomer unit in the polymer chain. Since the formation of R<sup>•</sup> from the initiator I proceeds much more slowly than the reaction of R<sup>•</sup> with monomer, the first step is rate determine & controls the rate R<sub>i</sub> of formation of active centre is defined as;

$$R_i = \frac{d[R^\bullet]}{dt} \dots\dots\dots 3$$

If it is assumed that rate constant K<sub>p</sub> for propagation is independent of the length of the growing, chain, then propagation can be represented by a single general reaction e.g.



In which the initiator fragment capital R has been omitted for clarity. The amount of monomer consumed in the initiator stage is negligible compared to the one consumed by the growing chain & so the rate of consumption of monomer is giving by;

$$\frac{-d(m)}{dt} = K_p[M_1][M] + K_p[M_2^\bullet][M] + K_p[M_i][M]$$

$$= K_p[M][M_1] + [2] + \dots\dots\dots + [M^\bullet] + \dots\dots\dots$$

If concentration of [M<sup>•</sup>] is the total concentration of four radical specie i.e.

$$[M^\bullet] = \sum_{i=1}^{\infty} [M_i]$$

then rate of formation



$$-d[M]/dt = K_p[M][M^0]$$

Kinetics of termination can be represented by considering;



$K_{tc}$  &  $K_{td}$  are rate constant of combination and disproportionation respectively. The overall rate at which radicals are consumed is given by;

$$-d[M^0]/dt = 2K_{tc}[M^0][M^0] + 2K_{td}[M^0][M^0]$$

The factor of 2 that was used is due to the fact that 2 growing chain of any length are consumed by each termination reaction. The equation can be simplification into;

$$-d[M^0]/dt = 2K_t[M^0]^2$$

where  $K_t = K_{tc} + K_{td}$   
 $K_t = \text{overall constant}$

Degree of polymerization

The number average degree of polymerization is denoted by  $\bar{X}_n$  of the polymer produce.

It is given by;

$$\bar{X}_n = \frac{\text{moles of monomer consumed in unit time}}{\text{moles of polymer formed in unit time}}$$

From the basis of simple kinetic scheme, it can be shown that;

$$\bar{X}_n = \frac{K_p[M][M^0]}{K_{tc}[M^0]^2 + 2K_{td}[M^0]^2}$$

$$K_{tc}[M^0]^2 + 2K_{td}[M^0]^2$$

The denominator takes into account the fact that combination produces only one polymer molecule whereas disproportionation produces two. Using steady state conditions, growing chain monomer or active center monomer can be substituted leading to;

$$[M] = \frac{k_p [M]_0}{\left\{ (k_t + k_{td}) [M]_0 \right\}^{1/2} \left( \frac{k_t}{2} \right)^{1/2}}$$

$$k_t = \frac{k_p^2}{k_t + k_{td}}$$

$k_t$  is fraction of termination reaction that proceeds by disproportionation. i.e.  $k_t = \frac{k_{td}}{k_t + k_{td}}$

When termination occurs by combination only,  $k_t = 1$  and when it occurs only by disproportionation,  $k_t = 0$ .

Auto- acceleration

Read – up

There is a simple experimental evidence to support that;

$$k_p \propto [M]_0 \quad \& \quad [M]_0^{1/2}$$

Chain transfer

Read – up

During some polymerization, growth of a chain may be terminated by chain transfer to monomer which kills the active site and begins a new one.

Inhibition and retardation

Read up

Certain substances react with the free radical active centers to produce specie which are incapable of initiating polymerization. If the reaction is highly efficient, polymerization is prevented and the substances is said to be an inhibitor. When the reaction is less efficient or yields species that slowly re-initiate polymerization, the rate of polymerization is reduced and substances is known as a retarder.

Retardation of rate constant

In other to use equation for the rate and degree of polymerization ( $\bar{P}_n$ ) predictively it is necessary to know the value of the individual rate constant for the particular polymerization of interest

Read up

Effect of temperature on rate constant

The temperature dependence on the rate of polymerization and the degree of polymerization arise from the dependent upon temperature.  $T_1$  of the individual rate constant. This is define in terms of the appropriate Arrhenius equation.

$$k_p = A_p e^{-E_p/RT}$$

$$k_t = A_t e^{-E_t/RT}$$

$$k_{tr} = A_{tr} e^{-E_{tr}/RT}$$

$$k_{tc} = A_{tc} e^{-E_{tc}/RT}$$

Methods for performing free radical polymerization

There are four commonly use method four performing free radical polymerization

1. Bulk polymerization
2. Solution polymerization
3. Suspension polymerization
4. Emulsion polymerization

Read – up

Ionic polymerization

Chain polymerization of definite monomers can also be effected via active centers which presses an ionic charge.

Read

Cationic polymerization

It is a chain reaction and can also be considered in terms of initiation, propagation and termination stages.

Read – up

Anionic polymerization

Read up

Stereochemistry of polymerization

Read up

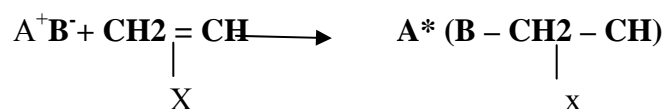
Ziegler, matha co-ordination

Read up

Methods of performing free radical polymerization and brief knowledge on cationic, anionic polymerization.

Anionic polymerization

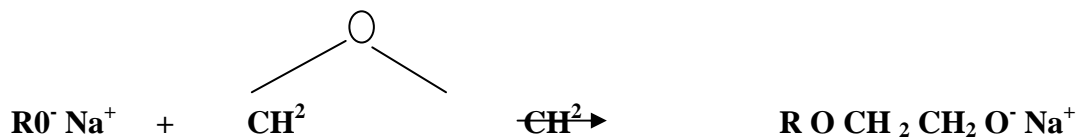
- Propagation is anionic
- Less used in industry than free radical polymerization because;
  1. Monomers do not undergo anionic polymerization
  2. Rigorously pure monomers have to be used
  3. Strict temperature control is necessary.
- If used, it does not give good control of the molecular weight (MW) of the polymer with little branching
- Initial step is generation of anion with a strong base  $\square^-$



e.g



For cyclic monomers having heteroatom, weaker alkali metal hydroxides (alkoxides) with suitable



If anionic polymerization is performed in a non – reacting solvent and in absence of impurities, there is no termination step and is therefore called “living polymerization”

Cationic polymerization

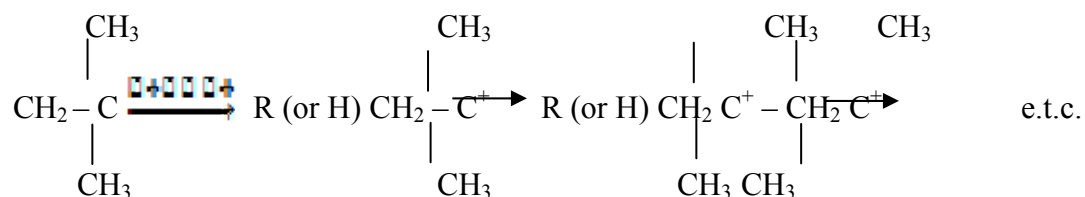
- Growing chain is a cation
- Initiators are gotten from lewis acids together with traces of a co-catalyst.



- If too much H<sub>2</sub>O is added, it will act as a catalyst poison.

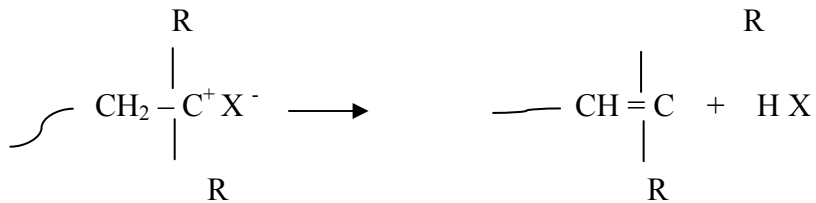


- Acid catalyst initiate polymerization by electrophilic attack on the monomer, e.g. with isobutylene

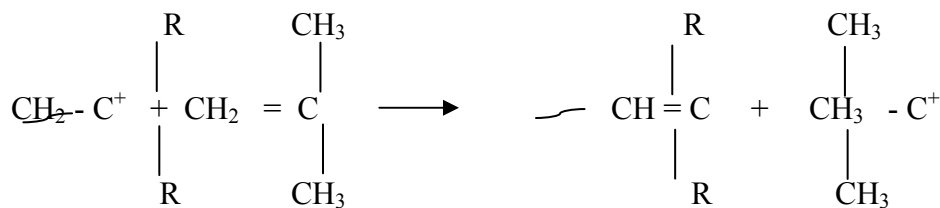


- It produces only low MW with oligomers e.g. propylene give oils which are mixtures of dimers, trimers and tetramers.

- Most saturated cyclic compounds containing hetero atoms, e.g O, S, NR will polymerize cationically if the cyclic strain is sufficient e.g. THF, ethyleneoxid and cyclic imines.
  - Termination cannot be by coupling like in free – radical polymerization but by ;
1. Internal attack by associated anion



2. By chain transfer with an incoming monomer thus Starting a new growth centre.



- Though not as easy to perform as with anionic polymerization living polymerization via cationic growth is possible.

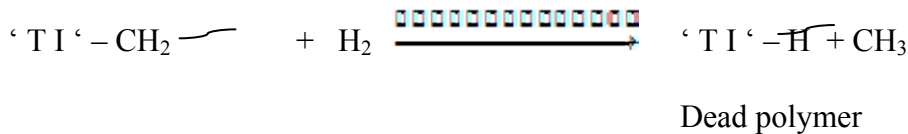
### Ziegler – matta polymerization or coordination polymerization

Due to amount of polymer produced, it out weights all other methods because of commercial production of ethylene and propylene. Polymerization involves transition metal TM centre (groups 4, 5, and 6) together with a co- catalyst (main group metal alkyl). C0-catalyst serves as an activator or alkylating agent and the TM as growth centre.

- Nature of polymer produced can be altered because;
1. TM are variable oxidation state and
  2. Differing co-ordinating liquids
- Heterogenous systems are used industrially. E.g. with  $\text{TiCl}_3 + \text{AlEt}_3$

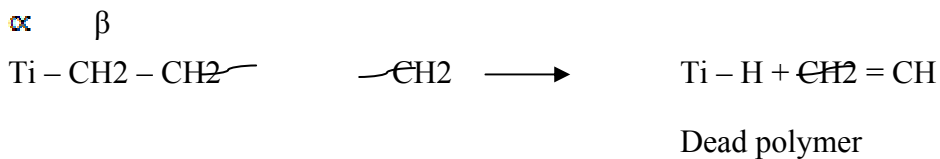
Termination occurs in two ways

- a. Adding a chain transfer agent e.g. hydrogen



Ti - H act as a new centre for polymerization.

- b. Decomposition of growing polymer chain by  $\beta$  - hydrogenation elimination.



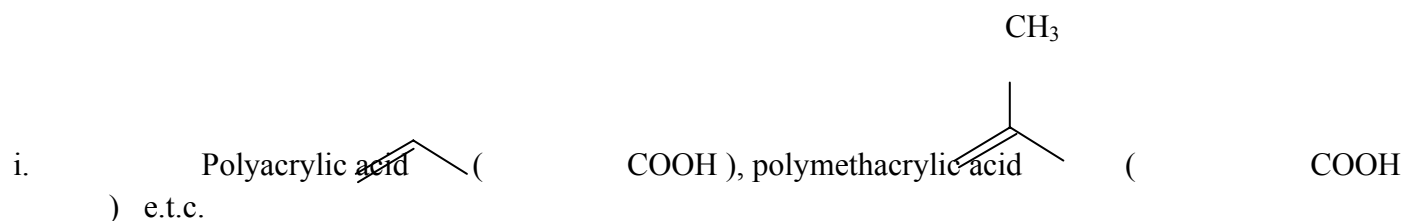
- Mode of chain termination occurs at higher temperature
- Because catalyst systems is sensitive to impurities, excess aluminum alkyls are used as scavengers, e.g. using Ti/A/ ratio of 1/10.

### Polymerization techniques

1. Bulk polymerization: no solvent or diluents is used, just the monomer (liquid or gas) and the catalyst. Polymer (and catalyst) can be soluble in the liquid monomer.
  - Problem encountered is increase in viscosity during polymerizations leading in poor mixing and heat transfer.
  - Auto - acceleration (trommsdorf effect) occurs because initiation and propagation proceed as normal but termination step is inhibited because of high viscosity.
  - Bulk polymerization involves;
    - i. Bulk gas - phase polymerization for polymerization of ethylene and propylene.
    - ii. Fluidized - bed technique.
2. Solution polymerization: uses solvent which is miscible with monomer and resulting polymer is also soluble.
  - Increase in viscosity also occurs
  - Auto - acceleration also take place but not as prevalent in bulk method.

Impurities in solvent can affect chain transfer, poisoning of catalyst, e.t.c.

- Solvent can be H<sub>2</sub>O or organic based
- Monomers and their polymers soluble in H<sub>2</sub>O includes;

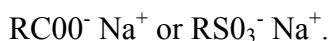


Monomer and polymers soluble in organic solvents are;

- i. Polystyrene
- ii. Poly(methylmethacrylate)

Advantage of H<sub>2</sub>O as solvent is that;

- i. It is cheap
- ii. No fire risk
3. Suspension polymerization: also called bead or pearl polymerization because of the smooth spherical shape of the polymer particles produced.
  - Catalyst is soluble in monomer which is suspended as small droplets in the solvent (H<sub>2</sub>O) phase by vigorous agitation added by adding suspending agents which prevent monomer from coagulating together.
  - Heat of the reaction is reduced by refluxing
  - Viscosity is low
4. Emulsion polymerization: used for latex polymers having colloidal polymer particle.
  - System contains two liquid phases consisting of liquid monomer or solution of monomer in diluents and H<sub>2</sub>O.
  - H<sub>2</sub>O is the continuous phase i.e. it is in excess and polymer is insoluble in H<sub>2</sub>O.
  - Mixture is vigorously agitated and emulsifier is used often an anion (e.g. Na salts of long chain carboxylic or sulphonic acids,



Advantages and disadvantages

Method	Techniques	Advantages	Disadvantages



1.	Bulk	Batch	1. Low impurity level	1. Thermal control difficult
		Continous	2. Casting possible	2. Autoacceleration possible
2.	Solution		1. Improved thermal control	1. Isolation difficult
		2. no solvent purification, recovery e.t.c.	2. Requires agitation and monomer recycling	
3.	Suspension	1. Improved thermal control.	1. Difficult to remove solvent	
		2. Used with high m.p polymers	2. Solvent recovery is costly	
4.	Emulsion	1. Low viscosity	1. Sensitive to agitation rate	
		2. Easy thermal control	2. Particle size difficult	
		1. Low viscosity	1. High cost	
		2. Good thermal control	2. Emulsifiers, surfactor and coagulents must be removed.	

### Effect of temperature on polymers

Viscosity of any substance at its melting temperature,  $T_m$  is  $\sim 10^3$  poise. However, when non-polymeric materials are heated to  $20 - 50^\circ\text{C}$  above  $T_m$ , viscosity increases to 1-100 poise while polymer with high MWs fall to  $10^5$ - $10^0$  poise

Autoacceleration (Gel effect, Trommsdorff Norrish effect).

Is a dangerous reaction behavior that can occur in free radical polymerization systems. It is due to the localized increases in viscosity of the polymerizing systems that slow termination reaction.

Autoacceleration of the overall rate of a free radical polymerization system has been noted in many bulk polymerization systems e.g. polymerization of methyl methacrylate deviates from classical mechanism behavior around 20% conversion causing rapid increase in molecular weight of polymer. This increase is accompanied by large rise in temperature. If heat dissipation is not adequate.

- Autoacceleration of polymerization systems can cause metallurgic failure of the reaction vessel.

Trommsdof and Norrish discovered that autoacceleration is caused by;

1. Increase in termination rate caused by increasing viscosity of polymerization.