# CHAPTER - 1

# INTRODUCTION

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## Introduction

The field of Polymer science has grown very large indeed and the polymers in modern world have been placed in a high esteem because of their increasing usefulness in every sphere of life. This is not only true for developed countries, but even in countries like India and other third world countries polymers have emerged as an active discipline of modern science. The industrial landscape too is vibrant with major investments in the offing in the area of commodity-engineering and speciality polymers.

## 1.1 What are Polymers ?

According to IUPAC definition 'a polymer is a substance composed of molecules characterised by mutiple repetition of one or more species of atoms or groups of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or few of the constitutional units'.

More simply a polymer can be defined as a large molecule built up by the repetition of small simple chemical units.

### 1.1.1 What are Copolymers ?

Polymeric susbstances containing two or more chemically different types of repeating units are termed as copolymers.

### 1.1.2 Classification of polymers

For the convenience various ways are adopted for the classification of polymers.

1.1.2a According to 'origin' polymers are classified as

(i) natural polymers and (ii) synthetic polymers.

(i) Natural polymers : These are isolated from natural materials, e.g. cotton, silk, wool, rubber, etc.

(ii) Synthetic polymers : These are synthesised from low molecular weight compounds e.g. polyethylene, poly(vinylchloride), nylon, terylene etc.

1.1.2b Considering the 'nature of the polymer back bone', polymers are divided in to

(i) organic polymers and (ii) inorganic polymers

(i) Organic polymers : These are the polymers whose back bone chain is essentially made of carbon atoms. The atoms attached to the side valencies of the back bone carbons are, usually hydrogen, oxygen, nitrogen etc. This is the largest class of polymers, e.g. nylon, rubber etc.

(ii) Inorganic polymers : These polymers generally do not contain any carbon atom in their back bone chain e.g. glass, silicon rubber etc.

1.1.2c Polymeric materials are also classified into two groups according to their thermal response.

(i) thermoplastic polymers and (ii) thermosetting polymers.

(i) Thermoplastic polymers : The polymers which soften on heating and stiffen on cooling are termed as thermoplastics e.g. polyethylene, poly(vinyl chloride), nylon etc.

(ii) Thermosetting polymers : The polymers which undergo some chemical changes on heating and convert themselves into infusible mass are called as thermosets ; e.g. phenol-formaldehyde resins.

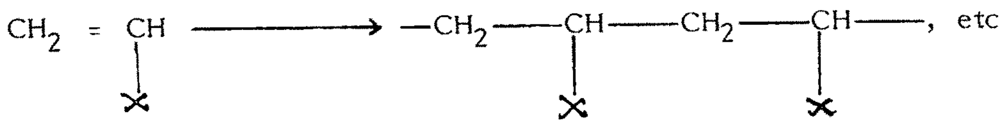
1.1.2.d All the synthetic polymers irrespective of their classes as organic, inorganic, thermoplastic and thermosetting are further classified by Carothers [1] as,

(i) condensation polymers and (ii) addition polymers.

(i) Condensation polymers : The polymers in which the molecular formula of the structural unit (or units) lacks certain atoms present in the monomer from which it is formed, or to which it may be degraded by chemical means are called condensation polymers. Condensation polymers are formed from the monomers bearing two or more reactive groups of such a character that they may condense intermolecularly with the elimination of a by-product, often water. Polyesters and polyamides are the examples of such class. A polyester is formed by typical condensation reactions between bifunctional monomers, with the elimination of water.

$$\begin{array}{l} x\ HO - R - OH \ + \ x\ HOOC - R' - COOH \longrightarrow \\ HO\ [- R - OCO - R' - COO - ]\, x\ \ H \ + \ (2x-1)\ H_2O \end{array}$$

(ii) Addition polymers :The polymers in which the molecular formula of the structural unit (or units) is identical with that of the monomer from which the polymer is derived are termed as addition polymers. Addition polymers consist of those derived from unsaturated monomers, such as vinyl compounds.



$$\underset{\displaystyle X}{CH_2 = \underset{|}{CH}} \longrightarrow -CH_2 - \underset{\displaystyle X}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle X}{\underset{|}{CH}} - ,\ \text{etc}$$

X may be halogen, phenyl or acetoxy, etc.

### 1.1.3 Copolymerisation

Simultaneous polymerisation of two or more monomers in the given reaction mixture, to produce copolymers is termed as copolymerisation.

Copolymerisation is the most general and powerful method of achieving desirable changes in polymer properties and is widely used in the production of various commercial polymeric materials and also in fundamental investigations of structure - property relationships. Copolymerisation influences the symmetry of the polymer chain and modulates both intramolecular and intermolecular forces and hence alters the properties such as melting point, glass transition temperature, crystallinity, stability, elasticity, permeability and chemical reactivity.

There is practically unlimited scope for variation in polymer structure and polymer properties through copolymerisation. In fact, the number of the technically important copolymers far surpasses that of the important homopolymers.

### 1.1.4 Classification of copolymers:

Exclusive classification of copolymers based on the morphology and arrangement of the monomeric units in the copolymer is as follows:

(a) random copolymers : in which the distribution of two repeating units in the polymer is in a statistically random fashion along a linear chain. For two monomers A and B it can be shown as

-A-B-B-B-A-B-A-A-B-A-B-B-A-B-A-A-B-A-B-

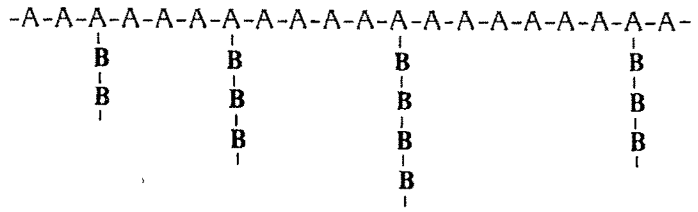
(b) alternating copolymers : in which the two repeating units are distributed alternately throughout the polymer chain,

-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-

(c) block copolymers : in which a sequence of block of one repeating unit is followed by a sequence or block of another unit which in turn is further followed by a block of the first repeating unit and so on,

-B-B-A-A-A-A-A-A-A-B-B-B-B-B-A-A-A-A-B-B-B-B-B-

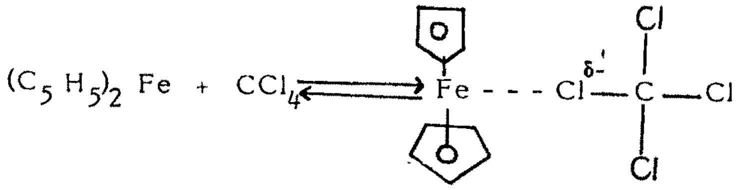
(d) graft copolymers : in which a long or short chains of one type of monomer units are attached to a polymeric back-bone consisting of another monomeric unit.



### 1.1.4a. Random Copolymers :

Random copolymers are formed when the product of the reactivity ratios of the two monomers ($r_1r_2$) is one, or less than one i.e. $r_1r_2 \leqq 1$. In the former case two types of monomer units show the same preference for adding one of the monomers over the other and they will be arranged at random along the chains in relative amounts determined by the composition of the feed and the relative reactivities of the two monomers. When $r_1r_2 < 1$, one of the monomers show higher preference to add with other kind (i.e. $M_1$ prefers to add $\overset{\text{to}}{\wedge}$ $M_2$ but not to $M_1$). Methyl methacrylate and acrylonitrile has this tendency of addition.

Synthesis of random copolymer is comparitively easy. Most of the vinyl monomer pairs have the tendency to copolymerise in statistically random way. Random copolymers can be synthesised in various ways viz. free-radically e.g. using benzoyl peroxide, [2], or with ionic mechanism e.g. using phenyl magnesium bromide [3], or with charge transfer mechanism, e.g. using ferrocene and carbon tetrachloride [4]. The charge transfer mechanisam for copolymerisation of methyl methacrylate (MMA) and acrylonitrite (AN) is shown below



$\longrightarrow (C_5H_5)_2Fe^+ + Cl^- + \cdot CCl_3$

$\cdot CCl_3 + x\ MMA + yAN \longrightarrow MMAx\ ANy\cdot$

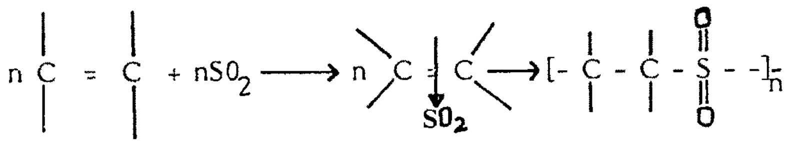
$\cdot CCl_3 + m\ MMA + n\ AN \longrightarrow MMA_m\ AN_n\cdot$

$MMAx\ ANy\cdot + MMAm\ ANn\cdot \longrightarrow MMAx{+}m\ ANy{+}n$

The free radical formation and polymerisation is discussed in details in section 1.2.1.a. and 1.2.3.

### 1.1.4b. Alternating Coplymers :

Alternating copolymers are formed in the case of monomers where the product of the reactivity ratio's ($r_1r_2$) is very close to zero or almost zero i.e. $r_1r_2 = 0$. Perfect alternation takes place when $r_1=r_2=0$. Copolymerisation of maleic anhydride with either stilbene or allyl acetate may be cited as example closely resembling the case of alternation in copolymerisation. Almost a perfect brand of alternation is shown by copolymers of sulfur dioxide and certain olefins, cyclo olefins or vinyl compounds. The alternation is thought to arise as a consequence of self polymerisation of 1:1 complex formed insitu between the olefin or related monomer (donor) and sulfur dioxide (acceptor)

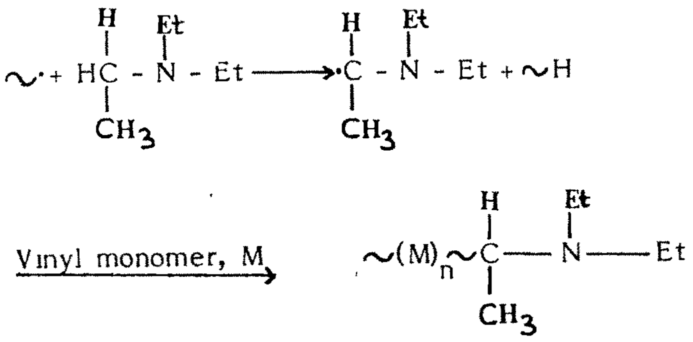


Acrylonitrile undergoes alternating copolymerisation with alkyl vinyl ketone ($r_1r_2=0.0004$). Monomers which do not homopolymerise will readily copolymerise with strict regularity of alternation.

### 1.1.4c. Block Copolymers

Although the copolymer structures resulting from the graft and block copolymerisation processes are quite different the former being a chain branching process and the latter a chain extension process, both may be considered as a chain modification processes differing only in direction. Block copolymers are usually prepared by polymerising a second monomer in the presence of preformed polymer of a different kind of monomer, and the process generally depends on the presence of labile sites particularly sensitive to radical attacks at chain ends of the reactant macromolecule.

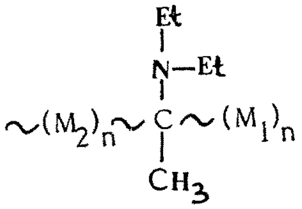
Block copolymers can be prepared by using effective transfer agent such as tertiary amine. When a vinyl polymerisation is carried out in the presence of sufficiently high concentration of tertiary base, each polymer chain may contain a terminal base residue according to the following scheme,



$$\sim\cdot + \mathrm{HC(H)(CH_3)-N(Et)-Et} \longrightarrow \cdot\mathrm{C(H)(CH_3)-N(Et)-Et} + \sim\mathrm{H}$$

$$\xrightarrow{\text{Vinyl monomer, M}} \sim(\mathrm{M})_n\sim\mathrm{C(H)(CH_3)-N(Et)-Et}$$

The nitrogen containing polymer is a macromolecular transfer agent, and functions as such in a second polymerisation. If two different monomers $M_1$ and $M_2$ are used in the two steps, a block copolymer should be formed, each molecule containing a chain of $M_1$ units joined to a chain of $M_2$ units by tertiary base fragments,



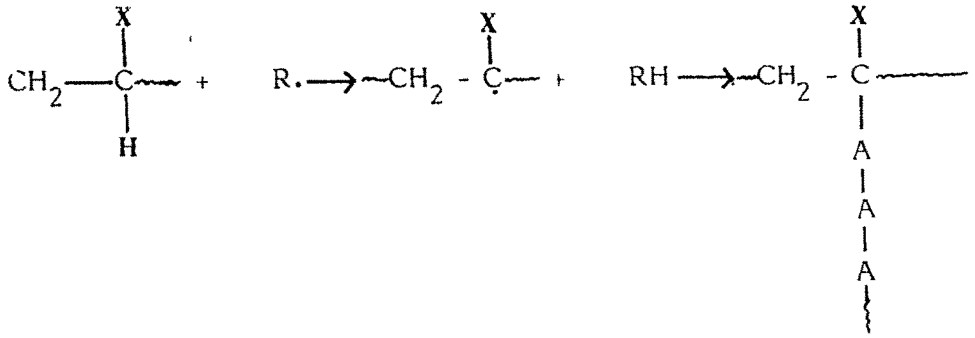
$$\sim(\mathrm{M_2})_n\sim\mathrm{C(CH_3)(N(Et)-Et)}\sim(\mathrm{M_1})_n$$

In choosing monomer combination to produce only block copolymers the following precautions have to be taken : (1) $M_1$ should readily undergo chain transfer with the amine because the concentration of amine groups in the second polymerisation is low : (2) chain transfer to the backbone in the second step, which would result in graft formation should not be an important reaction (3) the reaction products should be readily separable, (4) the back bone polymer and $M_2$ must be mutually soluble, or soluble in an inert solvent.

Studies of block copolymers are very much limited in comparison with those of graft copolymers because formation of block copolymers depends solely on the presence of reactive groups or labile atoms at chain ends of the linear polymers.

### 1.1.4d. Graft Copolymers :

They differ from block copolymers only in labile site, sensitive to radical attack. In this case, the labile sites are along the chain axis, which are attacked by radicals and branching of another monomer starts at these points. Graft copolymerisation usually involves polymerisation of a monomer onto other polymer back bone. The various reactions associated with polymerisation process can be utilised for the synthesis of graft copolymers. Most graft copolymers are formed by free radical polymerisation and often the major activation involves chain transfer. The reaction given below involves generation of a radical site on the preformed polymer by a chain transfer mechanism and then growth of a new polymer structure from that new radical site.



$$CH_2-\overset{X}{\underset{H}{C}}\sim + R\cdot \longrightarrow \sim CH_2-\overset{X}{\dot{C}}- + RH \longrightarrow \sim CH_2-\overset{X}{\underset{\substack{A\\A\\A}}{C}}-$$

The homopolymers and copolymers under present study are addition type and hence synthetic details of only addition polymerisation are discussed below.

## 1.2 Initiators used for addition polymerisations

Addition polymerisation can be carried out by using

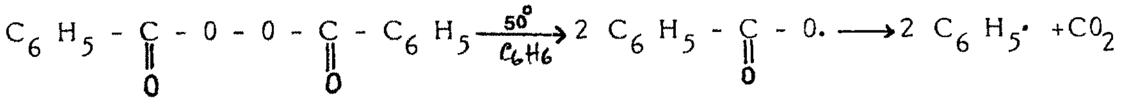
a) chemical initiators and b) photo-initiators :

### 1.2.1 Chemical initiators :

Chemical initiators are mainly grouped as

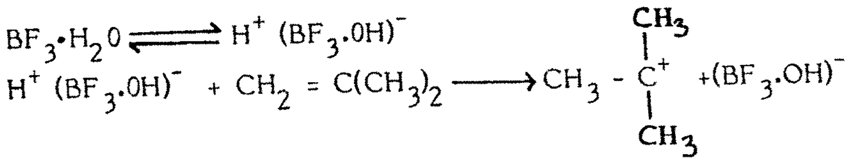
a) free radical, b) cationic and c) anionic

a) Free radical initiators : Free radical initiators are peroxides (such as benzoyl peroxide, di-t-butyl peroxide (DTBP), and hydroperoxide (such as t-butyl hydroperoxide, TBHP) and azo compounds (such as azobisisobutyronitrile AIBN). The peroxides decompose to give free radicals under optimium reaction conditions : e.g. benzoylperoxide decomposes as shown below.



$$C_6H_5 - \underset{\underset{0}{\|}}{C} - 0 - 0 - \underset{\underset{0}{\|}}{C} - C_6H_5 \xrightarrow[C_6H_6]{50^\circ} 2\,C_6H_5 - \underset{\underset{0}{\|}}{C} - 0\cdot \longrightarrow 2\,C_6H_5\cdot + C0_2$$

b) Cationic initiators : Protonic acids such as $H_2S0_4$, $HCl0_4$ or Lewis acids like $AlCl_3$, $BF_3$, $TiCl_4$, $SiCl_4$, and activated clays (attafulgite, montmorillonite, silicic acid) are cationic initiators. Except protonic acids, rest all are electron acceptors. These initiators first form a complex with a co-catalyst like $H_20$, alcohol or acetic acid and initiation occurs through transfer of a cation (carbonium ion). For $BF_3$ the initiation is shown below with isobutylene.



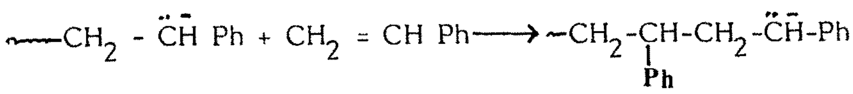
$$BF_3\cdot H_20 \rightleftharpoons H^+\,(BF_3.0H)^-$$

$$H^+\,(BF_3.0H)^- + CH_2 = C(CH_3)_2 \longrightarrow CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} + (BF_3.OH)^-$$

c) Anionic initiators : Basic compounds such as amides, alkoxides, alkyls and aryls of alkali metals and different Grignard reagents are used as catalyst for anionic polymerisation of monomers having electron withdrawing substituents. Here the catalyst breaks up into cation and anion under reaction conditions and the anion adds to the double bond of the monomer to generate a carbanion as the active centre of chain growth,

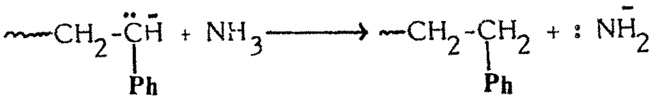
$$KNH_2 \rightleftharpoons K^+ + :NH_2$$

$$:\bar{N}H_2 + CH_2 = CH\text{-}Ph \longrightarrow H_2N\text{-}CH_2\text{-}\ddot{\bar{C}}H\ Ph$$



$$\sim CH_2 - \ddot{\bar{C}}H\ Ph + CH_2 = CH\ Ph \longrightarrow \sim CH_2\text{-}\underset{Ph}{CH}\text{-}CH_2\text{-}\ddot{\bar{C}}H\text{-}Ph$$

further termination can be achieved as follows

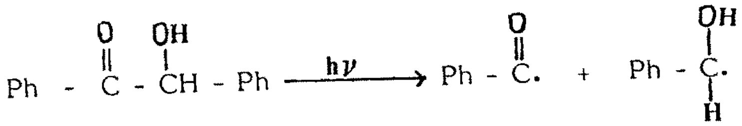


$$\sim CH_2\text{-}\underset{Ph}{\ddot{\bar{C}}H} + NH_3 \longrightarrow \sim CH_2\text{-}\underset{Ph}{CH_2} + :\bar{N}H_2$$

## 1.2.2 Photo initiators :

Some polymerisation reactions can be initiated by the influence of a) uv-radiation, b) high energy radiation.

By absorbing uv-radiation photosensitised compounds decompose into free radicals which initiate polymerisation. For example benzoin and benzophenone derivatives such as 2,2'- dimethoxy-2- phenyl acetophenone (DMPA), benzophenone (BP), 4-benzoyl benzoic acid (BBA), 3,3,4,4-benzophenone tetracarboxylic acid dianhydride (BTCD) etc. are good photo-initiators.



$$Ph - \overset{O}{\overset{\|}{C}} - \overset{OH}{\overset{|}{C}H} - Ph \xrightarrow{h\nu} Ph - \overset{O}{\overset{\|}{C}}\cdot + Ph - \underset{H}{\overset{OH}{C}}\cdot$$

Benzoin

High energy radiation includes principally $\alpha$-particles, $\beta$-rays, $\gamma$-rays and X-rays. These forms of energy are so powerful that the mechanisam and the result of their interaction with matter is usually quite different than that of uv-light. Most often, the energy absorbed by the molecule is so excessive that an electron is not just ejected into higher energy state, but it is completely ejected from the molecule. Electron ejection and ionization of a stable molecule produces a radical-cation containing one unpaired electron and a positive charge. However, overall process is quite complex and involves many more steps in production of various free radicals. Details are discussed by Lenz [5].

**As the present work is based on free radical polymerisation process, details of only free radical addition polymerisation are discussed below.**

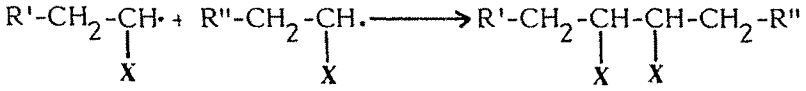
### 1.2.3 Kinetic aspects of free radical addition polymerisation

Free radical addition polymerisation involves three major stages (i) initiation (ii) propagation and (iii) termination.

In the process of initiation, active sites or radicals are formed through the interactions of an initiator system (chemical as well as photochemical), with the monomer.

The propagation step involves a series of reactions whereby the monomer reacts with other monomeric or polymeric species. If the reacting monomer is vinyl or acrylic in character, as in the acrylates, then the reaction proceeds to produce a head-to-tail polymer almost exclusively.

In the termination step radical sites in the polymer are destroyed by a bimolecular reaction, since their disappearance involves spin pairing. Termination can be achieved by either of two processes. Firstly, two radicals can simply combine together in a combination reaction, resulting in the formation of a head-to-head linkage ;



$$R'\text{-}CH_2\text{-}\underset{X}{CH}\cdot + R''\text{-}CH_2\text{-}\underset{X}{CH}\cdot \longrightarrow R'\text{-}CH_2\text{-}\underset{X}{CH}\text{-}\underset{X}{CH}\text{-}CH_2\text{-}R''$$

Alternatively, a hydrogen atom can be transferred from one radical to another giving two polymer molecules, one saturated and the other possessing an olefinic double bond at one end. This process is termed as 'disproportionation termination'.

$$R'\text{-}CH_2\text{-}\underset{X}{CH}. + R''\text{-}CH_2\text{-}\underset{X}{CH}. \longrightarrow R'\text{-}CH_2\text{-}\underset{X}{CH_2} + R''\ CH_2{=}\underset{X}{CH}$$

The kinetics of vinyl polymerisation of various monomers varies considerably with the nature of the monomers and the conditions of the polymerisation.

**Initiation :**

For chemically initiated systems, the first step in initiation is the decomposition of the initiator. I , into two radicals, R. ;

$$I \longrightarrow 2\ R.$$

Thus the rate of production of radicals may be expressed as

$$d\,[R.]\,/\,dt = 2K_1\,[I] \qquad (1.1)$$

where ; t = time and $K_1$ = reaction constant.

The radical R., is capable of initiating the chain reaction. The rate of initiation, $R_i$, of chain radicals can be given;

$$R_i = d\,[M.]\,/\,dt = 2.f.K_1\,[\,I\,] \qquad (1.2)$$

Where f is a factor which represents the fraction of primary radicals, R . , which initiate chain growth.

**Propagation :**

In each step of propagation reaction the monomer units are used. The rate of propagation, Rp, can be expressed as ;

$$Rp = -d[M]/dt = [M](K_1[M_1\cdot] + K_2[M_2\cdot]\cdots) \qquad (1.3)$$

for the process,

$$M_1\cdot + M \xrightarrow{k_1} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{k_2} M_3\cdot \quad \text{etc.}$$

In simple kinetic treatments it is necessary to assume that the rate constants are identical, i.e.

$$K_1 = K_2 \cdots\cdots = K_n = K_p$$ , the propagation constant.

The rate of propagation may now be written as

$$Rp = -\frac{d[M]}{dt} = Kp[M][M.] \qquad (1.4)$$

Where [M.] is the total concentration of radicals taking part in the reaction.

**Termination :**

If termination is assumed to take place through radical ends coming together so as to annihilate both, it can be represented as,

$$Mn\cdot + Mm\cdot \xrightarrow{Kmn} M_{n+m}$$

The loss in radicals is given as

$$-\frac{d[M.]}{dt} = 2K_{mn}[M_n^{\cdot}][M_m^{\cdot}] \qquad (1.5)$$

Where $K_{mn}$ is the termination constant ($K_t$).

The rate of termination can now be taken to be independent of molar mass of the radical species.

Equation (1.5) can now be written as

$$-\ d[M\cdot]/dt = 2K_t[M.]^2 \qquad (1.6)$$

## 1.3 Prediction of instantaneous copolymer composition

The relative rates of incorporation of comonomers A and B are not, in general, equal to their relative concentrations in the initial mixture [ 6 ]. Thus the copolymer formed at any instant differs in composition from the feed mixture, and the feed composition changes continuously through out the reaction process.

A central problem of copolymerisation theory has been the prediction of copolymer compositon given a fixed, or instantaneous feed composition. The products of copolymerisation, like those of any chemical reaction may be dictated either by the kinetics or by the thermodynamics of the reaction. With few exceptions , chain-growth copolymerisation products are kinetically determined. So instantaneous copolymer composition can be predicted by a set of different equations that describe the rates of monomer consumption. Development of these equations requires an appropriate kinetic model of the copolymerisation process. Most published models have been developed to treat copolymerisation via radical intermediates, but they are potentially applicable to any chain growth copolymerisation.

### 1.3.1 The Terminal Model

Mayo and Lewis in 1944 formulated a model for the copolymerisation process, for their work on the radical copolymerisation of styrene and methylmethacrylate [ 7 ], in which the rate constant for addition of each monomer was assumed to be dependent on the identity of the terminal unit on the growing chain. Thus four propagation rate constants are required.

$$\sim\sim\sim M_1\cdot + M_1 \xrightarrow{K_{11}} \sim\sim\sim M_1 M_1\cdot$$

$$\sim\sim\sim M_1\cdot + M_2 \xrightarrow{K_{12}} \sim\sim\sim M_1 M_2\cdot$$

$$\sim\sim\sim M_2\cdot + M_1 \xrightarrow{K_{21}} \sim\sim\sim M_2 M_1\cdot$$

$$\sim\sim\sim M_2\cdot + M_2 \xrightarrow{K_{22}} \sim\sim\sim M_2 M_2\cdot$$

Where $M_1$ and $M_2$ represent chain radicals having monomers $M_1$ and $M_2$ respectively, as their terminal, free-radical bearing units.

The rates of monomer disappearance are given as

$$- d [ M_1 ] / dt = K_{11} [M_1\cdot][M_1] + K_{21} [M_2\cdot][M_1] \tag{1.7}$$

$$- d [ M_2 ] / dt = K_{12} [ M_1\cdot ][ M_2 ] + K_{22} [ M_2\cdot ] [ M_2 ] \tag{1.8}$$

Where $[M_1]$ and $[M_2]$ are monomer feed concentrations and $[M_1\cdot]$ and $[M_2\cdot]$

are the concentrations of the growing radicals with terminal residues derived from $M_1$ and $M_2$ respectively. Dividing equation (1.7) by equation (1.8) the molar ratio of $M_1$ and $M_2$ in the copolymer is obtained

$$\frac{d[M_1]}{d[M_2]} = \frac{K_{11}[M_1\cdot][M_1] + K_{21}[M_2\cdot][M_1]}{K_{12}[M_1\cdot][M_2] + K_{22}[M_2\cdot][M_2]} \tag{1.9}$$

Assumption of steady state concentrations of $M_1$ and $M_2$ takes the form

$$K_{21}[M_2\cdot][M_1] = K_{12}[M_1\cdot][M_2] \tag{1.10}$$

and the copolymer composition is thus obtained as,

$$\frac{d[M_1]}{d[M_2]} = \left(\frac{[M_1]}{[M_2]}\right) \cdot \left(\frac{r_1[M_1]/[M_2] + 1}{[M_1]/[M_2] + r_2}\right) \tag{1.11}$$

Or,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \tag{1.12}$$

Where $r_1$ and $r_2$ are reactivity ratios.

$$r_1 = K_{11} / K_{12} \quad \text{and} \quad r_2 = K_{22} / K_{21} \tag{1.13}$$

The quantity given in equation (1.11) represents the ratio of the two monomers in the increment of polymer formed when the ratio of unreacted monomers is $[M_1] / [M_2]$. The former ratio obviously differes in general from the latter ; hence the unreacted monomer ratio will change as the polymerisation proceeds, and this will give rise to a continually changing composition of the polymer being formed at each instant.

The composition of the monomer feed and of the polymer formed may be expressed as mole fractions instead of mole ratios used above. To this end, $F_1$ represent the fraction of monomer $M_1$ in the increment of copolymer formed at a given stage in the polymerisation. Then

$$F_1 = d[M_1] / d[M_1] + [M_2] = 1-F_2 \qquad (1.14)$$

Letting $f_1$ and $f_2$ represent the mole fractions of unreacted monomers $M_1$ and $M_2$ in the feed ,

$$f_1 = [M_1] / [M_1] + [M_2] = 1-f_2$$

We obtain from equation (1.12)

$$F_1 = ( r_1 f_1^2 + f_1 f_2) / ( r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2) \qquad (1.15)$$

It is apparent that the mole fraction $F_1$ in general will not equal $f_1$ ; hence both $f_1$ and $F_1$ will change as the polymerisation progresses.

Equation (1.15) has been used in some modified form in section 2.4.8 to calculate the reactivity ratios of acrylonitrile and methyl methacrylate.

### 1.3.2 **Penultimate Model.**

Menz, Alfrey and goldfinger [ 8 ] in 1946 suggested that the relative rates of monomer addition at the ends of growing polymer chains are dependent not only on the identity of the terminal unit, but also on the identity of the preceding, or penultimate one. These authors cited no experimental evidence in support of their suggestion, but it is certainly plausible. In examination of the growing chain end in a copolymerisation for derivation of the expression of copolymer composition for penultimate model, the following eight distinct propagation steps must be considered.

$$\sim M_1M_1\cdot + M_1 \xrightarrow{K_{111}} \sim M_1M_1M_1\cdot$$

$$\sim M_1M_1\cdot + M_2 \xrightarrow{K_{112}} \sim M_1M_1M_2\cdot$$

$$\sim M_2M_1\cdot + M_1 \xrightarrow{K_{211}} \sim M_2M_1M_1\cdot$$

$$\sim M_2M_1\cdot + M_2 \xrightarrow{K_{212}} \sim M_2M_1M_2\cdot$$

$$\sim M_1M_2\cdot + M_1 \xrightarrow{K_{121}} \sim M_1M_2M_1\cdot$$

$$\sim M_1M_2\cdot + M_2 \xrightarrow{K_{122}} \sim M_1M_2M_2\cdot$$

$$\sim M_2M_2\cdot + M_1 \xrightarrow{K_{221}} \sim M_2M_2M_1\cdot$$

$$\sim M_2M_2\cdot + M_2 \xrightarrow{K_{222}} \sim M_2M_2M_2\cdot$$

As discussed earlier, the molar ratio of the monomers in the copolymer is given by the ratio of rates of monomer consumption.

$$\frac{d[M_1]}{d[M_2]} = \frac{K_{111}[M_1M_1\cdot][M_1]+K_{211}[M_2M_1\cdot][M_1]+K_{121}[M_1M_2\cdot][M_1]+K_{221}[M_2M_2\cdot][M_1]}{K_{112}[M_1M_1\cdot][M_2]+K_{212}[M_2M_1\cdot][M_2]+K_{122}[M_1M_2\cdot][M_2]+K_{222}[M_2M_2\cdot][M_2]} \tag{1.16}$$

Assumption of steady state concentrations of each of the four propagation centers leads to

$$[M_1M_1\cdot] = \frac{K_{211}[M_2M_1\cdot][M_1]}{K_{112}[M_2]}$$

$$[M_2M_2\cdot] = \frac{K_{122}[M_1M_2\cdot][M_2]}{K_{221}[M_1]}$$

$$[M_1M_2\cdot] = \frac{[M_2M_1\cdot](K_{211}[M_1] + K_{212}[M_2])}{K_{121}[M_1] + K_{122}[M_2]}$$

$$[M_2M_1\cdot] = \frac{[M_1M_2\cdot](K_{122}[M_2] + K_{121}[M_1])}{K_{211}[M_1] + K_{212}[M_2]}$$

Substitution of these steady state concentrations into equation (1.16) and introduction of the reactivity ratios,

$$r_{11} = K_{111} / K_{112} \quad : \quad r_{21} = K_{211} / K_{212}$$

$$r_{22} = K_{222} / K_{221} \quad : \quad r_{12} = K_{122} / K_{121}$$

gives the copolymer composition as

$$n = d[M_1] / d[M_2] = \frac{1 + \frac{r_{21} x (r_{11} x + 1)}{r_{21} x + 1}}{1 + \frac{r_{12}(r_{22} + x)}{x (r_{12} + x)}} \qquad (1.17)$$

Where $x = [M_1] / [M_2]$

If $r_{22} = r_{12}$ in equation (1.17) it follows after rearrangement like.

$$n-1 = \frac{r_{21}\, x\, (r_{11}\, x + 1)}{r_{21} x + 1} \qquad (1.18)$$

Barb [9] utilized this equation in interpreting the data of Ham and Fordyce [10] for styrene and fumeronitrile with moderate agreement. For this copolymerisation the conventional copolymerisation equation does not apply; because the chain rich in fumeronitrite and containing styrene as the last added unit exhibit greatly decreased reactivity with fumeronitrite monomer. In our study we could not use this model due to difficulties in determination of rate constants.

### 1.3.3 **The Complex participation model :**

According to some authors [11-15] the very regular copolymer structures obtained from olefin : $SO_2$ copolymerisations arose from concerted additions of 1:1 complexes of the monomers, evidence for which was available from optical spectroscopy. This mechanism was generalised in 1971 by Seiner and Litt [16-19] for copolymerisations in which chain growth occurs via competitive additions of free and complexed monomers. The following eight propagation steps were considered ,

$$
\begin{aligned}
&\sim\sim M_1\cdot + M_1 \xrightarrow{K_{11}} \sim\sim M_1M_1\cdot\\
&\sim\sim M_1\cdot + M_2 \xrightarrow{K_{12}} \sim\sim M_1M_2\cdot\\
&\sim\sim M_2\cdot + M_1 \xrightarrow{K_{21}} \sim\sim M_2M_1\cdot\\
&\sim\sim M_2\cdot + M_2 \xrightarrow{K_{22}} \sim\sim M_2M_2\cdot\\
&\sim\sim M_1\cdot + \overline{M_2M_1} \xrightarrow{K_{1C2}} \sim\sim M_1M_2M_1\cdot\\
&\sim\sim M_1\cdot + \overline{M_1M_2} \xrightarrow{K_{1C1}} \sim\sim M_1M_1M_2\cdot\\
&\sim\sim M_2\cdot + \overline{M_1M_2} \xrightarrow{K_{2C1}} \sim\sim M_2M_1M_2\cdot\\
&\sim\sim M_2\cdot + \overline{M_2\;M_1} \xrightarrow{K_{2C2}} \sim\sim M_2M_2M_1\cdot
\end{aligned}
$$

where $\overline{M_1M_2}$ represents the monomer complex. These authors suggested that such a kinetic scheme might describe copolymerisations of weakly interacting monomers, in which the concentration of the complex is so low that normal copolymerisation competes with complex addition to the growing chain end.

Because of the complexity of the model as well as nonsuitability for the present system the model was not useful for the determination of reactivity ratios. Hence details are not discussed here.

## 1.4 Rate of Copolymerisation

The rate of copolymerisation in binary system depends not only on the four propagation steps (section 1.3.1) but also on the rates of initiation and termination. To simplify matters, the rate of initiation may be made independent of the monomer composition by choosing an initiator which releases primary radicals that combine efficiently with either monomer [20]. The spontaneous decomposition rate of the initiator should be substantially independent of the reaction medium, as otherwise the rate of initiation may vary with the monomer composition.

The rate of initiation ($R_i$) of chain radicals of both types $M_1$ and $M_2$ is then fixed and equal to 2.f.Kd [ I ], or twice the rate of decomposition of the initiator I if the efficiency 'f' is equal to unity. The relative proportion of two types of chain radicals created at the initiation step is of no real importance, for they will be converted one into other by the two cross propagation reactions.

Two steady state conditions apply to the total radical concentration and to the concentrations of the two radicals separately. Three types of terminations must be considered, involving all possible pairs of radical types. The steady state condition as applied to the total radical concentration requires that the combined rate of termination shall be equal to the combined rate of initiation, i.e.

$$R_i = 2K_{t11}\,[M_1\cdot]^2 + 2K_{t12}\,[M_1\cdot]\,[M_2\cdot] + 2K_{t22}\,[M_2\cdot]^2 \qquad (1.19)$$

Where $K_{t11}$ and $K_{t22}$ are the bimolecular termination constants for reactions between like radicals and $K_{t12}$ applies to the cross reaction.

For steady state condition we have seen in equation. (1.10) (section 1.3.1) that

$$K_{21}\,[M_2\cdot]\,[M_1] = K_{12}\,[M_1\cdot]\,[M_2] \qquad (1.10)$$

If $[M_2\cdot]$ in equation (1.19) is eliminated through the use of equaiton (1.10), then on solving for $[M_1\cdot]$ we obtain

$$[M_1\cdot] = (R_i/2)^{1/2}\Big\{K_{t11} + (K_{t12}\,K_{12}/K_{21})\,([M_2]/[M_1]) + (K_{t22}\,K_{12}^2/K_{21}^2)\,[M_2]^2/[M_1]^2\Big\}^{-\frac{1}{2}} \qquad (1.20)$$

The total rate of polymerisation $(R_p)$, obtained by adding equations (1.7) and (1.8) (section 1.3.1) and then eliminating $[M_2\cdot]$ through the use of equation (1.10) is

$$R_p = -\frac{d([M_1]+[M_2])}{dt} = \frac{r_1[M_1]^2 + 2\,[M_1][M_2] + r_2\,[M_2]^2\,(R_i^{1/2}/\delta_1)}{\left\{r_1^2\,[M_1]^2 + 2\,(\Phi r_1 r_2\,\delta_2/\delta_1)\,[M_1][M_2] + (r_2\delta_2/\delta_1)^2[M_2]^2\right\}^{1/2}} \qquad (1.21)$$

Where

$$\delta_1 = (2K_{t11}/K^2_{11})^{1/2};\quad \delta_2 = (2K_{t11}/K^2_{22})^{1/2}$$

$$\Phi = K_{t12}\,/2K_{t11}^{1/2}\quad K_{t22}^{1/2}$$

The $\delta$ values simply represent the reciprocals of the well known kinetic parameter $K_p/(2K_t)^{1/2}$ for homopolymerisation of the individual monomers and $\Phi$ represents the ratio of half the cross termination rate constant to the geometric mean of the termination rate constants for like radicals. A value of $\Phi$ greater than one $(\Phi>1)$ means that cross termination is favoured and less than one $(\Phi<1)$ means just the opposite. The values of $\delta_1$ and $\delta_2$ can be conveniently obtained from the studies of rates of homopolymerisation of

$M_1$ and $M_2$ using the general relation.

$$-d \ln [M_1] / dt = R_1^{1/2} \delta$$

The ratio of homopolymerisation rates $-d\ln [M_1]/dt$ and $-d\ln[M_2]/dt$, under equivalent initiation conditions equals the ratio $\delta_2/\delta_1$. Thus rate measurements on the pure monomers yield two of the quantities $R_i^{1/2}/\delta_1$ and $\delta_2/\delta_1$ required in equation (1.21).

The monomer reactivity ratios $r_1$ and $r_2$ can be determined from copolymer composition studies. With a knowledge of $\Phi$ value the overall rate of copolymerisation ($R_p$) can be determined from equation (1.21) We have determined the overall rate of polymerisation of the system acrylonitrile methyl methacrylate copolymerisation process using equation (1.21) and is discussed later in section (2.4.15)

### 1.5. Poly(methyl methacrylate)

Poly(methyl methacrylate) is an important commercial plastic material. It has good optical properties and can exhibit almost perfect transmission in the wavelength region of 360 to 1000 mμ. The pure form of PMMA also transmits extensively in the ultra-violet range. It has excellent heat stability. Because of these properties MMA has been copolymerised with variety of monomers. Some of the significant work done is discussed below.

#### 1.5.1 Copolymers of methyl methacrylate and styrene

Copolymers of methyl methacrylate and styrene have been one of the most fascinating fields of research for the investigators and perhaps one of the most widely studied systems of all vinyl polymers. Mayo and Lewis [ 7 ] synthesised the copolymers of methyl methacrylate and styrene using benzoyl peroxide initiator at 60° and observed that the monomer reactivity ratios were independent of the composition of the monomer mixture. Yakovleva et al. [21] studied the radiation induced copolymerisation of methyl methacrylate and styrene in ethylchloride at a temperature of -78° to +25° and observed that the copolymerisation proceeds by a carbonium ion mechanism. They observed that the relative amount of styrene in the polymer increases with decreasing temperature for all monomer mixtures especially at -78°. Mitsengendler et al. [22] synthesised graft copolymers of methyl methacrylate and styrene by the reaction between polystyrene lithium and poly(methyl methacrylate) with 100% yield. John and coworkers [23] synthesised copolymers of methyl methacrylate (MMA) and styrene by both solution and bulk polymerisation techniques. The copolymers were transparent and thermoplastics in nature. Daniella et al. [24] synthesised block copolymers of MMA and styrene in tetrahydrofuran at -70° using either K-derivative of iso-propylbenzene or the di-Na-tetramer of α-methyl styrene as initiator. They determined the copolymer heterogeneity by light diffusion in different solvents. Yanes and Radriguez [25] synthesised the copolymers of MMA and styrene by suspension polymerisation using $(NH_4)_2S_2O_8$ as catalyst. Bararnovskaya et al. [26] studied the compositional heterogeneity of the statistical copolymers of MMA and styrene by nephelometry. Pluymer and Smets [27] synthesised copolymers of MMA and styrene by anionic radical propagation in the presence of lithium dispersion. Norkima and others [28] investigated the physico- chemical properties of MMA and styrene copolymers during multistage copolymerisation using benzoyl peroxide as initiator.

Shaikh et al. [29] synthesised block copolymers of MMA and styrene using a bifunctional initiator 4.4'-azobis (-4-cyano-valeryl) benzoyl peroxide. Johnson et al. [30] studied the influence of temperature on the reactivity ratios for the free-radically initiated copolymerisation of MMA and styrene. Nippon steel chemical Co. Ltd. [31] manufactured copolymer of MMA and styrene with low level of yellowing by continuous bulk polymerisation using BHT as a stabilizer. Bataille and Granger [32] synthesised alternating copolymers of MMA and styrene using zinc chloride as a complexing agent in aqueous medium and determined the rate of polymerisation. They also observed that the yield increased with increasing zinc-chloride concentration and reaction time, and decreased with increasing water content. Meijis and Rizzardo [33] synthesised the copolymers of MMA and styrene using α-benzyloxy styrene as chain transfer agent which proceeded via an addition fragmentation mechanisam. Nigam et al. [ 34 ] carried out the graft copolymerisation of MMA and styrene in the presence of peroxide at 60-150° for 2 hours. The resulting graft copolymer showed good impact resistant and transparency. They have also studied the kinetics of alternating copolymers of MMA and styrene using β-picolinium -p-chlorophenyl cyclide as radical initiator at 55, 60 and 65° for 3 hours [35]. Kandil and El-Gamal [36] studied the infra-red spectroscopic analysis of free radically synthesised poly (methyl methacrylate -co-styrene). They used IR spectra to get information about both the copolymer composition and the triad sequence distribution. Lin Dar et al. [37] studied the radical copolymerisation of 4-methyl styrene and MMA in benzene at 50° using AIBN initiator. They determined the reactivity ratios of the monomers which were in good agreement with literature values and conform with the Q-e scheme. Suzuki et al. [38] synthesised block and graft copolymers of MMA and styrene using polymeric peroxide which have several 0-0 bonds per mol. Most of the block copolymers were A-B type and they were effective emulsifiers for immiscible liquids. Badnarek et al. [39] studied the effects of solvents and monomer composition of MMA and styrene using tert-butoxy, methyl and phenyl radicals as initiators. The relative reactivities of these radicals were also established. Eastmond et al. [50] synthesised block copolymers of styrene and MMA by polymerising bromine terminated polystyrene (molecular weight $\ngtr$ 20000) and MMA using $Mn_2\ (CO)_{10}$ as a free radical polymerisation catalyst.

Van Beylen et al. [41] studied the developments in anionic polymerisation of MMA and styrene. Their study included longevity of living polymers, polymerisation involving bivalent cations and initiation of polymerisation by ion-pair complexes with co-ordinating agents. Polymers with suitable compositions and high flow for the injection molding of transparent articles were prepared by Gerecke [52] through aqueous polymerisation of 3-50% styrene with 97-50% MMA in the presence or absence of surfactants at concentration below the critical miceller concentration. Shaaban et al. [53] carried out the copolymerisation of MMA and styrene with AIBN initiator in the presence of $CuCl_2$ and observed the effect of $CuCl_2$ on the rates of copolymerisation and the reactivity ratios of the monomers.

Sadao Mori [44] determined the chemical composition and molecular weight distributions of high conversion styrene-methylmethacrylate copolymers by liquid adsorption and size exclusion chromatography. Fallon et al. [45]

studied the copolymerisation of MMA and styrene and their thermal degradation. O'Driscoll and Huang [46] studied the copolymersiation of MMA and styrene with particular attention to gel effect. They also studied the rate of copolymerisation which was initiated with 2.2'-azodi-isobutyrate at 60°.

## 1.5.2 Copolymers of methyl methacrylate and methacrylic acid

Comparitively less work has been done on the methyl methacrylate-methacrylic acid copolymers. Kalinushkin and Raybov [47] studied the thermal degradation of the above system with special emphasis on the products formed during degradation and mechanism of vacuum thermal degradation of the copolymer by a tagged atom method. Jamieson and Mcneil [48] synthesised the above copolymer using AIBN initiator and diphenyl picryl hydrazyl as inhibitor at 50° to restrict the conversion below 5%. They also studied the thermal degradation of the products using thermogravimetry and thermal volatilization analysis. Leplyanin et al. [49] synthesised the copolymers of MMA and methacrylic acid with controlled composition through bulk polymerisation in the presence of 3-methyl - 1,4,6-heptatrienes or 1,3,6-octatrienes. Gritter and co-workers [50] studied the pyrolytic decomposition of MMA-methcrylic acid copolymer and analysed the degradation prodcuts by gas chromatography and mass spectroscopy. Frolova and Koryakina [51] studied the thermal degradation of self-extinguishing methacrylic acid-MMA copolymers containing 20% bromo ethyl bromopropyl chloro ethyl phosphate as fire-proofing agent and they observed that during thermal degradation the latter has been converted completely to the gaseous phase at 270° where the reaction of a flame is inhibited. Kuryzhova et al.[52] studied the suspension polymerisation of MMA-methacrylic acid copolymer inthe presence of Poly(2-acrylamido-2-methyl propanesulfonic acid) Na-salt or MMA-2-acrylamido-2-methyl propane sulfonic acid copolymers. Shapiro et al. [53] studied the role of dispersion medium in chain formation of suspension copolymers of MMA and methacrylic acid and observed that the sequence distribution depended on the polarity of the dispersant. Bugner [54] synthesised block copolymers of MMA-methacrylic acid by selective cleavage of methacrylate esters.

### 1.5.3 Copolymers of methyl methacrylate and other acrylates

Copolymers of MMA-methyl acrylate have also drawn the attention of the researcher. However, significant amount of work has not been done on this system. Mikko shima and Akira Kotera [55] have studied the copolymerisation kinetics of MMA and methyl acrylate by a deuterium tracer method. They have examined two serieses of copolymers ; methylacrylate-deutero-methylmethacrylate and deutero methyl acrylate-methylmethacrylate. The copolymers were synthesised in sealed ampules in the presence of nitrogen without adding catalyst at 130°. Guseva et.al. [56] synthesised MMA-methyl acrylate copolymer by suspension polymerisation method with some modification of the general process applicable for preparation of copolymers based on MMA and esters of acrylic acid, so as to obtain a colourless copolymer suitable for preparation of articles by pressure casting by introducing higher alcohols e.g. octyl as plasticizers, esters of phthalic acid as stabilizers and derivatives of amino coumerines as clarifiers. Suzuki and Ota [57] studied the bulk polymerisation of MMA-methylacrylate in the presence of ditertiary butyl peroxide radical initiator by stirring at 160°-200° and obtained a copolymer having degree of polymerisation 1190 containing reduced amount of oligomers such as dimer, trimer and tetramer.

Copolymers of MMA-glycidylmethacrylate are also important in their own way. Sorokin et al. [58] studied the copolymerisation of MMA-glycidylmethacrylate in different solvents like dioxane, toluene and cyclohexane using benzoyl peroxide as initiator. They used different proportion of monomers and observed that the poly-dispersity increased regularly from pure poly (glycidyl methacrylate) to pure poly(methyl-methacrylate). Also when the quantity of benzoyl peroxide was increased from 0.1 mole percent to 0.4 mole percent, polydispersity was observed to be increased. Leemans et al. [59] synthesised water-soluble amphiphilic block copolymers of sulfonated glycidyl methacrylate and methylmethacrylate by living anionic polymerisation of MMA and glycidyl methacrylate and subsequent selective modification of oxirane groups of glycidyl methacrylate block into hydroxy fulonate groups by a phase transfer catalysed sulfonation reaction. These amphiphilic block copolymers displayed surface-active behaviour in water and were characterised by a critical miceller concentration. Yasaki et al. [60] studied the viscoelastic behaviour of copolymers of MMA and butyl methacrylate. They measured the shear creep compliance for six kinds of copolymers above the glass transition temperature. Vlcek et al. [61] studied the copolymerisation of MMA with 2-methoxy ethyl methacrylate initiated by lithium-tert-butoxide in benzene and observed that the copolymerisation proceeded in 2-stages separated by a plateau on the conversion curve. Matsumoto et al. [62] studied the solvent effects on the gelation in the copolymerisation of MMA with trimethylol propane trimethacrylate in dioxane or n-butyl acetate. They also studied the gelation in the copolymerisation of MMA with oligoglycol dimethacrylates [63]. Zhu and Hamielee [64] studied the radical copolymerisation of MMA with ethylene glycol dimethacrylate in an adiabatic reaction and developed a polymerisation model. They also measured the free radical concentration for bulk copolymerisation of the above system initiated with 0.3% (w/w) AIBN at 70° over entire concentration range with an online ESR spectrometer [65].

### 1.5.4 Some Other Copolymers of methyl methacrylate.

Methyl methacrylate forms innumerable copolymers with different monomers. Some of them are discussed below. Walling [66] studied the copolymerisation of MMA and vinyl acetate and determined the propagation rate constant ($K_p$) of the system. Ziazova [67] studied the derivatographic study of thermal stability of MMA-N-ethylol methacrylamide copolymers. Vasilova and Kucher [68] determined the constants K and $\alpha$ of the Mark-kuhn-Houwink equation for acrylonitrile-MMA-styrene ternery copolymer system having different compositions in pyridine, chloroform, 1,2-dichloro ethane tetrahydrofuran, 1,4-dioxane, DMF, chlorobenzene, MEK, DMSO, toluene, ethylbenzene and benzene. Ashamov et al. [69] studied the radiochemical copolymerisation of MMA with tetrafluoro ethane and observed that the copolymer had higher thermal stability than MMA homopolymer. Eginbaev and Ayepbergenov [70] studied the role of introduction of aromatic hydrocarbons such as benzene during radical polymerisation of MMA with vinylbutyl ether.

## 1.6 Polyacrylonitrile :

Polyacrylonitrile is unsuitable as a conventional thermoplastic due to its inheritant colouration and infusibility on heating. If is difficult to mold and to produce polymers with good molding characteristics, hence acrylonitrile is usually polymerised in the presence of a suitable comonomer. Some of its copolymers studied so far are discussed below.

### 1.6.1 Acrylonitrile - Styrene Copolymers

Acrylonitrile-Styrene copolymers have optical clarity, good processibility and are relatively inexpensive and hence have wider application range. Copolymers of acrylotrile (AN) and styrene are widely studied. Some of which are mentioned here. Mayo and co-workers [ 7 ] synthesised the copolymers of AN and styrene using benzoyl peoxide as free radical initiator, and determined the reactivity, ratios of the monomers and the rate of copolymerisation. Molnar and Riley [71] synthesised thermally initiated non-catalyzed AN-styrene polymers in the presence of $NH_3$ or an amine which is volatile at the polymerisation temperature to prevent polymer formation on the walls of the polymerisation vessel. Findley [72] in 1960 synthesised a resinous copolymer of AN and styrene by heating water 180, styrene 70, AN 30, Na-dodecylsulfonate 4, $K_2S_2O_8$ 0.3 and tert-dodecyl mercaptan 0.3 part at 50° for 12 hours to form a dispersion. The dispersion was coagolated by hot aqueous sodium chloride, washed, filtered and dried. After milling the thermoplastic obtained, showed good impact strength as well as thermal properties.

Guzman and Gomez Fatau [73] synthesised block copolymers of AN and styrene by anionic copolymerisation using Na-naphthalene initiator at 70°. They confirmed that no hompolymer of AN was formed. Foster Grant Company [74] synthesised thermoplastic copolymers of AN and styrene by aqueous suspension polymerisation using aliphatic peroxide catalyst having the general formula $[Me(CH_2)_nCO]_2O_2$ where n = 2. Dawan and Smets [75] studied the copolymerisation of AN-styrene, AN-MMA using phenylmagnesium bromide as anionic initiator and calculated the reactivity ratios. Beevers and White [76] studied the X-ray scattering of AN-styrene copolymers and obseved that X-ray results showed a transition from the double scattering peak in the polystyrene to the single peak of PAN. Andreas Hunyan et al. [77] synthesised high molecular weight copolymers of AN-styrene by polymerising the monomers in DMF for 4-20 hours using AIBN initiator at 50°. Seymour et al. [78-81] studied entensively the copolymerisation of AN-styrene using Zinc chloride. They synthesised alternating and random copolymers by controlling the polymerisation temperature. They also synthesised block copolymers of AN-styrene by using macroradicals of styrene in propanol. Burton and

Werner [80] studied the copolymerisation of AN with styrene in the presence of zinc chloride and various H-donors (e.g. cyclohexane, octane, isooctane, decalin) and observed that the rate of copolymerisation increases with the concentration of the H-donor at constant concentration of comonomers in acetone in the presence or absence of free radical source (AIBN initiator). Friztche and Malsch [82] synthesised the block copolymers of AN-styrene by using a living macro anions prepared from styrene or its derivatives and copolymerising it with acrylonitrile. Zaitseva et al. [83] studied the copolymerisation of AN-styrene with high degree of conversion and calculated the constants K and $\alpha$ in the Mark-Kuhn-Houwink equation for weight average molecular weight ($\bar{M}w$). Gandhi et al. [84] studied the copolymerisation of AN-styrene in benzene at 50° using cobalt acetylacetonate-triethylaluminium, a Zeigler-Nata initiator. They determined the overall activation energy of the polymerisation. Lakshminarayan et al. [85] synthesised copolymers of AN and styrene and grafted them on to casein. Hill and co-workers [86] studied the mechanism of bulk copolymerisation of AN and styrene at 60°. Tanczos et al. [87] investigated the effect of molecular inhibitor in the bulk copolymerisation of AN and styrene as well as AN and methyl acrylate. They studied the stoichiometry of the inhibitor reaction in the presence of p-nitroso-dimethyl aniline and p-nitroso diphenyl aniline as inhibitors. Hatate et al. [88] studied the rate of copolymerisation of AN with styrene involving minute amounts of either monomer. Podosenova and co-wokers [89] studied the kinetics for the calculation of process velocity and the molecular weight distribution of the products of copolymerisation of styrene and AN in the presence of rubber. Kalyanam et al. [90] computed the reactivity ratios of AN and styrene from the $^{13}C$ NMR spectra of copolymers prepared by using cobalt acetyl acetonate-triethyl aluminium initiator system and compared with the free radical initiator such as AIBN. Seganova and Georgiev [91] carried out the redox initiated copolymeristion of AN with styrene in the presence of benzoyl peroxide and dimethyl aniline. Prementine [92] studied the photolysis of 2,2'-azo-bis [(2-$^{13}$C) propionitrile] in a mixture of styrene and acrylonitrile which led to free-radical copolymerisation. Rashid [93] studied the thermal copolymerisation of AN with styrene in the presence of some complexing agents ($CoCl_2$, $ZnCl_2$ and $CrCl_3$).He observed that the reactivity ratios in the polymerisation were unaffected by the presence of inorganic salts.

Goh et al [94] studied the copolymerisation of AN and styrene and examined the miscibiity of the copolymer with polymethacrylates containing sterically hindered amine groups. Dmitrenko et al. [95] studied the copolymerisation of AN and styrene initiated by the redox decomposition of hydroperoxide grafted to the surface of sulfur dioxide fillers such as finely dispersed Aerosil A-175 and microfibrous sivol, treated by trichloronorbornenylsilane, and subsequent ozonisation. They determined the reactivity ratios and kinetics of styrene and AN in the copolymerisation and proposed a mathematical model for calculating the initiation effectiveness and decomposition constants of grafted hydroperoxide. Yan et al. [96] studied the copolymerisation of AN and styrene by homogeneous rare earth co-ordination catalysts $ML_3$-Al (iso-Bu)$_3$-$CCl_4$, where M is lanthanide metal and L is a legand.

### 1.6.2 Acrylonitrile-methylacrylate copolymers.

Acrylonitrile methylacrylate copolymers are important acrylic fibers and are used for industrial purposes. Copolymes of this system are discussed below.

Ohta et al. [97] synthesised a solution useful for manufacturing of of acrylic fibers by copolymerising AN, methylacrylate (MA) and sodium alkyl sulfonate in AC$NMe_2$ by heating at 50° for 4 hours. Buskina et al. [98] examined the copolymerisation of AN with MA in sodium thiocyanate solution on addition of various amounts of non-textile wastes from silk manufacture containing fibroin and sericin in the presence and absence of itaconic acid. Aqueous suspension polymerisation of AN with MA and styrene was carried out by Standard Oil Co [99] and they also separated the residual monomers from the copolymers. Czajlik et al.[101] studied the composition of AN-MA copolymers formed under different conditions in DMF at 50°. Kryuchkova et al. [100] sysnthesised a latex by emulsion polymerisation of AN with MA in aqueous poly(vinyl alcohol) at 71° for 110 min. Volkova et al. [102] studied the viscosity of spinning copolymer solution of AN, MA and itaconic acid prepared by polymerising the monomers at 70-90° in aqueous NaSCN in the presence of AIBN initiator.

We have seen above the glimses of the works done on two important copolymeric systems involving MMA and AN independently. The copolymers of these two monomers (MMA and AN) are studied extensively and the review of the work done is discussed here.

## 1.7 Review of the works on Methyl methacrylate-Acrylonitrile copolymers.

A lot of work has been done on the system methyl methacrylate-acrylonitrile using different initiators and solvents. The works include all three types of copolymers i.e. random, block and graft copolymers [103-165].

Lewis et al. [2] synthesised the copolymers of MMA and AN using benzoyl peroxide as free radical initiator and determined the reactivity ratios of the monomers, their relative reactivities and rates of polymerisation. Foster [103] studied the copolymerisation of MMA and AN by anionic mechanism catalysed by sodium in liquid ammonia. He determined the relative reactivity ratios of the monomers and compared the results with those obtained by free radical mechanism. The results were significantly different for the same system. Bamford et al. [105, 107, 111, 112] extensively studied the copolymerisation of MMA and AN. They synthesised block and graft copolymers by tertiary base method using triethylamine as a chain transfer agent and described the size and composition distributions in block copolymers and illustrated the statistical characteristics of the copolymers and concluded that the block copolymers prepared by tertiary base method were markedly heterogeneous with respect to size and composition. Baxendale and Madaras [106] copolymerised methylmethacrylate and acrylonitrile in aqueous solution at room temperature in the presence of an emulsifying agent, using redox cataylst, ferrous ion and hydrogen peroxide. They have calculated the rate and extent of conversion of monomers to polymers and also the heats of copolymerisation and concluded that the heats of copolymerisation lie between those of the respective homopolymerisations. Henglein et al. [110] synthesised the graft copolymers of MMA and AN in 20% methanol. Zutty and Welch [113] studied the copolymerisation of MMA and AN using metal alkyls as catalysts. They synthesised copolymers at 25° at approximately 1% conversion per hour and the metal alkyls used were alkyl derivatives of Li, Na, Be, Mg, B, Al, Zn, and Cd. Their calculated reactivity ratios agreed with the published values.

Findley [72] synthesised a hard non-rubbery copolymer of MMA and AN with a high impact strength by copolymerising MMA with $\leq$ 25% AN. He used the reaction mixture having a composition of $H_2O$ 180, MMA 90, AN 10, Na- stearate 4.2, Na-dodecyl benzene sulfonate 1, tert-dodecyl mercaptan 0.3 and $K_2S_2O_8$ 0.4. Beevers et al. [114,115] synthesied random, block and graft copolymers of MMA and AN using tertiary base like triethyl-amine as chain transfer agent. They compared the physical properties of these three types of copolymers which include X-ray scattering and glass transition temperature. They concluded from their observation that the refractive index and hence the density of the block copolymers was slightly higher than that of the corresponding random copolymer and the glass transition temperature of the block copolymers were intermediate between those of PMMA and PAN, whereas the random copolymers have glass transition temperature which fall below that of either homopolymer. Their results also showed that acrylonitrile block, to a large extent, governed the properties of block copolymers. Ceresa [116] synthesised block copolymers of MMA and AN by mechanicochemical technique by masticating PMMA in the viscoelastic state and adding AN as the plasticising agent. His investigation of the copolymerisation products indicated the formation of two distinct block copolymers (simple structure and sandwich) which were synthesised by shear dependent mechanism. Lang et al. [117] synthesised moldable, strong thermoplastic copolymer by copolymerising MMA 5-75%, AN 15-50% and a small weight percent (0.5) of styrene. Radiation induced ionic copolymerisation of MMA and AN was carried out by Yoshizo Tsuda [118] and observed that the copolymerisation proceeded through a free radical mechanism in DMF and toluene as well as in bulk. Miyama and Fujimoto [119] studied the heats of copolymerisation of MMA.and AN and found that the heat of copolymerisation for this system was 28.4 K cal $mol^{-1}$ whereas the heat of polymerisation of MMA was 13.0 K cal $mol^{-1}$ and that of AN was 17.3 K cal $mol^{-1}$. His results suggest that, the ceiling temperatures for copolymerisation reactions should be considerably higher than those of homo polymerisations. Scholtan and Marzolph [120] studied solution properties of MMA-AN copolymers and determined the value of K and $\alpha$ by computing the intrinsic viscositiy in DMF at 20° and molecular weights by light scattering technique. Yazawa et al. [122] synthesised copolymer of MMA and AN having a degree of polymerisation 1465 by using 20% $(NH_4)_2S_2O_8$ in aqueous solution. Dawans and Smets [75] synthesised the copolymer of MMA and AN using phenyl magnesium bromide as anionic initiator and calculated the reactivity ratios. They observed that copolymers with a high content of MMA show stereoregular isotactic sequencies, while copolymers with high AN content are usually coloured. Cotten and Schneider [123] synthesised the copolymer of MMA and AN in DMF and fractionated the copolymer first into 7-8 primary fractions and then to a total of 40-50 secondary fractions and then they tried to correlate the change of polymerisation conditions with the molecular weight distribution of the resultant copolymer and so also on the physical properties of the final product. Matsuda et al. [124] carried out the copolymeristion of MMA and AN in liquid $SO_2$ using $[Me_2\ C(CN)N:]_2$ as catalyst and observed that the reaction rate constants were not changed by the addition of ammonium salts. Roehm and Hass [125] synthesised the said copolymer using benzylidene (or thiophenylidene) dimethacrylate and 2,2'-azo diisobutyronitrile as initiator. The copolymers synthesised were suitable for injection molding after addition of plasticiser. Mezhirova et al. [126, 133] studied the copolymerisation of the above system in triethylamine under the influence of $\gamma$ -rays at -78°, -56° and 0° and observed that the copolymers formed at -78° were enriched in the nitrile component. They have also calculated the monomer reactivity constants. Masakazu et al. [127] synthesised the copolymer of MMA and AN with 98% yield, with molecular weight 105,000, by photo-polymerisation process using 60% aqueous $ZnCl_2$, 30% aqueous $H_2O_2$ and 33% aqueous HCl at 30-40° for 3 hours. Radiation induced copolymerisation was carried out by Yoneho Tabata et al. [128] over a wide range of temperatures. They calculated the apparent activition energy of copolymerisation and reactivity ratios of the monomers. They also observed that the rate of copolymerisation decreases linearly with molar concentration of AN in the liquid state copolymerisation at 15° and increases linearly with concentration of AN in the solid state at -78°. Bero and co-workers [129] investigated the continuous copolymerisation of MMA and AN in a heterogeneous system, in a tank type reactor using an aqueous solution of potassium persulphate $K_2S_2O_8$, an aqueous solution of potassium pyrosulfite ($K_2S_2O_5$) and an aq. solution of Mohr salt acidified with sulfuric acid. They observed that the reaction rate of copolymeristion is directly proportional to the concentration of the comonomers in the reactor and is also proportional to the residence time to the -0.65 power.

Funt and Williams [130] carried out electro-initiated anionic polymerisation of MMA and AN in dimethyl formamide saturated with sodium nitrate and observed in the polarographic measurements that the chain initiation proceeded by direct addition of an electron in the double bond. Laczkowski et al. [132] studied the continuous copolymerisation of MMA and AN in aqueous solution. They determined redox potential of the copolymerisation initiated by the system $K_2S_2O_8$ - $K_2S_2O_7$ - Mohr salt using a pH meter with Pt and Ag/AgClKCl electrodes. They observed that the potential was not related to the copolymerisation rate or extent of conversion. Luskin [134] studied the kinetics of the copolymerisation of MMA and AN and determined the ratio of Termination rate constants ($\Phi$) of MMA-AN copolymer system in copolymerisation reactions and the value of $\Phi$ was 6-24. Mosevich and Arbuzova [135] synthesised the copolymers of MMA and AN in bulk and in solution using benzoyl peroxide or cyclohexylpercarbonates at 45-120° and determined the reactivity ratios of the monomers. Grassie and Farish [136] studied the photodegradation of the copolymers of MMA and AN and observed that the volatilization of the copolymers to give methylmethacrylate almost exclusively was accompanied by a rapid decrease in molecular weight of the residue. Jean and co-workers [137] studied the distribution of the sequences of MMA units in the copolymers of MMA and AN and observed the effects of the penultimate units on the reactivity of the growing radicals. Kiyosho et al. [138] studied the copolymerisation of MMA and AN at 60° using AIBN initiator in different solvents and studied the effects of solvents and observed that the reactivity ratios of the monomers were largely influenced by the heterogeneity of the reaction system rather than polarity of the solvent. Noboru and Dakichi [139] studied the copolymerisation of MMA and AN initiated by palladium chloride-$H_2O$ catalyst system. They observed that the monomer-copolymer composition curve for $PdCl_2$ - $H_2O$ system was similar to that of radical copolymerisation system.

Block copolymers of MMA and AN were synthesised by Tadashi and Tomio [140] using a multimetallatable compound (e.g. active methylene compound) as initiator. Huang [141] carried out the photosensitized copolymerisation of MMA and AN by ultraviolet radiation in the presence of benzoin at lower than room temperature to give fibers and sheets with improved whiteness and physical properties. Trung and Chapiro [142] studied the radio-chemical grafting of acrylonitrile on poly(methylmethacrylate) and determined the glass transition temperature ($T_g$) of the graft copolymer and observed that $T_g$ increased with MMA content in the graft copolymer and a small minus glass transition temperature was observed for graft copolymer containing 9% acrylonitrile. Zafar and co-workers [143] studied the effects of solvent on radical copolymerisation of MMA and AN and observed the variation in nitrogen content of the copolymer with the change in solvent. Seymour et al. [144] synthesised block copolymers of MMA and AN by using macroradicals prepared by AIBN initiated polymerisation of MMA in inert atmosphere and in poor solvents or theta ($\theta$) solvents below theta temperature and at temperature below the glass transition temperature of PMMA.

Shimosaka and Osaki [145] synthesised transparent vinyl resin of MMA and AN, insoluble in its monomers, by heterogeneous bulk copolymerisation using 0.0001 to 5% radical scavanger under oxygen containing atmosphere. They used AIBN and m-phenylene diamine initiator for copolymerisation at 50° for 16 hours. Kimura et al. [146] investigated the copolymerisation of MMA and AN in the presence of Cu-II chelates of Poly(vinyl amine) and 1,3-diaminopropane in aqueous and DMF solutions and concluded through spin trapping and gelation studies that the copolymerisation was initiated by trichloromethyl radical formed. Sengupta and Palit [147] synthesised graft copolymers of MMA and AN by treating PAN with $H_2S$ to form a thiamide group followed by grafting with monomer MMA in the presence of halogen.

Szafko and Manczyk [148, 156] carried out the copolymerisation of the AN-MMA system and determined the initiation rate in the AIBN initiated copolymerisation in DMF and using the stable radical PhN(0): $CMe_2$ $CH_2$ $CMe_2$ N(Ph)O. as inhibitor. They observed that the initiation rate depends on the composition of the monomer mixture. Barton et al. [149] investigated the rate of photochemical (uv) polymerisation of AN with MMA in the presence of naphthalene catalyst and observed that the polymerisation rate increased with increasing concentration of AN in the feed mixture. Firsov et al. [150] studied the copolymerisation of MMA and AN in respect of heterogeneity, reactivity ratios and mechanisms for the radical co-ordination polymerisation at 60° in the presence of $ZnCl_2$ coordination catalyst and benzoyl peroxide. They observed that the appearance of heterogeneity (caused by coordination inclusion of $ZnCl_2$ in the growing chain) leads to increased rate of copolymerisation for systems containing a polar and non-polar monomers and decreased polymerisation rate for systems containing both polar monomer.

Yamaguchi and co-workers [151, 153] synthesised block copolymers of MMA and AN in the presence of acetanilide dilithium salt or dilithium trans $\beta$-methyl cinamanilide. Cattiaux et al. [152] studied the copolymerisation of MMA and AN in DMF and THF at 60° and observed the resonance pattern of methoxy and methine proton.

Radhakrishnan et al. [154] studied the thermal analysis of oxidised poly(acrylonitrile-co-methylmethacrylate) in air at 80 - 200° and observed that the exothermic peaks in DTA increased with increasing oxidation temperature. Hassler and Thompson [155] sysnthesised the copolymers of MMA and AN by polymerising AN with 20-40% MMA and got clear, tough castings. They also noticed little change in storage modulus and loss in colour apparently due to inappreciable ring formation, upon heat treatment of the copolymers for 24 h at 125° and for 5 h at 160°. Manczyk and Szafko [157] determined the rate of initiation in the copolymerisation of MMA and AN in the presence of the inhibitor, 4-hydroxy-2,2,6,6-tetramethyl piperidine-1--oxyl. Konsulav and his co-workers [158] studied the changes in size and morphology of AN - MMA sodium vinyl sulfonate copolymer particles with respect to polymerisation time using optical and electron microscopy. Staynov [159] investigated the effects of polymer concentration on the structural mechanistic properties of fibers prepared from 94:6 acrylonitrile methyl methacrylate copolymer of different molecular weights. Mogenstern and co-workers [160] studied the copolymerisation of AN with MMA or other acrylates in DMF by tert-BuOLi at -30° to +10° and calculated the chemical heterogeneity and copolymer structure.

Ye Dakeny et al. [161] investigated the copolymerisation of MMA and AN in the presence of titanocene dichloride and observed that the irradiation of light is a prerequisite for the copolymerisation. They also determined the mole fractions of monomers in the copolymer by $^1H$ NMR and the monomer reactivity ratios by four methods. Zaitseva et al. [162] studied the pohtopolymerisation of MMA and AN in the presence of benzoyl peroxide and AIBN and observed that chain termination was bimolecular and diffusion controlled. Dass and Sarmah [4] synthesised the copolymer of MMA and AN initiated with a mixture of ferrocene and carbon-tetrachloride as charge transfer agent in dimethyl sulfoxide at 60° and determined the reactivity ratios of the monomers.

Novoselova et al. [163] synthesised graft copolymers of MMA and AN by a two stage process involving initial formation of living polyacrylonitrile and subsequent addition of poly(methyl methacrylate) in the presence of lithium catalyst. Cywar and Tirrel [164] carried out the copolymerisation of MMA and AN initiated by photolysis of 1,1'- azobis (2-phenyl ($^{13}$C)) ethane at 35° in benzene and determined the relative end group concentrations. Fukumoto et al. [165] synthesised hydrophobic copolymers of MMA and AN as membrane material which are suitable for hemodialysis membrane with good permeability of solutes and mechanical strength.

A summary of the work done on MMA - AN polymeric system is given in the Table 1.1 for easy references.

## Table 1.1

**Survey of work done on the MMA-AN System**

| Sr. No. | Initiator used | Copolymer synthesised | Remarks | Reference |
|---|---|---|---|---|
| 1 | Benzoyl peroxide | random | Compared the monomer reactivity ratios of radicals. | 7 |
| 2 | Na-in liquid ammonia (carbanion mechanism). | random | relative reactivity ratios were determined | 103 |
| 3 | Triethylamine | block and graft | Study of size and composition distribution and kinetics. | 105,107<br>111,112 |
| 4 | Ferrous ion and $H_2O_2$ (redox system) | random | rate and extent of copolymeristion was studied | 106 |
| 5 | Metal alkyls like alkyl derivatives of Li, Na, Be, Mg etc. | random | reactivity ratios | 113 |
| 6 | $K_2S_2O_8$ | - | high impact strength copolymer | 72 |
| 7 | Triethylamine | random, block and graft | comparison of the physical properties Tg, X-ray diffraction and refractive index. | 114,115 |
| 8 | Mastication process (no initiator) | block | two distinct block copolymer (simple and and sandwich type) | 116 |
| 9 | - | random | copolymer with high ultimate elongation (moldable strong thermo plastic) | 117 |
| 10 | Radiation induced | random | copolymer synthesised by free radical and in bulk | 118 |
| 11 | $(NH_4)_2S_2O_8$ | random | - | 122 |
| 12 | Phenyl magnesium bromide | random | observed stereoregular isotactic sequencies in copolymers with high MMA content | 75 |

| | | | | |
|---|---|---|---|---|
| 13 | - | random | effect of molecular weight distribution on physical properties. | 123 |
| 14 | $[Me_2\ C(CN)\ N:]_2$ | random | - | 124 |
| 15 | 2,2'-azobis-iso butyronitrile | - | copolymers suitable for injection molding | 125 |
| 16 | $Et_3N$ under influence of $\gamma$-ray | random | determination of monomer reactivity ratios | 133 |
| 17 | $ZnCl_2/H_2O_2$ | random | - | 127 |
| 18 | $\gamma$-ray | random | study of activation energy and monomer reactivity ratios | 128 |
| 19 | $K_2S_2O_8$, $K_2S_2O_5$ and $Fe^{+2}$ | random | rate of copolymerisation was determined | 129 |
| 20 | Electro-initiation (DMF+$NaNO_3$) | random | molecular weight independent of composition distribution and monomer concentration | 130 |
| 21 | $K_2S_2O_8$-$K_2S_2O_7$ (Redox system) | - | redox potential of the copolymerisation | 132 |
| 22 | Benzoyl peroxide or cyclohexyl percarbonates | random | reactivity ratios | 135 |
| 23 | - | random | photodegradation | 136 |
| 24 | - | random | sequence distribution in the copolymer | 137 |
| 25 | AIBN | random | dependence of reactivity ratio on the heterogeneity of the reaction system. | 138 |
| 26 | $PdCl_2$ - $H_2O$ | random | - | 139 |
| 27 | Active methylene compound | block | - | 140 |
| 28 | UV-radiation (Benzoin) | - | fibers and sheets with improved whiteness and physical properties. | 141 |
| 29 | Radiation induced | graft | determined glass transition temperature | 142 |

| | | | | |
|---|---|---|---|---|
| 30 | Radical | random | effect of solvents on the copolymerisation | 143 |
| 31 | AIBN and Macroradicals of PMMA | block | - | 144 |
| 32 | AIBN and m-phenylene diamine | - | transparent resin of MMA and AN | 145 |
| 33 | Cu-II chelates of poly(vinylamine) $CCl_4$ | random | - | 146 |
| 34 | $Cl_2$ | graft | - | 147 |
| 35 | AIBN | random | rate of initiation in copolymerisation | 148<br>156,157 |
| 36 | Photochemical (UV) and naphthalene catalyst | random | study of rate of copolymerisation | 144 |
| 37 | $ZnCl_2$ + benzoylperoxide | random | role of heterogeneity in the rate of copolymeristion | 150 |
| 38 | acetanilide dilithium salt | block | - | 151,153 |
| 39 | | random | resonance pattern of methoxy and methine proton. | 152 |
| 40 | | random | thermal behaviour of oxidised polymer | 154 |
| 41 | - | random | clear, tough castings | 155 |
| 42 | - | random | size and morphology of copolymers | 158 |
| 43 | - | random | the effect of polymer concentration on structural mechanistic properties | 159 |
| 44 | Tert-Buo-Li | random | chemical heterogeneity and structure | 160 |
| 45 | Titanocene-dichloride | random | monomer reactivity ratios. | 161 |
| 46 | Benzoyl peroxide and AIBN | random | study of chain termination | 162 |

| | | | | |
|---|---|---|---|---|
| 47 | Ferrocene and $CCl_4$ | random | rate of polymerisation and reactivity ratios. | 4 |
| 48 | BuLi | graft | - | 163 |
| 49 | 1,1'-azobis(1-phenyl-($13_C$) ethane | random | determination of relative end group concentration. | 164 |
| 50 | - | - | Hydrophobic polymer suitable for hemodialysis membrane. | 165 |

## 1.8 Proposed work

Acrylonitrile homopolymers show high melting points high melt viscosity and poor thermal stability resulting into its limited applications. Copolymerisation of acrylonitrile with other monomers overcomes these limitations of acrylonitrile and simultaneously the uncommon and desirable properties of acrylonitrile can be incorporated into various melt processible resins. Copolymer properties such as rigidity, chemical resistance, melt viscosity, stability and permeability generally vary with acrylonitrile content. Molding and processing of polyacrylonitrile is difficult due to its high glass transition temperture which restricts its applications. It has been shown that by copolymerising acrylonitrile with methyl methacrylate the glass transition temperature can be drastically lowered.

Poly (methyl methacrylate) is a good plastic material. It is widely used as a molded and fabricated plastics of many kinds. The crystal clarity, light weight, outstanding weather resistance and strength of poly(methyl methacrylate) have resulted in extensive uses of this polymer in aircraft glazing, in signs, in lighting and in the architectural, transportation and home appliance. Copolymers of MMA and AN are extensively studied. From the literature survey we can see various methods adopted and initiators used for the synthesis of the copolymers. Most of the work is oriented towards the determination of reactivity ratios and rate of copolymerisation. Physico-chemical properties are the limiting factors for the applications of the polymers. The placement of monomer units in the copolymers has significant role to play in it. Hence we have attempted to study the effect of variation in sequence arrangement of the monomer units in the copolymers on the physicochemical properties. For this purpose random and graft copolymers of MMA and AN are synthesised. The experimental conditions are optimised and the resulting products are characterised through various techniques. Emphasis is given towards viscosity studies, thermal studies and differential refractive indices. Attempts are also made to determine the size of the polymer molecules in the solution. Most of the work reported so far involves synthesis in the solvents like DMF. We have tried here toluene as a reaction medium for the comparison of the results.

Details of the works are discussed in preceding sections.

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