CHAPTER – 1

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1.1 General Introduction :

"I am inclined to think that the development of polymerization is, perhaps, the biggest thing chemistry has done, where it has had the biggest effect on everyday life. The world would be a totally different place without artificial fibers plastics, elastomers etc." so said Lord Todd[1], the then President of Royal Society of Chemistry, in 1980. There is probably no one who will disagree with it. The polymerization process has become important ever since Goodyear's discovery of vulcanization of rubber in 1839 and also the conversion of styrene to a gelatinous mass in the same year by Simon. Berthelot applied the term *"polymerization"* to the above mentioned processes in 1866. Afterwards Hyatts invented plasticized cellulose nitrate in 1870, Bouchardat polymerized isoprene to a rubber like substance in 1879, poly(methacrylic acid) was synthesized in 1880 by Fitting and Engelhorn. Chardonnet manufactured man-made fibres in 1884, Backeland synthesized phenolic resins in 1909. Since then the pace of polymer science and technology has been accelerating dramatically. This explains why our age is termed the "*polymer age*". Polymers, in performance characteristics, offer unique properties, application prospects and diversity, they also offer novelty and versatility which is not found in any other class of materials.

The quest for new materials has been with us from ancient times. Polymers, though introduced in the materials field in a meaningful manner only very recently, occupy a major place and position in our life today. To name a few desirable properties – high strength, light weight, good flexibility, special electric properties, semiconducting, high temperature stability, resistance to chemicals, amenability for quick and mass production and for fabrication into complex shapes in a wide variety of colour – some polymers will almost always meet your requirement. Polymer can be converted into strong solid articles, flexible rubber–like masses, soft and resilient foams, smooth and fine fibres, clean and clear glass-like sheets, swollen jelly-like food materials and so on. They can be used to bond objects, seal joints, fill cavities, bear load – in fact, anything from clothing the naked to powering a space vehicle to even replacing a human organ[2]. It may be said without exageration that at present polymers have penetrated into almost all branches of industry, construction, agriculture, and biomedical sciences.

The science of macromolecules is divided between biological and non-biological materials[3]. Each is of great importance. Biological polymers form the very foundation of life and intelligence and provide much of the food on which man exists. Generally, polymers are the synthetic materials used for plastics, fibers and elastomers, with a few naturally occuring polymers, such as rubber, wood, and cellulose, included. Today these substances are truly indispensable to mankind, being essential to clothing, shelter, transportation and communication, as well as to the convenience of modern living. Despite the great deal of attention given at the present time to the building of regular molecular construction in chains of monomers, efforts to produce new polymers have not lessened. One of the most important tasks in this field is the synthesis of polymers that continue to have strength and functionality while in service but "*degrade*" after use[4].

General polymer science has contributed immensly to the understanding of structures and functions of biological polymers. Apart from the interest that biodegradable polymers have generated, interest also exist in a wide variety of biological and biomedical problems wherein the specific chemical and physical properties of polymers play an important role. Biomedical implants, prosthesis, artificial organs fall in this category as well as polymer bound drugs, fertilizers and pesticides[5]. It is challenging for the chemists today to mimic with synthetic polymers some of the remarkable adaptations of biopolymes. Biodegradability is one such phenomenon. The study of biodegradation of polymers is multi disciplinary and the subject cuts across the barriers in chemistry, microbiology, medicine and agricultural science. The rapid progress of polymer science has made it necessary to synthesize polymers that undergo degradation in the physiological environment or by microbial action in the soil[6]. Hence biodegradation is the most desirable long term future solution and this area of research and development has gained importance in recent years.

1.2 Classification of Polymers :

Polymer is a generic name given to a vast number of materials of high molecular weight. These materials exist in countless forms and numbers because of a very large number and types of atoms present in their molecules[3,7]. Polymers can have different molecular and chemical structures, physical and solution properties, thermal and mechanical behaviours, etc. Because of these functional and structural diversity of polymers, they can be classified under convenient heading[8,9] based on : (a) their origin, (b) mode of formation, and (c) geometric shape.

(a) **Origin** :

Depending on their origin, polymers can be divided into three main groups.

(i) **Natural polymers** : They are isolated from natural materials, usually of complex chemical structures e.g. protein, polysaccharide, gums, etc.

(ii) **Semisynthetic polymers** : They are chemically modified natural polymers such as hydrogenated, halogenated or hydro-halogenated natural rubbers, cellulose e.g. cellulose nitrate, cellophane, leather, etc.

(iii) **Synthetic polymers** : They are prepared by polymerization of low molecular weight compounds e.g. polyethylene, polystyrene, polyvinyl acetate, terylene, nylon, etc.

(b) **Mode of Formation** :

Based on stoichiometry of the polymerization, the polymer can be classified into two broad classes as :

(i) **Condensation polymers** : in which the molecular formula of the structural unit(s) lacks certain atoms present in the monomer from which it is formed e.g. polyamides, polyesters, polyurethanes, etc.

(ii) **Addition polymers** : in which the molecular formula of the structural unit(s) is identical with that of the monomer from which the polymer is derived e.g. polyethylene, polystyrene, polyacrylamide, etc.

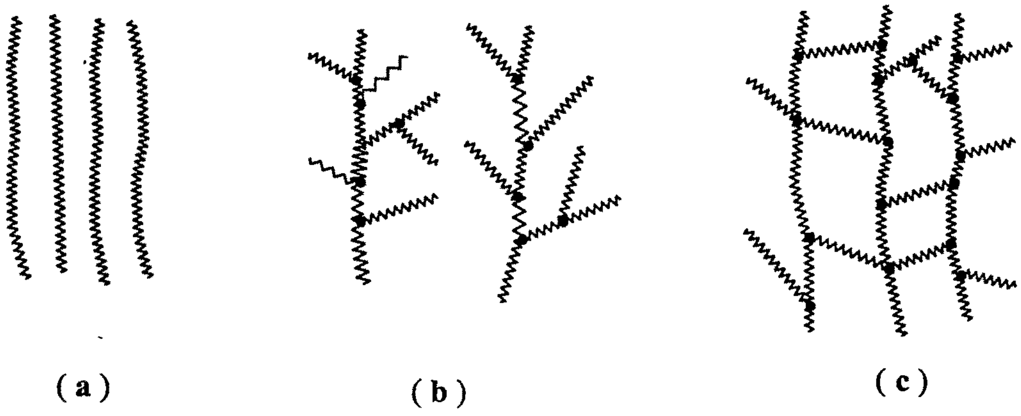
(c) **Geometric Shape** :

Beside the specific arrangement of the monomer units in the macromolecular chain, it is important to establish the geometrical shape of the macromolecule. According to the shape of the macromolecules, polymers are classified into three major classes as illustrated in Fig. 1.1.

(i) **Linear polymers** : They can schematically be represented by lines of finite length (Fig. 1.1a) e.g. high density polyethylene, polyvinyl chloride, nylon-6, etc.

(ii) **Branched polymers** : They can be schematically represented by lines of finite length with short or long branch structures of repeat units (Fig. 1.1b) e.g. linear low density polyethylene.

(iii) **Cross-linked polymers** : These polymers are composed of macromolecular chains joined together with transverse chemical bonds or cross-linked (Fig. 1.1c) e.g. wood, PF resin, vulcanized rubber, etc.



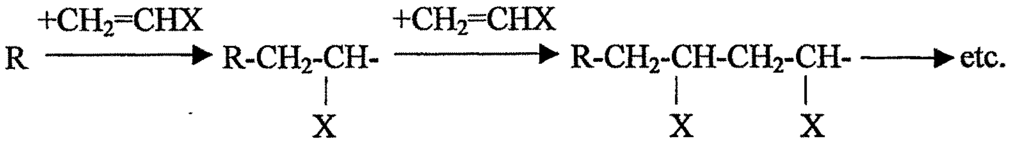
(a) (b) (c)

Figure 1.1: Schematic representation of the structure of (a) linear, (b) branched and (c) cross-linked or network polymers.

1.3 Synthesis of Polymers :

The process of synthesizing polymers is called polymerization. Generally it is defined as "*the fundamental process by which low molecular weight compounds are converted into high molecular weight polymers*"[2]. Depending on the mode of formation of polymers in 1929 W.H.Carothers[10] suggested a classification of polymers into two groups : addition and condensation polymers. The unsaturated monomers are converted to (carbon chain) high molecular weight polymers through addition polymerization process. A large number of different class of unsaturated monomers, such as olefin, α-olefins, diolefins and vinyl compounds readily undergo this type of (chain) polymerization. On the other hand, bifunctional or multifunctional molecules condense intermolecularly with the elimination of some small molecules such as water, hydrochloric acid, ammonia, methanol etc. and form (hetero chain) high molecular weight polymers. This is called condensation polymerization e.g. formation of polyamide from diamine and dicarboxylic acid.

The radical polymerization of vinyl monomers is the most versatile method of producing carbon backbone polymers, both industrially and in the laboratory. The use of free radical attack on monomer double bonds to initiate chain polymerization dates back to atleast 1838 when the free radical polymerization of vinylidene chloride was reported[11]. Indeed, a range of monomers including vinyl chloride[12], styrene[13], methacrylic acid[14] and methyl acrylate[15] were polymerized prior to 1900 ! The mechanism of radical polymerization has been the object of continuous study since its discovery. The following free radical chain mechanism, first suggested by Taylor and Bates[16] to explain the polymerization of ethylene induced by free radicals in gas phase and independently proposed by Staudinger[17] for liquid phase polymerizations, offers an explanation for the above general characteristics of vinyl polymerizations



$$R \xrightarrow{+CH_2=CHX} R\text{-}CH_2\text{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-} \xrightarrow{+CH_2=CHX} R\text{-}CH_2\text{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-}CH_2\text{-}\underset{\displaystyle X}{\underset{|}{CH}}\text{-} \longrightarrow \text{etc.}$$

Where X is a substituent which may be H, CH_3, C_6H_5, Cl, $OCOCH_3$, $COOCH_3$, etc. The chain propagation step consists essentially of free radical attack at one of the double bonded carbon atoms of the monomer and the active centre shifts uniquely to the newly added monomer, which is thereby capable of adding another monomer, etc. Like all chain reactions, the overall polymerization involves at least two other processes : chain initiation and chain termination[18]. The nature of these processes depends on the conditions employed. The average molecular mass and polydispersity of the polymer mixture formed depend on the reaction kinetics, which therefore has a decisive effect on the properties of the end products[19,20].

(a) Factors Determining Radical Chain Polymerization and the Properties of the Resulting Polymers :

(i) Monomer structure :

The polymerizability of unsaturated compounds depends on the arrangement of their double bonds, and on the nature and number of their substituents[3]. The general regularities of the effect of structure of unsaturated compounds on their polymerizability were first established by S. Lebedev[3]. He suggested that thermodynamically, the polymerization of a monomer is possible if it involves a decrease of free energy :

$$\Delta G = \Delta H - T\Delta S$$

where ΔG = change in free energy of the system,

ΔH = change in enthalpy of the system, and

ΔS = change in entropy of the system.

Polymerization of unsaturated hydrocarbons involves opening of one double bond and formation of two simple C-C bonds. The energy change associated with going from monomer to polymer and the appearance of stresses on formation of the polymeric chain from substituted olefins owing to interactions between side groups (steric effect) decided whether polymerization is feasible or not e.g. in α,α-diphenylethylene and vinylidene bromide, the energy loss due to steric effect may be so high that polymerization become thermodynamically impossible.

The double bond of ethylene is not polarized. Asymmetric introduction of substituents changes the electron density of the double bond and accordingly the polarized state of the molecule. The higher the degree of polarization of the monomer, the higher will be its reactivity and accordingly the rate of initiation of its polymerization.

(ii) **Initiator** :

The rate of decomposition of initiators depends, apart from their chemical nature, on the reaction temperature and the solvents used. This means that the same initiator in a given solvent decomposes at different rates at different temperatures; and the same initiator at a given temperature will have different decomposition rates in different solvents. The number of free radicals formed as a result of decomposition of the initiator increases with initiator concentration. This means a large number of active centres and hence a faster overall rate of polymerization. The molecular mass of the resulting polymer decreases with rising temperature.

(iii) **Temperature** :

The rate of polymerization increase with temperature. A rise in the rates of active centre formation and chain propagation increase the overall rate of conversion of monomer into polymer. However, a rise in termination rate retards polymerization process, shortens the reaction chain and decreases the molecular mass of the resulting polymer. Increasing the propagation rate results in a longer reaction chain and a higher molecular mass of the polymer. At low temperature reaction may not occur. That is an optimum temperature is required.

(iv) **Solvent** :

Solvent used in polymerization may act, in general, as mere diluents and sometimes also as chain transfer agent. But it is otherwise very likely that different solvents bring about different degrees of deviation from normal kinetics for a given initiator – monomer combination depending on chemical nature of the solvents and level of dilution. Enhancement of rate of chain initiation is manifested through an enhanced rate of polymerization and this may arise as a consequence of solvent-induced increase in initiator efficiency[21] or due to the increase in the value of the initiator decomposition rate constant, i.e. for solvent causing an increase in rate of radical generation[22]. On the other hand, interaction of an active centre or a growing chain with the solvent led to chain transfer, resulting in low molecular mass polymers. Sometimes, the polymerization of many monomers in solvent also accomplish chain transfer to polymer to form branch polymers. However, in general, if polymerization is carried out in a solvent, the overall rate of polymerization and the molecular mass of the resulting polymer increase with monomer concentration[22].

(v) **Pressure** :

A pressure of several atmosphere (atm) or even tons of atmosphere has practically no effect on polymerization. However, high or extremely high pressure (3,000 to 5,000 atm or more) speed up polymerization considerably. Since, the volume change on polymerization is usually negative, an increase in pressure favour the formation of polymer and is accompanied by an increase in the ceiling temperature, often 15-20°C per 1,000 atm. Nicholson[23] reported polymerization of styrene at higher pressure. He observed that the rate of dissociation of initiator is reduced, but the rate of polymerization is sufficiently increased to outweigh this, the overall polymerization rate being seven to eight times higher at 3,000 atm than at ordinary pressure. Also, the rate of termination, being diffusion controlled, is decreased. A particular feature of polymerization under pressure is that the reaction rate increases but the molecular weight of the resulting polymer does not decrease.

(vi) **Atmosphere** :

Atmospheric oxygen is a well known inhibitor of[24] polymerization. The inhibiting action of oxygen is due to its biradical nature. Oxygen reacts with a chain radical to produce a peroxy radical of low reactivity in the first step. This peroxy radical reacts with a growing free radical form dead peroxide containing polymer chain. To get high molecular weight polymer, it is necessary to avoid contact with atmospheric oxygen. This is why radical polymerization is generally carried out under nitrogen atmosphere[2].

(vii) **Inhibitor** :

Inhibitors are chemical substances which when present in the monomer or in the polymerization system, suppress the chain growth process to different degrees, usually by reacting with the initiating radicals or with some other radicals and converting them to non-radical species or inactive radicals. Before polymerization of monomers, it will have to be freed from the inhibitors. This is done either by distilling the monomer or by washing the monomer with an aqueous solution of sodium or potassium hydroxide. However, inhibitors are also used in the polymer system for the purpose of arresting the polymerization beyond a certain conversion limit.

(viii) **Reaction medium** :

Polymerizable systems are of great interest because they offer practical advantages in industrial applications. Among these are polymerization in which the monomer is carried in an emulsion, suspension and solution phase. However, most condensation polymerization are conveniently done by employing bulk or the solution technique. Some of the advantages and disadvantages of these systems are presented in Table 1.1.

(ix) **Termination** :

After termination, any further addition of the monomer units to the growing chain is stopped, and the growth of the polymer chain is arrested. Depending on factors such as temperature, time, monomer and initiator concentrations, there exists a statistical probability of the two growing chains coming close to and colliding with each other. When such a collision takes place the following two reactions occur, resulting in the arrest of the chain growth :

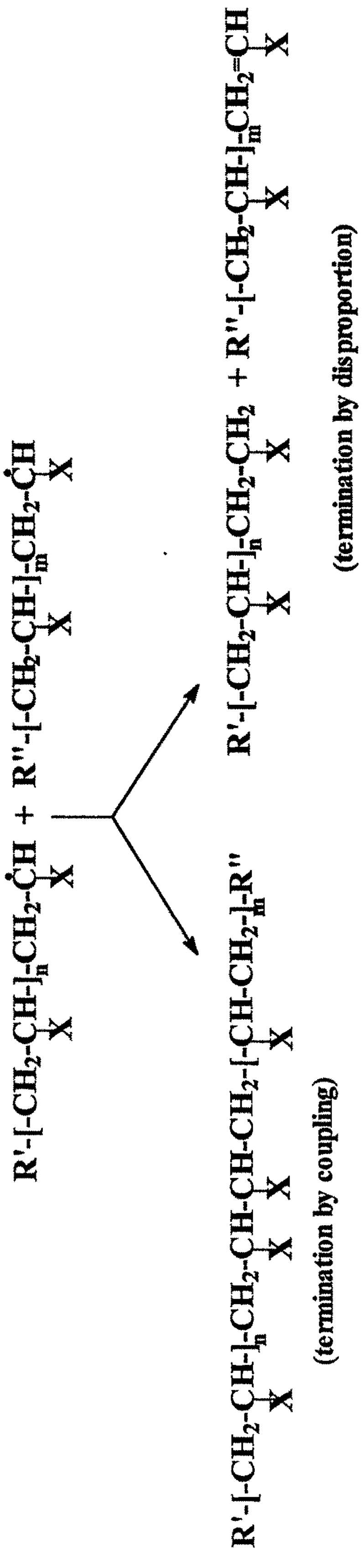

R'-[-CH2-CH-]n-CH2-CH• + R''-[-CH2-CH-]m-CH2-CH•
X X X X
R'-[-CH2-CH-]n-CH2-CH-CH-CH2-[-CH-CH2-]m-R''
X X X X
(termination by coupling)
R'-[-CH2-CH-]n-CH2-CH2 + R''-[-CH2-CH-]m-CH2=CH
X X X X
(termination by disproportion)

Table 1.1 : Comparison of Polymerization Systems[18] :

Type	Advantages	Disadvantages
Bulk	• Minimum contamination i.e.high purity product. • Simple equipment for making castings.	• Strongly exothermic. • Broad molecular-weight distribution at high conversion. • Complex if small particles required.
Solution	♦ Inert solvent medium control increasing viscosity. ♦ Solvent promote a proper heat. ♦ Solution may be directly usable.	♦ Difficult to get very high molecular weight product. ♦ Require isolation of the product from solution. ♦ Not very useful for obtaining dry polymer because of difficulty of complete solvent removal.
Suspension	▯ Ready control of heat of polymerization. ▯ Suspension or resulting granular polymer may be directly usable.	▯ Only water-insoluble monomer can be polymerized. ▯ Continuous agitation required. ▯ Contamination by stabilizer possible.
Emulsion	■ Rapid polymerization to high molecular weight and narrow distribution. ■ Emulsion may be directly usable.	■ Contamination with emulsifier, etc. almost inevitable, leading to poor colour and colour stability. ■ Washing, drying and compacting may be required.

Ref.18 : F.W.Billmeyer, Jr., In Text Book of Polymer Science, 3rd Edn., Wiley, New York, 1994, p.127.

(b) Homo- and Copolymerization :

Homopolymerization is a process which allows simple low molecular weight substance (i.e. single monomer) to combine and form a complex high molecular weight substance (i.e. homopolymer). On the other hand, the simultaneous polymerization (copolymerization) of two or more monomers to form polymers which are composed of more than one kind of repeating unit is called a copolymer[10]. Copolymerization of vinyl monomers is characterized by the flexibility of different combinations of reactants and reaction conditions. Consequently, a wide variety of product properties can be tailored through proper understanding of the process and adequate control[25]. In the 1930s it was found that the composition of copolymers of vinyl and diene monomers differed markedly from that of the feed monomers and cannot be deduced from the homopolymerization rates of the monomers involved[11]. Staudinger (1939) fractionated a vinyl chloride – vinyl acetate copolymer made from a mixture of equimolar quantities of the two monomers. He found no polymer containing equal amount of each monomer[26]. At the same time, acrylic esters were found to enter copolymers with vinyl chloride faster than did the second monomer. The first polymer formed was rich in the acrylate, later, as the amount of acrylate in the monomer system was depleted, the polymer become richer in vinyl chloride. Homopolymerization of maleic anhydride and α-methyl styrene are very difficult, though they copolymerize readily with styrene and acrylates[27,28].

(i) <u>Copolymerization composition equation</u> :

The monomer reactivity ratios $r_1(=k_{11}/k_{12})$ and $r_2(=k_{22}/k_{21})$ are the ratios of the rate constant for a given radical adding its own monomer to the rate constant for its adding the other monomer. The reactivity of the monomer can be elucidated from studies on the composition of their copolymers. The relationship between instantaneous copolymer composition and monomer feed composition is given by the following differential equation[29]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (1)$$

where M_1 and M_2 represent the two comonomers.

Equation (1) is the copolymer equation in terms of the molar concentrations of the monomers. It is usually more convenient to express this relationship in terms of the mole fraction in both feed and copolymer. The feed mole ratio for monomer 1 is given by

$$f_1 = 1\text{-}f_2 = \frac{[M_1]}{[M_1] + [M_2]} \qquad (2)$$

The instantaneous copolymer composition is given by

$$F_1 = 1\text{-}F_2 = \frac{d[M_1]}{d[M_1]+d[M_2]} \qquad (3)$$

From which

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (4)$$

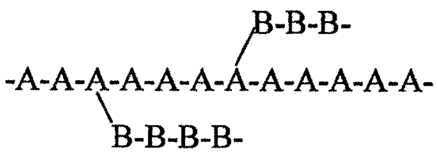
Equation (4) deals with the instantaneous composition of the copolymer. Since the comonomers generally do not enter the polymer in the same ratio as in the feed, the latter will drift in composition as copolymerization proceeds, becoming depleted in the more reactive comonomer. As a result, the higher the monomer conversion, the more heterogeneous is the product. It is therefore customary in fundamental studies to limit the conversion to below 10%[30]. On the other hand, lower the conjugation effect in the monomer, the higher will be the reactivity of the radical formed from it e.g. vinyl acetate (VAc), a monomer of low activity, can give a very active free radical. On the other hand, the active styrene monomer gives an inactive free radical. Thus, the rate of reaction of chain propagation depends on the reactivity of both the monomer and the free radical. A polarized monomer molecule will react more readily with a free radical.

The determination of reactivity ratios which provide important information concerning the behaviour of monomers and growing chains has required the determination of the overall comonomer composition of copolymers prepared from a series of feed ratios. Elemental analysis, IR, UV and NMR spectroscopy are most commonly used techniques. A number of computation and graphic methods such as those of Finemann-Ross and Kelen-Tudos were used to do this computation.

(ii) Application of copolymer composition equation :

The copolymer equation has been found applicable to almost all comonomer combinations and equally applicable and relevant to radical, cationic and anionic systems, despite wide variations in r_1 and r_2 values depending on the mode of chain propagation. If $r_1 > 1$, it means that the tendency of M_1 is to add preferentially to monomer M_1 instead of M_2. If r_1 has a value of less than unity, it means that M_1 adds to monomer M_2 preferentially. If $r_1 = 0$ it shows that M_1 is incapable of undergoing homopolymerization independently and prefers to alternate with another monomer, regardless of the composition of the monomer feed. A copolymer system is said to be ideal when the two radicals show the same preference for adding one of the monomer over the other. In this cases $r_1r_2 = 1$. The end group on the growing chain has no influence on the rate of addition, and the two types of units are arranged at random along the chain in relative amounts determined by the composition of the feed and the relative reactivities of the two monomers. Most actual cases lie between the ideal and alternating systems : $0 < r_1r_2 < 1$. A third possibility, with both r_1 and r_2 greater than unity, corresponding to the tendency to form block copolymer. Hence from the view point of chain architecture (sequence arrangement of monomeric units along the chain), copolymers composed of chemically different monomers can be classified into four categories i.e. random, alternate, block and graft copolymers[31,32].

- Random copolymers : where arrangement of the two monomers A and B along the chain are random fashion as
  -A-A-B-A-A-B-A-B-B-A-B-A-B-B-
- In case of an alternate copolymer the structure will be –
  -A-B-A-B-A-B-A-B-A-B-A-B-A
- Whereas a block copolymer will have a structure of –
  -A-A-A-B-B-B-B-A-A-A-B-B-B-B-
- The structure of the graft copolymer is likely to be



1.4 Polymer Characterization Using Various Techniques :

Polymer characterization is an essential step in working with the polymer[33]. The analysis of polymer systems continues to be a rapidly developing field of research particularly as many new applications become available with both new and established techniques that are capable of handling many of the intractable polymer systems. For the potential uses and commercial applications of new polymeric materials, it is desirable to characterize them for chemical composition, tacticity, sequence distribution of the monomer units in the polymer chain and correlate them with the physical and chemical properties of these copolymers[34]. Generally, these polymers were characterized by the following techniques.

(a) Elemental Analysis :

In past, elemental analysis techniques have been widely used to determine the chemical composition of the polymers. Percentage nitrogen present in the homo, co and tercopolymers of acrylamide, acrylonitrile, 2-vinyl pyrrolidone, 4-vinyl pyridine etc. with other vinyl monomers can be determined by the Kjeldahl[35] or Dumas methods. Nitrogen content in polyamide were also determined by using the above methods. Minor quantities of nitrogen may be determined by the Kjeldahl method in a procedure developed by Majewska[35]. Recently, Srivastava et al.[36] have reported the acrylonitrile content from N% and Cr content by gravimetric analysis in order to calculate the reactivity ratios of the tercopolymers of styrene-acrylonitrile-chromium acrylate. Ternary copolymerization of the three systems butyl methacrylate-, butyl acrylate- and styrene- with tributyltin methacrylate-acrylonitrile have been studied by Ghanem and others[37], and the tercopolymer composition of each system was determined through tin and nitrogen analysis. Bajaj et al.[38] have reported the determination of reactivity ratios of solution polymerized copolymers of acrylonitrile with various vinyl acids i.e. acrylic acid, methacrylic acid and itaconic acids by CHN, IR and ^{1}H-NMR analysis. The reactivity ratios thus obtained by different methods were found to be in good agreement with each other. Apart from C,H,N even Cl has been analysed for reactivity ratio determination for 7,7,8,8-tetrakis (ethoxycarbonyl) quinodimethane-maleic anhydride and 2-chloroethyl vinyl ether or p-chlorostyrene tercopolymers as reported by Iwatsuki et al.[39].

McCormick et al.[40] estimated the composition of copolymers and tercopolymers of acrylamide, acrylic acid and N-[(4-decyl)phenyl] acrylamide by a combination of elemental analysis and UV spectroscopy. W.M.Kulicke and coworkers[41] investigated the C:N ratio from elemental analysis to determine the composition of poly(acrylamide-co-sodium acrylate)s copolymer. The variation in feed ratios and the resultant copolymer compositions as determined by elemental analysis (C,H,N and S) for the random copolymers of acrylamide with sodium-2-sulfoethyl methacrylate and with sodium-2-acrylamido-2-methylpropane have been reported by McCormick and Chen[42].

(b) Spectroscopy :

(i) Infrared (IR) spectroscopy :

During the past four decades infrared spectroscopy has been established as a versatile and widely used technique for structural elucidation[1]. A substantial amount of literature exists regarding the use of infrared spectroscopy to determine the molecular structure and composition of polymers by analysing the characteristic vibrations of fundamental groups[43-46]. The majority of the functional groups present in polymers give characteristic bands in the infrared spectral region, thus facilitating their identification. Furthermore, the intensities of the characteristic bands are related to the concentrations of the functional groups in question, thus providing the basis for quantitative analysis[46]. The importance of IR spectroscopy is considerably enhanced by its ability to provide detail information on the microstructures and their relationships to the macroscopic properties of polymers[47]. This includes the way in which successive monomer units add on to the existing chain, both in the case of homo and copolymers, the configurational and conformational structures of the chains and the identification of defect structures and chain end-groups[47,48]. The determination of the crystallinity of polymer samples using IR spectroscopy has been extensively reviewed by Zerbi[49]. Numerous qualitative and quantitative applications have been reported[50,51]. They cover hydrocarbon and vinyl polymers and copolymers, the wide field of ester resins, polyurathenes, polyamides, polycarbonate, polyethers, polysulphones and fluoropolymers. Recently, the advent of Fourier transform infrared spectroscopy (FTIR) has brought about a revival of interest in IR spectroscopy as a characterization technique[52]. The increase speed and higher signal-to-noise ratio of FTIR relative to dispersion infrared has lead to a substantially greater number of applications of infrared in polymer research[52]. A sound understanding of the mechanisms whereby polymers degrade thermally and photochemically is of great importance for their commercial usage and FTIR spectroscopy offers considerable potential for studying the complex reactions occuring in the degradation of polymers. Coleman and Sivy[53] have extensively reviewed the degradation mechanism of acrylonitrile homopolymer and their copolymers with methacrylic acid (MMA), acrylamide (AM) and vinyl acetate (VAc) as well as their tercopolymers with VAc and itaconic acid. FTIR spectroscopic techniques have extensively been used to elucidate structure of homopolymers, copolymer and polymer blend systems by a number of workers[54-56]. Huang et al.[57] have confirmed the hydrolysis of vinyl acetate segment to vinyl alcohol in styrene-co-vinyl acetate block copolymer by appearance and disappearance of carbonyl peaks using FTIR spectroscopy. Martuselli and coworkers[58] have used FTIR spectroscopic technique to get direct indication of the existence of a copolymeric phase, in accordance with the indirect evidence provided by the calorimetry and the subsequent morphological investigation. The effect of tacticity on infrared spectrum of polyvinyl acetate (PVAc) was studied by Fujii[59]. He assigned the band at 1125 cm^{-1} corresponding to the conventional atactic PVAc. This band becomes weaker with decrease of syndiotactic structure and a new band appears at 1190 cm^{-1}. Apparently these two bands are associated with the syndiotactic and isotactic structure of the polymer, respectively. Beside the tacticity, crystallinity of polyvinyl alcohol was measured by using FTIR spectroscopy[60].

(ii) Nuclear magnetic resonance (NMR) spectroscopy :

Since 1960 the nuclear magnetic resonance (NMR) spectroscopy has become a major tool for the study of chain configuration, sequence distribution, and microstructure in polymers[61]. It is also established as a most effective and significant method for observing the structure and dynamics of polymer chains both in solution and in the solid state[62]. The stimulus for this growth was the demonstration in the early 1960s that high resolution ^{1}H-NMR could be used to determine the tacticity of some acrylic and vinyl homopolymers, and to assess the distribution of monomeric units in some simple addition copolymers[63,64]. The first major advance in the NMR technology was made in 1970s with the development of Fourier transform (FT) technique in NMR spectroscopy[65]. A significant increase in the sensitivity as compared to the conventional continuous wave method, resulted in the NMR spectroscopy of rare nuclei, particularly ^{13}C-NMR, which is essential for polymer studies. ^{13}C-NMR spectroscopy offers several advantages over ^{1}H-NMR for a polymer chemist[66,67]. ^{13}C resonance can be used to directly determine the skeleton of the polymer molecule. The resonance lines are narrow and the chemical shift range (in ppm) is much larger than for ^{1}H resonances. Furthermore, the shift depends on the structure of the molecule for upto three bonds in all directions from the site of interest. This means each shift becomes specific, and the structure can be easily assigned, frequently without any ambiguity[65]. The nearly complete absence of ^{13}C-^{13}C coupling broad band, decoupling of ^{13}C-^{1}H couple, avoidance of saturation using the pulse technique, add to the numerous advantages of ^{13}C over ^{1}H NMR spectroscopy. The main information that can be obtained from ^{13}C spectra are : absolute identification of specific arrangement of groups and microstructure of polymers, branching in macromolecules, analysis of sequence in copolymers, distinction between block and random copolymers, and analysis of microtacticity. High resolution ^{13}C spectroscopy in the solid state, achieved using high power proton decoupling, ^{1}H-^{13}C cross-polarization, and magic angle spinning (MAS) also has generated much interest to the determination of polymer structure[68].

Recent progress in high resolution NMR spectrophotometer having superconducting magnet permit greater sensitivity and resolution and thus offer more detail analysis of microstructures in polymers. The versatility of a 500 MHz spectrometer for microanalysis is recently reviewed by Hatada and coworkers[69]. One of the straight forward application of NMR microanalysis to polymer characterization is the molecular weight determination through end group analysis. The quantitative determination of the relative intensities of the signals due to the end group compared to that of the signals due to the monomeric units is a simple and straight forward way to determine the number average molecular weight (M_n)[70]. For example, the ^{1}H-NMR spectrum of the PMMA in nitrobenzene-d_5 shows distinct signals due to t-C_4H_9 (initiator fragment at end of the polymer chain) and OCH_3 (in monomeric units). The relative intensity of these signals provides the M_n :

$$M_n = I\,(OCH_3) / I\,(t\text{-}C_4H_9) \times 3 \times 100.14 + 58$$

The M_n values thus determined by 100 MHz ^{1}H-NMR spectroscopy agree well with those determined by gel permeation chromatography (GPC) and vapor pressure osmometry (VPO)[71]. Kitayama et al.[72] analyzed graft copolymers of PMMA macromonomer and MA monomer by ^{1}H-NMR spectroscopy for the determination of number of branches and M_n.

NMR chemical shift prediction by quantum chemical calculation and the γ-gauche effect method has become a useful approach for the stereochemical assignments of vinyl polymers. Recent successful ^{13}C-NMR assignments based on γ-effect and the rotational isomeric model were demonstrated for a series of polyolefins : poly(1-pentene) to poly(1-octene)[73]. Bovey[74] has examined tacticity data by stereochemical assignment of ^{1}H- and ^{13}C-NMR spectra of various vinyl polymers. Two dimensional NMR spectroscopy has recently been used to make absolute tacticity assignments. One of the earliest successful example is ^{1}H COSY analysis of polyvinyl alcohol[75]. Chang et al.[76] applied ^{13}C-^{1}H COSY to identify the ^{1}H and ^{13}C resonances belonging to the m and r diads in poly(vinyl amine). Advantages of two dimensional NMR spectroscopy have been successfully applied to the copolymer of vinylidene chloride and isobutylene for the assignment of monomer sequence of this copolymer[77]. Recently, Ernst and coworkers[78] demonstrated two dimensional ^{1}H spin-diffusion experiments for the investigation of miscibility in a blend of poly(methyl vinyl ether) and polystyrene. Brar and Dutta[79] have assigned the overlapping ^{13}C-NMR spectra of the acrylonitrile-glycidyl methacrylate copolymers without ambiguity with the help of DEPT experiments. The various compositional / configurational sequences were assigned to triad, tetrad and pentad sequences with the help of the inverse HETCOR (HSQC, heteronuclear single quantum correlation) and DEPT experiments. 2D inverse-HETCOR and TOCSY (total correlation spectroscopy) experiments were used for complete assignments of the overlapping and broad proton spectra of the copolymers. ^{13}C-NMR investigation used for the determination of the sequence distribution of poly(acrylamide-co-sodium acrylate) copolymers prepared in inverse microemulsions has been reported by Candau and coworkers[80]. The effect of reaction medium (i.e. solution and inverse emulsion) on reactivity ratios of both the monomers were seen. Bajaj and others[81] also calculated the tacticity and sequence length distribution of acrylonitrile-co-vinyl acids (i.e. itaconic acid, acrylic acid and methacrylic acid) copolymers using ^{13}C-NMR spectroscopy from C≡N and CH signals. Messiha et al.[82] have worked on estimation of the composition of tercopolymers of N-acryloyloxyphthalamide and N-methacryloyloxyphthalamide with methyl acrylate, methyl methacrylate and acrylonitrile by using ^{1}H-NMR spectroscopy. A recent report by Heatley and coworkers[83] discuss the sequence distribution using solution state ^{1}H-NMR spectroscopy and morphological changes occuring during surface erosion using solid state ^{1}H- and ^{2}H-NMR spectroscopy. The erosion of the melt fabricated polyanhydride copolymers formed from 1,3-bis(p-carboxyphenoxy) propane and sebacic acid were carried out in pH 7.4 phosphate buffer at 37°C.

(c) Thermal Analysis :

Thermoanalytical techniques are being extensively used for polymer characterization. The temperature dependence of some mechanical / physical properties and their relationship to polymer structure[84] is important. These involve a group of techniques in which properties are measured as a function of time or temperature, keeping every other variable constant[86]. Amongst them are the most common techniques like Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC).

(i) Thermogravimetric analysis (TGA) :

The three main reasons for the widescale use of TGA in polymer analysis are : phase changes can be studied via the heats of transitions, temperature affects the rate of reaction of most chemical processes, and complex molecules can be studied from fragments produced by pyrrolysis[87]. A thermal analysis curve is interpreted by relating the measured property versus temperature data of chemical and physical events occuring in the sample. Thermogravimetry is, in principle, a simple technique that provides kinetic information on the degradation, oxidation, evaporation, or sublimation of samples in any condensed form[88]. In thermogravimetry, the sample is heated and weighed continuously to study polymer degradations. The mass loss observed in TGA can be due to the decomposition and evolution of gases from solids[89]. The most common usage of TGA is in measuring the thermal and oxidative stability of polymers under working conditions. It is also used to investigate the thermal decomposition of polymers and associated kinetic parameters[90,91] i.e. the reaction order, frequency factor and activation energy. Evaluation of these parameters are important in elucidating the mechanism involved in polymer degradation.

Varma and coworkers[92] have used TGA technique to evaluate activation energy for the degradation of methyl methacrylate-2-ethylhexyl methacrylate (MMA-co-EHMA) copolymers. A decrease in thermal stability was observed by an increase in EHMA content. Varma et al.[93] also investigated the thermal behaviour of copolymers of MMA with iso-octyliso-decyl methacrylate using dynamic thermogravimetry, mass spectroscopy and pyrolysis gas chromatography. The degradation in homopolymers as well as copolymers proceeded by predominant loss of monomer (depolymerization). A good review on thermal degradation of linear vinylic polymers in dynamic conditions has been published by Schneider[94].

(ii) Differential scanning calorimetry (DSC) :

Differential scanning calorimetry (DSC) has also become an indispensable tool for polymer characterization over the last two decades. As almost all physical or chemical change occurs with a change in enthalpy, all changes can be followed by calorimetry. Similarly, thermal properties expressed through enthalpy, entropy and Gibbs energy can be evaluated by calorimetry using heat capacity and heat of transition measurements from O°K to the temperature in question[95,96]. DSC is often used in conjunction with TGA to determine if a reaction is endothermic such as melting, vaporization and sublimation or exothermic such as oxidative degradation[97]. It is also used to determine the glass transition temperature (T_g) and measure the specific heat changes in the T_g region, where there is an abrupt energy change[98]. The apparent T_g varies with sample thermal history, rate of cooling and subsequent heating. The sample and the reference material are maintained at an isothermal condition by the required flow of electric energy, as they are heated or cooled at a linear rate. The heat flow is recorded directly ($\Delta H/\Delta t$) in mcal/sec as a function of temperature in a DSC unit[96].

David et al.[99] have investigated the miscibility of the polymers (polycaprolactum and polyvinyl alcohol) in the amorphous part of the blend by using DSC, optical microscopy, FTIR and solid state-NMR techniques. DSC study carried out for all the extruded films of poly(lactic acid) and polyvinyl acetate (PVAc) blends were amorphous and the blends were compatible as only one glass transition temperature was observed[100]. He also reported that the mode of degradation differs for the aged and deaged samples. Li and others[101] have used various techniques such as SEC, DSC, WAXD, IR and NMR to monitor the change in molar mass, thermal stability, degree of crystallinity and composition on degradation of polylactic acid / polyethylene oxide / polylactic acid triblock copolymers. Recently, based on Ozawa equation, Chee et al.[102] have developed a novel approach to study the non-isothermal kinetics of polymers using DSC methods. A semicrystalline polyimides prepared from 1,3-bis(4-aminophenoxy) benzene and 3,3',4,4'-biphenyltetracarboxylic dianhydride was subjected to various cooling rates (2 to 200°C/min) from the melt[103]. A unique feature of this polyimide in DSC trace was the quenching of the polymer from the melt, even at very high cooling rates, did not result in an amorphous polymer, implying a very high crystallization rate from the melts.

(d) Solution Properties :

Rheology is important for polymer solution[1]. The most useful and common method employed in this is the dilute solution viscometry. The solution viscosity is helpful to determine polymer molecular weight and it has been well recognized since the early work of Staudinger and has continued to be useful even today[104,105]. The simplicity of measurement of viscosity molecular weight and its usefulness is so much that the viscosity measurement constitutes an extremely valuable technique for characterization of polymers[106]. This quantity provides a wealth of information relating to the size of the polymer molecule in solution,, including the effects upon chain dimensions of polymer structure, molecular shape, degree of polymerization and polymer-solvent interactions[107]. The viscometry depends on several factors, namely, the nature of the polymer and that of the solvent, polymer concentrations, the polymer molecular weight, and also the temperature[108]. The branching in the polymer chain increases the segment density within the molecular coil. Thus a branched molecule occupies a smaller volume and has a lower intrinsic viscosity than a similar linear molecule of the same molecular weight[105]. In case of copolymers, the presence of second monomer causes the dilute solution behaviour far more complex than that of the homopolymers. Copolymer composition and composition distribution, and the sequence length distributions of the two co-units are the most obvious additional factors which affect the intrinsic viscosities of copolymers. However, interactions between unlike segments, and preferential interaction of solvent molecules with one of the co-units are also of considerable importance. The use of a solvent which is a good solvent for both the corresponding homopolymers is strongly recommended. This is particularly important for block and graft copolymers, since they undergo aggregation / micellization when the solvent is a good solvent for one homopolymer but a poor solvent for the other[109,110]. Recently, many researchers used mixed solvents to study the viscosity behaviour in solution[111,112]. The rise in temperature of polymer solution generates two effects opposing each other[113]. The variation of intrinsic viscosity $[\eta]$ with temperature is dependent upon the relative importance of the following two properties : Firstly, on increasing the temperature, the solubility or solvent power generally increases which may lead to uncoiling of polymer chains and hence lead to increase in $[\eta]$ values. On the other hand, the rise in temperature may lower the rotational barrier, thereby enhancing the degree of rotation about a skeletal bond forcing the molecular chain to assume more compact coiled conformation. This results in a decrease in $[\eta]$ with increase in temperature[113,114]. The polyelectrolyte solutions show increase in viscosity because of the variations in the degree of dissociation of their ionizable side groups[115,116] and their interactions with the solvent. This data can be treated by the empirical relation proposed by Flory to determine $[\eta]$. This effect can be suppressed by use of 0.1 to 1.0 $mol.dm^{-3}$ inert electrolyte as the solvent and intrinsic viscosity can be easily evaluated[117]. The viscosity characteristics of polyamide solutions show unique dependence on time[118]. Many studies have been carried out on the complexities of the solution behaviour of PAM and its copolymers[119,120]. Vangani and Rakshit reported the viscosity behaviour of homopolymers of 2-ethyl hexyl acrylate and its copolymers with acrylamide (AM), acrylonitrile (AN) and methyl methacrylate (MMA)[113]. Radic and Gargallo[121] have studied the solution behaviour of mono- and diitaconates copolymerized with vinyl pyrrolidone. The effect of side chain length on viscosity behaviour and unperterbed dimension of the copolymers were investigated. The intrinsic viscosity of sodium polyacrylate in sodium bromide solution as a function of molecular weight was reported by Noda and coworkers[116]. The effect of two nonionic surfactants $C_{12}E_5$ and $C_{12}E_8$ on the viscosity of hydrophobically modified sodium polyacrylate was determined. The differences in viscosity between the two surfactants was observed due to change in alkyl group to surfactant ratio[122]. Kansara et al.[111] have studied the solution behaviour of poly(2-methyloxy cyanurate) in various solvent systems to get an insight on the conformational behaviour of this polymer. Recently, the characterization of branched polyethyleneimine (polyelectrolyte) have been carried out by means of viscometry as well as by laser light scattering at 35°C. The weight average molecular weight, M_w, the second virial coefficient, A_2^*, the Z-average radius of gyration, R_G, the Z-average effective hydrodynamic radius, R_H, the intrinsic viscosity $[\eta]$, and the Huggins coefficient, K_H, were all determined in 1M aqueous NaCl solvent.

(e) Morphology :

(i) Scanning electron microscopy (SEM) :

In the last few years the scanning electron microscopy (SEM) has been widely used, particularly to examine the morphology of polymers[124]. It has the advantage of an enormous depth of focus and wide range of magnifications. This equipment has been used for three dimensional observation of polymers[125]. The material unsuitable for replication or those which have too much geometric relief also could be examined[125]. The SEM is used almost exclusively for studies of polymers; adhesives, dental filling, filled polymers, glass-fiber rainforced plastics, organic coatings, fracture mechanics, foam plastics etc. In case of adhesive, the SEM images indicate whether the bonds themselves fail under stress, or if it is either the bulk phase of the adhesive or the adjoining material that breaks away. The SEM is again an excellent research tool in dentistry, to determine surface and bonding strengths of these polymeric materials, and their adhesion to the natural tooth material as a function of surface preparation and subsequent treatments. The effect on adhesion of varying the structure of the anodic film and the topography of the polymer surface in contact with this anodized aluminium was studied in detail using scanning electron microscope[126]. Filled and fiber-reinforced plastics can be fruitfully investigated with the SEM by observing exposed and fracture surfaces made at room temperature and at liquid nitrogen temperature which can explain polymer performance in actual usage. Organic coatings may be studied with the SEM to arrive at a better understanding of pigment dispersion, flow and adhesion of binder to pigment and substrate, blistering, and cracking or swelling of paint films in water. The presence of succinic anhydride causes a finer dispersion of ethylene-co-vinyl acetate in polyamide and was investigated using calorimetry and scanning electron microscopy[127]. Polymer foams, extrusion or molding performance of plastics may be monitored with the SEM. Qutubuddin et al.[128] investigated morphology of the composites resulting from microemulsion polymerization of styrene and acrylamide using anionic, cationic and zwitterionic surfactants. The SEM studied reveal that the morphology behaviour of the composites are strongly influenced by the type of surfactants.

de Souza and Baird[129] has reported the use of SEM technique to study the morphology developed during the injection moulding of poly(ether imide) and the thermotropic liquid crystalline polymers (i.e. vectras A and HX100) blends which is important to understand the mechanical properties of the blends. Krause et al.[130] used SEM technique to examine the surfaces of the ethylene-co-vinyl acetate copolymers with different topography. This was because of the different methods of preparation. Melt processed and annealed films had surface structures that looked like spherulites whereas solution and spin cast films appeared to consist of thick fibres with no definite spherulitic structures. The formation of stable macroradicals of poly(vinyl acetate) by heating vinyl acetate (VAc) and 2% tert-butyl peroxypivalate was monitored by yield, dilatometric rate data, and scanning electron micrographs[131]. The SEM investigation reveal that the size of the spheres in which VAc macroradicals polymerized was independent of the viscosity but appears to be related to the solubility parameters of the poor solvent.

(ii) Wide angle x-ray diffraction (WAXD) :

The x-ray diffraction technique is important to investigate morphological studies of polymer particularly with bulk specimens. Much information can be derived concerning the size of crystallines and relative amounts of order and disorder in the samples on the atomic and molecular scale[132]. It has been applied primarily to crystalline or semicrystalline polymers and leads directly to structural interpretations in terms of two phases like crystalline and amorphous[133]. The diffraction of x-rays from crystalline polymers gives rise to sharp diffraction lines. The detail information on the state of order of a crystalline material may be obtained from the analysis of the intensity, position, and line width of the diffraction lines. The degree of crystallinity and texture of the crystals (i.e. the shape and size of the crystallites, their forms of aggregation and their aggregation in bulk sample) in the polymeric material may be studied as functions of the preparative procedure. In some instances it has been applied to completely amorphous polymers in an attempt to derive structural information[133], since all amorphous polymers exhibit one or two halos at equivalent Bragg spacings of between about 3 and 10 Å. By the position (i.e. Bragg angles) and intensity of the diffraction, it is possible to deduce information concerning the unit cell dimensions, molecular geometry and packing of the chains[132].

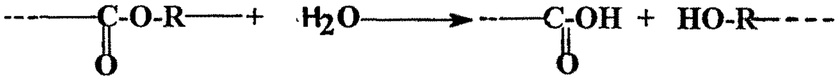
Stein and his coworkers[134,135] reported dynamic x-ray diffraction to study the changes of orientation with time in the crystalline regions. Very recently, Hudson et al.[136] investigated morphology of diacrylate copolymer network [4,4'-bis(acryloyloxy) biphenyl-co-4,4'-bis(6-(acryloloxy)hexyloxy)bisphenyl] formed in liquid crystalline medium. The morphology of this polymer networks were manipulated by blending different monomers of nearly equal reactivity and copolymerizing them in appropriate conditions. The WAXD profiles of the specimens of pure poly(ethylene terphthalate) (PET) and statistical copolyester containing 60 mol% p-oxybenzoate and 40 mol% ethylene terphthalate were measured in situ as a function of temperature[137]. The well developed crystalline diffraction peaks was observed in pure PET whereas diffraction peaks relevant to the copolyester are quite few and small The mechanical properties exhibited by thermotropic liquid crystalline polymers / poly(ether imide) blends was extensively studied using x-ray diffraction, blend rheology and interfacial energy measurements[129]. The rates of enzymatic erosion with change in crystallinity of the films of (3-hydroxybutyric acid) homopolymer and their copolymers with 3-hydroxyvaleric acid were studied by x-ray crystallography[138].

1.5 Polymer Degradation :

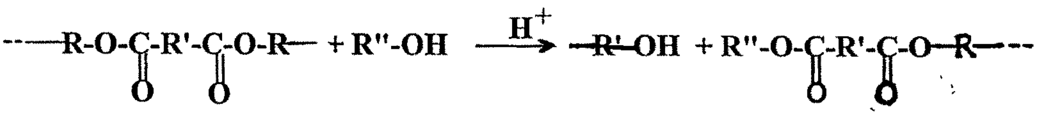
All polymers are degraded eventually within the environment to which they are exposed during their life cycle. Though there is considerable variation between polymers in their resistance to degradation, eventually important properties of every polymers are affected adversely as those chemical reactions responsible for degradation process occur[3]. The polymer degradation process is characterized by an uncontrolled change in the molecular weight or constitution of the polymer[139,140]. It is difficult to give a clear definition of polymer degradation. In a broad perspective, it is the undesirable change that occurs in a polymer affecting its physical and chemical properties. Degradation of polymers occurs because of the effect of environment such as, heat, light, high energy radiation, atmospheric oxygen, ozone, moisture, acids, alkalies and other chemicals, mechanical forces, microorganisms etc. on the polymer. The backbone structures of different polymers tend to degrade by two distinct mechanisms / processes i.e. hydrolytic or thermal process.

(i) **Random degradation** : Any chain rupture or scission occurs at random points along the chain, leaving fragments that are usually large compared to monomer units. The hydrolytic degradation of polymers e.g. polyester, polyamide takes place randomly. Drop in molecular weight is quite severe and drastic even for limited degradation of polymers.

- **Polyester**

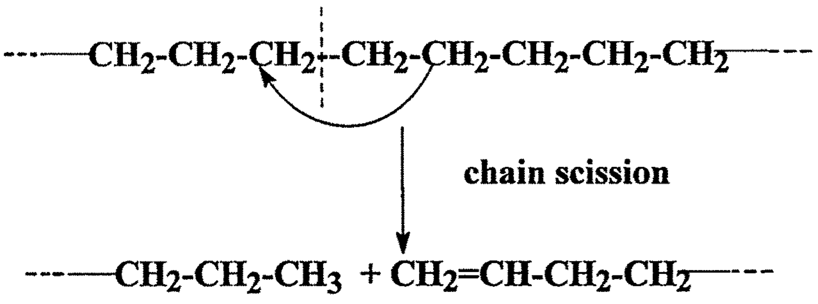


$$\text{---}\underset{\underset{O}{\|}}{C}\text{-O-R—} + H_2O \longrightarrow \text{---}\underset{\underset{O}{\|}}{C}\text{-OH} + \text{HO-R---}$$



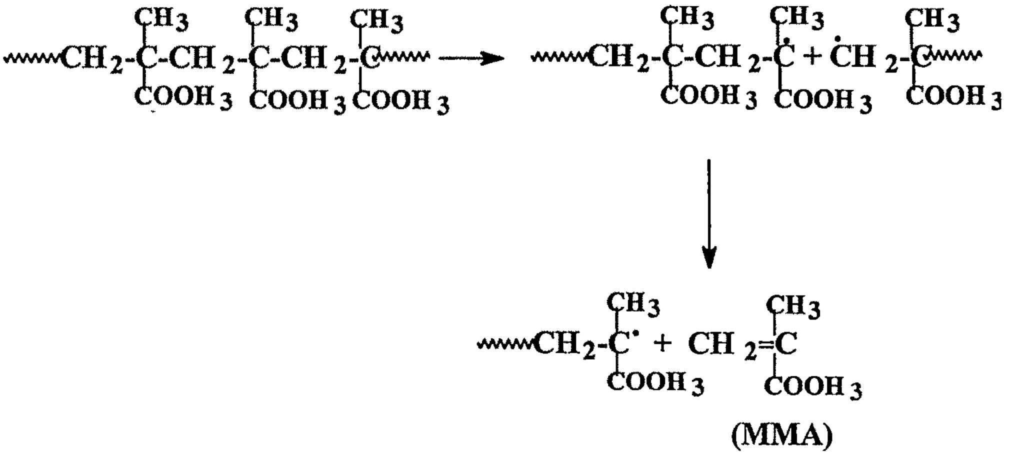
$$\text{---R-O-}\underset{\underset{O}{\|}}{C}\text{-R'-}\underset{\underset{O}{\|}}{C}\text{-O-R—} + \text{R''-OH} \xrightarrow{H^+} \text{—R'-OH} + \text{R''-O-}\underset{\underset{O}{\|}}{C}\text{-R'-}\underset{\underset{O}{\|}}{C}\text{-O-R---}$$

- **Polyethylene**



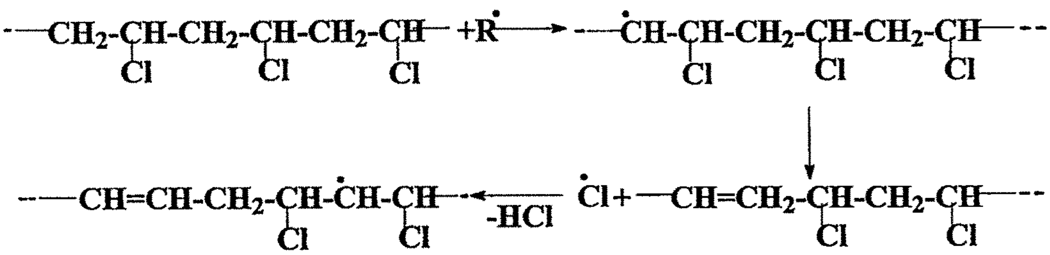
$$\text{---}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{---} \xrightarrow{\text{chain scission}} \text{---}CH_2\text{-}CH_2\text{-}CH_3 + CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{---}$$

(ii) **Chain-end degradation** : In this process, the degradation starts from the chain ends, resulting in successive release of the monomeric units. The result is that the molecular weight of the polymer decreases slowly and a large quantity of the monomer is liberated simultaneously. PMMA is prone to degradation under heat to yield MMA monomer.

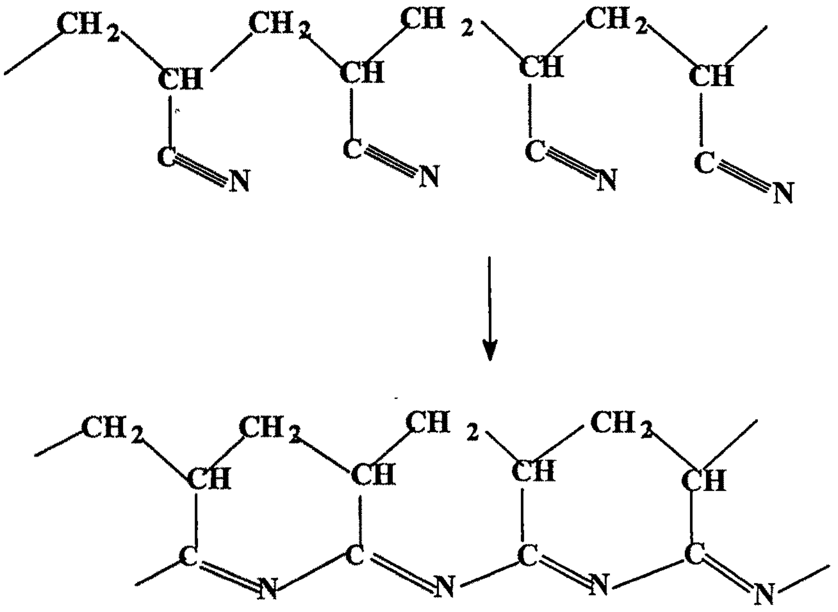


(a) Thermal Degradation :

Degradation of polymers at elevated temperature may follow either '*unzipping*' or the '*random*' route. The '*unzipping*' mechanism gives the pure monomer, while random degradation reaction are basically substituent reactions in that the substituents attached to the main polymer chain backbone are partially or totally modified or eliminated. This leads to major changes in the chemical nature of the repeat units in the macromolecular structure and the volatiles liberated in such cases are chemically unlike the monomer. In the absence of oxygen, poly(vinyl chloride) degrades thermally by sequential elimination of hydrogen chloride which leads to discoloration[141,142].

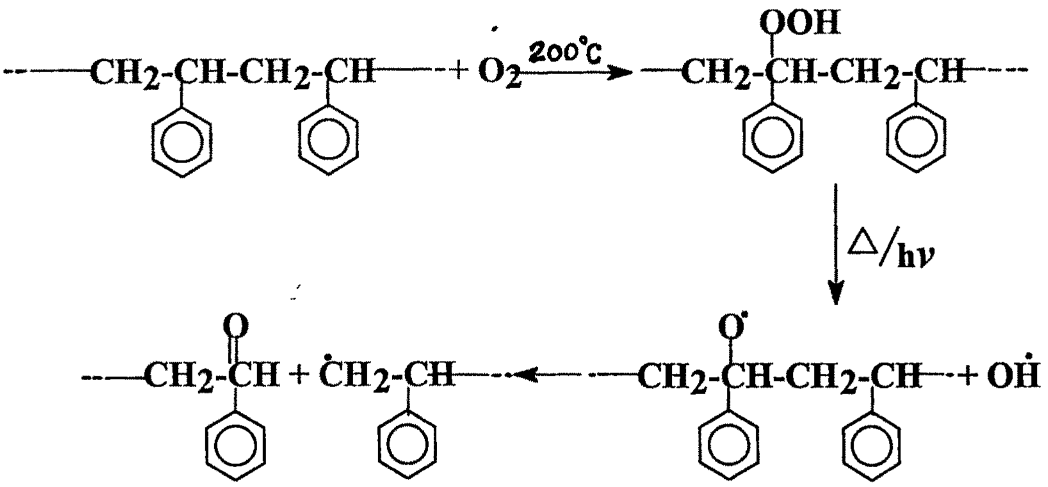


On heating, PAN undergoes cyclization with few volatile products such as ammonia and hydrocyanic acid[143].

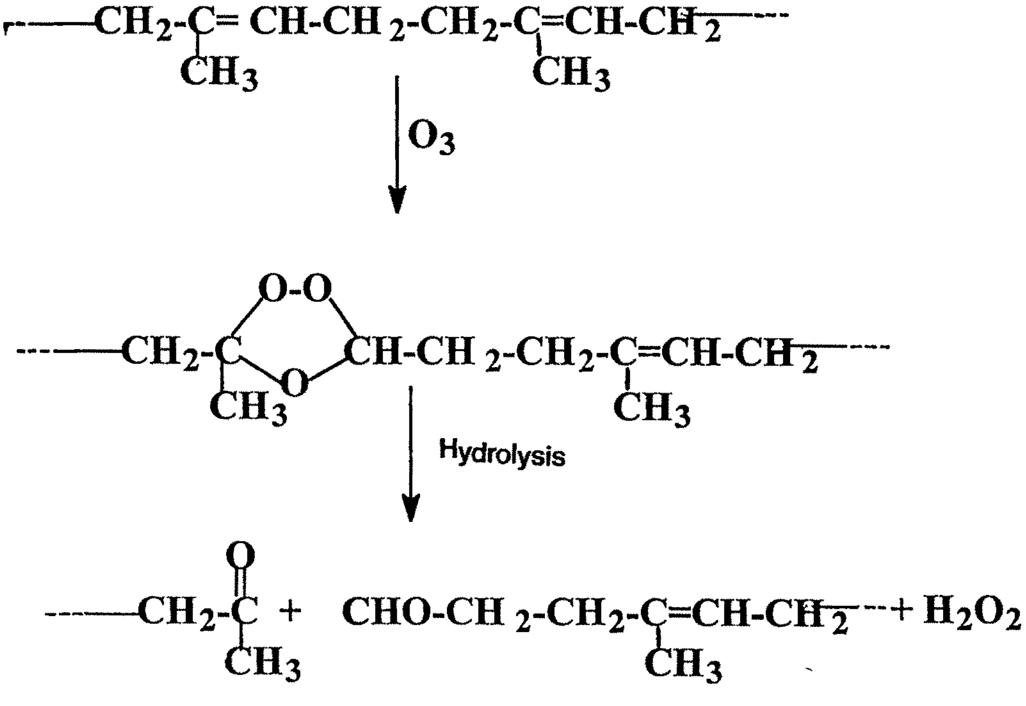


(b) Oxidative Degradation :

Oxidative degradation usually leads to hardening, discolouration as well as surface changes. The primary attack by oxygen leads to hydroperoxidation and the hydroperoxides formed subsequently decompose radically under heat / light with the onset of a chain process that ultimately results in chain degradation[144,145].



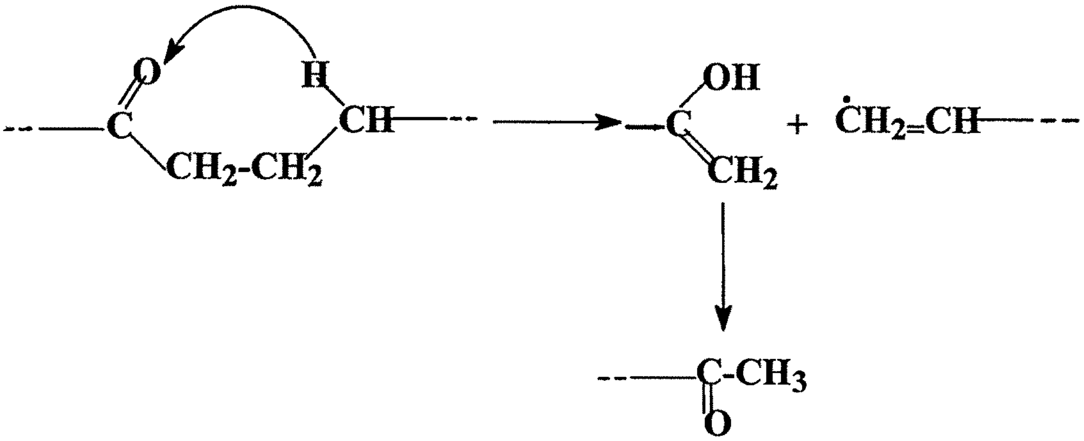
Atmospheric ozone adds itself to the double bond of many elastomer or unsaturated polymers to form an ozonide followed by hydrolysis which cleaves the original double bond (from which the ozonide is formed) to produce ketonic and aldehydic groups[2].



(c) Photochemical Degradation :

Photodegradation of polymers is of great practical importance because of the light – polymer interaction. Degradation by light is rather selective in nature. Specific groups would absorb light of given wavelengths and induce degradation (reactions occuring upon irradiation of polymers). Photodegradation of polymers play an important part in ageing processes, and often determine the lifetime of natural and synthetic fibres, rubber, goods, plastics and coating. The chief process causing the change in properties of the polymer is in most cases the photochemical chain reaction of scission of its molecular chains, activated by atmospheric oxygen[146].

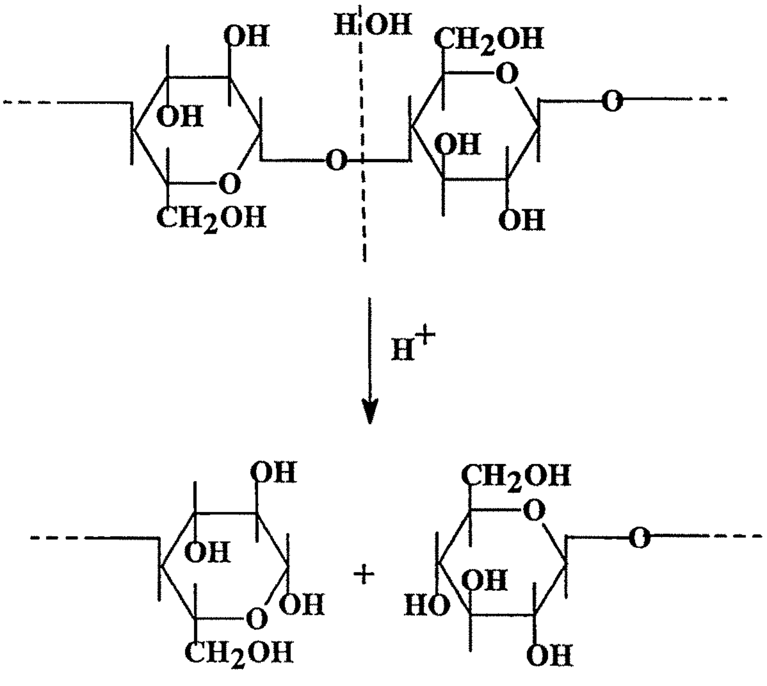
The polymers containing unsaturation, aromatic or carbonyl group, homolytic bond fusion etc. will occur readily to give free radicals. These radicals can then react with any oxygen present, leading to the oxidation of polymer chain. This is the phenomenon of '*ageing*' or '*weathering*' occasioned by irradiation with sunlight. The carbonyl group present in ethylene-co-carbon dioxide copolymer, make it more photo-labile, on exposure to UV irradiation a methyl ketone and a vinyl unsaturation are generated[147].



(d) Chemical Degradation :

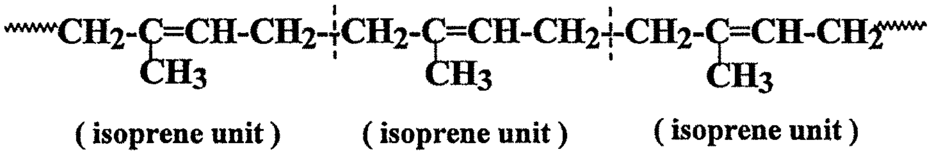
Chemical degradation proceeds under the action of polar substances such as water, acids, amines, alcohols, or oxygen. The most common type of chemical degradation of polymers is 'hydrolysis' – cleavage of a chemical bond with addition of a water molecule. Hydrolysis is catalyzed by hydrogen or hydroxyl ions. The hydrolysis of some polymers is accelerated in the presence of natural catalysts, namely, enzymes, which act selectively on the nature of the functional groups and bonds it is composed of. Hydrolysis of side functional groups changes the chemical composition of the polymer; hydrolysis of bonds in the main chain results in degradation and lowers the molecular mass of polymer.

Of great practical importance is the hydrolysis of natural polyacetal-polysaccharides. Complete hydrolysis of starch and cellulose gives glucose.



(e) Mechanical Degradation :

Agitation, grinding or extrusion, vigorous stirring or beating and mastication of rubber are well known methods for effecting the mechanical degradation of the polymer[148,149]. The basic phenomenon in all these is same; namely, to subject the polymer to a very powerful shearing force that breaks the molecule. In rubber i.e. polyisoprene, the bonds which are most vulnerable for scission are the CH_2-CH_2 links between the isoprene units. These bonds in the susceptible regions cleave when the polymer is subjected to mechanical stresses in the form of milling or mastication. The net effect is that the big molecule is broken or scissioned into small parts i.e. isoprene units[150].



$$\sim\sim CH_2-\underset{CH_3}{C}=CH-CH_2 \vdots CH_2-\underset{CH_3}{C}=CH-CH_2 \vdots CH_2-\underset{CH_3}{C}=CH-CH_2\sim\sim$$

Polyisoprene

(f) Biodegradation :

For many biomedical, agricultural and ecological purposes, it is preferable to have a biodegradable polymer that will undergo degradation in the physiological environment or by the microbial action in the soil. The term '*biodegradable polymer*' refers to a polymer which undergoes enzymic degradation in the physiological or microbial environment and where the secretion of degrading enzyme(s) is linked to a chemically recognizable cleavage of the molecular structure of the polymer[151,152].

It must be recognized herewith that evolutionary forces in microbiological development and the ability of microorganisms, essentially soil borne, to dramatically degrade the newer synthetic plastics will be governed by the gradual introduction of these new synthetic polymers into the soil, water and other habitats of these organisms. These evolved organisms eventually can be expected to be better indicators for determining the vulnerability of new polymeric materials[153]. The biodegradation of polymers proceeds via hydrolysis and oxidation. Most of the biodegradable synthetic polymers and biopolymers contain hydrolysable groups along the main chains. Initial studies of biodegradation mechanisms were motivated by biomedical applications of biodegradable polymers[154].

Biodegradation results when the organisms (i.e. bacteria, fungi and algae) secrete extracellular depolymerises which degrade the polymer into low molecular weight, water soluble species which are then readily absorbed through the cell wall and metabolized. Under aerobic conditions, the degradation products are carbon dioxide, water and some organic material. Methane is the main degradation product under anaerobic condition[155,156].

Microbial degradation of natural polymers involves initial hydrolysis of these polymers by water-soluble extracellular enzymes to yield low molecular weight oligomers, which are then taken inside the cell. These low molecular weight oligomers are further hydrolyzed and oxidized by various intracellular enzymes. On the other hand, most synthetic carbon-based polymers are inert towards microorganisms in the form in which they are initially produced. In order that the carbon nutrients which they contain can be made available to the biological cell, they must be first transformed by a variety of chemical reactions to low molecular weight metabolites that can be absorbed by the cell[157]. These reactions are sometimes induced by oxidative enzymes, following the colonization of cells on the surface of the polymer. This is in turn followed by surface erosion[158].

For example, in case of elastomeric poly(hydroxy butyrate) (PHB) and poly(hdroxy butyrate-co-hydroxy valerate) (HB/HV) copolymers, it has been shown that biodegradation occurred in aerobic and also in anaerobic microbially active environments. According to Cox, the degradation rate of these polymers depends on moisture level, nutrient supply, temperature and pH[159]. Biodegradation appeared to proceed by colonization of the polymer surface by bacteria or fungi, which secreted an extracellular depolymerase capable of degrading the polymer in the vicinity of the cell. The soluble degradation products were then absorbed through the cell wall and metabolized. Accordingly, enzymatic activity resulted in surface erosion and the thickness of PHB injection moulded bars gradually decreases with time in an aerobic environment[159].

In case of polyvinyl alcohol (PVA), it is first oxidized into β-diketone by PVA-oxidase or PVA-dehydrogenase, followed by means of β-diketone hydratase to cleave the polymer chain[160]. Suzuki et al.[161] formulated the following scheme of degradation of polyvinyl alcohol by a *Pseudomonas* strain(Fig. 1.2).

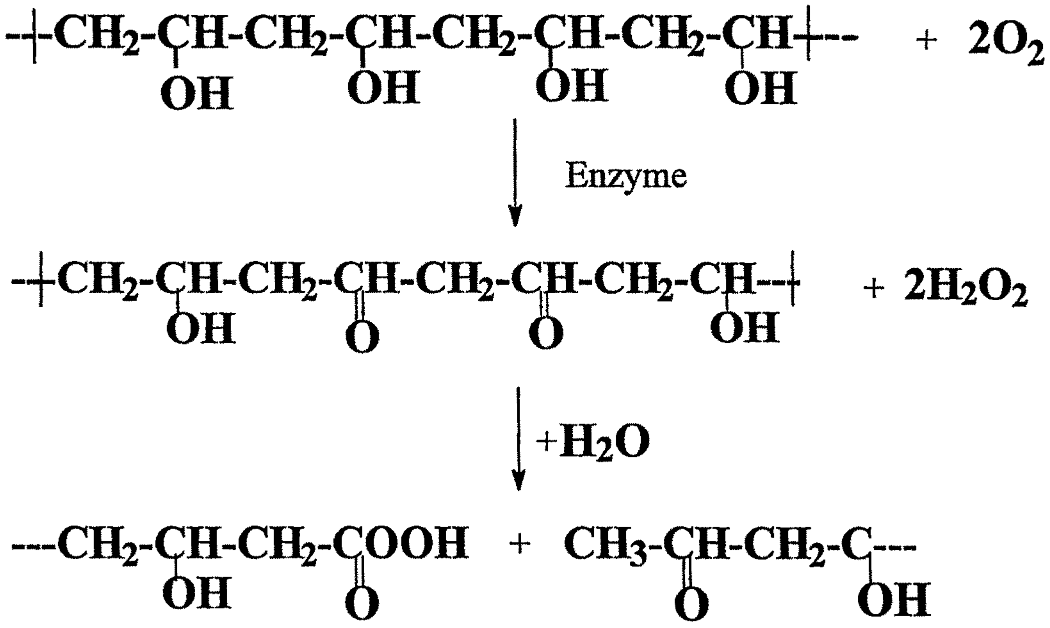


Figure 1.2 Mechanism of polyvinyl alcohol degradation by*Pseudomonas strain.*

Hatakeyama et al.[162] synthesized poly(3-methoxy,4-hydroxy styrene). The biodegradation of this polymer was expected because of its pendant guaicyl group. The polymer was decomposed in the soil and the organisms effective for the degradation were '*Moraxell*' and '*Penicillium*' species. The degradative pathway proposed is shown in Fig. 1.3.

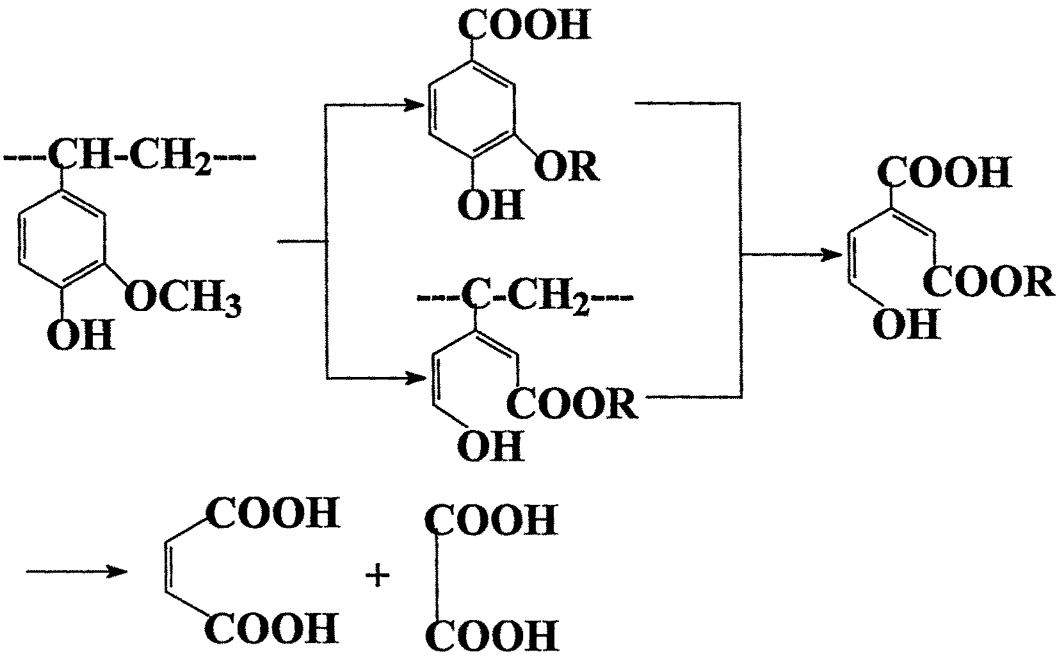


Figure 1.3 : Degradation pathway of poly(3-methoxy,4-hydroxy styrene) by *Moraxell* and *Penicillium* species.

It is also quite apparent that for the case of polymer (i.e. for both plastics and water solubles), all environmental degradation options as shown schematically in Figure 1.4 are applicable[163].

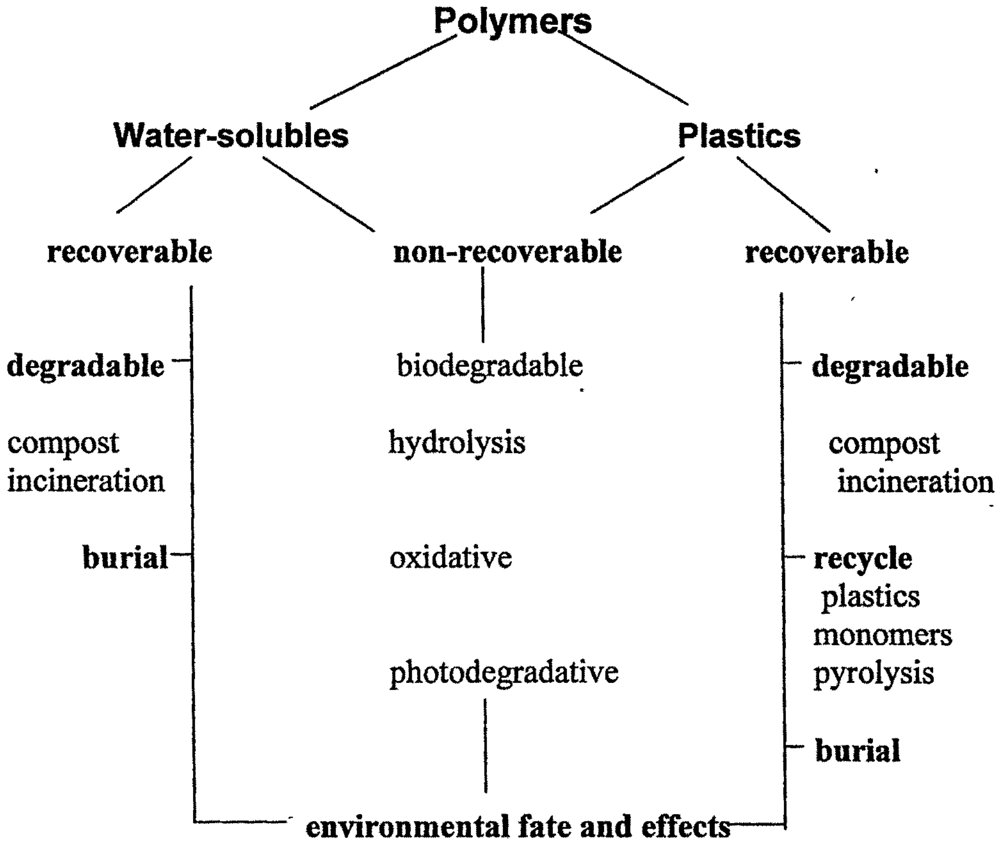


Figure 1.4 : Polymer waste-management options.

1.6 The Prospects for Biodegradable Polymers :

It is now almost fifty years since the first intentionally degradable plastic was made[164]. Since the time, increasing concern has been expressed by environmentalists about the escalation of plastic litter in the sea and on land[165] and with it has come the need to find more effective ways of dealing with plastic waste and litter. ***'Biodegradable'*** polymers such as polyolefins, polyesters, polyanhydride, polylactones, polyamides, etc. have been widely evaluated in at least four main fields : packaging material; mulching films in agriculture; disposable items in waste and litter where they will be mineralized (totally degraded) saprophytically, and in medical applications i.e. '*in vivo*' application in the human and animal body, where degradation must proceed in a way resembling parasitic process[166].

It is now widely recognized that along with the importance of synthetic polymers possessing long term stability, there is also a need for polymers that break down in a controlled manner specifically for controlled degradation under the inherent environmental stress in biological systems either unaided or by enzyme-assisted mechanisms. Medical applications of these materials have led to significant developments, such as the controlled release of drugs, fertilizers and pesticides, absorbable surgical implants, skin grafts and bone plates[167]. Recent interest in polymer waste management for packaging materials has also added incentive to the research on biodegradable polymers. This is because of the current commercial and widely used plastic products which were developed for their durability and resistance properties, and after disposal they are visible in the environment as litter and they contribute to landfill overcapacity[168].

1.7 Biodegradable Polymers : Possible Approaches :

Biodegradable polymers are norm in nature and it would seem reasonable to imitate this feature in designing new polymers. The current attempts to develop biodegradable polymers have centered mainly around the following areas :

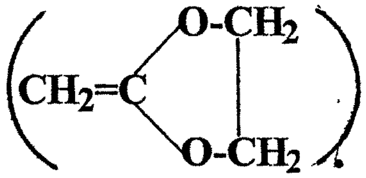
i) Synthesis of new biodegradable polymers
ii) Modification of natural polymers
iii) Modification of synthetic polymers
iv) Formulation of biodegradable polymer composites

The biological susceptibility of common synthetic polymers was reviewed by Heap and Morell[169] in 1968, Rodriquez[170] in 1971, Coscarelli[171] in 1972, Potts[172] in 1978, Kuster[173] in 1979, Kumar et al.[174] in 1983 and Amass and others[175] in 1998.

Polymers with an ester group on the backbone are often more prone to the biodegradation but at the same time are often less suitable than hydrophobic polymers for many technical applications. In 1962, polyglycolide (PGA) was developed as the first synthetic biodegradable polymer[176]. Slow-release system (i.e. bioabsorbable suture) is prime application where PGA has been useful. Incorporating two chemically different monomers in the same polymer chain is a well-established means of modifying polymer properties. This approach has been used for some time to obtain lactide / glycolide copolymers with properties between those of polylactide and polyglycolide homopolymers[176,177]. The rate of degradation of polylactide is increased by incorporating glycolide units into the polymer chain while the solubility of the polyglycolide is increased by incorporating lactide units into the chain structure. These copolymers have very good characteristics in applications where stiffer polymers are required.

Polymerization of ε-caprolactone and polymer properties were reviewed in detail by Brode and Koleski[178]. Polycaprolactone (PCL) have been shown to be biodegradable in both soil burial and fungal growth studies[179]. The polycaprolactone, an inherently susceptible material that can be tailored for the slower or faster rates of degradation, shows its potential utility as a biodegradable seeding container[180]. For packaging applications, by far the most promising possibilities today are based on poly(hydroxy butyrate) (PHB) and poly(hydroxy valerate) (PHV). The physical and mechanical properties of PHB can be regulated simply by changing the amount of hydroxy valerate (HV) unit in the P(HB-HV) copolymer and this copolymer is a potential biodegradable substitute for PP[181,182].

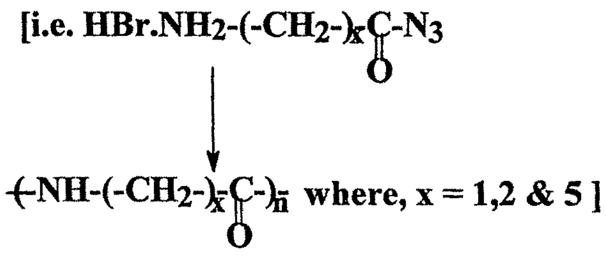
Addition polymers have generally been resistant to biodegradation, since the carbon-to-carbon bonds in the backbone are not very susceptible to enzymatic attack. Bailey et al.[183,184] reported for the first time an elegant way of introducing an ester functional group into the backbone of an addition polymer by a free radical process. One of the monomers investigated was ethylene ketene acetal



Polymerization of this monomer using free radical initiator (i.e. benzoyl peroxide at 140°C) gave a high molecular weight polyester. Since ethylene ketene acetal also copolymerizes with number of other vinyl monomers, it makes possible to prepare series of biodegradable polymers[183,184].

Very recently, aliphatic poly(ester-amides) containing α-hydroxy or α-amino acid moiety have been studied for their potential biomedical applications. Gansolves et al.[185] synthesized biodegradable poly(ester-amides) using anionic ring-opening copolymerization of ε-caprolactum and ε-caprolactone at 100-160°C with sodiocaprolactum as a catalyst. Helder and coworkers[186] studied the '*in vitro*' degradation of non-alternating glycine/DL-lactic acid copolymers. Barrows and others[187] also synthesized a series of alternating poly(ester-amides) by using two-step polycondensation reaction from glycolic acid, diamine, and diacoyl chloride and investigated the '*in vivo*' degradation of the copolymers for the purpose of developing new surgical implants. Tokiwa et al.[188] showed that poly(ester-amides), made by amide-ester interchange reactions of nylons and polycaprolactone, were degraded by lipase.

Bailey et al.[189] reported the synthesis of a new class of biodegradable polyamides viz. poly(β-alanine) (nylon-2), polyglycine (nylon-3), poly(ε-amino caproic acid) (nylon-6) etc., which by impressive chemistry, achieve both hydrophilicity and biodegradability. These polypeptides were synthesized through the polymerization of amino acid azide hydrobromide



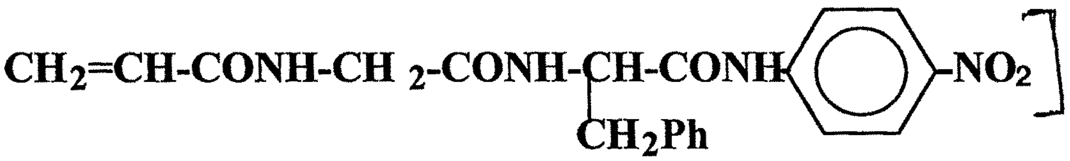
$$[\text{i.e. } HBr.NH_2\text{-}(\text{-}CH_2\text{-})_x\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}N_3 \;\longrightarrow\; \text{-}(\text{-}NH\text{-}(\text{-}CH_2\text{-})_x\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-})_n \text{ where, } x = 1,2 \;\&\; 5\,]$$

The copolyamide containing two different amide bonds (i.e. nylon 2/6 and nylon 3/4/6) were also reported[190] to be biodegradable (under aerobic conditions) based on the measurement of the release of carbon dioxide. A glycine containing polyamide i.e. nylon 266 [e.g. poly(N-(6-glycyl aminohexyl)adipamic acid] were prepared by interfacial polymerization of N-glycyl hexanediamine with adipoyl chloride for their potential use in replacing commercial non-biodegradable nylons in packaging and marine applications[191].

Incorporation of certain functional groups into polymers can markedly increase the activity of the carbon chains and hence increase the susceptibility of chain cleavage. Poly(alkyl-2-cyanoacrylate) was degraded and absorbed rapidly with acute tissue reaction[192]. Introduction of these cyanoacrylate moieties in the polymers, which form highly polarized polymers exhibiting reduced electron density on alternate carbon atoms and which have been postulated to undergo a reverse Knoevengel condensation reaction resulting in carbon-carbon bond scission[193].

Chiellini et al.[194] have reviewed the synthesis and semi-synthesis of multifunctional polymers and evaluated with the biodegradation and bioerosion. They have also assessed their potential of the polymers for controlled drug release in pharmaceutical and agricultural areas and in particular focussed on hydrophilic and/or water-soluble polymeric materials. Suzuki et al.[161,162] discussed the biodegradability of such water-soluble polymers as polyacrylamide (PAM) and polyvinyl alcohol (PVA) and the effect of ozonization on their biodegradability. Shimao and Kato also reported degradation of PEG and PVA in mixed cultures.

Copolymerization of a common monomer with a monomer possessing a polar functional group (i.e. acrylic acid) offers a conceivable route to enhance biodegradability; the polar functional groups might serve as points of attack for microbial enzymes[195]. Courtney et al.[196] reported biological degradation of acrylonitrile-acrylic acid and acrylonitrile-dimethylaminoethyl methacrylate copolymers. The degradation of these copolymer films has been studied in a continuous '*in vitro*' rumen system. Fu and Morawetz[197] developed a new monomer [L-phenyl alanine p-nitroanilide i.e.



$$CH_2{=}CH\text{-}CONH\text{-}CH_2\text{-}CONH\text{-}\underset{CH_2Ph}{CH}\text{-}CONH\text{-}C_6H_4\text{-}NO_2]$$

and copolymerized it with a large excess of acrylamide or acrylic acid. These polymers were shown to be susceptible to enzyme attack and the rates of degradation depend on composition and constitution of monomeric units present in the polymers.

The conventional polymers (PE, PP, PVC, etc.) can be made biodegradable by incorporation of cofactor (i.e. biodegradable additives) which utilized by microorganisms leads to physical embrittlement of the remaining polymers and hence induce degradation. For example, starch-polyethylene composites, prepared by conventional compounding and processing, resulted in biodegradable paper like materials[198]. The use of biodegradable additives such as starch and cellulose, in combination with PVA as a synthetic film forming material, has been proposed as a route to degradable mulch or barrier layers for use in disposable diapers and sanitary napkins[199]. PVC compositions filled with starch or with starch graft copolymers[200] are readily attacked by microorganisms. When a biodegradable additive is employed, probably only the additive undergoes degradation, a porous and mechanically weakened but undegraded polymer is left behind. While the increased surface area of the residual polymer would be expected to enhance biodegradability, there is as yet little convincing evidence that the remaining polymer is truly biodegradable.

1.8 Aim and Scope of the Present Work :

Synthetic polymers, natural polymers and modified natural polymers are widely used throughout most of the world today and contribute enormously to the quality of life in the industrial world and are helping to raise living standards in the '*Third World*'. Because polymer properties are readily controlled by their chemical composition, synthetic method and manufacturing processes, they are used as commodity plastics, in such diverse applications as packaging, personal care products, construction of automobiles, computers, houses, clothing, etc. They are also used as speciality additives in many applications such as water-soluble polymers in detergents, paints, adhesives, coatings, cosmetics, pharmaceuticals, lubricants, concrete, etc. and in medical applications for drug delivery, temporary and permanent prostheses, such as sutures and bone replacements, as well as in agricultural applications like mulching films, controlled release pesticides and fertilizers, respectively. However, it is observed that most synthetic polymers are not biodegradable because they have not been on the earth long enough to have microorganisms evolve to utilize them as food. Of course, all naturally occuring polymers such as starch, cellulose, proteins, nucleic acids and lignin are biodegradable.

The earliest studies on the biodegradation of polymers were performed to prevent or to retard polymer degradation by microorganisms. Today however, a new field of research has developed, which is concerned with the synthesis of biodegradable polymers. This field of research growing rapidly because of the strong demand for such polymers as biocompatible materials for specific medical applications, such as sutures, surgical implants, and formulations of drugs with controlled release. Research on these materials continues at an extraordinary pace. One of the important current incentives for the study of biodegradable polymers is, of course, the potential for their easy disposal and biodegradation under natural environmental conditions.

In the present study, different types of experimental techniques have been applied to characterize various synthesized homo-, co- and tercopolymers as well as to understand the topology of these polymers. Results of investigations comprising the above aspects are presented and discussed. It is hoped that this would provide a comprehensive background for the fundamental understanding of polymer synthesis, characterization and their biodegradability as well as mutual stability when it is in service, which are essential criterion for their practical applications.

The thesis is organised in seven Chapters : Introduction, Materials and Methods, Four Chapters of experimental results and discussions and the last Chapter of Summary and Conclusions, as detailed in the contents.

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