CHAPTER - I

INTRODUCTION

INTRODUCTION

Polymer science is one of the most active and promising fields of science covering multitude of topics from natural polymers such as proteins, nucleic acid, cotton, wool, cellulose, silk,leather etc.that are of prime importance for living systems, and synthetic high polymers have assumed a significant role in man´s economy and modern civilization.

Polymers exhibit unique physical properties such as high tensile strength, elasticity, light weight, good flexibility. Good electrical resistance is an important property of majority of polymers and hence they are useful as insulating materials and as dielectrics. Polymers can be fabricated into various shapes and in a wide variety of colours. Polymers can be converted into strong solid articles, flexible rubber like masses, soft and resilient foams, rigid and light foams, smooth and fine fibers, clean and crystal clear glass like sheets, jelly like food materials,etc.

Polymers have found applications in almost every walk of life. Because of desirable properties at low cost, polymers have replaced metals and wood as light structural materials in cars, furniture and building materials. They are widely used in transportation, modern dresses, communication, water management, fisheries, public health, electrical and textile industries, for storage purpose, in medicine and surgery, and in agriculture and so on.

Most of the commercially available polymers are homopolymers, that is , they are derived from only one type of monomer. The range of useful properties and applications of homopolymers can be further extended by formation of a copolymer which combine properties not attainable with simple homopolymers.

1.1 Copolymers

A polymer built up from two or more small, simple structural repeating units is called copolymer. A copolymer molecule is composed of two or more monomers covalently linked together. Thus, copolymer is not an alloy or a blend of two homopolymers. The copolymers are further classified into random, alternating, graft and block copolymers.

1.2 Random and Alternating Copolymers

The copolymers consisting of two or more monomer units arranged in a statistical random fashion along the backbone are called as random copolymers.

~~~~~~~~ A A B A B A B A B A A A B ~~~~~~

On the other hand, in alternating copolymers the two monomer units, in equimolar amounts, are placed in a nonrandom regular alternating manner.

~~~~~~~~ A B A B A B A B~~~~~~

Both random and alternating copolymers are synthesized by the simultaneous polymerization of two monomers. The placement of monomer units along the polymer chain and the composition of copolymer is determined by the copolymerization reactivity ratios of the monomers. The monomer reactivity ratio(r) is defined as the ratio of the rate constant for a reactive propagating species adding its own type of monomer to the rate constant for its addition of other monomer. The tendency of two monomers to copolymerize is noted by (r) values between zero and unity (1).

Alternating copolymers are rare because of the stringent requirement of a pair of monomers (A and B) with highly specific copolymerization reactivity ratios (r1 , r2)

When both r1 and r2 are equal to zero, each of the two types of propagating species preferentially adds the other monomer with the result that the two monomers enter into the copolymer in equimolar amounts in a non-random alternating arrangement along the copolymer chain. An example of this type of copolymer is the styrene maleic anhydride copolymer. It is highly alternating in nature. Alternating copolymer can also be synthesized by step growth reactions. For example, alternating copolycarbonate of hydroquinone-bisphenol-A is synthesized by first forming the dichloroformate of one of the monomer and condensing this intermediate with the second monomer.

Various ionic, free radical, addition and ring opening polymerization techniques, as well as many step growth reactions are employed in the synthesis of random copolymers. Typical examples of random copolymers are

i) copolycarbonates formed by the phosgenation of mixtures of bisphenol-A and hydroquinone.

ii) styrene-acrylonitrile copolymers formed by free radical initiation.

Physical and chemical properties like mechanical properties, glass transition temperatures, permeability, chemical resistance etc. of alternating or random copolymers lie in between those of the two corresponding homopolymers prepared from the two monomers. Both, the alternating and the random copolymers contain very short sequential runs of particular monomer units and therefore, are unable to enforce microphase separation. The result is that they exhibit single phase morphology which manifests into optical transparency in amorphous system.

If a monomer is copolymerized with another monomer then the crystallinity of the homopolymer can be reduced. For example, copolymerization of ethylene and propylene produces copolymers ranging from partially crystalline plastics to amorphous elastomers.

1.3 Graft and Block Copolymers

In contrast to the random and alternating copolymers discussed above graft and block copolymers contain long sequential run of the same monomer unit. In the case of graft copolymers, segments composed of a particular monomer are connected as side chain to the main chain comprised of another type of monomer units.Thus, a graft copolymer may be viewed as a branched polymer where the main chain (backbone) and the side chains differ in constitutional or configurational features. A graft copolymer can be schematically shown as

```
------X X X X X X X X X Z X X X X X X X X X X  ----
                        Y
                        Y
                        Y
                        ¦
```

Here, the main chain, the side chain and interconnecting unit are represented by the sequence of X monomer units, that of Y monomer units and the z unit, respectively. The backbone and the side chains may both be homopolymeric, or one homopolymeric and other copolymeric or both may be copolymeric but of different chemical compositions.

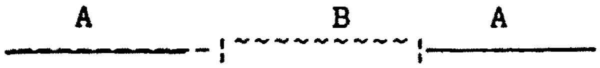
Block copolymers have considerably long sequential run of the same monomer unit following that of the another monomer unit. Thus a block copolymer is a linear copolymer made up of two or more polymers joined end-on-end (2 ,3 ,4).

There are different architectural types of block copolymers as shown schematically.

i)

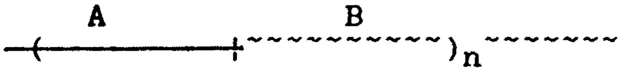
A-B diblock copolymer

ii)



A-B-A triblock copolymer

iii)



-(- A-B-)-$_n$ multiblock copolymer

1.3.1 Methods of Preparation

Unlike random/alternating copolymers, graft and block copolymers cannot be prepared by simultaneous polymerization of two monomers. Graft and block copolymers have been reviewed (2,3,5,6). Both the graft and the block coploymers can be synthesized by radical, ionic or ring opening initiation of a monomer in the presence of a preformed polymer containing appropriate reactive sites.In the case of graft copolymers, the reactive sites are located along the preformed polymer backbone while the use of a prepolymer with the reaction sites located at the chain ends results in block copolymers. In addition coupling or condensation reactions between functional polymers can be used to obtain block copolymers and, to some extent, graft copolymers.

1.3.1.1 Free Radical Polymerization

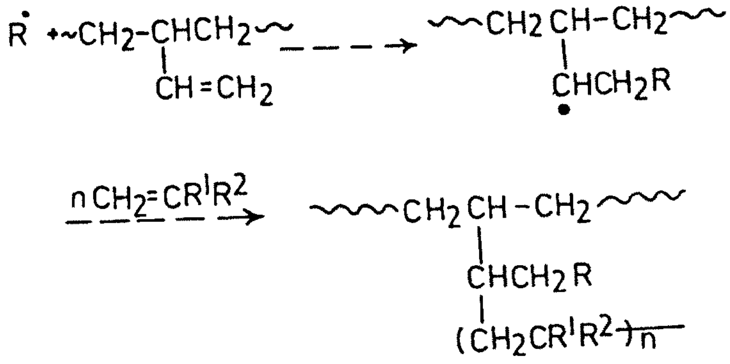
A polymer containing labile hydrogen is subjected, in presence of an olefinic monomer, to radical generating treatments. Grafting of styrene onto poly butadiene(7) serves as an example. Radicals are generated by using peroxide initiators or irradiation or thermal methods. The radicals formed in the system can undergo several reactions (8),

(a) add monomer to form homopolymer chains

$$\dot{R} + CH_2 = CR^1 R^2 \dashrightarrow R - CH_2 - \dot{C}R^1 R^2$$

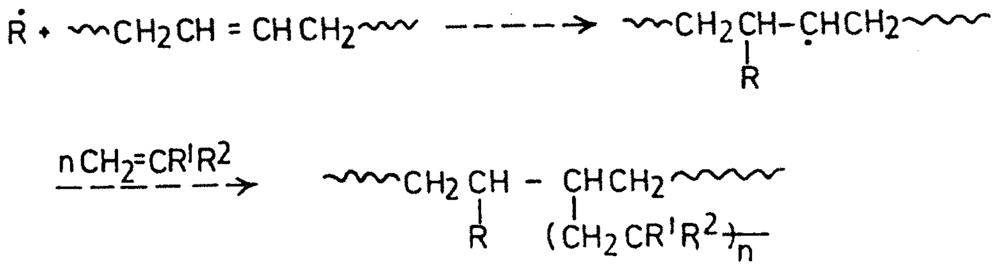
Scheme 1

(b) add to vinyl side groups in the polydiene and add more monomer to form graft copolymer .



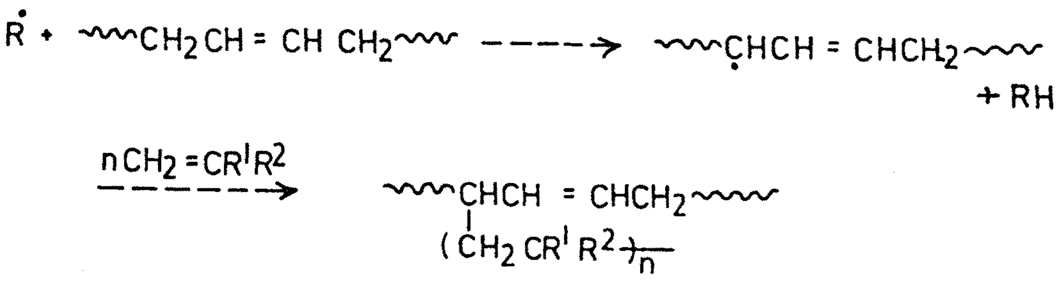
Scheme 2

(c) add to in-chain double bonds and then add more monomer to form graft copolymer



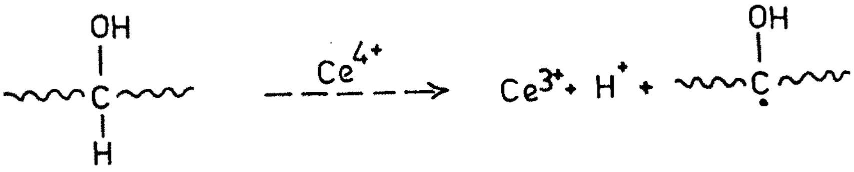
Scheme 3

(d) abstract a labile hydrogen (allylic hydrogen) and then add monomer to the resulting allylic radical to form graft copolymer.



Scheme 4

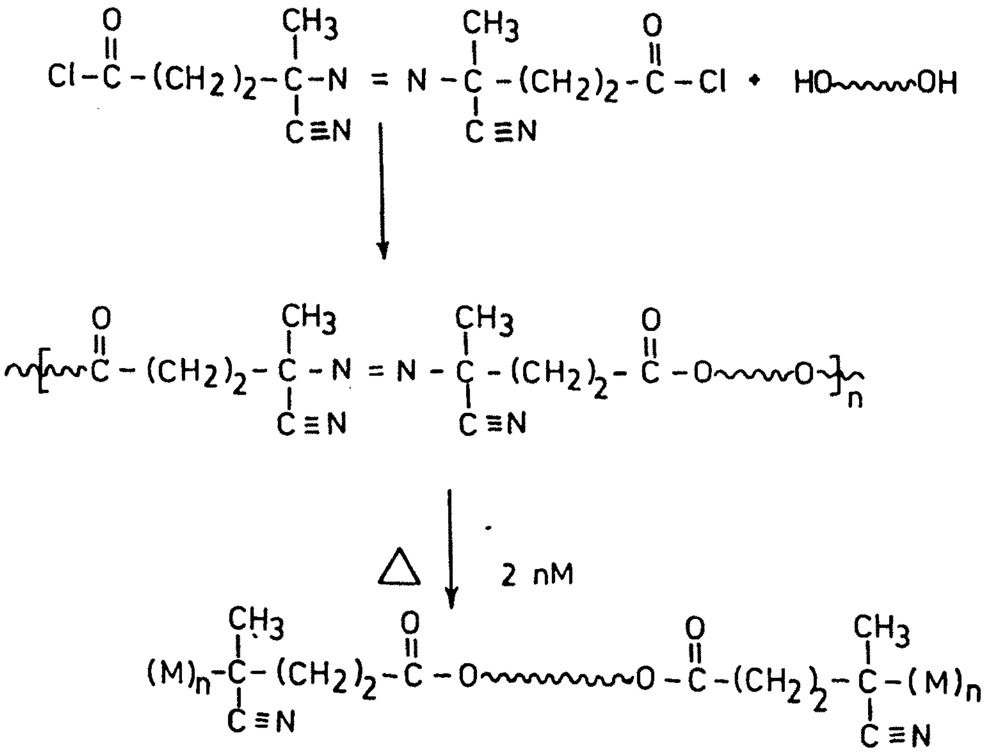
The labile hydrogen may also be abstracted by the growing chain (chain transfer to polymer). Free radical grafting methods produce material contaminated with homopolymers. Homopolymer formation can be minimized by redox reactions which generate radical initiation sites singly on the backbone polymer without any accompanying small radicals that can initiate homopolymerization. Vinyl monomers were grafted on hydroxyl containing polymers, such as cellulosics, starch and poly (Vinyl alcohol) by oxidising backbone hydroxyl groups with metal ions (e.g. Co^{3+},Ce^{4+},Mn^{3+}, V^{5+} and Fe^{3+}) (9 - 11).



Scheme 5

Termination by coupling results in crosslinked products.

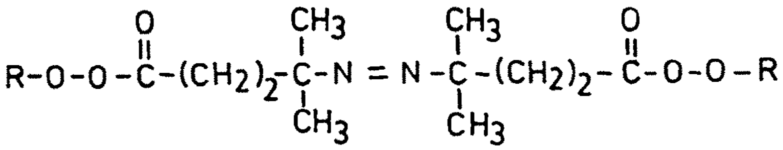
In order to synthesize block copolymers it is necessary that the radicals are generated only at the chain ends of a preformed polymer, so that the subsequent initiation and polymerization of a second monomer results in block copolymers. This has been achieved by using polymers containing in – chain initiating groups which upon dissociation give polymer segments with terminal radical sites. Reaction of hydroxyl terminated polymer with 4, 4-azobis-4-cyano-valeryl chloride results in chain extended polymer which on thermal decomposition of azolinks in the presence of vinyl monomer gives block copolymers (3,12).



ABA triblock copolymer

Scheme 6

Initiators with two different initiating groups e.g. peroxide and azo or of the same type, but with different rates of decomposition can be used to obtain block copolymers.



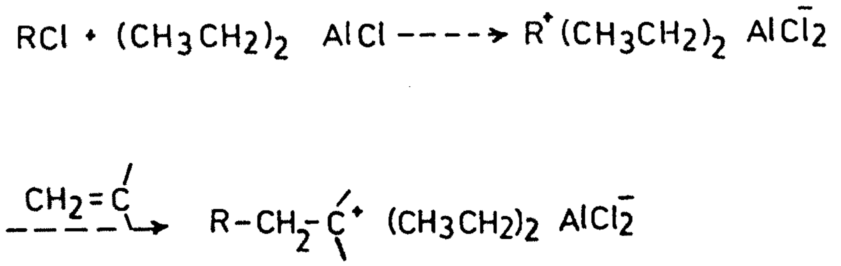
$$R{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}N{=}N{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}(CH_2)_2{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}R$$

where R = t-butyl (13,14), benzoyl(15), p-nitrobenzoyl or chlorobenzoyl (16) have been used to synthesize block copolymers. Diperoxide initiators containing peroxide groups of different thermal stability have been used to prepare styrene-methylmethacrylate block copolymers (3).

1.3.1.2 Cationic Polymerization

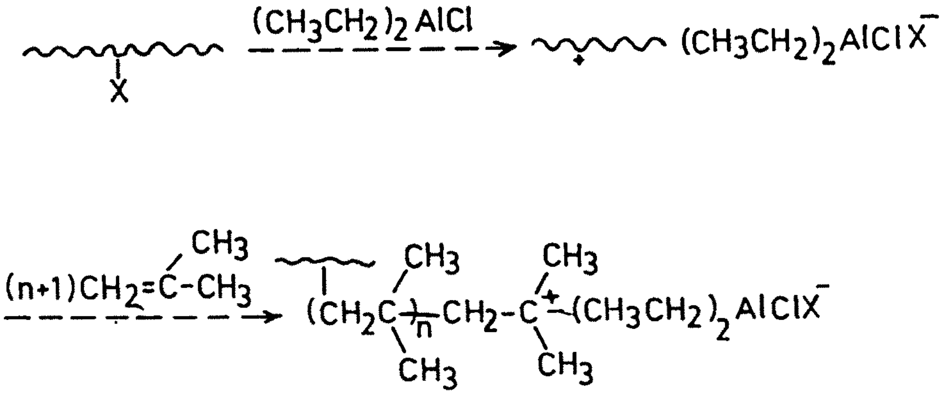
Olefinic monomers with electron donating substituents such as styrene, alkyl vinyl ethers, isobutylene or cyclic ethers e.g. THF undergo cationic polymerization.

A variety of initiator-coinitiator systems are used to initiate cationic polymerization. One of such system involves alkyl aluminium compounds, e.g. $(CH_3CH_2)_2AlCl$, $(CH_3CH_2)_3Al$, $(CH_3)_2AlCl$ in conjugation with cationogens such as tertiary, benzylic or allylic chlorides.



Scheme 7

Such system is free from the effect of protic impurities. Polymers with halogenated backbone such as polychloroprene (17-24), chlorinated styrene-butadiene rubber(24), chlorinated (23,25,26) and brominated (24) butyl rubber, chlorosulfonated polyethylene(27) and chlorinated polybutadiene(24) have been grafted with different monomers. Initiation reactions between labile alkyl halides and various Lewis acids were utilized.



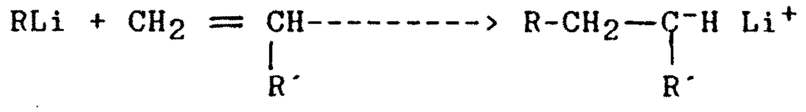
Scheme 8

Polymers with terminal halogen groups can be used as cationogens in conjugation with alkyl lithium compounds to prepare block copolymers. Lewis acids do not initiate homopolymer chain growth in the absence of reactive alkyl halides.

1.3.1.3 Anionic Polymerization

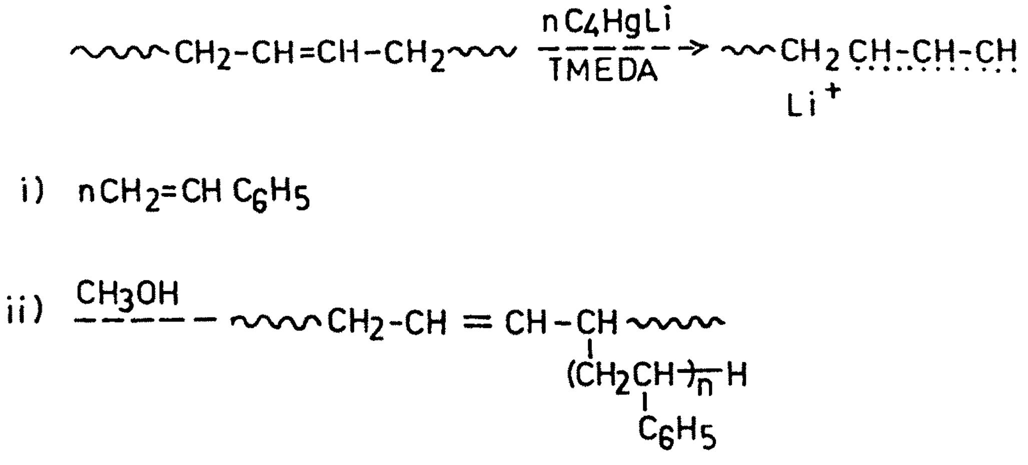
Olefinic monomers with electron defficient substituents such as styrene, butadiene, etc. are susceptible to anionic polymerization.

Strong bases are used for initiating anionic polymerization. Organomatallic compounds, especially alkyllithiums are mostly used as initiators.



$$RLi + CH_2 = \underset{R'}{CH} \text{---------}> R\text{-}CH_2\text{—}\underset{R'}{C^-}H\ Li^+$$

Polybutadiene and polystyrene have been metalated by reaction with chelated organolithium (alkyllithium complexed with N, N, N´, N´-tetramethylethylene diamine, TMEDA) compounds followed by grafting reactions of styrene (28-30)

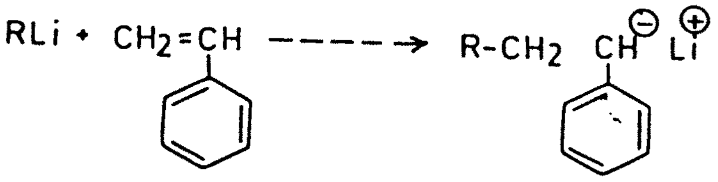


Scheme 9

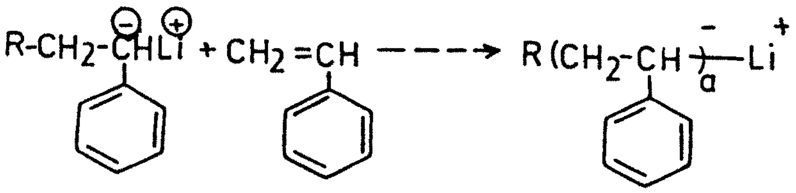
It is important in this reaction to ensure that all of the organolithium reagent is consumed in the metallation step so that homopolymerization is minimum.

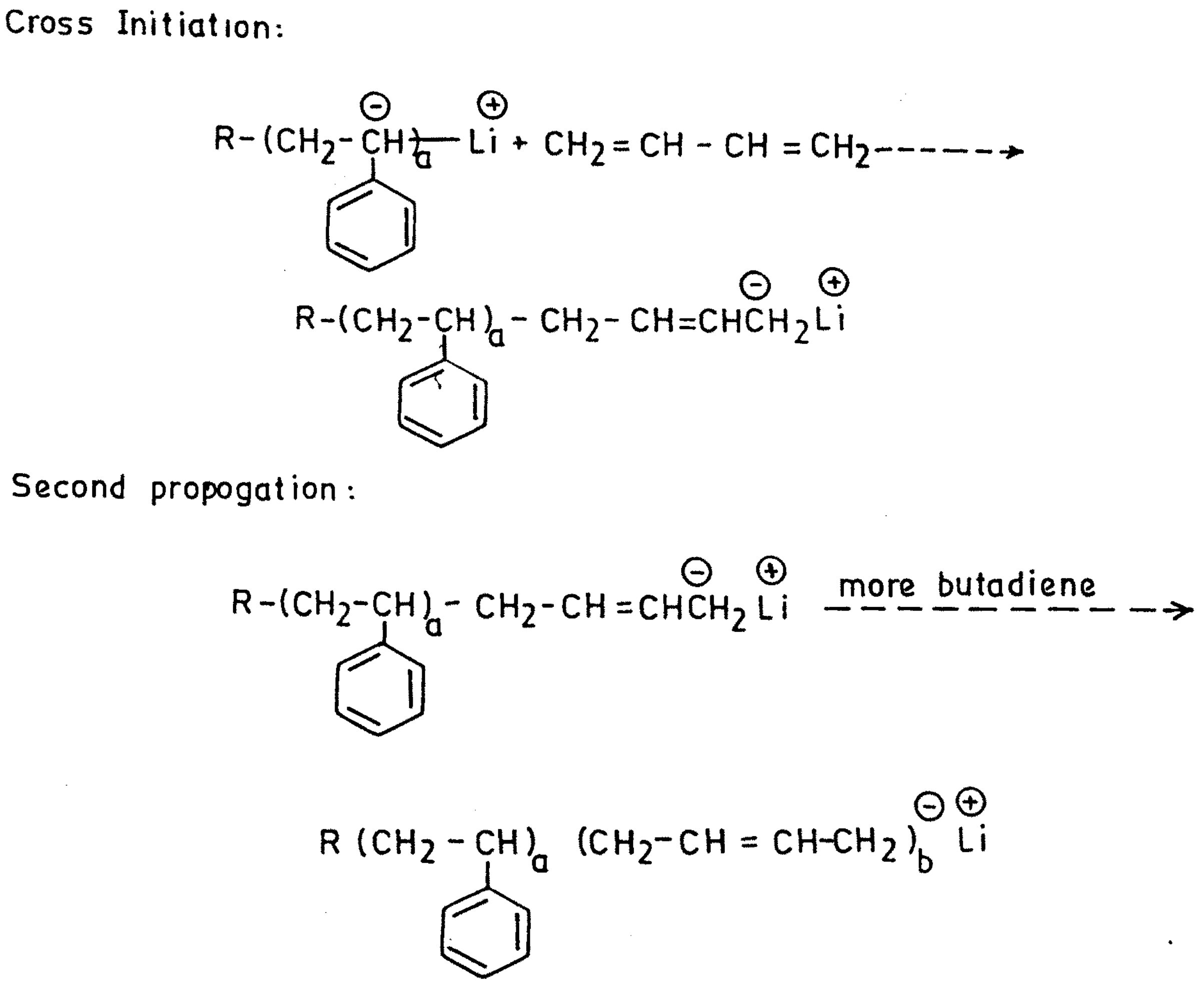
The special feature of anionic polymerization is that they, usually, are devoid of termination reactions and are, therefore, referred to as living polymerization. Absence of termination step produces well defined blocks with a control over block length which is determined simply by monomer / initiator ratio. Also very narrow molecular weight distributions are possible. The synthesis of block copolymers by anionic method involves sequential addition of desired monomers. For example, styrene- butadiene block copolymer can be prepared by using alkyllithium initiators as follows.

Initiation:



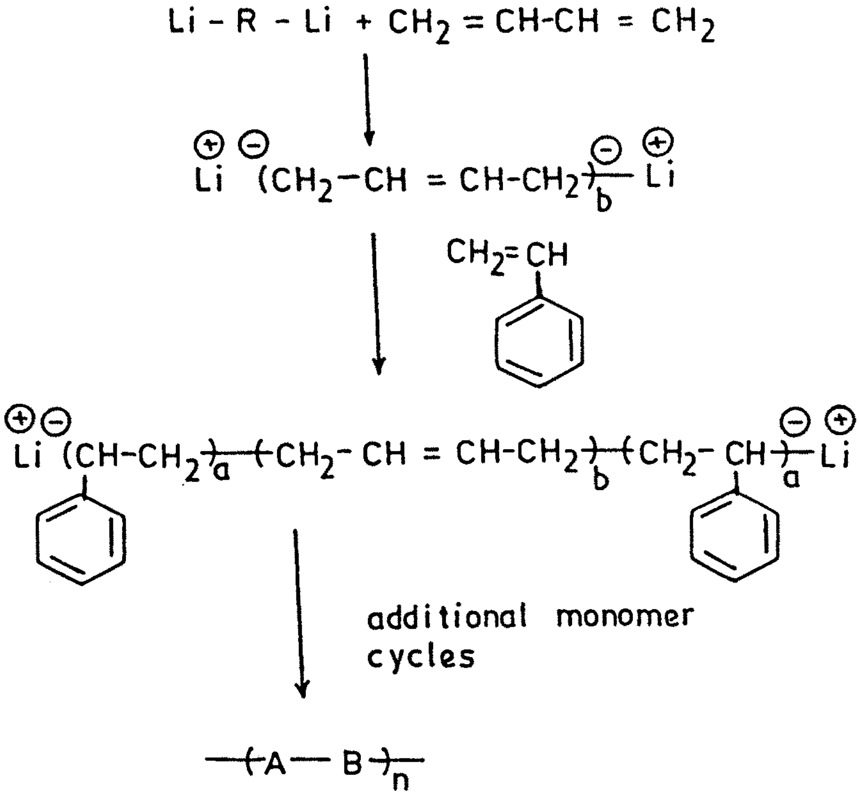
First propogation:





Scheme 10 (Ref. 2)

The reverse monomer addition sequence can also be used. Triblock and multiblock copolymers can also be prepared by using difunctional initiators.

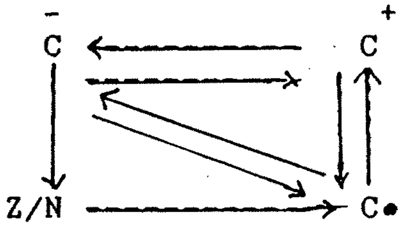


Scheme 11(Ref.2)

However, this technique requires ultrapure reagents and solvents, high vacuum and low temperatures and usually limited to dienes and styrene monomers, though some cyclic sulfides and cyclic ethers polymerize well by this technique.

In order to synthesize styrene-methylmethacrylate block copolymer by this technique certain precautions have to be taken (2). Styrene must be polymerized first because poly(methyl methacrylate) anion is not sufficiently basic to initiate styrene polymerization. Since, polystyrene anion attacks the ester group of methylmethacrylate it must be capped with 1,1-diphenylethylene before methylmethacrylate is added.

The nature of active centre of a propagating chain can be altered to another type of active centre as shown schematically

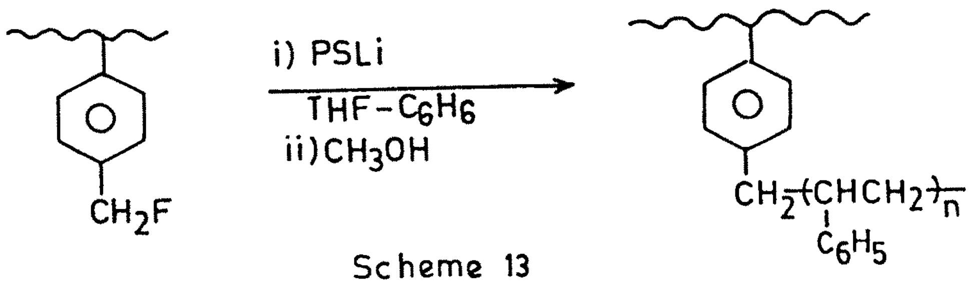


Scheme 12

Such transformation reactions have been reviewed (3). This approach greatly extends the range of possible monomer combinations in a block copolymer synthesis.

1.3.1.4 Condensation and Coupling Reactions

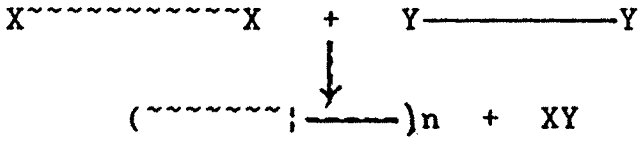
This method is the less frequently used method for the preparation of graft copolymers. One example is the grafting of living anionic polymers onto polymer backbones with reactive halogen or epoxide functionalities (8).



Scheme 13

Condensation and coupling reaction is the most commonly used method to synthesize block copolymers. Functionally terminated oligomers, also termed as telechelic polymers can be prepared in a variety of ways. In the step- growth polymerizations, the polymer bears the end groups of the monomer used in excess. In the chain polymerizations, the desired terminal functional group is obtained either by choice of initiator or by capping the propagating chain with an appropriate reagent. Reactions of functionally terminated oligomers which involve formation of intersegment linkages yield block copolymers.

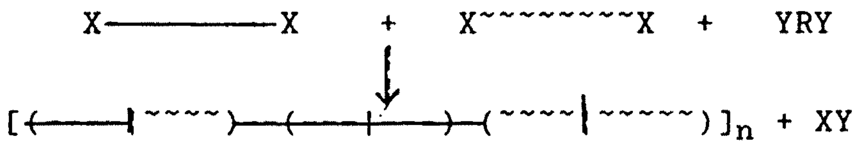
Monofunctioal oligomers are used to prepare A-B diblock and A-B-A triblock copolymers, while difunctional oligomers are used in preparation of -(A-B)$_n$, multiblock copolymers. Perfectly alternating (A-B)$_n$ multiblock copolymers are obtained when oligomers with mutually ractive groups are used. Such oligomers can only react with each other and not with themselves (2).



Scheme 14 (Ref.2)

The average molecular weights of the blocks are identical with those of the corresponding oligomers.

Two differnt oligomers with same terminal functional groups are linked by using appropriate coupling agents. If the oligomers are similar in reactivity towards the coupling agent,they are incorporated in the block copolymer molecule in a statistical or random fashion.

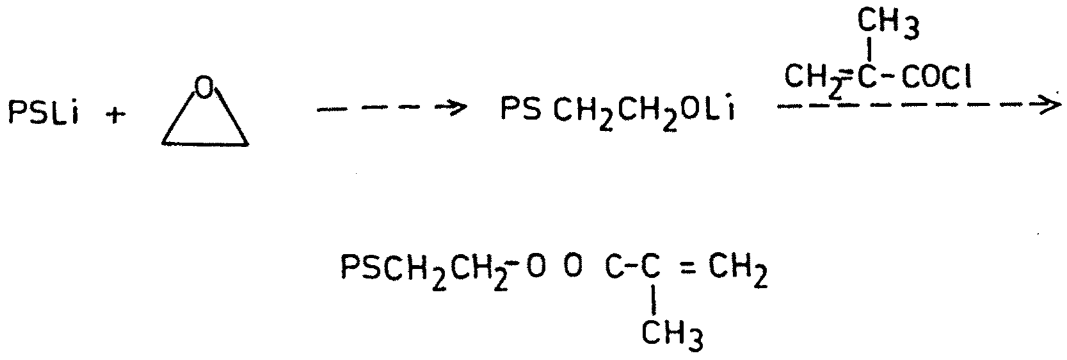


Scheme 15(Ref.2)

In this case the average molecular weight of blocks is higher than those of corresponding oligomers (2).

1.3.1.5 Miscellaneous Methods

Graft copolymers can be synthesized by polymerization of macromonomers. Macromonomers can be prepared by free radical or ionic methods and subsequently copolymerized with a backbone forming comonomer using free radical or ionic polymerization methods to give comb-type graft copolymers (8). Thus, methacrylate terminated polystyrene is prepared (Scheme 16) (31),



Scheme 16

which can form comb-type graft copolymers with vinyl monomers. This method gives graft copolymers with well characterized graft chains. A large number of macromonomers have been reported (8).

Polymer growth from oligomer end groups yields block copolymers. In this method a preformed polymer with end groups that can initiate polymerization of other monomer is employed. Both addition / ring opening oligomers and step growth oligomers can be used to initiate polymerization of addition / ring opening monomers or step-growth monomers (2).

1.3.2 Properties of Graft and Block Copolymers

Copolymerization is a widely used method for modifying polymer properties. Both, graft and block copolymers display properties that are different from the properties of the respective homopolymers from which they are made up of. The polymer components of graft and block copolymers are usually thermodynamically incompatible owing to the long sequential run of monomer units. The thermodynamic incompatibility forces phase separation in solid state or in concentrated solutions. However, because of the presence of intersegmental linkages the phase separation is on micro scale in contrast to polymer blends. In a few cases, where the component polymers have identical values of solubility parameter, both graft and block copolymers are known to exhibit single phase morphology (2).

The morphology of graft and block copolymers is determined by several factors including the relative concentration of the components, the differential solubility parameter, and the method of specimen fabrication. The component in larger concentration forms the continuous phase. The differential solubility parameter (δ) is defined as the difference between solubility parameter of the respective components. The larger the value of (δ) greater is the phase separation.

When the concentration of both the components is nearly equal, phase continuity depends upon the methods of specimen fabrication and can be altered by choice of suitable solvent. The component which is more soluble in the solvent used for casting will form the continuous phase. Methylmethacrylate-natural rubber graft copolymers have been shown to exhibit such behaviour (2,32). Thus, it is possible to control properties such as modulus and permeability by controlling the morphology of the copolymer.

The physical, rheological, optical, and transport properties of graft and block copolymers are direct consequence of the two phase morphology. The thermal properties of graft and block copolymers, unlike those of random / alternating copolymers, resemble those of physical blends displaying the characteristics of both the components. Thus, they display multiple thermal transitions such as glass transitions and/or crystalline melting points, characteristic of each components. Because of the small domain size, they are optically transparent when the components are amorphous.

Graft copolymers can be blended well with their respective homopolymers. Technologically important graft copolymers are high impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene graft copolymer (ABS).

From mechanical property point of view, block copolymers may be divided into two classes- rigid and elastomeric (2). Rigid materials may be comprised either, of two `hard´ segments or a hard segment and a minor proportion of "soft" segment. A ´hard´ segment is defined as the one that has T_g or T_m above room temperature, while a soft segment has Tg or Tm below room temperature. Elastomeric block copolymers have a soft segment together with minor proportion of hard segments. Block copolymers with both soft segments offer no mechanical property advantages.

Rigid block copolymer composed of two hard segments improve heat distortion temperature (HDT), creep, stress-relaxation resistance. The presence of intersegment linkages and good interphase adhesion retain the inherent ductility of the segments in contrast to physical blends which are brittle.

The toughness of a brittle rigid polymer is improved by block copolymerization with a minor fraction of a soft segment. These types of polymer form the technologically important class of polymers-toughned thermoplastic resins.

Thermoplastic elastomers,another technologically important class of polymers are block copolymers comprised of a soft segment with a minor proportion of hard segment. They combine mechanical properties of a crosslinked rubber with the processing behaviour of linear thermoplastic polymers. Examples are styrene-butadiene block copolymers and segmented polyurethanes or polyesters.

A high degree of structural control and integrity is necessary in order to achieve the ultimate properties inherent in such two phase systems. It is in this respect that block copolymers offer a clear advantage over graft copolymers. It is feasible to have a better control over sequence architecture, segment length and spacing, polydispersity and homopolymer contamination in case of block copolymer synthesis than graft copolymer synthesis.

1.4 Starch and Cellulosic Based Graft and Block Copolymers

1.4.1 Starch

Starch is naturally occuring renewable polymer. All cells of green plants, wheat, barley, maize, potatoes and arrow root are the sources of starch. Starch can be manufactured from corn or other starchy materials by rupturing cell walls when the enclosed starch granules get exposed which are washed to remove cellulose.

Cereal or plant from which starch can be manufactured is washed with water when sticking dirt is washed away. When rice is used as a raw material it is treated with dilute caustic soda solution before washing to remove gum and gluten (cellulose and protein materials). After washing it is disintegrated mechanically when paste like mass called pulp is obtained, from which starch can be obtained.

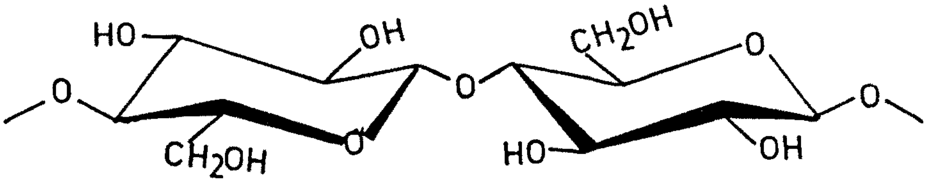
Soluble starch can be obtained by heating ordinary starch with 10% hydrochloric acid for 24 h and then precipitating with alcohol. Starch granules vary in shape and size with source.

Normal corn starch is composed of 20-30% of the linear polysaccharide amylose and 70-80% of the branched polysaccharide amylopectin (33). Each of these are made up of about 500-1000 glucose units. In one of the several ways of separation of these components n-butyl alcohol is added to a hot colloidal solution of starch in water and the mixture is cooled. α-Amylose gets precipitated and is removed. Amylopectin is recoverd from the mother liquor by adding methanol.

Starch is the most valuable constituents of food such as rice, bread, corn flour, potato, etc; it can be used in large quantities for the manufacture of glucose. It forms the basis of brewing industry as raw material in the manufacture of alcohol. Starch is used for the manufacture of dextrin and adhesives. It is used in paper industry for sizing paper, and also in textile industry for giving a finish to cotton fabrics. In laundry, starch is used as a stiffening agent. Starch is used in calico-printing as a thickening agent for colours.

1.4.2 Cellulose

Cellulose is the principal carbohydrate of plant origin. It is a naturally occuring renewable polymer. Cellulose from different plant sources may vary in molecular weights, degree of molecular orientation and morphological structure. The chemical structure of cellulose from different plant sources is the same . In cellulose the D-anhydro glucose units are joined by β-1,4-glucosidic bonds.



Cellulose is very important in the manufacture of regenerated fibers for textiles and other cellulosic products. Cotton, the most harvested fiber, is the world's largest source of textile , industrial and biomedical fibers.

The viscosity average molecular weight of natural cellulose can range as high as 8,00,000 with a degree of polymerization in range of 5,000 .

The range of use of starch and cellulose can be increased by

(i) chemical modification which may be either simple derivatization or reactions leading to graft and block copolymers,(ii) blending with natural /synthetic polymers .

Cellulose and starch based block and graft copolymerization with synthetic polymers have remarkable properties. The special properties of graft /block copolymers of cellulose that lead to proven applications are changes in solubility, permeability, compatibility and the mosaic structure of the solid state . The cellulose and starch are responsible for the biodegradability of block/graft copolymers containing these components .

1.4.3 Graft Copolymers

Graft copolymers of cellulose (34), cellulose derivatives and lingo celluloses (35) have been reviewed.

Among all the methods to prepare cellulose graft copolymers, free radical initiation is the most widely used technique. In some cases , macro cellulosic radicals are formed directly and initiate polymerization of vinyl monomers onto cellulose. In other cases free radicals are formed which may abstract hydrogen atoms from cellulose to form macro radicals.

A number of vinyl monomers like styrene, vinyl acetate, acrylonitrile, methylmethacrylate, methylacrylate, acrylamide, acrylic acid have been grafted. Free radical initiation can be classified into two,

i)initiation by chemical methods. ii)initiation by irradiation.

In the irradiation method cellulosic macro radicals are produced by gamma (Cobalt 60) and electron beam irradiation.

The various steps are as follows :

Initiation

$$C \dashrightarrow C^{*} \dashrightarrow \dot{C} + \dot{H}$$

$$M \dashrightarrow M^{*} \dashrightarrow \dot{M} + \dot{H}$$

$$I \dashrightarrow I^{*} \dashrightarrow \dot{I} + \dot{H}$$

$$C + \dot{I} \dashrightarrow \dot{C} + IH$$

Propogation

$$M + \dot{I} \dashrightarrow \dot{M} + IH$$

$$\dot{C} + M \dashrightarrow C\dot{M}$$

$$C + \dot{M} \dashrightarrow C\dot{M}$$

$$C\dot{M} + nM \dashrightarrow C\dot{M}n+1$$

$$\dot{M} + nM \dashrightarrow \dot{M}n\ +1$$

Termination

$$\dot{C} + \dot{C} \dashrightarrow C2$$

$$\dot{C} + \dot{M} \dashrightarrow CM$$

$$C\dot{M}m + C\dot{M}n \dashrightarrow C_2Mm+n$$

$$\dot{M} + \dot{M}n \dashrightarrow Mn+1$$

Chain transfer

$$\dot{C} + S \dashrightarrow C + \dot{S}$$

$$\dot{S} + M \dashrightarrow S + \dot{M}$$

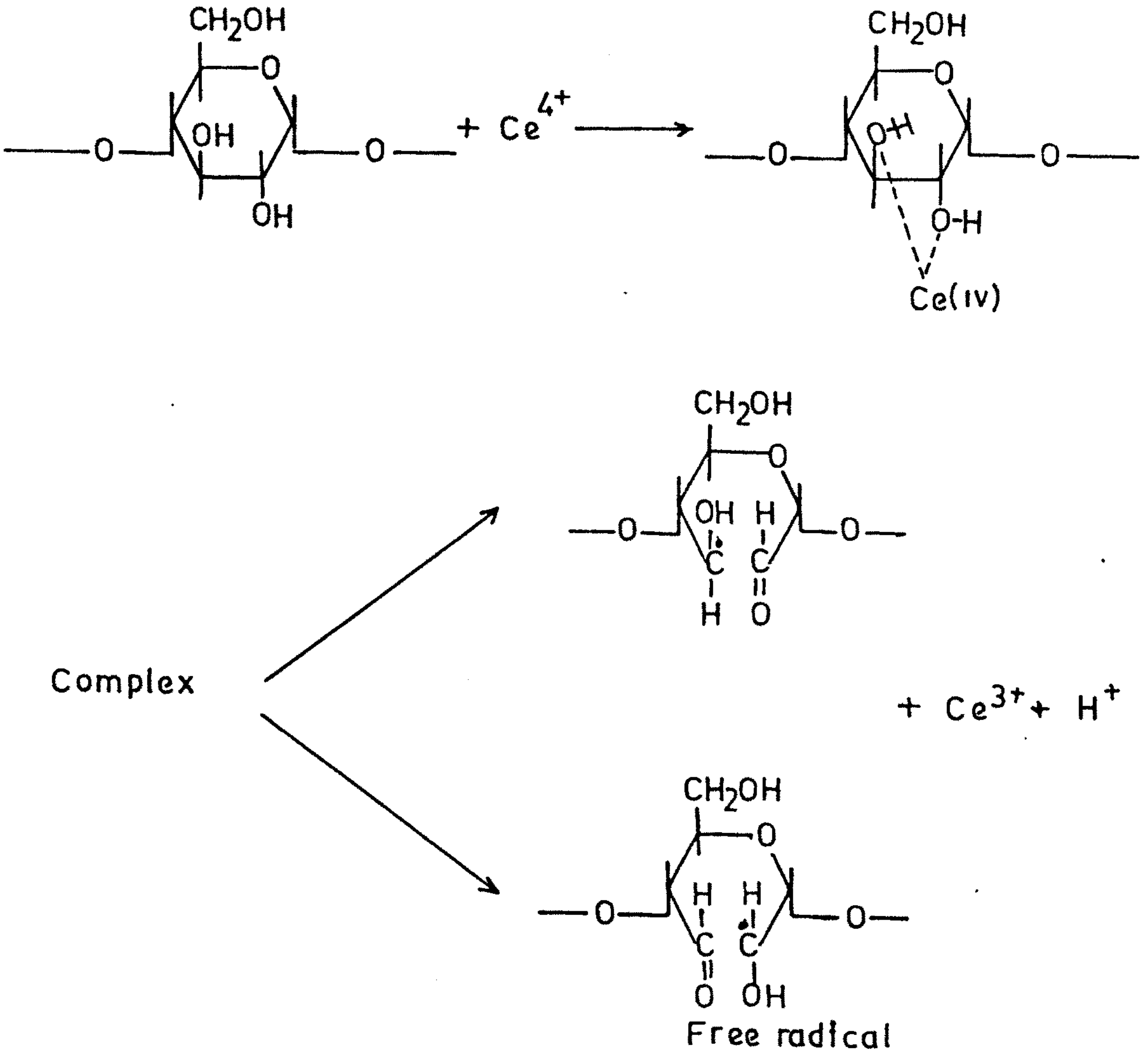
Where C = cellulose, M = vinyl monomer, S = solvent,

I = sensitizing initiator. * - indicates active state.

All these reactions are likely to occur in the one step process where solution of vinyl monomer is in contact with cellulose, when the free radicals are formed. In two step process, where macro cellulosic radicals are initially formed and afterwords the cellulose is brought in contact with a solution of vinyl monomer, many of these reactions may not occur and less homopolymer is obtained, which is primarily due to chain transfer reactions.

Graft polymerization of styrene on to cellulose by gamma ray, mutual irradiation technique was also studied in a homogeneous medium where the cellulose solvent system used was SO_2-dimethylamine-dimethylsulphoxide (36).

Perhaps the most widely used method of chemical initiation is the reaction of cellulose with cerric ammonium nitrate dissolved in dilute nitric acid. This was suggested by Mino and Kaizerman (37). The initiation of graft copolymerization by cerric ions may be shown to occur as :



Cellulose free radical + monomer -----> graft copolymer

Photoinduced graft copolymerization of vinyl monomer onto cellulose is generally carried out in the presence such photosensitizers as hydrogen peroxide (38), dyes (39), metal ions (40). The grafting efficiency is low in above. It can be increased by initiation with photolysis of functional group introduced in cellulose.

Homogeneous graft copolymeriztion of cellulose has been reported. Cellulose was dissolved in a dimethylsulfoxide-paraformaldehyde solvent system. The vinyl monomers grafted were methylacrylate (41), methylmethacrylate (42), and the initiation was carried out by using ammonium persulfate, benzoyl peroxide or azobisisobutryronitrile.

Miyamoto et al have reported graft copolymers of cellulose with polypeptides and evaluated their blood compatibility (43). Cellulose-g-poly (γ-benzyl-L-glutamate) copolymers were prepared by ring opening polymerization of γ-benzyl-L-glutamate — N-carboxy anhydride (γ-BLG-NCA) by amino groups of amino ethyl cellulose.

Cellulose-g-polystyrene has been prepared by anionic polymerization technique (44). It involved three steps i)preparation of "Living" polystyrene by anionic polymerization,

ii)introduction of tosyl group on to cellulose backbone by chemical modification, and iii)reactions of modified cellulose with "Living" polystyrene under homogeneous conditions involving nucleophilic displacement of tosyl groups. This technique offers the advantage of control over graft chain length and minimum homopolymer contamination.

1.4.4 Block Copolymers

The simplest method of synthesis of block copolymers of cellulose derivatives was reported by Ceresa in which mastication of cellulose derivatives like methyl, ethyl, benzyl ethers of cellulose and cellulose acetate in the presence of vinyl monomers yield the respective block copolymers. During mastication cellulose backbone is cleaved generating free radicals which polymerized the vinyl monomer.

Block copolymers in which one of the block components is an unsubstituted poly or oligosaccharide such as cellulose or amylose or derivatives of poly or oligosaccharide, such as cellulose triacetate or amylose triacetate have been reviewed (45).

The chemical method to produce multiblock copolymers (segmented) of cellulose derivatives was developed by Steinmann (46). Cellulose triacetate was first hydrolysed in acidic medium at 60 °C which resulted in cleavage of glucosidic linkages to yield hydroxyl terminated low molecular weight cellulose triacetate. Water content of the reaction system is very important factor. A small amount of water in the system is essential to prevent acetylation of the hydroxyl end groups formed by hydrolysis, while water in excess of 0.6% results in hydrolysis of acetyl blocking groups. The functionally terminated cellulose triacetate was then reacted with a diisocyanate capped hydroxy terminated polyester oligomer to yield segmented polyurethanes. This approach of cellulose block copolymer synthesis was extended by Gilbert and Stannett (47-53). They prepared block copolymers using cellulose triacetate, 2,3,6- tri-o-methyl cellulose, amylose triacetate and 2,3,6-tri-o-allyl-amylose as one of the block components and polymeric diols as the other block component. Diisocyanate coupling agents such as diphenyl methane 4,4′- diisocyanate (MDI) or tolylene-2-4 diisocyanate(TDI) were used.

Another approach to the synthesis of carbohydrate based block copolymers involves first forming a polysaccharide block with reactive end group that is used to initiate polymerization of a second block. Douy and Gallot (54, 55) described a novel procedure for the synthesis of amphipathic block copolymers containing a hydrophilic polysaccharide block and a hydrophobic polypeptide block. The polysaccharide block was derived from a glycoamino acid OB isolated from hen egg-white ovomucoid. The peptide block was a poly(γ- benzyl- L glutamate). The glycoamino acid OB has an asparagine residue at one end. The amino function of asparagine was used to initiate the ring opening polymerization of -benzyl-L-glutamate-N-carboxyanhydride (γ—BLG-NCA) to give polypeptide block. This approach was adopted to the synthesis of cellulose triacetate-poly (γ-benzyl-L-glutamate) block copolymer (56).

1.5 Scope of Present Investigation

Methylmethacrylate has been graft copolymerised onto cellulose using several initiation techniques such as irradiation (57-59), mechano-chemical (60-61) ,photo induced (62-64),and chemical(35, 65-69). Acrylonitrile starch graft copolymer have also been reported (70). In all these cases graft copolymerization reactions have been carried out in heterogeneous medium.

The present investigation was undertaken to synthesize starch and cellulose based graft and block copolymers, by using coupling reactions of preformed block components.

Acetylated starch and ethyl cellulose (EC)were grafted with polymethylmethacrylate (PMMA). Carboxy terminated and hydroxy terminated polymethylmethacrylate were synthesized by free radical initiation in the presence of appropriate chain transfer agents (71) which were subsequently coupled with the remaining hydroxyl groups of acetylated starch/ethyl cellulose. Tolylene-2,-4-diisocyanate was used as coupling agent in grafting hydroxy terminated polymethylmethacrylate.

Similarly, hydroxy terminated cellulose triacetate was coupled with carboxy terminated and hydroxy terminated polystyrene to obtain cellulose triacetate polystyrene(CTA-PS) block copolymers.

All the graft and block copolymer were characterized by chemical and spectroscopic methods. Starch based copolymers were examined for biodegradability.

All these materials are film formers, hence can find applications as membranes in seperation technology. EC-PMMA graft copolymers can find applications as materials for dental fillings. CTA-PS block copolymer can replace cellulose acetate in reverse osmosis membrane applications. Incorporation of starch /cellulose component can impact biodegradability to these materials.