CHAPTER – I
1.1. INTRODUCTION

The chemistry of macromolecular compounds is at the present time one of the most vigorously developing branch of chemistry, the rapid rate of its development can be accounted for by the fact that synthetic chemistry of polymers involving the manufacture of plastics, synthetic fibres and synthetic film forming materials. A number of advances in polymer science have been observed recently. Polymers have excellent thermal and oxidative stability for use in high performance aerospace applications; engineering plastics-polymerers designed to replace metals; non-flammable polymers including some that emit a minimum of smoke or toxic fumes. In its turn, it plays an important role in the development of many branches of new engineering and modern industries; aviation, automobiles and radio technical machineries.

A polymer is made of many units or "-mers" and they are generally hydrocarbons or derivatives joined together in distinct repeating patterns. Each link of the chain is the "mer" or basic unit, which is made of carbon, hydrogen, oxygen, and /or silicon. To make the chain, many links or "-mers" are hooked or polymerized together. Polymerization can be demonstrated by linking strips of construction paper together to make paper garlands or hooking together hundreds of paper clips to form extended chains. The reaction by which small molecules combine with each other to form macromolecule is called polymerization. Polymers are materials with seemingly limitless uses. The polymers have the following general characteristics:
• Polymers have average molecular weight, such as weight average molecular weight \((M_w)\), number average molecular weight \((M_n)\), viscosity average molecular weight \((M_v)\) and sedimentation average molecular weight \((M_z)\).

• Polymers do not have sharp melting point but a softening temperature range.

• Polymers do not have saturation point

• Polymers have high viscosity.

• Polymers can be very resistant to chemicals.

• Polymers can be both thermal and electrical insulators.

• Generally, polymers are of low density with varying degree of strength

• Polymers can be processed in various ways to produce thin film, fibres or very intricate parts.

The field of polymerization was initiated by H. Staudinger, W. H. Carothers and propagated by a number of eminent scientists like P. J. Flory, R. W. Lenz, and H. F. Mark without termination. Today, this excellent branch of chemistry has developed so much that even approximately 55 journals of polymer science around the globe, have become insufficient. The progress of chemistry of macromolecules results from increasing number of new initiators like substituted benzophenones peroxo dicarbonate, ylides (1); and polymers like Star Polymers, Polymer Liquid Crystals (PLC), Plasma Polymerization, Atom Transfer Radical Polymerization (ATRP) etc.

**STAR POLYMERS**

Star polymers are a class of branched macromolecules, which typically consist of number of linear polymer arms joined together by a central core. These polymers have
attracted much attention in research as new polymer materials due to their various functions and properties stemming from their unique three dimensional structures (2). Well-defined star poly(1,3-butadienes) with up to even 128 arms have been successfully synthesized by this end coupling reaction (3). The synthesis of star polymers involve living polymerization techniques such as ATRP, anionic, cationic and ring opening metathesis polymerization (4). The physical properties of star polymers are unique and quite different from those of linear polymers.

Multi-arm star polymers have been the subject of a great deal of interest for the past few decades, with considerable attention given to the dilute solution properties of these materials. (5,6). Star polymers with up to 270 arms have been successfully produced (7). Synthesis of these materials has been primarily through the addition of p-divinylbenzene or chlorosilanes to anionically polymerized styrene, butadiene or isoprene.

Several researchers have been interested in the development of rodlike star polymers. L. Mathias et al. (8,9) synthesized a four-arm polyaramid star via a palladium-catalyzed carbonylation-condensation route. M. Sawamoto et al. (10) in 2001, prepared star-shaped polymers that consist of well-defined poly(methyl methacrylate) arms and a microgel core of a divinyl compound by RuCl₃ (PPh₃)₃ catalysed living radical polymerization. These star shaped polymers had the arms number of 10-30 and Mₘ> 10⁵.

Star polymers containing chemically different arms have been designated as miktoarm (mixed) star polymers. They reveal interesting properties in the solid state as well as in solution due to their unique architectures. These are the materials, which are of interest because of their unique spatial shapes and lower viscosity compared with that of
linear polymers with similar molecular weights. These have narrow molecular weight distribution and are used as phase transfer catalyst, viscosity modifier for paints and coatings. These are also used to enhance tensile strength, thermoplastic nature and electrical conductivities. The structure of different kinds of star polymers are shown:

![Structures of different kinds of star polymers](image)

**Fig 1: Structures of different kinds of star polymers**

**POLYMER LIQUID CRYSTALS**

Polymer liquid crystals (PLCs) are a class of materials that combine the properties of polymers with those of liquid crystals. These "hybrids" show the same mesophases characteristic of ordinary liquid crystals, yet retain many of the useful and versatile properties of polymers.

For flexible polymers to display liquid crystal characteristics, rod-like or disk-like elements (called mesogens) must be incorporated into their chains. The placement of the mesogens play a large role in determining the type of PLC that is formed. Main-chain
polymer liquid crystals (MC-PLCs) are formed when the mesogens are themselves part of the main chain of a polymer. Conversely, side chain to the polymer by a flexible "bridge" called the spacer. Other factors influencing the mesomorphic behaviour of polymers include the presence of long flexible spacers, a low molecular weight, and regular alternation of rigid and flexible units along the main chain.

The behaviour of polymer liquid crystals is characterized by a wide variety of unexpected phenomena, many of which remain unexplained. One of the most intriguing phenomena associated with PLCs is the observation of banded texture, which significantly affects the mechanical properties of PLCs fibred and films (11).
PLASMA POLYMERIZATION

Plasma polymerization is a procedure, in which gaseous monomers, stimulated through plasma, condense on freely selectable substrates, as high cross-linked layers. Condition for this process is the presence of chain producing atoms, such as carbon, silicon or sulphur, in the working gas. As the monomer molecules in plasma, for the most part, become shattered into reactive particles, there remain at most, only partially preserved chemical structures of the output gases in the product, which results in cross-linked and disordered structure (illustration). Structural preservation and cross-linking gradients can be controlled through process parameters, such as pressure, working gas-flow and applied electrical output; gradient layers can be constructed; i.e. with increasing degree of cross-linking over the thickness. The plasma polymers result special layer characteristics with excellent coating adhesion on almost all substrates, which are chemically, mechanically and thermally stable. Plasma polymer coatings are scratch resistant and corrosion protective.

Fig. 1.1- Comparison of the structures of plasma polymers and conventional polymers
ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

Atom transfer radical polymerization is a controlled/ "living" polymerization based on the use of radical polymerization to convert monomer to polymer. Although many of the polymer types described have been prepared using other living polymerizations, researchers have been striving to develop a living radical polymerization for nearly 40 years. An alternative was sought because other types of living polymerizations are severely limited by many factors: only a small number of monomers can be used, the reaction are sensitive to moisture, and two or more monomers cannot be randomly copolymerized. Radical polymerization, in contrast, can polymerize hundreds of monomers, can copolymerize two or more monomers, and can be performed in water as emulsions or suspensions. Controlled / "living" radical polymerization promised to overcome these limitations and provide a method to maximize the potential of living polymerizations.

The K. Matyjaszewski and J. Xia research group was the first to develop a controlled/ "living" polymerization that used a simple, inexpensive polymerization system. It is capable of polymerizing a wide variety of monomers, is tolerant of trace impurities (water, oxygen, inhibitor), and is readily applicable to industrial processes. The system that was developed was termed Atom Transfer Radical Polymerization (ATRP). ATRP is a robust system that has generated much interest among polymer chemists in both industry and academia. Science Watch, a trade Journal has recently listed three ATRP papers among the top ten cited papers in chemistry today.
The control of the polymerization afforded by ATRP is a result of the formation of radicals that can grow, but are reversibly deactivated to form dormant species. Reactivation of the dormant species allows the polymer chains to grow again, only to be deactivated later. Such a process results in a polymer chain that slowly, but steadily, grows and has a well-defined end group (for ATRP that end group is usually an alkyl halide).

The initiator is generally a simple, commercially available, alkyl halide. The catalyst is a transition metal that is complexed by one or more ligands; the catalyst does not need to be used in a one-to-one ratio with the initiator but can be used in much smaller amounts. The deactivator can be formed in situ, or for better control, a small amount (relative to the catalyst) can be added. Additionally, the catalyst is tolerant of water and trace amounts of oxygen.

Although other controlled radical polymerization systems have been reported by various groups, ATRP remains the most powerful, versatile, simple, and inexpensive. Only ATRP has been able to polymerize a wide range of monomers including various styrenes, acrylates and methacrylates as well as other monomers such as acrylonitrile, vinyl pyridine and dienes. ATRP commonly uses simple alkyl halides as initiators and simple transition metals (iron, copper) as the catalysts. These catalysts can be used in very low amounts, whereas, other controlled polymerization system require the use of expensive reagents in much higher concentrations.

**YLIDES**

Ylides are 1,2-dipolar compounds in which carbanion is covalently bonded to a positively charged hetero atom. These have been reported as potential radical initiators in
the domain of polymer science. In most cases heteroatom were non-metal like N(12); S(13); P(14). The use of metalloids such as the arsenic hetero atom is rare (15), perhaps because of poisonous character of arsenic and the difficulties associated with the synthesis of arsonium ylide. The interaction of $\pi - \pi$ overlap between hybrid $sp^2$ orbitals and the larger as well as more diffused 4d orbitals of arsenic atom may lead to the formation of free radicals. p-Acetyl benzylidene triphenyl arsonium ylide (p-ABTAY) was chosen as a new radical initiator for the copolymerization of vinyl monomers with linalool. The added advantages are, it is economical and enhances the alternating tendency of copolymers.

**TERPENOID POLYMERS**

Nearly all terpenoids are constituents of essential oils of many plants, have carbon skeleton made up of isoprene units. The application of terpenoids in the organic chemistry have been well documented. Recently, the polymerization of terpenoids have attracted polymer chemists because few terpenoids yield optically active and functional copolymers. A few polymer chemists have examined isoprene and $\alpha/\beta$-pinene for homo (16,17) as well as copolymerization (18), but no attention has been devoted on polymerization of acyclic monoterpenoids, as they do not undergo homopolymerization due to steric hindrance low stabilization energy between monomer and free radicals in transition state and excessive chain transfer.

Linalool, an optically active acyclic monoterpenoid, includes two double bonds and one tertiary alcoholic group. It is, therefore, susceptible to polymerization and is of great interest to investigate its copolymerization with vinyl monomers. Further, the copolymers formed are significant to study the kinetics, mechanism and its characterization due to
functional properties and optical activeness.

\[
\text{OH} \\
\text{Linalool}
\]

Acyclic monoterpenoids, linalool, as a new novel monomer, has been used for the synthesis and characterization of co/terpolymers with vinyl monomers such as acrylonitrile, styrene, methyl methacrylate, acrylamide, n-butyl acrylate and vinyl acetate in the presence of free radical initiator such as benzoyl peroxide, azobisisobutyronitrile and p-acetyl benzylidene triphenyl arsonium ylide. The kinetics and mechanism of co/terpolymerization of above systems have been investigated. The copolymer(s) have been characterized by using modern techniques like of Fourier-Transform Infrared spectroscopy (FTIR), \(^1\text{H}\) and \(^{13}\text{C}\)-Nuclear Magnetic Resonance (\(^1\text{H}\)-NMR, \(^{13}\text{C}\)-NMR), Gel Permeation Chromatography (GPC), Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC).

Synthetic polymers are currently being used as a construction material for home appliances, furnishing, domestic and industrial buildings, fabrics and transportation vehicles. The main reason for increasing use of polymers is their lightweight, ease of production and design flexibility. Good optical properties and mechanical properties like high tensile and impact strength, high softening point, durability (retention of optical and
mechanical properties, collection of little dirt) are some of the requirements of a polymer in such applications.

Alkyl itaconate has been copolymerized with a variety of vinyl monomers to yield copolymers with improved melt flow indices, better impact strength, abrasion resistance and heat characteristics. The ability to tailor the rigid and stable itaconate alone or in combination with styrene to fit specific application requirement such as outstanding clarity and dimensional stability and the unusual chemical and light stability of this class of materials has spurred its growth and have made itaconate esters prime candidates for numerous and diverse applications.

Incorporation of vinyl monomers such as styrene, vinyl chlorides, alkyl acrylates/methacrylates, n-aryl maleimides etc. in the itaconate backbone have been carried out in the past with an aim to improve some of the properties. Such copolymers find applications in the field of plastics, paints, binders for ceramics, viscosity index improvers, adhesives, automotive coatings and substitute for glass in solar collectors (19-30).

During the last few years, interest in the properties and applications of monoesters and diesters derived from itaconic acid has increased, because itaconic acid is obtained commercially by a fermentation process (31) but also as a consequence of great variety of polymers that can be prepared due to two lateral esterifiable groups in the monomer (32-33). Recently keen attention has been paid to dialkyl itaconate esters (DRI) since they are radically polymerized at moderate rates to yield polymer of high molecular weights in spite of two bulky substituents (34-41). Furthermore, one can regard poly (itaconic acid diesters) as poly(alkyl methacrylates) in which one hydrogen of the α-methyl group is replaced by a
second ester group and, as might be expected, poly(di-n-alkyl itaconates) exhibit many of the properties associated with the poly(alkyl methacrylates) (42-43). Copolymerisation and reactivity ratio data have been reported for monomethyl itaconate with styrene (44). Itaconic anhydride has also been used as a comonomer with several vinyl monomers including styrene (45-46).

An increase in the chain length of alkyl group is expected to affect the rate of copolymerization, as well as thermal, mechanical and optical properties of the copolymers. In order to modify the impact behaviour of polystyrene while keeping its useful properties (i.e. optical clarity, environmental stability) it is necessary to incorporate only low mole fractions of comonomers in the polystyrene. It was, therefore, considered of interest to make a comprehensive study of copolymerization behaviour of alkyl itaconate with styrene. Comonomers, hexyl itaconate, (HI), octyl itaconate, (OI), decyl itaconate (DI), dodecyl itaconate (DDI), tetradecyl itaconate (TDI), Cetyl itaconate (CI), stearyl itaconate (SI) were selected to study the effect of structure of comonomers on the rate of copolymerization and on the properties of copolymers.

A review of the state-of-art regarding the copolymerization of alkyl itaconate and styrene monomers with particular reference to alkyl (itaconate) is described in the following section. Scope of the present work, objectives and the plan of the thesis are given in later sections.

1.2 ALKYL ITACONATE MONOMERS

The properties and polymerization of itaconic acid and its derivatives has been reviewed for the period up to 1970 by Tate (47). Other studies have since been reported and information is available covering the physical properties (48-51) such as dilute
solution behaviour (52-56), polyelectrolyte and ion exchange properties (57-61), biological and anti-tumor behaviour (62-63) and response to high energy radiation (64) of these materials.

1.2.1 Structure

Alkyl itaconate esters are unsymmetrically substituted ethylene, and can be represented by the generic formula.

\[ \begin{align*}
  &\text{H} \quad \text{O} \\
  &\text{a} \quad \text{CH}_2 \quad \text{C} \quad \text{O} \quad \text{H}_2\text{C} \quad (\text{CH}_2)_n \quad \text{CH}_3 \\
  &\text{C} \quad \text{c'} \quad \text{e'} \quad \text{f} \\
  &\text{b} \quad \text{O} \\
  &\text{a'} \quad \text{CH}_2 \quad (\text{CH}_2)_n \quad \text{CH}_3
\end{align*} \]

The identity of \((\text{CH}_2)_n\) groups determine the properties of both the monomers and the polymers. The esterification of itaconic acid has been done by using alcohols having a long chain. Following methods have been used for the preparation of alkyl itaconates:

a) Direct esterification of itaconic acid

b) Transesterification using alkyl esters of itaconic acid and appropriate alcohol

The most commonly used method is direct esterification and the commonly used catalyst includes: sulphuric acid, p-toluene sulphonic acid, and sulphonic acid functional cation exchange resins. The water formed in the direct esterification is azeotropically removed by carrying out the reaction in refluxing toluene in the presence of a polymerization inhibitor like hydroquinone (65).
1.3 **STYRENE**

It may well be argued that the history of polystyrene is more closely bound up with the history of the twentieth century than is the case with any other plastics material. After the war however there was a large surplus capacity of plant for the manufacture of styrene and polystyrene together with a great deal of knowledge and experience that had been collected over the war years. It was therefore found possible to produce polystyrene, not as an expensive electrical insulator, but as a cheap general purpose thermoplastic. Because of such desirable characteristics as low cost, good mouldability, excellent colour range, transparency, rigidity and low water absorption, polystyrene became rapidly developed. For many purposes, however, it was considered to be unacceptably brittle and this led to the development of the rubber-modified high-impact polystyrene (HIPS) and to the complex ABS, AMBS and MBS materials. These developments, together with the considerable success of expanded polystyrene as both insulation and packaging material,
have led to the plastic materials based on styrene becoming a most important group of thermoplastics. World production capacity of polystyrene, including high impact polystyrene but excluding Eastern bloc capacity, is somewhat in excess of $6 \times 10^6$ tonnes, which rates it fourth after polyethylene, poly(vinyl chloride) (PVC) and polypropylene in tonnage terms. About 60% of this production (in Western Europe at least) is high impact polystyrene rather than the general purpose material. Major producers include Ato Chimie (Lacqrene), BASF (Polystyrol), Dow (Styron), Hoechst (Hostyren), Monsanto (Lustrex), and Montedison (Edistir).

In addition, production of ABS and related materials (such as SAN and ASA) in the western world was estimated at $2 \times 10^6$ tonnes in 1986, of which some 85-90% was accounted for by ABS alone. For expanded polystyrene the figure is now believed to be in excess of $1 \times 10^6$ tonnes. The rarely used systematic IUPAC name for polystyrene is poly-(1-phenylethylene).

### 1.3.1 Preparation of Styrene

In 1786 William Nicholson wrote a Dictionary of Practical and Theoretical Chemistry. In this work Nicholson mentions that a chemist named Neuman, on distillation of storax (a balsam derived from the tree Liquamber Orinetalis), had produced fragrant empyreumatic oil. In 1839 E. Simon carried out some similar experiments, apparently quite independently, and again obtained this essential oil, which he called styrol. In 1845 M. Glenard and R. Boudault reported the production of styrol (now known as styrene) by dry distillation of dragons blood, a resin obtained from the fruit of the Malayan rattan palm.
In 1869 Berthelot reported the production of styrene by dehydrogenation of ethylbenzene. This method is the basis of present day commercial methods. Over the years many other methods were developed such as the decarboxylation of acids, dehydration of alcohols, pyrolysis of acetylene, pyrolysis of hydrocarbons and the chlorination and dehydrogenation of ethylbenzene.

There are today two methods of interest, (a) the laboratory preparation, and (b) commercial preparation.

1.3.2 Laboratory Preparation of Styrene

The principal constituent of storax is cinnamic acid and for laboratory purposes styrene is still most easily obtained in high purity by dry distillation of cinnamic acid and its salts under atmospheric pressure.

\[
\text{Dry} \quad \text{Distill} \quad \text{CH}=\text{CH}_{2} + \text{CO}_2
\]

The cinnamic acid is readily prepared by heating benzaldehyde with acetic anhydridic and sodium acelate (the Perkin Reaction)

\[
\text{CH} = \text{CHCOOH} \quad + \quad \text{CH}_3\text{COO}^+ \quad \text{CH}_3\text{COOH}
\]
1.3.3 Commercial Preparation

The bulk of commercial styrene is prepared by, the Dow process or some similar system. The method involves the reaction of benzene and ethylene to ethylbenzene, its dehydrogenation to styrene and a final finishing stage. It is therefore useful to consider this process in each of the three stages.

1.3.4 Preparation of ethylbenzene

Ethylbenzene is prepared by reaction of ethylene and benzene in the presence of a Friedel-Crafts catalyst such as aluminium chloride at about $95^\circ$C

\[
\text{C}_6\text{H}_6 + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_8\text{H}_{10}
\]

To improve the catalyst efficiency some ethyl chloride is added which produces hydrochloric acid at the reaction temperature.

The purity of the ethylene is not critical providing that acetylene is not present. The normal purity of ethylene used is about 95%. The purity of the benzene is somewhat higher at about 99% and it is important here that sulphur, as impurity, should be below 0.10%.

After passing through the reaction chamber the products are cooled and the aluminium chloride, which is in the form of a complex with the hydrocarbons, settles out. The ethylbenzene, benzene and polyethylbenzene are separated by fractional distillation, the ethylbenzene having a purity of over 99%. The polyethylbenzene is dealkylated by
heating at 200°C in the presence of aluminium chloride and these products together with the unchanged benzene are recycled.

Plants have now been installed by some manufactures to produce ethylbenzene via catalytic reforming process. The reforming process is one, which converts aliphatic hydrocarbons into a mixture of aromatic hydrocarbons. This may be subsequently fractionated to give benzene, toluene and a xylene fraction from which ethylbenzene may be obtained.

1.3.5 Dehydrogenation

\[
\begin{align*}
\text{C}_2\text{H}_5 \quad & \quad 630^\circ\text{C} \quad & \quad \text{CH} = \text{CH}_2 \\
\end{align*}
\]

**Ethyl benzene** \hspace{2cm} **Styrene**

Styrene is produced from ethylbenzene by the process of dehydrogenation.

This is an endothermic reaction in which a volume increase accompanies dehydrogenation. The reaction is therefore favoured by operation at reduced pressure. In practice steam is passed through ethylbenzene in order to reduce the partial pressure of the latter rather than carrying out a high temperature reaction under partial vacuum. By the use of selected catalysts such as magnesium oxide and iron oxide a conversion of 35-40% per pass with ultimate yields of 90-92% may be obtained.
1.3.6 Styrene purification

The dehydrogenation reaction produces 'crude styrene' which consists of approximately 37.0% styrene, 61% ethylbenzene and about 2% of aromatic hydrocarbon such as benzene and toluene with some tarry matter. The purification of the styrene is made rather difficult by the fact that the boiling point of styrene (145.2°C) is only 9°C higher than that of ethylbenzene and because of the strong tendency of styrene to polymerise at elevated temperatures. To achieve a successful distillation it is therefore necessary to provide suitable inhibitors for the styrene, to distil under a partial vacuum and to make use of specially designed distillation columns.

In one process the crude styrene is first passed through a pot containing elemental sulphur, enough of which dissolves to become a polymerization inhibitor. The benzene and toluene are then removed by distillation. The ethylene is then separated from the styrene and tar by passing this through two distillation columns each with top temperatures of about 50°C and bottom temperatures of 90°C under a vacuum of about 35mmHg.

Styrene is a colourless mobile liquid with a pleasant smell when pure but with a disagreeable odour due to traces of aldehydes and ketones if allowed to oxidize by exposure to air. It is a solvent for polystyrene and many synthetic rubbers including SBR but has only a very limited mutual solubility in water.
1.4 COPOLYMERISATION

Copolymerisation is the most general and powerful method of bringing about systematic changes in polymer properties and is widely used in the production of commercial polymers and in fundamental investigation of structure–property relationship. Copolymerisation modifies the symmetry of the polymer chain and modulates both intramolecular and intermolecular forces, so properties such as melting point, glass transition temperature, crystallinity, solubility, elasticity, permeability and chemical reactivity may be varied within wide limits (66).

Several monomers that do not homopolymerise or produce low molecular weight polymers might undergo copolymerisation to yield good polymers, provided that the comonomers are properly selected. For example maleic anhydride does not homopolymerise but undergoes copolymerisation with styrene and other suitable monomers to produce commercially useful materials (67-68). N-substituted maleimides are known to homopolymerise both free radically and anionically to give low molecular weight polymers (69), however it has been copolymerized successfully with a variety of vinyl monomers to give high molecular weight products.

Monomeric itaconate esters copolymerize with several other vinyl monomers to increase the range of available polymer properties. By judicious adjustments of the amount of each type of monomer, polymers of desired properties can be prepared. Polymers of this class are noted for their water-clear colour and retention of their properties upon ageing under severe service conditions. Small amounts of specially functionalized monomers are often copolymerized with itaconate monomers to modify or improve the properties of the
polymer directly or by providing sites for further reactions.

In the copolymerization reaction of alkyl itaconate with styrene, the repeating units are expected to have the following structure.

\[
\begin{align*}
\text{benzene} & \quad (\cdot \text{H}_2\text{C} - \text{CH}_2\cdot)^x \\
\text{alkyl itaconate} & \quad (\cdot \text{H}_2\text{C} - \text{C} - \text{O} - \text{O})^y
\end{align*}
\]

1.5 KINETICS OF RADICAL (CO) POLYMERISATION

In the homopolymerization of dialkyl itaconates (DRI) overall rate of polymerization (\(R_p\)) is reported to be proportional to the square root of initiator concentration, indicating that bimolecular termination occurs in these polymerization systems. However, the orders with respect to the monomer are higher (between 1.6 and 2.0) than those observed for usual polymerization of vinyl monomers (70-72).

From \(R_p\) and initiation rate of polymerization (\(R_i\)) of some DRIs together with the concentration of propagating polymer radicals determined from e.s.r. Spectroscopy, DRIs have homopropagation (\(k_p\)) and homotermination (\(k_t\)) rate coefficients lower than those found for the usual vinyl monomers, which indicates that steric effects of the substituents play an important role in both homopropagation and homotermination rate constants (73-75). The overall activation energy of the polymerization is lower than those
observed for conventional monomers such as methyl methacrylate or styrene. In order to explain such behaviour individual kinetics coefficients for each step of free radical homopolymerization have been determined (76-78).

On the other hand, a slight variation of homopropagation rate coefficients is noted on changing the monomer concentration, but efficiency factor and termination rate coefficients decrease with an increase of the monomer concentration. This has been described to the increase of the medium viscosity and/or chain length dependence. It is well known termination rate coefficient is dependent on the chain length and Sato et al (79) found a slope of −0.65 in the plot of termination rate coefficients vs chain length. This value is higher than those found for methyl methacrylate (−0.15) or for styrene [−0.24] (80-81). Thus the large chain length dependence of the termination rate coefficients seems to originate mainly from the dependence of termination rate on the monomer concentration. Besides, the kinetics parameters are modified as a function of the carbon number of the ester alkyl group. Thus propagation and termination rate coefficients are reduced with an increase of the carbon number of the alkyl substituents, but the decrease of termination rate coefficients is larger than that for the propagation rate coefficient, giving rise to an increase of the overall rate of polymerization when the length of alkyl substituents increases (82-84).

Although no kinetics mechanisms have been studied, copolymerization of some DRI with styrene (S) has shown that the apparent copolymerization rate increase with the increase of (S) concentration in the feed (85-87). The structure of alkyl substituents in the itaconate esters does not change the values of the reactivity ratios significantly when S is used as comonomer, and the observed Q/e values indicate that DRI is an electron–acceptor
and conjugative monomer. On the other hand, the relative reactivity of DRI towards polystyrene radical was found to decrease slightly by the introduction of electron donor and sterically hindered alkyl group (88).

Only a few and opposite reactivity ratio values (89) for the free - radical polymerization of DRI with methyl methacrylate (MMA) have been reported, the values obtained for Q and e parameters being very different from those obtained from the copolymerization with S. Furthermore, critical tests of terminal or other kinetic models for the overall copolymerization rate of DRI have not been examined.

The central equation of "classical free-radical polymerization kinetics' relates the rate of polymerization \( R_p \) with the concentrations of the reactants e.g. monomer concentration \([M]\) and initiator concentration \([I]\).

\[
R_p = \frac{d[M]}{dt} = k [M][I]^{1/2}
\]

Here \( k \) denotes the overall rate constant of polymerization and contains the elementary reaction rate constants of the chain initiation \( f_k d \) (\( f = \) cage efficiency ; \( k_d = \) decomposition rate constant of the initiator), the chain propagation \( k_p \), and the chain termination \( k_t \):

\[
K = \left( \frac{2 f k_d k_p^2}{2k_t} \right)^{1/2}
\]

However, deviations have been observed which were mostly explained by side reactions. The chain termination is a diffusion controlled reaction and the dependence of \( k_t \)
on steric factors has been substantiated by studying the effect of alkyl group on the
reactivity of alkyl itaconate monomers by several workers (90-93) concluded that the
propagation rate constant remains constant with increasing length of alkyl (ester) group in
alkyl itaconate, whereas the termination rate constant decreases as a result of the increased
steric effect of the alkyl group. Since the viscosity of alkyl itaconate monomers increase
with the number of carbon atoms in the alkyl group, it is quite likely that the termination in
these polymers is diffusion-controlled.

Polymerization of several alkyl itaconate (alkyl group from C$_1$ – C$_4$) by
azobisisobutyronitride (AIBN) at 60°C was investigated by Otsu et al (94). The rate of
polymerization increased with increasing length of the alkyl group. Authors have
suggested that the radical reactives of alkyl itaconate depend on the polar characteristics
of alkyl group but are independent of steric factors. Inchenko et al (95) studied
polymerization kinetics of methacrylate of C$_{12}$ –C$_{16}$ alcohols at 363-378 K in toluene in the
presence of BPO as an initiator and dodecyl mercaptan as molecular weight regulator. An
increase in temperature increased the consumption of the monomer. The activation energy
of the polymerization was 95.4kJ/mole group.

1.6 CHARACTERISATION

1.6.1 Structural Characterization

Analytical techniques used for the determination of copolymer composition include
elemental analysis (96) infrared absorption spectroscopy, magnetic resonance spectroscopy
and pyrolysis gas chromatography. UV absorption (97-100) and IR spectroscopy (101-103)
have provided limited sequence information because these two methods require the two
monomers to have absorbing structures, which are significantly different. $^1$H-NMR and
$^{13}$C – NMR methods are widely applicable to copolymer analysis and are particularly valuable for its rapidity and simplicity. These methods are used for determining the copolymer composition (104-107), and for characterizing the monomer sequence distribution (108-115). Compositional analysis of methyl methacrylate –styrene random copolymers by uv spectrophotometer (at 260nm), $^1$H-NMR and IR (at 1730 cm$^{-1}$) have been accomplished by Mori, and reported an excellent agreement between these three methods.

Characterization and composition determination of copolymers of MMA has also been done by pyrolysis followed by analysis of products using gas-liquid chromatography (116-118) Haslam et al. (119) and Radell et al. (120) were among the early workers who investigated the application of gas chromatography to the separation and identification of pyrolysis products. They demonstrated that gas chromatography coupled with a controlled temperature pyrolysis technique can be employed as a rapid semi quantitative method for the determination of the composition of mechanical mixture of acrylic and methacrylic polymers.

1.6.2 Thermal Behaviour

Glass transition temperature of poly (di-n-alkyl itaconates), have been studied largely by Cowie (121-123). From these studies it follows that $T_g$ values of poly (DRI) decrease monotonically with increasing chain length of di-n-alkyl substituents from methyl to hexyl derivatives. When the length of the single bonded carbon atoms of alkyl groups increase from seven to eleven, poly (DRI) shows two apparent glass transitions $T_g^u$ and $T_g^l$, where $u$ refers to the higher temperature. $T_g^l$ has been ascribed to the independent micro-Brownian motion of a side chain occurring below the conventional main chain
relaxation $T_g^u$. Itaconate derivates containing n-alkyl ester side chain of twelve or more single bonded carbon atoms displayed a pronounced melting point but no $T_g$.

Although some copolymerization and reactivity ratio data of di-n-alkyl itaconate with other monomers like styrene (124-126), have been reported, to our knowledge only the thermal stability and glass transition of thermally cross-linkable methyl methacrylates based copolymers containing monomethyl itaconate or itaconic anhydride as comonomers have been described (127). Also random copolymers synthesized from mixtures of dialkyl itaconate esters have been studied (128). Thus, copolymers obtained using dimethyl itaconate as comonomer 1 and di-n-heptyl itaconate as monomer 2 show two transition temperatures. The position of lower transition is approximately composition independent but the inflection diminishes in intensity as concentration of the longer side chain comonomer decreases. The position of the higher transition of the referred copolymers and those of the copolymers obtained from di-n-propyl itaconate with di-n-octyl itaconate are dependent on the copolymer composition. It increases as the content of copolymer became richer in the shorter side chain component (128).

Thermal stability of the copolymers was determined by recording TG/DTG traces in nitrogen atmosphere. The relative thermal stability of the copolymers was compared by comparing the initial decomposition temperature ($T_i$), temperature of maximum rate of weight loss ($T_{max}$), final decomposition temperature ($T_f$) and percent weight loss at 500°C.

DSC scans of copolymers and homopolymers were recorded to study the effect of the copolymer composition and comonomer structure on the glass transition temperature of the copolymers.
1.7 RECTIVITY RATIOS

A considerable amount of research effort has been directed to develop methods for estimating reactivity ratios from the experimental data (129-139). Different procedures for calculation of monomer reactivity ratio exist using the differential or integral form of the copolymerization equation. These include approximation, linearization intersection and curvefitting.

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

Where \([M_1]\) and \([M_2]\) are the concentrations of monomer 1 and 2 in the initial feed and \(r_1\) and \(r_2\) are the reactivity ratios of two monomers respectively. For all the copolymer systems, described above the values of the product \(r_1 r_2\) are not far from unity, indicating thereby that these systems approximate to the ideal copolymerization. Extremely low reactivity ratio (\(r_2\)) observed in this system can be attributed to the general problem of allylic polymerization.

Besides depending upon the nature of the monomer, reactivity ratio also depends on the nature of the solvent. For example in radical copolymerization of MMA with 1-naphthyl methacrylate in benzene, chlorobenzene and o-dichlorobenzene at 50\(^\circ\)C, marked effect of solvent on both \(r_1\) and \(r_2\) was observed. This was correlated with the variation in the polarity of the solvents (140).
From knowledge of reactivity ratios in copolymerization, the Q and e values of Alfrey-Price equation can be determined (141-144). Although extensive studies have been carried out for copolymerization of dialkyl itaconates with variety of vinyl monomers. However no systematic studies have been carried out to investigate the effect of length of alkyl side chain in itaconate esters on the copolymerization behaviour & thermal behaviour etc.

1.8.1 Objectives

1. Synthesis and characterization of alkyl itaconate monomers of following structure.

\[
\begin{align*}
\text{a} & \quad \text{b} & \quad \text{O} & \quad \text{c} & \quad \text{e} & \quad \text{f} \\
\text{CH}_2 & \quad \text{C} & \quad \text{O} & \quad \text{H}_2\text{C} & \quad (\text{CH}_2)_n & \quad \text{CH}_3 \\
\text{a'} & \quad \text{H} & \quad \text{C} & \quad \text{C} & \quad \text{O} & \quad \text{CH}_2 & \quad (\text{CH}_2)_n & \quad \text{CH}_3 \\
\text{H} & \quad \text{H} & \quad \text{O} & \quad \text{CH}_2 & \quad (\text{CH}_2)_n & \quad \text{CH}_3 \\
\end{align*}
\]

Where

- \( n=4 \), n-hexyl itaconate (HI)
- \( n=6 \), n-octyl itaconate (OI)
- \( n=8 \), n-decyl itaconate (DI)
- \( n=10 \), n-dodecyl itaconate (DDI)
- \( n=12 \), n-tetradecyl itaconate (TDI)
- \( n=14 \), n-cetyl itaconate (CI)
- \( n=16 \), n-stearyl itaconate (SI)

(Letters in parentheses indicate the letter designation of the alkyl itaconate monomers).
2. Copolymerisation studies using free radical initiator (azobisisobutyronitrile).
   i. To study the effect of structure of the comonomer, temperature and initiator concentration on rate of polymerization.
   ii. Structural characterization of copolymers and determination of monomer reactivity ratios.
3. Studies of the effect of structure of copolymers on thermal behaviour.

1.8.2 Plan of the Thesis

Besides this introductory chapter and literature survey, the thesis contains four more chapters.

The synthesis, characterization of alkyl itaconate and copolymerization studies are described in chapter II of the thesis. Esterification of itaconic acid with the corresponding alcohols in the presence of p-toluene sulphonic acid was used for synthesizing the monomers. Characterization of monomers was done by spectroscopic methods i.e. FTIR and \(^1\)H- NMR.

Homopolymerization and copolymerisation of alkyl itaconate with styrene was carried out in bulk and/solution (using THF as solvent) in N\(_2\) atmosphere at 60\(^0\) C using azobisisobutyronitrile (AIBN) as an initiator. The effect of structure of comonomer, initiator and temperature on the rate of free radical copolymerization of a 2:1 molar ratio of HI: styrene, OI: styrene, DI: styrene, DDI: styrene, TDI: styrene, CI: styrene and SI: styrene was followed by gravimetric method.
Structural characterization of copolymers is described in chapter III of the thesis. The copolymer composition was determined from $^1$H-NMR spectra using Grassie and ratio methods. From the copolymer composition, reactivity ratios $r_1$ (styrene) and $r_2$ (comonomer) were calculated using Fineman-Ross and Kelen-Tudos method. The Q and e values of comonomers were also determined using Alfrey-Price equation.

Molecular characterization was done by intrinsic viscosity measurements. Intrinsic viscosity [$\eta$] of the copolymers was determined in tetrahydrofuran (THF) at $30 \pm 1^\circ$C using an Ubbelohde suspension level viscometer. Molecular weight and molecular weight distribution (MWD) of these copolymers was determined by using waters 600 GPC and polystyrene standards for calibration.

Thermal behaviour of the homopolymers and copolymers of alkyl itaconate form the basis of chapter IV of the thesis. Thermal stability of copolymers was evaluated in nitrogen atmosphere using Dupont 1090 thermal analyzer having 951 TG module at a heating rate of $10^\circ$C/mn. Summary and discussion highlighting the salient features of the work are given in chapter V of the thesis. Suggestions for future work are also given. References are given at the end of the thesis.