

INTRODUCTION

CHAPTER I

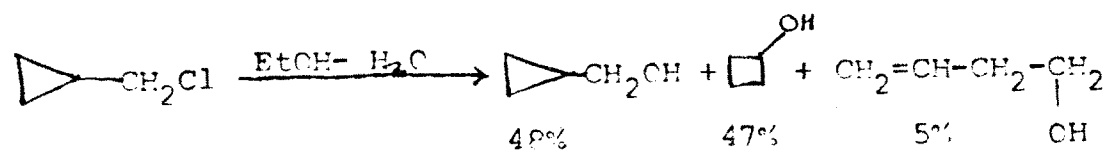
INTRODUCTION

Ring opening reactions are observed in molecules having strained ring structure, and the process of ring opening results in easing out strain earlier prevailing in the ring structure. Ethylene oxide undergoes various ring opening reactions to afford alkenes, β -hydroxy esters, halohydrins, mercaptans etc., mainly because 60° angle (between oxygen atom and carbon atoms) represents a large departure from the tetrahedral angle. The counterpart of ethylene oxide, (ether), is much less reactive than ethylene oxide (1). Cyclopropane which is even more strained than ethylene oxide, gets cleaved very easily than would be expected for an ^{acyclic} alkane. Other compounds having a three membered ring structure are also reactive. As the size of the ring becomes larger, the compound tends to be less reactive due to lesser ring strain. Six membered rings are practically strainless. In general it can be said that for ring opening reactions entropy factor (change in entropy) is favourable to make reaction feasible by lowering of free energy of the product (opened structure) in comparison with that of the cyclic structure.

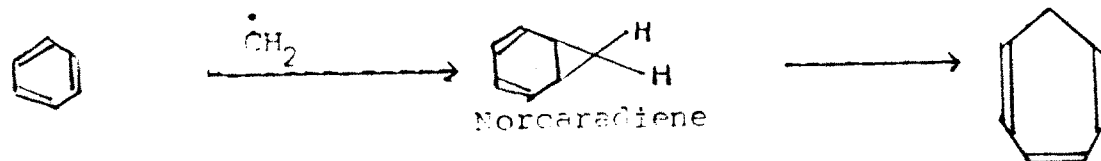
In some cases, reactions are accompanied by releasing of ring strain by ring expansion, hence the products include ring

structures larger than those of reactants. Some cases are listed below.

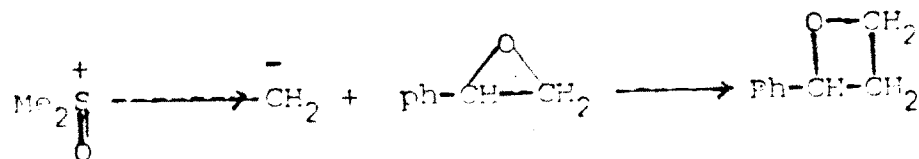
- 1) When cyclopropyl chloromethyl substrates are solvolysed, the products include 3 membered hydroxymethyl cyclopropane as well as cyclobutanol in equal amounts (2).



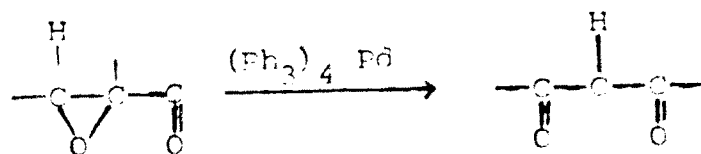
- 2) Carbenes often add to the size of aromatic rings, carbenes react with benzene to form cycloheptatriene (3).



- 3) Dimethyl sulphonium methylide when reacted with epoxides, oxetanes are obtained (4).



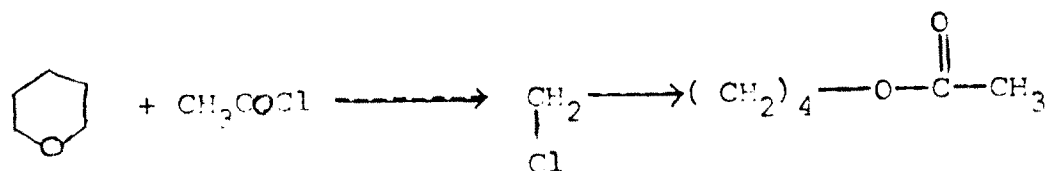
- 4) Certain transition metal catalysts convert α - β epoxy ketones to β - diketones (5,6).



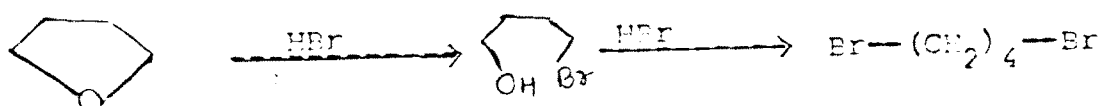
1.1 RING OPENING REACTIONS

Some reactions are mentioned below

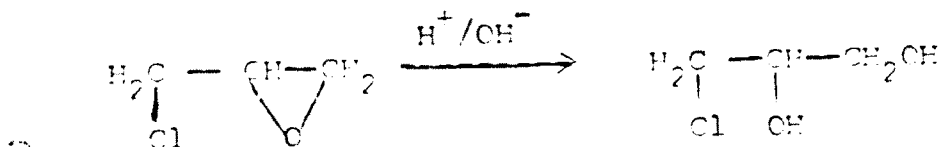
- a) Synthesis of 5-chloro pentyl-acetate : 5-chloro-pentyl-acetate is prepared from the reaction between tetrahydropyran and acetylchloride (7).



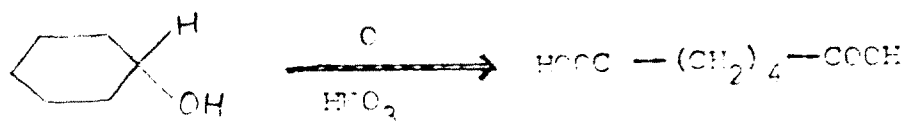
- b) Synthesis of α - ω Dihalides : Cyclic ethers (Tetrahydrofuran, Tetrahydropyran) are readily cleaved by hydrobromic acid to yield α - ω dihalides.



- c) Synthesis of Vicinal Diols : Oxiranes undergo ring opening to give vicinal diols (8).



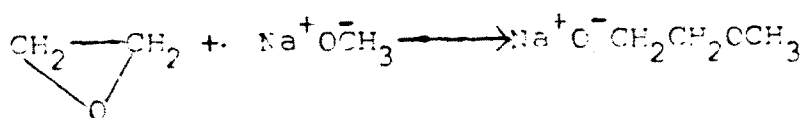
- d) Synthesis of Adipic Acid : Adipic acid is synthesized by oxidation of cyclohexanol by nitric acid (9).



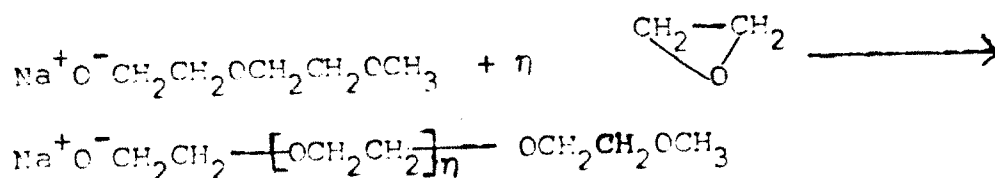
1.2 RING OPENING POLYMERIZATION :

Monomers having a ring structure may undergo ring opening polymerization if conditions are favourable. Cyclic compounds such as lactones, lactams and oxiranes can be opened up by aqueous alkali or acids to form intermediates with active ends capable of undergoing further polymerization. It may be noted that 4 and 8 membered lactones possessing a strained ring structure can be polymerized by ring opening. On the other hand 5 membered lactone is rather difficult to undergo polymerization. The mechanism of ionic ring opening polymerization can be explained by considering the example of polymerization of ethylene oxide. Sodium ethoxide (containing traces of methanol) dissolved in dioxane, attacks the oxirane ring and an acyclic anion is generated. This anion further attacks other molecules of ethylene oxide and gets added on with the simultaneous formation of bigger anions. The process goes on and on. Termination of the growing chains can be effected, when the anion is caged by adding a proton.

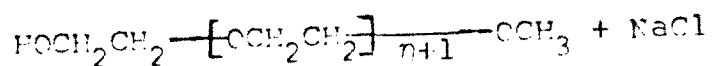
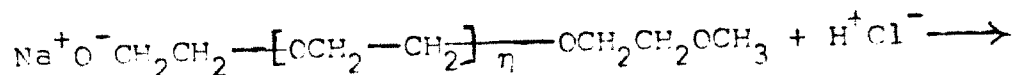
Initiation : -



Propagation : -



Termination : -

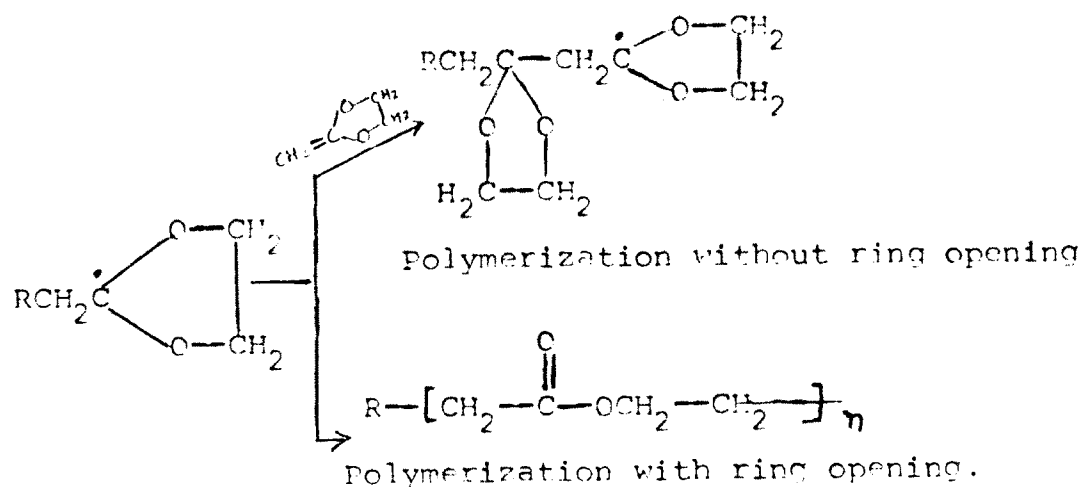


The ionic ring opening polymerization of heterocyclic compounds such as ethylene oxide, tetrahydrofuran, ethyleneimine, B-propiolactone and caprolactam, as well as the Ziegler-Natta ring opening of cyclic alkenes such as cyclopentene and norbornene are well known.

1.3 RADICAL RING OPENING POLYMERIZATION :

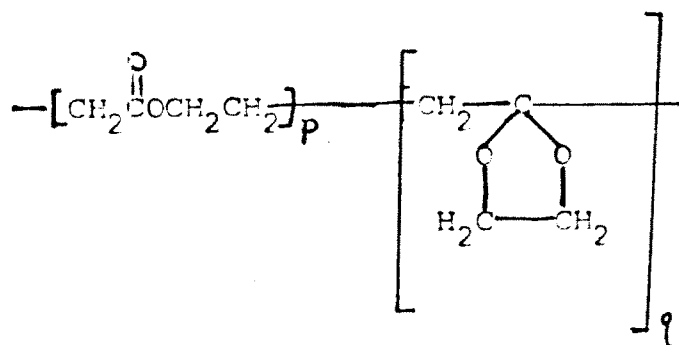
Radical ring opening polymerization reactions are rather rare. Cyclic ketene acetals undergo radical ring opening polymerization. Bailey (10) reported polymerization of cyclic ketene acetal (2-methylene-1,3-dioxolane), with the mechanism as..





The above mentioned mechanism of ring opening polymerization can be explained on the basis of higher thermodynamic stability of carbon-oxygen double bond over that of carbon-carbon double bond (11). (The former is stable by at least 50-60 Kcal/mole). It was observed that the polymerization of 2-methylene-1,3-dioxolane resulted in a polymer containing ester linkages in the backbone of the polymer as well as oxolane linkages. The extent of ring opening was confirmed by IR, NMR spectroscopy and by chemical analysis. Basic hydrolysis of the polymer formed, resulted in cleavage of the ester groups, keeping the oxolane groups intact. The polyester formed by radical ring opening polymerization is difficult to be synthesized by other routes i.e. from condensation of hydroxybutyric acid or ring opening polymerization of γ -butyrolactone.

Thus the structure of the polymer can be represented as,

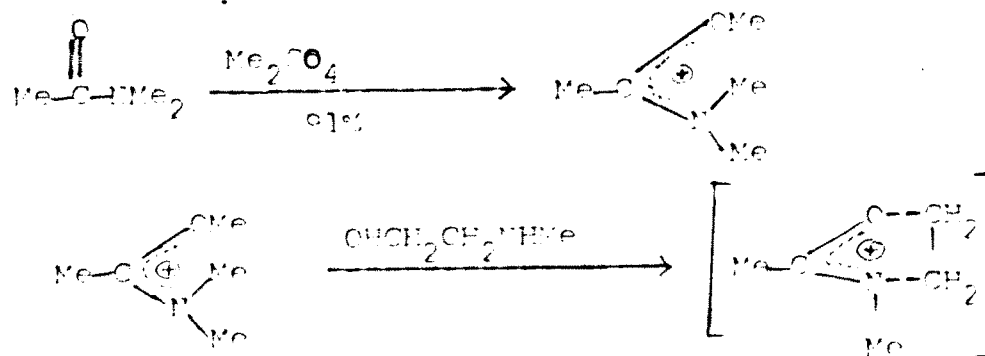


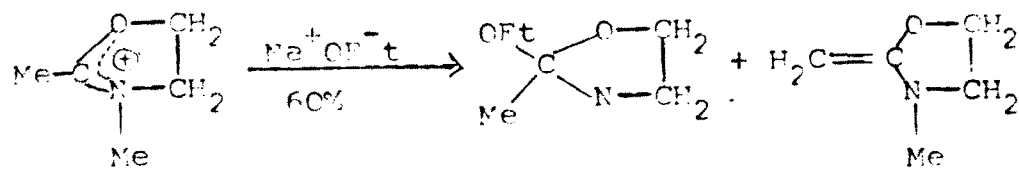
The polymer formed can be regarded as copolymer.

Additional cyclic ketene acetals (12-14) were reported to undergo radical ring opening polymerization. They included oxolanes such as 4-phenyl-2-methylene-1,3-dioxolane, 4-methyl-2-methylene-1,3-dioxolane, 4,5-dimethyl-2-methylene-1,3-dioxolane, 4,5-tetramethyl-2-methylene-1,3-dioxolane and oxanes such as 4,6-dimethyl-2-methylene-1,3-dioxane, 2-methylene-1,3-dioxane, 5-diethyl-2-methylene-1,3-dioxane. Even seven membered cyclic ketene acetals were reported to undergo radical ring opening polymerization. One of them was 2-methylene-1,3-dioxo-5-pene.

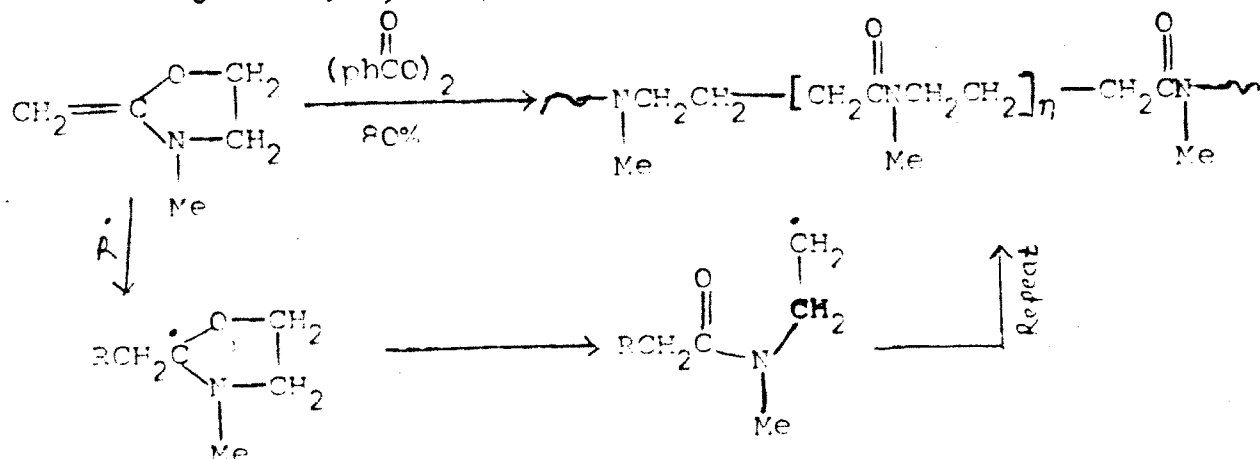
1.4 NITROGEN AND SULPHUR ANALOGS OF CYCLIC KETENE ACETALS

The Nitrogen analog of 2-methylene-1,3-dioxolane was prepared by substituting 2-N-methylamino ethanol for the ethylene glycol.

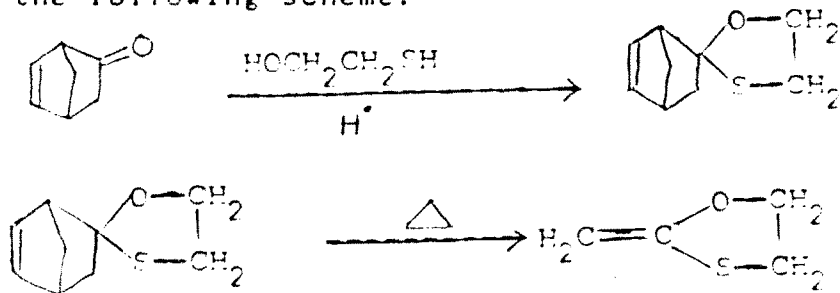




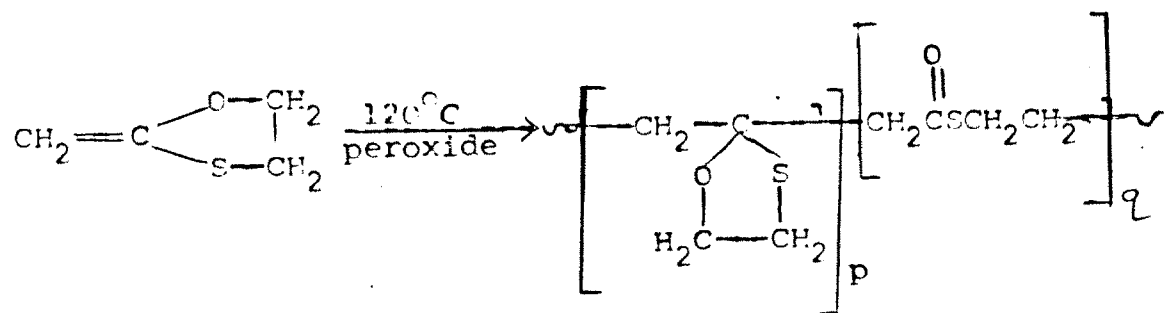
Radical ring opening polymerization of this monomer was carried out using benzoyl peroxide as an initiator.



The sulphur analog of 2-methylene-1,3-dioxolane was prepared according to the following scheme.



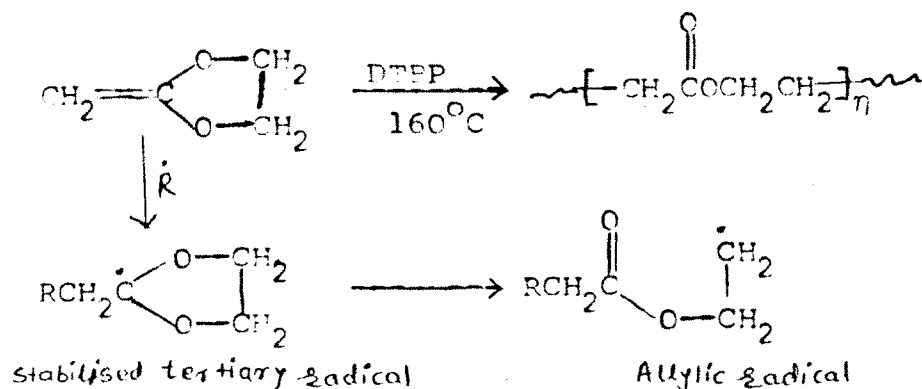
Radical chain polymerization of this monomer resulted in a 'copolymer' (15)



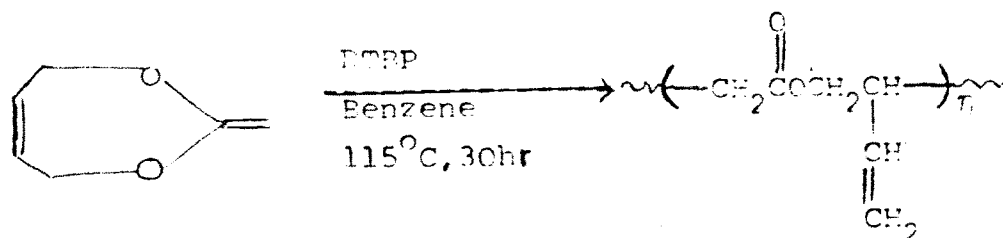
1.5 MECHANISM OF FREE RADICAL RING OPENING OF 2-METHYLENE-1,3-CYCLIC KETENE ACETALS

It was observed that generally an alkyl group in the 4 position of 2-methylene-1,3-dioxolane promoted moderately the extent of ring opening while phenyl group on the 4 position did so substantially. Also the size of the acetals seemed to have a role to play in the extent of ring opening in that, a seven membered ring promoted the extent of ring opening more than that by a six membered and a five membered ring respectively. In addition, the effects tended to be additive.

In the case of cis-4,5-diphenyl-2-methylene-1,3-dioxolane the presence of cis-phenyl groups ensured quantitative ring opening in both homopolymerization and copolymerization. It was inferred that substituents such as phenyl group in the 4 position of cyclic ketene acetals stabilised the open chain radical and thus facilitated quantitative ring opening.

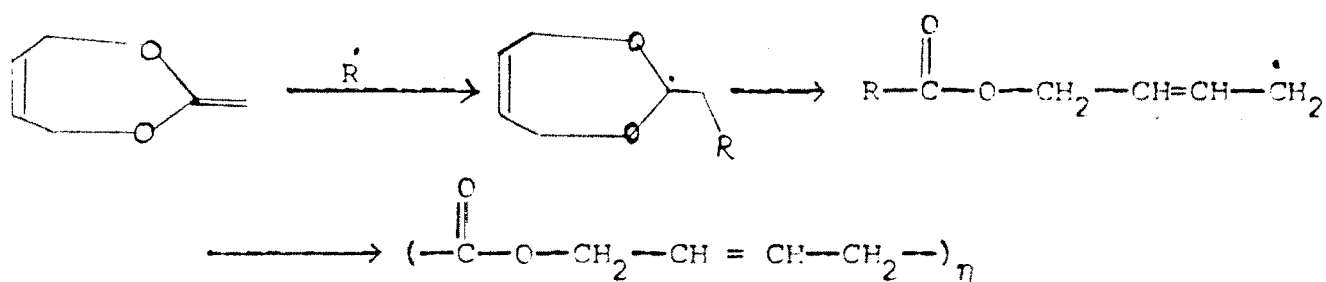


Since the direct addition of cyclic stabilised tertiary radical to the monomer during polymerization is a bimolecular process, the rate of this process would decrease on dilution. This eventually would help in a higher extent of ring opening, as conversion of cyclic radical to open chain radical being a unimolecular process, dilution has no effect on its rate. However this mechanism seemed to be greatly oversimplified as polymerization of 2-methylene-1,3-dioxo-5-pene polymerized with radical ring opening mechanism to give 100% ring opening with only the vinyl containing structure (100% 1:2 addition) being formed.

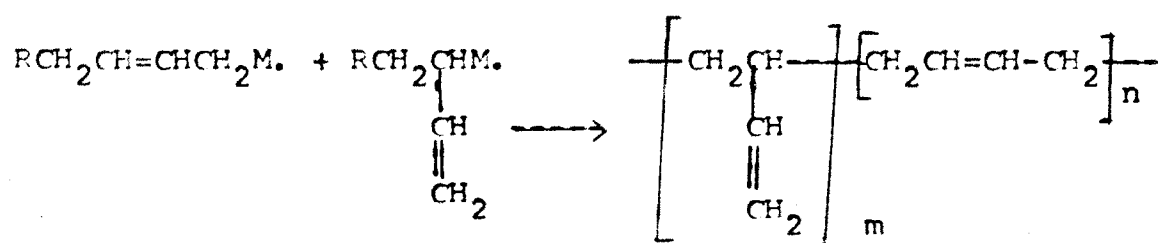
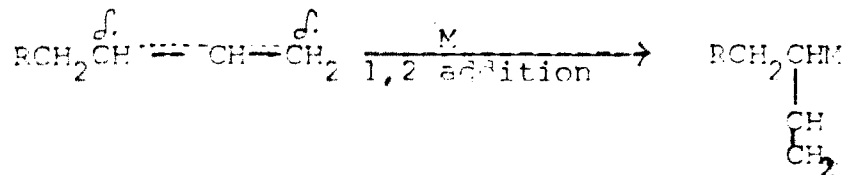
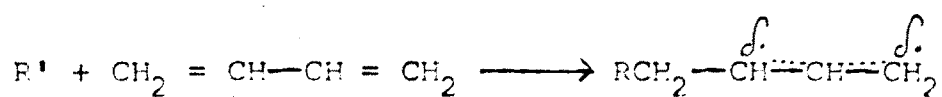


The result was surprising according to the traditional mechanism the free radical would have added to the ketene acetal double bond to form a stabilised tertiary radical. Subsequently the ring would have opened with the formation of ester group to generate a

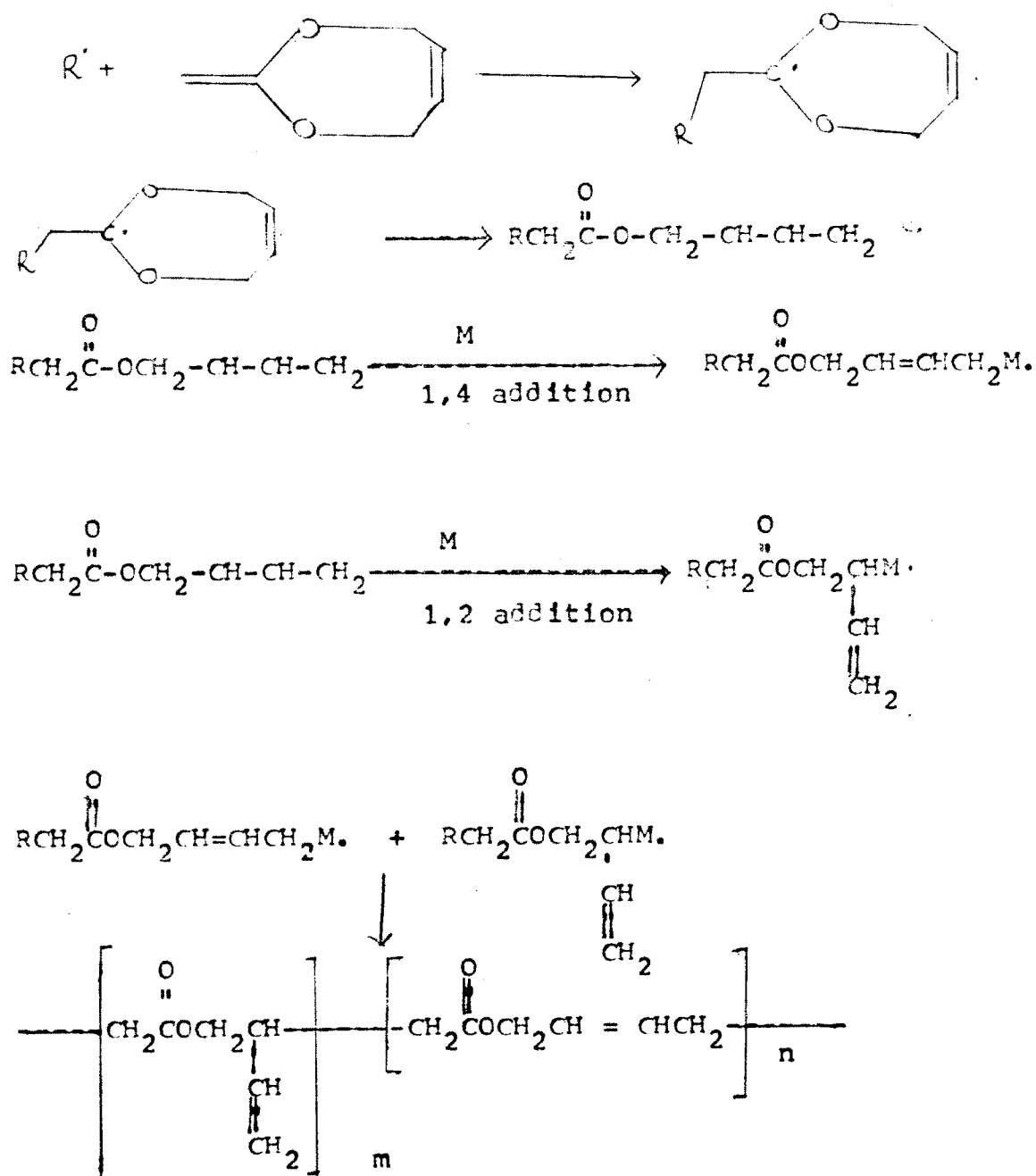
new allylic radical. The traditional mechanism is depicted below



As soon as the allylic radical forms, the end of the growing polymer chain would be expected to be similar to that present in the polymerization of butadiene as given below



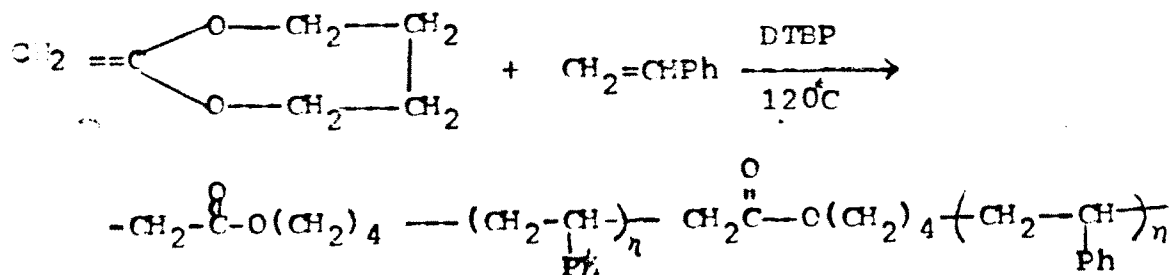
In the case of cyclic ketene acetal polymerization it can be expected that the allylic radical may undergo both 1:4 addition and 1:2 addition.



The results obtained were in obvious contradiction to the expected mechanism because the polymer obtained was not a 'copolymer'. Also the product obtained was thermodynamically less stable. Therefore it can be concluded that the radical formed by ring opening is never really free and that the process is somewhat concerted. Alternatively it can be said that the bond making step involving a second monomer occurs at, nearly the same time as bond breaking step.

1.6 COPOLYMERIZATION OF CYCLIC KETENE ACETALS : -

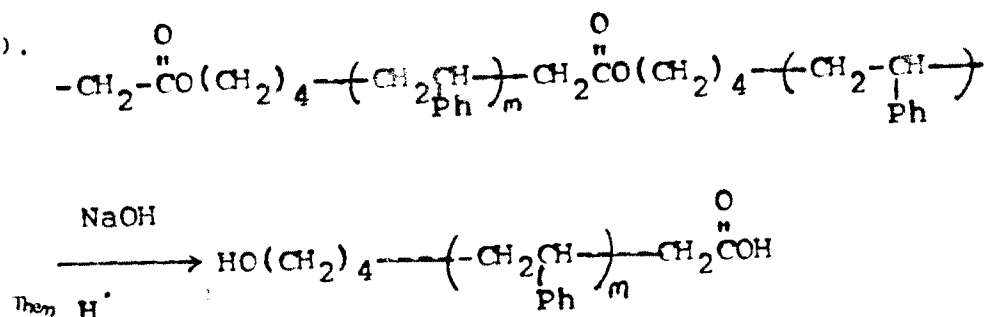
Reactivity : - Cyclic ketene acetals copolymerise with all common monomers to give copolymers with an ester, an amide or thioester linkage in the backbone of the chain, e.g. 2-methylene 1,3 dioxepane copolymerises with styrene to produce the copolymer as indicated below



1.7 APPLICATIONS : -

1) Synthesis of functionally terminated oligomers:- Most functionally terminated oligomers are made commercially by ionic addition polymerization or condensation reactions rather than by

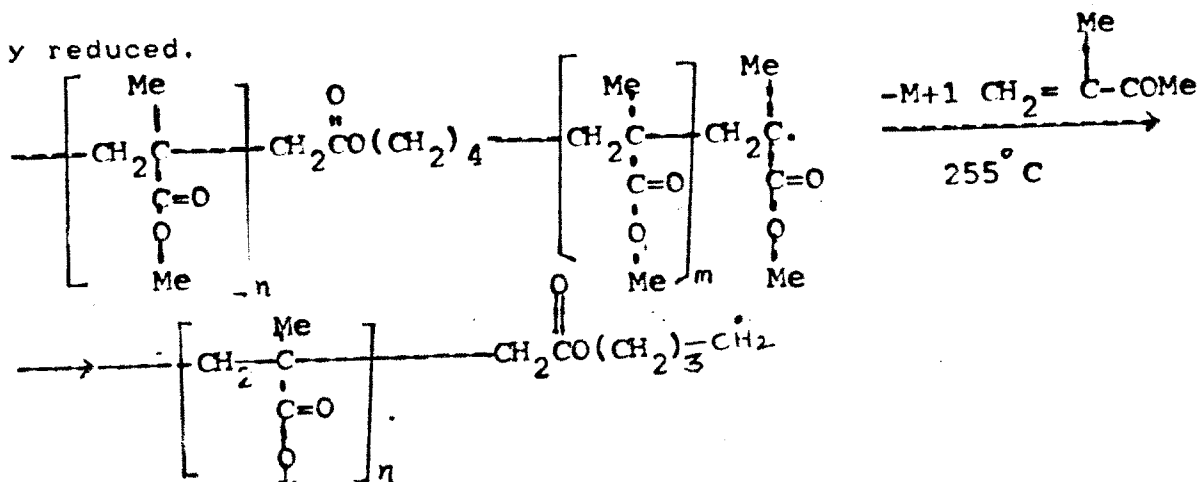
convenient and inexpensive free radical process. The seven membered cyclic ketene acetal mentioned above (2-methylene 1,3 dioxepane) can be copolymerized with styrene, vinyl acetate, ethylene, vinyl chloride etc. to give copolymers with ester groups in the main chain. Hydrolysis of resultant copolymer may result in a functionally terminated oligomer. Thus a very general method has been developed for the synthesis of wide variety of oligomers within a desired molecular weight range (16-18).



2) Biodegradable polymers : - All naturally occurring polymers, such as, starch, cellulose, proteins, nucleic acids and lignin, are biodegradable. On the other hand, synthetic polymers especially, addition polymers are quite resistant to biodegradation . If an easily hydrolysable group such as an ester group could be introduced into an addition copolymer by radical ring opening polymerization, a wide variety of biodegradable polymers could be prepared.

3) Increased thermal stability of copolymers : - Many polymers such as poly (methyl methacrylate), tend to decompose by reverse polymerization (unzipping) process. If a small amount of cyclic

monomer is copolymerized with ring opening into a backbone of PMMA. The degradation (unzipping) can be stopped or can be greatly reduced.



Copolymers of MMA and 2-methylene-1,3-dioxepane, were prepared which showed a significant increase in thermal stability. Other monomers were also used for this purpose (19).

1.8 ELECTROCHEMICAL POLYMERIZATION

Electrochemical Synthesis : - General Introduction :

There has been a growing awareness of the relevance of electrochemistry as a useful interdisciplinary field with applications for physicists, metallurgists and biologists and polymer chemists among others. Its applications in energy conversion and storage syntheses extraction and surface finishing are also factors contributing to its increasing popularity.

The earliest work reported in electrochemical synthesis of organic compounds was that of Haber, Thatcher, and Kolbe (20). However not much work was made following that till forties. Some of the pertinent facts concerning electrochemical synthesis are

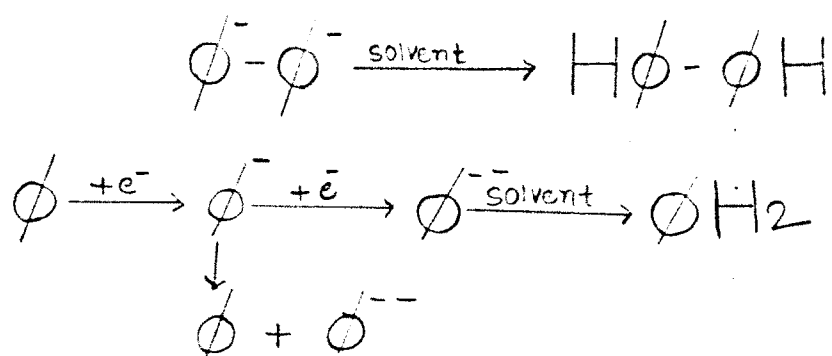
- i) Reaction selectivities may be achieved by precise control of the electrode potential.
- ii) Synthesis involving thermally sensitive compounds can be realized.
- iii) Stoichiometric amount of oxidants and reductants are not required, thus the risks of contamination of the reaction products are minimised.
- iv) The course of the reactions can be monitored with coulometers relatively easily.
- v) The increase in the cost of chemicals has been much more than the increase in the cost of electricity over the recent years.

Like conventional reactions of organic compounds, electrochemical reactions proceed through either carbanion, carbocation or free radical intermediates which can be detected by spectroscopic techniques such as NMR, ESR, UV and IR with optically transparent electrodes. However in most of the cases, the involvement of these intermediates is inferred (21) from the nature of the products and by analogy to known reactions.

1.8.1 Carbanions and Carbanion Radicals :

It has been reported that aromatic hydrocarbons are reduced in aprotic solvents (dimethylformamide, acetonitrile, dimethyl sulphoxide, propylene carbonate etc.) in two one-electron steps

forming the carbanion radicals and dicarbanions. The outcome of the reduction process depends on the nature of the solvent and time scale of the experiment. The addition of the first electron leading to the formation of an anion-radical is reversible. The anion-radical formed on a larger time scale, might pick up one more electron or might undergo dimerization, or disproportionation. The resulting dianion might abstract protons even from the aprotic solvent, forming dihydroaromatic or dihydrodiaromatic compounds.

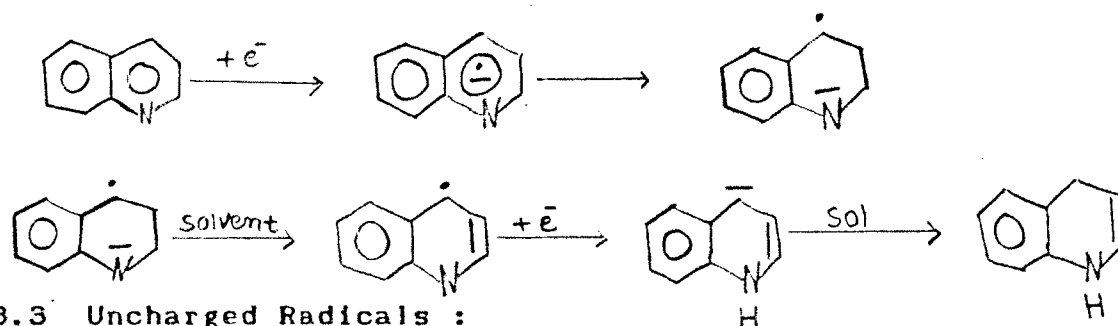


1.8.2 Carbocations and Carbocation Radicals :

With regard to the formation of carbocation and carbocation radicals, the report on their formation from an aromatic hydrocarbon by a two-electron step oxidation is rather scanty. The reason for this is their lower stability than anion counterparts. However several cases of multielectron oxidations have been reported. In the electrooxidation of aliphatic hydrocarbons (22) alkyl halides (23) etc, carbocation formation has been observed.

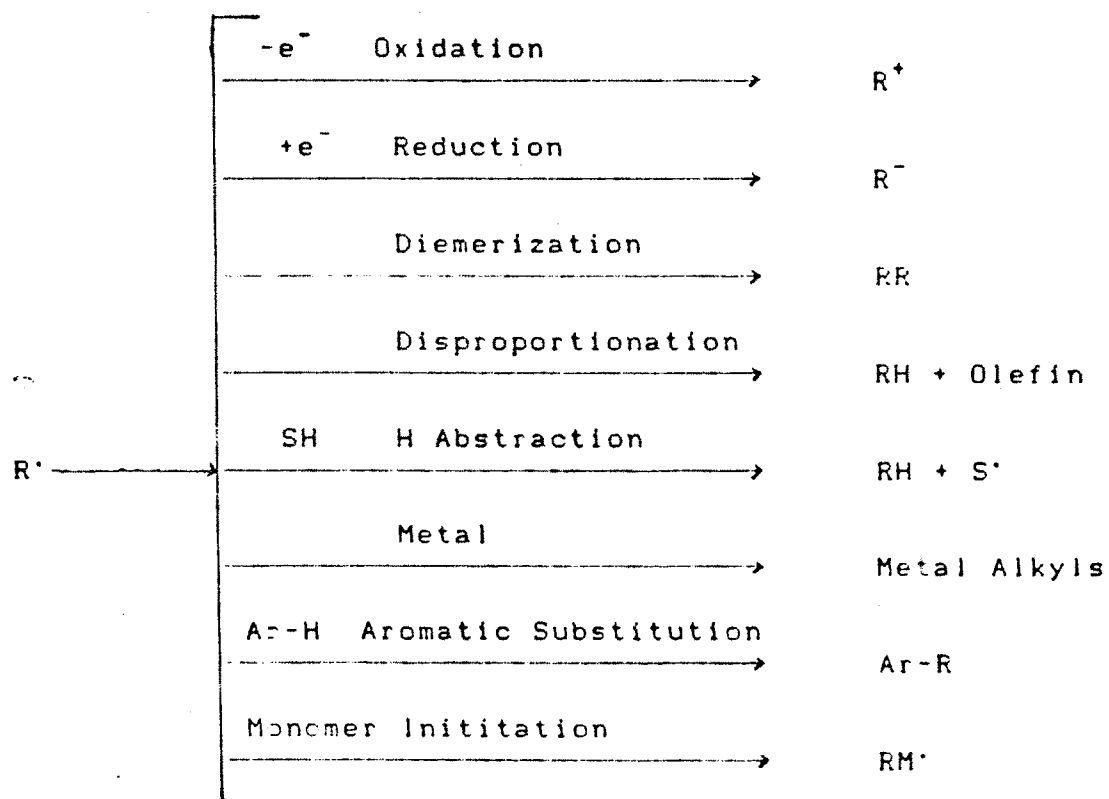
In the electrode reactions of organic compounds containing

nitrogen, charged and uncharged intermediates have been noted. For instance, negatively charged species were formed during the reduction of quinoline (24) in aprotic solvents. After proton abstraction from the solvent and additional electron transfer, the final compound was found to be dihydrocompound.



1.8.3 Uncharged Radicals :

Uncharged radical intermediates are reactive and can undergo various reaction paths as indicated below.



The free radicals may also get adsorbed on the electrode. This adsorption phenomenon is responsible for the high catalytic activity of electrodes such as platinum black, as well as for the variation of products obtained with different electrode materials. For example in the oxidation of carboxylic acids the use of platinum electrodes gives rise to products, resulting from alkyl radicals, whereas the use of carbon electrodes leads to products through the formation of carbocations.

1.8.4 Electroinitiation of Polymerization Reactions :

The possibility of a reaction between the electrochemically generated radicals and olefins to initiate polymerization is attractive. Electroinitiated polymerization may involve either the direct activation of the monomer or the generation of an active species from the medium which starts the polymerization reaction. Compared with thermal polymerization, the electrolytic polymerization can occur under milder conditions resulting in cleaner products. The mechanism of electrochemical polymerization is similar to that of the conventional polymerization except for the initiation step. Once the initiating radical or ion is formed electrochemically, the further course of the reaction is essentially unaffected by the passage of current.

Polymerization by electrochemical techniques can be studied with different aspects in view,

(i) The rate of the reaction may be controlled by the programming the current-time profile.

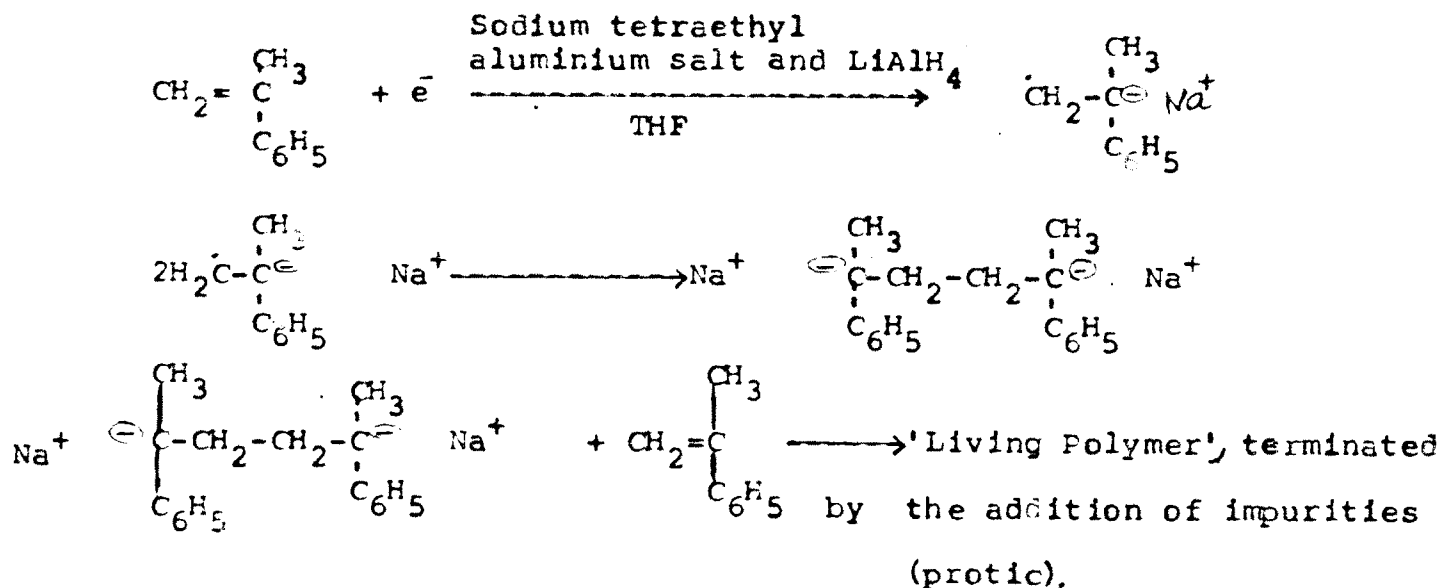
(ii) The molecular weight distribution may be controlled by variation of applied current.

(iii) The molecular architecture of the polymer may be influenced by the conditions of electrolysis.

(iv) Copolymers which are difficult to prepare conventionally may be synthesised.

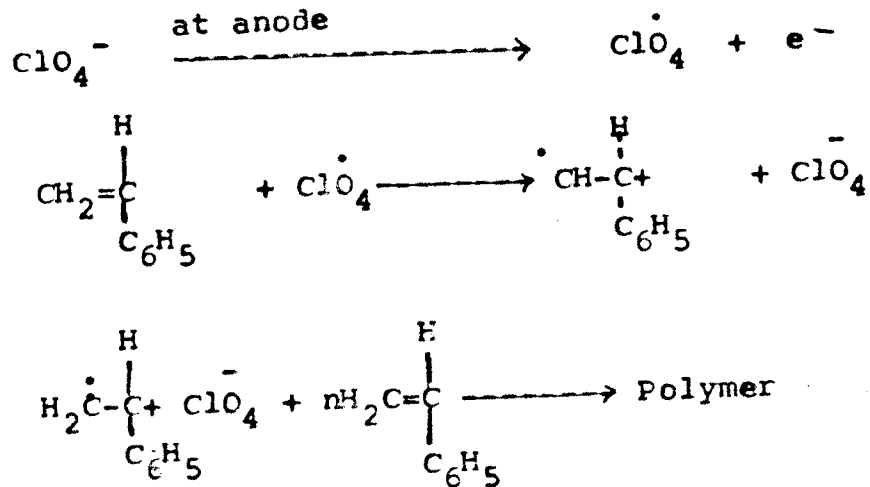
A few examples of electroinitiated polymerization are as given below :

(a) Through Radical Anions : α -methylstyrene, in tetrahydrofuran undergoes polymerization in presence of sodium tetramethyl aluminium salt and lithium aluminium hydride (25).



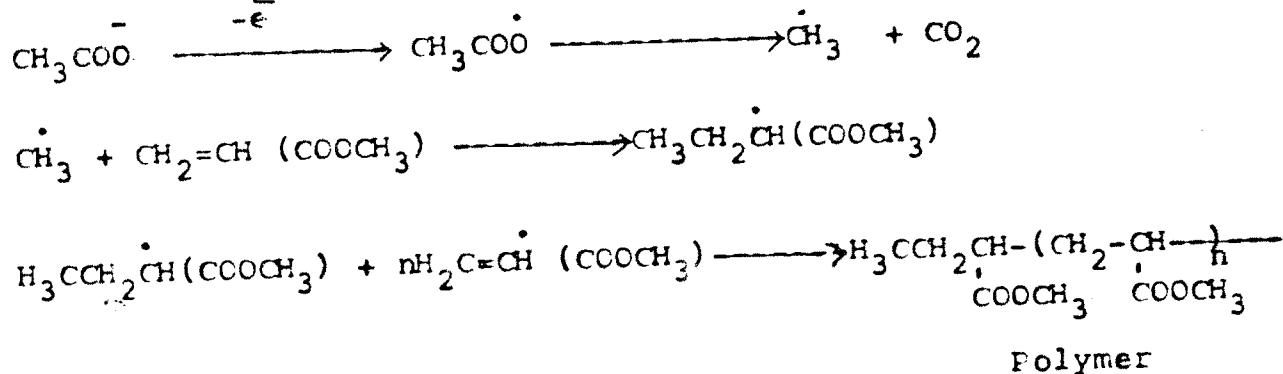
(b) Through Radical Cations : Styrene (26) in methylene chloride

 containing tetrabutylammonium perchlorate as supporting
 electrolyte forms polystyrene.



(c) Through Free Radicals : Electrolysis of potassium acetate

 in presence of methyl acrylate gives poly (methyl acrylate) (27).



A comprehensive review (28) has been devoted to the investigations on the electroinitiated polymerization of monomers such as methyl methacrylate (MMA), acrylonitrile (AN), 1,3-butadiene, pyridine and acrylic acid carried out by various

workers.

Since the present work deals with the electroinitiated polymerization, it is considered pertinent to review the earlier work.

Electrolytic polymerization of AA has been achieved in aqueous solutions in presence of potassium persulphate (29) potassium acetate-acetic acid (30) potassium trifluoroacetate-acetic acid (31) tetramethyl ammonium perchlorate-zinc perchlorate ethylene glycol-sodium acetate and ethylene glycol-barium perchlorate. Bhadani and coworkers have reported the polymerization of AA under aqueous (32) and non-aqueous (33,34) conditions using tetraalkyl ammonium salts and sodium nitrate as supporting electrolytes. PAA has been electrodeposited as a coating on metal cathodes from aqueous solutions of AA containing zinc chloride (35) and on carbon fibres from aqueous solutions containing acrylic acid (36) Ehrig and Kundal (37) have reported the formation of the polymer of diacetone acrylamide as a coating on the cathode by electrolysis of an aqueous solution of the monomer. Subramanian and coworkers have extensively investigated the polymerization of vinylmonomers such as acrylamide, acrylonitrile, methyl methacrylate and styrene to form polymer coatings on copper, aluminium, steel and carbon electrodes (38,39).

The electroinitiated oligomerization of MA in methanol in presence of lithium acetate has been reported by Albeck and

Karoly (40). Albeck and coworkers (41,42) have reported the electrolytic polymerization of methyl acrylate, ethyl acrylate, methyl methacrylate and ethyl methacrylate in various alcoholic solvents in presence of lithium acetate.

The electrolysis of an aqueous solution of potassium acetate in the presence of VAc was found (43) to produce PVAc at the anode. The kinetics of electroinitiated emulsion polymerization of VAc (44) and the copolymerization of VAc (45) with styrene, methyl methacrylate and acrylonitrile have been investigated. Copolymerization involving the monomers AA, MA and VAc has not been reported.

1.9 SCOPE OF THE PRESENT WORK :

The present work is undertaken to synthesize monomers that would undergo radical ring opening polymerization by electrochemical initiation. Following monomers are synthesized

- 1) 2,2-diphenyl-4-methylene-1,3-dioxolane
- 2) 2-methyl-2-phenyl-4-methylene-1,3-dioxolane

Since the work on cyclic ketene acetals has been limited with regard to method of thermal polymerization, it is proposed that electrochemical polymerization be studied.