

CHAPTER - 1

GENERAL INTRODUCTION

of polymerization. For example, free radical reaction which are based on the thermal decomposition of a labile compound have the inherent limitations that they cannot be carried out below the temperature of decomposition of the labile compound. Further, once the reaction starts, its further control is rather difficult and can be stopped only by adding some inhibitor which will contaminate the product. These difficulties do not arise in the electrochemical process where the polymerization reaction can be started and stopped at ease with the switching on and switching off the current. Further, the rate of the reaction can be controlled simply by programming the current-time profile. These considerations also apply to ionically initiated processes carried out electrochemically through the generation of ionic initiating species.

Again the control of the molecular weight distribution can be achieved with greater ease by manipulation of the concentration of the growing ends through the variation of the impressed current. Further a system containing several monomers, preferential initiation of a particular monomer may be achieved through the voltage or potential control. The method does not limit itself to linear polymerization alone but also may be applicable for the modification of formed polymers by inducing cross-linking, grafting, block formation or degradation by electrochemical means.

Basically the electroinitiated polymerization owes its origin to the electrochemical reactions that take place at the electrode

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surfaces either with the monomer or with the supporting electrolyte or with a combination of both giving rise to initiating species for the polymerization reaction. There are several mechanistic pathways for such polymerization.

- i) Electron transfer at the electrodes may form a free atom such as hydrogen atom, a radical or sometime a radical-anion or radical-cation; each of these in turn may add to the monomer and propagate the polymerization reaction. Sometimes direct electron transfer to the monomer from an electrode, i.e., cathode may occur where the potential required for such transfer is less than those required for other competing species present in the system resulting in the formation of a radical-anion which may take part in the propagation step.
- ii) Electrochemical polymerization may also occur through the generation of a stable initiating species (such as a redox initiator) at the electrodes, this is equivalent to the electro-chemical formation of an initiator in situ.
- iii) Electrolysis may also cause indirect polymerization by the removal of the inhibitor(s) from the reaction medium by their electrolytic destruction and thus cause the onset of uninhibited conventional thermal polymerization.

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iv) There is a kind of electropolymerization which is quite different from the type described above and this results when high electric field is applied to a conventional thermally initiated polymerization process. Here the field influences the course as well as the rate of electropolymerization by exerting an electrostatic effect on the monomer and the initiating species.

Due to the existence of these various mechanistic possibilities, the study of electrochemical polymerization is often a complex and a challenging job, and hence needs intensive investigations from various angles.

#### 1.2 GENERAL ASPECTS OF POLYMERIZATION PROCESS :

For the last few decades or so the subject of polymer chemistry has developed into a vast field whose various aspects have been well documented in many standard text book and monographs [2-10].

Polymer, by definition, is a large chain molecule built up by the repetition of small and simpler chemical units called monomers and the process through which this takes place is known as polymerization. In certain cases, the repetition is linear and in other cases the chain may be branched or inter-connected to form three dimensional net works. The length of the polymer chain is specified by the number of repeated units in the chain and is called as the degree of polymerization (DP). The kinetic chain length ( $\bar{V}_n$ ) represents the number