CHAPTER - I

INTRODUCTION
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Polymer science and chemistry during its brief life time of five decades has seen the development of synthetic elastomers that equal or exceed nature's product in abrasion resistance, tensile strength, high temperature performance and degradation resistance; the development of a molecular theory of rubber elasticity, truly a triumph of statistical mechanics; the development of synthetic fibres that now clothe a significant fraction of the world's population; the emergence of plastics as structural or protective elements for the sheltering of man; the use of polymeric films and materials for artificial hearts, kidneys & blood dialysis, the synthesis of stereospecific polymers which come close to the duplication of nature in chemical modeling; and countless other areas where low density, optical clarity, dielectric activity, corrosion resistance, biological inertness, ease of fabrication or other specific properties dictate the use of high polymers.

One primary characteristic, their high molecular weights, distinguishes polymers from all the simple substances. Staudinger\(^1\) in a very act of coinining the term macromolecules, provided the seed for an intellectual revolution that was soon to have vast consequences, both scientific and technological.

Ideally Carothers\(^2\) first classified polymers into two main groups; addition & condensation polymers, based on the numbers of atoms present in repeating unit of polymer, which are
same or fewer in comparison to monomer, respectively. In recent years, the emphasis has been changed to classify polymers according to whether the polymerization occurs in a stepwise fashion or in a chain growth process by Lenz. The chain growth polymerization invariably proceeds by free radicals; ionic or transitional metal (co-ordination) catalysts. The chain initiation being achieved by the addition of an active initiator which reacts with the monomer to produce an active centre. The addition of further monomer molecules to the resulting active centre proceed in a series of rapid propagation steps until termination occurs. Besides this, the radical polymerization has also been attempted by heat (thermal), light (photo) and various radiations.

In general, free radical polymerization is more versatile than any other methods because it can be accomplished in bulk, in solution, in emulsion; in the solid or in the gas phase.

Commercially vinyl monomers occupy an important place in the history of polymer science. They have become increasingly important due to their commercial uses; and much research has been done on their polymerization than with other monomers.

The free radical polymerization of vinyl monomers was first reported well over 100 years ago, but reproducible high molecular weight polymers have been synthesized by this route only within the past 30 years or so. The reliable application of this type of polymer synthesis had to await the recognition
by Staudinger in 1920 and later by Kharasch & Flory.

The huge volume of work has been published in the past on the polymerization of vinyl monomers, using various types of free radical initiators like peroxides (ROOR), hydroperoxides (ROOH), azocompounds, redox initiators, organometallic compounds etc. They are thermally unstable and decompose into radicals at the specific temperatures. The newly invented radical initiators are benzoin methyl ether, tetraphenyl phosphonium salt, 7-picoline-bromine charge transfer complex, peroxodiphosphate sodium thiosulfate redox system, iodine monochloride and ylide (triphenylphosphonium ethoxycarbonylmethylide).

The scope and usefulness of the ylides in the synthetic organic chemistry were exploited by Wittig in his organic reactions named Wittig reactions. The Wittig reaction, involving a condensation elimination between a phosphonium ylide and an aldehyde or ketone to form an olefin and a phosphine oxide, is named after Professor George Wittig of the University of Heidelberg. The role of the Wittig reaction has been established firmly in the arsenal of synthetic organic chemistry as an important method for the preparation of olefins.

Although the field of ylide chemistry dates back to the 19th century, it did not become a part of the main stream of polymer chemistry until the early 1970s. In recent decade
chemists have seen an expansion in this area of research which has resulted in development of the novel branch of polymer chemistry for the preparation of new polymers of better quality with end applications in various fields. This significant branch of the polymer chemistry is now developing extensively and its considerable expansion in the polymer field may be expected, since a number of problems have not been fully elucidated as yet and have been by no means completely realised. Amongst such are the application of ylide as initiator or accelerator or retarder; the preparation of functional polymers carrying ylide structure in the polymer chain; and the mechanism of various polymerization reactions involving ylide.

Thus the present monograph entitled "Studies on polymerization of vinyl monomers in presence of heterocyclic ylide", demonstrates both fundamental and theoretical studies together on kinetics and mechanism of the polymerization of vinyl monomers with the use of heterocyclic ylides. This leads major contribution in the detailed study of the polymerization of methyl methacrylate, vinyl acetate and methyl acrylate with the use of α- or β-picolinium-p-chlorophenacylide and imidazolium-p-chlorophenacylide as initiator. In case of MA the added advantage is that α-PCPY solves the problem regarding autoacceleration up to a certain extent. On the other hand, with electron donating monomer like styrene, they act either as a initiator or as an accelerator.
Thus, the analysis of the results of the study of polymerization involving ylide, indicates a considerable progress in the understanding of many aspects of the polymerization. The intensities of the study of this field for elucidation of fairly general characteristics of these process requires further concerted studies by the chemists specialising in the field of polymerization with the use of ylides and in the polymer chemistry.