



## I N T R O D U C T I O N

The science of polymer chemistry which started with Staudinger's pioneering work in the period 1920-1930 has over the years undergone intense diversifications both conceptually and materially. The concept of the radical chain polymerization has given way to that of non-radical chain polymerizations involving the carbonium ions, oxonium ions (cationic polymerization) and the carbanions (anionic polymerization). The subsequent developments leading to co-ordination polymerization [K. Ziegler (1955) and G. Natta (1955)] and synthesis of stereoregular polymers [C.E. Schildknecht (1947)] using organometallic, Ziegler-Natta and other related catalyst systems followed by the discovery of charge-transfer polymerization [L. P. Ellinger (1963)] by organic and inorganic electron acceptors have imparted to the field of polymers a rigid stature with substantial practical importance both academically and from the technological point of view.

The chemistry of cationic polymerization to which incidentally the present work is related, has in the words of Kennedy [J.P. Kennedy (1975)] undergone "consolidation to the point that the field has become a visible coherent entity with solid scientific foundation and a promising future. The modern era in this field is best characterized by the great variety of

emerging research avenues and the concurrent developments of a variety of industrial ventures". Despite these amazing developments further work is still warranted in many specific areas of the chemistry of cationic polymerization. Thus, the fundamental kinetic and mechanistic aspects of cationic polymerization yet pose problems which call for new thinking, new experimentation and more cautious interpretations. The reason for this is constituted on the one hand by the rapidly growing number of cationically polymerizable monomers with varied degrees of structure and reactivity and on the other hand by the discovery of novel initiators/catalysts for the polymerization. All monomers possess varied degrees of initiator/catalyst specificity and all initiators are characterized by their different extents of monomer selectivity. The situation is all the more complicated by the fact that the scope of an individual initiator or a catalyst may be further enhanced through appropriate modifications by conventional modifiers and more interestingly, through the use of suitable co-initiators. The work highlighted in the present thesis attempts to bring to focus some new observations along these lines in respect of the polymerization of alkyl vinyl ethers. The selectivity of these monomers in regard to the initiators/catalysts including some organic and inorganic oxychlorides, 3d-transition metal oxides and the effect of appropriate modifications of these systems with organometallic compounds have been examined.

For a proper appraisal of the significance of the work thus accomplished, it is necessary to keep abreast of the pertinent developments in this field and the conclusions reached thereof. Sections I and II of this chapter are intended to highlight respectively the present status of the cationic polymerization of vinyl monomers in general and of alkyl vinyl ethers in particular.