

CHAPTER - I

INTRODUCTION

Chain reaction polymerization is known to occur by several mechanisms other than those involving free radicals. Prominent among these are reactions in which the chain carriers are carbonium ions (cationic polymerization) or carbanions (anionic polymerization). In addition, spectacular developments commencing with the discovery of coordination catalysts by Ziegler and Natta and supported metal oxide catalysts and others have added to the list of non-radical chain processes.

The subject of addition polymerization initiated by free radicals is now far developed and rather well-understood. In contrast, non radical ionic or coordination polymerizations still present problems yet to be understood, interpreted and reinterpreted. Consequently, despite the significant bulk of data already accumulated on these topics, the diverse results obtained, mutually contradictory interpretations presented and other related difficulties frequently necessitate further investigations in these fields¹.

Of the various significant recent developments in these directions the one which is of primary concern from the point of view of the present work - is the cationic charge transfer polymerization^{2,3} of some heterocyclic vinyl monomers - the most important example being N-vinyl carbazole (here-in-after called NVC). This may be brought about by organic

electron transfer agents^{2,3} and also by some oxidising metal salt systems^{4,5}.

Although controversies still remain⁶ as regards the exact mechanism by which these polymerizations proceed in NVC system, the situation nevertheless appears to be in general more clearcut than that in the other alternative mode of its polymerization by aprotonic acid systems, via the heterolytic fission of the vinyl double bond⁷. There is a surprising paucity of systematic studies on the latter type of polymerization of NVC⁷. In fact, very few aprotonic type of catalyst systems has been explored. Moreover, the scanty experimental reports available on a few of these systems add to the confusion of the overall situation rather than its clarification⁷.

The work embodied in the present thesis is an endeavour to enlighten these aspects of NVC polymerization catalysed by some hitherto unstudied metal salt systems⁸, suggested by Biswas and Chakravarty.

For a critical appraisal of these features it is necessary to keep in view the significant developments and conclusions revealed in the relevant literature. Section I of this chapter is devoted to a brief survey of the pertinent features in the kinetics, mechanism and other relevant features of cationic polymerization in general. Section II summarises the recent developments in the cationic and charge transfer polymerization of NVC.