

P R E F A C E.

The work reported in the thesis is the fourth phase of the research programme on polymerisation of vinyl esters undertaken by the Department of Applied Chemistry. The first three phases were studies on : (1) Vinyl benzoate, (2) Vinyl n-butyrate, Vinyl-isobutyrate, Vinyl n-Caproate, Vinyl isocaproate, (3) n-butyl methacrylate, isobutyl methacrylate. The object of our study on vinyl propionate is to elucidate the mechanism of polymerisation by free radicals. The behaviour of this monomer in copolymerisation with other monomers is also studied. There is hardly any published work on this monomer. The polymerisation-kinetics of vinyl acetate has also been studied to throw some light on the complexity in the behaviour of this monomer and to compare these two nearest homologues under identical conditions of polymerisation.

In Chapter I, the work done on vinyl esters during the past decade is briefly reviewed. The basic concepts in the kinetics of polymerisation, which we need in our work, are explained. In Chapter II, we study the reaction kinetics of vinyl propionate in bulk phase using benzoyl peroxide and 2,2' azo-bis-isobutyronitrile as initiators respectively. The dependence of R_p , rate of polymerisation, on $[M]$ and $[I]$ is discussed and a comparative study of $K = K_p(K_i/K_t)^{\frac{1}{2}}$.

is made for the two initiators. The chain lengths and some related constants are evaluated. In Chapter III, we study the reaction kinetics of vinyl propionate in solution phase using four solvents and AIBN initiator. For comparison, we have studied the reaction kinetics of vinyl acetate also, using the same solvents and AIBN and Bz_2O_2 initiators. The mechanism of polymerisation is proposed on the basis of the studies in Chapters II and III. In Chapter IV, we study the copolymerisation of vinyl propionate with four monomers and calculate the reactivity ratios. In Chapter V, the main conclusions arrived at in the thesis have been summarised.