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Cationic Polymerisation

Initiation Processes with Alkenyl Monomers

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Preface

Initiation of cationic polymerisation is arguably the most difficult single elementary reaction step studied in polymer science as a whole. But the publication, in this issue of *Advances in Polymer Science*, of an unusually comprehensive review, does not rest on the plea of *complexity*: on the contrary the justification lies in the degree of *order* which the authors have induced in the wider field of cationic polymerisation as a whole. Just what it is that cationic initiation initiates, emerges in a better light almost everywhere.

This review has clearly matured on the basis of long and arduous experience. Years ago, Cheradame and Sigwalt demonstrated the occurrence of initiation by direct acid-base reaction between a Lewis acid and a vinyl monomer, while Gandini and Plesch first put pseudocationic polymerisation involving propagation by undissociated ester intermediates on the map. Each of the two authors of this review was, accordingly, trained by one of the pioneers of cationic polymerisation. From them they learned the rigorous vacuum techniques which no other methods have yet been able to displace. The recent explosion of interest in cationic research does not, however, stem from further refinements in the clean handling of sensitive materials. Wistfully, in this respect, the authors record a steady decline in standards. As a result, spectacular improvements due to modern spectroscopic stopped-flow methods, and to instrumental advances in unravelling chemical mechanisms generally, have perhaps been slower than elsewhere to emerge in studies of cationic polymerisation mechanism. Only in 1976 do we find – in the work of Kunitake and Takarabe – ‘the first thorough examination of the kinetics of initiation’ of a dimerisation (!) based on spectroscopic stopped-flow measurements.

While generous with praise, Cheradame and Gandini are often sceptical and sometimes scathing. Where they themselves merely speculate, they say so clearly, and are worth listening to. Their text bears the imprint of wide experience in chemical mechanistics, far transcending the field under review. Many other reactions are drawn in to help us understand cationic polymerisation: the addition of iodine or acids to olefines, or Friedel-Crafts reactions, are among the many examples. As a result, the authors are able in several places to suggest new mechanistic schemes, and to support often quite comprehensive novel formulations by recalculations based on literature data.

Initiation mechanisms are everywhere elucidated by their integration into the complex overall rate behaviour of cationic polymerisation. Propagation rates determine yields and conveniently multiply the measurable effects of initiation. Termination steps contribute their effects to the jigsaw of cationic polymerisation, and even various kinds of cationic grafting reactions are covered. There can be few reviews punctuated by so many specific proposals for timely research, not only by academics, but also sometimes for possible industrial development.

To combine an impeccably systematic account with imaginative presentation is not the least merit of this book, which may be studied with profit by chemists who pursue elusive intermediates in any field.

M. Gordon