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Book review

Reactivity, Mechanism and Structure in Polymer Chemistry, edited by A.D. Jenkins and A. Ledwith, John Wiley and Sons, London, New York, Sydney, Toronto, xvii + 613 pp., 1974, £13.00.

The purpose of this book is to present a comprehensive view of reaction mechanisms and structure in polymer chemistry, and to correlate this with the current state of knowledge in organic reaction mechanisms. The title is somewhat misleading, however, since only the mechanisms of chain reaction polymerizations are included, while step reaction polymerizations are omitted. Further, the book is concerned mainly with vinyl-type polymerizations. Ring-opening polymerizations are given their due billing only in the last chapter *Thermodynamics of Addition Polymerization Processes*, and are dealt with only briefly in the cationic polymerization chapter, and are given some mention in the chapter on anionic polymerization.

With these exceptions, the book does give a rather detailed treatment of the following subjects. In Chapter 1, *General Aspects of Reactivity and Structure in Polymerization Processes*, N.C. Billingham and A. Ledwith give a good general overview of the types of polymerization reactions and polymer structure. J.M. Tedder presents a clear summary of the types of reactions characteristic of free radicals in Chapter 2, *The Reactivity of Free-Radicals*. Chapter 3, *Organometallic Derivatives of Transition Metals as Initiators of Free-Radical Polymerization*, by C.H. Bamford provides a detailed account of the reactions of organometallics which produce free radicals. This chapter should be of special value and interest to those doing work in the area. Some possible reaction mechanisms in certain systems are ignored, however. For example, an S_N2 mechanism for the reaction of tetrakis(triphenylphosphine)nickel(0) with carbon tetrachloride is not considered, even though a large negative entropy of activation for this reaction has been observed (p. 84).

In Chapter 4, *Reactivity of Polymer Radicals in Propagation and Transfer Reactions*, A.D. Jenkins gives good treatment of the mechanisms involved in homo- and co-propagation reactions. Unfortunately, virtually no discussion of the influence of charge transfer complexes in copolymerization is presented. A detailed review of the Bamford—Jenkins—Johnston approach (p. 127) to radical reactivity is given, but only superficial coverage of the other schemes are offered. An excellent presentation of *The Influence of Chain Structure on the Free-Radical Termination Reaction* is given by A.M. North in Chapter 5. In Chapter 6, *The Influence of Pressure on Polymerization Reactions*, by K.E. Weale affords an interesting account of an area of polymer chemistry which is not widely studied. A good blend of theoretical and practical information on *Emulsion Polymerization* is offered by W. Cooper in Chapter 7.

The treatment of *Carbonium Ions* in Chapter 8, by R. Baker is somewhat superficial and is void of any quantitative information on reactivity. In the

following chapter (9) on *Reactivity and Mechanism in Cationic Polymerizati* by A. Ledwith and D.C. Sherrington, much of the information on carbonium ions is repeated and elaborated upon with a considerably more detailed treatment of theory. The overall coverage is good, but there are some mistakes in the structures and electron book-keeping which are of prime importance in such a discussion. The review of *Carbanions* in Chapter 10 by E.C. Dart is quite good. It is a little annoying, however, to find the references out of orde in the first few pages. Chapter 11, *Anionic Polymerization* by A. Parry provides a good account of the essential features of anionic polymerization mechanisms. The discussion of the effects of solvent and cation on the rate of propagation is not given as much coverage as it deserves in such a presentatior however.

Chapter 12 on *Reactivity and Mechanism in Polymerization by Complex Organometallic Derivatives* by A. Ledwith and D.C. Sherrington generally provides one of the most comprehensive recent summaries of the essential features of the Ziegler—Natta catalysts. The description of the mechanisms of diene polymerization is not as clear as it could be. This is partly because there are some mistakes in the structures in the diene section as well as elsewhere, where it is important that accurate and good stereochemical drawings be made available to the reader. Chapter 13, *Reactivity and Mechanisms with Chromium Oxide Polymerization Catalysts*, by D.R. Witt is written with reference to only seven of the papers on this catalyst! Also, it would have been advantageous to have included the supported nickel catalysts in this chapter.

Chapter 14, *Interaction of Light with Monomers and Polymers*, by F.C. DeSchrijver and G. Smets, provides a somewhat rambling account of photochemical processes in high polymers. This chapter, which was intended to provide "a comparative and critical survey of existing data", is more of a presentation of facts than didactic. In an attempt to bring the chapter right up to date, a last reference was added which included twenty-three publications all of which were erroneously cited as dealing with aryl azide decomposition. P.L. Luisi and F. Ciardelli give an excellent account of the *Configuration and Conformation in High Polymers* in Chapter 15. It is especially important that these authors carefully (and correctly) defined configuration and conformation, provided a clear account of configuration using the *R*, *S* notation, and gave the relationship of both configuration and conformation to optical activity. A clear and concise presentation of the *Thermodynamics of Addition Polymerization Processes*, is provided by K.J. Ivin in Chapter 16. Author and subject indices for the book are included.

Overall, this is a very good collection of chapters on the most important aspects of vinyl polymerization, and is a book which every polymer chemist should have available. Inorganic and organometallic chemists involved in vinyl polymerization will find this book invaluable. Unfortunately, it does not provide the most up-to-date information. Most of the references are not later than 1970.

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