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Book review

Emulsion Polymerization: A Mechanistic Approach

R. G. Gilbert
Academic Press, London, 1995
362 pages, £55.00
ISBN 0-12-283060-1

Emulsion polymerization is one of the most important industrial organo-chemical reactions. It is widely used for the large-scale production of synthetic rubbers and of many polymers used as plastics. Much of the immediate product of such reactions is in effect an intermediary in the production of the bulk solid polymer. However, a proportion of the reaction product is used directly as synthetic latices, following appropriate after-treatment, for applications such as surface coatings, textile treatments, paper coatings, adhesives, carpet backing, and the manufacture of latex foam rubber. In view of the great industrial importance of the reaction, it is hardly surprising that there has been a proliferation of publications relating to it in recent years. Many of these publications have described what are essentially empirical contributions to our knowledge. However, valiant efforts have also been made to understand the mechanism of the reaction in terms of fundamental physical and chemical concepts, and to interpret the properties of the reaction product in the light of the mechanisms which led to its formation. Foremost amongst those seeking to extend fundamental understanding in this area is a group working at the University of Sydney, Australia. Professor Gilbert is a prominent and highly respected member of that group. The book under review provides a very convenient summary of much of the important research which has been undertaken in this field by them in recent years, as well as providing a wider overview. As such, it is warmly to be welcomed and recommended to all those who have an interest in understanding the mechanism of this reaction. It should be especially useful to those who aspire to employ such understanding in seeking rational bases for improving the properties and performance of their reaction products.

Chapter 1 of this book deals with various introductory matters, such as the nature of emulsion polymerization reactions, and the advantages and disadvantages of this method of effecting free-radical addition polymerization. It also provides a useful 'guided tour' of the reaction, introducing the reader to the three conventional stages or 'intervals' of a typical emulsion polymerization reaction, namely, particle nucleation, particle growth after the cessation of particle nucleation, and particle growth after the disappearance of monomer droplets. Chapter 2 discusses the fundamental thermodynamic and kinetic considerations which control the steps of an emulsion polymerization reaction. The problem of obtaining reliable values of the rate coefficients for the basic steps of a free-radical polymerization reaction is well-illustrated by Figure 2.7, which shows the spread of published results for k_p for methyl methacrylate at 25°C and 30°C, as given in the latest edition of the well-known *Polymer Handbook*. Table 2.1 summarizes values, obtained by pulsed-laser polymerization and believed to be reliable, for the Arrhenius parameters for k_p for some of the common monomers which are polymerized in the emulsion mode. The discussion of this matter is illustrative of the emphasis which is evident throughout this book upon accuracy and reliability. Chapter 3 expounds the theory of the kinetics of particle growth. Chapter 4 deals with the applications of this theory, and the conclusions drawn therefrom concerning mechanism. The models introduced in Chapter 3 are here shown to be predictive, and to be sufficiently well-tested against experimental results as to enable the dominant processes in particle growth to be identified in a given reaction system. Chapter 5 applies these concepts to the evolution of particle-size distribution, and Chapter 6 applies them to the evolution of molecular-mass distribution. Chapter 7 deals with the matter of the mechanism of particle nucleation. Although it may seem strange—even perverse—to relegate the first step of the reaction to the final chapter, there are sound reasons for doing this; these are discussed at the start of Chapter 7.

There is a great deal of mathematical analysis in the text. The author is unnecessarily apologetic about this; it is inevitable in a book which aims for precision and accuracy in a field in which the prediction of quantitative properties such as reaction rates, particle-size distributions and molecular-mass distributions is a necessary concomitant of mechanistic understanding. To assist the reader, important equations have been boxed; it is suggested that, initially at least, these equations be taken on trust. In general, the level of mathematics required for understanding of the text does not appear to be unduly high; it is therefore to be hoped that most readers will wish to go beyond taking key equations on trust. However, the mathematical notation does appear to be unduly complicated in places. The difficulties of developing a satisfactory notation in a complex subject such as emulsion polymerization are well known, but the reviewer wonders whether subscripts and superscripts such as 'initiator', 'thermal', 're-entry' and 'micelle' are really helpful; they certainly make for difficulty in writing equations manually. The text is illustrated by numerous diagrams. Some of these betray Bob Gilbert's whimsical sense of humour; they are all the more effective for that. Production of the book is generally satisfactory. A minor criticism is that the term 'molecular weight' has been retained, rather than replacing it by the more modern alternatives 'relative molecular mass' or (preferably) 'molecular mass'.

Throughout the book, there are indications concerning the directions which future fundamental research in this field might take. One possible area to which the reviewer missed reference is that of the application of chaos theory. Certainly, industrial experience indicates that some emulsion polymerization reaction systems can show sensitive dependence upon initial conditions of the type which chaos theory seeks to address.

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