THE CHEMISTRY OF
RADICAL
POLYMERIZATION
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Acknowledgments

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In recent years, the study of radical polymerization has gone through something of a renaissance. This has seen significant changes in our understanding of the area and has led to major advances in our ability to control and predict the outcome of polymerization processes. Two major factors may be judged responsible for bringing this about and for spurring an intensified interest in all aspects of radical chemistry:

Firstly, the classical theories on radical reactivity and polymerization mechanism do not adequately explain the rate and specificity of simple radical reactions. As a consequence, they can not be used to predict the manner in which polymerization rate parameters and details of polymer microstructure depend on reaction conditions, conversion and molecular weight distribution.

Secondly, new techniques have been developed which allow a more detailed characterization of both polymer microstructures and the kinetics and mechanism of polymerizations. This has allowed mechanism-structure-property relationships to be more rigorously established.

The new knowledge and understanding of radical processes has resulted in new polymer structures and in new routes to established materials; many with commercial significance. For example, radical polymerization is now used in the production of block copolymers, narrow polydispersity homopolymers, and other materials of controlled architecture that were previously available only by more demanding routes. These commercial developments have added to the resurgence of studies on radical polymerization.

We believe it is now timely to review the recent developments in radical polymerization placing particular emphasis on the organic and physical-organic chemistry of the polymerization process. In this book we critically evaluate the findings of the last few years, where necessary reinterpreting earlier work in the light of these ideas, and point to the areas where current and future research is being directed. The overall aim is to provide a framework for further extending our understanding of free radical polymerization and create a definable link between synthesis conditions and polymer structure and properties. The end result should be polymers with predictable and reproducible properties.

The book commences with a general introduction outlining the basic concepts. This is followed by a chapter on radical reactions that is intended to lay the theoretical ground-work for the succeeding chapters on initiation, propagation, and termination. Because of its importance, radical copolymerization is treated in a separate chapter. We then consider some of the implications of these chapters by
discussing the prospects for controlling the polymerization process and structure-property relationships. In each chapter we describe some of the techniques that have been employed to characterize polymers and polymerizations and which have led to breakthroughs in our understanding of radical polymerization. Emphasis is placed on recent developments.

This book will be of major interest to researchers in industry and in academic institutions as a reference source on the factors which control radical polymerization and as an aid in designing polymer syntheses. It is also intended to serve as a text for graduate students in the broad area of polymer chemistry. The book places an emphasis on reaction mechanisms and the organic chemistry of polymerization. It also ties in developments in polymerization kinetics and physical chemistry of the systems to provide a complete picture of this most important subject.

Graeme Moad
David H Solomon
Preface to the Second Edition

In the ten years since the first edition appeared, the *renaissance* in Radical Polymerization has continued and gained momentum. The period has seen the literature with respect to controlled and, in particular, living radical polymerization expand dramatically. The end of 1995, saw the first reports on atom transfer radical polymerization (ATRP) and in 1998 polymerization with reversible addition fragmentation chain transfer (RAFT) was introduced. The period has also seen substantial development in nitroxide-mediated polymerization (NMP) first reported in 1987 and discussed in the first edition. A new generation of control agents has added greater versatility and new applications. The area of living radical polymerization is now responsible for a very substantial fraction of the papers in the field. In this edition, we devote a new chapter to living radical polymerization.

The initial thrust of work in the area of living radical polymerization was aimed at capitalizing on the versatility of radical polymerization with respect to reaction conditions and the greater range of suitable monomers as compared to anionic systems. Anionic polymerizations were seen as the standard. This has now changed, and living radical polymerizations are now seen as offering polymers with unique compositions and properties not achievable with other methodologies. Living radical polymerization has also been combined with other processes and mechanisms to give structures and architectures that were not previously thought possible. The developments have many applications particularly in the emerging areas of electronics, biotechnology and nanotechnology.

A small change has been made to the title and the text of this edition to reflect the current IUPAC recommendation that radicals are no longer ‘free’. Of the classical steps of a radical polymerization, while there remains some room for improvement, it can be stated that we now have methodologies that give control over the termination and initiation steps to the extent that specific structures, molecular weight distributions, and architectures can be confidently obtained. The remaining ‘holy grail’ in the field of radical polymerization is control over the stereochemistry and regiospecificity in the propagation step. Although some small steps have been taken towards achieving this goal, much remains to be done.

The last ten years have also seen significant advances in other areas of radical polymerization. Chapters one through eight have been updated and many new references added to reflect these developments.

Graeme Moad
David H Solomon

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