PRINCIPLES OF
POLYMER CHEMISTRY

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Preface

IT WAS the author's privilege to hold the George Fisher Baker Non-resident Lectureship in Chemistry at Cornell University during the spring of 1948. This book had its inception at that time. The uncompleted manuscript was laid aside shortly thereafter, and the work was not resumed until 1951. During the intervening years much new material became available from the ever-increasing literature, and major revision of manuscript and outlines consequently was necessary. The momentum of extensive investigations on the kinetics of addition polymerization, undertaken in various laboratories at the close of the war, carried this phase of the subject to an advanced stage of development. The material on dilute polymer solutions, appearing in the later chapters, had to be completely recast and expanded in the face of recent theories and experiments. The book consequently goes considerably beyond the Baker lectures both in scope and in the inclusion of new developments.

The field of polymer science has grown very large indeed, and it would scarcely be possible in a single volume to do justice to all the excellent researches in various branches of the subject. Even with a less ambitious objective, selection of material to be included is difficult and an element of arbitrariness is unavoidable. The author has been guided in his choice of material by a primary concern with principles. Out of the vast research effort carried on by many investigators over the past twenty years, and especially during the last decade, certain reasonably well-defined generalizations have emerged. It was felt that the time had come when these should be brought together in a book. In accordance with this objective, experimental results have been introduced primarily for illustrative purposes and to develop the basis for these principles. Descriptions of the properties of specific polymers and extensive cataloging of accumulated data, except as they may serve the foregoing objective, lie outside the intended scope

of this project. Some of the more important experimental methods are summarized, but there has been no attempt to offer detailed descriptions of apparatus or procedures.

Even in the selection of that which may be regarded as having achieved the status of a principle, the author admittedly exercised arbitrary judgment, and to a degree that may evoke censure. In particular, he may be criticized for myopic preoccupation with his own work. While granting that the allegation may be well founded, he would nevertheless call attention to the desirability of a unified point of view in a book of this sort, and he could scarcely have hoped to maintain a proper perspective from the outlook of someone else. However this may be, it is undeniably true that some important subject matter has been omitted. The subject of mechanical properties has been slighted, dynamic behavior having been omitted altogether. Originally a chapter on these topics was contemplated, but before Chapter XIV was completed the book had considerably exceeded its projected size and the author's patience. He therefore sought a measure of comfort in the dubiously tenable position that the subject of dynamic properties, being in the process of rapid growth on the one hand while deficient in theoretical interpretations on the other, should perhaps be postponed for some other volume, or possibly for a revision of this one—preferably by another author.

There are two introductory chapters. The first presents an interpretation of early developments which proved rewarding to the author, though it may seem an unnecessary embellishment to some readers. The second chapter, written primarily for the newcomer, is intended to set forth essential definitions and elementary concepts. The next three chapters deal with polymerization and copolymerization reaction mechanisms and kinetics. Chapters VI through IX cover the broad field of polymer constitution, including structure, molecular weight determination, and molecular distribution. The final five chapters treat molecular configuration and associated properties of polymers and their solutions. Familiarity with the material ordinarily included in courses in organic chemistry, physical chemistry, physics, and calculus are prerequisites, and some knowledge of thermodynamics and statistical mechanics is assumed in the later chapters. Explanation of standard topics belonging to these fields has not, in general, been attempted; the consultation of textbooks by the reader to the extent required seemed a preferable solution. No previous knowledge of polymers has been assumed, and the various chapters are addressed primarily to the beginner. At the same time it is hoped that some of the subject matter may prove useful to the experienced investigator as

well. Certain derivations, possibly of less interest to the general reader, have been included in Appendixes to a number of the chapters. In addition to the usual indexes, a glossary of the more widely used symbols has been included.

The author takes pleasure in acknowledging the generous assistance of many of his colleagues. He is especially indebted to Prof. P. Debye, who tendered the invitation to the Baker Lectureship; to Drs. T. G. Fox, Jr., L. Mandelkern, W. R. Krigbaum, and A. R. Shultz, whose expertly conducted investigations while officially collaborators of the author are repeatedly referred to in this book; to Prof. R. M. Fuoss for many valuable criticisms of the manuscript and to Prof. H. A. Scheraga and Dr. L. Mandelkern for reading and criticizing portions of the manuscript; to Dr. Helen Bedon, Mr. T. E. Dumitru, and Mr. A. T. McIntyre for proofreading and assistance with the indexing.

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PRINCIPLES OF POLYMER CHEMISTRY

CHAPTER I

Historical Introduction

THE hypothesis that high polymers are composed of covalent structures many times greater in extent than those occurring in simple compounds, and that this feature alone accounts for the characteristic properties which set them apart from other forms of matter, is in large measure responsible for the rapid advances in the chemistry and physics of these substances witnessed in recent years. This elementary concept did not gain widespread acceptance before 1930, and vestiges of contrary views remained for more than a decade thereafter. The older belief that colloidal aggregates, formed from smaller molecules through the action of intermolecular forces of mysterious origin, are responsible for the properties peculiar to high polymers is repudiated by this hypothesis. Such characteristic properties as high viscosity, long-range elasticity, and high strength are direct consequences of the size and constitution of the covalent structures of high polymers. Intermolecular forces profoundly influence the properties of high polymers, just as they do those of monomeric compounds, but they are not primarily responsible for the characteristics which distinguish polymers from their molecularly simple analogs. As a corollary of the prevailing viewpoint, the forces binding atoms of high polymers to one another, i.e., the covalent bonds, may be considered entirely equivalent to those which occur in analogous monomeric substances; intermolecular forces likewise are of a similar nature.

The implications of the foregoing concept have profoundly influenced modern trends in polymer research. If polymers owe their differences from other compounds to the extent and arrangement of their "primary valence" structures, the problem of understanding them is twofold. It is necessary in the first place to provide appropriate means, both experimental and theoretical, for elucidating their macromolecular structures and for subjecting them to quantitative characterization. Secondly, suitable relationships must be established to express the de-