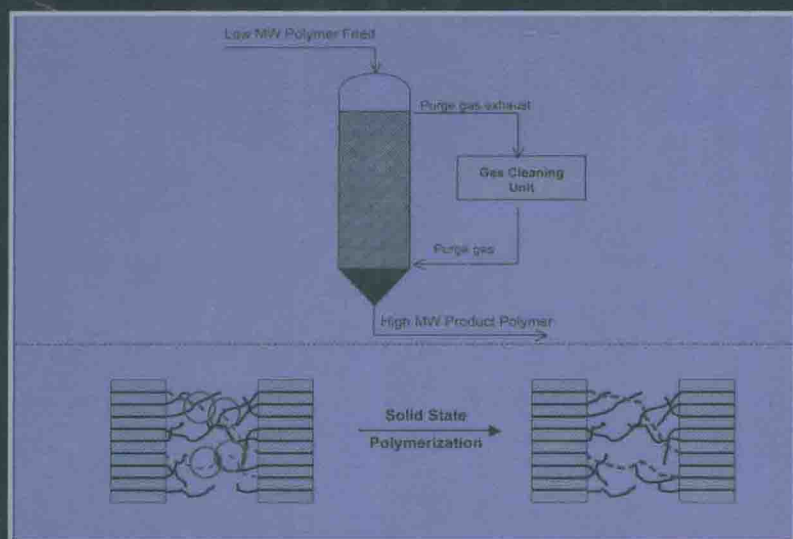


SOLID STATE POLYMERIZATION



Edited by
CONSTANTINE D. PAPASPYRIDES
STAMATINA N. VOUYIOUKA

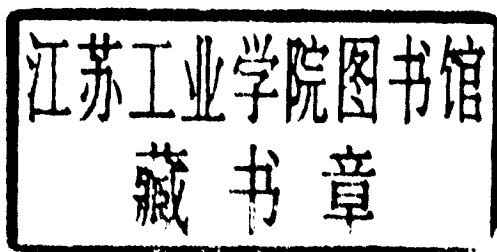
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School of Chemical Engineering
National Technical University of Athens



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SOLID STATE POLYMERIZATION

To my wife Dida
—CDP

To my mother Anastasia
—SNV

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PREFACE

Solid state polymerization (SSP) constitutes a valuable technique used industrially mainly for condensation polymers such as polyamides and polyesters. It involves heating the starting material in an oxygen-free atmosphere (i.e., under flowing gas or high pressure or in vacuo), at a temperature below the melting point, increasing the molecular weight of the product while the material retains its solid shape. Its advantages over conventional melt-phase operations are the low polymerization temperatures, eliminating decomposition and undesirable by-product formation, the simplicity and low cost of process equipment, and the less expensive catalyst systems required.

SSP technology dates from 1940 and the first relevant patents of Flory (1939) and Monroe (1962) issued in an increase in prepolymer molecular weight via reactions in the solid state. Since then, the industrial scale for polyamides has been expanded to include PA 66, PA 6, and polyesters such as PET, and their use in overall polymerization layouts is often stated as drying or finishing. In parallel to its application, extensive research is on going in universities and in industry to understand the reaction mechanism and to optimize the process, especially with regard to the low reaction rates and sintering problems. The amount of open literature, especially patents, has increased steadily since 1995, and its investigation has spread to the majority of issues of most immediate concern, since it is an indispensable part of polymer production lines.

The answer to the question “Why study SSP in 2009?” is that the value of SSP lies beyond its obvious role as an extension of conventional polymerization techniques. It can also be used as a recycling method, through which the

molecular weight of the postconsumer material is increased, thus permitting processing without severe recycled material deterioration. It offers a feasible tool with which to investigate polymer behavior during polymerization or subsequent processing, due to its simplicity regarding technical requirements. For example, the catalytic performance of organic substances can be tested primarily in SSP and extrapolated further with regard to activity in the melt-phase reaction. Even more, the mechanisms prevailing in a solid-phase reaction can be used and interpreted to overcome a series of problems during conventional polymerization and processing.

In our experience, SSP comprises an “exciting” technique for a student or researcher because it combines fundamentals of polymer science, chemistry, physical chemistry, and engineering. In Chapter 1, the complexity of the process is highlighted and how it involves both chemical and physical steps combined with process mechanisms and apparatus is discussed. These SSP steps are found to control the reaction rate separately and/or jointly, depending on the starting material type and process conditions (i.e., temperature, initial stoichiometry and crystallinity, reacting particle size distribution, condensate content in the surroundings, catalysts presence, etc.). The physical chemical aspects of the process are described further in Chapter 2, where the concept of end-group diffusion is indicated as being the primary difference from melt-phase technique. The reacting system morphology shows how it can influence SSP kinetics, and a model is constructed to predict molecular weight achieved. In the following chapters, SSP kinetics are investigated further, also considering other possible rate-controlling steps, such as chemical reactions and by-product removal. Polyesters and polyamides are examined as prevailing SSP polymers. Especially for polyamides, examples are given where SSP serves as a tool to investigate the effect of additives on polymerization rates.

As depicted in SSP kinetics, the slow process rate handled using catalysts and relevant systems is discussed in Chapter 5, covering metallic, nonmetallic, reactive, and inert additives. In Chapter 6 we describe a specialized application of SSP conducted under high pressure on a laboratory scale. It is shown how SSP can serve as a tool to examine the differences in a series of polyamide monomers and polymers in terms of monomer polymerizability, polyamide structure, and degree of orientation. Finally, Chapters 7 and 8 cover engineering aspects regarding process modeling and industrial application. The relevant knowledge can serve as a guide to develop SSP reactors and design pertinent plants.

Based on the book's structure, we have gathered and filtered the literature available on the SSP technique. It is hoped that the reader will find information not only to comprehend the pertinent polymerization technique, but also to initiate future investigations, since it is our belief that SSP processes consist of a continuously developing field.

Finally, we wish to cordially thank the indispensable contribution of each chapter author, with whom we enjoyed an excellent collaboration. Also, our warm thanks to the members of the staff at Wiley for all their help and guidance.

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July 2008*

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1

FUNDAMENTALS OF SOLID STATE POLYMERIZATION

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1.1. INTRODUCTION

1.1.1. Polymers and Plastics

Plastics are indispensable contemporary materials used in nearly all areas of daily life, and their production and fabrication are major worldwide industries. The key word related to plastics is *polymers*, organic substances that are built up by small molecules (monomers) joined together with covalent bonds and forming long carbon or heteroatom chains (macromolecules). There may be hundreds, thousands, ten thousands, or more monomers linked together in a polymer molecule, as noted by the Greek root of the word *polymer*, meaning “many parts.” Plastics are highly modified polymeric materials that have been or can readily be formed or molded into useful shapes, and a typical commercial plastic resin may contain one or more polymers in addition to various additives and fillers.

Although humankind has used natural polymers, such as animal skins, silk, cellulose, and natural rubber since prehistoric times, the birth of plastics may be traced back to the mid-nineteenth century. More specifically, the true nature of polymer molecules was elucidated in 1920 by the pioneering work of Herman Staudinger, who proposed and defended the macromolecular structure of polymers, differing from the then- prevailing theory that polymers are colloids. Distinct milestones in plastics history (Fig. 1.1) include development of the vulcanization process by Charles Goodyear, transforming the latex of natural rubber to a useful elastomer for tire use; the invention of celluloid, the first

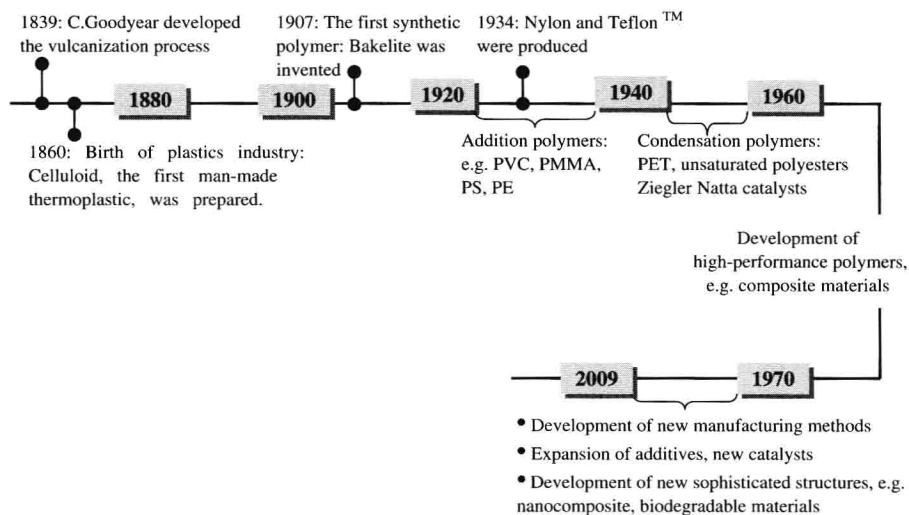


Fig. 1.1. Major milestones in plastics history.