POLYMER REACTOR ENGINEERING

Edited by C. McGreavy

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Preface

Approximately half of the world production of the petrochemical industry (more than 100 million tonnes) is in the form of polymers, yet it would probably surprise most people to learn how much their lifestyle depends on polymers ranging, as they do, from detergents, kitchenware and electrical appliances to furnishings and a myriad other domestic goods. Still less are they likely to be aware of the extensive part they play in engineering applications for mechanical machine components and advanced high performance aircraft.

This versatility derives from the fact that polymeric materials are made up of a range of molecules of varying length, whose properties are related to molecular structure and the proportions of the chains in the mixture. For example, polypropylene is a commodity polymer which is produced in hundreds of different grades to meet specific market requirements. This depends on the catalyst as well as the operating conditions and reactor design.

A major area for growth is in substituting polymers for conventional materials such as ceramics and metals. Not only can they match these materials in terms of mechanical strength and robustness but they have very good resistance to chemical attack. Polyamides, for example, are widely used for car bumpers and new polymers are being developed for engine manifolds and covers. In 1993 there is, typically, 100 kg of various polymers used in cars and this is continually increasing, giving a net weight reduction and hence better fuel economy.

The properties of polymers can be further enhanced and extended by the use of additives such as carbon fibres. The resulting materials can meet very demanding duties for engineering components in high performance aircraft. There has also been a spin-off from these developments into sporting goods, such as skis, fishing rods, tennis racquets and bicycles, and there is also the possibility of usage in superconducting switching devices. The possibilities for growth and development are endless and there is a need to develop the reactor technology to respond to this. The challenge is to provide a framework for solving the design problems where the reaction stages play the leading role.

To try to achieve these goals, this book covers the basic background in polymer chemistry by summarizing the main types of polymer reactions. This is followed by a general outline of the methods used to characterize polymers in relation to the nature of the molecular chains. A further chapter deals with the mathematical methods of describing the final molecular mixture in terms of suitable statistical functions related to mean chain length as well as size

distribution. A general description of how the kinetic models are used in standard reactor designs is also given and linked to an extended account of some of the modern control schemes which can be used to produce high quality polymers.

To emphasize that there is a strong interaction between the process and mechanical design, two case studies are given, which illustrate the complexities arising, even in stirred tank reactors, when the heat transfer and agitation problems are taken into account. There is also a brief treatment of reaction injection moulding to illustrate non-conventional reactor design. Finally, a brief account of the design of a recycling process is presented to illustrate the life-cycle concept.

Within the scope of this book, it is only possible to raise an awareness of the challenge of polymer reactor engineering. The essential concept is to realize that every problem needs to be treated individually. This book provides the link between chemistry, polymer processing and materials engineering to ensure that high quality, engineered products can be manufactured.

Mr Ilias Dawood is gratefully thanked for drawing the illustrations in chapters 1 and 2, and some of those in chapter 6.

<div align="right">C. McG.</div>

Contents

1 Uses and applications of polymers

A. F. JOHNSON

1.1 Introduction

1.1.1 History

Our knowledge of chemistry has been built almost entirely on the detailed study of small molecules. It is not particularly surprising that, in order to gain a fuller understanding of the physical world, most attention has been given to model systems which lend themselves readily to theoretical predictions and experimental measurement. What is surprising, however, is that during the last decade of the century so little is still known about very large synthetic molecules when one considers their importance to our everyday existence. In the preface to his splendid monograph entitled *Mega Molecules*, Hans-Georg Elias points out that 'All life is based on big molecules...' [1]. This is not an exaggeration and he amply supports the statement by suggesting that humans, animals and plants would not exist were it not for macromolecules lending support to the physical structures of each. No life could propagate without macromolecular DNA and RNA. Our diet would not contain meat, eggs, cereal, vegetables or fruit if there were no macromolecules. It is unlikely we would live in houses of the type we know if there were no macromolecules since wood and many stones consist of macromolecules. Without macromolecules we would have no clothes since all fibres are formed from macromolecules; there would be no cars as there would be no tyres, no photographic film, no microelectronics. The list is almost endless.

The macromolecules which occur in nature have evolved over millions of years and their molecular structure is often very complex and precisely 'tailored' for the particular role they play in our existence, e.g. the sequencing of structural units in DNA in relation to heredity. In this brief overview, attention is limited to macromolecules which can be synthesized in the laboratory and ultimately in a production scale chemical plant, i.e. those macromolecules or polymers which *Homo sapiens* has endeavoured to construct for his own purposes. These molecules usually have a much simpler molecular structure than naturally occurring macromolecules and are often called polymers (from the Greek for *many* (poly) and *part* (mer)), although they too fall into the overall classification of macromolecules.

The first 'synthetic' polymers were obtained by chemical modification

of naturally occurring materials. The nitration of naturally occurring cellulose (cotton, wood) was first reported in 1836 and this 'synthetic polymer' which could be thermally deformed (thermoplastic) was in commercial production for knife handles and spectacle frames by 1869. The acetate derivatives of cellulose, which are also thermoplastic materials, were discovered in 1865, but did not come into commercial production until 1927 when it was realized that these materials had good film-forming and fibre-forming properties which made cellulose acetate suitable for use in packaging, photographic film, and synthetic fibres. Natural rubber, now known to be essentially *cis*-polyisoprene, was discovered in 1839 and became commercially important in the 1850s with the discovery of the vulcanization process which turned the natural polymer into a crosslinked elastomer suitable for use in motor car tyres. Many other synthetic thermoplastic polymers were discovered in the 1800s and commercialized in the early 1990s–for example, polyvinyl chloride (1838, 1914), polystyrene (1838, 1939), poly(methyl methacrylate) (1880, 1928), where the first date mentioned refers to the date of discovery and the second to the approximate date of commercialization. Thermosetting polymers, i.e. polymers which are crosslinked during the cure process and therefore do not subsequently deform readily with increasing temperature, were discovered at a later date. For example, alkyd resins (1901, 1926) were used for coating purposes and phenol formaldehyde resins (1906, 1909) found significant applications as an insulator in the electrical industry.

The early synthetic polymers were all discovered and used before there was any real understanding of the chemistry whereby these materials were produced, before there was any meaningful concept between the molecular structure and properties of the polymers, and long before there was any understanding of the importance of chemical engineering principles for the controlled synthesis of the products on a large scale. Graham discovered in 1861 that a number of substances, e.g. gelatine, differed markedly in their diffusion properties in water from that of inorganic salts and sugars. These materials were rightly considered to have a high molecular weight, but the high molecular weight was incorrectly ascribed to the fact that many small molecules physically associated to form larger aggregates. This interpretation of the observed phenomenon was not surprising since at that time 'the colloidal state of matter' was in vogue, i.e. the belief that all substances could, under the right conditions, be transformed to a colloidal or aggregated state and, conversely, all colloidal substances were aggregates of simpler molecules. In 1922 cellulose was still regarded as an aggregated or colloidal cyclic tetrasaccharide.

In the 1920s, Staudinger [2] first suggested that macromolecules were not simple aggregates but could exist in their own right. They could not be reduced to the smaller molecules from which they were derived without the destruction of their unique macromolecular chemical identity. It is now well established that macromolecules, and polymers in general, derive their properties from the

linking together of numerous smaller molecules by primary chemical bonds to form long, high molecular weight linear molecules, or three-dimensional network structures of infinite molecular weight, but more than a decade was to pass before Staudinger's ideas were adopted as these early workers did not have access to the large range of instrumental techniques that are now available. In particular, it was not a simple task to measure the molecular weight of a substance with any accuracy when the molecular weight was very high, and the concepts of chain addition reactions and step polymerization processes did not exist. The early history of synthetic polymer chemistry is well described by Flory [3] in his textbook published in 1953, which has become a classic and marks the turning point in the quantitative understanding of polymerization processes and the characterization of the molecular weights of polymers for the majority of practising polymer scientists.

1.1.2   Purposeful synthesis of polymers

During the last three decades significant strides have been made towards a meaningful understanding of many aspects of polymer science and technology. The chemistry, physics and processing of polymeric materials have been well described in a number of texts [4–17]. There is less ready access to information concerning polymerization reactors [18–20], partly because much of the significant work has been carried out in industry and the information is of a proprietary nature, and partly because an understanding of the complexities of the polymerization reactor, and the role played by the reactor and the physical condition employed in any given system on the molecular characteristics of the product, has required the development of user friendly computational methods. Appropriate computational methods and hardware have only become readily available in recent years. The empiricism which characterized much of the early work involving the synthesis and scale-up of polymerization processes has not been removed completely, but there is now a growing awareness of some of the essential principles which have to be understood in order to produce well 'tailored' synthetic polymers, i.e. polymers that have exactly the right molecular characteristics to match the desired end-use for the material. In particular, it is timely to ask what the chemical engineer can contribute to the purposeful synthesis of polymers.

This chapter introduces some basic concepts although the coverage is necessarily abbreviated. The sole aim will be to establish a framework on which the study of polymerization processes might be based. Some of the points raised will be considered in later chapters; others will require much wider reading to establish the extent of their treatments.

1.1.3   Molecular structure and physical properties of polymers

The relationship between the molecular characteristics of polymers and their solid-state, solution, or melt properties is very complex. Much is now known

about commodity or high-tonnage materials (e.g. polyethylene, polystyrene, cellulose acetate, polyesters, etc.) as many of these have been known for some time. In general, less is known about speciality or effect polymers (e.g. conducting polymers, photoresponsive polymers, biocompatible polymers, liquid crystalline polymers, etc.) which might be produced in small quantities for high-added-value low-volume applications. There are numerous molecular features which can have an impact on the observed physical behaviour of polymers and some of the more important will be outlined below. Usually, it is necessary to reach some form of compromise in the design and synthesis of a polymer for a given end-use, as changing the molecular structure or composition in order to achieve one desirable property often causes a loss in some other property. This is very simply illustrated in Figure 1.1.

Many of the desirable features of a polymer (e.g. tenacity or mechanical strength of a fibre) are derived from the fact that the molecules have a high molar mass [21, 22]. One might expect that an ever-increasing molecular mass might give ever-increasing tenacity or mechanical strength. To an extent this is true but the relationship between properties and molar mass is not linear. Moreover, it becomes increasingly difficult to process polymers which have a very high molar mass and the ease of processing decreases significantly as the size of the polymer chains is increased. The target is usually the optimum molar mass which gives good physical properties and good processing properties. It is not always easy to decouple all the different variables that can be found in polymers in order to assess the quantitative impact on observed
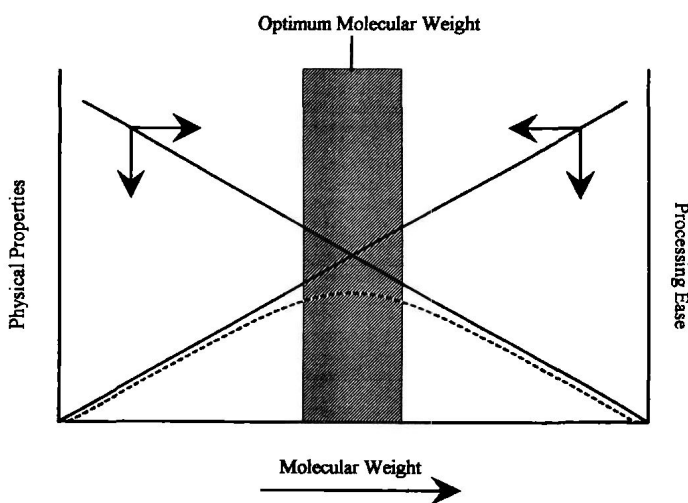

Figure 1.1 Diagrammatic illustration of the way in which the mechanical properties of a polymer might increase with molecular weight and the processing properties might decrease with increasing molecular weight. The optimum overall properties are at some compromise molecular weight shown by the maximum in the dotted curve.

properties, but some of the main structural features of polymers which should be taken into account are outlined below.

1.1.4 Homopolymers and copolymers

Some of the more obvious variations which might be achieved with one chemically distinct type of structural unit in the chains are as shown in Figure 1.2.

When only one type of repeat unit is found in a polymer chain it is described as a homopolymer. This illustration uses 25 units in every case so that the degree of polymerization (i.e. number of repeat units in the polymer) is the same for each. As can be seen, polymers may be linear, branched, ring- or star-shaped. The length of branches may be the same or different in the branched and star-shaped molecules.
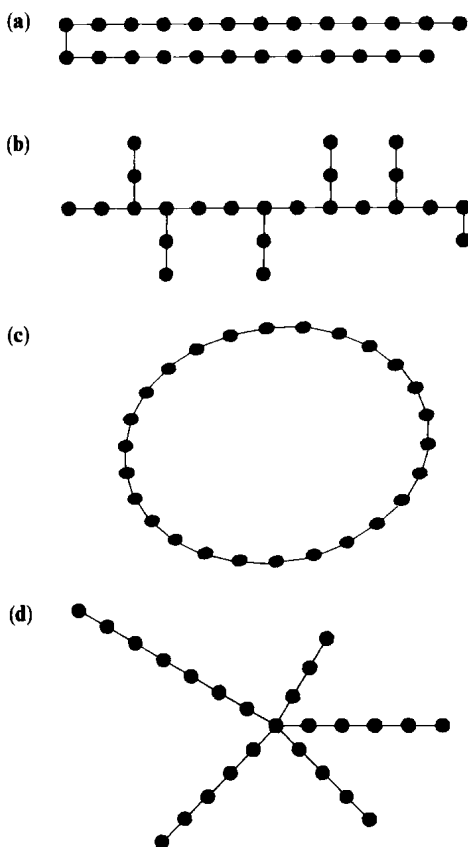
Figure 1.2   The homopolymers illustrated are: (a) linear molecule, (b) branched molecule where the branch chains are short, (c) large cyclic molecule, (d) a star-shaped molecule with arms of different size. All the molecules illustrated have the same degree of polymerization (25 repeat units).
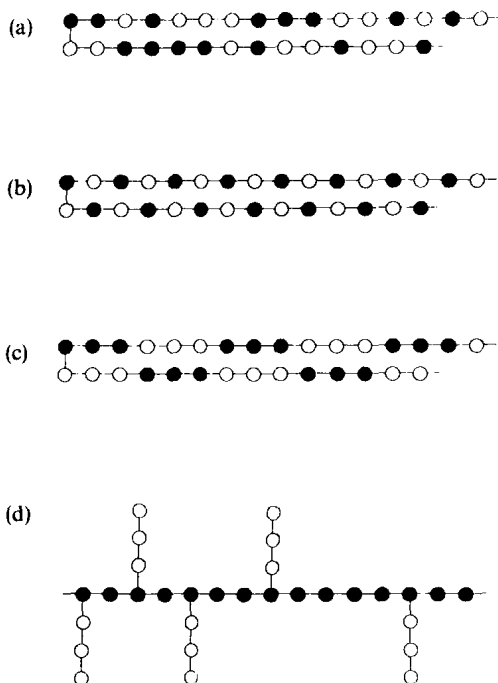
Figure 1.3 The copolymers illustrated are: (a) statistical copolymer, (b) alternating copolymer, (c) linear segmented block copolymer in which the block sequence lengths are the same, and (d) a graft copolymer in which grafted chains are the same size. All the polymers illustrated have a 50/50 composition of the two components and all have the same degree of polymerization (total number of repeat units).

When two chemically distinct units are used to construct a polymer, an even greater variety of structures is possible, some of which are shown in Figure 1.3.

Chains containing two types of structural unit are described as copolymers or binary copolymers. In the illustration 15 structural units of each type are used. When all copolymer molecules have exactly the same number of structural units they all have the same degree of polymerization, the same molar mass, and the same composition. The repeating units can be distributed along linear polymer chains in a manner which obeys some statistical law (statistical copolymers), randomly distributed (random copolymers), arrayed alternately along the chain (alternating copolymers) or combined in two distinct blocks (block copolymers). When two different monomers are used to produce branched or block copolymers a considerable variety of structures and composition distributions is possible.

The statistical nature of polymerization processes is such that it is not possible to synthesize homopolymers or copolymers with precisely equal chain lengths or chains which contain precisely the same number of different repeat units in each chain. Hence, polymers of the type illustrated in Figures 1.2 and 1.3 will actually have some form of molar mass distribution which

will stem directly from the nature of the chemistry used to construct the polymers and the influence of the reactor on the polymerization statistics.

When a polymer comprises molecules of the type illustrated in Figures 1.2 and 1.3, it would in principle be possible to form them thermally if they were solids (e.g. injection mould, blow mould or thermoform) or dissolve them in a solvent to form a solution, since the only attraction holding the molecules together would be secondary bonding forces such as van der Waals forces, dipolar interactions or hydrogen bonding forces. Polymeric materials that can be shaped by applying heat are described as *thermoplastic*. If polymer molecules are held together by primary bonds of a similar strength to those holding the repeat units together, e.g. covalent bonds, then the polymer is described as crosslinked. Crosslinked polymers have an infinitely high molar mass and cannot be processed by conventional methods or be dissolved in a solvent. Crosslinked polymers are known as *thermosets* because it is not possible to shape them by the application of heat. Some crosslinked polymers have good elastomeric properties, e.g. vulcanized natural rubber which comprises essentially linear chains of polyisoprene chemically crosslinked by sulphur.

1.2 Polymerization

1.2.1 *Chain and step polymerization reactions*

The chemical structure of a repeat unit in a polymer produced from low molar mass precursors is dependent on the type of chemistry used to build up the chain structure. The monomers which are commonly used to construct polymer chains may be vinyl or diene compounds, ring compounds or functionalized compounds which require two or more coreactants in order to form a polymer. Some typical precursors are shown in Figure 1.4.

There are two major kinetic mechanisms for the formation of a polymer, namely, chain polymerization reactions and step polymerization reactions. Typically, vinyl and diene monomers will undergo polymerization by a chain mechanism. Monomers containing, for example, –OH and –COOH functionality will polymerize by a step kinetic mechanism. Ring monomers can polymerize by either a chain or step polymerization mechanism depending on the precise nature of the monomer and method used to start the polymerization reaction.

It is essential to understand the precise nature of these two very different kinetic processes in order to design and control appropriate polymerization reactors. However, in order to understand more fully the correlations between polymer molecular structure and properties, it is sufficient to examine the nature of the repeat units which are introduced into a linear polymer chain by each mechanism. The dynamic and thermodynamic characteristics of chain