Stoyko Fakirov

Fundamentals of Polymer Science for Engineers

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Front Cover
Synthesis, processing and application
of polymers – the use of plastics and
their composites in civil Airbus 350
and Boeing 787 is 53 % and 50 %,
respectively.

To my beloved wife Olia, for her inspiration, support and patience

Contents

Preface

Regardless of the fact that, with respect to the subject of study, polymer science belongs among the oldest since its subject is living matter, but as an individual science it was formulated very recently, less than 100 years ago. This happened between 1920 and 1930 thanks to the continuous and systematic efforts of the German chemist *Hermann Staudinger*.

Another peculiarity of polymer science is the fact that its further establishment and development was driven mostly by chemists. Only after World War II, when the commercial production of synthetic polymers boomed, did engineers join the research of polymers, particularly in the mechanical characterization of polymer materials.

Due to the attractive properties of synthetic polymers as materials, they quickly found wide applications parallel to classical materials and even started to replace them. What is more, in many cases they possess a combination of properties which is unknown for common natural materials. In this way, step by step, polymer material science became a subject of study for engineers and physicists.

During 50 years of being involved in polymer research, mostly structure–properties relationships, I have had the chance, particularly during the last two decades, to work together with mechanical engineers in the area of polymer composites. From my contacts with engineering students while advising their Master or PhD theses, I gained the impression that their knowledge of polymer science is very limited. As a rule, they do not have the chance to get any systematic information on polymer science and for this reason they apply their knowledge of metals when dealing with polymer materials.

Possibly, the curriculum of engineering students is overloaded and it is not possible to offer them a specialized course on polymer science. At the same time, it could hardly be accepted as a normal situation when an engineering student is working 3–4 years on his polymer-oriented PhD dissertation without having a good idea about the glass transition temperature of polymers, about the basic difference between polyethylene and poly(ethylene terephthalate), or about the nature of high elasticity and polymer processing. What is more, some basic knowledge about polymers, including their synthesis and chemical properties is needed also by engineers researching polymer materials. Good examples in this respect include polymer composites, whose mechanical performance depends mostly on two basic factors – the aspect ratio of the

reinforcing component and the adhesive quality between the matrix and the reinforcement. As a rule, adhesion is poor because the two components are chemically different and seizing or compatibilizers are used to improve the situation. At the same time, dealing with polymer–polymer or single polymer composites based on condensation polymers (e.g., polyesters and polyamides) or involving cellulose- or protein-based fibers, the chemical interactions between matrix and reinforcement possibly result in the establishment of chemical bonds between them. In the author's opinion, this potential for drastic improvement of the interfacial adhesion quality between matrix and reinforcement is not explored enough by the composite community mostly because of a lack of chemistry knowledge among the engineers involved in this type of research.

Possibly, some solution to the current situation could be the offer of a specially prepared textbook to engineering students involved in polymer research. In this they can find very basic knowledge on the synthesis, properties, processing, and application potentials of polymer materials. Just such an attempt is undertaken in the current book. A feature of the book is the author's approach of continuously comparing the *physical* properties of polymers with those of low molecular weight substances and materials. This is done because of the author's belief that these physical properties demonstrate in the best way the specific properties of polymers, as compared with low molecular weight substances. For this reason, the consideration of a given phenomenon starts with describing the situation in the case of low molecular weight substances, followed by analyzing the characteristic features of the same phenomenon when dealing with high molecular weight substances. A good example in this respect is the *crystallization phenomenon* – the specific characteristic features of polymer crystallization are discussed after introducing the same phenomenon in the case of low molecular weight substances.

Another feature of the textbook is that it is not intended for chemists but for readers dealing mostly with polymers as materials. In addition, as mentioned above, a good idea about the specific characteristic features of polymers could be obtained by considering their physical properties. For this reason, the book starts by discussing the physics and physical properties of polymers. Further, some terms, definitions, or statements are repeated in the text on purpose, because they are considered very important and have to reach the reader, who is unlikely to systematically read the whole book.

Auckland, Spring 2017   *Stoyko Fakirov*

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Further, my thanks go to Prof. M. Chanda from the Indian Institute of Science, Bangalore, India, whose excellent textbook has been used intensively during the preparation of this text as well as for his valuable suggestions for improvement of the current textbook.

I would like to express my appreciations to my colleagues and good friends, Prof. Dr. Dr.h.c. K. Friedrich, co-founder of the Institute for Composite Materials at the Technical University of Kaiserslautern, Germany, Prof. Dr. H.-J. Radusch from the Martin Luther University of Halle, Germany, and Prof. Dr. Dr.h.c. J. Karger-Kocsis from the Budapest University of Technology and Economics, Hungary, all of them being engineers researching polymer materials, for their kind acceptance to read the manuscript, as well as for making interesting suggestions aiming at improvement of the book.

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To all of them – my sincere thanks!

Part One

Introduction

If you once enter in the world of polymers,
You will never leave it.
T. Tsuruta

1

Introduction

1.1 Milestones in the Development of Polymer Science

Regarding its subject of study, *polymer science* belongs to the oldest fields of science (existing since the times when living cells appeared), while as a separate, well-defined science it was formulated less than 100 years ago – between 1920 and 1930 – thanks to the pioneering works of the German chemist *Hermann Staudinger* (Figure 1.1). Polymer materials have always been used by human beings without having any idea what differs these materials from the others. The situation did not change even when the first synthetic polymer material was prepared around 1910 by *Leo Baekeland –Bakelite*.[1] First, Baekeland produced soluble phenol-formaldehyde shellac called "Novolak", but later he succeeded in preparing a hard plastic material.

Bakelite continues to be used for wire insulation, brake pads and related automotive components, and industrial electric-related applications. Bakelite stock is still manufactured and produced in sheet, rod and tube form for industrial applications in the electronics, power generation, and aerospace industries, and under a variety of commercial brand names.

Baekeland was a very talented chemist with an extremely strong feeling for commercially important products. But as a matter of fact, he did not contribute to the creation of polymer science in any theoretical aspect such as, for example,

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1 *Baekeland* was already a wealthy person due to successful sales of his first serious discovery – the photographic paper Velox. *E. Kodak*, the designer of the first photographic camera, was so impressed by the new material that he immediately signed a check of one million dollars! In this way Baekeland, who expected to get at least US$ 10 000, was able to organize at home a chemical laboratory with all necessary equipment. The most important apparatus was the autoclave needed just for studying the condensation reaction between phenol and formaldehyde. Baekeland's initial intent was to find a replacement for shellac, a material that was in limited supply because it was made naturally from the excretion of lac bugs. The germ of his idea came in the chemistry library where he found that the German chemist *Bayer* studied the same reaction and obtained a solid, non-soluble product which he could not remove from the reaction flask, so he threw it away together with the glass flask. *Baekeland* decided that this was what he needed, and he started a systematic study leading to the creation of Bakelite. Phenolic resins have been commonly used in ablative heat shields. Soviet heat shields for warheads and spacecraft re-entry consisted of asbestos textolite, impregnated with Bakelite.
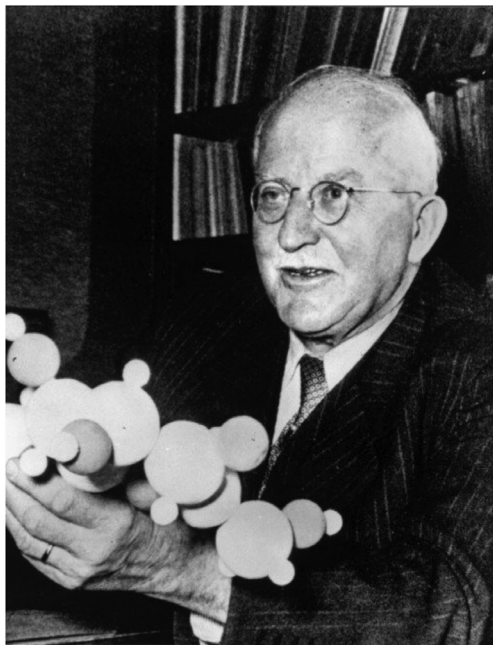
Figure 1.1 H. Staudinger (1881–1965), the *"father of polymer science"* who received the Nobel Prize in 1953 for his studies.

trying to answer such questions as how does the molecular structure of polymeric substances differ from that of other substances.

It must be stressed that his target was completely different – to create a new material with a well-defined combination of properties needed for a particular application. And he completed his task in an excellent way! Today we know that even if he tried to perform theoretical research, he could hardly have the same success he achieved in material synthesis. This is because his polymer, Bakelite, belongs to a special group of polymers characterized by a rather dense molecular cross-linking, that is, the single molecular chains are connected *via* covalent bonds, forming in this way a giant three-dimensional (3-D) molecular network, where separate linear molecules with a strictly defined start and end no longer exist. What is more, the cross-linked polymers do not display the typical and unique properties of polymers as the non-cross-linked ones do. So, the answer to the question regarding why the molecular structure of polymeric substances differs from that of other substances was given by Hermann Staudinger, who was working around the same time.

Staudinger had been studying natural products as cellulosic derivatives, natural rubber, and others, and particularly their solutions. Thus he got the impression that in these solutions one deals with larger "particles" than in solutions of low molecular weight substances. By the way, the same observation had been made much earlier, around the mid-nineteenth century when the colloid chemistry was formulated and such solutions were called "lyophilic colloids." Staudinger went further, suggesting that these "particles" are giant molecules comprised of a large number of atoms bonded *via* covalent bonds; and this met a negative reaction

Figure 1.2 W. Carothers (1896–1937), the inventor of nylons and neopren.

from the scientific world. The leading chemists and physicists of that time were against him, stating that it was not possible that such a large number of atoms could be bonded in one molecule.[2]

Staudinger did not abandon his idea, and step by step, he gathered arguments in favor of his hypothesis which, around 1930, was accepted world-wide. As a matter of fact, he formulated a new science, *polymer science* suggesting and proving that polymers are comprised of large molecules consisting of a huge number of atoms connected to each other by *covalent bonds.* In this way he demonstrated the basic difference in the molecular structure of polymers and low molecular weight substances.

The most serious support for Staudinger's concept was made in 1930 by the American chemist *Wallace Carothers* (Figure 1.2). Carothers was a group leader at the DuPont Experimental Station laboratory, near Wilmington, Delaware, where most polymer research was done. Carothers was an organic chemist who, in addition to first developing Nylon, also helped lay the groundwork for Neoprene. After receiving his PhD, he taught at several universities before he was hired by DuPont to work on fundamental research. In his research, Carothers showed even at this time the high degree of originality which marked his later work. He was never content to follow the beaten path or to accept the usual interpretations of organic reactions. His first thinking about polymerization and

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2 "Dear Colleague, Leave the concept of large molecules well alone . . . there can be no such thing as a macromolecule." It is said that this advice was given to H. Staudinger just 90 years ago, after a major lecture devoted to his evidence in favor of the macromolecular concept (Olby, 1970).

the structure of substances of high molecular weight began while he was at Harvard.

As a matter of fact, the systematic studies at Du Pont on the condensation process with the aim to prepare a synthetic macromolecules allowed Carothers to start on polyesters using diacids and diols. The obtained products were not of commercial interest because of their low melting temperatures and problems with their low hydrolytic stability. The commercial success came with polyamides – Nylon 6 and Nylon 66 in the mid- to late 1930s.

The commercially important polyester, the poly(ethylene terephthalate), was developed in the United Kingdom around 1940 in a programme initiated by *J. R. Whinfield*. Its commercialization was handled by Du Pont and ICI (UK) since they had a current agreement for joint work on this topic.

Polyesters and polyamides, being the subject of Carothers' studies, are examples of condensation polymers formed by step-growth polymerization. Carothers worked out the theory of step-growth polymerization and derived the *Carothers equation* which relates the average degree of polymerization to the fractional conversion (or yield) of monomer into polymer. This equation shows that, for a high molecular weight, a very high fractional conversion is needed (for step-growth polymer only).

Carothers had been troubled by periods of depression since his youth. Despite his success with Nylon, he felt that he had not accomplished much and had run out of ideas. His unhappiness was compounded by the death of his sister and on the evening of 28 April, 1937 he checked into a Philadelphia hotel room and committed suicide by drinking a cocktail of lemon juice laced with potassium cyanide.

In this way, after the successful synthesis of linear polyesters and polyamides, the further establishment and development of polymer science involved many talented chemists from Europe and the United States. One of the first achievements was the demonstration that the macromolecules are not rigid, non-flexible, rod-like formation, as wrongly suggested by H. Staudinger[3] but are extremely flexible formations.

The application of physics and physical chemistry to macromolecular systems dates back to the early attempts made in the late nineteenth century to understand the unusual properties of natural polymers, such as rubber, polysaccharides, and proteins. However, it was not until the 1920–1930 period that *Meyer* and *Mark* in Germany began to establish the structure of cellulose and rubber with the use of X-ray diffraction techniques. Explanations of rubbery elasticity in terms of polymer conformations were put forward by *Kuhn*, *Guth*, and *Mark* between 1930 and 1934. Kuhn, in particular, was the first to apply statistical methods to the study of macromolecules.

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3 As mentioned above, the main subject of Staudinger's studies were the derivatives of cellulose. Only many years later it was found that these polymers belong to the class of *liquid-crystalline polymers* which are characterized by "solid" non-flexible, rod-like molecules. In addition, Staudinger studied their behavior in solutions, mostly during flow, and found that they behave as crystallizable substances demonstrating light birefringence in flow. He could not accept that a flexible chain would be able to demonstrate this phenomenon, while a rod-like molecule would do.

The application of light scattering to macromolecular systems was made by *Debye* during World War II. It was also during this period that *Flory* began a series of investigations into the applications of statistical methods, conformational analysis, and other fundamental physicochemical techniques to polymer science. During the early 1950s, *Watson*, *Crick*, *Wilkins*, and particularly *Franklin* successfully applied X-ray diffraction analysis to the structure determination of biological polymers, such as deoxyribonucleic acid (DNA), hemoglobin, and insulin.

Single crystals of polyethylene were first reported by *Keller*, *Fischer*, and *Till*[4] independently from each other in the same year, 1957. This discovery was possible thanks to the development of electron microscopy. The more recent introduction of solid-state nuclear magnetic resonance (NMR) methods in the 1980s has had a major impact on polymer structural analysis.

Regarding the synthesis of polymers it has to be noted again that a number of important new polymers were prepared and commercialized in the period between 1890 and 1930, many of which were based on the use of chemical reactions (acetylation, nitration) carried out on cellulose. It is perhaps astonishing to realize that most of these technological developments occurred during a time when the polymeric nature of these products was not recognized or believed.

The 15 years between 1930 and 1945 represent the springboard for the development of modern synthetic polymer chemistry, as can be concluded from Table 1.1, which summarizes the development of polymer synthesis.

The development of polymer synthesis in the period 1945 to 1960 was accelerated by the large-scale availability of new monomers from the petrochemical industry, coupled with a series of key scientific discoveries. These include the pivotal development by *K. Ziegler* and *G. Natta* of organometallic compounds as initiators for the polymerization of ethylene and catalysts for the stereoregular polymerization of other olefins.

By the late 1980s it was already evident that polymer science was entering a new phase. This phase of synthetic polymer chemistry involved a subtle shift in emphasis. Many of the most accessible (and inexpensive) "commodity" polymers have now been studied in detail and their applications have been developed extensively. Interest is now focusing on the synthesis and study of entirely new polymers that have specialized, high performance properties, such as very high strength, temperature stability, oil and fuel resistance, biomedical compatibility. In parallel, newer methods of synthesis are developing.

The 1990s and early 2000s saw numerous additional advances. New polymer architectures were developed such as star and dendrite structures, as well as new types of block and graft copolymers. Hybrid polymer-ceramic materials were prepared further, as were polymers for use as semiconductor resists, electro-luminescent materials, electrolytes in batteries, and proton-conducting membranes in fuel cells. The interface between biology and medicine continues to be strengthened by intensive research on micelles, vesicles, microspheres, hydro gels, and biocompatible surfaces. Thus, it is clear that polymer science continues to be a vibrant and expanding field with an increasing influence on all other scientific

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4 Keller (1957), Fischer (1957), and Till (1957).

Table 1.1 Approximate sequence of polymer synthesis development.

Time	Development
1838, 1839	Polymerization of vinyl chloride and styrene; vulcanization of rubber
1868	"Celluloid" (cellulose nitrate plus camphor)
1893	Rayon (regenerated cellulose)
1910	Styrene-diene copolymers; phenolic resins
1914	Cellulose acetate as aircraft "dope"
1920	Cellulose nitrate lacquers (automobiles)
1924	Cellulose acetate fibers
1927	Cellulose acetate plastics; poly(vinyl chloride) manufacture
1929	Urea-formaldehyde resins
1930	General acceptance of the macromolecular hypothesis
1931	Poly(methyl methacrylate)
1936	Poly(vinyl acetate) and poly(vinyl butyrate) in laminated safety glass; Nylon 66
1937	Polystyrene manufacture
1939	Melamine-formaldehyde resins; neoprene rubber; polysulfide rubber (Thiokol)
1939–1945	Manufacture of polyethylene (UK); polybutadiene rubber (Germany); acrylonitrile-butadiene rubber (Germany); polyurethanes (Germany); styrene-butadiene rubber (USA); polyisobutylene (butyl rubber; USA)
1945–1960	Epoxy resins, acrylonitrile-butadiene-styrene polymers, polyesters, polyacrylonitrile, polysiloxanes (silicones), linear polyethylene, polypropylene, "living" anionic polymerizations, cationic polymerizations, polyoxymethylene, polycarbonates, polyurethane foams, fluorocarbon polymers
1960–1980s	*cis*-Polyisoprene rubber, *cis*-polybutadiene rubber, ethylene-propylene rubber, polyimides, poly(phenylene oxides), polysulfones; styrene-butadiene block copolymers, aromatic polyamides, aromatic ladder polymers, group-transfer polymerization, cyclopolymerizations, olefin metathesis polymerization, polyphosphazenes, polysilanes
1980s–2000s	ADMET polymerizations, atom radical polymerizations, polymerizations in super-critical CO_2, poly(phenylenevinylenes), polyaniline, poly-(ferrocenophanes), non-linear optical polymers, telechelic polymers, dendrimers, ceramers, living polymerizations to polyphosphazenes, polyester synthesis in bacterial cells, and metallocene catalysts

and engineering fields that make use of polymeric materials. In fact, it has become the central science on which nearly every other scientific and technological field depends. This trend is expected to continue for the foreseeable future.

Another unique characteristic feature of polymer science and technology is the fact that the number of synthetic commercially manufactured polymers has remained almost constant during the past decades. At the same time, the need for polymeric materials with new or improved properties is steadily increasing. Their satisfaction, as the experience during the past decades has demonstrated, takes place not *via* the synthesis of new unknown polymers but through the modification of commercially available ones.

The modification approaches used are mostly of a physical type, such as blending, reinforcement, drawing, controlling the crystallization process, and so on. Combining such approaches of physical modification it is possible to compete in some cases with the mechanical performance of traditional non-polymeric materials, or to create a material with a combination of properties unknown for traditional materials. But it has to be stressed that, as a rule, the plastic materials comprising polymers only are characterized by inferior mechanical properties. Therefore, to meet the demands of industry for strength and stiffness they have to be reinforced. Excellent mechanical properties have been achieved with the more traditional fiber reinforcements such as glass or carbon, but increased focus on the complete lifecycle of a product leads to concerns about recycling and environmental impact. This interface between polymer chemistry, engineering, rheology, and solid-state science is often described under the general umbrella term of *material science*. The period since the mid-1960s has seen a striking growth of interest in material science aspects of polymer science as investigators seek to improve the properties of well-known synthetic polymers. This type of work is likely to become even more important as technology continues to demand new materials with improved properties at a time when most of the readily available organic polymers have already been commercialized.

Materials science includes the fields of metals, ceramics, and a wide range of inorganic semiconductors, optics, and electro-optical materials, as well as polymers. Many modern devices and constructs combine and utilize materials from all four of these large areas. It seems clear that the technological future of polymer science will require a close interaction between the synthetic chemist on the one hand and the physical chemist and material scientist on the other.

Concluding this short historical overview on the rise of polymer science it should be stressed that, regardless of the fact that polymer science is extremely young (less than 100 years development), it has achieved remarkable results. Very soon after its formulation, Staudinger organized the first world-wide scientific journal on polymers, named "*Die Makromolekulare Chemie,*" followed by the second journal "*Die Angewandte Makromolekulare Chemie.*" In the United States similar activities were developed by *H. Mark* who used to work in Europe contributing to the establishment of polymer science and later immigrated to the United States. There he organized the "*Journal of Polymer Science*" (in three editions) and the "*Journal of Applied Polymer Science*" as well as the first "*Encyclopedia of Polymer Science and Technology.*" He also founded the first Polymer Institute at Brooklyn Polytechnic. Nowadays the scientific journals dealing with polymer science and technology are more than 100.

In this relatively short period of development the remarkable achievements of polymer scientists were awarded with *Nobel Prizes*. Their names are:

1) *Hermann Staudinger*, 1953, for his work in macromolecular chemistry,
2) *James Watson*, *Francis Crick*, and *Maurice Wilkins*, 1962, jointly, for their 1953 determination of the structure of DNA,
3) *Karl Ziegler* and *Giulio Natta*, 1963, jointly, for polymer synthesis techniques,

4) *Paul John Flory*, 1974, for theoretical and experimental work in polymer chemistry,
5) *Bruce Merrifield*, 1991, for synthesis on a solid matrix,
6) *Pierre-Gilles de Gennes*, 1991, for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers,
7) *Alan G. MacDiarmid*, *Alan J. Heeger*, and *Hideki Shirakawa*, 2000, jointly, for electrically conductive polymer,
8) *Y. Chauvin*, *R. H. Grubbs*, and *R. Schrock*, 2005, jointly for metathesis reactions.

In addition, many of the prizes in medicine are related to polymers/macromolecules.

In these concluding remarks it seems worth mentioning also the following facts. As noted earlier, polymers are all around us. Over 100×10^9 lb (50×10^6 t) of synthetic polymers are produced annually in the United States (Table 1.2), and growth of the industry is continuing at a fast rate. There is every reason to believe that this polymer age will continue as long as petroleum and other feed stocks are available and as long as consumers continue to enjoy the comfort, protection, and health benefits provided by elastomers, fibers, plastics, adhesives, and coatings. The 100×10^9 lb of synthetic polymers consumed each year in the United States translates to over 300 lb for every man, woman, and child in the United States. This does not include paper- and wood-related products, natural polymers such as cotton and wool, or inorganic polymers.

The number of professional chemists directly employed with polymers as part of their interest and assignment is estimated to be 40–60% of all chemists. As the

Table 1.2 United States production of plastics (2010).

Plastics		Production (millions of pounds)
Thermosetting resins	Epoxies	610
	Ureas and melamines and phenolics, miscellaneous.	12 600
	Total	13 210
Thermoplastics	Low density polyethylene	6700
	High density polyethylene	16 900
	Linear low density polyethylene	13 800
	Polypropylene	17 300
	Polystyrene	5000
	ABS and styrene-acrylonitrile	2600
	Polyamides, nylons	1000
	PVC and copolymers	14 000
	Other thermoplastics	14 800
	Total thermoplastics	90 000
Grand total		103 000