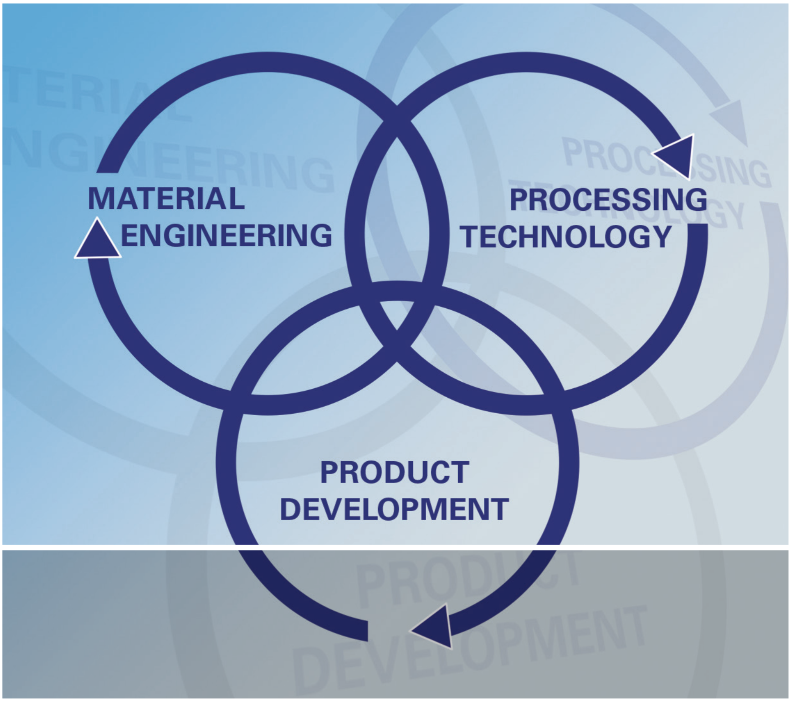
Christian Bonten

Plastics Technology

Introduction and Fundamentals



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Hanser Publishers, Munich Hanser Publications, Cincinnati

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Distributed in the Americas by:
Hanser Publications
414 Walnut Street, Cincinnati, OH 45202 USA
Phone: (800) 950-8977
www.hanserpublications.com

Distributed in all other countries by:
Carl Hanser Verlag
Postfach 86 04 20, 81631 Munich, Germany
Fax: +49 (89) 98 48 09
www.hanser-fachbuch.de

Library of Congress Control Number: 2019946865

Editor: Dr. Mark Smith
Production Management: Jörg Strohbach
Coverconcept: Marc Müller-Bremer, www.rebranding.de, Munich
Coverdesign: Max Kostopoulos
Typesetting: Kösel Media GmbH, Krugzell
Printed and bound by Hubert & Co. GmbH und Co. KG BuchPartner, Göttingen
Printed in Germany

ISBN: 978-1-56990-767-2
E-Book ISBN: 978-1-56990-768-9

Preface

Immediately after I started working at the University of Stuttgart in late summer 2010, I revised the course “Fundamentals of Plastics Technology” with the help of my scientific staff. Since then, this important course has been held unchanged in Stuttgart for a long time. During the revision we not only updated figures and contents, but also gave the course a new structure, which I – inspired by didactic seminars of the German University Association – consider more contemporary. Numerous film sequences used in the lectures enable the students to understand the contents more quickly and deeply. I am convinced that the students in my course become well equipped with a comprehensive, fundamental knowledge of plastics and plastics technology for their upcoming professional life. If students want to deepen their knowledge of the subject, they can do so in the three main areas of “Materials Engineering”, “Processing Technology”, and “Product Engineering” in other courses later on.

This introductory and fundamental lecture series in Stuttgart is an elective course with four lessons per week for master students of process engineering, mechanical engineering (e. g. production engineering, automotive engineering), materials science, as well as of technology management. The course is actually aimed at technically educated students, but in the meantime non-technical students (economics, environmental issues) choose the course as well. While about 100 students had this subject examined after the 2010 winter semester, the number was growing year by year subsequently. The increasing interest of highly motivated and disciplined master’s students led me to supplement the figures with continuous text and publish them in the form of a book the first time in 2014.

In winter 2012/13, students started asking me about the critical topics that are “heard in the media”. I decided to get to the bottom of the topics “environmental pollution”, “toxins in plastics”, “bioplastics”, and “life cycle analyses” right down to the original sources and to prepare this as a part of the course as well. These topics form the final chapter “plastics and the environment” of this book, and I have the impression that factual information is the best means of clarification. The reader may decide whether I have succeeded in dealing with the topics in a factual way.

I was a little surprised when, just one and a half years after the start of sales of the first German edition, the publisher asked me to prepare the second one. The many reviews that were sent to the publisher were all positive, contained valuable suggestions and encouraged me to continue this book the same way. Since 2016, more than 500 students chose the course underlying this book in structure and content and also encouraged me to continue teaching in this way. In the second German edition, I concentrated on individual additions, revisions, and updates, as well as the correction of several errors.

In the meantime, I am being asked by university professors from all over the world to give not only scientific presentations, but master's courses about plastics technology there as well. Since not everyone speaks German and I usually do not speak their native language, I often hold the course in English. To help the students with the rework, I have decided to translate the second edition of this book into the English language and made only minor changes.

I would like to thank the publisher for their trust and advice as well as for offering this book in color and hardcover. I would also like to thank my supporting staff members, who have carefully worked through and gave valuable hints on mistakes and the comprehensibility of the text of the first and second German editions. Technical staff members supported me with figures and photos from their daily work. The students Adriana Steinitz and Lisa Schleeh greatly helped me with translation of the text and the figures.

I am sure that with the knowledge of the book I will give every reader/student the opportunity to quickly gain a foothold in the plastics industry and to enable her or him to decide early on in which application plastics can do great things.

Stuttgart, September 2019

Univ.-Prof. Dr.-Ing. Christian Bonten

The Author: Prof. Christian Bonten

University Professor Dr.-Ing. Christian Bonten heads the Institute for Plastics Technology (Institut für Kunststofftechnik; IKT) in Stuttgart, one of the leading German research institutes in the field of plastics technology. After studying mechanical engineering in Duisburg/Germany and plastics processing at the University in Aachen/Germany, Prof. Bonten received his doctorate in the field of welding plastics under supervision of Prof. Ernst Schmachtenberg. After several years of technical responsibility and later business responsibility at the chemical company BASF and the bioplastics manufacturer FKuR, he was appointed Director and Head of the IKT by the University of Stuttgart in 2010. The institute works in all areas of plastics technology: materials engineering, processing technology, and product engineering.

How to Use This Book

The special feature of this book is the use of so-called Quick Response Codes (QR codes), which were developed more than 30 years ago in Japan. In this book they are used to connect a smartphone with the YouTube channel of the IKT and to run a film or animation matching the topic. This offers the fusion of the “frozen” printed book with the highly mobile possibilities of the new media.

QR codes allow the transmission of information by scanning – very similar to the bar codes on food packaging, but with a higher information density. They are a square matrix of black and white dots, which represent the coded data in binary code. Nowadays you do not need a special scanner any more, but simply scan the code with the camera of your smartphone using suitable software (an “app”).

To use the barcodes, a corresponding app (to be found e.g. under the search terms “QR code reader” or “QR code scanner”) must be installed, if the smartphone does not already have it “on board”. Of course, the smartphone must have Internet access in order to access the IKT YouTube channel. After starting the app, the QR code should be targeted in the search field: the information is usually recognized quickly and the appropriate YouTube movie runs automatically. Some of the movies have a soundtrack, so: speaker on!

A video can be played here.

A video can be played here.

http://www.ikt.uni-stuttgart.de/links/Videolinks/Hinweis

If teachers in schools or similar non-commercial entities want to make use of the figures used in this book, we will be happy to send them in high resolution. We kindly ask to make sure that the “Source: C. Bonten, Plastics Technology, 2019, Hanser” is always mentioned.

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1 Introduction

"What do you think of when you hear the word 'plastic'?" is often the first question to my master's students at the University of Stuttgart. Interestingly, most of them think first of all about application areas (lightweight construction, automobiles, aircraft, but also packaging and thermal insulation), then about the subdivision into thermoplastics, elastomers, and thermosets, which they may have remembered from high school. Sometimes they think of processing terms such as injection molding or extrusion, but compared to previous years, the topics of plasticizers, recycling, and environmental pollution only emerge later and later.

Plastics already seem to be such an integral part of everyday life that every student associates them with something useful and does not necessarily burden them with a "cheap" image. In this introduction, we first want to take a look at the young history of plastics and their current fields of application, before presenting the special significance of plastics for design-influenced products.

■ 1.1 Plastics – Material of the Modern Age

The earth is presumably 4.54 billion years old, plants (flora) originated only 540 million years ago, fungi, lichens, and the first animals (fauna) appeared about 440 million years ago.

Homo sapiens sapiens, i. e. the intelligent, modern human being, has existed for about 40,000 years and in this short period of time – from a world-historical point of view – has created amazing things.

The Copper Age, the last phase of the Stone Age, was followed by the Bronze Age (Figure 1.1). Bronze is an alloy consisting of at least 60% copper and also contains tin. Bronze is regarded as the first alloy specifically produced and used by humans, an achievement that already required metallurgical knowledge. Finally, the Bronze Age was gradually replaced by the early Iron Age (Hallstatt period). Iron and its alloys required even more metallurgical knowledge and higher temperatures, which finally enabled even more superior weapons and tools such as those of the ancient Romans.

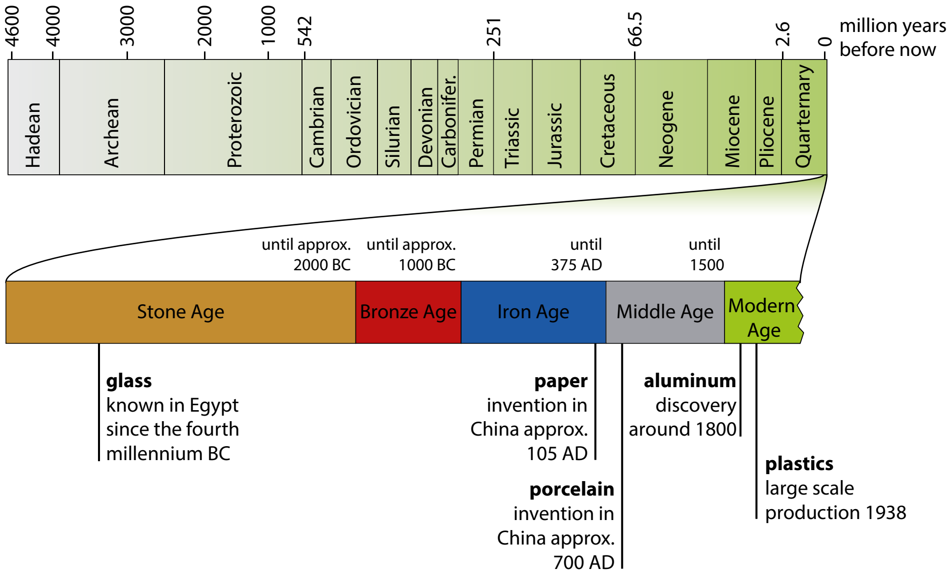

Figure 1.1 Chronology of development of different materials in human history

For over a millennium, actually no new material in the “known world” (from a European perspective, i. e. Europe, Africa, Middle East) was invented. It was only at the beginning of the 18th century that J. F. Böttger and E. W. von Tschirnhaus “invented” European porcelain (which already existed in China for about 1000 years). Aluminum was first produced at the beginning of the 19th century, and in the middle of that century the early plastics were introduced (however, it took until the middle of the 20th century to implement production on a large scale).

Due to the strong and increasing use of plastics, there are historians who already speak of the “plastics age”. In 1983, the worldwide consumption of plastics reached 125,000,000 m^3, for the first time, exceeding that of iron [1]. In the history of plastics, a distinction is made between four eras [2]:

- Origins (until 1839),
- The era of imitation fabrics (1839 to 1914),
- Era of substitutes (from approx. 1914 to approx. 1950),
- The era of materials with new properties (from around 1950).

The Era of Imitation Materials

At the beginning of the history of plastics there was an ecological problem, which is not strange to us even today. Due to the strong demand for ivory for balls for the billiards game popular in the USA, the elephants in Ceylon, today's Sri Lanka, were already close to extinction in the second half of the 19th century.

An American inventor, J. W. Hyatt, succeeded in 1867 in synthesizing a substitute, celluloid. But celluloid was not only attractive for billiard balls, but also for the inexpensive imitation of luxury products made of ivory, tortoiseshell, nacre, or horn for all kinds of everyday objects (Figure 1.2). The invention of G. Eastman, the head of the Kodak Group, who patented photographic film in 1884, has an even more epochal significance: thin strips of celluloid as a carrier for a light-sensitive layer [1].

Figure 1.2 Celluloid: replacement for expensive natural materials [Image source: Deutsches Kunststoffmuseum (German Plastics Museum)]

It was similar with the development of Bakelite®, the first fully synthetic phenolic resin-based plastic, by the Belgian Leo Hendrik Baekeland at the beginning of the 20th century. The heat distortion resistant, electrically insulating, and lightweight material was ideal for the still young electrical engineering industry for use as a housing material for radios and telephones (Figure 1.3) and for even more complex geometries of switches and lamp sockets (Figure 1.4). Electrical devices spread rapidly at that time.

Figure 1.3
Telephone housing made of Bakelite [Image source: Deutsches Kunststoffmuseum (German Plastics Museum)]

Figure 1.4
Bell button to call for domestic servants [Image source: Deutsches Kunststoffmuseum (German Plastics Museum)]

The Era of Substitute Materials

Even before World War I, the German Fritz Klatte took the first steps towards the industrial production of one of the most important mass plastics of the 20th century: polyvinyl chloride (PVC), which was invented by the Frenchman Henri Victor Regnault but could not be produced in large quantities until then.

The mechanical properties and the resistance of this material to chemicals and environmental influences as well as its low-cost production made it universally applicable: from acid-resistant protective gloves to bags and suitcases made of imitation leather. The vinyl record replaced the record made of shellac, a secretion of special lice, and spun on every turntable until well into the 1980s [1].

The Era of Materials with New Properties

Even before the First World War, these pioneers were often dependent only on empiricism, on ideas and experiments, in order to make new inventions in the field of plastics. This changed in 1922 when Professor Hermann Staudinger from Freiburg, Germany, explained the processes involved in the formation of polymers and plastics with his theory of macromolecules (Nobel Prize 1953).

It is therefore not surprising that numerous new substances were developed in the 1930s: polymethyl methacrylate (PMMA; “Plexiglas®”) from Röhm (now Evonik), polystyrene (PS) from BASF (now INEOS), polyethylene (PE) from Imperial Chemical Industries (now Akzo Nobel), and the polyamide (PA) with the brandname Nylon® from DuPont as well as with the brandname Perlon®, at the same time invented by the University of Stuttgart chemist Paul Schlack [1].

After stagnation during the Second World War, the triumph of plastics was unstoppable. Otto Bayer had already developed polyurethane by the end of the 1930s. In the 1950s there were numerous applications for soft and rigid polyurethane (PUR) foams, mostly upholstered furniture and sporting goods.

In 1949, Fritz Stastny of BASF created a very lightweight material with expanded polystyrene (EPS; Styropor®) through his process of foaming polystyrene. It was immediately used for shock-absorbing packaging of sensitive goods and for thermal insulation. In 1953, Karl Ziegler patented a safe and inexpensive process for the production of polyethylene (PE) that made this plastic truly marketable (Nobel

Prize 1963 together with Giulio Natta). To this day, polyethylene and polypropylene (PP) are by far the most widely used materials [1].

Hermann Schnell at Bayer succeeded in synthesizing polycarbonate (PC) in 1953. It combines transparency with very good mechanical properties. The material is valued as an alternative to glass in the construction industry and for housings for electrical appliances, usually also blended with ABS. Today, shatterproof headlamp diffusers made of polycarbonate ensure greater safety and lower weight in cars. From around 1982 it was used in large quantities for the manufacture of optical data carriers. The Compact Disc (CD) almost completely replaced the proven vinyl record made of PVC, followed by DVD and Blu-ray Disc [1]. Today, however, these are increasingly being replaced by solid state disks (SSDs) that contain little plastic.

1.2 Applications of Plastics

Plastics are increasingly being used for passenger transport because their low mass forces also reduce inertia (so-called “lightweight” construction, although inertia is not equal to weight). If inertia is reduced, sportier driving is possible for a given engine power, or alternatively the engine power and therefore the use of resources can be reduced.

Figure 1.5 shows selected examples of vehicles and aircraft whose plastic content is constantly increasing. For example, below right, the A350 series from Airbus is shown, which now consists of more than 50% by weight carbon fiber reinforced plastics.

Figure 1.5 Application of plastics in passenger transportation [Image source: Deutsche Bahn AG, BMW AG, Honda Motor ltd., Airbus AG]

The largest area of application for plastics is light food packaging, illustrated in Figure 1.6 using the example of films and plastic bottles. For many people, it is not immediately obvious which benefits are provided by packaging. On closer inspection, it becomes clear that plastic packaging with minimal input quantities provides a “shield” over the goods to be protected whose material or energetic efficiency cannot be achieved by other packaging materials. Section 6.3 deals with this more in detail.

Figure 1.6 Packaging made of plastic

Using the example of European plastics consumption, Figure 1.7 shows that packaging is a very important area of application for plastics, followed by use in the construction industry, e.g. as insulating material, for pipelines, or as heat-insulating material for window frames. This is followed by vehicles and electrical engineering applications.

It is particularly noticeable that packaging is more likely a short-lived application of plastics; on the other hand, plastics in the construction sector are used for 50 years or longer. Here one already notices the dilemma under which this class of material suffers. On the one hand the product should disappear as soon as possible after usage (packaging); on the other hand it should be usable as long as possible (building industry).

The term “other” is used, for example, to describe the areas of application: sports and leisure, furniture, toys, and medical technology. It becomes clear that there is actually hardly any industry in which plastics are not used!

Figure 1.8 shows sports and leisure applications; most of them would be inconceivable without plastics. The images shown here have also been selected for their design and color variety: While technical components, which are hardly visible, are designed according to the technical requirements and usually dyed black, consumer products are often fashionably designed and dyed.

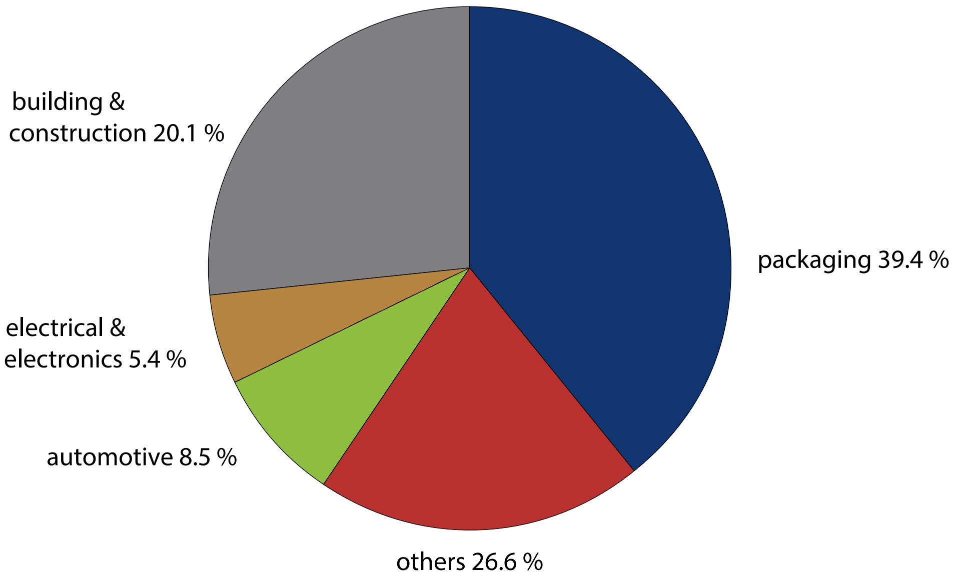

Figure 1.7 Application of plastics in Europe 2014 [3]

Figure 1.8 Application in the sports sector

1.3 Plastics and Design

Many consumer-related products use design as a unique selling point (e.g. Apple®, Samsung®, but also BRAUN® and Rimowa®). In some cases, technology and quality alone can no longer clearly differentiate a company from the competition. Plastics are the “chameleon of materials” and are therefore a material that designers like to use. The early plastics made it possible to imitate precious natural materials such as horn, tortoiseshell, nacre, and ivory (see above), and even modern plastics allow the imitation of many other high-quality materials.

What also makes plastic components so attractive is not only the lower weight, but also the usually lower component costs. The low-cost primary forming process, which we will get to know in Chapter 4 “Processing Technology”, allows a wide variety of forming options and thereby freedom of design (see also Chapter 5 “Product Development”). Both are particularly attractive for engineers and industrial designers.

The “cost-effective” aspect has certainly led to the fact that plastics had for a long time a “cheap” image compared to other materials. Today, plastic products are increasingly being processed into high-quality design products without losing their material identity. Plastics are less and less substitutes for other materials than a previously “non-existent innovation material” [4].

The design of a vehicle interior, the coordinated color scheme, the feel, and the sound are an experience that can hardly be associated with a “cheap” one (Figure 1.9): almost everything here is made of plastic.

Figure 1.9 High-quality vehicle interior made of various plastics [Image source: BMW AG]

Designers particularly like the fact that plastics can be colored (Figure 1.10), which is hardly possible with any other material. Lunch boxes, ballpoint pens, shower gel bottles, and many other plastic products are available in a wide range of colors and color combinations.

With the coloring, the more expensive painting step can be saved on the one hand, whereas on the other hand the component retains its color even if the surface is damaged. This is an advantage used, for example, by Japanese motorcycle manufacturers, who switch from painted sheet metal parts – where technically possible – to UV stabilized colored plastic components. The result is not only the above-mentioned aesthetic advantages after scratches, but also a far lower component weight at lower manufacturing costs.

Figure 1.10 Everyday objects in different colors, shapes, and surfaces

The variety of shapes has always inspired designers and artists. Figure 1.11 shows “La Chaise” by the engineer and artist couple Charles and Ray Eames from 1948, which for decades existed only as a model and was exhibited in museums. At the beginning of the 1990s, the German-Swiss furniture manufacturer Vitra dared to invest in its series production with modern materials and certainly does not regret it today.

Figure 1.11 Aesthetic shape of “La Chaise” [Image source: Vitra AG]

Figure 1.12 shows the world-famous cantilever chair of the Dane Verner Panton. First he made it as a prototype from glass fiber reinforced plastic (GFRP) manually on a one-sided wooden mold and showed it to his friends. Their approval encouraged him to start series production and he found a daring company in Vitra AG, which made the chair from polyurethane with the support of Bayer AG (Section 4.3.4). It had to be sanded, primed, and painted afterwards. The chair was so well received that even larger quantities were thought of and injection molding (see Section 4.2) came into the game.

Although a lot of money had to be invested in the injection mold, there was no longer any need for reworking and the color was already included in the material. BASF now supported the realization with its UV-resistant acrylic ester-styrene-acrylonitrile (ASA). At the end of the 1990s – as part of a retro wave – the chairs were reissued, but now injection molded from long glass fiber-reinforced polypropylene (PP-LGF) with a matte surface.

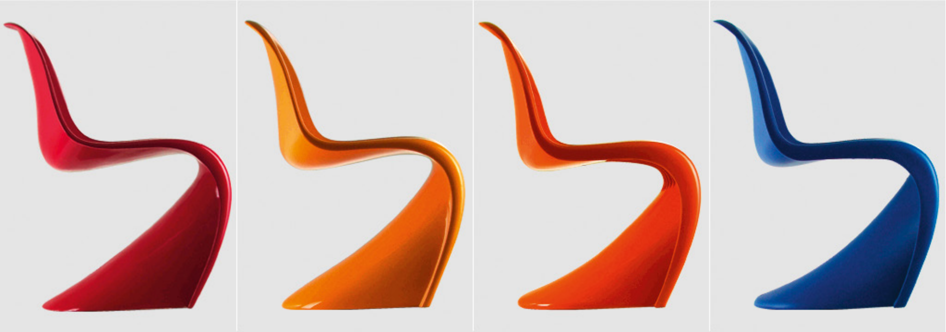

Figure 1.12 Different stages of the Panton chair [Image source: Vitra AG]

1.4 References

[1] N. N., *"http://www.deutsches-kunststoff-museum.de,"* 2014. [Online]. Available: *http://www.deutsches-kunststoff-museum.de/rund-um-kunststoff/zeittafel-zur-geschichte/*. [Accessed April 8, 2014].

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2

Fundamentals

For the engineer working with plastics, an introduction to polymer chemistry is a necessary basis, because the properties as a material, during processing, and in the finished component depend strongly on the structure and molecular shape of the polymers.

This chapter also refreshes some of the basic principles of material mechanics necessary for understanding this class of materials, aiming towards better comprehension and prediction of their special features, e. g. under the influence of time and temperature.

2.1 From Monomer to Polymer – Basics of Polymer Chemistry

We will now get to know the origin of the monomers and the three most important polyreactions, clarify the molar mass and molar mass distribution of polymers, and gain a better understanding of the acting binding forces. Afterwards, the so-called primary, secondary, and tertiary structure of polymers will be discussed, since not only the atoms of the polymer chain, but especially also their arrangement strongly influences the later material properties.

2.1.1 Origin of Monomers

Since the end of the Second World War, at the beginning of the modern era of plastics, crude oil has been used as a raw material for polymer chemistry. In a refinery, crude oil is distilled (sorted according to molecule size), cracked (split into smaller molecules), reformed (molecules partially converted), and refined (purified). Substances such as gases, gasoline (petrol), heating oil, bitumen, lubricating oil, and coke (chain length increasing) and – depending on where the oil is found – more or less sulfur is produced.

Ethene and propene – two volatile gases – can be extracted from the crude petroleum called naphtha. In the past, these gases were called ethylene and propylene, names that have survived in plastics technology and polymer chemistry to this day, and were initially waste materials that were incinerated without generating useful energy. For a long time, however, naphtha has been used to produce polymers.

Synthetic polymers are formed from smaller molecles, the so-called monomers ("mono"; Greek: one, alone, "mer", Greek: part, fraction), in the form of threads. If only a few (e. g. 10) smaller molecules are strung together, so-called oligomers are formed; they are of a wax-like and partly sticky consistency. If at least 1000 atoms are linked by chemical bonds, one speaks of polymers ("poly"; Greek: a lot). These very long molecules are also called macromolecules ("macros"; Greek: large, wide, long).

Figure 2.1 shows that not only ethene and propene, but also other chemicals are obtained from crude oil, which are raw materials for other polymers. With only a few raw materials (crude oil, natural gas, rock salt, sulfur, water, air), a chemical company can produce about 30 important monomers from which polymers of all kinds and with a wide range of properties can be produced. In the meantime, BASF has outsourced or sold the business of some of the polymers described to subsidiaries: however, this does not mean that it does not continue to supply the raw materials for these polymers.

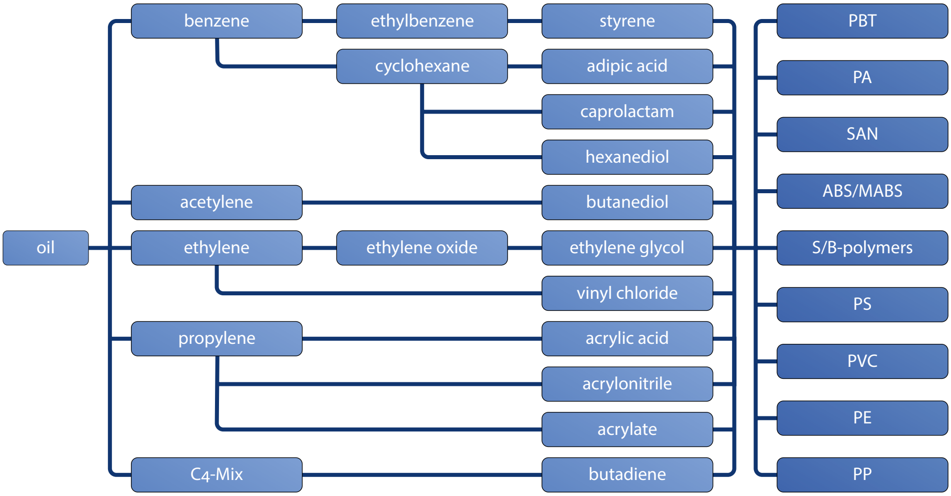

Figure 2.1 Polymer production routes [Image source: BASF SE]

Since oil reserves will become scarcer and more expensive in the long term, it makes sense to try to produce more and more polymers from renewable raw materials (Figure 2.2). Biosynthesis either takes place in nature itself (examples of natural polymers are proteins, cellulose, spider silk) or is deliberately induced in bioreactors:

- Biopolymers from plants (e. g. rubber trees)
- Biopolymers from animals (e. g. chitin, casein)
- Biopolymers from microorganisms (e. g. synthesis of PHB)
- Bio-monomers from microorganisms (e. g. fermentation of starch to lactic acid and later synthetic polymerization to polylactic acid PLA)
- Bio-monomers from plants (e. g. bio-ethanol from sugar becomes bio-polyethylene)

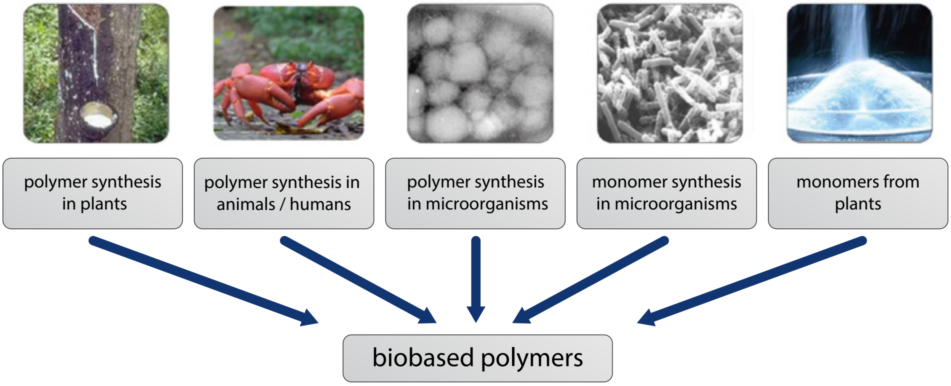

Figure 2.2 Synthesis of biobased polymers [Image source: IGVP, Univ. Stuttgart]

The example of five possible routes in Figure 2.3 shows which bio-based chemicals and polymers can be produced from glucose, a simple sugar. Glucose is mainly produced by plants using photosynthesis from sunlight, water, and carbon dioxide (CO_2) and can be used by all living organisms as a source of energy and carbon.

However, glucose is usually not freely available, but occurs as a disaccharide (lactose, beet sugar) or in its long-chain polymer form (such as starch, cellulose, etc.), which are both reserve substances and components of the cell structure in plants. When humans, animals, fungi, and bacteria ingest food, the long-chain saccharides are first broken down by enzymes into glucose monosaccharide before they are metabolized.

In Section 6.3, we will discuss bio-based polymers and bio-based plastics more in detail.

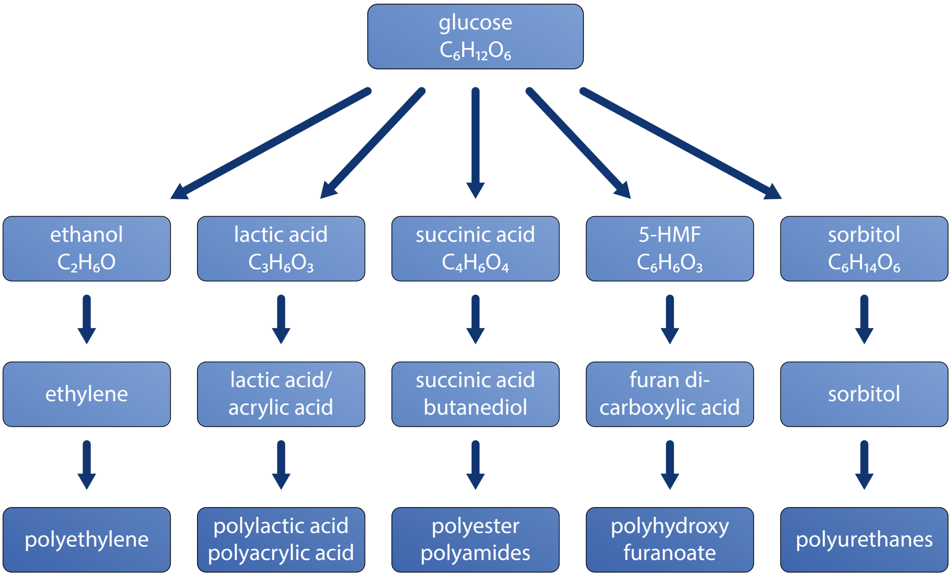

Figure 2.3 Polymers based on glucose [Image source: IGVP, Univ. Stuttgart]

2.1.2 Polymer Synthesis

The three most important chemical reactions (polyreactions) which cause monomers to react to form polymers are polymerization, polycondensation, and polyaddition. While polymerization is a chain growth reaction in which unsaturated monomers are combined to form polymers, polycondensation and polyaddition are step growth reactions in which different molecules react alternately to form a long molecular chain. Both step growth reactions are similar, but while polyaddition does not split off any by-products, polycondensation produces by-products such as water, hydrogen chloride, ammonia, and alcohols, which must be removed to continue the reaction.

2.1.2.1 Polymerization

Polymerization is explained here using the example of a radical polymerization (Figure 2.4). In radical polymerization, a radical generator, the so-called initiator, provides radicals, i.e. molecules with free/unpaired electrons, which attack the C=C double bond in monomers such as ethene. The initiator “grabs” an electron of this double bond and forms a bond with the monomer. This step is called a chain start.

By binding to the initiator, the monomer itself becomes a radical and therefore forms a bond with an adjacent monomer. This in turn becomes a radical and looks for a next partner. The molecular chain becomes longer and longer, which is called a chain growth reaction. The growth of the chains is often terminated by recombination, i. e. the radicals of two molecular chains form a chemical bond.

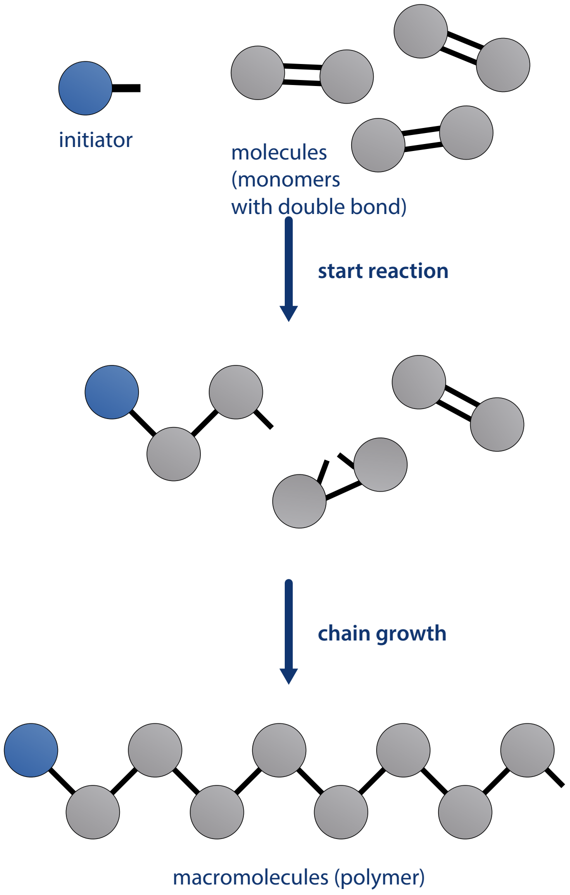

Figure 2.4
Schematic process of radical polymerization

QR-Code 2-1

The production of polyethylene originating from ethylene is shown, as an example of the radical polymerization.

http://www.ikt.uni-stuttgart.de/links/Videolinks/Polymerization

The length of the molecular chains is determined by the concentration of the initiator. The higher the initiator concentration, the more chains are started at the beginning of polymerization and the less monomers are available per chain. The molecule chains therefore remain shorter with the addition of more initiator.

A polymer with *n* repeating units is formed from *n* monomers (Figure 2.5). The monomer is usually a hydrocarbon. The simplest suitable hydrocarbon is ethene (formerly: ethylene).

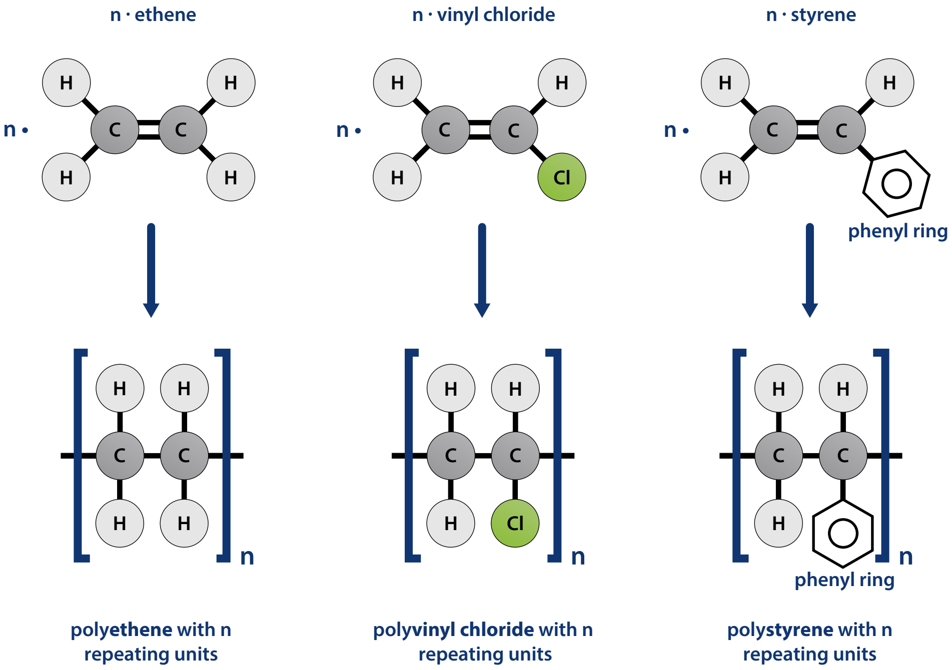

Figure 2.5 Structural formulas of different monomers and their corresponding polymers

A hydrogen atom is often replaced by a characteristic atom or group of atoms, the so-called substituent, which changes the chemical designation of the monomer. The replacement (substitution) of an H-atom with a Cl-atom results in the monomer chloroethene (trivial name: vinyl chloride). Substitution by a phenyl ring yields phenylethene (trivial name: styrene). From this, polyethylene (PE), polyvinyl chloride (PVC), and polystyrene (PS) are produced by radical polymerization.

For some polymerization reactions there are special catalysts, so called organometallic compounds which produce a polymer with a particularly regular structure. The monomer can only be coupled to the chain in a very specific way. The type of bond between catalyst and chain is called a coordinative bond and is therefore called a coordinative polymerization. Important organometallic compounds are Ziegler-Natta catalysts and metallocene catalysts. (The scientists Karl Ziegler and Giulio Natta were awarded the Nobel Prize in 1963 for their work on these catalysts.)

2.1.2.2 Copolymerization (Special Form of Polymerization)

If polymers in their chain reaction are not composed of one type of monomer but of different monomers, the reaction is called copolymerization. The macromolecules are called copolymers. The incorporation of two (rarely three) different monomers greatly influences the properties of the polymer. The sequence of monomer building blocks in the chain can be statistical, alternating, or blockwise (so-called block copolymers) (Figure 2.6). Graft copolymers are a special form of copolymers. These are polymers with a homogeneous main chain onto which shorter side chains of another type of monomer are grafted.

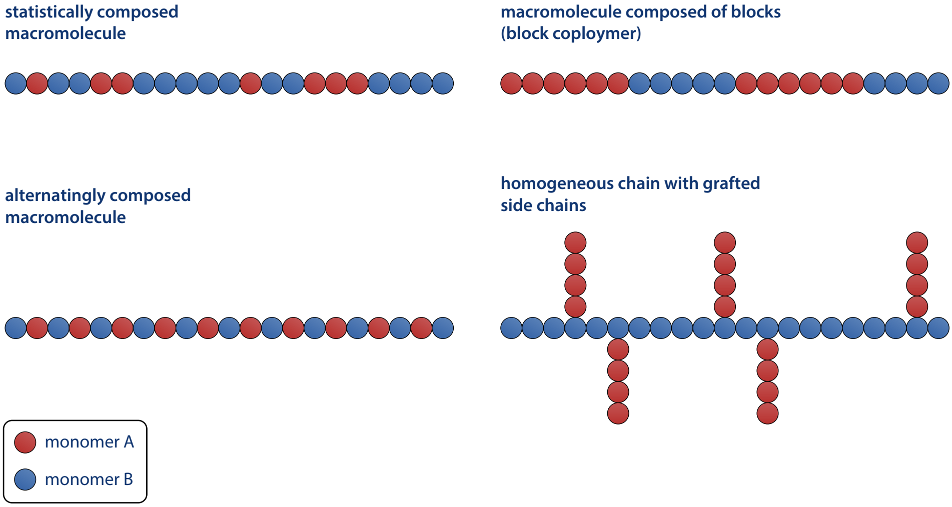

Figure 2.6 Types of copolymerization

It is not intended here to give the impression that this is a step growth reaction of two different monomers. Copolymerization is also a chain growth reaction, only with two different monomers. It should also be pointed out that the physical (not chemical!) mixture of different polymers is not the same as a copolymer. Polymer mixtures are also referred to as polymer blends, occasionally also as polymer alloys. These are discussed in Section 3.3.2.3.

2.1.2.3 Polycondensation

Polycondensation is a step growth reaction of multifunctional molecular building blocks. In Figure 2.7, two bifunctional molecules react to form a polymer and form a by-product, which must be removed in order not to slow down the reaction. Low molar mass by-products such as water, ammonia, and hydrogen chloride are formed. If the by-products are not removed, the reaction process is interrupted.

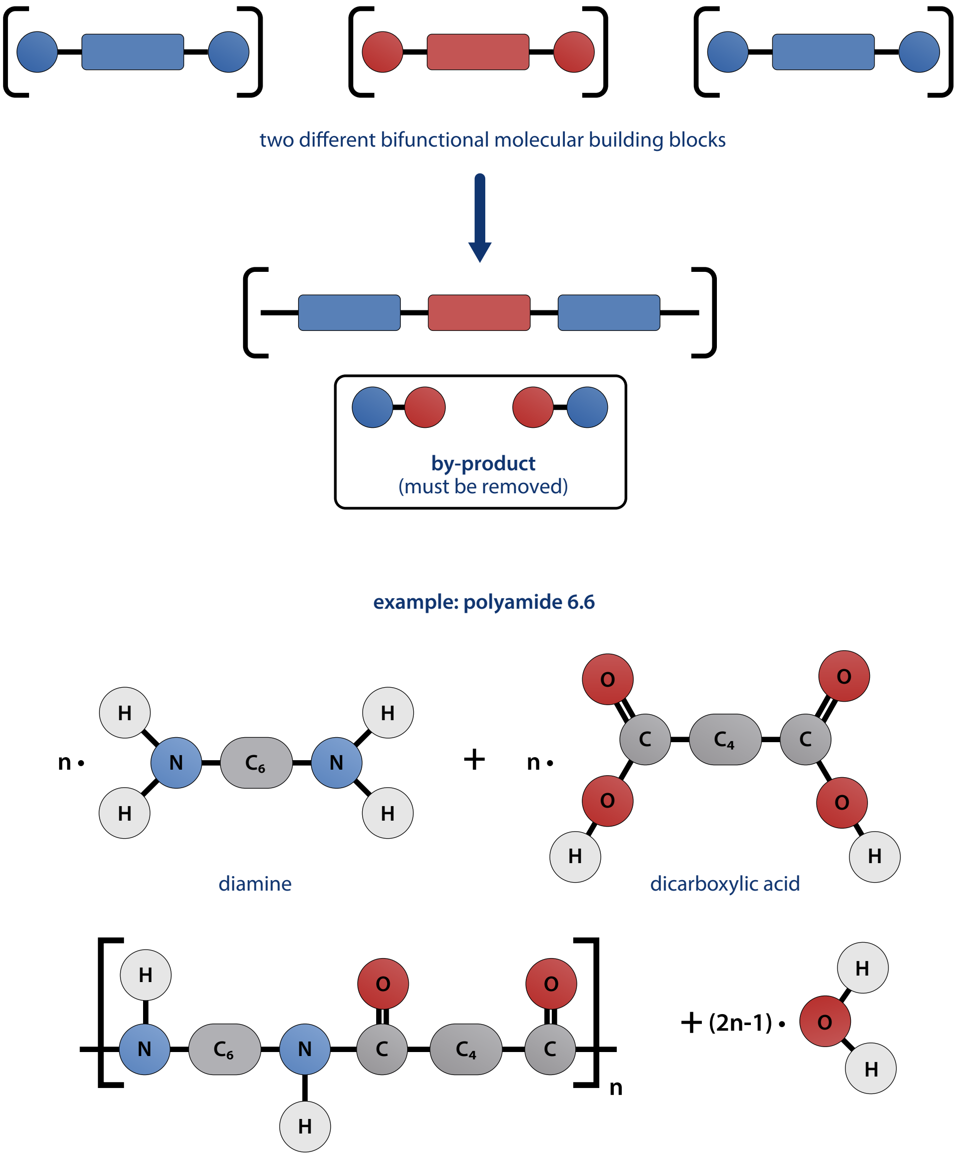

Figure 2.7 Polycondensation

In this way, polyamide 6.6 (PA66), for example, is produced from a bifunctional amine (1,6-diaminohexane) and a bifunctional carboxylic acid (e. g. adipic acid). A macromolecule with an amide group (CONH) is formed and water is removed as a by-product.

As distinguished above, polycondensation is a step growth reaction since, in addition to the reaction of individual bifunctional monomers with an existing chain, two chains of any length can also react with each other to form an even longer chain. In comparison to radical polymerization, this does not lead to the termination of chain growth, since the chain ends still have functional groups and can therefore continue to react with bifunctional monomers, oligomers, and polymers.

QR-Code 2-2

The polycondensation of heptanedioic acid and 1,6-hexanediamine is shown.

http://www.ikt.uni-stuttgart.de/links/Videolinks/Polykondensation

2.1.2.4 Polyaddition

In the polyaddition step growth reaction, two different multifunctional molecular building blocks (Figure 2.8, here bifunctional) also react with each other. However, no by-product is formed. The coupling of the reactive monomers results from the change of place of one or more atoms, preferably hydrogen atoms, which detach relatively easily from their respective end groups (–OH, –NH_2, –COOH). An example is the polyaddition of bifunctional isocyanate with a bifunctional alcohol to polyurethane. Polyurethane is specifically discussed in more detail in Section 4.3.4 “Polyurethane Processing”.

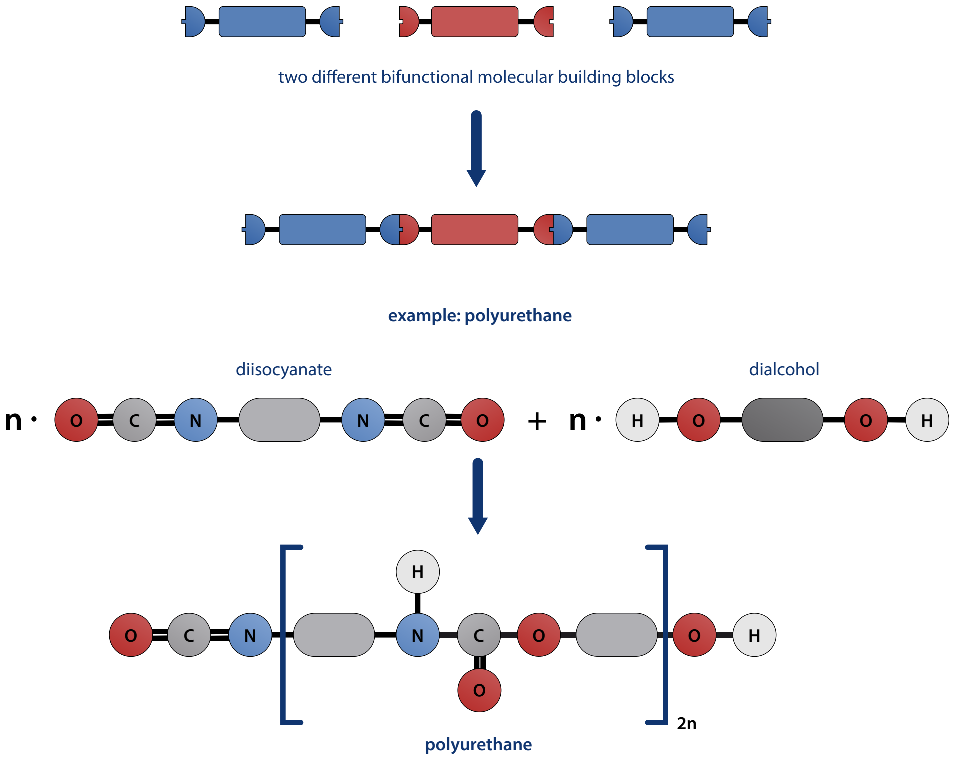

Figure 2.8 Polyaddition

QR-Code 2-3

The polyaddition reaction is explained using the example of an epoxy resin.

http://www.ikt.uni-stuttgart.de/links/Videolinks/Example-of-Polyaddition

2.1.3 The Molar Mass of Polymers

It may be known from school lessons that the molar mass, formerly called molecular weight, can be determined from the sum of the masses of the individual atoms. The molar mass of a macromolecule can now be calculated by addition of the molar masses of the individual monomer units. For this, however, it must be known how often the monomer units are contained in the polymer chain. This number is called the degree of polymerization n. Since not all polymer chains have the same length, n is always only an average value.

Since the chain length can only be an average value, the molar mass of a polymer can only be an average value as well. In reality, there is a molar mass distribution, i.e. shorter chains, medium-long chains, and longer chains. An example of such a molar mass distribution is shown in Figure 2.9.

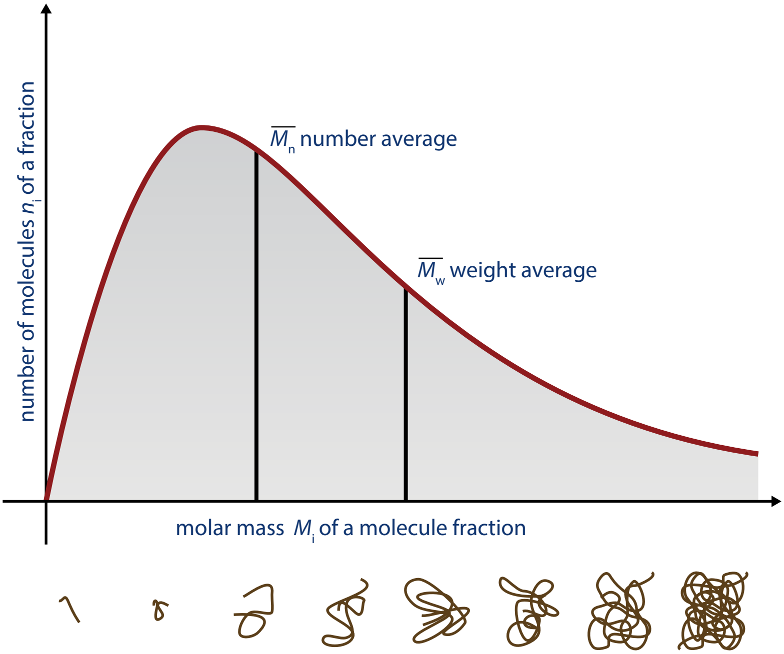

Figure 2.9 Example of a molar mass distribution of a polymer

So there are few molecules with very low molar mass (see coordinate origin) and few with very high molar mass (running to the right). In between, there is a characteristic distribution, which has its maximum at one point. Since some properties of the polymers and the plastics produced from them correlate with the molar mass, knowledge of them is very helpful.

But how can such a distribution be summed up in a single number? It turns out that some properties depend on the so-called molar mass number average $\overline{M_n}$ and others on the so-called molar mass weight average $\overline{M_w}$. The number average is simply the sum of the mathematical product of the number of single molecules present n_i times the molar mass M_i, divided by the sum of the number of single molecules n_i.

$$\overline{M_n} = \frac{\sum_{i=1}^{k} n_i M_i}{\sum_{i=1}^{k} n_i} \tag{2.1}$$

The weight average additionally takes into account the weight of the counted molecule lengths and is defined by the mass fraction m_i of the macromolecules with the molar mass M_i.

$$\overline{M_w} = \frac{\sum_{i=1}^{k} m_i M_i}{\sum_{i=1}^{k} m_i} \tag{2.2}$$

The wider the molar mass distribution, the further apart the values of weight and number averages are. The polydispersity results from the quotient of the two mean values. Instead, $\left(\frac{\overline{M_w}}{\overline{M_n}}\right)$, the so called “non-uniformity” U, is also often given.

$$U = \frac{\overline{M_w}}{\overline{M_n}} - 1 \tag{2.3}$$

The difference can be clearly explained by analogy with a purse with coins (Figure 2.10). The 2 Euro (€2) coins correspond to particularly long chains (high molar masses) and the 1 cent (€0.01) coin to very short chains (low molar masses). The number average is the average value of a coin and is calculated from the total value of the coins divided by the total number of coins:

$$\overline{M_n} = \frac{\sum_{i=1}^{k} n_i M_i}{\sum_{i=1}^{k} n_i} = \frac{\sum_{i=1}^{k} m_i}{\sum_{i=1}^{k} n_i} = \frac{5\cdot 0.01 + 15\cdot 0.02 + 27\cdot 0.05 + 32\cdot 0.1 + \ldots}{5 + 15 + 27 + 32 + \ldots} = \frac{50}{159} = 0.31 \qquad (2.4)$$

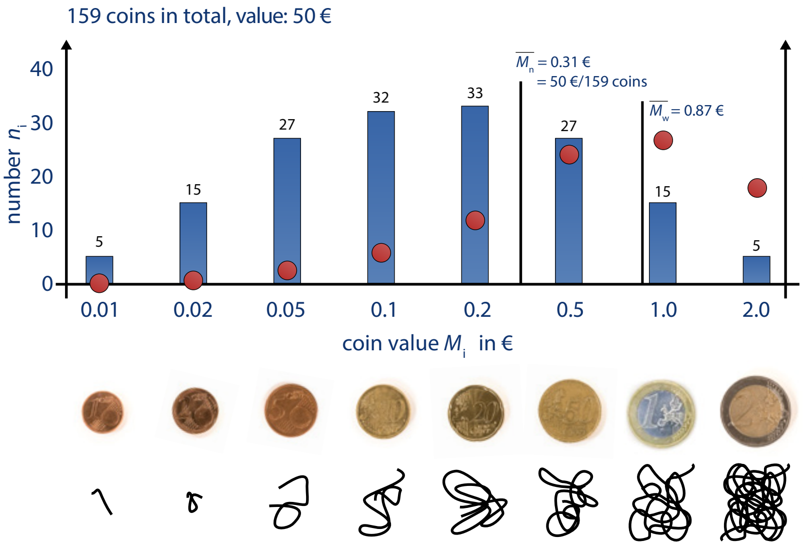

Figure 2.10 Descriptive explanation of average value and distribution

The average value of each coin is €0.31.

The weight average can be calculated by letting the individual coin stacks participate in the formation of the total sum, not in the ratio of the effective particle numbers (number of coins), but by weighting the coin stacks. This means that the ratio of the sum of all stack values is formed by the total sum (value) of the coins.

It is assumed that in the wallet there are not:

Table 2.1 Determination m_i Using Coins as an Example

n_i	M_i	m_i
5 coins at	0.01	0.05
15 coins at	0.02	0.30
27 coins at	0.05	1.35
32 coins at	0.10	3.20
etc.		

but rather:

$m_i \cdot M_i$	m_{F1}
0.05 · 0.01	0.0005
0.30 · 0.02	0.0060
1.35 · 0.05	0.0675
3.20 · 0.10	0.3200
etc.	

m_{F1}: stack value

The following applies to the weight average:

$$\overline{M_w} = \frac{\sum_{i=1}^{k} m_i M_i}{\sum_{i=1}^{K} m_i} = \frac{\sum_{i=1}^{k} m_{F^I}}{\sum_{i=1}^{k} m_i} = \frac{0.0005 + 0.0060 + 0.0675 + 0.3200 + \ldots}{50} \tag{2.5}$$

$$= \frac{43.46}{50} = 0.87$$

Therefore, the weight average value of each coin is €0.87.

Since the molar mass of the polymer is an important criterion for various properties of the later plastic, the most important methods for their determination will be briefly presented here.

Measurement with the Capillary Viscometer

The molar mass of the polymer can be determined using a capillary viscometer, e.g. the Ubbelohde viscometer (Figure 2.11). The polymer must first be dissolved using a suitable solvent. Now a defined volume of this solution is allowed to flow through a capillary of the viscometer and the time required is measured.

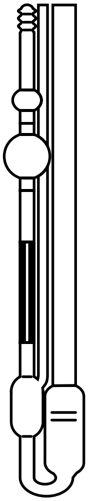

Figure 2.11
Ubbelohde viscometer

With the help of physical correlations and mathematical relationships, the so-called limiting viscosity number (“Staudinger index” $[\eta]$) can ultimately be calculated.

For real macromolecules, the Mark-Houwink relationship applies, with which the number-average molar mass is calculated:

$$[\eta] = K \cdot \overline{M_n}^{\alpha} \tag{2.6}$$

K and α are characteristic parameters which are listed in the literature for a large number of polymer solvent systems at different temperatures. For linear, unbranched molecules (see “secondary structure” below), α has values between 0.5 and 1.

This method is a relative method. The quality of the determination of $\overline{M_n}$ depends, among other things, on the agreement of the test conditions and the molar mass distribution (polydispersity) of the respective polymer.

In addition, the polymer can also be melted instead of brought into solution and can also be pressed through a capillary. However, gravity is not sufficient to determine this so-called melt flow index (MFI) and the force of some weight plates is used to help. The results can be determined quite quickly, but do not give a value for a molar mass, but rather only an indirect statement. Further details are given in Section 3.1.6 “Rheometry – Measurement of Flow Properties”.

Measurement with Size Exclusion Chromatography

The measurement using size exclusion chromatography (SEC) provides an exact molar mass distribution and can also determine absolute molar masses using light scattering detectors. The polymer to be measured is applied in solution to a separation column with a porous structure and passes through it sequentially (Figure 2.12).

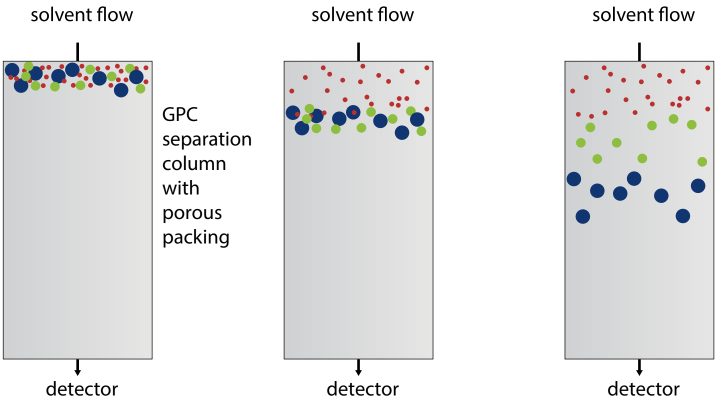

Figure 2.12 Size exclusion chromatography (SEC)

The principle of size exclusion chromatography: Large macromolecules only have a few pores in which they can be deposited. This is why they are detected relatively quickly by the continuous solvent stream and rinsed out of the separation column first. The smaller a macromolecule is, the more often it can settle in a pore on its way through the separation column. This means that the smaller the macromolecules, the later – i.e. with a time delay – they leave the column.

2.1.4 Binding Forces and Brownian Molecular Movement

As a basis for understanding the molecular binding forces in polymers, it is necessary to provide a reminder of the different binding forces between atoms:

Metallic Bonds

In the metallic bond, the electrons can move freely in a metal lattice (atomic lattice) (Figure 2.13). The valence electrons (outer electrons) of the metal atoms can easily be separated from the atom because they are only bound weakly. A lattice of positively charged metal ions, the so-called atomic bodies, forms in the metal. The “electron gas”, named after the physicist Enrico Fermi, consists of free outer electrons. The high electrical conductivity, magnetism, and also the high thermal conductivity of metals are the result of this free mobility.

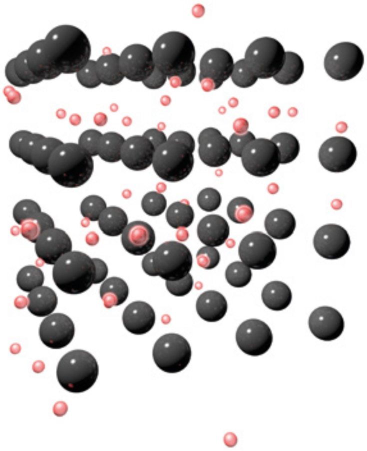

Figure 2.13
Metallic bonds

Atomic Bond

The atomic bond is a chemical bond and is also called the main valence bond (chemical primary valence bond). Atomic bonds are formed especially between non-metals and share at least one binding electron pair of the outer electrons (valence electrons) (Figure 2.14). The atoms in the macromolecules of polymers are linked by main valence bonds.

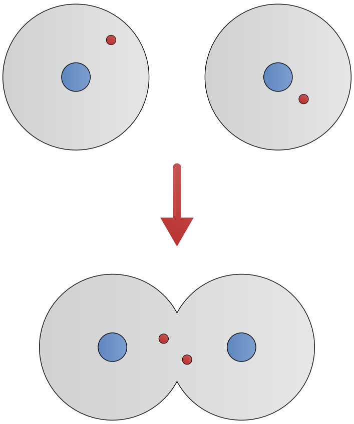

Figure 2.14
Atomic bond, using the example of a hydrogen molecule H_2 (also: covalent bond, main valence bond)

Further terms for atomic bonds or main valence bonds are: covalent bonds, homopolar bonds, and electron pair bonds. An atomic bond has a certain direction of action, i.e. it is a directional bond and therefore determines the geometric structure of a compound (in contrast to an electron gas). The strength of a bond is described by the binding energy. The formation or breaking of an atomic bond is called a chemical reaction.

Once more repeating school material, a reminder of the binding nature of these often-used elements is provided here. In general, atoms (elements) strive to take up a noble gas electron configuration when forming a chemical bond (shell model: eight outer/valence electrons; except hydrogen: two outer electrons). Electrons are always arranged in pairs. Unbound outer electrons of one atom therefore enter into a “partnership” with those of another atom – a molecule is formed. The binding energy of main valence bonds can have values from 40 to 800 kJ/mol.

The number of atomic bonds an atom can form is called valency or binding capacity. It depends on the number of outer electrons. The “8-minus-*n*” rule applies to the binding capacity of a covalently bonded atom of the IV – VII main groups of the periodic table, with *n* equal to the outer electron number of the corresponding atom. For chlorine (Cl), oxygen (O), nitrogen (N), and carbon (C) with 7, 6, 5, and 4 outer electrons, respectively, a binding capacity of 1, 2, 3, and 4 is calculated. The hydrogen atom strives for the configuration of helium (noble gas) with 2 outer electrons and can thus take up 1 electron within a chemical bond. This means that hydrogen is monovalent. Since sulfur (S) stands in the main group VI of the 3rd period, this can additionally form 6 bonds.

The macromolecules of a polymer are formed by such atomic bonds. The fragment of a polyethylene macromolecule shown in Figure 2.15 consists of about 70 ethylene monomer units. Most polyethylenes even have 100,000 repeating units. However, these cannot be shown here.

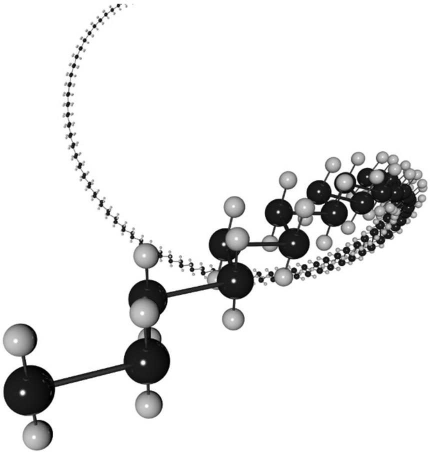

Figure 2.15
Fragment of a polyethylene macromolecule

Polymers are organic compounds because they are based on carbon. Besides carbon (C), important components of organic compounds are hydrogen (H), oxygen (O), and nitrogen (N). In polymers, the heteroatoms chlorine (Cl), fluorine (F), sulfur (S), and silicon (Si) are occasionally used as well.

2.1.4.1 Intermolecular Physical Bonds

Physical bonds are secondary valence bonds . They describe the type and size of the attraction forces existing between the polymer chains. Further terms for secondary valence bonds are: intermolecular forces, secondary valence forces, and secondary bonds. These attractional forces are strongly distance-dependent and 2 to 2000 times weaker in relation to the main valence bonds.

Dipole-Dipole Forces

Dipole-dipole forces consititute a very strong secondary valence bond. They occur between molecules with permanent dipole moments. The dipole moments derive from the different electronegativities of the chemical elements. In polyvinyl chloride (PVC), for example, the chlorine atom is more electronegative than the carbon and the hydrogen atoms (Figure 2.16, left) and therefore attracts their electrons (in the orbital model, this corresponds to an asymmetric electron cloud).

This creates a permanent dipole: attraction forces, the so-called dipole-dipole forces, arise between the dipoles of neighboring polymer chains. Their binding energy is 1/50 to 1/200 of a main valence bond.

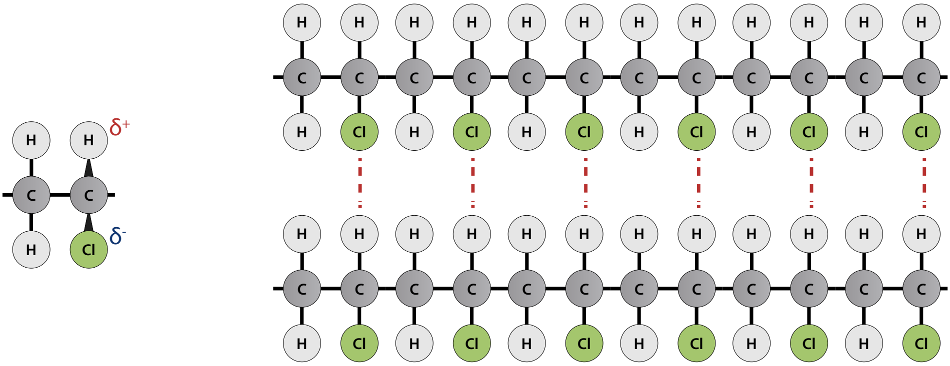

Figure 2.16 Dipole-dipole forces

Hydrogen Bonds

Hydrogen bonds are a special form of the dipole-dipole bond and are formed by a hydrogen atom covalently bonded to a much more electronegative atom (e.g. O, N, F) whose common electrons are shifted in the direction of this atom (Figure 2.17).

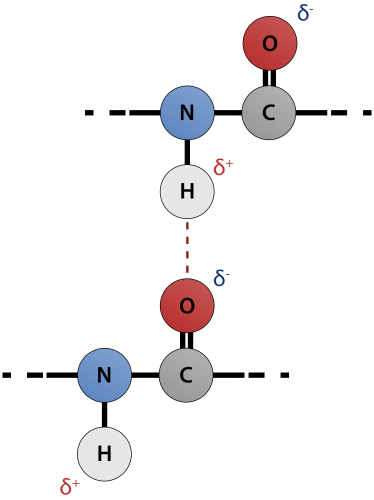

Figure 2.17 Hydrogen bonds

The hydrogen atom, which is partially positively charged by the electron shift, is more strongly bound to another electronegative atom of a second macromolecule and thus acts as a "hydrogen bridge" between the two molecule chains. With ~20 kJ/mol, this strongest type of intermolecular force reaches the order of weak main valence bonds. Figure 2.18 shows hydrogen bonds in polyurethane (PUR) and polyamide (PA).

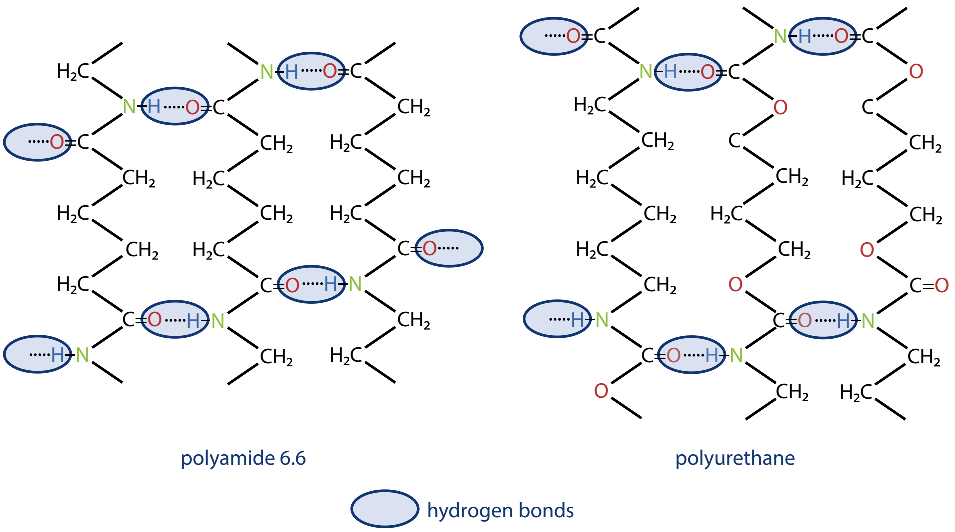

Figure 2.18 PA66 and PUR as examples for formation of hydrogen bonds

Induction Forces

Induction forces are very weak secondary valence bonds. Molecules with permanent dipoles can cause electron shifts in adjacent nonpolar molecules and thus induce dipole moments. The binding energy is only 1/500 to 1/2000 of a main valence bond.

In summary, the following applies to the secondary valence forces already listed: a prerequisite for the occurrence of dipole-dipole forces and/or induction forces is the presence of permanent dipoles.

Dispersion Forces

With binding energies of 1/500 to 1/1000 of a main valence bond, dispersion forces (also Van der Waals forces, London dispersion forces) are also very weak. By random movement of the electrons and the resulting deformations of the electron cloud, momentary dipoles are formed even in non-polar molecules. These rapidly varying dipoles, which compensate each other to zero on a time average, also induce dipoles in the neighboring molecules in the rhythm of their own frequencies, but they are not permanent.

To illustrate this, Figure 2.19 shows spheres strung together as atoms which are connected to each other by main valence bonds and form polymer chains. Between the polymer chains there are secondary valence forces of different kinds, depending on the atoms of the polymer chain.