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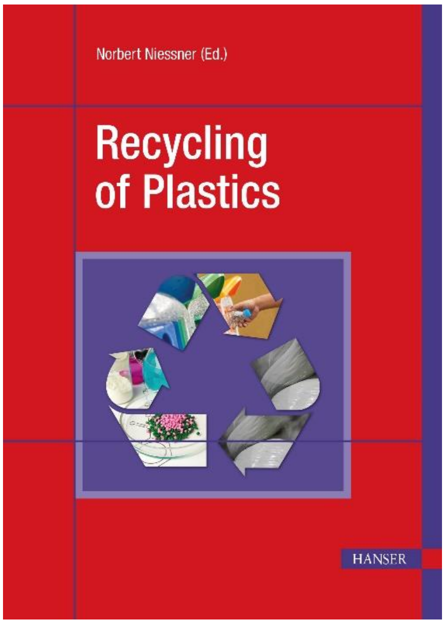

# Sample Pages

# Recycling of Plastics

Norbert Niessner

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# Preface

Plastics have offered and still offer an unprecedented step-up in quality of life. Their beneficial effects range from reduction of food waste by extension of shelf life, affordable healthcare measures through mass production of diagnostics or infusion kits, significant carbon dioxide savings through lightweight applications in automotive and aircraft, up to a wide range of electronic gadgets in lightweight yet stiff and tough protective housings. A replacement or even no-plastics strategy would not only affect lifestyle, but also increase the emission of greenhouse gases such as carbon dioxide significantly.

At the same time it is clear that environmental pollution by plastic parts must not continue as it has done until now. While recovery of precious metals – even from landfills – is already in place in many parts of the world, it is about time to treat plastic items at the end of their normal lifecycle not as waste anymore, but as a source of precious raw materials. Plastics are not the problem, but rather insufficient collection schemes and recycling initiatives.

This book intends to show the state of the art in plastics recycling, the value chains, the challenges, and the solutions. The following paragraphs give a very condensed overview of the contributions and their authors (those who (co)wrote more than one contribution are mentioned just once here – see the table of contents or "The Authors" for a more complete survey).

We introduce structure-property relationships in plastics with a contribution by leading polymer scientists from Bayreuth University (Prof. Hans-Werner Schmidt Tristan Kolb, and Andreas Schedl), will touch the economics and deep-dive into the important topics of legislation and political/legal boundaries, contributed by two major stakeholders in this field (Accenture with Michael Ulbrich, Marvin Stiefermann, and Sören Hörnicke, and BASF SE with Klaus Wittstock and Victoria Wessolowski). By this dual approach we emphasize the overarching importance of politics and legislation for the successful, global implementation of plastics recycling.

LCA contributions by BASF SE (Prof. Peter Saling), NMB (Thomas Neumeyer, Regino Weber), and TU Braunschweig (Prof. Stephan Scholl, Mandy Paschetag, and Hannes Schneider) complete the first part (Part A).

The recycling chapters will be introduced by Prof. Christian Hopmann, Prof. Rainer Dahlmann, and Martin Facklam (IKV Aachen), followed by a split into mechanical and advanced recycling (by chemistry-based measures), including contributions by Prof. Achim Schmiemann (IFR); Marco Amici (INEOS O&P); Prof. Thomas Schröder (ikd Darmstadt); Hermann van Roost (SCS Brussels); Eike Jahnke and Bianca Wilhelmus (INEOS Styrolution); Hannah Mangold and Caroline Beyer (BASF); Jason Leadbitter (INEOS INOVYN); Prof. Dieter Stapf (KIT); Prof. Thorsten Gerdes, Achim Schmidt-Rodenkirchen, Stephan Aschauer, and Klaus Hintzer (InVerTec); Adrian Griffiths, Stephanie Loo, and Alejandro Sánchez (Recycling Technologies); and Carsten Eichert and Vitalij Salikov (Rittec). A section on the dissolution technology is provided by the Fraunhofer Freising team around Andreas Mäurer and Martin Schlummer.

Contributions by two key representatives from the recycling and sorting industry – by Jürgen Ephan and Arne Köhne (REMONDIS) and Jürgen Priesters (TOMRA) – complement the view on the value chain, introduced by Raphael Kiesel.

We conclude our book with contributions on reuse examples, design for recycling, and future developments from Prof. Volker Altstädt, Prof. Holger Ruckdäschel, Tobias Standau, Matthias Mühlbacher, Josefa Nüßlein, Robin Fachtan (NMB), and Eric Homey.

Our book is written for the decision makers in companies, public institutions, and government/administration, for the student, as well as for the experts from academia and industry. We hope that all stakeholders will receive a comprehensive overview, allowing the identification of the best solution for each recycling challenge.

*Norbert Niessner*, Editor August 2022

# Foreword

Recycling of plastics is a very important topic for society, policymakers, and industry.

Plastic is a material we use every day. It helps feed the world sustainably, keeps us warm, allows us to get from A to B, and even saves lives. We cannot achieve our climate ambitions without plastics.

But we also know that plastics, plastics production and plastics waste management must be sustainable.

To transition to the EU's net zero emissions goals by 2050 requires the European plastics system to realize drastic emissions reductions across the entirety of the value chain, from raw materials to end-of-life. The stakes are high as we know societal sustainability goals, triggered by new EU legislation and consumer/citizen demand, are not just confined to Europe but impact global trade systems too.

Circularity is absolutely fundamental to our industry's transition. It is the most important medium-term lever and recycling is an essential component of circularity. "Reshaping Plastics", an independent report commissioned by Plastics Europe in 2022, concluded that by 2050 the plastics system could achieve 78% circularity with 48% being recycled.

Plastics Europe and our members recognize systemic change is essential to achieve this and needs to be accelerated. European plastics manufacturers are already undertaking huge investments and a far-reaching reorganization of their production and technology base to increase circularity and support recycling.

But we are under no illusions about the scale and complexity of this transition. The European plastics system is extremely diverse and complex. We are talking about multiple supply chains, delivering thousands of products and a plethora of industrial and consumer applications. There is no silver bullet solution.

Whilst plastics manufacturers have a very important role to play in supporting the transition to net zero, we represent only one part of the European plastics system. We do not have all the answers or levers to the recycling challenges we and the plastics system face and cannot do it alone.

Policymakers also have a vital role to play. Accelerating the transition requires an enabling policy framework that incentivizes and fosters a climate of creative collaboration and competition. One that helps to maximize investment and innovation from both private and public actors.

Deeper collaboration between the plastics industry, value chain, policy makers, increased investment and innovation – all of this is vital and it has to be based on a deeper and science-based understanding of the challenges and opportunities that we face in relation to recycling. This is why I welcome this book.

Packed with vital insights and detailed analysis, “Recycling of Plastics” is an invaluable resource for all of us as we rise to the collective challenge and opportunity of creating a circular plastics economy.

Happy reading!

Virginia Janssens

Plastics Europe – Managing Director

# Foreword 2

Plastics are ubiquitous in our everyday lives. Economically, they are one of the most prolific materials, with above average global growth rates surpassing other key materials such as paper, glass, or aluminum.

This is not least due to the remarkable properties of plastics, which bring many benefits to the individual consumer as well as society as a whole. For example, plastics are used in packaging to protect goods, also helping to reduce food waste, and to build lighter and more fuel-efficient vehicles, helping to reduce greenhouse gas emissions.

However, more recently, the focus of the public perception of plastics has shifted towards their end of life. Globally, only a small portion of plastic waste is collected, sorted, and recycled, while too much of it is still incinerated, landfilled, or, even worse, leaked into the environment. Policymakers, NGOs, plastic users and end consumers, as well as investors increasingly demand that the plastics industry accepts its share of responsibility and takes concrete action against plastic pollution and greenhouse gas emissions by transitioning from a linear to a circular economy.

Indeed, circularity is an integral aspect of sustainability. Implementing "reduce, reuse, and recycle" (3R) is one key approach to addressing the urgent need to mitigate climate change, in line with the Paris Agreement at a global level, as well as, more specifically, the European Green Deal and the Circular Economy Action Plan (CEAP) at the European Union (EU) level. Our common goal must be a circular, net-zero carbon plastics economy. In the end, further increasing collection, sorting, and recycling of plastic waste will be instrumental to achieve this, in addition to reuse models and renewable materials. This includes standardizing and designing plastic products to increase their ability to be recycled and incorporate recycled content, with closed-loop systems as the ultimate goal, where they are the most sustainable solution.

Also in support of fact-based policy and other decision making, industry will continue to contribute to meeting expectations regarding transparency. This includes aspects such as data collection, traceability, monitoring, and accountability, as well as providing comprehensive scientific evidence on the life cycle impacts of its products.

The global transition to a sustainable, circular economy cannot be achieved with isolated solutions. Within an enabling policy framework, cooperation along the value chains is key to achieve these objectives. In the EU, the Circular Plastics Alliance (CPA) and polymer value chain associations such as PETCORE (PET), PCEP (PE, PP), Vinylplus (PVC), and SCS (Styrenics) are visible examples of such cooperation.

This book provides a strong fact base for all stakeholders involved or interested in the circular economy for plastic. To help to better understand feasibilities, limitations, and opportunities, it lays out the potential of existing mid- and long-term solutions, enabling conditions, as well as trends and future developments. This includes standardization and the huge but not yet fully tapped potential of design for recycling.

Against the backdrop of the above-mentioned as well as more recent developments, the release of this book is timely, as it presents a technology roadmap and possible choices regarding circular feedstocks, which will also help to meet the urgent strategic needs to save fossil resources such as crude oil and natural gas.

I hope that with its diverse content and contributing authors, this book may inspire all its readers to closely communicate and collaborate with each other. With commitment, concrete action, and solutions, together we can deliver an answer to the dual challenge of climate change and plastics pollution by realizing the circular economy for plastics.

Jens Kathmann

Secretary General, Styrenics Circular Solutions (SCS)

# The Authors

## The Editor

**Norbert Niessner**

Dr. Norbert Niessner is Innovation Director at INEOS Styrolution. He is a Chemistry graduate from Marburg University, Germany, at which he also obtained his PhD in Polymer Chemistry. From 1989 to 1990, he worked as a post-doctoral fellow at IBM Almaden Research Labs in San Jose, California. After joining BASF in 1990, he held several positions in R&D and marketing & sales in Europe, as well as in Asia. In 2011, he joined the newly created BASF/INEOS joint venture "Styrolution", now a 100% INEOS company.

During his career, Dr. Niessner gained experience in building and leading global R&D and business management teams in the polymers industry worldwide, with focus Europe and Asia. In terms of patents/applications, he is one of the leading inventors in styrenic polymers. His publication/patent list comprises more than 300 tech/scientific papers, book chapters, and original inventions. Special fields of interest are, amongst others, liquid crystalline polymers, development of world-scale polymer manufacturing technologies and product lines, polymers for 3D printing, and advanced recycling technologies.

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* Order according to chapter/section number.

# Glossary

| | |
|---|---|
| AA | Acrylic acid |
| ABS | Acrylonitrile–butadiene–styrene copolymer |
| AN | Acrylonitrile |
| API | A measure of how heavy or light a petroleum liquid is compared to water: if API > 10, then the liquid is lighter and floats on water; if API < 10, it is heavier and sinks |
| APC | Aliphatic polycarbonates |
| ASR | Automotive shredder residue |
| ASTM | American Society for Testing and Materials; international standardization organization |
| BGL | British Gas Lurgi Process |
| BHET | Bis(2-hydroxyethyl) terephthalate |
| BHETA | Bis(2-hydroxyethylene) terephthalamide |
| BMBF | German Ministry of Education and Research |
| BMC | Bulk molding compound |
| BPA | Bisphenol-A (monomer for polycarbonate) |
| BTX | Benzene, toluene, xylenes fraction |
| CAPEX | Capital expenditure |
| CEAP | EU Circular Economy Action Plan |
| CEFIC | European Chemical Industry Council |
| CFC | Carbon fiber composites |
| CFF | Circular footprint formula |
| Citeo | Non-profit company founded from the merger of Eco-Emballages and Ecofolio |
| $CO_2e$ | Carbon dioxide equivalents |
| CPA | Circular Plastics Alliance of EU Commission |
| CPE | Chlorinated Polyethylene |
| CPO | Circular Polyolefins Project |
| CSS | EU Chemicals Strategy for Sustainability |
| CW | Commercial waste / consumer waste[1] |

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1) Which definition applies is given in the relevant chapter.

| | |
|---|---|
| DEHP | Diethyl hexyl phthalate (plasticizer) |
| DfR | Design for recycling |
| DfS | Design for sustainability |
| DMT | Dimethyl terephthalate |
| DSC | Differential scanning calorimetry |
| DSD | Duales System Deutschland – German collection system |
| DSP | Selective dissolution and precipitation |
| ECHA | European Chemicals Agency |
| ED | Endocrine disruptor |
| EEA | Eco efficiency analysis |
| EfW | Energy from Waste |
| EG | Ethylene glycol |
| EGMA | Ethylene–glycidyl methacrylate |
| EHS | Environment, health, safety |
| EHS&S | Environment, health, safety, and sustainability |
| ElektroG | German Electrical and Electronic Equipment Act |
| ELV | End-of-life vehicle |
| EPA | U.S. Environmental Protection Agency |
| EPC | Engineering, procurement, construction |
| EPDM | Ethylene–propylene–diene terpolymer |
| EPM | Poly(ethylene-co-propylene) |
| EPR | Extended producer responsibility |
| EPS | Expanded polystyrene |
| ETICS | External Thermal Insulation Composite System |
| EVA | Ethylene–vinyl acetal copolymer |
| EVOH | Ethylene–vinyl alcohol copolymer |
| FBP | Final boiling point of a distillation fraction |
| FBR | Fluid-bed or fluidized-bed reactor |
| FDA | US Food and Drug Administration |
| FEP | Freshwater eutrophication potential |
| FFF | Fused filament fabrication, a 3D printing technology |
| GewAbfV | German industrial waste ordinance |
| GHG | Greenhouse gas |
| GMA | Glycidyl methacrylate |
| GWP | Global warming potential |
| GPPS | General purpose polystyrene |
| Green Dot | German dual system of waste collection (“Grüner Punkt”) |
| HALS | Hindered amine light stabilizer (UV stabilization additives) |
| HBCDD | Hexabromocyclododecane (flame retardant) |
| HCFC | Hydrochlorofluorocarbon |
| HDPE | High-density polyethylene |

| | |
|---|---|
| HEMA | Hydroxyethyl methacrylate |
| HIPS | High-impact polystyrene |
| HSP | Hansen Solubility Parameter |
| HTW | High-temperature Winkler process |
| IBP | Initial boiling point for a distillation fraction |
| ISO | International Organization for Standardization |
| KrWG | Kreislaufwirtschaftsgesetz (German circular economy law) |
| LB | Liquid boards |
| LCA | Life cycle analysis |
| LCI | Life cycle inventory |
| LCIA | Life cycle impact analysis |
| LDPE | Low-density polyethylene |
| LLDPE | Linear low-density polyethylene |
| LWP | Lightweight packaging waste |
| LWP-SR | Lightweight packaging waste sorting residue |
| MA | Maleic anhydride |
| MERF | Material recovery facility or multi reuse facility |
| MFI | Melt flow index |
| MMA | Methyl methacrylate |
| MP | Mixed plastics |
| MRF | Multi reuse facility |
| MSW | Municipal solid waste |
| MSWI | Municipal solid waste incinerator |
| NIR | Near infrared technology (used for e.g. plastics sorting) |
| NGO | Non-governmental organization |
| ODP | Ozone depletion potential |
| OECD | Organization for Economic Co-operation and Development |
| OEFSR | Organization Environmental Footprint Sector Rules |
| OEM | Original equipment manufacturer |
| OPEX | Operational expenditure |
| PA | Polyamide |
| PAr | Polyarylate |
| PBAT | Poly(butylene adipate)-co-terephthalate |
| PBS | Polybutylene succinate |
| PBT | Persistent, bioaccumulative and toxic substances |
| PBT | Polybutylene terephthalate |
| PC | Polycarbonate |
| PCB | Paper and cardboard |
| PCB | Printed circuit boards |
| PCB | Polychlorinated biphenyl |
| PCR | Postconsumer recycling |

| | |
|---|---|
| PE | Polyethylene |
| PEF | Polyethylene furanoate |
| PEFCR | Product Environment Footprint Category Rules |
| PET | Polyethylene terephthalate |
| PHA | Polyhydroxyalkanoate |
| PHB | Polyhydroxybutyrate |
| PIC | Prior informed consent |
| PIR | Postindustrial recycling |
| PLA | Polylactic acid |
| PMMA | Poly(methyl methacrylate) |
| PO | Polyolefin |
| POM | Polyoxymethylene |
| POP | Persistent organic pollutant |
| PP | Polypropylene |
| PPE | Poly(2,6-dimethyl-1,4-phenylene ether) |
| PPO | Polyphenylene oxide, often synonymous with PPE |
| PPP | Polluter pays principle |
| PPWD | EU Packaging & Packaging Waste Directive |
| PRO | Producer responsibility organization |
| PS | Polystyrene |
| PVC | Polyvinyl chloride |
| PTFE | Polytetrafluoroethylene |
| PTT | Polytrimethylene terephthalate |
| PUR | Polyurethane |
| RDF | Refuse derived fuel (waste fraction) |
| R&D | Research and development |
| REACH | EU Registration, Evaluation, Authorization, Restriction of Chemicals |
| RED | Relative energy difference |
| RHW | Residual household waste |
| RPW | Residual plastics waste |
| RVM | Reversed vending machine |
| SAN | Styrene–acrylonitrile copolymer |
| SBC or SBS | Styrene–butadiene block copolymer |
| SCS | Styrenics Circular Economy |
| SDGs | UN Sustainable Development Goals |
| SEBS | Hydrogenated styrene–butadiene block copolymer |
| SF | Substitute fuels |
| SHVC | Substances of very high concern |
| SMA | Styrene-maleic anhydride copolymer |
| SMC | Sheet molding compound |
| SMMA | Styrene-methyl methacrylate copolymer |

| | |
|---|---|
| SPE | Society of Plastics Engineers |
| Sphera | Provider of Environmental, Social and Governance (ESG) performance and risk management software, with a focus on EHS&S |
| SPI | Sustainable Products Initiative |
| SR | Shredder residues |
| SRF | Solid recovered fuel |
| SSP | Solid state polycondensation |
| SVZ | Sekundärverwertungszentrum (secondary reutilization center) |
| TBS | Tracer based sorting |
| TEM | Transmission electron microscopy |
| TPA | Terephthalic acid |
| TPE | Thermoplastic elastomer |
| TRL | Technology readiness level |
| TÜV | Technischer Überwachungs-Verein (German Technical Inspection Association) |
| UVP | Unique value proposition |
| VerpackG | Verpackungsgesetz (German packaging act) |
| vPvB | Very persistent, very bioaccumulative substances |
| WEEE | Waste from electrical and electronic equipment |
| WFD | EU Waste Framework Directive |
| WTE | Waste-to-energy (incineration with energy recovery) |
| XPS | Extruded polystyrene |
| ZSVR | German Central Packaging Register |

# Contents

# PART A

## Fundamentals; Legislative, Economic, and Political Considerations; LCA

# 1

# Introduction

Norbert Nießner

The plastics story is a success story. Already the alchemists dreamt of creating new matter having special, exceptional properties. The area of synthetic polymers started with a secret recipe, developed by businessman and alchemist Bartholomäus Schobinger and disclosed to Benedictine monk Wolfgang Seidel in 1530 [1]. Schobinger treated cheese several times with boiling water, while he decanted the milky part and collected the thick slurry. The slurry was separated and could subsequently be cast into any shape. The new material was a substitute for natural materials like cattle horn.

In the 19th century, breakthrough inventions paved the way towards plastics. Some highlights:

- 1823: Charles Mackintosh fabricated the first waterproof raincoat based on natural rubber.
- 1835: Eduard Simon extracted styrene from the *Styrax* tree; it would become the building block for polystyrene in the late 1920s.
- 1839: Charles Goodyear invented the “vulcanization” (chemical cross-linking) of natural rubber with sulfur and founded the basis for the tire industry.
- 1846: Christian Friedrich Schönbein developed nitrocellulose by treating celluloses with sulfuric and nitric acid. A weakly nitrated cellulose recipe became the basis for *collodion*.
- 1856: Alexander Parkes invented cellulose polymers.
- 1870: John Wesley Hyatt invented *Celluloid*, based on nitrocellulose. Billiard balls made of this material could explode after collision.
- 1872: Johann Friedrich Wilhelm Adolf von Baeyer produced the first phenol-formaldehyde resin.

The first half of the 20th century paved the way for synthetic polymers becoming “mass polymers”:

- 1907: Leo Hendrik Baekeland optimized the process conditions of the phenol-formaldehyde condensation and created the first fully synthetic resin, *Bakelite*.
- 1911: Chemist Richard Escales created the German word *Kunststoffe* for synthetic matter.

- 1920: Hermann Staudinger founded the modern polymer science, being awarded with the first Nobel Prize for macromolecular chemistry in 1953.
- 1929: Hermann Mark received a patent on synthetic styrene, as basis for polystyrene (patented 1930).
- 1931: Otto Röhm developed synthetic glass from methyl methacrylate (Plexiglas®, first industrial production 1935).
- 1935: Wallace Hume Carothers invented polyamide-66 (nylon).
- 1936: First industrial polystyrene production at BASF, Germany.
- 1937: First polyethylene pilot plant at ICI, UK; Otto Bayer invented polyurethane; first industrial PVC production in Germany.
- 1947: DuPont developed the engineering plastic polyformaldehyde.
- 1949: Fritz Stastny invented expandable polystyrene (Styropor®).
- 1953: Karl Ziegler polymerized ethylene with his catalysts at ambient temperature and pressure.
- 1956: Giulio Natta polymerized propylene, based on Ziegler catalysts.

## 1.1 Industrial Aspects

Since then, synthetic polymers showed an unprecedented growth, as can be seen in Figure 1.1.

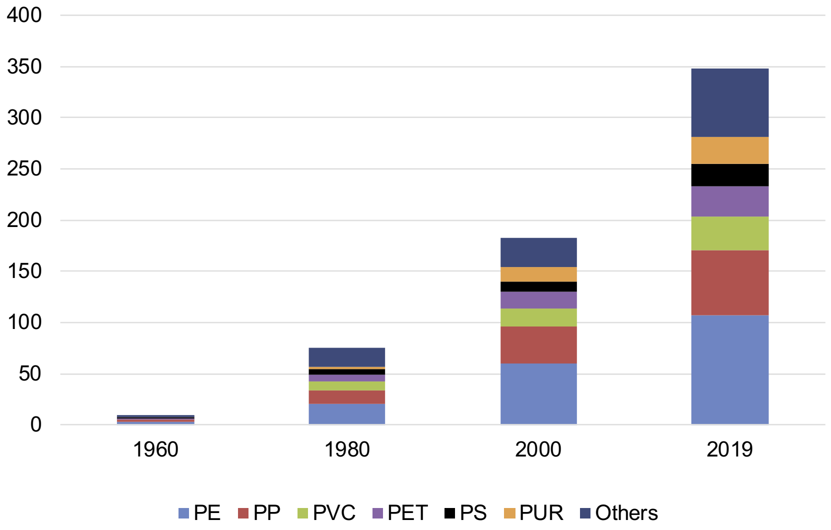

**Figure 1.1** Global annual primary plastics production in million t/a [2–4]

The driving force for these lightweight, artificial "plastics" was not only the substitution of heavier, traditional materials like wood, glass, or metal. The main motivation was the myriad of application developments that allow today's modern lifestyle. Examples are given below, with discussion of the possibilities for recycling these products.

- Housings for household goods and electronic equipment: typically, several plastics types are combined in one application. As with PET bottle recycling it is possible to sort out large parts made of a single material (such as refrigeration in-liner, made of polystyrene; or vacuum cleaner housing made of ABS or polypropylene, as shown in Figure 1.2) and to selectively recycle such materials. Mechanical recycling – potentially in combination with an "impact booster" to compensate for loss in impact resistance during thermal treatment in recycling processes – is the choice here.

**Figure 1.2** Refrigerator in-liner (left) and vacuum cleaner housing (right) as examples for plastics in household goods [3] (Picture source: INEOS Styrolution (left) and Obak/Shutterstock.com (right))

- Medical applications, from infusion sets to therapeutic devices: such products are often incinerated, for obvious reasons. However, a potential recycling pathway could be thermal depolymerization, which works especially well with polymers having a low ceiling temperature $T_c$ – such as PMMA or polystyrene, see Figure 1.3. As many parts of infusion sets (drip chamber, clamp) are made of polystyrene or related materials, depolymerization could become a promising recycling pathway, once fully commercially established.

**Figure 1.3** Medical applications: drip chamber from infusion sets (left), transparent housings and connectors (middle), and lab ware for diagnostics (right) [3] (Picture source: INEOS Styrolution (left and middle) and Shutterstock.com (148514897, right))

- High-strength fiber composites for lightweight aircraft and automotive applications, e. g. wind shields for trucks or carbon-reinforced automotive body panels, see Figure 1.4: While sorting and recycling of automotive parts has a long and successful history, products based on glass fiber or carbon fiber reinforced composites can in many cases only be downcycled. Especially in the case of non-melting, thermoset (duroplastic) matrix polymers, the parts are crushed, and long fibers are chopped into short fibers and hence lose their value in mechanical reinforcement. The emerging “organosheets” (thermoplastic based fiber composites) might have an advantage here, because at elevated temperatures, the polymer matrix melts, allowing for a separation of matrix and fibers. For thermoset parts, solvolysis pathways are under development, cleaving the otherwise unprocessable matrix back into its monomers, which can be recovered, purified, and reused.

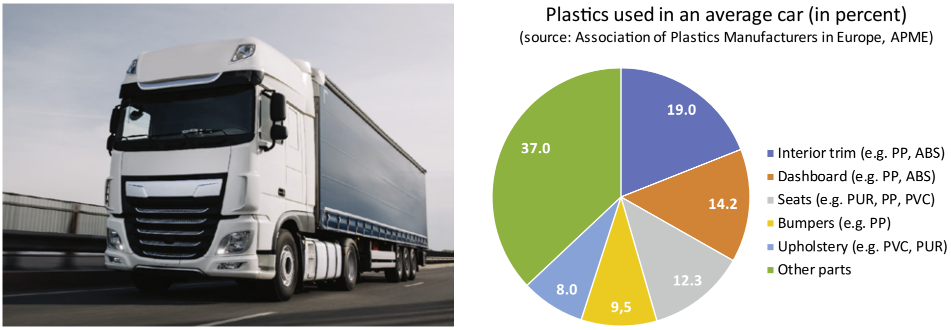

**Figure 1.4** Truck plastics parts are partly made from thermoplastic polymers and partly from thermoset (often fiber reinforced) plastics to guarantee high strength at lowest possible weight. Approx. 7% of the global plastics consumption is used for the automotive and two-wheeler industry. A large portion are exterior trim applications [3] (Picture source: BoJack/Shutterstock.com (left))

- Synthetic fibers, securing supply of textiles way beyond the availabilities of natural fibers
- Synthetic rubber and artificial leather
- Toy building bricks
- Lightweight, transparent, and safe plastic bottles: PET bottles are a great example of a commercially and ecologically feasible substitution of traditional materials (here: glass, see Figure 1.5). Due to its excellent combination of impact resistance, thermal and mechanical stability, transparency, low weight, and organoleptically neutral behavior, PET is the choice for packaging mineral water, soft drinks, etc., safely and economically, while providing several established as well as new ways for recycling. The classical recycling path comprises the introduction of cleaned, shredded bottle grade flakes into new PET, prior to manufac-

turing of the bottles in a stretch-blow process. The fact that PET – as an important member of the class of polycondensates – is prone to hydrolytic degradation is addressed by subjecting post-consumer PET bottle granules to a post-condensation process to increase the molecular weight. Finally, polycondensates like PET can be cleaved into their building blocks and hence be subjected to depolymerization recycling.

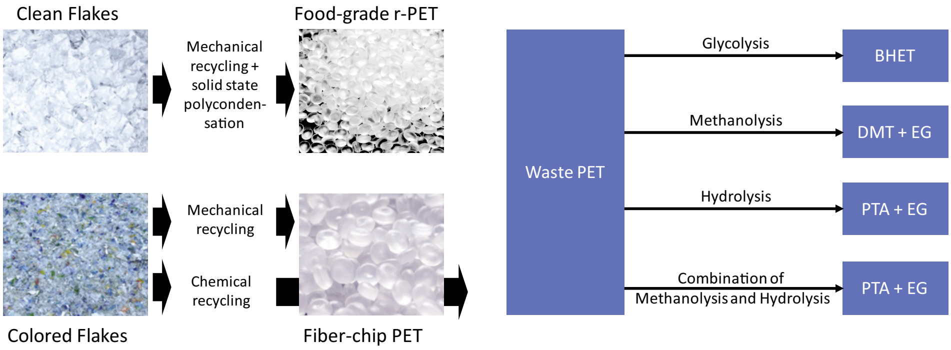

**Figure 1.5** Schematic representation of PET bottle recycling: mechanical recycling (left), depolymerization (solvolysis) (right) [3] (Picture source: Nutthpol Kandaj/StanislauV/RecycleMan/Afanasiev Andrii/Shutterstock.com (left) and INEOS (right))

- Multilayer packaging: transparent and tough, barrier against oxygen and water, thermoformable, and lightweight. Multilayer packaging allows safe storage of food (see Figure 1.6), and represents the best possible combination of weight and packaging efficiency (shelf life). However, it presents a recycling challenge: a delamination of layers, followed by mechanical recycling by product class is not possible. However, feedstock recycling (thermal decomposition and feed-back of small molecules into existing chemistry infrastructure) is an option.

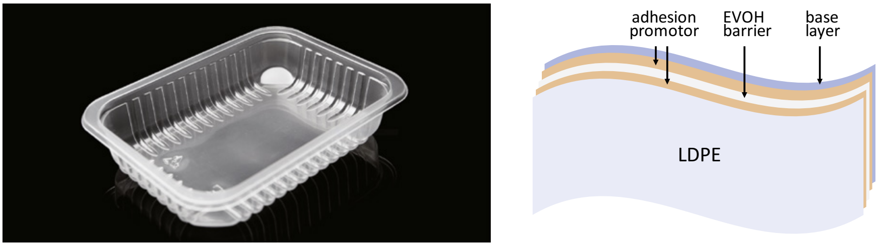

**Figure 1.6** Multilayer packaging: transparent and tough, barrier against oxygen and water, thermoformable, and lightweight. Allows safe storage of food [5] (Picture source: nikkytok/Shutterstock-com (left) and INEOS Styrolution (right))

In line with those application developments went the development of new and/or improved processing technologies, such as the following:

- Blown film and sheet extrusion (Figure 1.7)

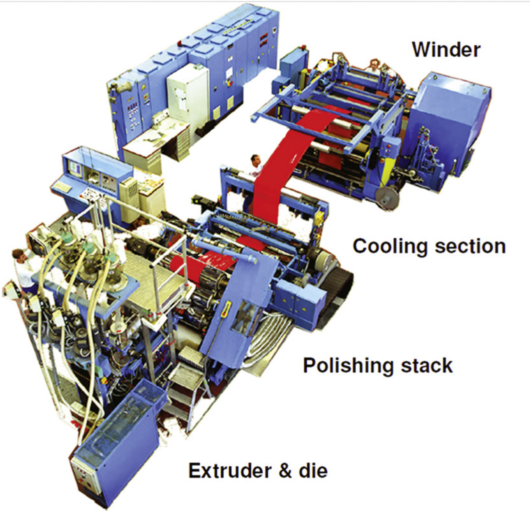

**Figure 1.7**
Sheet extrusion of polymers [3] (courtesy of Neue Materialien Bayreuth GmbH)

- Blow molding of hollow plastic parts
- Fiber composite manufacturing for large, lightweight automotive parts
- Advanced injection molding technologies, allowing addition of gases and co-injection of different thermoplastics (Figure 1.8)

**Figure 1.8** Advanced injection molding machine, allowing addition of gases and co-injection of different thermoplastics (courtesy of Neue Materialien Bayreuth GmbH)

Hence, the development of new plastics created a flourishing industry continuously striving for improvement, efficiency, and high-quality in the processing of plastics, which in itself spurred the development of performance-optimized materials.

To round up the plastics story, we have to take into consideration that even modern electronics would not have been possible without polymer-based photolithography, and protection of ships, bridges, and other steel construction would not be possible without high-performance coatings, based on polymer formulations. The construction of our tallest buildings worldwide would not be possible without polymer-based additives allowing high flow and pumping of concrete over several hundreds of meters in height.

Taking all this together, polymers and plastics are those materials that determine more than anything else our modern lifestyle with increasing health, wealth, and wellbeing even for the poor in this world. *"Plastics have made it possible for us to push the limits and go further, faster and safer than we have dared to go before"* [6].

## 1.2 Plastics Pollution

Parallel to the unique success story of plastics, focus was laid largely on "linear economics". But since the 1970s, a major revolution, thinking in terms of "circular economy" and reuse of plastics, can be observed. Unfortunately, globally still only a limited amount of end-of-life plastic products are recovered and recycled or used for thermal recovery. The remaining part of the plastic waste ends up in landfills, where it can be carried away by winds, or even in rivers or the ocean. Together with carelessly discharged plastic (e. g., packaging and construction materials), plastic waste enters the environment from year to year. Since plastic degrades slowly, its accumulation in marine, freshwater, and terrestrial ecosystems is of increasing scientific and public concern.

**Figure 1.9**
Accumulation of (mainly) plastic garbage on the ocean (Picture source: Iurii Stepanov/Shutterstock.com)

Today, between 4 and 12 Mt/a of plastics enters the ocean (Figure 1.9 and Figure 1.10).

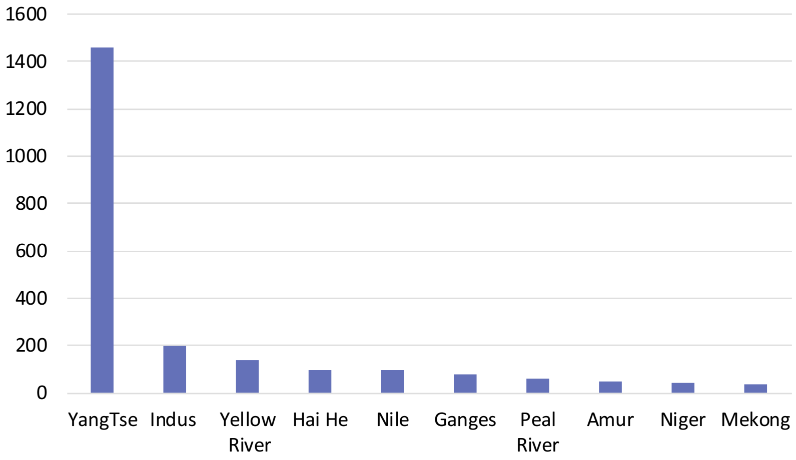

**Figure 1.10** Amount of plastics waste (in kt/a) entering the ocean from major rivers [7]

The global plastic pollution and ubiquitous distribution came along with the observation that plastic in the environment does in general not tend to vanish by UV or other types of degradation. Rather than degrading, plastic mostly disintegrates into smaller particles.

More specifically, a combination of mechanical abrasion, UV radiation, and (micro) biological degradation in the environment causes the formation of tiny plastic fragments/particles, which are termed “secondary microplastic”. Fibers from synthetic clothes, which are released by washing and enter aquatic ecosystems via sewage treatment plants, can also be assigned to “secondary microplastic”. Apart from these, the so-called “primary microplastic” is designed and produced on purpose: such microparticles are broadly applied, for example in industrial cleaners and personal care products (toothpaste, facial and body scrubs, etc.). Virgin plastic pellets, which serve as precursor for manufactured plastic products, are also classed as “primary microplastic” [8]. Such particles can accumulate in organisms and hence become part of the food chain.

As a consequence, do we need to phase out and avoid plastics in future? And what are the materials that (re)substitute plastics? Are bio-plastics the solution to the waste problem? Prof. Gerrit Luinstra, chair of technical polymers at Hamburg University, recently mentioned in an interview: *“Unfortunately it is often much easier to change materials, rather than human behavior. Plastics are basically great materials. We should treat them as if they were gold”* [9].

In a recent “TED Talk”, Prof. Kim Ragaert explained it like this: *“Imagine, someone parked a car in the middle of a highway. Who is to blame: the car or the idiot who left the car there?”* [10].

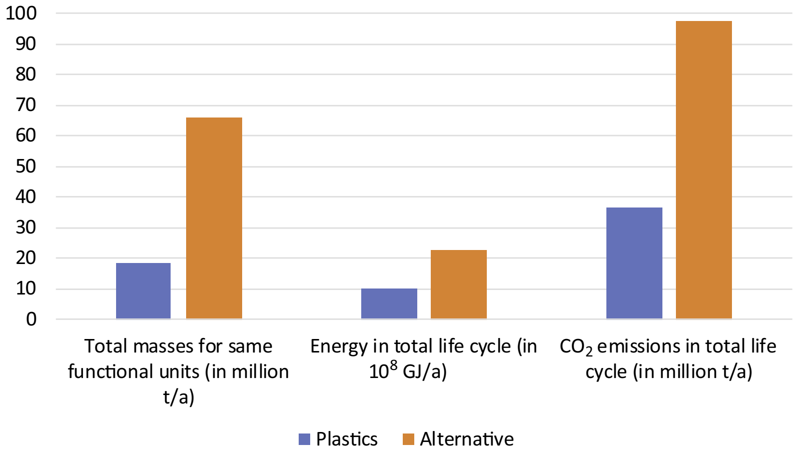

**Figure 1.11** What is the environmental impact of switching parts of the plastic production to alternative materials [10]

In the same event, Prof. Ragaert (Maastricht University – Chair of Circular Plastics) outlined the consequence of re-substitution of plastics by traditional materials – knowing however that many of today’s applications exist only because polymers as unique building blocks make them possible. The result is overwhelming (Figure 1.11): a multiple of energy will be required, and triple the $CO_2$ emissions would have to be accepted if we substitute all plastics with metal, glass, wood, etc. This scenario impressively shows what we would have to expect with a plastics ban. Therefore – and especially in the light of finding low $CO_2$ solutions for our planet – we need to make use of the energy and $CO_2$ savings potential offered by modern plastics. And – at the same time – we need to bundle all our forces to treat plastic parts at the end of their lives not as waste, but as precious resources for the next cycle. Only then we will master the challenge of reducing greenhouse gas emissions while not compromising our modern lifestyle.

## 1.3 Plastics Pollution: Bio Solution?

At this stage we briefly want to enter the discussion on bio-based or bio-degradable plastics. While in some people's minds "bio-plastics" will overcome the major challenges created by plastics, others believe that their $CO_2$ footprint is not always as favorable as it seems at first glance, and, except for the routes to produce such plastics from second- and third-generation feedstock [11], there might as well be competition with food in growing plants as the source for such plastics. Figure 1.12 and Figure 1.13 show two important types of bioplastics and outline their formation, properties, and major applications.

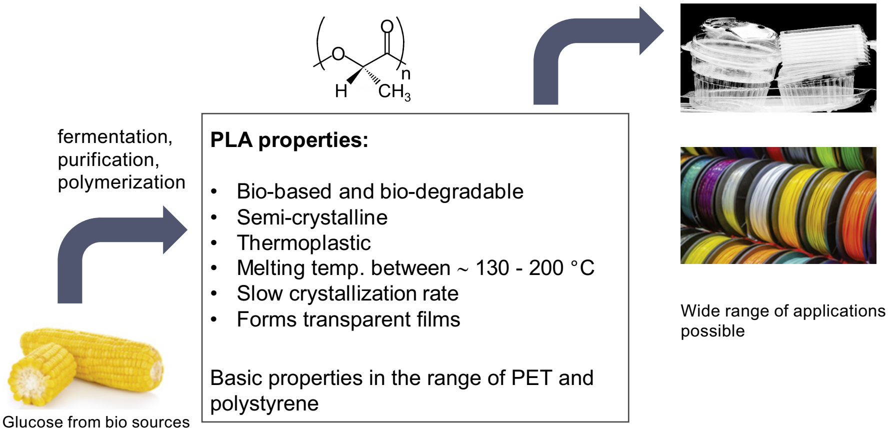

**Figure 1.12** Formation, properties, and applications of PLA (polylactic acid) [3] (Picture source: rakasina/Shutterstock.com (left), Konektus Photo/Shutterstock.com (top right), MarinaGrigorivna/Shutterstock.com (mid right))

Bio-degradable plastics are a special case and qualify for those applications with a more or less controlled shelf life, temperature, and/or residence time in the environment. Such bio-degradable plastics typically require a controlled, humid, and oxygen-enriched environment at elevated temperatures over several days to degrade [12]. These conditions, however, can often not be realized in today's day-to-day infrastructure. For this reason, although bio-degradable plastics are an important part of today's plastic product portfolio, they cannot be regarded as the universal solution against plastic pollution.

Degradation of conventional plastics (those with only C–C bonds in the main chain) has been reported [13]. This field of research is comparably young, and gives hope for new solutions to today's waste problems. However, a holistic insight into all major degradation products, their accumulation in the environment, and the effect, for example, on microorganisms is still pending.

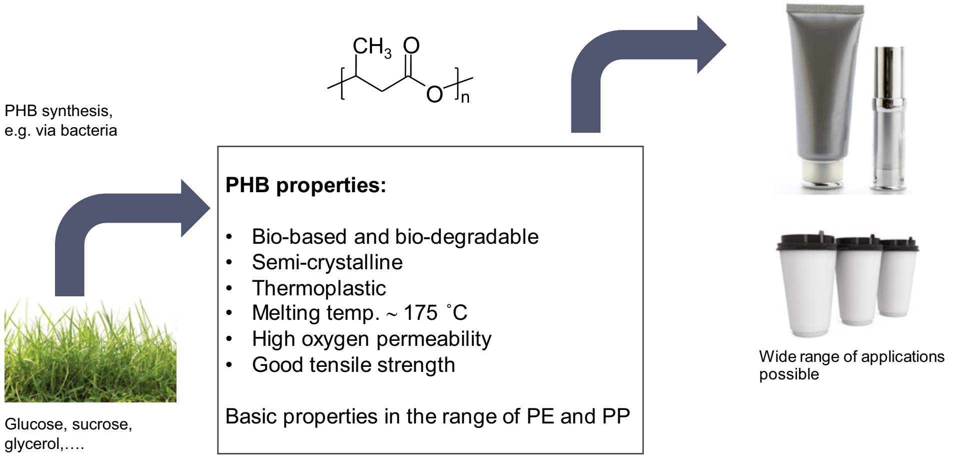

**Figure 1.13** Formation, properties, and applications of PHB (polyhydroxybutyrate) [3] (Picture source: Pornsawan Baipakdee/Shutterstock.com (left), Lifestyle Travel Photo/Shutterstock.com (top right), CG_dmitriy/Shutterstock.com (mid right))

Another strong trend is the use the existing petrochemical infrastructure with refineries and steam crackers to produce monomers. By the example of “styrenic polymers”, the process is explained as follows (Figure 1.14):

- Everything starts with the biomass source. Food crops and/or products from food crops like vegetable oil are obvious sources. However, the cultivation of such crops for biopolymer production competes with food production. Therefore research groups are developing concepts to start with non-food bio sources (second generation) and even crops from specially engineered plants, like algae reactors (third generation).
- Classical monomers like ethylene, propylene, styrene, acrylonitrile, or butadiene can be produced by using plant biomass as starting material and eliminating oxygen during chemical conversion to the desired monomers. Such multi-step conversions often consume high amounts of energy and/or result in rather moderate yields.
- Alternatively, bio-based monomers can be produced using existing chemistry infrastructure, requiring to convert bio-mass (e. g., palm oil) into hydrocarbons by chemical treatment (e. g., hydrogenation).
- Due to the conversion of carbohydrates (general formula $C_nH_{2n}O_n$) to mostly hydrocarbons, a large weight-% of the bio-based mass is lost.
- Such processes are currently typically available in a pilot scale or small commercial scale only.

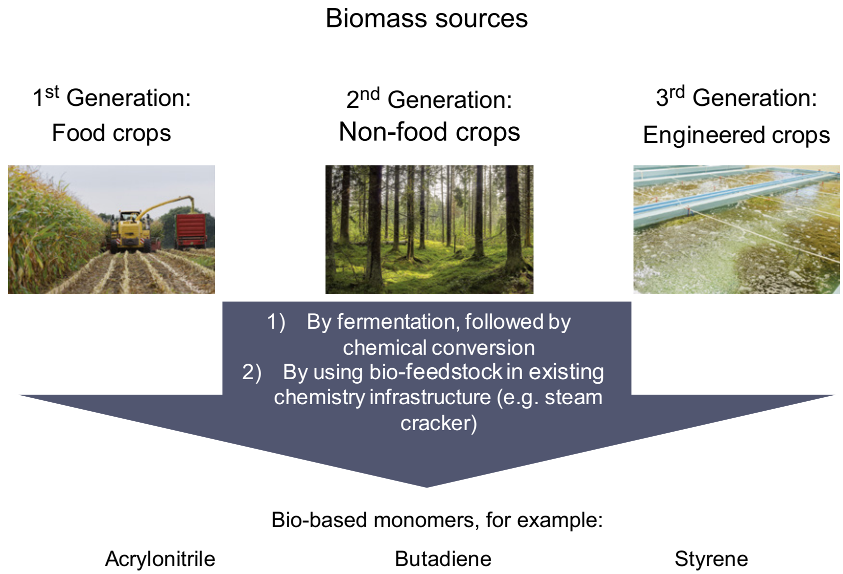

**Figure 1.14** Current status of bio-based monomers for the example of ABS (acrylonitrile-butadiene-styrene) [3] (Picture source: Claudia Harms-Warlies/Shutterstock.com (left), Lillac/Shutterstock.com (mid), Pataporn Kuanui/Shutterstock.com (right))

As bio-based polymers are made of fresh biomass, common understanding is that such polymers show the same high $^{14}C$ isotope content as the biomass source. Hence, some polymer producers demonstrate the bio content of their products via $^{14}C$ measurement. For bio-polymers produced “on purpose”, such as polylactic acid (PLA), this concept works. However for the sake of fast implementation of biomass-based feedstock in existing commodity plastics, it is necessary to co-feed such bio-based feedstock, together with fossil based feedstock, using the large, existing chemical infrastructure. As the supply of bio-based feedstock is still not sufficient to cover the demand of traditional polymers, it is economically not yet always feasible to run such large scale polymerization reactions in existing plants based on 100% bio-feedstock.

A probably more feasible and smarter alternative to the direct polymerization of bio monomers is the “mass balance concept” (Figure 1.15): Here, the large industrial equipment is used for making “bio-attributed” polymers. Both the fossil-based feedstock and the bio-based feedstock (usually available in smaller amounts) are fed into a steam cracker, producing naphtha, which is subsequently converted into monomers. By a certified process, the bio-molecules entering the steam cracker are – by an accounting process – attributed to an equivalent amount of downstream monomers, and later on to the respective polymers. It is not guaranteed that you can find those bio-molecules in your polymer by $^{14}C$ isotope counting. But it is certified that an equivalent amount of bio-based monomer/polymer has been produced.

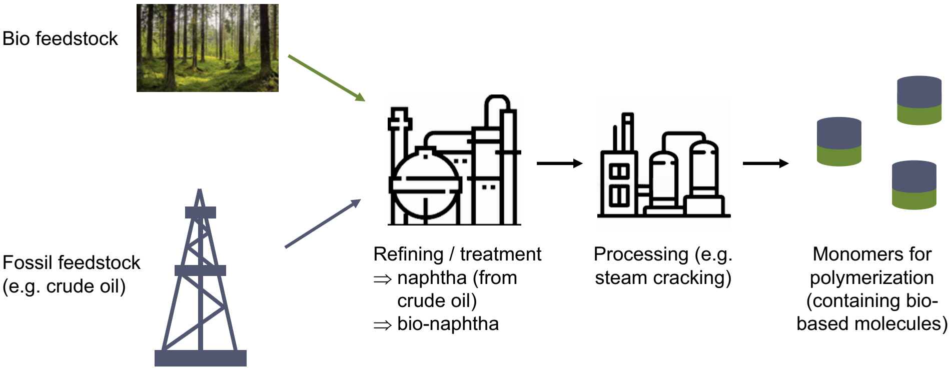

**Figure 1.15** Schematic description of bio-based monomers for existing polymers: defined and controlled content of bio-based product in final product [3] (Picture source: Lillac/Shutterstock.com (top left))

The benefits of such a process are:

- Use of existing infrastructure
- No "green-washing": the amount of monomer/polymer that has been produced based on bio-feedstock input to the steam cracker is certified.
- Especially in these times of establishing a circular economy and moving away from a linear economy, the availability of adequate bio-feedstock does not yet reach the availability of crude oil based feedstock. Nevertheless, we can in principle use any bio-based feedstock quantity to produce bio-attributed polymer in the corresponding quantity.

A schematic depiction of the process is given in Figure 1.16.

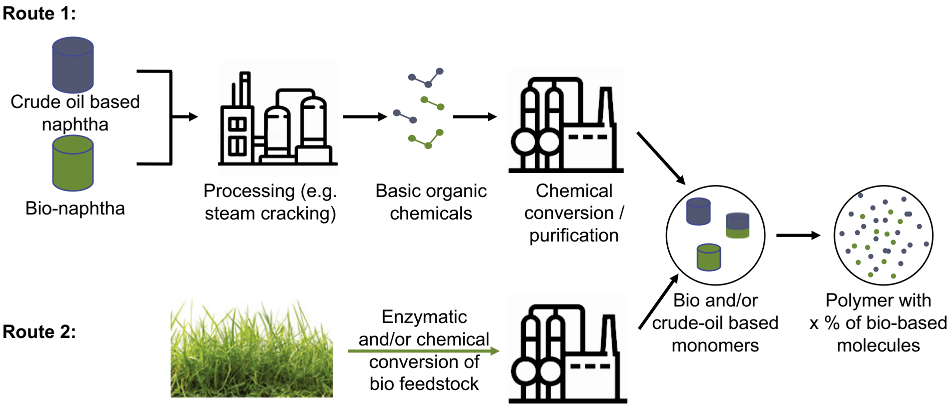

**Figure 1.16** Schematic description of bio-mass balance: fluctuating and uncertain content of bio-based monomers in final product; therefore, allocation of bio-molecules per certificate [3] (Picture source: Pornsawan Baipakdee/Shutterstock.com (bottom left))

Bringing all aspects together, we have a set of measures that can help us to reduce the environmental impact of plastics. However, along with strengths and opportunities, every measure also shows certain weaknesses and threats, as outlined in Table 1.1 to Table 1.5 (distinguishing between "weaknesses" and "threats" is difficult, and therefore both are placed in the same column).

**Table 1.1** Direct Substitution of Fossil-Based Raw Materials by Bio-Based Building Blocks, Examples: Butadiene from Bioethanol, Acrylonitrile by Fermentation of Biomass (via Glycerol)

| Strengths | Weaknesses/Threats | Opportunities |
|---|---|---|
| ▪ Drop-in solution, same properties of the resulting polymers<br>▪ No need to change polymerization technology | ▪ Often many reaction steps, sometimes low yield<br>▪ Processes mostly still under development/ at lab or pilot scale<br>▪ High cost compared to established fossil based solutions<br>▪ It is questionable whether it is economically and ecologically meaningful to eliminate approx. 60–70 wt% of a bio-based molecule in order to convert it into a "classical" monomer with C=C bond | ▪ Independence of fossil feedstock<br>▪ "Green" source |

**Table 1.2** Bio Attribution: Bio-Based Feedstock Is Used in an Upstream Process Part (e. g., in the Production of Naphtha), Resulting in Monomers and Polymers Containing a Defined Amount of Bio-Based Carbon. The Mass-Balance of this Procedure is Certified by Independent Institutes

| Strengths | Weaknesses/Threats | Opportunities |
|---|---|---|
| ▪ Drop-in solution, same properties of the resulting polymers<br>▪ No need to change polymerization technology | ▪ Might require special cracker set-up<br>▪ Requires bio-feedstock treatment to meet cracker-feed specifications"<br>▪ Possibly feedstock competition to food or energy crops | ▪ Independence of fossil feedstock<br>▪ "Green" solution |

**Table 1.3** Dedicated Bio-Based Polymers

| Polymer | Strengths | Weaknesses/ Threats | Opportunities |
|---|---|---|---|
| PHA (polyhydroxyalkanoate) | ▪ Broad feedstock base<br>▪ Low oxygen and water permeability | ▪ High investment for commercial plants | ▪ Biodegradable under controlled conditions |
| PHB (polyhydroxybutyrate) | ▪ Feedstock can be biomass waste<br>▪ Good mechanical & thermal properties | ▪ High investment for commercial plants | ▪ Biodegradable under controlled conditions |

| Polymer | Strengths | Weaknesses/ Threats | Opportunities |
|---|---|---|---|
| PLA<br>(polylactic acid) | - Already established | - High investment for commercial plants<br>- Partly high injection molding cycle times | - Biodegradable under controlled conditions |
| PBAT<br>(poly(butylene adipate)-co-terephthalate) | - High toughness | | - Biodegradable under controlled conditions |
| PEF<br>(polyethylene furanoate) | - Good barrier, thermal & mechanical properties<br>- Made by chemical reaction, not microbiotic | - High investment for commercial plants, multi-step process | - Partly improved properties compared to PET |
| PET<br>(polyethylene terephthalate) | - Ethylene glycol can be made from bio sources | - TPA unit based on bio sources still challenging | - "Drop-in" for existing PET applications |
| APC<br>(aliphatic polycarbonates) | - Very good optical and mechanical properties | - Currently only partially bio-based | - Already used in automotive applications |
| PTT<br>(polytrimethylene terephthalate) | - Better tensile strength, flexural strength, and stiffness than PBT | - TPA unit based on bio sources still challenging | |
| PA | - Sustainable "bio" PA grades often based on castor or palm oil | - Multi-step process | - Drop-in solution for many applications |
| PBS<br>(polybutylene succinate) | - Mechanical properties between PE and PP and can be improved by blending | - High investment for commercial plants | - Biodegradable under controlled conditions |

**Table 1.4** Carbon Capture and Utilization: $CO_2$ is Collected at Stationary Sources (such as Power Plants, Municipal Waste Incineration or as By-Product in Chemical Reactions) and/or Converted into Platform Chemicals

| Strengths | Weaknesses/Threats | Opportunities |
|---|---|---|
| - Removal of $CO_2$, positive effect on global warming | - High energy demand; energy should come from renewable sources<br>- Chemical conversion: "green" hydrogen required, produced with renewable energy<br>- Processes and technology still under development<br>- Uncontrolled release of $CO_2$ needs to be strictly avoided | - No competition to food; uses a "waste" gas<br>- Positive examples exist: e. g. "Carbon4PUR", Covestro<br>- Positive examples: lab production of industrially relevant intermediates via electrochemistry of $CO_2$ |

**Table 1.5** Lignin-to-Chemicals: Conversion of the Phenolic Natural Polymer Lignin, Which is the Second Most Unused Biomass Waste, into Aromatic Chemicals

| Strengths | Weaknesses/Threats | Opportunities |
|---|---|---|
| ▪ Sustainable solution (reducing GHG emissions)<br>▪ Approx. 9 million t lignin waste from industry available per year | ▪ Pretreatment necessary<br>▪ Pyrolysis can lead to high coke/char amount<br>▪ Low yield of aromatic oil compared to other oils<br>▪ Contamination from salts, carbohydrates, particulates, volatiles possible | ▪ Practically unlimited bio resources |

The mentioned options to integrate bio-based content or $CO_2$ into plastics are versatile and quite different in their characteristics. This makes it difficult to compare the specific energy consumption, $CO_2$ savings, and other environmental impacts for all options.

A generally accepted tool to compare environmental impacts is the “life cycle analysis” (“LCA”, see also Chapter 6 of this book). While LCA comparison of related processes (e. g., various recycling methods) are already complex enough, we would therefore suggest to assess the options to integrate bio-based content or $CO_2$ qualitatively:

- Direct substitution of fossil-based raw materials by bio-based building blocks (Table 1.1) seems to be the easiest way to save $CO_2$ emissions. However, the direct routes often require a multistep synthesis and yield/energy requirements counterbalance the positive effect of $CO_2$ reduction. Examples for bio-based routes to formerly fossil-based raw materials:
  - *Ethylene* can be obtained by fermentation of e. g. sugarcane and separation of the resulting bio ethanol, followed by dehydration [14].
  - *Terephthalic acid* (used as comonomer in PET) can be produced e. g. from the biomass-derived furfural. Furfural can be oxidized and dehydrated into maleic anhydride, which reacts in a Diels-Alder reaction with furan. The dehydration of that Diels-Alder (DA) adduct results in the formation of terephthalic acid [15].
  - *Butadiene* can be produced by dehydrogenation of ethanol to acetaldehyde, followed by aldol condensation and dehydration in a one-pot process over a $MgO\text{-}SiO_2$ catalyst (Lebedew process) with up to 70% yield [16]. A different pathway leads from ethanol over butanediol to butadiene via dehydration [17].
  - *Styrene* can be obtained via pyrolysis of biomass to a mixture of benzene, toluene, and xylene (BTX) and subsequent reaction of benzene with ethylene to form styrene [17]. One biotechnological route is the deamination of L-phenylalanine to trans-cinnamic acid by Phenylalanine Ammonia Lyase (PAL), an enzyme present in yeast *Rhodotorula glutinis* and in *E. coli* [18].

  - *Acrylonitrile* (e.g., used to produce SAN and ABS) can be produced via several routes, for example: 1) by oxidative decarboxylation of glutamic acid (chemical or biotechnological route), followed by a decarbonylation-elimination step, 2) by oxidation of a mixture of glycerol, ammonia, and air, and further conversion into acrylonitrile in a multistep reaction [19].

Except the ethylene formation from bio-ethanol, most of these reactions have not yet reached fully commercial (world) scale, and hence bio-based “classical” monomers are still under broad investigation.

- The use of bio-naphtha (Table 1.2) in a bio-attribution process seems to be a most straightforward method to save $CO_2$ emissions. Such a process is mainly based on the existing (modified) petrochemical infrastructure. Together with best suitable recycling methods, this combination of measures would be an efficient start of a true circular economy. Note: today’s petrochemical infrastructure is so large that it cannot be fully operated based on bio-feedstock. Hence the products (e.g., monomers for plastics) would be based on a mix of fossil and bio-based feedstock, and such bio-based molecules can then only be allocated to the corresponding amount of products in a certified process [20].
- The use of bio-based plastics as substitute for existing plastics is an alternative that is most easily understood by consumers as a sustainability measure (Table 1.3). The strength of this route is the direct allocation of bio-molecules to plastics [21] and the possibility to measure the bio-based content via the radio carbon ($^{14}C$ isotope) method. Nevertheless this approach often is in competition with food, at least as long as the feedstock materials are the commonly used crops, sugarcane, etc. It is a frequent misperception that bio-based plastics are always bio-degradable too. And if they are, the degradation process often requires quite optimal conditions to be completed within weeks or months, such as elevated temperature and air supply, available only at selected industrial facilities but not in the typical landfill site or even residential gardens. Last but not least, also bio-plastics should be subject to recycling, because with degradation, the material will be lost for the production of new polymers.
- Carbon capture and utilization (CCU, Table 1.4) measures deal with physical “lock-down” or chemical conversion of $CO_2$ in order to reduce the man-made climate change. Examples are storage of large amounts of $CO_2$ in subterranean caverns, and conversion of $CO_2$ into insoluble carbonates (“CarbFix”, [22]) or other chemicals. While a safe storage of large amounts of $CO_2$ poses a specific challenge, the conversion to chemicals is a proven path forward (examples given in [23]). As $CO_2$ is a “low energy” molecule, it requires high energy reaction partners (plus, potentially, catalysts) to convert this greenhouse gas into chemicals otherwise being produced based on fossil feedstock. Recently, the electrocatalytic reduction of carbon dioxide, powered by renewable electricity, to produce valuable feedstocks has been reported [24]. Such feedstocks could act as a $CO_2$ sink in converting them into plastics.

- By converting $CO_2$ into plant biomass and $O_2$, nature has successfully done this job already for millions of years. Therefore, forestation projects are a meaningful way to capture $CO_2$ sustainably, but as a self-regulating forest takes many decades to grow, it is a rather slow process.
- The “lignin-to-chemicals” route is highly interesting, as the starting material is readily available (Table 1.5). Whether or not the many different possible reaction products of lignin in a “bio refinery” will establish themselves as alternative to the traditional, crude oil based petrochemicals remains to be seen [25].

## 1.4 Recycling Methods: Closing the Loop

A circular plastics economy is not possible without recycling. Mechanical recycling of post-industrial and also post-consumer plastics has been practiced for many years now. While post-industrial thermoplastics are mostly reprocessed without property losses, mechanical recycling of post-consumer plastic waste often ended in “downcycling”. Mixed waste or contamination of the input resulted in properties inferior to virgin product properties. Examples:

- Mixed plastics to flower pots
- Bottle PET to fiber PET for clothing
- Materials formerly used for food packaging are reused in non-food applications like electronics housings

While there is nothing wrong with reuse of material in less demanding applications, a true circular solution however requires serving the high quality markets (such as food packaging or healthcare applications) with recycled material too. Especially in the light of demanding applications, advanced chemical recycling technologies were developed, such as the de-polymerization of PET, polystyrene, or PMMA, aiming to recover the respective monomer, which is re-polymerized to plastics with the same purity range as the original polymer, allowing them to be used for the same applications.

Recently, mechanical recycling methods experienced significant progress to achieving high purity plastics as well. The “super sorting” of post-consumer polystyrene waste (“supercleaning” technology of machine manufacturer Gneuss), followed by a thorough degassing step, is able to provide very clean polystyrene, suitable for food packaging applications. In cooperation with the Fraunhofer-Institut für Verfahrenstechnik und Verpackung IVV, SCS (Styrenic Circular Solutions) performed so-called challenge tests, which confirmed the ability of this new mechanical recycling technology to remove waste-stream induced impurities from polystyrene. The challenge test revealed the very good cleaning efficiency of the technology used, leading to excellent purity levels of the r-PS. This result is supported by the intrinsic properties of polystyrene being a low diffusion polymer, which prevents waste impurities entering into or migrate through the polymer matrix. The resulting quality of the r-PS provides producers of packaging for the food industry with utmost flexibility, as it can be used in their existing industrial production processes such as extrusion and thermoforming. Members of SCS delivered the proof of concept that mechanically recycled polystyrene can serve as a drop-in solution in form, fill, and seal (FFS) production lines. Multiple variants for packaging are possible: single layer, co-extrusion of the r-PS with virgin polystyrene, or use of the recyclate as middle layer between virgin polystyrene (A-B-A) [26]. The test results enable the first application for an opinion of the European Food Safety Authority (EFSA) on the use of recycled polystyrene (r-PS) as food contact material [26].

Additionally, dissolution technologies have developed during the past 30 years into a high quality and moderate energy consuming alternative to mechanical recycling. Several examples are known, like Polystyvert in Canada [27], Foam Cycle in the USA [28] or Fraunhofer in Germany [29], with the CreaSolv® process being one of the most prominent ones. This process, developed by Andreas Mäurer and Martin Schlummer of Fraunhofer-Institut Verfahrenstechnik und Verpackung IVV in Freising, Germany, uses the specific solubility of polymers in solvents and solvent combinations in order to separate dedicated plastic materials from a "mono" plastic application, from blends, or from coextrusion layer food packaging. Re-precipitation and work-up results in a thoroughly purified polymer. Dissolution is especially suitable for foam applications, such as XPS or EPS, used in clam shells, (food packaging) fish boxes, but also insulation for building and construction [30].

Similar to the pros and cons of the various routes of incorporating bio-based content into polymers and other chemicals, also recycling pathways have different strengths and weaknesses, as outlined in Table 1.6 to Table 1.8.

**Table 1.6** De-Polymerization Examples: Polystyrene or PMMA Cleavage Back into Their Monomers; Hydrolytic Degradation ("Solvolysis") of PET into Its Precursors

| Strengths | Weaknesses/Threats | Opportunities |
|---|---|---|
| ▪ Monomers are generated by cleavage of the polymer chain<br>▪ After purification and re-polymerization: basically same quality as "virgin" type polymer | ▪ Some sorting and conditioning of the post-consumer waste required<br>▪ Purification step of monomers required<br>▪ Scale is lower than world-scale production of monomers from crude oil | ▪ UVP for PS, PMMA due to their low $T_c$ (ceiling temperature)<br>▪ Various reactor types possible |

**Table 1.7** Mechanical Recycling

| Strengths | Weaknesses/Threats | Opportunities |
|---|---|---|
| - Cost-effective<br>- Established solution for industrial waste/off-spec. material<br>- Not much energy required | - No removal of contaminants like flame retardants<br>- Quality, lot-to-lot inconsistencies<br>- Material degradation possible after frequent cycles | - Food quality possible for polystyrene and PET in case of well sorted, washed and pure waste |

**Table 1.8** Dissolution Technology: A Post-Consumer Waste Is Subjected to Treatment with a Defined/Adapted Solvent. The Respective Polymer Is Selectively Dissolved, Re-Precipitated, and Recovered

| Strengths | Weaknesses/Threats | Opportunities |
|---|---|---|
| - No disintegration of the polymer<br>- Moderate energy consumption due to relatively moderate temperature | - By-products can be significantly reduced, but mostly not completely removed<br>- Scale is lower than world-scale production of polymers from crude oil | - Very selective for defined plastics |

In contrast to nature, technical solutions will probably never work with 100% yield and therefore not allow literally endless recycling circles, so process losses have to be replaced by new material. Even so, above mentioned recycling processes typically show a significant lower environmental impact than the production and linear use of plastics, while contributing to reducing litter at the same time.

## 1.5 Summary

Plastics offered and still offer an unprecedented step-up in quality of life. Their beneficial effects range from reduction of food waste by extension of shelf life, affordable healthcare measures through mass production of diagnostics or infusion kits, significant $CO_2$ savings through lightweight applications in automotive and aircraft up to a wide range of electronic gadgets in lightweight yet stiff and tough protective housings. A replacement or even no-plastics strategy would not only affect lifestyle, but also increase the emission of greenhouse gases like $CO_2$ significantly.

At the same time it is clear that environmental pollution by plastic parts needs to be kept in check and hence must not continue as it has done until now. While recovery of precious metals – even from landfills – is already in place in many parts of the world, it is about time to treat plastics not as waste anymore, but as precious raw materials source. Plastics are not the problem, but rather insufficient collection schemes and recycling initiatives.

This book is more than a compilation of state-of-the-art recycling technologies: it starts with the fundamental understanding of plastics structure/property relations, deep-dives into economic, legal and political boundary conditions, and explains methods and results of life cycle analyses in order to identify the best recycling solutions for our environment. The in-depth look into the complete value chain – from collection, sorting, cleaning up to applications, design-for-recycling and new developments – provides a holistic view on this topic, beyond the pure technical perspective.

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# 2

# Introduction to Major Thermoplastic Polymers in the Context of Recycling

Tristan Kolb, Andreas Schedl, Hans-Werner Schmidt

This chapter gives a basic insight into thermoplastic polymers, their architecture, polymerization mechanisms, and solid state morphology. Further, it focuses on the degeneration of the polymers during processing and use. The last part gives a brief overview of the most important thermoplastic polymer types.

Based on their origin, polymers are usually classified into biopolymers and synthetic polymers. Biopolymers are naturally occurring polymers, like proteins, polynucleotides (e. g., DNA and RNA), polysaccharides (e. g., starch, glycogen, cellulose, and chitin), and natural resins (e. g., amber, mastic, and shellac). In contrast, synthetic polymers are created by chemical reactions from petroleum-based and (increasingly nowadays) natural building blocks. In this chapter, we will focus on synthetic polymers, with their wide industrial application.

The breakthrough for industrial polymers was the discovery in 1839 of rubber vulcanization by Charles Goodyear, who obtained elastomers from the cross-linking of natural rubber with sulfur [1]. Since that time, the world of polymers has grown continuously to over 200 different polymer types today, with large differences in properties allowing a broad spectrum of applications in all fields of our daily life including packaging, construction, automotive, electronics, agriculture, and medical devices.

Polymers often replace conventional materials, for example billiard balls formerly made from ivory were later produced from celluloid. Celluloid was one of the first commercial polymers, and was prepared from a mixture of nitrocellulose and camphor. Consequently, the demand for ivory was reduced and with it the need for elephant hunting. Depending on their property profile, completely new applications have become possible, like polystyrene foam as an insulation material for buildings to reduce energy consumption for heating, or advanced food packaging to slow down food spoilage.

Key features of polymers are tailorable mechanical properties, availability in huge quantities, affordable price, and low density. The latter allows lighter parts and thus an energy conservation in their application, especially with respect to transportation. However, some further key features lead to a dilemma. The stability and durability of these materials allows on the one hand long-term usage in applications, but also causes on the other hand only very slow decomposition under natural conditions. This has provoked the current issue of plastics accumulation in the environment. This can be overcome if the polymer waste is completely collected, sorted, purified, and then treated as resource for recycling. The waste management as well as current and upcoming recycling methods are covered in the various chapters of this book.

## 2.1 Chemical Structure and Synthesis of Industrial Polymers

### 2.1.1 Polymer Architecture

Whether we consider any of the industrial polymer types, or one of the many biopolymer types, the fundamental architecture of a polymer is a long chain. These can form linear, star-like, branched, and cross-linked network architectures (Figure 2.1). The chain architecture has an enormous impact on the properties of the macroscopic material (e.g., different types of polyethylene, described in Section 2.3.2.1).

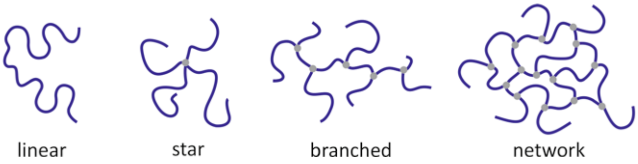
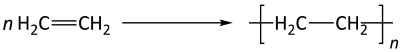


**Figure 2.1** Schematic illustration of the main polymer architectures (linear, star, branched, and network)

The long polymer chains are formed from small building blocks, the so-called monomers, which are covalently bound to each other. An example is shown in Figure 2.2 for the polymerization of the monomer ethylene to the polymer polyethylene.



$$n\,H_2C{=}CH_2 \longrightarrow \left[ H_2C{-}CH_2 \right]_n$$

**Figure 2.2** Polymerization of the monomer ethylene to the polymer polyethylene by forming covalent bonds between the monomer units

A further important structural feature of polymer chains is their configuration (Figure 2.3). This is relevant for vinyl monomers with substituents (e.g., the phenyl group in styrene or the methyl group in propylene). The orientation of such groups along the polymer chain can be controlled during the polymerization process. Hence, selective process conditions give access to a wide variety of materials with different properties while using the same monomer (e.g., different types of polypropylene, described in Section 2.3.2.2).

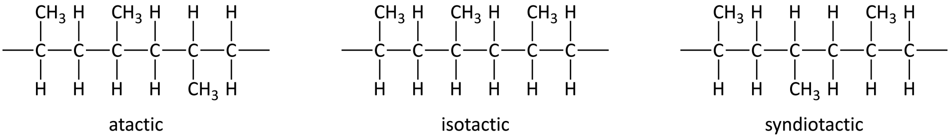


**Figure 2.3** Schematic representation of potential configurations, exemplified for polypropylene: Isotactic polymers have all their substituents on the same side along the chain. In contrast, syndiotactic polymers have alternating positions of the substituents along the chain. If a chain has no regularity, it is called atactic.

So far, we have focused on polymers that are built up from only one monomer. Beyond these so-called homopolymers, copolymers can be obtained from the polymerization of two or more monomers. The arrangement of the different monomers along the polymer chain can be controlled by synthetic procedures. For two monomers, the main sequences are random, alternating, and a block fashion (Figure 2.4). In random copolymers, the different monomers are arranged without any ordering along the chain. Alternating copolymers reveal a strict alternating arrangement of both monomers along the chain. Graft copolymers are composed of a backbone of one monomer and grafts of the second monomer. In block copolymers the monomers are arranged in blocks along one chain. An AB diblock copolymer is composed of a block of monomer A directly linked via one single bond to a block of monomer B. The concept of block copolymers can also be expanded to more sophisticated architectures with an arrangement of distinct blocks, such as an ABA triblock copolymer. A special type of block copolymers are segmented $(AB)_n$ copolymers. Here, several segments of different length are connected in one chain. By introducing a third monomer block, ABC triblock terpolymers are even accessible. Notably, the arrangement of monomer units within specific segments might lead to the formation of immiscible blocks which cause microscopic phase separation on the nanometer scale.

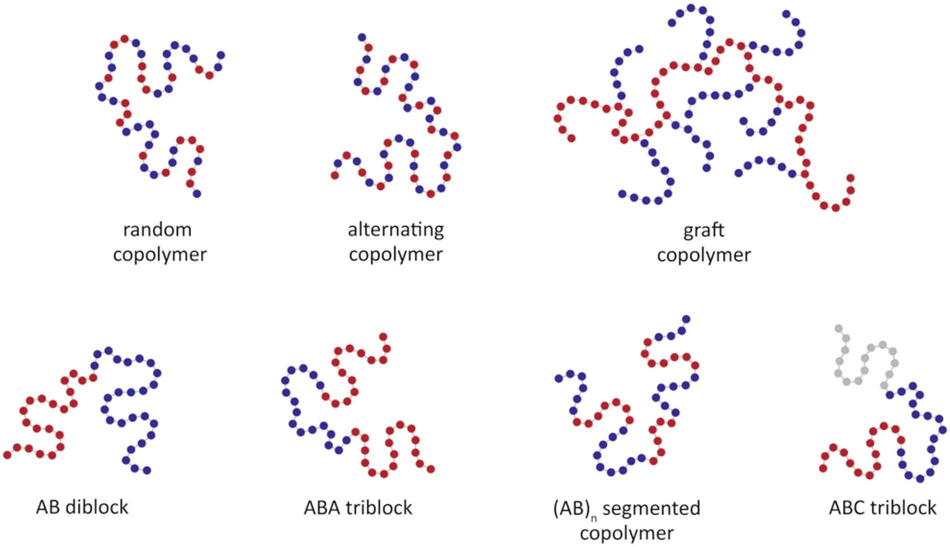


**Figure 2.4** Main possibilities for the sequence of two monomers in copolymers along the chain are random, alternating, graft, AB diblock, ABA triblock, and $(AB)_n$ segmented. In case of ABC triblocks, three monomers are used.

A blend of two different homopolymers is typically not homogeneously miscible. Instead, macroscopic phase-separated areas on the micrometer scale are formed. These so-called domains consist each of only one of these polymers. Block copolymers can be employed as compatibilizer and stabilize the morphology of blended systems. This technique is widely used to combine the properties of two polymer types in one product, while maintaining a good connection between the different phases, which is, for example, crucial for good mechanical properties. The physical background for the phase separation is based on the interaction forces between the different monomer units in the polymer chains. Mostly, the interactions between chain segments based on the same monomer are stronger than interactions between chain segments consisting of different monomers. Such so-called secondary interactions originate from the weak attractive forces between the chains, which occur beside the covalent bonds of the polymer chain. The responsible intermolecular forces originate from so-called van der Waals forces and hydrogen bonds.

The different van der Waals forces originate either from interactions based on spontaneous electron fluctuations (London dispersion forces) between atoms or chain segments, or permanent polarization of functional groups based on atoms with different electronegativity in the functional groups inducing induction forces and dipole–dipole interactions. All of these have in common that the strength of the interactions is strongly dependent on the distance between the respective parts of the chain segments. Consequently, their contribution rises with closer proximity of the polymer chains.

Hydrogen bonds (H-bonds) are defined by IUPAC as "an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation" [2]. They are formed, for example, between N–H groups and carbonyl groups, as depicted in Figure 2.5 for polyamides and polyurethanes. Since these forces are usually stronger than van der Waals forces, they have a large contribution to the properties of the respective polymers.

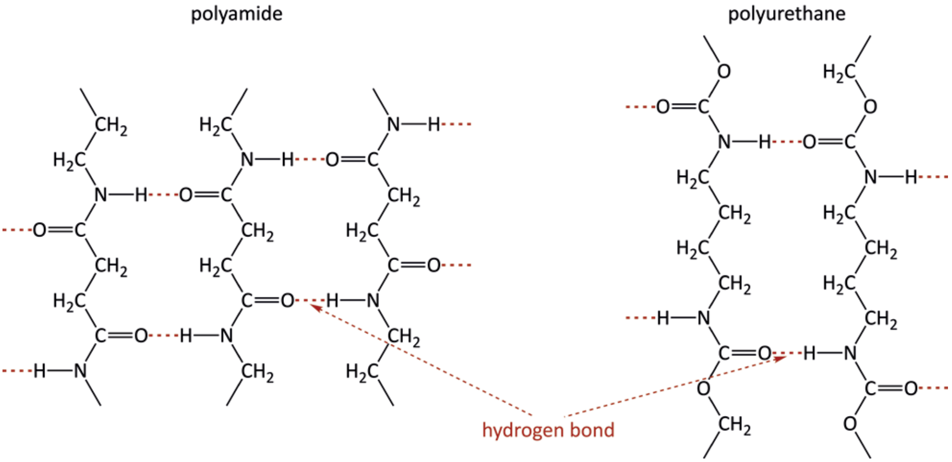


**Figure 2.5** Hydrogen bonds between N–H groups and carbonyl groups in polyamides and polyurethanes

Beside the mentioned interactions, a further mechanical contribution originates from chain entanglements. Polymer chains form random coils for entropic reasons and entangle with neighboring chains. Due to that, the chains can only move to a limited degree along each other (Figure 2.6). This results, for example, in the common viscous flow of molten polymers. The number of entanglements increases with the length of the polymer chains. Consequently, grades with a high molecular weight show higher viscosity than grades with a lower molecular weight.

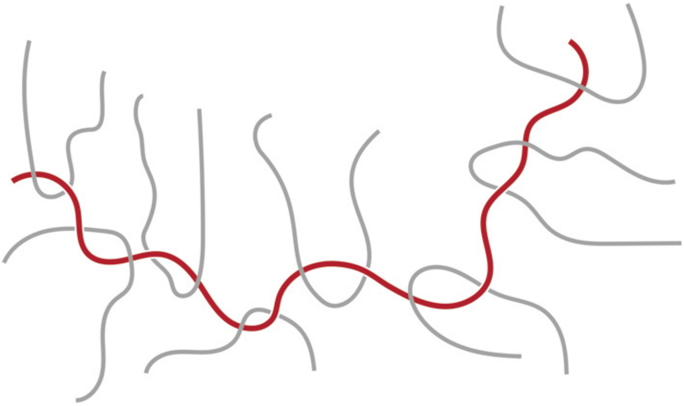


**Figure 2.6** Illustration of entanglements of a polymer chain with neighboring chains

## 2.1.2 Polymers in the Solid State

When polymer materials are cooled down from the molten state, the mobility of the chains decreases. Polymers can solidify in a random coil-like and entangled form, which is called the amorphous state (Figure 2.7(a)). It is characterized by being disordered and having an isotropic orientation, and thus a high entropy. An important characteristic for the description of that state is the glass-transition temperature $T_g$. At this temperature, chain segments start to get mobile and thus the material becomes (to a certain degree) flowable and formable.

Polymers can also form ordered structures in the solid state. Hereby, the chains are partially packed in a crystalline structure with a regular orientation, and thus the entropy is reduced. Consequently, the ordering process, the so-called crystallization, must provide a sufficient energy gain to result in an overall favorable process. The energy gain for the crystallization arises from the previously discussed secondary interactions such as van der Waals forces and H-bonds. The latter require that the functional units are correctly oriented with respect to each other. Consequently, an ordered hydrogen bond pattern is formed. In contrast to small molecules, polymer chains cannot crystallize completely from the molten state. The main reason is the presence of entanglements, which restrict complete crystallization. This leads to the formation of crystalline areas, the so-called lamellae. Within these lamellae, the chain segments are well orientated and closely packed. The chains leave the lamella and statistically re-enter at a different position within the same lamella or connect to different crystalline lamellae. Tie molecules between the crystalline parts are formed, which are important for the mechanical properties. Loops, tie molecules, and disordered chains form amorphous regions. This structure is illustrated in Figure 2.7(b). Imperfections in the chain such as branches are usually present in this amorphous region, since these do not allow a high degree of ordering of the respective chains. From a more macroscopic perspective, several of these crystalline lamellae are present within an amorphous matrix, as illustrated in Figure 2.7(c), which both are crucial for the mechanical properties of the material. Due to the coexistence of amorphous and crystalline regions, the materials are called “semicrystalline”. Such materials are characterized by the degree of crystallinity, which represents the fraction of the monomers in the crystalline areas to all monomers. It depends on the polymer class but also on the microstructure, such as the amount of branching (which typically ranges from 40% to 70% for semicrystalline thermoplastic polymers). Furthermore, the amorphous regions are characterized by the glass-transition temperature. The crystalline areas are characterized by the melting temperature $T_m$. For temperatures above $T_m$, a homogeneous melt is formed.

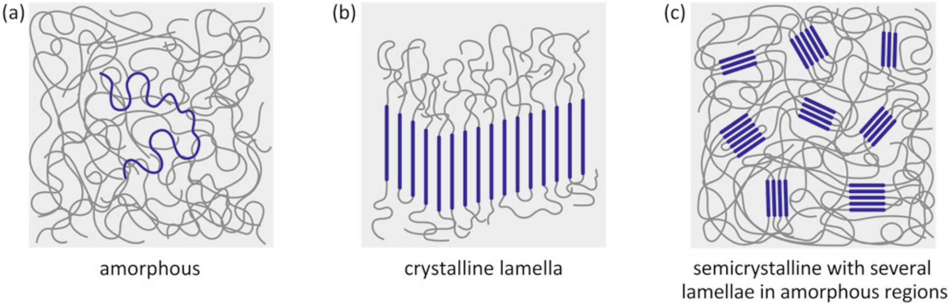


**Figure 2.7** Structures of solid-state polymers: (a) In amorphous polymers, the chains form coils entangled with neighboring chains; (b) crystalline lamella of polymer chains; (c) semicrystalline polymers feature several crystalline lamellae, which are separated by an amorphous matrix

## 2.1.3 Categorization of Polymers

The architecture of a polymer has a direct effect on the thermomechanical properties of the material. In general, there are three main categories of polymer materials:

- Thermosets
- Elastomers
- Thermoplastics (with the subcategory of thermoplastic elastomers)

*Thermosets* are based on a fully cross-linked polymer network. As the different chains are directly bonded to each other, such materials cannot be melted upon heating and thus cannot be reformed without destroying the polymer architecture.

To prepare such materials, usually a reactive resin is filled into a mold and subsequently cured to result in a high degree of cross-linking. After curing, such materials can only be reshaped by subtractive manufacturing.

*Elastomers* are polymer networks with a relatively small number of cross-linking points and a base polymer with a glass-transition temperature below the service temperature. Like thermosets, these materials are not meltable and hence not formable upon heating. In contrast to thermosets, they show an elastic behavior. Due to the low glass-transition temperature, the polymer chains have a certain mobility and hence allow a mechanical deformation of the material by a force. Since the chains are connected to each other, the original shape is restored upon releasing the force.

*Thermoplastics* can be shaped at elevated temperatures. This allows repeated melting and remolding. Thermoplastics consist of polymers with a linear or branched polymer architecture but are not cross-linked. Upon heating, the chains become more and more mobile, and so can move past each other and hence can be repeatedly formed into new shapes. Depending on their morphology in the solid state, thermoplastics are classified into amorphous and semicrystalline materials.

*Thermoplastic elastomers (TPEs)* combine elastic and thermoplastic behavior. This is achieved by a combination of hard and soft segments. The soft segments consist of an elastic main material with a low glass-transition temperature, which are physically cross-linked by hard segments (like crystalline structures or domains with a glass-transition temperature higher than the service temperature). The physical cross-links break up at elevated temperatures and thus the entire material can be processed in a thermoplastic manner. Upon cooling, the hard segments are formed again and provide the material with physical cross-links and thus the elastic behavior. Typically, a block copolymer architecture is used for TPEs, with one domain featuring the soft segment and one the hard segment.

### 2.1.4 Polymerization

The term “Polymerization” covers different chemical reactions leading to covalent bonds between monomer units and simultaneously forming polymer chains or networks. In general, these reactions can be categorized into *chain-growth polymerization* and *step-growth polymerizatio*n. These two types differ significantly in the mechanism of macromolecule formation. This is shown in Figure 2.8 for the chain length as a function of the conversion of monomers and functional groups, respectively.

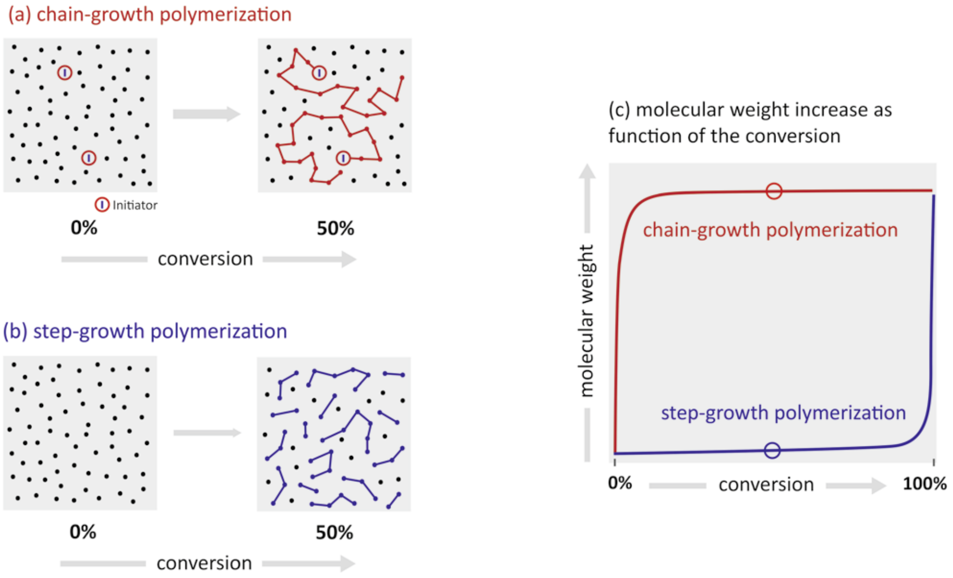


**Figure 2.8** Comparison of polymerization mechanisms: (a) Chain-growth polymerization; (b) step-growth polymerization; (c) the respective increase of the molecular weight as function of the conversion

Chain-growth polymerization starts from an active chain carrier formed by an initiator. A polymer chain is formed by the subsequent addition of monomers (Figure 2.8(a)). Typically, polymer chains with high molecular weight are formed even at a low monomer conversion (Figure 2.8(c)). In contrast, systems with step-growth polymerization follow a different mechanism. Instead of reactions taking place exclusively at the active chain carriers, all monomers and reaction products formed from them have a similar probability of reacting with each other. This leads to the formation of a broad variety of dimers, trimers, tetramers, and oligomers at low conversions during the polymerization (Figure 2.8(b)). High molecular weight polymer chains are formed at a very high conversion (Figure 2.8(c)).

### 2.1.4.1 Chain-Growth Polymerization

Chain-growth polymerization can occur at different kinds of active sites. This has a huge effect on the polymerization process, conditions, and the resulting polymer. Table 2.1 gives an overview of possible active sites and the derived classification. These classes will be discussed below.

**Table 2.1** Possible Active Sites for Chain-Growth Polymerization and the Derived Classification

| Active site | Classification |
|---|---|
| Radical | Radical polymerization |
| Anionic or cationic species | Ionic polymerization |
| Transition metal–carbon bond | Coordination polymerization |

### Radical Polymerization

Radical chain-growth polymerization consists of the reaction steps initiation, chain propagation, chain transfer, and chain termination. In the initiation step, a radical chain carrier is created. This can take place, for example, by the thermal decomposition of an initiator like azobisisobutyronitrile (AIBN) (Figure 2.9(a)). In the starting reaction the first monomer is added while maintaining the radical site (Figure 2.9(b)). This active chain end repeatedly adds monomers in the chain propagation step, building up the polymer chain (Figure 2.9(c)). Thereby, the active center at the chain end is maintained. However, such radical-carrying chain ends are very reactive and can be subjected to different kinds of further reactions. First of all, they can react with inactive molecules (e.g., low molecular weight species or any polymer chains present) and thereby transfer the radical species to these molecules (Figure 2.9(d)). This leads to cessation of the growth of the original chain. The active radical site is now located on the new molecule and a new chain can propagate from this site. If the transfer takes place to another chain, or even another position on the same chain, long and short branches are formed. Radical-carrying species can also react with each other and thereby terminate the active centers and hence the chain growth. If two radical chain ends react by forming a new covalent bond, the molecular weight of the resultant chain substantially increases in one step. This process is called recombination (Figure 2.9(e)). In a disproportionation reaction, one hydrogen atom (marked in red) is exchanged between two active chain ends. The radical character of both chains is lost, and thereby one saturated and one unsaturated chain is formed. The latter can react with another active radical site.

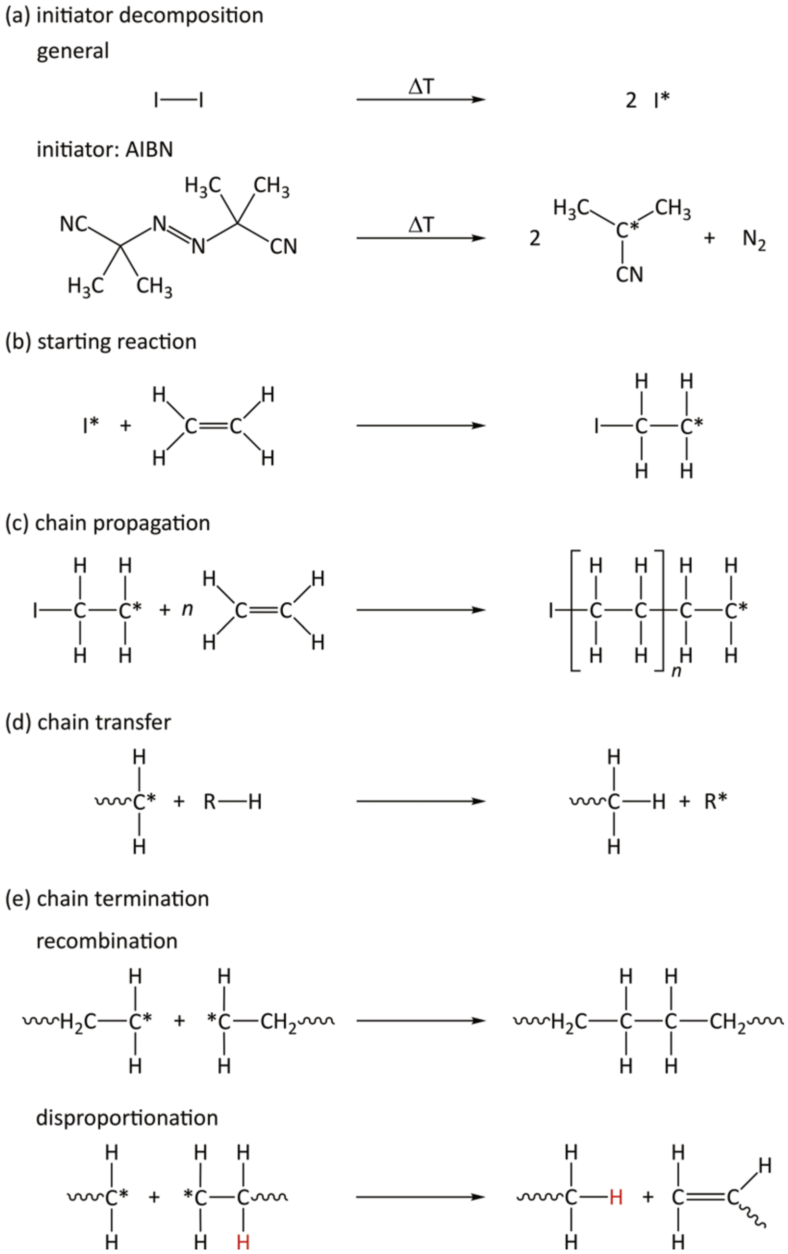


**Figure 2.9** Reaction mechanism of radical chain-growth polymerization: (a) Initiation, here also shown for AIBN as an example; (b) starting reaction; (c) chain propagation; (d) chain transfer; (e) chain termination by recombination or disproportionation

All reaction types can take place, with their distribution being determined by their reaction speeds. This leads to a characteristic variety of chain lengths and thus a broad molecular weight distribution. This is usually characterized by the average molecular weight. It can be affected, for example, by the reaction temperature or the amount of initiator. Higher initiator amounts and higher temperatures result thereby in lower molecular weights.

The molecular weight is one of the key parameters influencing processing and material performance. A higher molecular weight leads to higher mechanical strength, toughness, stress crack resistance, and heat deflection temperature. However, a higher molecular weight also increases the viscosity of the material in the melt and thus decreases the flowability of the material in the molten state. Consequently, high-molecular-weight materials are more difficult to process to specific shapes than low-molecular-weight materials.

### Ionic Polymerization

Ionic polymerization differs from radical polymerization by having a charged ion species or an ion pair as the active site. Depending on the charge of the active site, the reaction mechanism is further categorized into cationic and anionic polymerization.

Cationic polymerizations are initiated by a proton donor such as a strong acid (e. g., sulfuric acid) or Lewis acids (e. g., boron trifluoride) in combination with water. By reaction of the proton with the monomer, a carbenium ion is formed that can then propagate the chain by repeated reaction with further monomers. Side-reactions of the active chains can occur by a chain transfer reaction to the monomer or solvent, leading to transfer of the active center. Consequently, the growth of the original chain is stopped and a new chain can start from the active species formed. This mechanism is the main reason for the limitation of the resultant molecular weight, as termination reactions between active chain ends cannot occur due to electrostatic repulsion of the charged species. Controlled termination is usually carried out by addition of bases or water.

Anionic polymerizations are initiated by strong bases like sodium hydroxide, sodium alcoholates or organolithium reagents such as *n*-butyllithium. During initiation, they form carbanions with monomers. The carbanions can add further monomers and hence propagate the chain. Reaction of the carbanion species with polar molecules like water can take place und thus deactivate the active sites. Thus, such contaminations must be thoroughly removed prior to anionic polymerization. Analogous to the cationic polymerization, termination reactions between active chain ends cannot occur due to electrostatic repulsion of the charged specimen. Remarkably, this kind of polymerization can be performed with nearly complete exclusion of chain transfer. The active sites have a nearly unlimited lifetime and grow with a similar speed until all monomer is consumed. These "living polymers" feature the unique property of propagating further when more monomer is later added. This technique is usually applied in the production of block copolymers, where a second monomer is added to the living chain end. Polymers with a highly-defined narrow molecular weight distribution and architecture can be obtained in this manner.

### Coordination Polymerization

Coordination polymerization uses catalysts based on transition metals to form the polymer chain. The monomer is added at the active center of the catalyst and then inserted into the metal–carbon bond of the growing chain. The catalyst restricts possible orientations for the coordinated monomer by the presence of its ligands around the active center. This leads to inclusion of the monomers in (primarily) a selective manner, and hence buildup of a stereoregular polymer chain is possible. The most prominent examples are Ziegler–Natta catalysts, which are based on transition metal chlorides like titanium tetrachloride, which is activated by organoaluminum compounds like triethylaluminum. Thereby, the transition metal receives an alkyl ligand, but still features a free coordination position (Figure 2.10(a)). At this position, the monomer is coordinated (Figure 2.10(b)) and inserted, via a 4-center-4-electron transition state, into the metal–carbon bond (Figure 2.10(c)). After this insertion, the chain is elongated and the active catalyst center with a free coordination position is reformed (Figure 2.10(d)). The coordination polymerization is widely used, for example, for the production of unbranched high-density polyethylene, or stereoselective polymers like isotactic polypropylene.

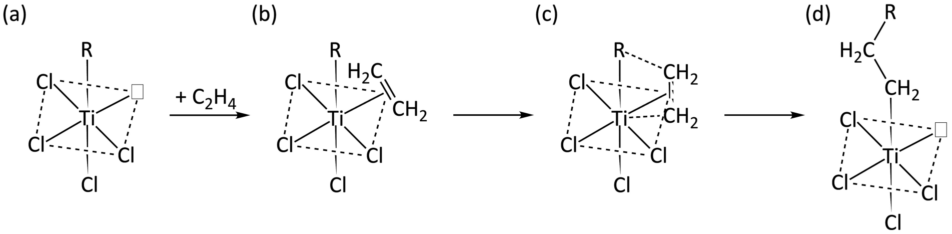


**Figure 2.10** Simplified mechanism for coordination polymerization: (a) Catalyst featuring a free coordination position and a metal–carbon bond to the growing chain R; (b) coordination of the monomer in the free coordination position; (c) insertion of the monomer into the growing chain via a 4-center-4-electron transition state; (d) restoration of the free coordination position of the active catalyst

### 2.1.4.2 Step-Growth Polymerization

Step-growth polymerization is based on the reaction of functional groups of bifunctional monomers. In a first reaction step, a dimer is formed. This is illustrated in Figure 2.11(a) for two different bifunctional monomers with two equal functional groups F and G, respectively. The reaction is also possible with only one bifunctional monomer, which carries both functional groups F and G (Figure 2.11(b)).

**Figure 2.11** (a) Formation of dimers by step-growth polymerization based on two bifunctional monomers with the functional groups F and G. (b) Formation of a dimer by a monomer featuring both functional groups

The dimers formed feature again two reactive functional groups at the ends, and thus can react with further monomers or oligomers. In general, the reactivity of the functional groups is similar regardless of their presence on monomers, dimers, trimers, or longer chains. At the outset, a large number of monomer molecules is present, and hence primarily oligomeric chains are formed at low conversion. At increasing conversion and hence higher concentrations of oligomer fragments, these increasingly react with each other, and form longer chains. Consequently, a very high conversion is needed to achieve a high-molecular-weight polymer by step-growth polymerization. Furthermore, it is essential to have equal amounts of functional groups F and G present in the polymerization, as otherwise only oligomers are formed, which will feature chain ends with the excess functional group. As these cannot react with themselves, the molecular weight is restricted. Linear polymer chains are obtained from bifunctional monomers. By the addition of trifunctional or even multifunctional monomers in different amounts, weakly or highly cross-linked networks can be synthesized.

Step-growth polymerization can be categorized into polycondensation or polyaddition reactions. In a polycondensation, two functional groups react with each other and thereby release a low-molecular by-product. In contrast, the reaction of the functional groups in a polyaddition takes place without the release of any by-product. In both cases, the main chain of the polymer typically contains heteroatoms. At such positions in some cases step-growth polymers are suitable for chemical recycling by hydrolysis of the respective unit. This differentiates them from radically prepared chain-growth polymers, which typically contain only carbon atoms in the main chain. Consequently, these polymer chains cannot be broken up by hydrolysis.

### Polycondensation

In a condensation reaction, two functional groups react with each other and form a condensation product by releasing a volatile low-molecular-weight by-product (Figure 2.12). The reaction kinetics depend strongly on the equilibrium between the sum of all educts and the sum of all products. To achieve a high conversion and hence a high molecular weight of the formed polymer, the equilibrium must be shifted to the product side. This is achieved by continuously removing the low-molecular-weight by-product. Typical polycondensation reactions involve, for example, the formation of amide linkages (resulting in *polyamides*), and ester linkages (resulting in *polyesters*).

$$\mathrm{R{-}X} + \mathrm{Y{-}R'} \rightleftharpoons \mathrm{R{-}R'} + \mathrm{XY}$$

**Figure 2.12** Equilibrium between educts and products in a condensation reaction by releasing a by-product

*Polyamides* can be formed by reaction of bifunctional monomers with carboxylic acid and amine functions while water is released as a low-molecular-weight by-product. The carboxylic acid function can also be substituted with its more active derivatives like acid halides or esters from low-boiling alcohols, resulting in formation of the respective hydrogen halide or alcohol during the reaction. The main industrial polymer classes of polyamides are aliphatic polyamides. Also, partially aromatic polyamides (named polyphthalamides) and fully aromatic polyamides are commercial products. Aliphatic polyamides are typically named according to the number of carbon atoms in the amine and the carboxylic acid monomer. Thus, polyamide 6.10 is synthesized from the 6-carbon amine hexamethylenediamine and sebacic acid, which contains 10 carbons (Figure 2.13).

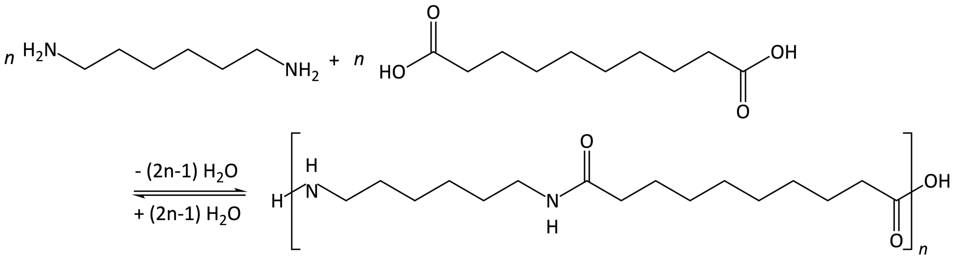


**Figure 2.13** Polycondensation of hexamethylenediamine and sebacic acid to polyamide 6.10. The first number represents the number of carbon atoms in the diamine, while the latter represents the number of carbons in the diacid.

Furthermore, polyamides can be synthesized from amino carbonic acids, like PA 12 from the 12-carbon monomer ω-aminolauric acid. Alternatively, PA 12 can be prepared by anion-initiated ring-opening polymerization of laurolactam, which follows the kinetics of chain-growth polymerization.

Partialy or fully aromatic polyamides contain aromatic monomers to a certain degree. The most prominent representative for fully aromatic polyamides (so-called polyaramides) is Kevlar®, which is prepared by the reaction of *p*-phenylenediamine and terephthaloyl chloride. Kevlar is typically used as high-performance lightweight fiber.

*Polyesters* are synthesized from monomers with carboxylic acid and alcohol functions, with water being released as a low-molecular-weight by-product (Figure 2.14(a)). Analogous to polyamides, the carboxylic acid function can also be exchanged with its derivatives like acid halides or esters (with low-boiling alcohols), resulting in the release of hydrogen halides or alcohols, respectively. From a chemical point of view, polycarbonates can be regarded as the diesters of a carbonic acid with a difunctional alcohol. Since the reactivity of the carbonic acid is quite low, they are usually created by the reaction of phosgene with the respective difunctional alcohol (Figure 2.14(b)) or by transesterification, for example of diphenyl carbonate with the respective difunctional alcohol.

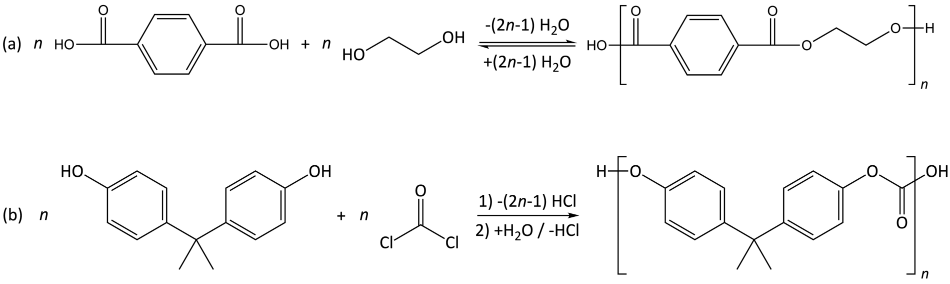


**Figure 2.14** (a) Polycondensation of terephthalic acid and ethylene glycol to polyethylene terephthalate (PET). (b) Polycondensation of bisphenol A with phosgene to polycarbonate (PC)

## Polyaddition

Like polycondensation, polyaddition follows a step-growth polymerization mechanism. However, the functional groups in a polyaddition react without the formation of any by-product. The most important polymer classes synthesized by this mechanism are polyureas, polyurethanes, and epoxy resins.

*Polyureas* are formed by the reaction of diisocyanates with diamines, resulting in the formation of urea groups (Figure 2.15(a)). In contrast, *polyurethanes* are formed by the reaction of diisocyanates with diols resulting in the formation of urethane groups (Figure 2.15(b)). Aliphatic amines, aliphatic alcohols, and aromatic or cycloaliphatic isocyanates are very reactive, and allow a rapid reaction even at room temperature. Furthermore, an anhydrous reaction procedure is required for non-foamed applications, since isocyanates are susceptible to side-reactions with water, forming carbon dioxide and amines. The carbon dioxide acts as a foaming agent and thus polyurea foams result.

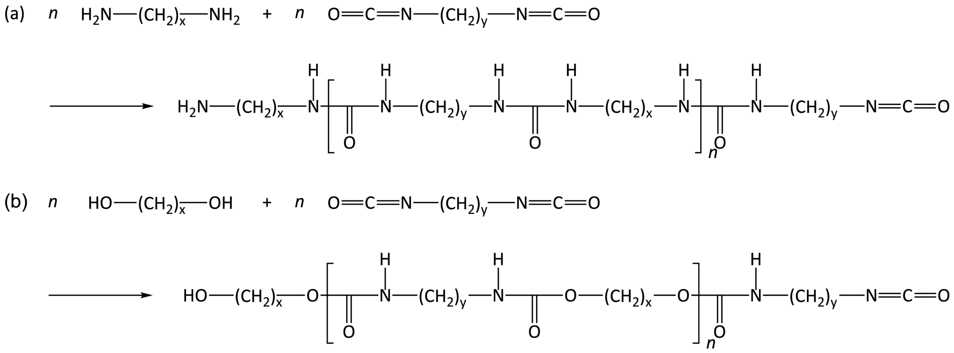


**Figure 2.15** Polyaddition of diisocyanates with diamines to polyureas (a), and with diols to polyurethanes (b)

*Epoxy resins* belong to the class of thermosets and are highly cross-linked. They are cured by a polyaddition reaction of multifunctional monomers with epoxy functions and amine functions, respectively. Thereby, the reaction of epoxy monomers with secondary amines leads to the formation of linear connections. The reaction with primary amines (Figure 2.16(a)) leads to the formation of secondary amines, which can subsequently react with further epoxy functions and thus result in a higher cross-linking density (Figure 2.16(b)). To obtain highly cross-linked thermosets, multifunctional monomers are additionally applied.

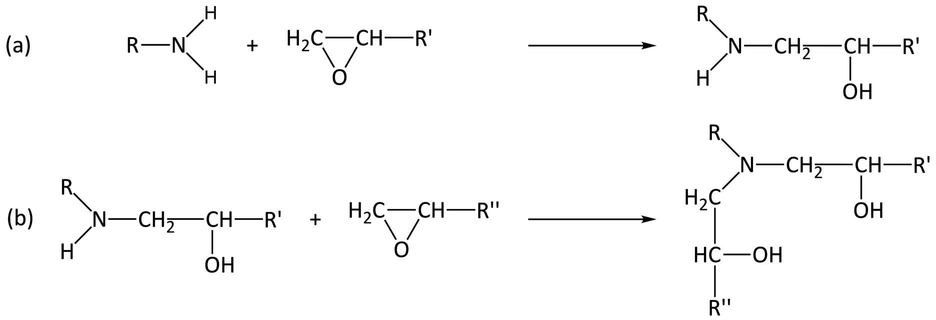


**Figure 2.16** Polyaddition of epoxy groups with primary amines (a), and successive reaction with further epoxide functions to chemical cross-linkages (b)

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