Chemistry with Polymers

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Many macromolecules still contain chemically reactive groups even after polymerization has taken place; under certain conditions, macromolecules can also be reactive chemicals. They do, however, have some special characteristics compared with reagents with a low molar mass. This chapter describes such reactive macromolecules and their peculiarities.

It is of fundamental importance to differentiate between two types of chemical reactions that macromolecules can undergo: intentional chemical reactions or undesired degradation processes. Specific stabilization strategies have been developed to inhibit unwanted degradation processes, and these are also dealt with in this chapter.

15.1 Polymer Analogous Reactions

Reactions that involve parts of macromolecules, but that do not change their degree of polymerization, are known as polymer analogous reactions. The hydrogenation of unsaturated bonds in the polymer backbone or the hydrolysis of side groups are examples of these kinds of reactions. Because the molar mass of the repeat unit usually changes during these reactions, the molar mass of the macromolecule does not remain constant (in contrast to the degree of polymerization).

From a synthetic polymer chemist's point of view, polymer analogous reactions are fundamentally different to reactions involving only small molecules in several ways:

- By-products are difficult to separate from the desired products so that only reactions that do not generate significant amounts of unwanted by-products are suitable for polymer analogous reactions.
- The solubility of a chemically modified polymer can be very different from that of the base polymer. This is especially pronounced if charged moieties are added to an uncharged polymer, for example, the hydrolysis of ester to carboxylate groups. This can make polymer analogue reactions difficult as, because of its reduced solubility, the polymer precipitates during the reaction, resulting in the unconverted functional groups no longer being easily available for reaction; the reaction does not go to completion and a chemically inhomogeneous product is formed. Chemically inhomogeneous products are also obtained if a poorly soluble polymer (e.g., cellulose) is made more soluble by modification. Nevertheless, in many technical processes, despite chemical inhomogeneity, an acceptable product can be produced so that some polymer analogous reactions gain considerable technical significance. Some examples of these reactions are dealt with more thoroughly in ▶ Sect. 15.1.3. However, polymer analogous reactions are not so often used in academia, where the goal is usually to produce a well-defined material.
- Because of the high local concentration of the group taking part in the reaction in the interior of the polymer random coil, in contrast to the "empty" solvent phase in between the coils, special kinetic features occur:
  - A preference for intramolecular reactions
  - An increase or decrease in the reaction rate

These effects are discussed in more detail in ▶ Sects. 15.1.1 and 15.1.2.

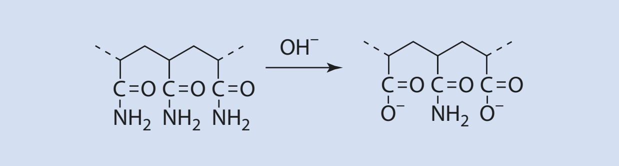


Fig. 15.1 Hydrolysis of polyacrylamide

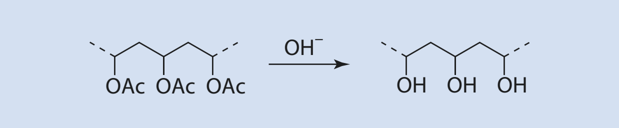


Fig. 15.2 Hydrolysis of polyvinyl acetate to polyvinyl alcohol. *Ac*: acetate

15.1.1 Special Kinetic Features of Polymer Analogous Reactions

In contrast to homogenous reactions of small molecules, the functional groups taking part in polymer analogous reactions are not evenly distributed throughout the reaction volume. Random polymer coils with high concentrations of functional groups are separated from one another by solvent. Because of the proximity of these functional groups there can be a strong impact on the kinetics of the reaction. This can result in the reaction being either retarded or accelerated.

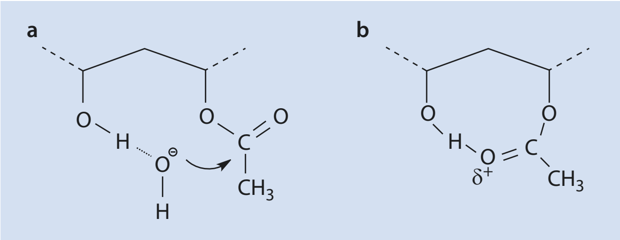
An example of a self-retarding reaction discussed in the following is the (technically insignificant) saponification of polyacrylamide (◘ Fig. 15.1). During alkaline saponification, negatively charged carboxylate groups are formed. These have an electrostatically repulsive effect on the attacking hydroxide ions so that the reaction of neighboring, unhydrolyzed groups is significantly slowed.

An amide group, such as the one shown in ◘ Fig. 15.1 which is flanked by two hydrolyzed, and thus negatively charged, groups, is electrostatically shielded from attack by a hydroxide ion because of the negative charges of these groups. This results in the reaction being slowed by a factor of 12 even at a degree of conversion as low as $p = 0.4$.

In contrast to this kind of retardation, an acceleration can also take place during polymer analogous reactions because of a high local concentration of functional groups. This is the case for the technically significant hydrolysis of polyvinyl acetate (◘ Fig. 15.2).

The OH functional groups formed during this reaction can—in contrast to the less polar acetate group—form hydrogen bonds with the attacking hydroxide ion. This favors the attack of these ions. As a result, an acetate group flanked by two groups which have already been hydrolyzed is around 100 times more reactive than without these neighboring groups. This is why a strong acceleration in the rate of conversion as the reaction proceeds is observed. A further effect, which can lead to an acceleration of the reaction, is the formation of a hydrogen bond between an acetate group and a neighboring hydroxyl group, leading to a positive polarization of the carbonyl group (◘ Fig. 15.3).

These kinetic effects have an important influence on the structure of the materials produced if the conversion is incomplete. During the hydrolysis of polyacrylamide, for



■ **Fig. 15.3** Hydrogen bonds in partially hydrolyzed polyvinyl acetate. (**a**) Stabilization of an attacking hydroxide ion. (**b**) Intramolecular activation of the carbonyl function by hydrogen bonding. *Ac*: acetate

example, there is a tendency for the reaction to take place with groups that are as far apart as possible. This means that a partially hydrolyzed polymer tends to have a structure more akin to that of an alternating copolymer. On the other hand, partially hydrolyzed polyvinyl acetate can be regarded as a block copolymer.

15.1.2 Intra- Vs. Intermolecular Reactions

As already mentioned in ► Sect. 15.1.1, the functional groups attached to a polymer molecule are not distributed evenly throughout the polymer solution. This inhomogeneity is especially pronounced in dilute polymer solutions. In very dilute solutions the distance between the polymer coils (and therefore their functional groups) is especially large, whereas the distance between the functional groups within the polymer molecules is, at least initially, independent of the dilution. Thus, intramolecular reactions are more likely to take place during reactions involving a multifunctional reagent which can react with more than one of the functional groups of the polymer molecules.

At high polymer concentration, intermolecular reactions, i.e., a linking of two polymer molecules, can occur to a lesser extent. Formally, this no longer qualifies as a polymer analogous reaction because the degree of polymerization significantly increases. To avoid such reactions, polymer analogous reactions are best carried out in dilute solution.

A technically important example of this type of intramolecular polymer analogous reaction is the esterification of polyvinyl alcohol (■ Fig. 15.4).

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The reaction is irreversible when carried out under alkaline conditions so that hydroxyl groups for which both neighboring groups have already reacted cannot react. For this reason, the reaction does not proceed to complete conversion with respect to the hydroxyl groups. It can be shown that the maximum conversion p_{max} is

$$p_{max} = 1 - \frac{1}{e^2} \approx 86.5\ \% \qquad (15.1)$$

Complete conversion can only be achieved if the reaction is reversible and "reaction defects," such as those shown in ■ Fig. 15.4, can be rearranged during the reaction process.

Polyvinyl butyral is widely used in the automobile industry to make laminated safety glass. Two glass panes are stuck to one another using a transparent film of polyvinyl butyral. The film is usually about 0.75 mm thick. In the event of mechanical damage the glass panes break but the glass splinters remain adhered to the polymer film. As a result, the material does not completely break, and the risk of injury from flying glass splinters is minimized.

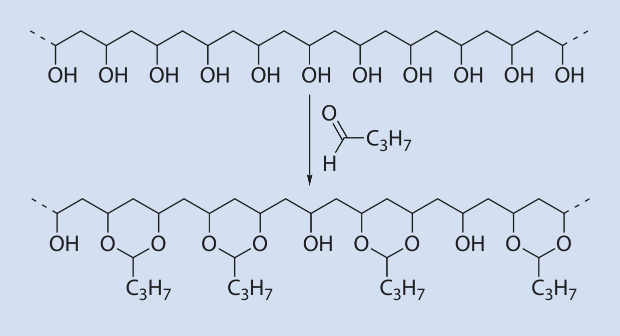


Fig. 15.4 Esterification of polyvinyl alcohol to polyvinyl butyral

15.1.3 Technically Significant Polymer Analogous Reactions

The aromatic side group of polystyrene can be chemically modified in many different ways. These reactions are often used commercially for polystyrene that has been cross-linked, for example, with divinyl benzene. As an example, the reaction of cross-linked polystyrene beads with sulfuric acid results in a sulfonic acid functionalized polymer network (Fig. 15.5) which can be used as a cation exchange resin.

Anion exchange resins can be made in a similar manner by chloromethylating polystyrene and subsequent reaction with a tertiary amine to yield quaternary ammonium functionalized polystyrene (Fig. 15.6).

The intermediate product, chloromethylated polystyrene, is also used as a resin for the Merrifield synthesis of peptides. The chloromethyl groups react with the amino groups of an amino acid to bind the peptide to the solid substrate.

Another macromolecule, often used for polymer analogous reactions, is cellulose, and cellulose derivatives have been technically significant for a long time because of its natural abundance. Cellulose is a polysaccharide consisting of β-1,4 linked D-glucose units (Fig. 15.7) leaving three hydroxyl groups available per monomer unit as reactive functional groups.

Cellulose Esters

The OH functional groups of cellulose can be esterified with a variety of different acids (Fig. 15.8).

The reaction of cellulose with nitrating acid gives so-called, nitrocellulose, which is well known as the main component of celluloid. Many everyday objects, in addition to film rolls, were made of celluloid in the nineteenth century and the early twentieth century. However, because of its flammability, it was soon replaced by other materials and now only has a few uses such as a raw material for paint.

Esterification of cellulose with acetic acid produces cellulose acetate. Textile fibers and cigarette filters are made from this biodegradable material.

The reaction of cellulose with carbon disulfide under alkaline conditions is of special interest. The resulting cellulose xanthate is sensitive to acid and can be transformed back into cellulose by lowering the pH. This permits cellulose xanthate to be spun from an acidic solution (▶ Chap. 17). During this process, the carbon disulfide is eliminated and cellulose fibers, known as rayon or artificial silk, are produced.

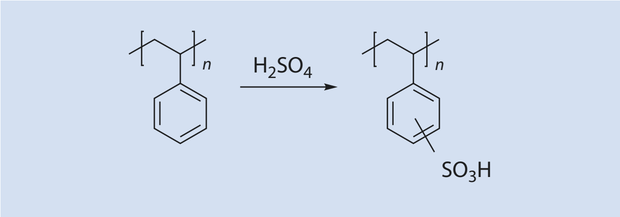


Fig. 15.5 Conversion of polystyrene with sulfuric acid

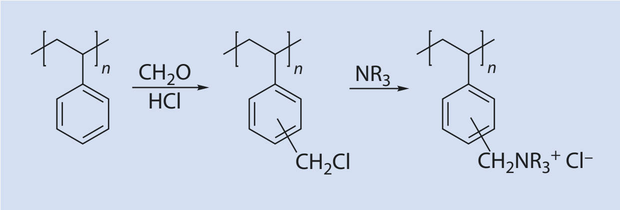


Fig. 15.6 Chloromethylation and amination of polystyrene

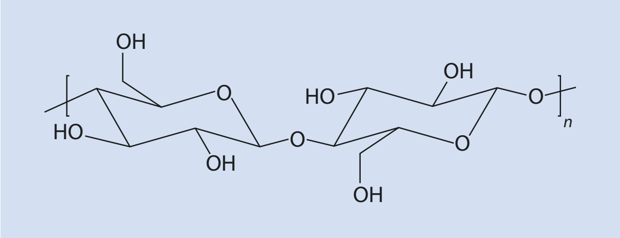


Fig. 15.7 Structure of cellulose and the D-glucose units

a

$$\text{Cell—OH} \xrightarrow{HNO_3/H_2SO_4} \text{Cell—ONO}_2$$

b

$$\text{Cell—OH} \xrightarrow{HOAc} \text{Cell—OAc}$$

c

$$\text{Cell—OH} \underset{H^+}{\overset{CS_2/NaOH}{\rightleftharpoons}} \text{Cell—OCS}_2\text{Na}$$

Fig. 15.8 Conversion of cellulose to (**a**) cellulose nitrate, (**b**) cellulose acetate, and (**c**) cellulose xanthate. *Cell-OH* cellulose

Cellulose Ethers

As well as from its reaction with acids, industrially important polymers also result from the etherification of cellulose with alkylating agents (Fig. 15.9). Thus the reaction of cellulose with alkyl halides yields a diverse selection of cellulose ethers. By employing ethylene oxide as reactant, hydroxyethyl cellulose is obtained. Another important reaction is the alkali catalyzed reaction with chloroacetic acid from which carboxy methyl cellulose (CMC) results.

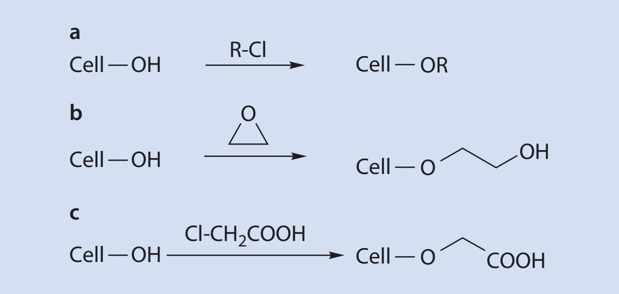


Fig. 15.9 Reaction of cellulose to (**a**) cellulose ethers, (**b**) hydroxyethyl cellulose (HEC), and (**c**) carboxymethyl cellulose (CMC)

These materials are functional polymers (▶ Chap. 19), for example as food thickeners (E466), stabilizers for suspensions of nano particles, glues, pharmaceutical additives, and flow improvers for concrete as well as for additives to textiles and paper. Cellulose ethers are also used as membrane substrates or, especially benzyl cellulose, as thermoplastic resins.

15.2 Cross-Linking Reactions

Cross-linking reactions result in covalent bonds between individual macromolecules and are thus, by definition, not polymer analogous reactions. However, the chemical cross-linking of polymers is also very important industrially, and has a great effect on their material properties, as mentioned briefly here:

- The glass transition temperature increases because of the decrease in the mobility of the polymer chains and the increasing molar mass which approaches an infinite value during cross-linking.
- The strength of the material increases.
- Because of the increase in molar mass, the solubility of the macromolecules decreases. When cross-linking is complete, the material is completely insoluble (▶ Chap. 1).

Industrially important cross-linking reactions of polymers are briefly discussed below.

15.2.1 Cross-Linking of Polyolefins

Polyolefins can be cross-linked in order to improve their material properties. This can be achieved chemically, thermally, or by radiation. These reactions usually take place radically (◘ Fig. 15.10).

15.2.2 Vulcanization of Rubber

The vulcanization of rubber is probably the oldest chemical reaction intentionally carried out on polymers (Goodyear 1844). Natural rubber, which is sticky and thus not particularly useful in its original state, is transformed into an everyday, essential material by reacting it, e.g., with sulfur (◘ Fig. 15.11). During this reaction the *cis*-polyisoprene chains are linked together by oligomeric sulfur bridges consisting of up to eight sulfur atoms.

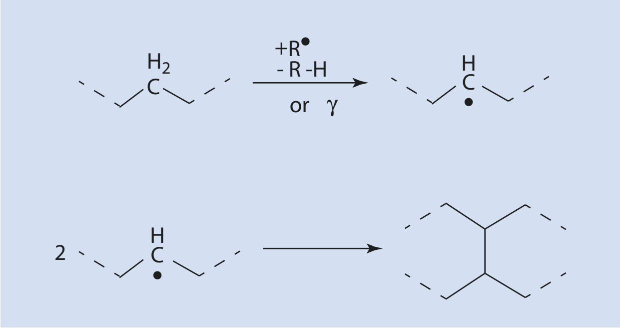


Fig. 15.10 Cross-linking of polymers by radicals or by radiation

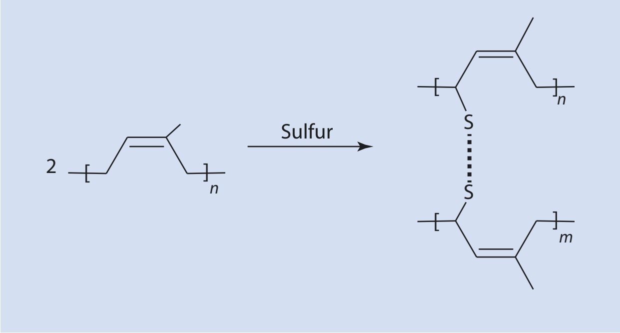


Fig. 15.11 Vulcanization of natural rubber (*cis*-polyisoprene)

15.2.3 Photoresists

The structuring of surfaces by light plays a crucial role in many industrial processes, especially in the electronics industry for the production of micro-structured electronic components. The structuring of polymeric surfaces can take place by a variety of means:

- Increasing the solubility by radiation
- Decreasing the solubility by radiation
- Direct removal with an intensive light beam

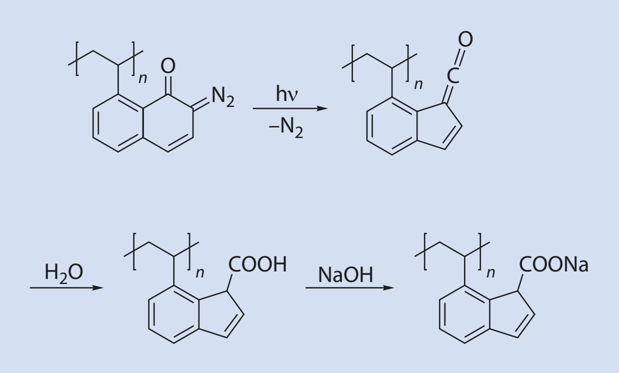
Polymeric surfaces, which interact with light in one of these ways, can be structured by simply exposing them to light through a mask. The structures accessible in this manner can be extremely small, which is an essential requirement for the production of microstructures. The processes of structuring and the materials used in these processes are now discussed in some detail.

15.2.3.1 Positive Resists

Polymers referred to as "positive resists" (*p-resists*) become more soluble on exposure to light of a suitable wavelength. An example is shown in Fig. 15.12.

The polarity of the molecule increases drastically as a result of the insertion of an ionic group. As a result, irradiated areas are soluble in polar solvents or water in contrast to those that have not been irradiated.

Fig. 15.12 Increasing polymer solubility by introducing a polar group with the aid of light



15.2.3.2 Negative Resists

So-called “negative resists” (*n-resists*) display exactly the opposite reaction when they are irradiated: they become insoluble. The easiest way to achieve this is by photochemical cross-linking (Fig. 15.13).

The material becomes insoluble in all solvents as a result of cross-linking so that the un-cross-linked macromolecules can be easily removed.

The basic procedure for the surface structuring of p- and n-resists is shown in Fig. 15.14. On the left a substrate is coated with an n-resin, which is soluble in its non-irradiated state. The irradiated regions are insoluble because of cross-linking after irradiation through a mask. In a further step, the regions which have not been irradiated, and thus remain soluble, are removed. A structured substrate remains. A similar procedure, but with a negative mask, can be employed for structuring using p-resins.

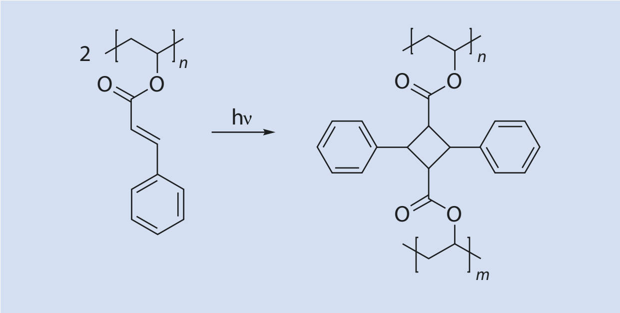
15.2.3.3 Polymers for Photoablation

By exposure to high-energy radiation, suitable polymers are broken down into small molecules. The low molar mass fragments are removed after irradiation. To obtain better defined structures, groups sensitive to radiation, such as triazene groups, can be included in the backbone of the macromolecules. When irradiated by a pulsed laser with a frequency in the nanosecond range, the surface becomes heated (in terms of atomic thermal motion) by the energy of the laser during each pulse. Because of the poor thermal conductivity of polymers, allowing only a slow energy transfer to the surrounding material, the energy from the laser is concentrated in a thin layer (around 1 μm for pulse lengths of 10 ns). The surface reaches very high temperatures during this process and instantaneous evaporation or disintegration of the material takes place. An example of a structure produced by laser ablation is shown in Fig. 15.15.

15.2.4 Paints

The paint on a modern automobile is about 110 μm thick so that per vehicle around 1 kg of paint is needed; nowadays, car paint comprises four layers (Goldschmidt and Streitberger 2002). The so-called *electrocoat* is galvanically applied directly onto the metal bodywork of the car. This electrocoat protects the car from corrosion. Then the *filler* is applied. The filler

Fig. 15.13 Reduction of polymer solubility by photochemical cross-linking



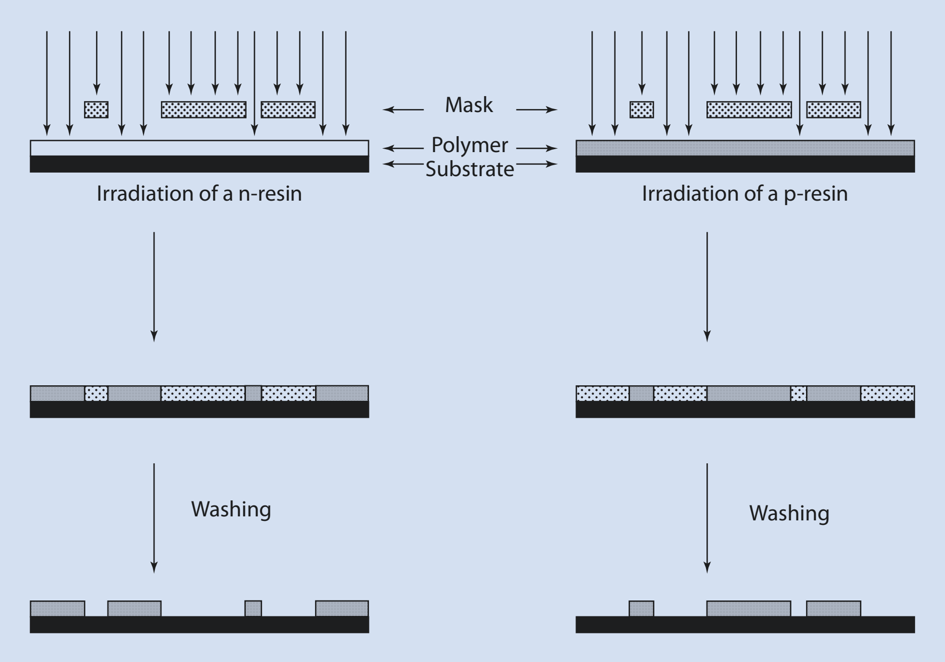


Fig. 15.14 Structuring surfaces covered with n- or p-resists

levels out any microscopic unevenness of the bodywork and the electrocoat and protects the vehicle from the impact of small stones in use. The pigments that give the vehicle its color are contained in the next layer, the *base paint*. The top layer, made up of *clear coat*, is of special importance for the appearance of the vehicle. It is responsible for the glossiness and scratch resistance of the varnish system and is made up of a layer of polymers produced from their monomers and reactive oligomers (so-called pre-polymers) during the varnishing of the bodywork surface. This process is a challenging one for every polymer chemist, as the reaction mixture must form a perfect, absolutely even layer as soon as the varnish hardens, regardless of whether the surface is flat or curved or whether it is vertical

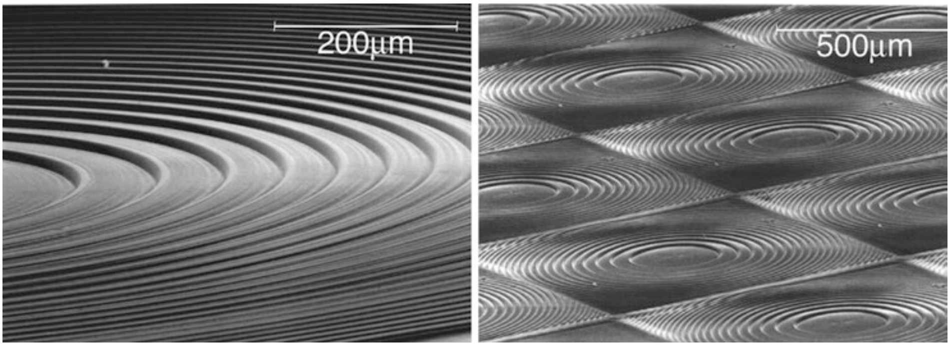


Fig. 15.15 Electron micrograph of a structure produced from a triazene functionalized polymer using pulsed laser ablation

Fig. 15.16 Pentaerythritol tetraacrylate as an example of a cross-linking monomer in clear coat varnishes

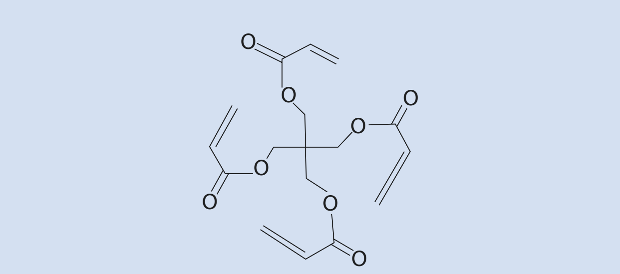
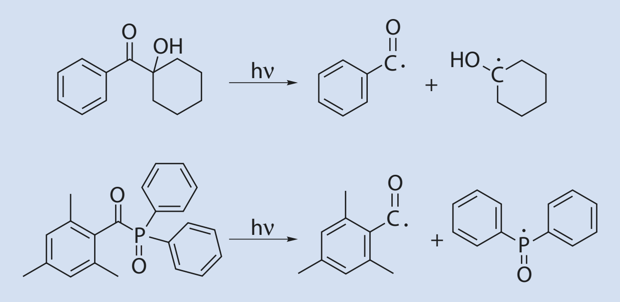


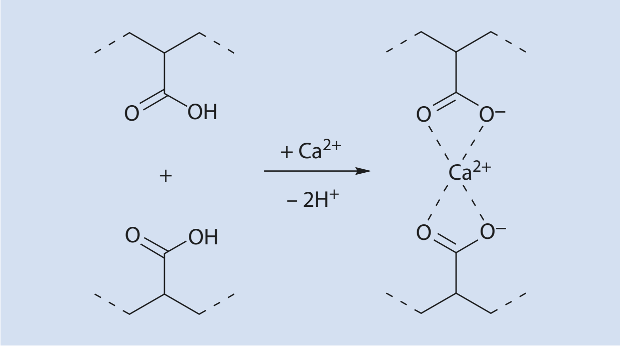
Fig. 15.17 Example photoinitiators and their decomposition products



or horizontal in relation to the ground. The varnish mixtures used for these top coats are extremely complex. An example of a monomer used in clear coat varnish is pentaerythritol tetraacrylate shown in Fig. 15.16.

The system quickly reaches its gelling temperature as the molecule has four reactive double bonds (▶ Sect. 8.3.4). Even if the transformation of all double bonds is not complete, in practice every molecule is integrated into the network via at least one double bond. Hardening can be initiated photochemically after the surface has been coated with the clear coat. To do this a so-called photoinitiator is added to the varnish which disintegrates into radicals when irradiated with light of a suitable wavelength and these trigger polymerization, or rather cross-linking. Two examples of these kinds of initiators and their decomposition products when irradiated are shown in Fig. 15.17.

Fig. 15.18 Physical cross-linking of acid functionalized polymers with calcium ions



The advantage of the photochemical cross-linking of such, highly functionalized systems is the rapid speed of the process. Depending on the type of system, a short flash of light is enough to transform a viscous, sticky monomer mixture into a hard, glossy, and scratch resistant surface.

15.2.5 Thermoreversible Cross-Linking: Ionomers

Chemical cross-linking reactions in which covalent bonds are formed are irreversible processes. The products generally have useful material properties; however, they are infusible and insoluble so they cannot be changed into a different shape by melting or dissolution. In contrast to this, there are materials which are reversibly cross-linked by non-covalent, physical cross-links. One particular example is materials cross-linked via ionic interactions, such as the copolymers of ethylene with 5–10 wt% acrylic acid. These macromolecules can be ionized using alkaline solutions and then cross-linked using multivalent ions such as Ca^{2+} (Fig. 15.18).

The ionic bonds formed function as cross-links at lower temperatures and impart properties to the material similar to those derived from covalent cross-links. These bonds dissociate at higher temperatures, in contrast to covalent bonds, so that the material can be melted and reshaped. New ionic links are formed again as the material cools.

15.3 Degradation Processes in Polymeric Materials

Similar to non-polymeric materials, which age over the course of time (they become rusty or weathered), most polymeric materials also show signs of ageing to a greater or lesser extent when exposed to the environment. Ageing can be brought about by:

- Temperature stress
- Light or UV radiation
- Oxygen
- Water (hydrolysis)
- Microorganisms (biodegradation)
- Mechanical stress

Fig. 15.19 Depolymerization of a polymer

$$\mathrm{P}_n \longrightarrow \mathrm{P}_{n\text{-}1} + \mathrm{M}$$

Fig. 15.20 Chain scission of a polymer

$$\mathrm{P}_{n+m} \longrightarrow \mathrm{P}_n + \mathrm{P}_m$$

The ageing of polymers involves in particular the following processes:

- Depolymerization
- Chain scission
- Oxidation and cross-linking

Cross-linking processes have already been dealt with in ▶ Sect. 15.2.

Depolymerization is, formally, the reverse of polymerization according to the equation shown in Fig. 15.19.

This process is only thermodynamically possible if the ceiling temperature of the material is exceeded or if the monomer is continually removed from the system by, for example, evaporation.

Whereas depolymerization leads to the monomer as one of the products, *chain scission* refers to the process whereby the polymer backbone is split somewhere along its length to yield two, usually, polymeric fragments. This process can be described as in Fig. 15.20.

These two degradation processes have different effects on the development of the molar mass distribution. With the assumption that the monomer molecules or the fragments remain in the system, then the number average of the degree of polymerization develops along a hyperbolic curve that is identical for both degradation mechanisms. However, the weight average of the degree of polymerization decreases significantly more quickly with chain scission than it does during depolymerization as is shown in Fig. 15.21 for the degradation of an oligomer P_n with $n = 13$. The reason for this is immediately apparent: if a monomer building block splits off from a polymer during depolymerization, then the weight average of the molar mass, or that of the degree of polymerization, is determined by the bigger molecule (▶ Chap. 3) and therefore only changes slightly. The weight average is therefore close to the original value for high degrees of polymerization. If, however, the same molecule is split in the middle because of a chain scission process, then two molecules that are roughly the same size are formed whose weight average degrees of polymerization are only half the size of that of the original macromolecule.

In general, the following applies: the closer the scission point is to the chain end, the smaller the effect on the weight average of the degree of polymerization. Conversely, if scission takes place in the middle of the chain, the difference between the various averages of the degree of polymerization is significantly smaller than that for depolymerization.

The courses of the different averages are shown in Fig. 15.21. In the case of chain scission, the curve for the weight average molar degree of polymerization can take on a slightly different course depending on how the process takes place as the position of scission is random during degradation. This, however, does not affect the validity of the statement in the previous paragraph.

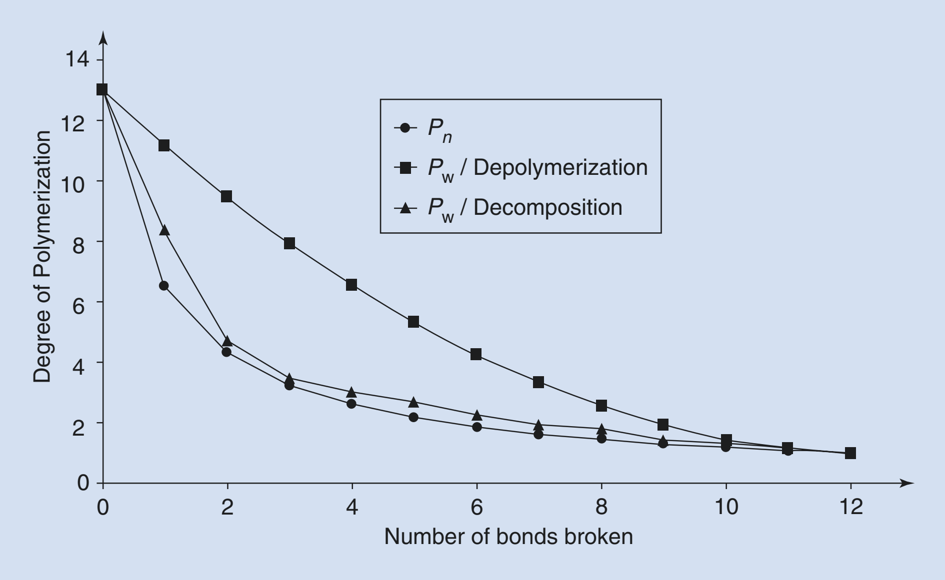


Fig. 15.21 Development of the number and weight average degrees of polymerization for a polymer with a degree of polymerization of 13 as a function of the mode of decomposition. The simulation assumes that all fragments remain in the system. P_n: number average degree of polymerization for both mechanisms (see text)

15.3.1 Degradation Mechanisms

Degradation processes that result in chain scission can take place with or without the participation of oxygen. In both cases, the first step of the process is the formation of radicals. This can take place thermally, photochemically, through the influence of gamma rays or electrons, and by oxidation. The polymer radical formed can then undergo a β-scission during which the degree of polymerization is reduced. During this process, the radical character of the system is not lost so that further radical reactions can take place. These processes are shown in Fig. 15.22.

A polymer radical can react in two different ways in the presence of oxygen, resulting in either an oxidative chain scission or peroxide formation.

The formation of peroxides occurs on the addition of a molecule of oxygen to the polymer radical. The peroxy radical formed in this process can then abstract a hydrogen atom from another polymer chain to form a hydroperoxide and a new polymer radical. This starts a chain reaction involving the absorption of oxygen and the formation of peroxides. This process is autocatalytic, and accelerates with time as the peroxides formed can generate new radicals. The peroxides produced can also rearrange into a ketone and an alcohol (Fig. 15.23).

The ketones formed during this process can take part in further scission reactions of the Norrish type when exposed to light. The Norrish-I-type reaction consists of an α-scission taking place and the generation of radicals which then initiate secondary reaction. In a Norrish-II-type reaction an excited carbonyl group abstracts a hydrogen atom from the γ-position (γ-H-abstraction) and the product decomposes to yield an α-olefin and a methyl ketone. These processes are shown in Fig. 15.24.

Fig. 15.22 Radical chain scission without oxygen

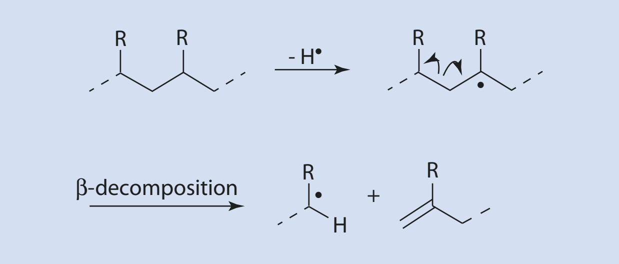


Fig. 15.23 Oxidation of polymer radicals

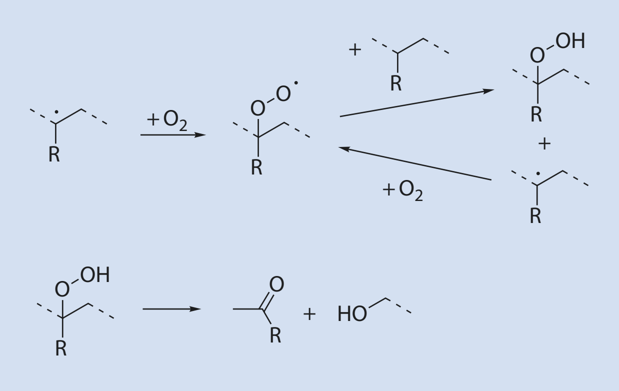
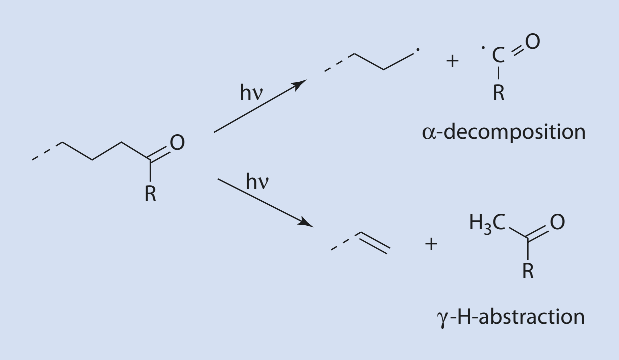


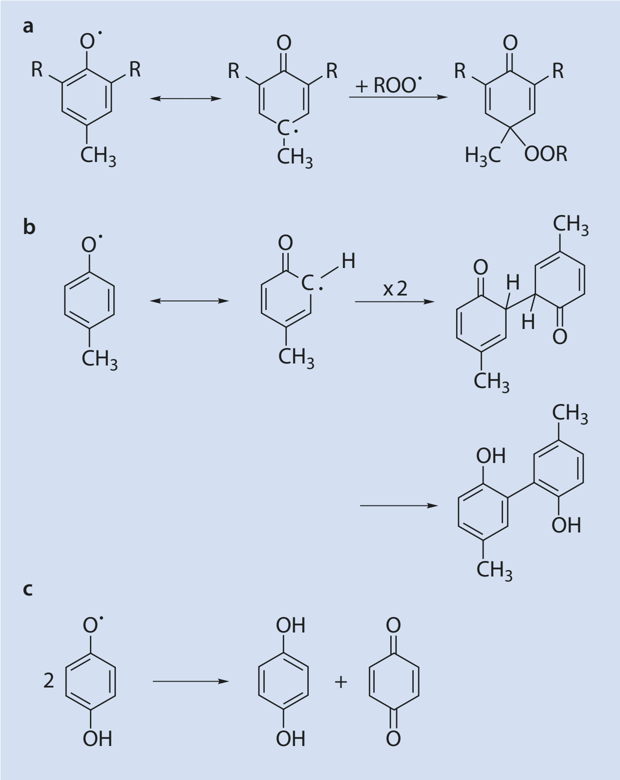
Fig. 15.24 Photochemical decomposition of polyketones via Norrish reactions



15.3.2 Stabilization of Polymers

Polymer materials can be stabilized by basically two types of compounds: antioxidants and UV stabilizers. These compounds are added to the polymer as additives during processing. A prerequisite for effectiveness is the miscibility of the additive with the polymer (► Chap. 2). It is particularly important when choosing additives to prefer those with a low tendency to crystallize; the additive's enthalpy of crystallization competes with the free enthalpy of the mixing process.

Fig. 15.25 Reaction mechanisms for phenolic antioxidants: (**a**) addition to a radical, (**b**) dimerization, and (**c**) disproportionation



Antioxidants are classified as primary or secondary. Primary antioxidants are used to intercept free radicals, formed via the mechanisms described above, and thus terminate any radical chain reactions. Secondary antioxidants reduce any peroxides that form.

15.3.2.1 Primary Antioxidants

Primary antioxidants are often sterically hindered phenols such as 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT). These substances saturate radicals by transferring a hydrogen atom and so terminate the reaction chain. The BHT radicals formed during this process take part in various follow-up reactions by combining with another radical, by dimerization, or by disproportionation (Fig. 15.25). The dimer is also an effective antioxidant.

15.3.2.2 Secondary Antioxidants

Sterically hindered amines, thioethers, or phosphites are used to reduce peroxides that have already been formed. A specific feature of amines is that they can react with peroxy radicals and with polymer radicals and can thus decrease the total radical concentration in the polymer. These processes are shown in Fig. 15.26.

As is evident from Figs. 15.25 and 15.26, antioxidants do not react catalytically, but stoichiometrically; i.e., they become completely consumed above a certain level of oxygen exposure. Once this level has been reached, the oxidation of the polymeric material takes place at the same rate as an unstabilized polymer. The period of use of the material is equivalent to the induction period of peroxide formation, i.e., the period of time in which

Fig. 15.26 Reduction of peroxides: (**a**) by tetramethyl piperidine (TMP) as an example of a sterically hindered amine, (**b**) by a thioether, and (**c**) by a triaryl phosphite

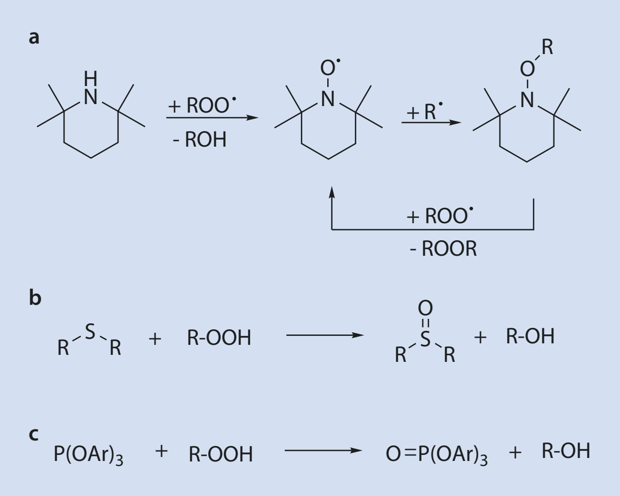
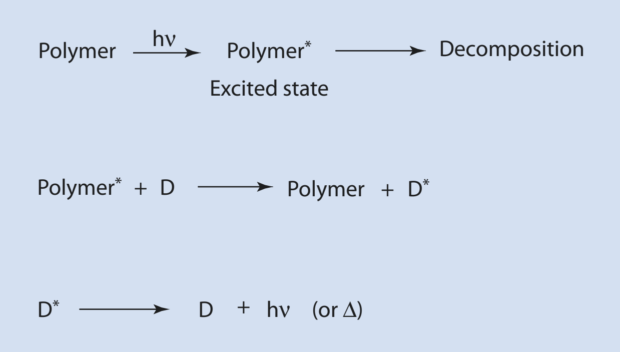


Fig. 15.27 Mode of action of UV-stabilizers. *D*: deactivator



the polymer is protected from oxidative stress by the remaining antioxidants. This time period can be lengthened by increasing the amount of additive. However, the amount is limited by the solubility of the additive and, if exceeded, the additive crystallizes or simply migrates out of the polymer. Too much additive can also, under certain circumstances, lead to detrimental side-effects, such as an increased absorption of water, oxygen, or other gases, together with changes in the mechanical or thermal properties (▶ Chap. 7).

15.3.2.3 UV Stabilizers

As light plays a significant role in many degradation processes, polymers can also be protected from degradation by UV-absorbing substances. How these so-called *UV stabilizers* function is shown in Fig. 15.27.

Initially, a chromophore in a polymer is excited by absorbing light. The excited chromophore then reacts, leading, for example, to the breaking of a bond. In the presence of a deactivator the excitation energy of the polymer can be transferred to the deactivator whereby the polymer reverts to its original state. The deactivation of the UV stabilizer can then take place either thermally or by the emission of light of a longer wavelength. In contrast to antioxidants, which are consumed by reaction with oxygen and radicals,

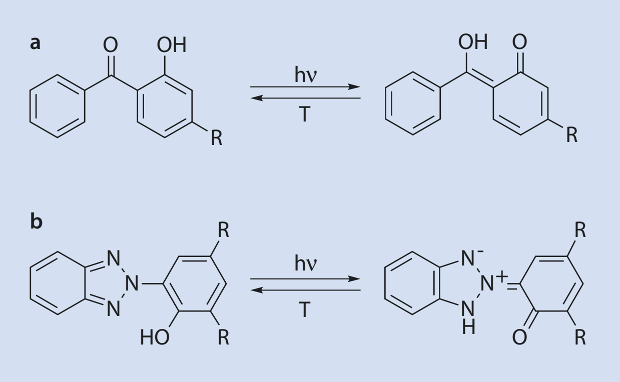


Fig. 15.28 Examples of UV-stabilizers. (**a**) 2-Hydroxy benzophenone. (**b**) Hydroxyphenyl benzotriazole

UV stabilizers can provide a high level of protection as long as no loss of stabilizer occurs, for example by desorption (migration).

Carbon black is the most common UV stabilizer. A good example of the use of carbon black is in car tires. These contain natural rubber, polybutadiene, and styrene-butadiene copolymers, all of which are susceptible to photoinduced, oxidative degradation because of the large number of double bonds along their polymer backbone. The UV stress of the material can be reduced by the addition of carbon black which provides for the long-term stability of the material. Absorbed UV light is simply converted into heat. As well as this, phenolic groups on the surface of carbon black act as radical traps (see above). The use of carbon black is responsible for the color of car tires.

Other examples of UV stabilizers are hydroxyl benzophenone or hydroxyphenyl benzotriazole. Fig. 15.28 shows examples of these UV absorbers.

References

Goldschmidt A, Streitberger HJ (2002) BASF Handbuch Lackiertechnik. Vincentz, Hannover
Goodyear C (1844) Improvement in India-rubber fabrics. U.S. Patent 3633