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Functional Polymers

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Classical polymer materials such as polyethylene and polyamide are familiar to all of us because of the multiplicity of uses in everyday life. Equally as omnipresent, but less well known, are the so-called functional polymers. As opposed to the structures previously discussed in ▶ Chaps. 13, 14, and 15, these polymers do not generally belong to the group of solid materials. Instead, these materials are mostly used in solution, where they induce a certain physical effect. Thus, most frequently it is not the polymer itself that is recognized but rather its effect or function—hence the name *functional polymers*. They are also referred to as *polymeric materials* or *effect substances* (Göthlich et al. 2005). Despite being so inconspicuous, many areas of our daily lives would be very different without them. For example, they are used in detergents, pharmaceuticals, and cosmetics.

As with most systems with which we come into contact in our daily lives, almost all environments in which functional polymers are used are aqueous, so most of these polymers are soluble in water. As demonstrated in ▶ Chap. 2, when a polymer dissolves in a solvent only a relatively small entropy gain is achieved. To reach the desired solubility in water, only relatively hydrophilic monomers can be considered; these interact, for example, via hydrogen bonds with water and are thus responsible for a favorable (negative) contribution to the free enthalpy of the solution. Such monomers are often electrically charged. The ionic polymers made from them are referred to as *polyelectrolytes*.

In principle, four different types of monomers are potential elements of functional polymers (◘ Fig. 19.1):

- Anionically charged, that is, acidic monomers such as acrylic acid
- Cationically charged, that is, alkaline monomers such as monomers carrying amino groups
- Electrically neutral, highly polar monomers, for example, vinyl pyrrolidone
- Zwitterionic monomers

Some examples of such monomers can be found in ◘ Fig. 19.1.

A substantial amount of the commercially available functional polymers are homo- and copolymers based on acrylic acid, vinyl pyrrolidone, and vinyl acetate. In addition, acrylate and methacrylate monomers play a vital role. Depending on their substituent, they can be hydrophilic (e.g., hydroxyethyl acrylate) or hydrophobic (e.g., lauryl acrylate). Cationic acrylates, based on amino functionalized acrylates, are common.

Zwitterionic monomers, such as the betaine presented in ◘ Fig. 19.1, have found only limited use to date. However, because of their unusual solubility behavior, they remain of interest. As opposed to most polymers, which are soluble in water and display an *upper critical solution temperature* and thus become insoluble above a certain temperature (▶ Chap. 2), zwitterionic monomers can give polymers that have a *lower critical solution temperature*, that is, a minimum temperature at which the polymer is soluble.

As well as the unsaturated monomers mentioned above, which are mostly radically polymerized in aqueous solution, some monomers are also used to make functional polymers, which are converted via a ring-opening polymerization (▶ Chap. 12), particularly ethylene oxide, ethylene imine, and oxazolines. Ethylene oxide can be polymerized both cationically and anionically and delivers a linear polymer that is soluble in water (◘ Fig. 19.2). Particularly important are polyethylene oxides with a lower molar mass, which are also referred to as polyethylene glycols. Industrially, anionic polymerization has achieved the greater relevance. In the polymerization of ethylene imine, the reaction is complicated because both the nitrogen atom of the monomer and that in the polymer are able to react with the active species (ammonium ion). The latter possibility leads to branched products, as demonstrated in ◘ Fig. 19.3.

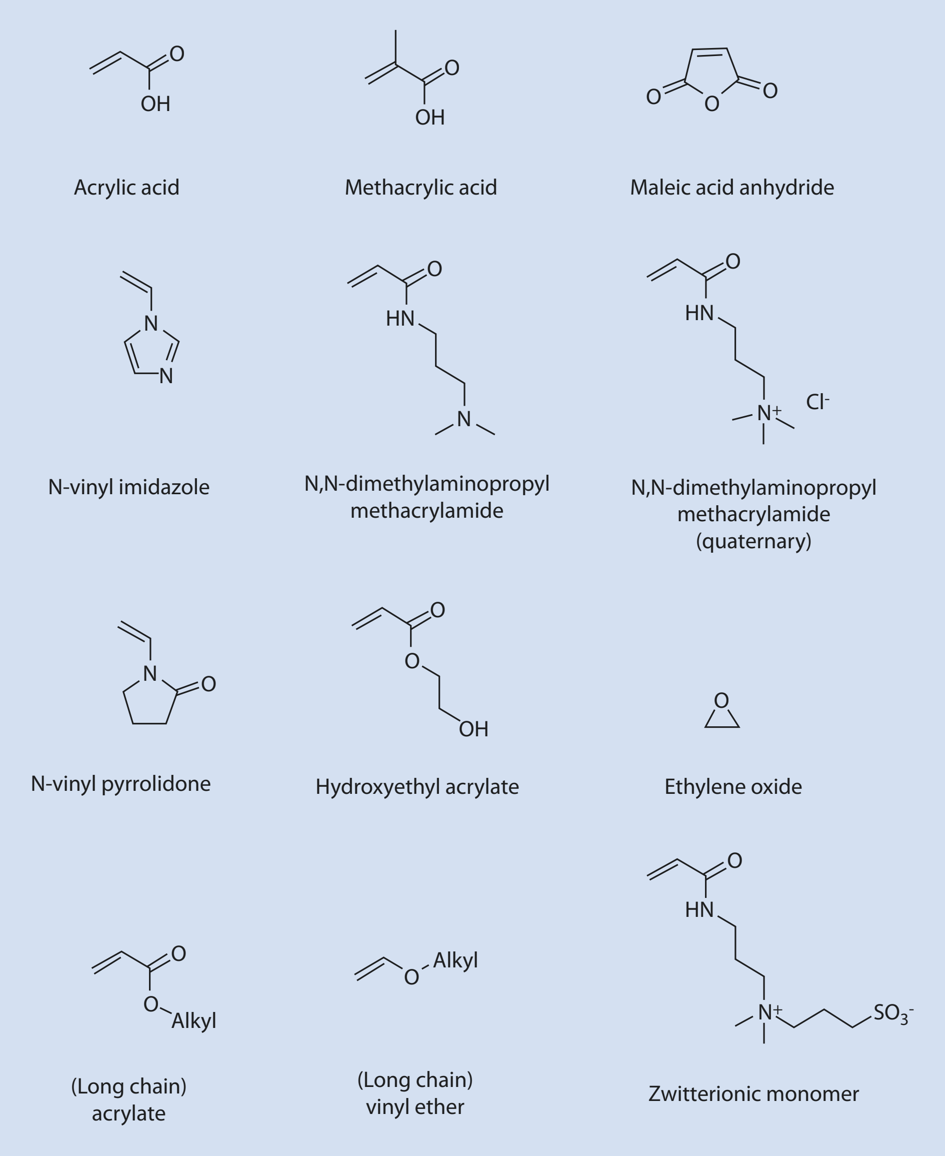
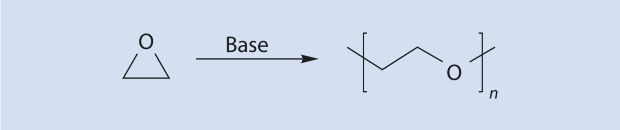


Fig. 19.1 Examples of monomers of functional polymers

Fig. 19.2 Polymerization of ethylene oxide to polyethylene oxide



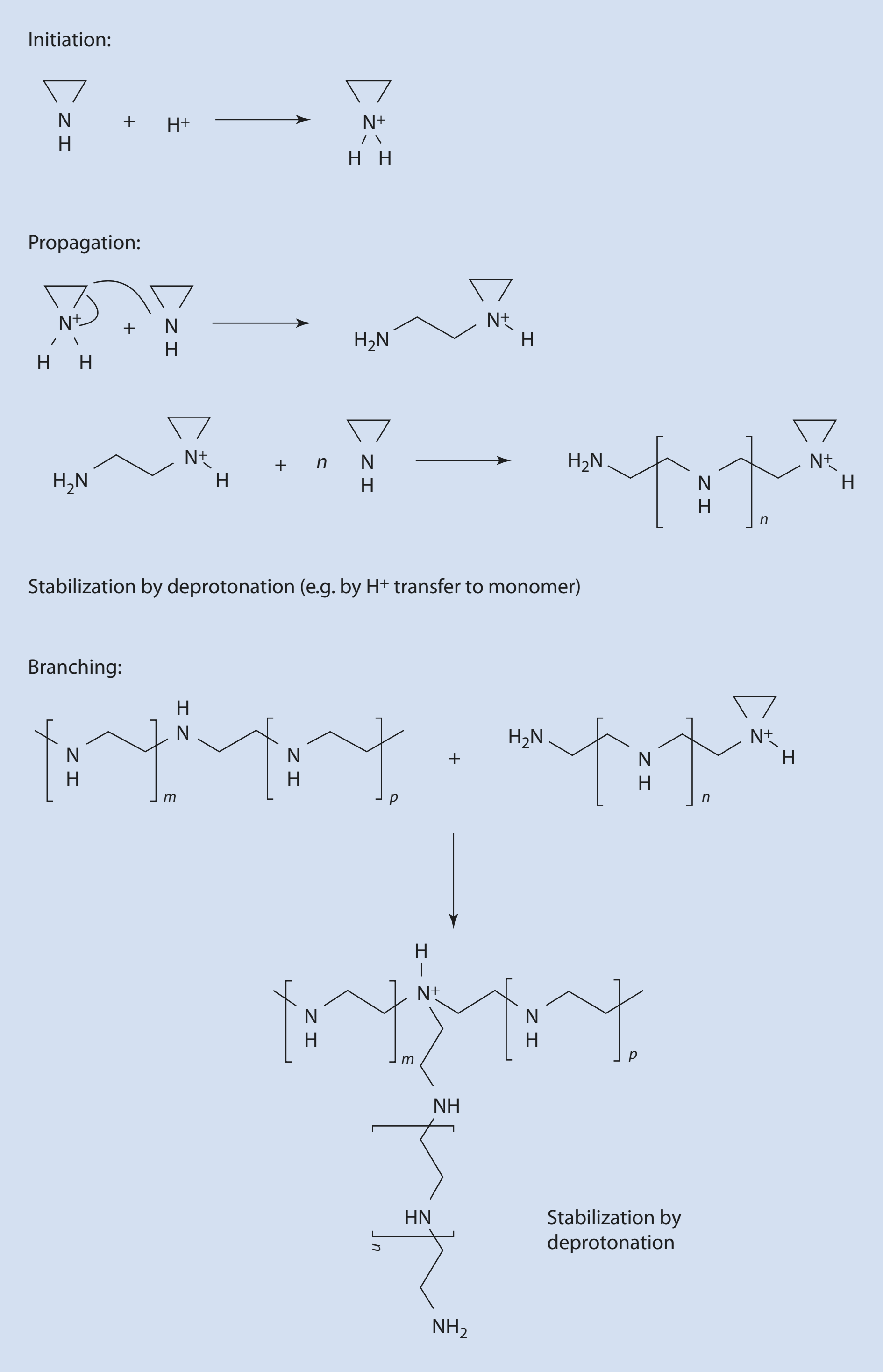
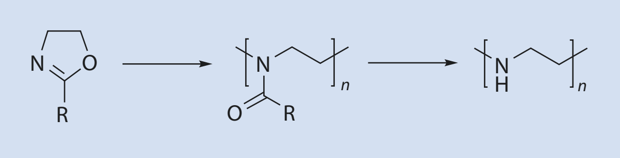


Fig. 19.3 Polymerization of ethylene imine to polyethylene imine



▪ **Fig. 19.4** Synthesis of linear poly(ethylene imine) by hydrolysis of a polyoxazoline

Linear polyethylene imine can be synthesized via a polymer analog reaction whereby an oxazoline monomer is cationically polymerized via ring opening (▶ Sect. 12.3) and subsequently hydrolyzed (▪ Fig. 19.4).

By copolymerizing the monomers shown in ▪ Fig. 19.1 with other monomers, a vast number of chemically varied polymer structures are accessible. The technical profile of these polymers can be additionally fine-tuned by selectively varying their molar mass.

In addition to the synthetic polymers discussed here, natural polymers or modified biopolymers, such as, for example, derivatives of cellulose (▶ Chap. 14), play an important role as functional polymers.

19.1 Polymer Dispersion Agents

One of the most important applications of functional polymers is the stabilizing of so-called *colloid systems*, which can also be referred to as dispersions. Here we are dealing with systems of two or more immiscible substances in which one material is finely distributed in the form of minute particles or droplets (dispersed phase) in the other (continuous phase) material. For reasons of clarity, the dispersed phase is often referred to as particles, although the models may also include emulsions.

Systems in which a solid is dispersed in a liquid are referred to as *suspensions*. If a liquid is homogenously and finely distributed in another liquid with which it is immiscible, it is referred as an *emulsion*.

In most cases, the only systems referred to as *colloid systems* are those whose dispersed particle diameters are less than 1 µm. Milk, in which small fat droplets are dispersed in water, is probably the most well-known example of a natural colloid system. Colloids are also technically of great importance. Thus, for example, all polymer dispersions which are produced via an emulsion polymerization and used, for example, as coating agents fall into this classification. It is also necessary to find a suitable method to disperse plant protection substances, which are often water insoluble, into stable, sprayable aqueous dispersions for convenient use by farmers.

Because of the large surface area of the colloid nanoparticles, the simple dispersion is, in most cases, thermodynamically unstable and requires stabilization. Without sufficient stabilization, the dispersion segregates into two macroscopic phases; for example, the oil droplets of an emulsion tend to float (cream) to the top of the system and finally coalesce into a separate phase. In general, the stabilization of a colloid system can occur in two ways:

- By electrostatic stabilization
- By steric stabilization

Electrostatic stabilization involves all particles being identical so that they repel each other electrostatically. The simplest approach is to adsorb charged molecules, for example, dodecyl sulfates, onto the dispersed particles. Once charged, the particles tend to assume the maximum distance from each other so that no flocculation or agglomeration of the particles takes place and the colloid stability is increased. Another approach to ensuring that the dispersed particles are mutually repulsive is to adsorb functional polymers onto their surface. Steric stabilization is discussed in detail below. It is also sometimes practical to stabilize colloids by the simultaneous adsorption of both polymers and ions—or of charged polymers. This approach is called *electrosteric stabilization*. For a more detailed study of colloid systems, the interested reader is referred to Tadros (2005).

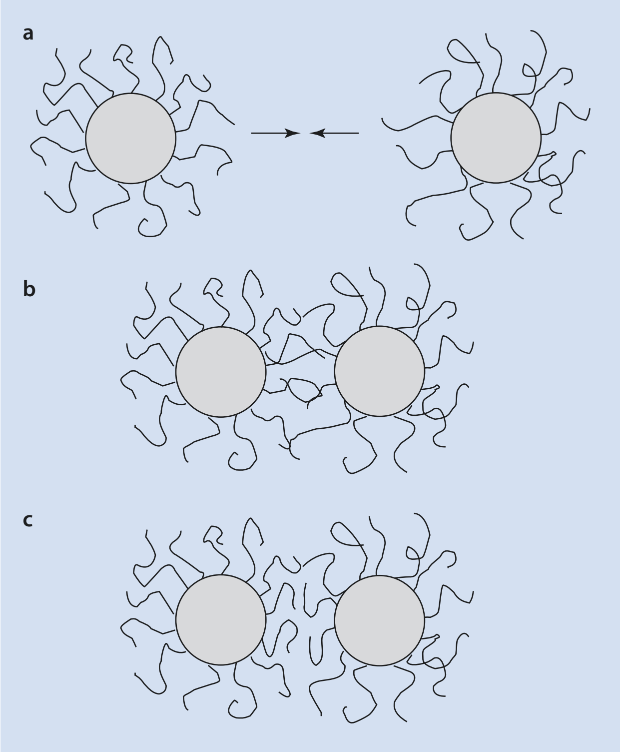
19.1.1 Steric Stabilizing of Colloid Systems: Protective Colloids

In ▣ Fig. 19.5 two colloid particles (not to scale) are shown which have been sterically stabilized by the adsorption of a polymer layer. For the steric stabilization of a particle with a diameter of 1 µm, the adsorbed polymer layer is ideally 5–10 nm thick. When two stabilized colloid particles approach each other, two unfavorable energy effects occur which impede or prevent close approach:

- The chains overlap (▣ Fig. 19.5b) and/or
- The adsorbed polymer layer is compressed (▣ Fig. 19.5c)

In both cases, the segment density between the particles increases. Both processes lead to a strong repulsion of the particles for two reasons:

▣ **Fig. 19.5** Scheme showing the processes occurring when two sterically stabilized colloid particles approach each other. (**a**) Starting condition. (**b**) Approach involving an entanglement of the polymer chains. (**c**) Approach involving a compression of the polymer chains



- The increased segment density between the particles leads to an osmotic pressure, which in turn results in the diffusion of solvent into the region between the particles and thus counteracts any further approach
- The configuration entropy of the chains decreases because of their reduced flexibility

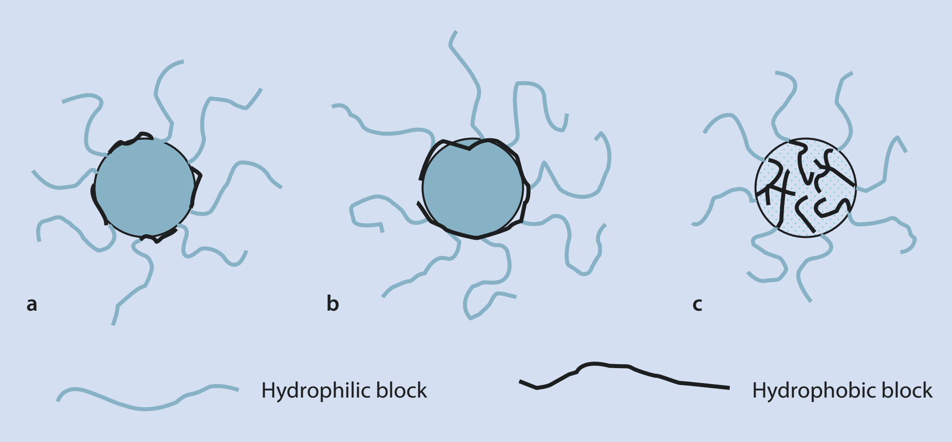
These repulsion effects are especially strong if the chains protruding into the continuous phase are very soluble in it so that they are highly solvated. On the other hand, the adsorption and thus the stabilization is obviously only effective if at least some subsection of the polymer also shows an affinity to the surface of the particle. Thus, *amphiphilic block copolymers* consisting of hydrophilic and hydrophobic blocks have proven to be particularly effective colloid stabilizers. In a similar manner, comb copolymers with a hydrophobic polymer backbone and hydrophilic side chains exhibit a marked tendency to adsorb onto the surface of particles or droplets.

The adsorption processes are shown schematically in ▣ Fig. 19.6. The thermodynamic driving force of the adsorption is both enthalpic and entropic in nature:

- The absorption of a polymer onto a surface involves a favorable entropy change, because *one* polymer chain at the surface of the particle supplants a larger number of solvent molecules
- The favorable enthalpy results, in the case of hydrophobic particles in water, for example, are that the hydrophobic areas of the polymer accumulate onto an equally hydrophobic surface or, in an emulsion, they can dissolve in an oil phase

Such amphiphilic steric stabilizers are also referred to as *protective colloids*. Technically, block copolymers consisting of ethylene oxide and propylene oxide are commonly used (▣ Fig. 19.7). In these polymers the hydrophobic propylene oxide middle section functions as an anchor group for the adsorption of the polymer on the surface, whereas the hydrophilic polyethylene oxide segments protrude into the water phase leading to steric stabilization.

Concrete plasticizers, such as those discussed in ▸ Sect. 19.1.2.3, are examples of amphiphilic comb polymers.



▣ **Fig. 19.6** Possibilities for adsorbed amphiphilic polymers. (**a**) Adsorption of an ABA-triblock copolymer on a particle. (**b**) Adsorption of a comb copolymer on a particle. (**c**) Adsorption of an AB-block copolymer to an oil droplet

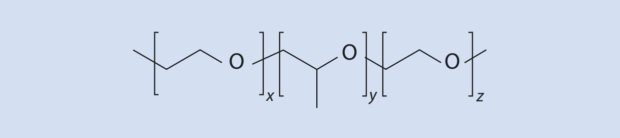


Fig. 19.7 ABA-triblock copolymer of ethylene oxide (forming the A-block) and propylene oxide (forming the B-block) as an example of a typical protective colloid

19.1.2 Applications of Polymer Dispersion Agents

In this section some important applications of polymer dispersion agents are discussed in more detail.

19.1.2.1 Paper Coatings

The surface of most paper one encounters in daily life is modified with a surface coating. This coating fulfills various functions, such as to generate gloss (common in illustrated magazines) or to reduce absorbency. The latter is an essential characteristic of writing and printing paper to prevent the ink or printing paste from running as they do on blotting paper so that a sharp printing image can be achieved.

A material often used for paper coating is so-called *China Clay*, a layered silicate with negatively charged surfaces and positively charged platelet edges. Thus the platelets tend to form a "house-of-cards" type structure (Fig. 19.8b). An extremely voluminous but mechanically fairly stable superstructure emerges. To destroy it and to transfer the layered silicate into a fluid form of low viscosity which can be spread onto the paper, a large amount of water must be added. Even at a water content of 40 wt% the mixture is still pasty and not fluid at room temperature. To obtain a spreadable mass using only water would require considerably higher amounts of water but these would then have to be evaporated in the finishing process which would be energetically unfavorable, time consuming, and expensive.

An alternative to using a dilute spreading mass is to add a small amount of polyacrylic acid with a molar mass M_w of ca. 2000 g/mol. Polyacrylic acid is largely in its dissociated form at a neutral pH and is thus negatively charged. For this reason it preferably adsorbs onto the positively charged platelet edges, neutralizing their positive charge. This leads to

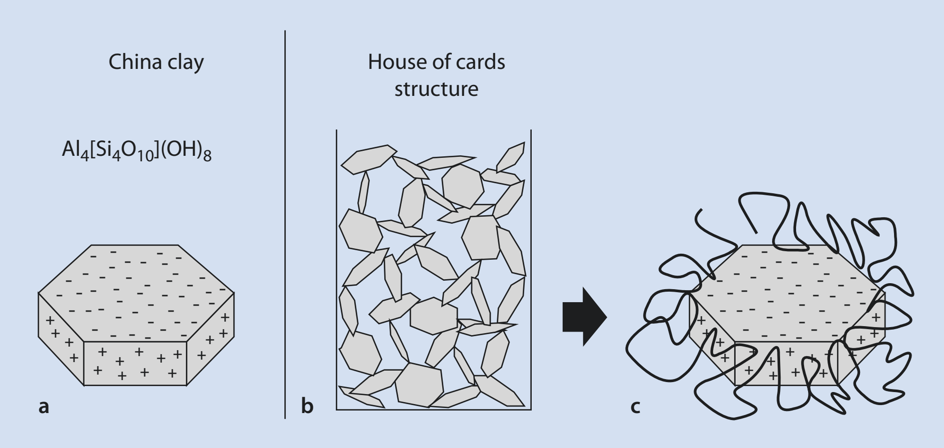


Fig. 19.8 (**a**) Surface charge distribution. (**b**) "House of cards" structure of China Clay. (**c**) Interaction of China Clay with polyacrylic acid

the collapse of the stable "house-of-cards" structure. The viscosity decreases rapidly to yield a relatively thin, spreadable paste, even at high solid contents. The mechanisms described here are shown schematically in ◘ Fig. 19.8.

19.1.2.2 Additives for Seawater Desalination

Clean drinking water is becoming an ever more valuable resource in view of an increasing world population and ecological and climatic changes. Especially in the countries of the Middle East, seawater desalination is employed to supply much of the water demand. The majority of desalination plants operate via reversed osmosis and large plants can desalt several hundred thousands of cubic meters of seawater per day. The remaining concentrated brine must be effectively prevented from crystallizing and clogging up the pipes. These residue dispersions can be stabilized by adding polymer dispersion agents to prevent agglomeration or precipitation on the walls. In this case too, negatively charged polyelectrolytes based on acrylic acid are commonly used. The working principal of these dispersion agents is similar to that shown in ◘ Fig. 19.8.

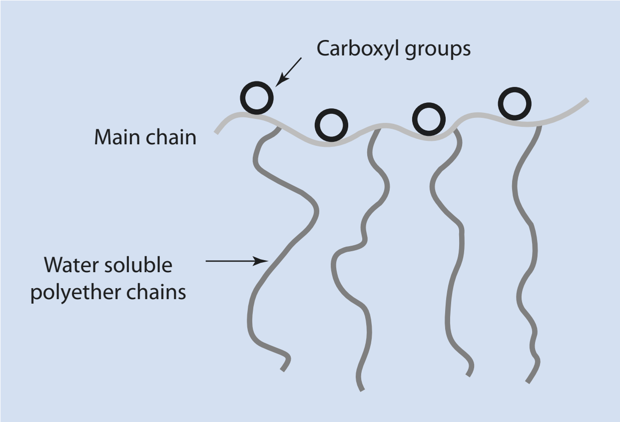
19.1.2.3 Plasticizers

Concrete is the largest volume industrially produced product in the world. Chemically, it is a mixture of cement, sand, gravel, and water. Cement is a heterogeneous mixture of various minerals based on the calcium aluminates, silicates, and sulfates. With water, this mixture forms hydrates in a strongly exothermic reaction whereby the mineral particles are joined to each other, leading to the increasingly solid material as the concrete sets. Because of the heterogeneity of the materials and the complexity of the various processes, the exact details have not yet been identified.

Notwithstanding, the addition of water to the above mixture has two effects: it makes the water available for forming the hydrates essential for the setting process and it turns the solids into a liquid facilitating rapid mixing and forming processes, for example, it can be poured into a shape before it solidifies—the so-called *hardening*. The amount of water added is critical for both the processability and the strength of the concrete. Although the flowability of the concrete increases with the amount of water added, only approximately 30 % water (relative to the mass of the concrete) is chemically bound as hydrate water in the end product; the rest evaporates over time. Too much water leads to an increased porosity and a decrease in the strength of the resulting concrete. For the production of high-performance concrete, necessary, for example, for the construction of skyscrapers, it is beneficial to limit the amount of added water to a minimum. To this end, polymer plasticizers are a good choice.

Functional polymers have been used as plasticizers for concrete for a long time. Older products of this type are sulfonated lignin, sulfonated melamine-formaldehyde-resins, or sulfonated naphthalene-formaldehyde-resins. Lignin sulfonate is a structurally ill-defined polymer that is negatively charged by its sulfonic acid groups. It is a by-product of paper production. Formaldehyde condensates are discussed in ► Chap. 8. These products are inexpensive but achieve only a limited effect. For high-performance *superplasticizers* for cases where high demands are placed on the hardened concrete, polycarboxylate ethers are commonly used. Polycarboxylate ethers are polymers based on carboxylic acids, for example, acrylic acid or methacrylic acid. These are copolymerized with a comonomer containing a hydrophilic polyethylene chain, a so-called *macromonomer* (◘ Fig. 19.9). A typical example of a macromonomer is polyethylene glycol, which has a functionalized group, such as an acrylate function, at one end. The resulting polymers have the structure of graft copolymers.

Fig. 19.9 Sketch showing the structure of a polycarboxylate ethers



This generic structure is extremely variable in detail. By varying the molar mass of the comb polymer and the number of polyether side chains and their length, the effect of the polymer on the hardening and setting process of the concrete can be influenced considerably and hence controlled. The ability to control the process is important in practice, as the demands on the hardening and setting kinetics vary considerably depending on the application. Whereas a manufacturer of ready-set concrete parts, who mixes the concrete and pours it into molds on site, requires the quickest possible setting in order to finish the product and to fill his forms anew, a producer of ready-mix concrete, who needs to transport his product to the desired site in a concrete transport vehicle, aims to achieve the opposite: obviously, the concrete should not harden in the transport vehicle. By varying the different parameters, the hardening and setting process kinetics can be controlled over a wide range, depending on the application.

As a mechanistic model of the liquefying effect, it is assumed that the polymer with its polycarboxylate backbone adsorbs onto the surface of the mineral particles of the concrete and the polyether side chains protrude into the aqueous phase. Because of the steric dispersion effect of the long polyether side chains, the cement particles are effectively held apart. This postpones the hardening of the concrete and enables a prolonged processing time (◘ cf. Fig. 19.6b).

19.1.2.4 Scale and Color Transfer Inhibitors

Functional polymers also play a large role in detergents. Modern heavy-duty detergents contain about 7 % of various polymers, which predominantly inhibit color transfer and scale development and should protect the textile becoming soiled. In the following, these functions are briefly discussed in more detail.

Scale Inhibitors

As in a seawater desalination plant, in the washing machine there is a danger that, over time, calcium and magnesium sediments build up in the machine components—especially on the heating elements—and compromise the performance of the equipment.

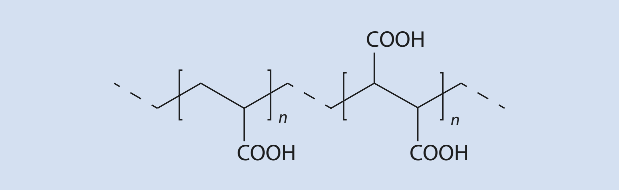


Fig. 19.10 Structure of acrylic acid-maleic acid copolymers

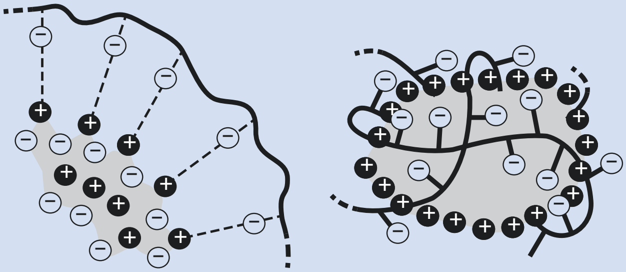
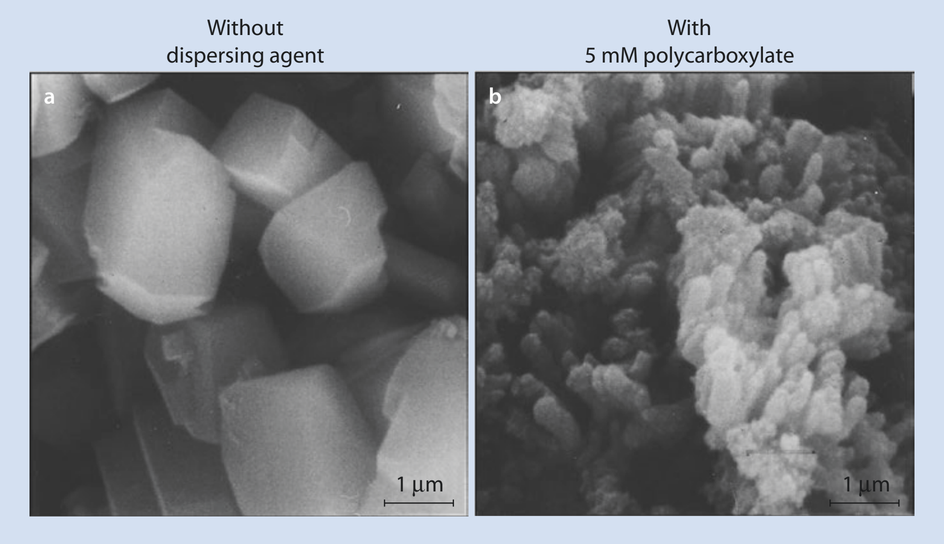


Fig. 19.11 Scheme showing the interaction of polycarboxylates with calcium or magnesium crystallites

Moreover, such fine precipitates can also settle on the textile material, reducing wear comfort. Adding negatively charged polyelectrolytes, such as those described in ► Sects. 19.1.2.1, 19.1.2.2, and 19.1.2.3, to the wash process can also prevent the development of scale. In detergents, statistical copolymers of acrylic acid with maleic acid are often used (Fig. 19.10), which (after neutralizing the carboxylic acid groups) have a particularly high charge density. Generally, the molar mass of the polymers used in detergents are a little higher than those used in paper coating.

The mode of action of these polymers presumably relies on several effects. As with all carboxylic acid groups, the carboxylate functions in the polyelectrolytes being discussed have a high affinity toward calcium and magnesium ions and so reduce the activity of these ions in the wash water (the so-called wash liquor). The carboxyl-functionalized polymers also effectively adsorb onto the surface of alkaline earth minerals. The absorbed polymer chains prevent the crystals from further growth. At the same time, as discussed above, the polymer serves as a dispersion agent and thus prevents the precipitation of sediment on surfaces (Fig. 19.11).

Two REM pictures of calcite crystals formed in the presence or absence of a polycarboxylate but under the same conditions are shown in Fig. 19.12; the effects are clearly visible. Because the polymer does not react stoichiometrically but rather in a comparatively small amount with the surface of the crystals, amounts of less than 1 ppm of polymer



■ **Fig. 19.12** REM-pictures of calcite crystals (**a**) in the absence and (**b**) in the presence of a polycarboxylate

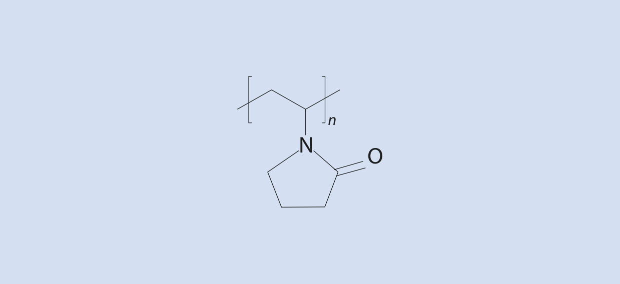
are sufficient for achieving a massive effect. In total, the crystallization of inorganic minerals can often be influenced or controlled considerably by adding dissolved polymers to crystallizing solutions. This has been discussed in numerous scientific papers (e.g., Cölfen 2003; Wegner et al. 2007; Huang et al. 2008).

Color Transfer Inhibitors

Another problem arising when washing colored textiles is color transfer, commonly referred to as "color running." This undesired effect arises because color molecules that have not adsorbed onto the surface of the textile permanently enough dissolve into the wash water during the washing process and re-adsorb onto differently colored or even white textiles in an equilibrium process. These processes can also be inhibited by using functional polymers; in this case, homo- or copolymers based on polyvinyl pyrrolidone (PVP) are effective (■ Fig. 19.13).

Despite lacking an electric charge, PVP is an extremely polar polymer because of the high dipole moment of the pyrrolidone group. This dipole moment enables a relatively stable complex formation with any color molecules in the wash water, reducing their concentration and their tendency to re-adsorb. ■ Figure 19.14 shows a model of such a colorant–PVP-complex. With its electroneutrality, the pyrrolidone group can interact with both ionic and neutral molecules so that a large number of colorants can be prevented from "color running" with this polymer.

Fig. 19.13 Structure of PVP



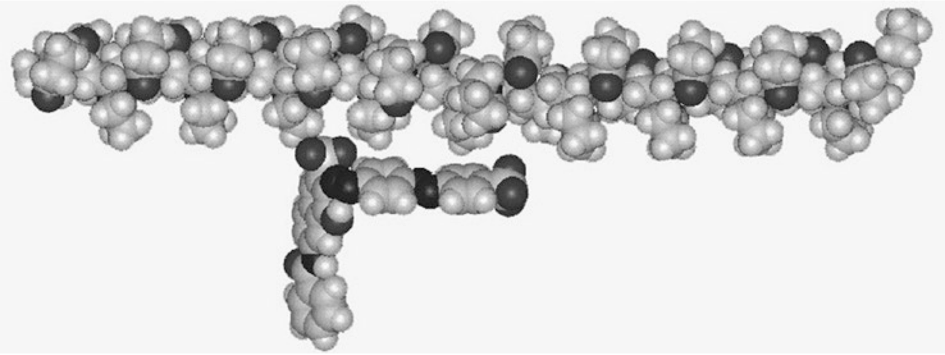


Fig. 19.14 Model for a PVP-complex with the Dye Direktrot 81

19.2 Flocculants

Polymer dispersion agents have been discussed in ▶ Sect. 19.1.2 but if the basic polymer structure is changed, functional polymers which have the exact opposite effect can be made. Such polymers are designed to cause colloidal systems to flocculate. To this end, the fact that such systems are usually thermodynamically unstable and sterically or electrostatically prohibited from coagulating by absorbed materials is exploited. If the activation barrier associated with this kinetic stabilization can be overcome, the system flocculates and the particles agglomerate.

Flocculation is of great importance in the field of wastewater treatment. A large portion of the pollutants in wastewater is present in the form of particles or droplets, which are colloidal and highly stabilized by negatively charged surfaces. These often extremely small particles are hard to remove from the wastewater. Filtering techniques can be ruled out because of the vast amounts that have to be treated. Techniques which precipitate the pollutant particles are more effective and result in purified water and a so-called sludge. The latter can be disposed of, for example, by incineration.

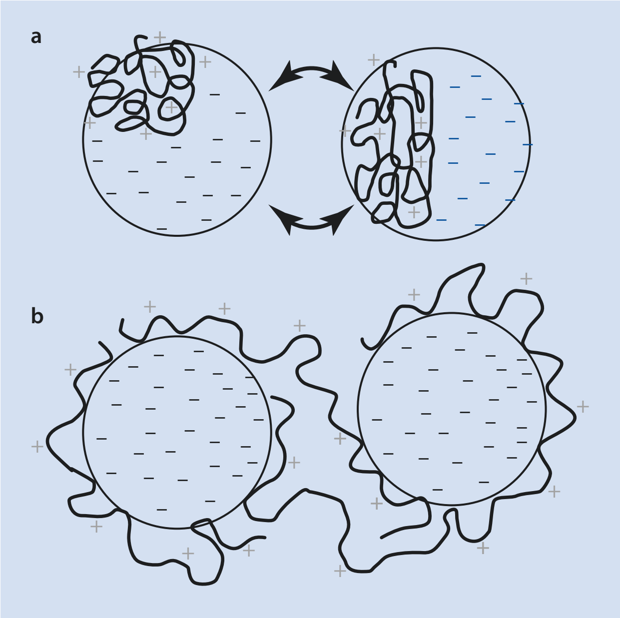


Fig. 19.15 Mechanisms of the flocculation employing high molar mass cationic polymers. (**a**) Mosaic adhesion. (**b**) Bridge building

Technically, the flocculation is often accomplished by the addition of iron salts. However, because of the high colloidal stability of the particles formed, they do not agglomerate effectively and the accumulating sludge still contains up to 90% water. For this reason, further polymer flocculating agents are added to induce improved aggregation. The goal of this second flocculation is to produce larger structures by destabilizing the system, which then sediments or can be separated more easily. For this application, copolymers based on acrylamide with cationic comonomers are used. Because of their positive charge these polymers adsorb onto the negatively charged surfaces of the pollutant particles very effectively. However, in contrast to the charged dispersion agents discussed in ▶ Sect. 19.1.2, for this application high molar mass polymers are generally employed.

The mechanism by which these polymers are believed to work is shown in Fig. 19.15. In principle, two mechanisms are discussed:

- With the so-called *mosaic adhesion* the polymers adsorb to only some areas of the particle surface. In these areas, the originally negative charge of the particles is locally reversed, which results in the system containing particles whose surfaces have both positively and negatively charged areas. The oppositely charged areas of two or more particles attract each other so that the particles—in analogy to the “house of cards” structure in Fig. 19.8b—agglomerate.
- For the so-called *bridging precipitation* it is assumed that a large molar mass polymer is adsorbed onto more than one particle to form “bridges”. Obviously, a relatively high molar mass is required for this to occur.

A great advantage of the second precipitation is the markedly reduced water content in the resulting sludge, which requires considerably less energy by incineration.

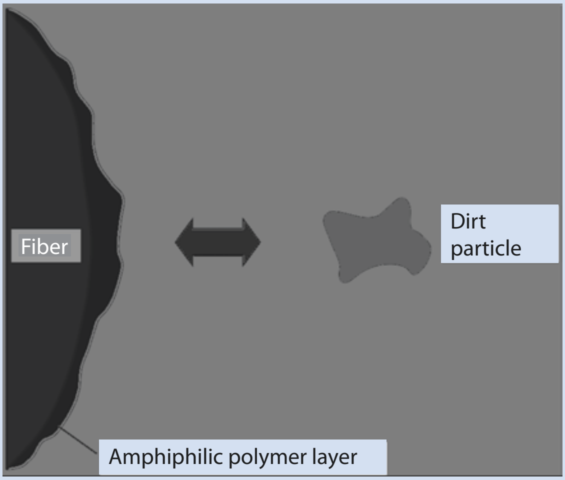


Fig. 19.16 Schematic diagram of the impregnation of textiles with amphiphilic polymers to protect against the adsorption of hydrophobic grime

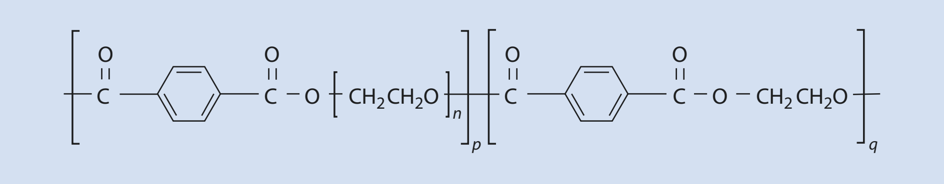
19.3 Amphiphilic Systems for Surface Functionalization

Amphiphilic polymers, polymers which have both hydrophilic and hydrophobic molecular parts, can be synthesized with different polymer structures. Statistical copolymers made of hydrophilic and hydrophobic monomers exhibit a relatively narrow sequence of these elements, whereas block copolymers are made up of a few, relatively large domains of different polarity. Graft copolymers have a similar structure, in which the hydrophilic branches are grafted onto a hydrophobic backbone or the other way round.

If such a polymer is adsorbed onto a surface with, for example, a hydrophobic character, then the hydrophobic parts of the polymer are orientated predominantly toward this surface whereas the hydrophilic parts face outward. Macroscopically, this leads to an alteration of the polarity of the surface, which is expressed, for example, in an altered wettability by water or organic solvents. Moreover, the tendency of further hydrophobic molecules or particles to adsorb onto the surface with reversed polarity is significantly reduced.

This effect is used technically, on a large scale, for textile impregnation. For this purpose, amphiphilic polymers can be used as additives in detergents. During the washing process they are organized onto the hydrophobic textile fibers and render them hydrophilic (Fig. 19.16). The adsorbed polymers have the effect that hydrophobic grime particles, such as oil droplets, which soil the textile as it is being worn, cannot bind onto the fabric as strongly because the adsorption of these hydrophobic grime particles onto the hydrophilized surfaces is energetically less favorable. Subsequently, they can be washed out considerably more effectively in the washing processes. For this reason, these macromolecules are referred to as *soil release polymers*.

Chemically, these polymers are generally copolyesters based on terephthalic acid, glycol, and polyethylene glycol (Fig. 19.17). By incorporating polyethylene glycol, the polyester becomes a block-structure in which the hydrophilic polyethylene glycol blocks are separated by hydrophobic polyethylene terephthalate structures. The block structure



■ **Fig. 19.17** Structure of soil release polyesters

can be effectively controlled by the molar mass of the polyethylene glycol used for the polycondensation and the molar ratio of glycol and terephthalic acid to polyethylene glycol.

The hydrophobic blocks adsorb as anchor groups effectively onto polyester fibers and polyester mix textiles, whereas the polyethylene terephthalate and glycol blocks are responsible for making the surface hydrophilic and thus impregnating the fabric. Similar effects are less strong on pure cotton because of its different surface structure.

19.4 Thickeners

As well as those applications already discussed, which rely on an interaction between polymers and surfaces, dissolved functional polymers can also have a strong physical effect on the total system. One profound effect is the polymer-typical increase of the solution viscosity (▶ Chap. 3). This thickening effect is used in many domestic products, for example, cosmetics, in which the system is required to have a viscous or gelatinous consistency.

In principle, every high molar mass, water-soluble polymer could be used as a thickener. However, it is often desired that the viscosity of the system is switchable, that is, it can be influenced by changing the intrinsic system parameters. With polyelectrolytes this can be achieved by varying the pH or the salt concentration. This is illustrated in ■ Fig. 19.18 with a polycarboxylic acid as an example.

At low pH values, the carboxyl functions of the polyelectrolyte are protonated and the polymer entanglements are electrically neutral. Thus, they are present simply as solvent swollen polymer coil (▶ Chap. 2). If the carboxyl functions are neutralized by adding a base, for example, NaOH, an increasing accumulation of negative charge builds up along the polymer chain. As these repel each other, the polymer chains spread out to reduce the interaction. At a certain point the chains overlap and the viscosity of the system increases. This effect is reversible by adding acid. Alkali salts, for example, sodium chloride lead to a similar effect which can be explained as follows.

The strength of the electrical field generated by an ion in solution is, intuitively, inversely proportional to the distance from the charge. Mathematically, this decrease can be described by an exponential function. Here the distance in which the potential of the electrical field falls by the factor of Euler's number (approx. 2,718, this means a decrease of approx. 63.2 %) is given by the so-called *Debye length* λ_d. This length is given by

$$\lambda_d = \sqrt{\frac{\varepsilon \cdot kT}{2N_A \cdot e^2 \cdot I}} \tag{19.1}$$

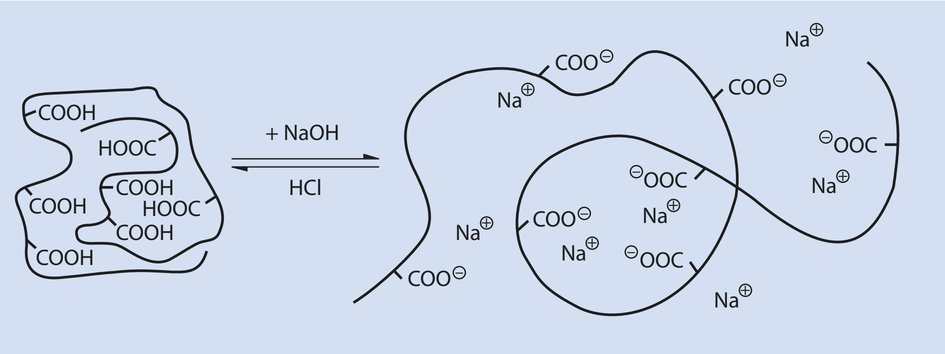


Fig. 19.18 Spreading of a polyelectrolyte coil by varying the pH

ε	Electrical permittivity
k	Boltzmann constant
N_A	Avogadro constant
e	Elementary charge
I	Ionic strength of the solution

For singly charged salts such as sodium chloride, the ionic strength equals the activity, and thus, approximately, the concentration of the salt. Equation (19.1) means that the electrical field of an ion falls at a higher salt concentration in a solvent. Thus the Debye length in a 0.001 M NaCl solution at 25 °C is ~10 nm and shortens to ca. 1 nm in a 0.1 M solution. Thus, the effective electrical field of the ion "shrinks." This effect is often termed a *shielding* of the electrical charges. As a result, the charges along the polymer backbone repel each other less if NaCl is added to the solution. This leads to the chains contracting and the viscosity decreasing. Many thickeners are therefore sensitive to the salt concentration of the solution.

The so-called *associative thickeners* are particularly effective. These are statistical copolymers consisting of a hydrophilic monomer, for example, acrylic acid, with a small amount of a non-polar comonomer, for example, a long-chain acrylate. If such polymers are dissolved in water, the alkyl moieties tend to agglomerate. If such an association occurs between various polymer chains, this results in a physical bridging between these chains and eventually leads to gel formation and a large increase in the viscosity of the system. Because of the extreme growth of the polyelectrolyte, polymer entanglements and the strength of such hydrophobic interactions in aqueous systems, minute amounts of thickeners (a few percent, sometimes even less) are enough to gel the complete system.

19.5 Super-Absorbents

In contrast to the soluble polymer systems discussed thus far, with the so-called *super-absorbents* we are dealing with cross-linked insoluble polymers. Such polymers can only swell in contact with a solvent. Although this effect is not pronounced for most polymers, super-absorbers are optimized to absorb a maximum amount of water. To achieve this goal, they are made from cross-linked polyacrylic acid which has been

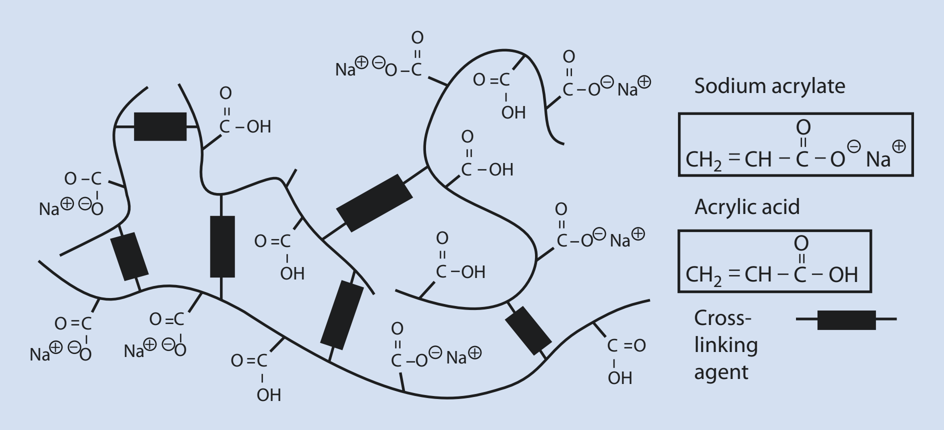


Fig. 19.19 Structure of cross-linked sodium polyacrylate (super-absorber)

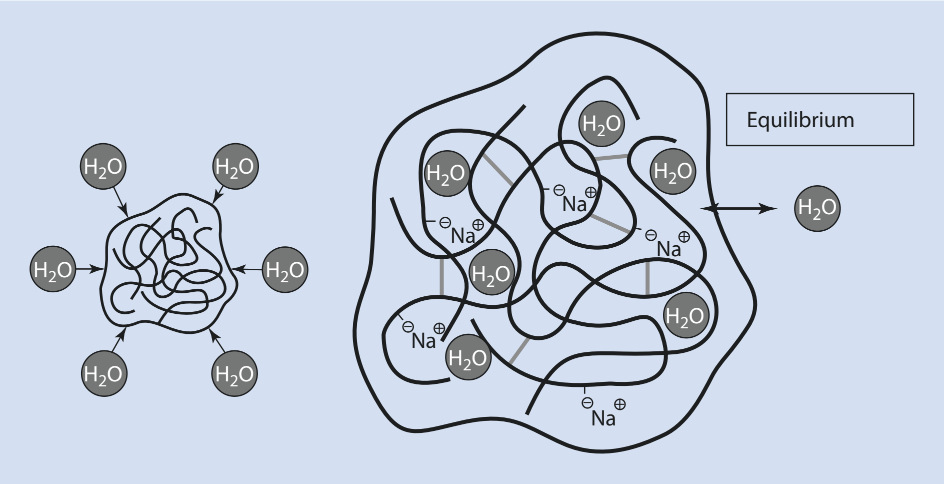


Fig. 19.20 Swelling of a super-absorber produced by osmosis

partially neutralized with sodium ions (Fig. 19.19). Because of their high internal salt concentration, a considerable osmotic pressure develops when they come into contact with water and the water is “sucked into” the gel particles. The gel particles swell dramatically. The water absorption is only halted when the restoring force built up by the chains becoming stretched between the cross-linking points is equal to the osmotic driving force (Fig. 19.20).

The main application of super-absorbers is diapers and other hygienic products. For these products, super-absorber particles are wrapped in a so-called *fluff* pulp (bleached, non-woven cellulose fibers). This textile ensures a rapid distribution of, in most cases, the suddenly increasing amounts of liquid, and the super-absorbers take care of its storage, making the article appear dry. Osmotically functioning super-absorbers show notable advantages in practice:

- The amount of liquid that can be absorbed is extremely large. Some super-absorbers can absorb up to a thousand times their own weight before they cease to swell. This results in a gel which consists of up to 99.9 % water but which feels dry on the outer surface.
- Because of the osmotic effect, the liquid is bound much more strongly to the absorber than is the case, for example, for absorption from the capillary action of a sponge. Thus, water absorbed by a super-absorber cannot be released by simply "squeezing," as it can with a sponge. For use in diapers this is a crucial factor, as the bound urine is not released as the baby moves about.

Further, volume-wise less important, applications of super-absorbers are their use as soil improvers in crop fields (preservation of moisture for dry periods), for moisture control in tunnel construction, and to prevent contact sweat in furniture seats.

19.6 Polymers for the Formulation of Active Ingredients

To conclude this chapter, the use of functional polymers in the area of formulation of active ingredients, particularly in pharmaceutical applications, is highlighted

In a typical tablet, that is, in a solid oral dosage form, functional polymers are used in the following applications.

19.6.1 Matrix Materials

Many pharmaceutical ingredients are already active in milligram amounts. As these minute amounts cannot be handled easily, polymers are used in which the active ingredients dissolve and become homogeneously distributed. Hereby the active ingredient is transformed into a form which a patient can handle. Such a "solid solution" can be imagined as a conventional solution of an organic material in a solvent, in which the solvent has been replaced with a polymer. Thus the active ingredient is no longer present in crystalline but in molecular form. An example for a suitable matrix material is the PVP mentioned above.

19.6.2 Coatings

Tablets covered in a smooth polymer coating can be swallowed more easily. Moreover, the coating can be colored. Colored tablets are easier for the patient to recognize, which reduces the danger of confusion. Furthermore, the often unpleasant taste of the active ingredients can be masked with a suitable coating. An example of a polymer suitable for pharmaceutical coating is a graft copolymer of vinyl acetate on polyethylene oxide, whereby the grafts have been hydrolyzed to vinyl alcohol (◘ Fig. 19.21 and ▶ Chap. 15).

Many oral pharmaceutically active ingredients are sensitive toward acid and should only be released after passing through the stomach. In these cases a coating is used which is resistant with respect to the stomach acid. Such polymers are usually insoluble in acid but soluble above pH 5.5. Such a pH-dependent solubility can be achieved by building carboxyl groups into the polymer. These are ionized at high pH levels and markedly

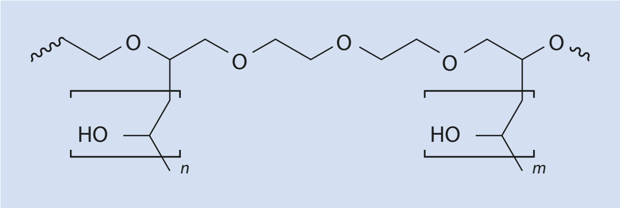


Fig. 19.21 Graft copolymer of vinyl alcohol (from vinyl acetate) and polyethylene oxide

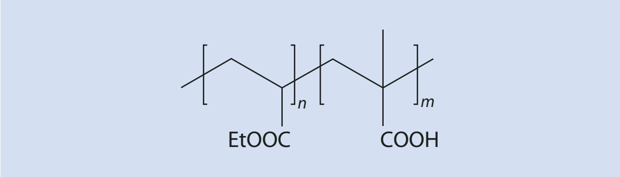


Fig. 19.22 Copolymer of methacrylic acid and ethyl acrylate as an example for a stomach acid-resistant tablet coating

increase the solubility of the polymer in water. Thus, for example, copolymers consisting of methacrylic acid and ethyl acrylate are employed (Fig. 19.22). Another area of application for such pH-sensitive coatings is the formulation of active ingredients which would otherwise damage the stomach lining.

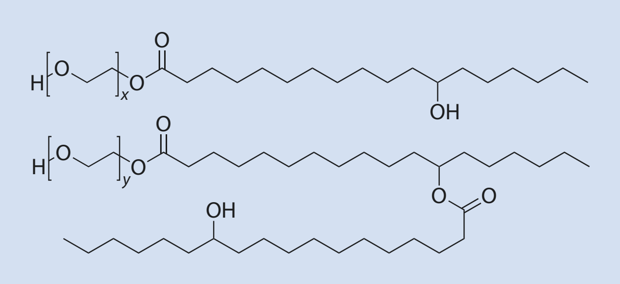
19.6.3 Exploders

Pharmaceutical tablets can also include so-called *exploders*. These can be, for example, cross-linked PVP. Analogous to the super-absorbers discussed in ► Sect. 19.5, these swell in contact with water and cause the tablet to disintegrate so that its contents can dissolve more rapidly.

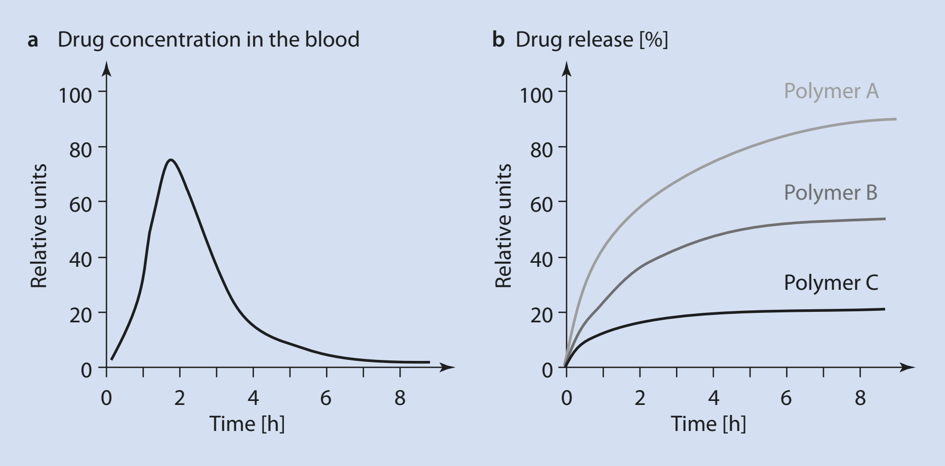
19.6.4 Solubilizers

Many active pharmaceutical ingredients—especially those which have only recently been discovered—have an unfavorable solubility in water and/or only dissolve slowly. Because an oral formulation must be taken up by the body within 24 h or risk being excreted, the speed with which an active ingredient dissolves can, under certain circumstances, limit its bioavailability. In many cases this problem can be solved with polymers which assist the dissolution process. In the same way as color transfer inhibitors, discussed in ► Sect. 19.1.2.4, solubilizers are capable of building water-soluble complexes with the active ingredient and thus increase its solubility and dissolution rate in aqueous media. A common solubilizing polymer certified for pharmaceutical use is polyethylene glycol esterified with a (monomeric or dimeric) stearic acid (Fig. 19.23). In addition, polymers have the advantage that they are usually relatively non-toxic, obviously a precondition for pharmaceutical use.

With an appropriate choice of formulation aids, the way the active ingredient is released can be significantly influenced. Thus, on the one hand a sudden, rapid release is



▪ **Fig. 19.23** Structures of the oligomeric main components of the pharmaceutical solubilizer Solutol HS 15®



▪ **Fig. 19.24** Graphs of different release profiles. (**a**) Instant release. (**b**) Retard formulation

possible. This is always desirable when symptoms need to be reduced rapidly and effectively. Examples are painkillers for acute pain or medication to treat allergic or epileptic attacks. Such formulations are referred to as *instant release* formulations. On the other hand, a steady release over the course of the day may be more appropriate. So-called *retard* formulations ensure a constant level of active ingredient in the body and thus reduce any side effects of any excess active ingredient shortly after intake. Both release profiles are displayed schematically in ▪ Fig. 19.24.

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