7 Inorganic Polysaccharide Esters

Polysaccharides form esters with any inorganic acid known. Examples of typical products are summarised in Fig. 7.1. The esters of nitric acid, phosphoric acid, dithiocarbonic acid and sulphuric acid have gained importance. Cellulose nitrate is commercially produced and used as, for example, film-forming component in lacquers and as explosive. However, the inorganic esters of cellulose and other polysaccharides have yet to be commercially exploited. Anionic functions such as sulphuric acid half esters are found in numerous naturally occurring polysaccharides. Typical examples are heparan and chondroitin [284].

Esters of polysaccharides with functional groups that can be split off by changing the conditions (pH value, medium, salt concentration) are used for shaping processes. The most important commercial example is the 3 000 000 t annual worldwide production of rayon via cellulose dithiocarbonic acid ester (xanthogenate). The cellulose xanthogenate is formed by treating cellulose with CS_2/NaOH, and dissolves in the surplus of aqueous NaOH during xanthogenation. The viscose process is described in detail in [285]. The conversion of polysaccharides with N_2O_4 in the presence of a polar aprotic solvent under dissolution yields the nitrite, which can be used for regeneration by applying a protic solvent [286, 287].

7.1 Sulphuric Acid Half Esters

Polysaccharides containing sulphuric acid half ester moieties constitute a complex class of compounds occurring in living organisms. They possess a variety of biological functions, e.g. inhibition of blood coagulation, or are a component of connective tissues [288]. These polysaccharides are usually composed of different sugars including aminodeoxy- and carboxylic groups containing RU, e.g. β-D-glucuronic acid or α-L-iduronic acid and *N*-acetyl-β-D-galactosamine [289].

Heparan sulphate is composed of α-L-iduronic acid and *N*-acetyl-β-D-galactosamine (Fig. 7.2A, [290]). The structure of heparin is similar to that of heparan sulphate but it contains higher amounts of sulphate groups and iduronic acid. The sulphate ester moieties are bound to position 3 of the L-iduronic acid and position 6 of the D-galactosamine. Moreover, the amino group is either acetylated or sulphated. Heparin is an important therapeutic anticoagulant and antithrombotic agent.

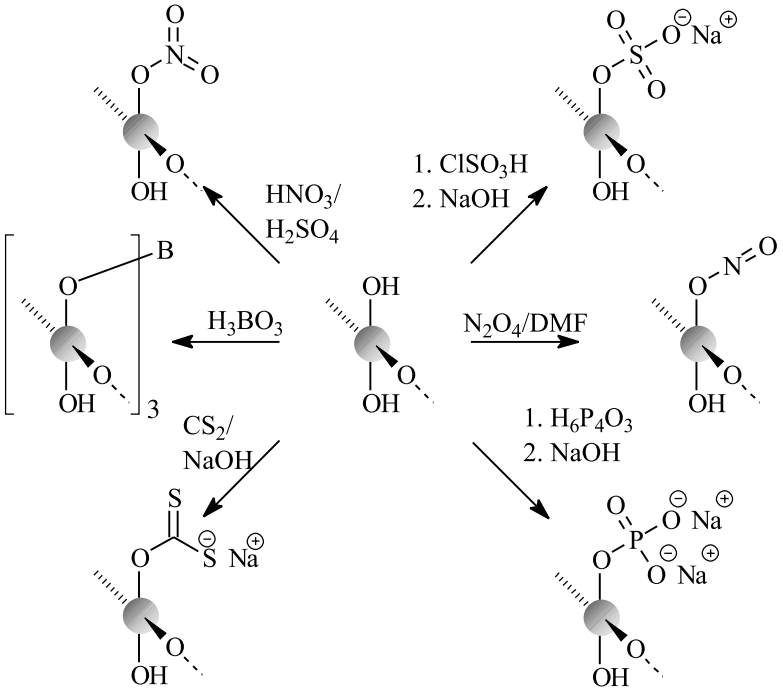

Fig. 7.1. Examples of polysaccharide esters of inorganic acids

The main sugar moieties of chondroitin, a component of cartilage and connective tissue, are β-D-glucuronic acid and *N*-acetyl-β-D-galactosamine connected via β-(1→3) linkages [291]. Sulphuric acid half esters are found at position 4 or 6 of the *N*-acetyl-β-D-galactosamine (see Fig. 7.2B for chondroitin-6-sulphate). Dermatan sulphate consists of L-iduronic acid, rather than D-glucuronic acid (Fig. 7.2C) [292].

Sulphuric acid half ester moieties are introduced in polysaccharides in order to render water-insoluble biopolymers soluble and to impart biological activity. For instance, curdlan, which is not very water soluble, gives clear solutions after introduction of a small amount of sulphuric acid half ester groups, as little as 4.4 mol% (DS 0.04) [293]. Consequently, sulphation of polysaccharides is an important path for structure- and property design.

Several homogeneous and heterogeneous synthesis paths have been developed for the preparation of artificially sulphated polysaccharides. The ester, in its H^+ form, is strongly acidic, which causes autocatalytic hydrolysis of the ester moieties and also chain degradation. Therefore, it is converted to the salt form, often the sodium salt, which is water soluble and stable in aqueous systems.

In general, sulphation can be accomplished using various reagents such as $ClSO_3H$, SO_3 and H_2SO_4. Treating polysaccharides with concentrated or slightly diluted H_2SO_4 may lead to sulphation. Under these conditions, a remarkable