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## 9 Polysaccharide Esters with Defined Functionalisation Pattern

Polysaccharide esters with a defined pattern of functionalisation are indispensable for the establishment of structure–property relations, e.g. for the solubility of cellulose acetate in function of the functionalisation pattern (Chap. 8). The defined functionalisation pattern may also yield unconventional thermal, optical and biological properties, as revealed for polysaccharide sulphuric acid half esters from dextran and curdlan with anti-HIV [421] and cancerostatic activity [422].

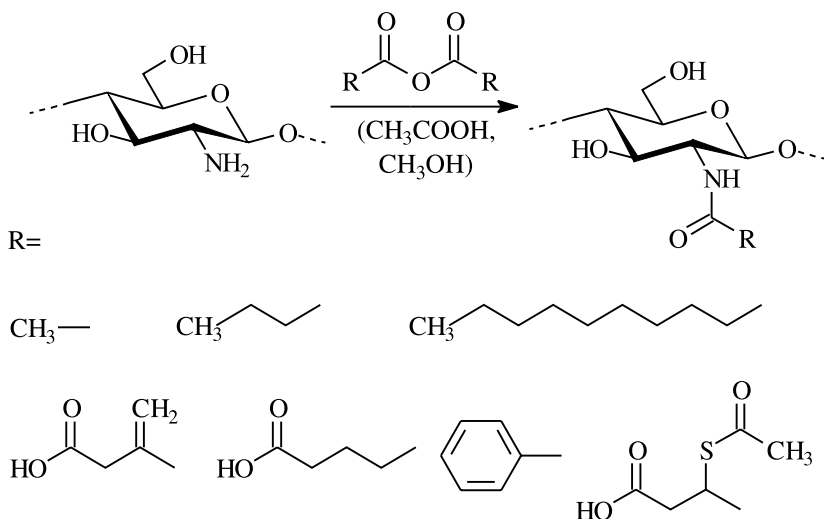
A number of approaches for the preparation of polysaccharide esters with a defined functionalisation pattern is known, applying mostly chemo- and regioselective synthesis and selective deacylation processes. Regioselective conversion may be realised by protective group techniques and so-called medium controlled reactions. However, the chemoselective functionalisation of polysaccharides has scarcely been exploited and is of special interest for the uronic acid-containing polymers, e.g. alginate, and for aminodeoxy polysaccharides (chitin and chitosan).

A selective esterification of the uronic acid units is discussed in Sect. 5.1.2. The polysaccharide is transferred into the acid form and then into the tetrabutylammonium salt, and finally this salt is converted homogeneously in DMSO with long-chain alkyl bromides (see Fig. 5.5, [5]).

In the case of chitin, the tailored modification is accomplished in different solvents (see Fig. 4.6). A number of valuable *N*-acetylated chitosan derivatives can be prepared in a mixture of methanol and acetic acid (Fig. 9.1, [423, 424]).

For polysaccharides containing exclusively hydroxyl groups, the modification reactions preferably occur at primary OH groups, especially if bulky carboxylic acid ester moieties are introduced.

A pronounced reactivity is observed for the OH group adjacent to the glycosidic linkage, due to electronic reasons. Consequently, for (1→4)- and (1→3) linked polysaccharides, e.g. curdlan, starch and cellulose, the rate of esterification is usually in the order of position  $6 > 2 > 3(4)$ . For polysaccharides with no primary OH group, esterification at position 2 is the fastest conversion. Dextran shows an acylation reactivity of the OH moieties in the order  $2 > 4 > 3$ . Reaction paths leading to alternative patterns of esterification are described in the following sections.



**Fig. 9.1.** *N*-acyl derivatives obtained by conversion of chitosan in acetic acid/methanol with carboxylic acid anhydrides

## 9.1 Selective Deacylation

Selective deacylation has been intensively studied for cellulose acetate. This is due to the fact that partially deacetylated cellulose acetates, e.g. cellulose diacetate, possess adjusted solubility (compare Table 8.1, Chap. 8) and can therefore be easily processed. The extent to which the polymer properties are controlled by the distribution of substituents within the RU is unknown. These properties may be additionally influenced by the distribution along the chain. Nevertheless, deesterification is used for the preparation of polysaccharide esters with unconventional functionalisation pattern within the RU. Polysaccharide acetates with adjusted functionalisation are valuable intermediates for the subsequent derivatisation, which leads (after adequate saponification) to subsequent derivatives with inverse functionalisation pattern. Cellulose triacetate is most commonly saponified directly (see Chap. 4). The hydrolysis is performed with aqueous  $\text{H}_2\text{SO}_4$  and cleaves the primary hydroxyls that can later be reesterified [425, 426].

Different functionalisation patterns are obtained under different hydrolysis conditions [151]. For acidic hydrolysis of cellulose triacetate to products with DS values down to 2.2, the rate of deacetylation in position 6 and position 2 is comparable. If hydrolysis continues, deacetylation in position 2 is more pronounced, i.e. the acetyl functions in 6 are the most stable [89, 427]. Deacetylation in position 3 is the fastest (Fig. 9.2A). A different behaviour is observed if the hydrolysis with acetic acid/sulphuric acid is carried out directly after the complete functionalisation of cellulose. The rate of reaction is comparable for all three positions over the whole range of DS (Fig. 9.2B). Thus, cellulose acetate samples with an even distribution of substituents on the level of the AGU are obtained.