
4 Esters of Carboxylic Acids – Conventional Methods

Esterification of polysaccharides with carboxylic acids and carboxylic acid derivatives is among the most versatile transformations of these biopolymers. It gives ready synthetic access to a wide range of valuable products. Commercial processes are carried out exclusively under heterogeneous conditions, due to the high viscosity of polysaccharide solutions, the high costs of solvents, and the ease of workup procedure in the case of multiphase conversions. One aims for completely functionalised derivatives because partial conversion leads mainly to insoluble polymers, specifically in the case of cellulose.

A variety of solvents have been studied and even special solvent mixtures established for homogeneous acylation at the laboratory scale. These homogeneous reactions permit synthesis of highly soluble, partially derivatised polymers and are the prerequisite for the application of “state of the art” organic reagents yielding broad structural diversity. For cellulose and chitin, the development of novel solvents heralded a new era of bio-based functional polymers. Both common organic solvents and multicomponent solvents are still widely studied for esterification procedures yielding novel structures.

4.1 Acylation with Carboxylic Acid Chlorides and Anhydrides

Conventional esterifications of polysaccharides are acylation procedures developed as heterogeneous processes, but now include homogeneous mixtures during the esterification, caused by the dissolution of the esterified product, applying usually carboxylic acid anhydrides or chlorides. In the case of sensitive acids, these reactive compounds are either expensive or inaccessible, and the anhydrides and chlorides of more complex acids are insoluble. Thus, conventional acylation is applied for the complete conversion of all hydroxyl groups of the polysaccharide with aliphatic (acetate to stearate) and aromatic acids (substituted benzoic acids). Over the last 60 years, an enormous amount of papers have been published (approximately 54 000 papers dealing with cellulose esters alone), and this chapter presents an overview of present general techniques and their specific potential.

4.1.1 Heterogeneous Acylation – Industrial Processes

The most common method for the acylation of polysaccharides is the reaction with carboxylic acid anhydride in heterogeneous phase (Fig. 4.1).

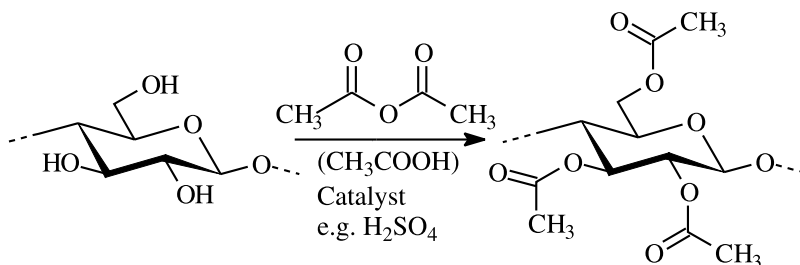


Fig. 4.1. Scheme of the conversion of cellulose with acetic anhydride/acetic acid

Cellulose acetate is the most commercially important polysaccharide ester of a carboxylic acid, and is prepared industrially or at the laboratory scale by conversion of cellulose with a mixture of acetic acid and acetic anhydride (10–40% excess to the amount needed for cellulose triacetate formation) in the presence of sulphuric acid as catalyst (up to 15%, w/w). It is assumed that intermediately the mixed sulphuric acid–acetic acid anhydride is formed (usually called acetyl sulphuric acid) generating an acetyl cation (Fig. 4.2, [85, 86]). Hence, during this conversion, a partial sulphation is observed that suppresses the formation of a real cellulose triacetate. Nevertheless, most of the sulphate groups introduced are exchanged by acetyl functions during the reaction or split off during the workup. In the case of starch, a dehydration (water content less than 3%) and conversion at reflux temperature is recommended for the formation of a starch triacetate [87].

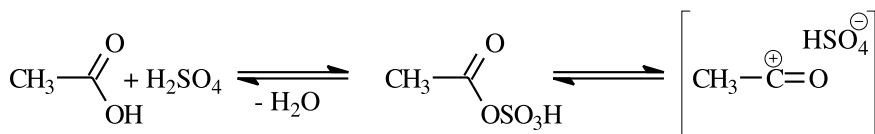


Fig. 4.2. Formation of the reactive, intermediately formed acetyl sulphuric acid

For better control of the reaction temperature and to diminish the amount of catalyst (as low as 1%, w/w H_2SO_4), acetylation can be carried out in methylene chloride, which is combined with the dissolution of the products formed in the final phase of the reaction. Most commercial cellulose acetate is produced via this route.

An alternative is the acetylation on the intact cellulose fibre (fibre acetylation) in an inert solvent such as toluene with perchloric acid as highly efficient catalyst [88]. The triester is obtained applying only 15 mg catalyst on 5 g cellulose in 40 ml acetylation mixture within 24 h at 32 °C. Moreover, the introduction of additional ester groups is avoided, as observed for sulphuric acid catalysis. This method is exploited if the superstructure of the polysaccharide should be retained, which is essential for a number of applications, e.g. as solid phase for chiral separation in chromatographic methods (see Chap. 10).