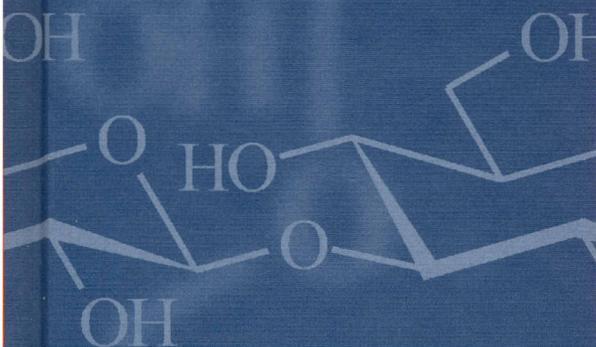


SPRINGER LABORATORY



T. Heinze · T. Liebert · A. Koschella

Esterification of Polysaccharides



 Springer

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Polyaccharides are unique biopolymers with an enormous structural diversity. Their domains of polysaccharides are formed biochemically by many organisms including plants, animals, fungi, algae, and microorganisms as storage polymers and structure-forming macromolecules due to their extraordinary ability for structural diversity by supramolecular interactions of variable types. In addition, polysaccharides are increasingly recognized as a substrate for biotransformation processes regarding, e.g., activity and selectivity. Although the naturally occurring polysaccharides are already outstanding, chemical modification can improve their given features and can even be used to make advanced materials.

Further expansion and diversification of polysaccharides represent the most versatile transformations as they provide easy access to a variety of biobased materials with reliable properties. In particular, state-of-the-art water chemistry can yield a broad spectrum of polysaccharide derivatives, as discussed in the frame of this book from a practical point of view but are currently only used under lab-scale conditions. In contrast, simple esterification of the most abundant polysaccharide cellulose and starch are commercially accepted procedures. Nevertheless, it is the author's intention to review classical concepts of esterification, such as conversions of cellulose to carboxylic acid esters (C_1 to C_6 acids including mixed derivatives of gluconic acid and cellulose nitrate, which are produced in large quantities. These commercial paths of polysaccharide esterification are carried out exclusively under heterogeneous conditions at least at the beginning of the conversion. The majority of cellulose acetate (about 30–500 t per year) is based on a route that includes the dissolution of the products formed [1–3].

Research and development offers new opportunities for the synthesis of polysaccharide esters resulting from:

- New reagents (ring opening, transesterification), enzymatic acylation and *in situ* activation of carboxylic acids
- Heterogeneous reaction paths, i.e., starting with a dissolved polysaccharide and new reaction media
- Regioselective esterification applying protecting-group techniques and protecting-group free methods exploiting the superstructural features of the polysaccharides as well as enzymatically catalyzed procedures

With regard to structure characterization on the molecular level most important are NMR spectroscopic techniques including specific sample preparation. Having