8 Structure Analysis of Polysaccharide Esters

For modified polysaccharides, the analysis goes far beyond the structural verification. The chemical structure of the ester function introduced, the DS, and the distribution of the functional groups at both the level of the RU and along the polymer backbone (Fig. 8.1) can strongly influence the properties and need to be determined comprehensively.

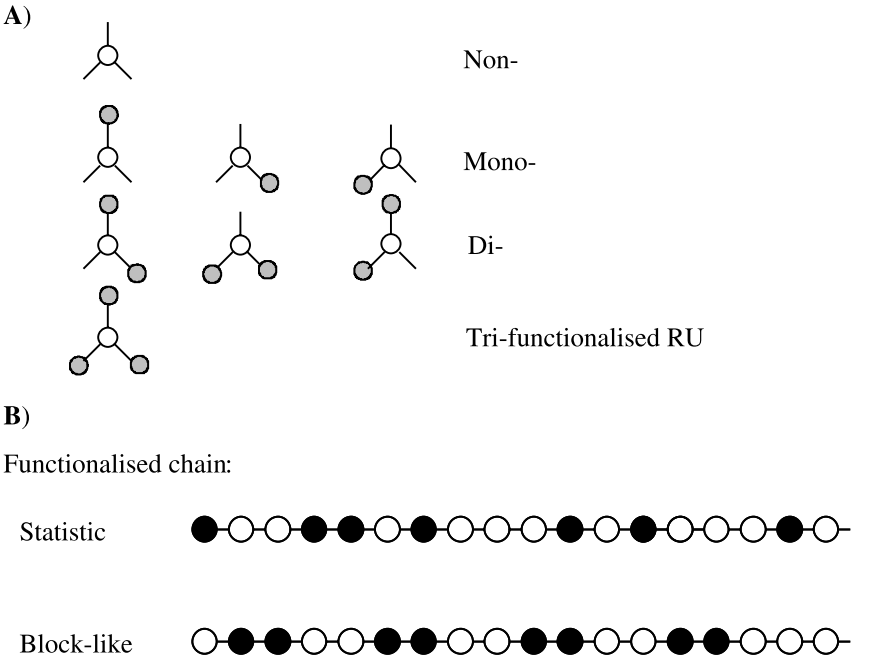

Fig. 8.1. Schematic plot of the possible patterns of functionalisation for the repeating units (**A**) and for the distribution along the polymer chain (**B**) of polysaccharides with three reactive sites

The chemical functionalisation may be associated with side reactions modifying the polymer backbone additionally, maybe to a rather low extent only. These "structural impurities" introduced have to be revealed as well because they are not removable from the polymer chain. Consequently, an efficient and reliable analysis (type of functionalisation, DS, the pattern of substitution) is indispensable for the establishment of structure–property relations of the modified polymers. The tailored modification of substitution patterns can be used to "fine tune" product properties, e.g. solubility behaviour, as shown for the water solubility of cellulose acetate in Table 8.1 [89].

Table 8.1. Water solubility of cellulose acetate: dependence on the pattern of functionalisation (adapted from [89])

Method[a]	Total DS[b]	Degree of acetylation at position[b]			Water-soluble fraction (%, w/w)
		2	3	6	
1	0.49	0.16	0.13	0.20	29
1	0.66	0.23	0.20	0.23	99
1	0.90	0.31	0.29	0.30	93
2	0.73	0.18	0.19	0.36	30
3	1.10	0.33	0.25	0.52	5

[a] Methods applied: (**1**) deacetylation of cellulose triacetate with aqueous acetic acid, (**2**) reaction of cellulose triacetate with hydrazine, and (**3**) acetylation of cellulose with acetic anhydride in DMAc/LiCl

[b] Determined by ^{13}C NMR spectroscopy

Analytical data are also necessary to confirm the reproducibility of a synthesis and the resulting product purity. Unconventional polysaccharide esters, e.g. with sensitive heterocyclic moieties, can often not be analysed by "standard methods" and this has required the development of new analytical tools.

Most of the structural features of the polymer backbone are accessible via optical spectroscopy, chromatography and NMR spectroscopy, as discussed in Chap. 3. Specific techniques useful to determine the result of an esterification, the DS, and the pattern of functionalisation are described herein. The evaluation of the pattern of functionalisation is illustrated in detail for the most important polysaccharide ester, cellulose acetate. Detailed spectroscopic data for other polysaccharide esters are given in Chaps. 3 and 5.

From the synthesis chemist's perspective, the most reliable, powerful and efficient method for the detailed structure elucidation at the molecular level is NMR spectroscopy. A number of interesting new chromatographic tools have been developed over the last two decades, with a potential of gaining defined structural information, but they are combined with a variety of complex functionalisation steps making them susceptible to analytical errors and, therefore, should be used only by experienced analysts.