

## 2 Structure of Polysaccharides

### 2.1 Structural Features

There is a wide range of naturally occurring polysaccharides derived from plants, microorganisms, fungi, marine organisms and animals possessing magnificent structural diversity and functional versatility. In Table 2.1, polysaccharides most commonly used for polymeranalogous reactions are summarised according to chemical structures. These include glucans (1–8), fructans (11), aminodeoxy glucans (12, 13), and polysaccharides with uronic acid units (14).

**Table 2.1.** Structures of polysaccharides of different origin

Polysaccharide Type		Source	Structure	Reference
Cellulose	1	Plants	$\beta$ -(1→4)-D-glucose	[6]
Curdlan	2	Bacteria	$\beta$ -(1→3)-D-glucose	[7]
Scleroglucan	3	Fungi	$\beta$ -(1→3)-D-glucose main chain, $\beta$ -(1→6)-D-glucose branches	[8]
Schizophyllan	4	Fungi	$\beta$ -(1→3)-D-glucose main chain, D-glucose branches	[9, 10]
Dextran	5	Bacteria	$\alpha$ -(1→6)-D-glucose main chain	[11]
Pullulan	6	Fungi	$\alpha$ -(1→6) linked maltotriosyl units	[12]
Starch		Plants		[13]
Amylose	7		$\alpha$ -(1→4)-D-glucose	
Amylopectin	8		$\alpha$ -(1→4)- and $\alpha$ -(1→6)-D-glucose	
Xylan	9	Plants	$\beta$ -(1→4)-D-xylose main chain	[14]
Guar	10	Plants	$\beta$ -(1→4)-D-mannose main chain, D-galactose branches	[15]
Inulin	11	Plants	$\beta$ -(1→2)-fructofuranose	[16]
Chitin	12	Animals	$\beta$ -(1→4)-D-(N-acetyl)glucosamine	[17]
Chitosan	13		$\beta$ -(1→4)-D-glucosamine	
Alginate	14	Algae	$\alpha$ -(1→4)-L-guluronic acid $\beta$ -(1→4)-D-mannuronic acid	[18]

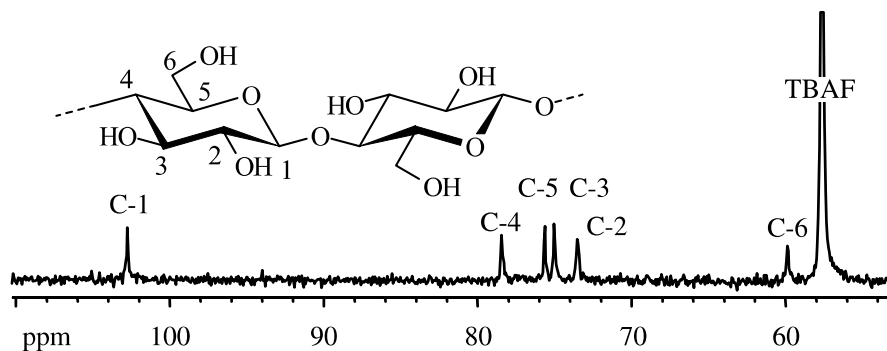
The common motifs are primary and secondary OH groups and carboxylic acid moieties, accessible to esterification, and  $\text{NH}_2$  groups for conversion to amides. In addition, comprehensive reviews about the molecular, supramolecular and morphological structures of the polysaccharides are available [9, 19–23].

### 2.1.1 Cellulose

Cellulose, the most abundant organic compound, is a linear homopolymer composed of D-glucopyranose units (so-called anhydroglucose units) that are linked together by  $\beta$ -(1 $\rightarrow$ 4) glycosidic bonds (Fig. 2.1). Although cellulose possesses a unique and simple molecular structure, very complex supramolecular structures can be formed, which show a rather remarkable influence on properties such as reactivity during chemical modification. The complexity of the different structural levels of cellulose, i.e. the molecular, supramolecular and morphological, is well studied [24]. The polymer is insoluble in water, even at a rather low DP of 30, and in common organic solvents, resulting from the very strong hydrogen bond network formed by the hydroxyl groups and the ring and bridge oxygen atoms both within and between the polymer chains. The ordered hydrogen bond systems form various types of supramolecular semicrystalline structures. This hydrogen bonding has a strong influence on the whole chemical behaviour of cellulose [25, 26].

To dissolve the polymer, various complex solvent mixtures have been evaluated and are most often employed in esterification reactions such as DMAc/LiCl and DMSO/TBAF. A well-resolved  $^{13}\text{C}$  NMR spectrum of the polymer dissolved in DMSO- $d_6$ /TBAF, including the assignment of the 6 carbon atoms, is shown in Fig. 2.1 [27].

The carbon atoms of position 2, 3 and 6 possess hydroxyl groups that undergo standard reactions known for primary and secondary OH moieties. Cellulose of various DP values is available, depending on the source and pre-treatment. Native cotton possesses values up to 12 000 while the DP of scoured and bleached cotton linters ranges from 800 to 1800 and of wood pulp (dissolving pulp) from 600 to 1200.



**Fig. 2.1.**  $^{13}\text{C}$  NMR spectrum of cellulose dissolved in DMSO- $d_6$ /TBAF (reproduced with permission from [27], copyright Wiley VCH)