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Thomas Heinze · Tim Liebert · Andreas Koschella

Esterification of Polysaccharides

With 131 Figures, 105 Tables, and CD-ROM

Springer

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Preface

The recent world attention towards renewable and sustainable resources has resulted in many unique and groundbreaking research activities. Polysaccharides, possessing various options for application and use, are by far the most important renewable resources. From the chemist's point of view, the unique structure of polysaccharides combined with many promising properties like hydrophilicity, biocompatibility, biodegradability (at least in the original state), stereoregularity, multichirality, and polyfunctionality, i.e. reactive functional groups (mainly OH–, NH–, and COOH– moieties) that can be modified by various chemical reactions, provide an additional and important argument for their study as a valuable and renewable resource for the future.

Chemical modification of polysaccharides has already proved to be one of the most important paths to develop new products and materials. The objective of this book is to describe esterification of polysaccharides by considering typical synthesis routes, efficient structure characterisation, unconventional polysaccharide esters, and structure-property relationships. Comments about new application areas are also included.

The content of this book originated mainly from the authors' polysaccharide research experience carried out at the Bergische University of Wuppertal, Germany and the Friedrich Schiller University of Jena, Germany. The interaction of the authors with Prof. D. Klemm was a great stimulus to remain active in this fascinating field. In addition, there is increasing interest from industry in the field of polysaccharides that is well documented by the establishment of the Center of Excellence for Polysaccharide Research Jena-Rudolstadt. The aim of the centre is to foster interdisciplinary fundamental research on polysaccharides and their application through active graduate student projects in the fields of carbohydrate chemistry, bioorganic chemistry, and structure analysis.

The authors would like to stress that the knowledge discussed in this book does not represent an endpoint. On the contrary, the information about polysaccharide esters provided here will hopefully encourage scientists in academia and industry to continue the search for and development of new procedures, products, and applications. The authors strongly hope that the polysaccharide ester information highlighted in this book will be helpful both for experts and newcomers to the field.

During the preparation of the book, the members of the Heinze laboratory were very helpful. We thank Dr. Wolfgang Günther for the acquisition of NMR

spectra, Dr. Matilde Vieira Nagel for preparing many tables and proofreading the text as well as Stephanie Hornig, Claudia Hänsch, Constance Ißbrücker, and Sarah Köhler for technical assistance. Special thanks go to Prof. Werner-Michael Kulicke, University of Hamburg, who encouraged us to contribute a synthetic topic to the Springer Laboratory series. Dr. Stan Fowler (ES English for Scientists) is gratefully acknowledged for proofreading the manuscript.

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Jena, February 2006

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Tim Liebert
Andreas Koschella

List of Symbols and Abbreviations

[C_4mim]Br	1-*N*-Butyl-3-methylimidazolium bromide
[C_4mim]Cl	1-*N*-Butyl-3-methylimidazolium chloride
[C_4mim]SCN	1-*N*-Butyl-3-methylimidazolium thiocyanate
Ac	Acetyl
AFM	Atomic force microscope
AGU	Anhydroglucose units
AMIMCl	1-*N*-Allyl-3-methylimidazolium chloride
APS	Amino propyl silica
Ara*f*	α-L-Arabinofuranosyl
Ara*p*	Arabinopyranosyl
AX	Arabinoxylans
AXU	Anhydroxylose unit
Bu	Butyl
Cadoxen	Cadmiumethylenediamine hydroxide
CDI	*N*, *N*′-Carbonyldiimidazole
CI-MS	Chemical ionisation mass spectroscopy
COSY	Correlated spectroscopy
CTFA	Cellulose trifluoroacetate
Cuen	Cupriethylenediamine hydroxide
DB	Degree of branching
DCC	*N*, *N*-Dicyclohexylcarbodiimide
DDA	Degree of deacetylation
DEPT	Distortionless enhancement by polarisation transfer
DMAc	*N*, *N*-Dimethylacetamide
DMAP	4-*N*, *N*-Dimethylaminopyridine
DMF	*N*, *N*-Dimethylformamide
DMI	1,3-Dimethyl-2-imidazolidinone
DMSO	Dimethyl sulphoxide
DP	Degree of polymerisation
DS	Degree of substitution
DQF	Double quantum filter
EI-MS	Electron impact ionisation mass spectroscopy
FAB-MS	Fast atom bombardment mass spectroscopy
FACl	Fatty acid chloride
FTIR	Fourier transform infrared spectroscopy

GA	α-D-Glucopyranosyl uronic acid
GalNAc	*N*-Acetyl-D-galactosamine
Gal*p*	Galactopyranose
Gal*p*N	Galactopyranosylamine
Gal*p*NAc	*N*-Acetylgalactopyranosylamine
GLC	Gas liquid chromatography
GLC-MS	Gas liquid chromatography-mass spectroscopy
GlcN	D-Glucosamine
GlcNAc	*N*-Acetyl-D-glucosamine
GlcA	Glucuronic acid
Glc*p*	Glucopyranose
GPC	Gel permeation chromatography
GX	4-*O*-Methyl-glucuronoxylan
HMBC	Heteronuclear multiple bond correlation
HMPA	Hexamethylphosphor triamide
HMQC	Heteronuclear multiple quantum coherence
HPLC	High-performance liquid chromatography
HSQC	Heteronuclear single quantum correlation
I_c	Crystallinity index
INAPT	Selective version of insensitive nuclei enhanced by polarisation transfer
Maldi-TOF	Matrix assisted laser desorption ionisation time of flight
Man*p*	Mannopyranose
MeGA	4-*O*-Methyl-α-D-glucopyranosyl uronic acid
MEK	Methylethylketone
MesCl	Methanesulphonic acid chloride
Methyl triflate	Trifluoromethanesulphonic acid methylester
M_w	Mass average molecular mass
n.d.	Not determined
Na dimsyl	Sodium methylsulphinyl
NBS	*N*-Bromosuccinimide
NIR	Near-infrared
Nitren	Ni(tren)(OH)2[tren=tris(2-aminoethyl)amine]
NMMO	*N*-Methylmorpholine-*N*-oxide
NMP	*N*-Methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
NOE	Nuclear Overhauser effect
NOESY	Nuclear Overhauser effect spectroscopy
PAHBA	*p*-Hydroxybenzoic acid hydrazide
PP	4-Pyrrolidinopyridine
Py	Pyridine
RI	Refractive index
RT	Room temperature
RU	Repeating unit
S_N	Nucleophilic substitution

TBA	Tetrabutylammonium
TBAF	Tetrabutylammonium fluoride trihydrate
TBDMS	tert-Butyldimethylsilyl
TDMS	Thexyldimethylsilyl
TEA	Triethylamine
TFA	Trifluoroacetic acid
TFAA	Trifluoroacetic acid anhydride
T_g	Glass transition temperature
THF	Tetrahydrofuran
TMA	Trimethylamine
TMS	Trimethylsilyl
TOCSY	Total correlated spectroscopy
TosCl	*p*-Toluenesulphonyl chloride
TosOH	*p*-Toluenesulphonic acid
Trityl	Triphenylmethyl
UV/Vis	Ultraviolet/visible
Xyl*p*	Xylopyranose

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