Chitin Chemistry

CHITIN CHEMISTRY

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In memory of my parents

Isobel M.L. Roberts (née Gunion)
(1904–89)

and

George A.E. Roberts
(1901–89)

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Foreword

Chitin is the second most important natural polysaccharide (cellulose being the first). But fundamental knowledge about chitin and its applications is frequently difficult to obtain.

Even though its original and spectacular properties have been recognised for a long time (it was first isolated by Braconnot in 1811), it seems that no great uses were made of these until comparatively recently.

The first review of chitin was presented by R. Muzzarelli in 1977. Subsequently, International Symposia on Chitin and Chitosan kept the information up to date. *Chitin Chemistry* answers the needs of people working in this field as well as those who want to develop new products for specific applications. The book gives an exhaustive overview of chitin and its derivatives. Both the solid state and the solution properties of chitin and chitosan are discussed.

The book is a very useful source of knowledge for everyone involved with chitin and its developments.

Professor M. Rinaudo
University Joseph Fourier of Grenoble

Preface

Although the isolation of chitin by Braconnot in 1811 preceded Payen's isolation of cellulose by some 30 years, the development of the chemistry of chitin and its industrial applications has lagged far behind that of cellulose. However the 1970s saw the beginning of an upsurge of interest in chitin chemistry, spearheaded by the publication of Professor Muzzarelli's two books, *Natural Chelating Polymers* (1973) and *Chitin* (1977), and the organisation of the 1st International Conference on Chitin/Chitosan in 1977. In the intervening period the chemical behaviour of these polymers has been studied intensively and the object in writing this book is to present an up-to-date, ordered, coherent and critical account of the chemistry of chitin and chitosan.

As indicated by the title, the book is concerned with the chemistry of these polymers and no attempt has been made to deal with their biology except for two topics, the chitin-protein complexes of native chitin and the biodegradation of chitin and chitosan, whose inclusion seemed particularly relevant. Furthermore, despite the considerable interest that exists in the commercial utilisation of the two polymers, their possible applications have not been discussed apart from a few brief references. Although there is a large and ever-increasing number of potential uses proposed for these polymers and their derivatives, particularly in the patent literature, most would appear not to be in use at the present time and I did not feel in a position to find the few needles in the numerous haystacks. However it is my hope that this book, by presenting a comprehensive account of their chemistry, may point the way to the development of useful applications for these most intriguing polymers.

Acknowledgements

My interest in chitin developed out of an earlier interest in cellulose and I am indebted to Dr Hal S. Blair of Queen's University, Belfast, who first introduced me to cellulose chemistry, and to Mr Eugene D. Klug who further stimulated my interest in it during the period that I was fortunate to work with him at Hercules Inc. I am also indebted to my former research students – Drs Graham K. Moore, Julian G. Domszy, Beryl D. Gummow, Ghobad G. Maghami, Kathryn E. Taylor and Ing. Irineu Batista – whose work has contributed much to my understanding of chitin.

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Glossary of Symbols and Abbreviations

<i>a</i>	exponent in the Mark–Houwink equation
AA	alginate acid
Am	Kuhn statistical chain element
BSA	bovine serum albumin
CD	circular dichroism
C.I.	Colour Index (published by the Society of Dyers and Colourists)
CMC	carboxymethyl cellulose
CP/MAS	cross polarisation/magic angle spinning
CS	cellulose sulphate
CSA	chondroitin sulphate A
CSC	chondroitin sulphate C
DCA	dichloroacetic acid
DCC	dicyclohexylcarbodiimide
DD	degree of deacetylation
DEAE cellulose	diethylaminoethyl cellulose
DIPEA	di-(prop-2-yl)ethylamine (di- <i>isopropylethylamine</i>)
DMAc	dimethylacetamide
DMF	dimethylformamide
DMSO	dimethylsulphoxide
DNA	deoxyribonucleic acid
DNase	deoxyribonuclease
DNFB	2,4-dinitrofluorobenzene
$\overline{DP}$	degree of polymerisation
$\overline{DP}_n$	number-average degree of polymerisation
$\overline{DP}_v$	viscosity-average degree of polymerisation
$\overline{DP}_w$	weight-average degree of polymerisation

DS	degree of substitution
DxS	dextran sulphate
EDTA	ethylenediaminetetraacetic acid (Na^+ salt)
EO	ethylene oxide
ESR	electron spin resonance
FTIR	Fourier transform infra-red
GC	gas chromatography
GCD	glycidol (2,3-epoxypropanol)
GC/MS	gas chromatography/mass spectroscopy
GLC	gas-liquid chromatography
GPC	gel permeation chromatography
GTMAC	glycidyltrimethylammonium chloride
GUA	poly(galacturonic) acid
HA	hyaluronic acid
HECh	hydroxyethyl chitosan
HEP	heparin
HMPA	hexamethylphosphoramide
IPA	2-propanol (<i>iso</i> -propanol)
IR	infra-red
K	constant in the Mark-Houwink equation
LC	liquid chromatography
LVN	limiting viscosity number
$\bar{M}_n$	number-average molecular weight
$\bar{M}_v$	viscosity-average molecular weight
$\bar{M}_w$	weight-average molecular weight
MCA	monochloroacetic acid
MS	moles of substitution
MWD	molecular weight distribution
NADH	nicotinamide adenine dinucleotide (reduced form)
NASA	1-naphthylamine-4-sulphonic acid
NCA	<i>N</i> -carboxyanhydride
NMP	<i>N</i> -methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
NSA	1-naphthol-4-sulphonic acid
Py	pyridine
RNA	ribonucleic acid
RNase	ribonuclease
SEM	scanning electron microscopy
TBA	2-methyl-2-propanol (<i>tert</i> -butanol)
TCA	trichloroacetic acid
TEA	triethylamine
THF	tetrahydrofuran
TLC	thin-layer chromatography
UV	ultra-violet

$[\eta]$	limiting viscosity number (formerly intrinsic viscosity)
$\eta_{(\text{inh})}$	logarithmic viscosity number (formerly inherent viscosity)
$\eta_{\text{sp}/c}$	viscosity number (formerly reduced viscosity)