This page intentionally left blank
Biopolymers: Biomedical and Environmental Applications
Biopolymers: Biomedical and Environmental Applications

Edited by
Susheel Kalia
Department of Chemistry, Bahra University, India

and

Luc Avérous
European Engineering School for Chemistry, Polymer and Materials, University of Strasbourg, France
Contents

Preface xvii
List of Contributors xxi

Part 1: Polysaccharides

1. Hyaluronic Acid: A Natural Biopolymer 3
   J. Schiller, N. Volpi, E. Hrabárová and L. Šoltés
   1.1 Glycosaminoglycans 4
   1.2 Hyaluronic Acid/Hyaluronan – Structure, Occurrence 7
   1.3 Hyaluronan Synthases 8
   1.4 Enzymatic Catabolism of Hyaluronan 10
   1.5 Oxidative Degradation of Hyaluronan 11
      1.5.1 Reaction of HA with HO\(^*\) Radicals 13
      1.5.2 Reaction of HA with HOCl 17
      1.5.3 Reaction of HA with Peroxynitrite 18
   1.6 Hyaluronan Degradation under Inflammatory Conditions 19
      1.6.1 Generation of ROS under \textit{In Vivo} Conditions 20
      1.6.2 Discussion of ROS Effects under \textit{In Vivo} Conditions 21
      1.6.3 Cell-derived Oxidants and Their Effects on HA 22
      1.6.4 Synovial Fluids 23
      1.6.5 Extracellular Matrix 23
   1.7 Interaction of Hyaluronan with Proteins and Inflammatory Mediators 24
      1.7.1 HA Binding Proteins and Receptors 25
      1.7.2 HA Receptors – Cellular Hyaladherins 25
      1.7.3 Extracellular Hyaladherins 26
   1.8 Hyaluronan and Its Derivatives in Use 26
      1.8.1 Viscosurgery 27
      1.8.2 Viscoprotection 27
      1.8.3 Viscosupplementation 28
      1.8.4 Vehicle for the Localized Delivery of Drugs to the Skin 28
      1.8.5 Electrospinning for Regenerative Medicine 28
   1.9 Concluding Remarks 29
   Acknowledgements 29
   References 30
2. Polysaccharide Graft Copolymers – Synthesis, Properties and Applications
B. S. Kaith, Hemant Mittal, Jaspreet Kaur Bhatia and Susheel Kalia

2.1 Introduction

2.2 Modification of Polysaccharides through Graft Copolymerization
   2.2.1 Graft Copolymerization Using Chemical Initiators
   2.2.2 Graft Copolymerization Using Radiations as Initiators

2.3 Different Reaction Conditions for Graft Copolymerization
   2.3.1 In Air (IA) Graft Copolymerization
   2.3.2 Under Pressure (UP) Graft Copolymerization
   2.3.3 Under Vacuum (UV) Graft Copolymerization
   2.3.4 Graft Copolymerization Under the Influence of γ-Radiations
   2.3.5 Graft Copolymerization Under the Influence of Microwave Radiations (MW)

2.4 Characterization of Graft Copolymers
   2.4.1 FT-IR
   2.4.2 13C NMR
   2.4.3 SEM
   2.4.4 XRD
   2.4.5 Thermal Studies

2.5 Properties of Polysaccharide Graft Copolymers
   2.5.1 Physical Properties
   2.5.2 Chemical Properties

2.6 Applications of Modified Polysaccharides
   2.6.1 Sustained Drug Delivery
   2.6.2 Controlled Release of Fungicide
   2.6.3 Selective Removal of Water from Different Petroleum Fraction-water Emulsions
   2.6.4 Removal of Colloidal Particles from Water
   2.6.5 Graft Copolymers as Reinforcing Agents in Green Composites

2.7 Biodegradation Studies

2.8 Conclusion

References

3. Natural Polysaccharides: From Membranes to Active Food Packaging
Keith J. Fahnestock, Marjorie S. Austero and Caroline L. Schauer

3.1 Introduction

3.2 Polysaccharide Membranes
   3.2.1 Permeative Membranes
   3.2.2 Iionically Conductive Membranes
   3.2.3 Polysaccharide Polymers
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 Permselective Membranes</td>
<td>63</td>
</tr>
<tr>
<td>3.4 Ionically Conductive Membranes</td>
<td>65</td>
</tr>
<tr>
<td>3.4.1 Cation Conductive Membranes</td>
<td>65</td>
</tr>
<tr>
<td>3.4.2 Anion Conductive Membrane</td>
<td>66</td>
</tr>
<tr>
<td>3.5 Polysaccharide Membranes: Synopsis</td>
<td>67</td>
</tr>
<tr>
<td>3.6 Active Food Packaging</td>
<td>67</td>
</tr>
<tr>
<td>3.7 Antimicrobial Films</td>
<td>68</td>
</tr>
<tr>
<td>3.7.1 Chitosan</td>
<td>69</td>
</tr>
<tr>
<td>3.7.2 Cellulose</td>
<td>76</td>
</tr>
<tr>
<td>3.8 Other Developments in Active Packaging:</td>
<td>77</td>
</tr>
<tr>
<td>Lipid Barrier</td>
<td>77</td>
</tr>
<tr>
<td>3.9 Food Packaging: Synopsis</td>
<td>77</td>
</tr>
<tr>
<td>3.10 Conclusion</td>
<td>78</td>
</tr>
<tr>
<td>References</td>
<td>78</td>
</tr>
<tr>
<td>4. Starch as Source of Polymeric Materials</td>
<td>81</td>
</tr>
<tr>
<td>Antonio José Felix Carvalho</td>
<td></td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>81</td>
</tr>
<tr>
<td>4.2 Starch Structure</td>
<td>83</td>
</tr>
<tr>
<td>4.3 Non-food Application of Starch</td>
<td>86</td>
</tr>
<tr>
<td>4.4 Utilization of Starch in Plastics</td>
<td>87</td>
</tr>
<tr>
<td>4.5 Some Features of the Physical Chemistry of Thermoplastic Starch Processing</td>
<td>89</td>
</tr>
<tr>
<td>4.6 Recent Developments in Thermoplastic Starch</td>
<td>92</td>
</tr>
<tr>
<td>4.7 Reactive Extrusion</td>
<td>93</td>
</tr>
<tr>
<td>4.8 Conclusion</td>
<td>94</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>95</td>
</tr>
<tr>
<td>References</td>
<td>95</td>
</tr>
<tr>
<td>5. Grafted Polysaccharides: Smart Materials of the Future, Their Synthesis and Applications</td>
<td>99</td>
</tr>
<tr>
<td>Gautam Sen, Ashoke Sharon and Sagar Pal</td>
<td></td>
</tr>
<tr>
<td>5.1 Introduction: Polysaccharides as a Material of the Future</td>
<td>99</td>
</tr>
<tr>
<td>5.2 Modified Polysaccharides</td>
<td>100</td>
</tr>
<tr>
<td>5.2.1 Modification by Insertion of Functional Groups onto the Polysaccharide Backbone</td>
<td>100</td>
</tr>
<tr>
<td>5.2.2 Modification by Grafting of Chains of Another Polymeric Material onto Polysaccharide Backbone</td>
<td>101</td>
</tr>
<tr>
<td>5.3 Characterization of Grafted Polysaccharides</td>
<td>110</td>
</tr>
<tr>
<td>5.3.1 Intrinsic Viscosity</td>
<td>110</td>
</tr>
<tr>
<td>5.3.2 Elemental Analysis</td>
<td>111</td>
</tr>
<tr>
<td>5.3.3 FTIR Spectroscopy</td>
<td>112</td>
</tr>
<tr>
<td>5.3.4 Scanning Electron Microscopy (SEM) Analysis</td>
<td>114</td>
</tr>
<tr>
<td>5.3.5 Thermo Gravimetric Analysis (TGA)</td>
<td>115</td>
</tr>
</tbody>
</table>
5.4 Application of Grafted Polysaccharides
   5.4.1 Application as Viscosifier
   5.4.2 Application as Flocculant for Water Treatment
   5.4.3 Application as Matrix for Controlled Drug Release
5.5 Conclusion
   References

6. Chitosan: The Most Valuable Derivative of Chitin
   Debasish Sahoo and P.L. Nayak
   6.1 Introduction
   6.2 Polysachharide
   6.3 Sources of Chitin and Chitosan
   6.4 Composition of Chitin, Chitosan and Cellulose
   6.5 Chemical Modification of Chitin and Chitosan
   6.6 Chitin – Chemical Modification
   6.7 Chitosan – Chemical Modification
      6.7.1 O/-N-carboxyalkylation
      6.7.2 Sulfonation
      6.7.3 Acylation
      6.7.4 Sugar-Modified Chitosan
   6.8 Depolymerization of Chitin and Chitosan
      6.8.1 Chemical Methods
      6.8.2 Physical Methods
      6.8.3 Enzymatic Methods
      6.8.4 Graft Copolymerization
      6.8.5 Chitosan Crosslinking
   6.9 Applications of Chitin and Chitosan
   6.10 Bio-medical Applications of Chitosan
      6.10.1 Gene Therapy
      6.10.2 Enzyme Immobilization
      6.10.3 Antioxidant Property
      6.10.4 Hypocholesterolemic Activity
      6.10.5 Wound-healing Accelerators
      6.10.6 Artificial Kidney Membrane
      6.10.7 Drug Delivery Systems
      6.10.8 Blood Anticoagulants
      6.10.9 Artificial Skin
   6.11 Miscellaneous Applications
   6.12 Antimicrobial Properties
   6.13 Film-forming Ability of Chitosan
   6.14 Function of Plasticizers in Film Formation
   6.15 Membranes
   6.16 In Wastewater Treatment
   6.17 Multifaceted Derivatization Potential of
      Chitin and Chitosan
   6.18 Conclusion
   References
Part 2: Bioplastics and Biocomposites

7. Biopolymers Based on Carboxylic Acids Derived from Renewable Resources
*Sushil Kumar, Nikhil Prakash and Dipaloy Datta*

- 7.1 Introduction 169
- 7.2 Carboxylic Acids: Lactic- and Glycolic Acid
  - 7.2.1 Lactic- and Glycolic Acid Production 170
- 7.3 Polymerization of Lactic- and Glycolic Acids
  - 7.3.1 Polymerization of Lactic Acid 171
  - 7.3.2 Polymerization of Glycolic Acid 178
- 7.4 Applications 180
- 7.5 Conclusions 181
  - References 181

8. Characteristics and Applications of Poly (lactide)
*Sandra Domenek, Cécile Courgneau and Violette Ducruet*

- 8.1 Introduction 183
- 8.2 Production of PLA
  - 8.2.1 Production of Lactic Acid 184
  - 8.2.2 Synthesis of PLA 186
- 8.3 Physical PLA Properties 190
- 8.4 Microstructure and Thermal Properties
  - 8.4.1 Amorphous Phase of PLA 192
  - 8.4.2 Crystalline Structure of PLA 193
  - 8.4.3 Crystallization Kinetics of PLA 194
  - 8.4.4 Melting of PLA 197
- 8.5 Mechanical Properties of PLA 197
- 8.6 Barrier Properties of PLA 199
  - 8.6.1 Gas Barrier Properties of PLA 199
  - 8.6.2 Water Vapour Permeability of PLA 201
  - 8.6.3 Permeability of Organic Vapours through PLA 202
- 8.7 Degradation Behaviour of PLA 203
  - 8.7.1 Thermal Degradation 204
  - 8.7.2 Hydrolysis 204
  - 8.7.3 Biodegradation 206
- 8.8 Processing 208
- 8.9 Applications
  - 8.9.1 Biomedical Applications of PLA 210
  - 8.9.2 Packaging Applications Commodity of PLA 211
  - 8.9.3 Textile Applications of PLA 214
  - 8.9.4 Automotive Applications of PLA 215
  - 8.9.5 Building Applications 215
  - 8.9.6 Other Applications of PLA 216
- 8.10 Conclusion 217
  - References 217
9. **Biobased Composites and Applications**

_Smita Mohanty and Sanjay K. Nayak_

9.1 Introduction 225
9.2 Biofibers: Opportunities and Limitations 226
  9.2.1 Chemical Composition of Biofibers 228
  9.2.2 Surface Modification and Characterization of Biofibers 232
  9.2.3 Physical and Mechanical Properties of Biofibers 234
9.3 Biobased Composites: An Overview 235
  9.3.1 Biobased Composites of Sisal Fiber Reinforced Polypropylene 237
  9.3.2 Innovations in Biobased Hybrid Composites 246
  9.3.3 Prototype Development and Future Recommendations 262
9.4 Conclusion and Future Prospects 262
References 263

Part 3: Miscellaneous Biopolymers

10. **Cassia Seed Gums: A Renewable Reservoir for Synthesizing High Performance Materials for Water Remediation**

_Vandana Singh and Pramendra Kumar_

10.1 Introduction 269
10.2 Cassia Seed Gums Based Flocculants
  10.2.1 Cassia angustfolia 272
  10.2.2 Cassia javahikai 273
  10.2.3 Cassia tora 276
  10.2.4 Mechanism of Dye Removal by Flocculants 276
10.3 Cassia Seed Gums Based Metal Sorbents
  10.3.1 Cassia grandis 278
  10.3.2 Cassia marginata 280
  10.3.3 Cassia javanica 283
10.4 Other Grafted Cassia Seed Gums
  10.4.1 Cassia pudibunda 286
  10.4.2 Cassia occidentalis 286
  10.4.3 Cassia siamea 286
10.5 Conclusion 286
References 287

11. **Bacterial Polymers: Resources, Synthesis and Applications**

_GVN Rathna and Sutapa Ghosh_

11.1 Introduction 291
11.2 Diverse Bacterial Species
  11.2.1 Polysaccharides 295
  11.2.2 Proteins 299
  11.2.3 Protein-polysaccharide and Lipopolysaccharides 299
  11.2.4 Polyesters 300
11.3 Methods to Obtain Bacterial Polymers 302
  11.3.1 Conventional Methods (extraction/isolation) 302
  11.3.2 Biosynthesis Methods 305
11.4 Tailor-made Methods 307
11.5 Applications 309
  11.5.1 Biomedical Applications 309
  11.5.2 Industrial Application 311
  11.5.3 Food Applications 311
  11.5.4 Agricultural Application 312
11.6 Conclusion and Future Prospective of Bacterial Polymers 312
References 312

12. Gum Arabica: A Natural Biopolymer 317
   A. Sarkar
   12.1 Introduction 317
     12.1.1 Natural Gums, Sources and Collection 319
   12.2 Chemistry of Gum Arabica 320
     12.2.1 Potential Use as Material 321
   12.3 Electroactivity of Gum 321
     12.3.1 Ionic Conduction in Electroactive Material 322
     12.3.2 Conduction Mechanism 323
     12.3.3 Ion Transference Number 323
     12.3.4 Conducting Ion Species in Gum Arabica 324
     12.3.5 Carrier Mobility in Gum Arabica 324
   12.4 Method of Characterization 325
     12.4.1 Microscopic Observation 325
     12.4.2 Microscopic Observations 326
     12.4.3 Thermodynamic Analysis 328
     12.4.4 Electrical Polarization and A.C. Conductivity 330
   12.5 Electronic or Vibrational Properties 338
   12.6 Enhancement of Electroactivity 342
   12.7 Application Potential in Material Science 344
     12.7.1 Gum Arabica and Its Scope of Application 344
     12.7.2 Biopolymer Gel 345
     12.7.3 Nanocomposites 351
     12.7.4 Metallic Sulphide Nanocomplex of Gum Arabica 352
     12.7.5 Development of Carbon Nanoparticle 356
     12.7.6 Photosensitive Complex 359
   12.8 Development of Biopolymeric Solar Cells 364
   12.9 Biomedical-like Application 370
   12.10 Conclusion 374
     Acknowledgements 374
     References 374

13. Gluten: A Natural Biopolymer 377
   S. Georgiev and Tereza Dekova
   13.1 Introduction 378
13.2 Gliadins 383
   13.2.1 Genetics and Polymorphism 384
13.3 Glutenins 387
   13.3.1 Gluten Polymer Structure 388
   13.3.2 Polymeric Proteins 389
   13.3.3 Structure 391
   13.3.4 Relationship to Wheat Quality 392
13.4 LMW-GS 393
   13.4.1 Structure 395
   13.4.2 Molecular Characterization of LMW-GS Genes 395
13.5 MALDI/MS: A New Technique Used to Analyze 397
   the Proteins in Plants
13.6 Albumins and Globulins 397
13.7 Wheat Gluten and Dietary Intolerance 398
13.8 Conclusion 399
References 399

14. Natural Rubber: Production, Properties and Applications 403
   Thomas Kurian and N. M. Mathew
   14.1 Introduction 403
   14.2 Rubber Yielding Plants 404
   14.3 History 404
   14.4 Plantation Rubber 406
   14.5 Rubber Cultivation 407
      14.5.1 The Para Rubber Tree 407
      14.5.2 Agro-climatic Requirements 408
      14.5.3 Planting 408
      14.5.4 Disease Control 408
      14.5.5 Tapping and Collection of Crop 410
   14.6 Biosynthesis of Rubber 412
   14.7 Chemistry of Latex 413
   14.8 Primary Processing 413
      14.8.1 Preserved and Concentrated Latex 414
      14.8.2 Ribbed Smoked Sheet 415
      14.8.3 Pale Latex Crepe and Sole Crepe 418
      14.8.4 Field Coagulum Crepe 418
      14.8.5 Technically Specified Rubber 419
   14.9 Current Global Status of Production 421
      and Consumption
   14.10 Properties of NR 421
   14.11 Blends of Natural Rubber 423
      14.11.1 Blends of Natural Rubber with Thermoplastics 423
      14.11.2 Preparation of Thermoplastic Natural Rubber 423
      14.11.3 Properties and Applications of TPNR 423
   14.12 Modified Forms of Natural Rubber 424
      14.12.1 Introduction 424
      14.12.2 Hydrogenated Natural Rubber 424
14.12.3 Chlorinated Natural Rubber 424
14.12.4 Cyclized Natural Rubber 425
14.12.5 Graft Copolymers Based on Natural Rubber 425
14.12.6 Epoxidized Natural Rubber 426
14.12.7 Ionic Thermoplastic Elastomers Based on Natural Rubber 427
14.13 Introduction to the Manufacture of Rubber Products 428
14.13.1 Processing Methods 429
14.13.2 Vulcanization Techniques 431
14.14 Applications of Natural Rubber 431
14.14.1 Dry Rubber Products 431
14.14.2 Latex products 432
14.15 Natural Rubber, a Green Commodity 432
14.16 Conclusions 433
References 433

15. Electronic Structures and Conduction Properties of Biopolymers 437
Mohsineen Wazir, Vinita Arora and A.K. Bakhshi
15.1 Introduction 437
15.2 Electronic Conduction in Proteins 438
15.2.1 Introduction 438
15.2.2 Investigations of Electronic Structure and Conduction Properties of Periodic and Aperiodic Polypeptides 439
15.2.3 Factors Affecting the Conduction Properties of Proteins 444
15.3 Electronic Conduction in DNA 447
15.3.1 Introduction 447
15.3.2 Mechanisms of Electron Transfer in DNA 447
15.3.3 Factors Affecting the Conductivity of DNA 448
15.3.4 Investigation of the Electronic Structure of DNA Base Stacks 448
15.4 Conclusions 453
References 454

Part 4: Biopolymers for Specific Applications

16. Applications of Biopolymers in Agriculture with Special Reference to Role of Plant Derived Biopolymers in Crop Protection 461
S. Niranjan Raj, S.N. Lavanya, J. Sudisha, and H. Shekar Shetty
16.1 Introduction 461
16.2 Biopolymers 462
16.3 Sources of Biopolymers 463
16.3.1 Plants 463
16.3.2 Microbes 464
16.3.3 Animals 466
16.3.4 Agricultural Wastes 466
xiv  CONTENTS

16.3.5 Fossils 466
16.4 Application of biopolymers in agriculture 467
16.5 Seed coating for value addition 469
16.6 Plant Derived Biopolymers in Plant Growth Promotion 470
16.7 Plant Derived Biopolymers in Plant Disease Management 474
16.8 Integrated Use of Plant Gum Biopolymers 476
16.9 Transgenically Produced Biopolymers 477
16.10 Conclusions and Future Prospects 478
References 479

17. Modified Cellulose Fibres as a Biosorbent for the Organic Pollutants 483
Sami Boufi and Sabrine Alila
17.1 Introduction 483
17.2 Cellulose Structure 484
17.2.1 Molecular Level 484
17.2.2 Supermolecular Structure 485
17.2.3 Ultrastructure 486
17.3 Application of Natural Lignocellulosic Materials as Adsorbents for Organic Pollutants 488
17.4 The Use of Modified Cellulose Fibres as a Sorbent for the Organic Pollutants Removal 491
17.4.1 Adsorption of Model Organic Compounds on Surfactant Treated Cellulose Fibres 491
17.4.2 Different Strategies of Surface Chemical Modification of Cellulose Fibres 497
17.5 Adsorption Properties of Modified Cellulose Fibres 509
17.5.1 Adsorption of Herbicides 512
17.6 Adsorption Isotherm Modelisation 514
17.7 Thermodynamic Parameters 516
17.8 Adsorption Kinetic Modelling 516
17.9 Column Studies 519
17.10 Column Regeneration 519
17.11 Investigation of Adsorption Mechanisms by Laser Induced Luminescence 520
17.12 Conclusion 521
References 522

18. Polymers and Biopolymers in Pharmaceutical Technology 525
István Erős
18.1 Introduction 525
18.2 Purpose of the Use of Polymers in Pharmacy and Medicine 526
18.2.1 Active Substances 527
18.2.2 Bases for Preparations 528
18.2.3 Filling, Binding, Stabilizing and Coating Materials 528
18.2.4 Polymers Controlling Drug Release 529
18.3 Administration of Active Substances through the Mucosa of Body Cavities with the Help of Polymers and Biopolymers 547
18.3.1 Mucoadhesion 548
18.3.2 Mucoadhesive Preparations in the Gastrointestinal Tract 549
18.3.3 Drug Administration through the Nasal Mucosa 550
18.3.4 Mucoadhesive Preparations on the Mucosa of the Eye 551
18.3.5 Mucoadhesive Preparations in the Rectum and in the Vagina 552
18.4 Conclusion 553
References 554

19. Biopolymers Employed in Drug Delivery 559
Betina Giehl Zanetti Ramos
19.1 Introduction 559
19.2 The Most Studied Biopolymers in Drug Delivery 560
19.2.1 Cellulose Derivatives 561
19.2.2 Biopolymers from Marine Source 563
19.2.3 Others Polysaccharides 565
19.2.4 Polyhydroxyalcanoates 569
19.2.5 Biopolymers from Proteins 570
19.3 Conclusion 571
References 571

20. Natural Polymeric Vectors in Gene Therapy 575
Patit P. Kundu and Kishor Sarkar
20.1 Introduction 575
20.2 Cationic Polymers 577
20.3 Natural Polymers as Nonviral Vectors in Gene Therapy 578
20.3.1 Chitosan 578
20.3.2 Gelatin 592
20.3.3 Alginate 593
20.3.4 Arginine 594
20.3.5 Collagen 596
20.4 Conclusions 599
References 599

Index 605
This page intentionally left blank
Preface

There is currently a tremendous interest in the latest information concerning polymer related topics. Experts predict the future availability of fossil resources (oil, natural gas and coal), which are not renewable, varies between one and three generations. Keeping in mind the deteriorating environmental conditions caused by many factors including advancements in science and technology, population expansion, global warming, etc, researchers all over the world have recently focused on biopolymers from renewable resources with much success.

This book focuses on different biopolymers and their applications in various fields. It highlights recent advances in technology in many areas from chemical synthesis and biosynthesis to end-user applications. These areas have not been covered in a single book before, and include information on biopolymers from chemical and biotechnological modifications, material structures, processing, characterization, properties, and applications.

Chapters cover nearly every conceivable topic related to polysaccharides, such as biofibers, bioplastics, biocomposites, natural rubbers, proteins, gums, and bacterial polymers. Given the global context it does not seem preposterous to consider the materials discussed as the polymers of the future.

The book distills recent research conducted by the scientific community. It is arranged in four parts. Part I, Polysaccharides, covers hyaluronic acid, chitin and chitosan, starch and other natural polysaccharides. Polysaccharides have received more attention due to their numerous advantages such as their renewability, non-toxicity, biodegradability and ready availability. This interest has resulted in a great revolution leading to polysaccharides becoming on par with, and even superior to, synthetic materials. That is why a plethora of research studies have been undertaken to understand the potential of these natural polymers.

Hyaluronic acid is a linear polysaccharide formed from disaccharide units containing N-acetyl-D-glucosamine and glucuronic acid. Since it is present in almost all biological fluids and tissues, hyaluronic acid-based materials are very useful in biomedical applications. After cellulose, chitin is the second most abundant natural polysaccharide resource on earth. Chitin and its de-acetylated derivative chitosan are natural polymers composed of N-acetylglucosamine and glucosamine. Both chitin and chitosan have excellent properties such as biodegradability, biocompatibility, non-toxicity, hemostatic activity and antimicrobial activity. Chitin and its derivatives are widely used in various fields of medicine.
Polysaccharides and their graft copolymers are finding extensive applications in diversified fields. The graft copolymerized and crosslinked polysaccharides are cost effective, biodegradable and quite efficient for use in technological processes. The end products obtained have improved properties that can be used in fields such as sustained drug delivery systems, controlled release of insecticides and pesticides to protect plants in agricultural and horticultural practices, release of water for plants during drought conditions, water treatment and membrane technology. Modified polysaccharides have found applications from permselective membranes to ionically conductive membranes for fuel cells.

Starch is the major carbohydrate reserve in higher plants and has been one of the materials of choice since the early days of human technology. Recently, starch gained new importance as a raw material in the production of bioplastics, in particular for use in the synthesis of monomers to produce polymers such as poly(lactic acid), and after chemical modification and thermomechanical processing, to produce the so-called thermoplastic starch.

Part II discusses bioplastics and biocomposites. One of the main environmental problems in industrial development is plastic waste and its disposal. An enormous part of scientific research has been directed towards environmentally benevolent bioplastics that can easily be degraded or bio-assimilated. High performance bio-based composites (biocomposites) are very economical and open up a wide range of applications.

Part III covers different biopolymers such as gums, proteins, natural rubbers and bacterial polymers and some of their applications. The genus Cassia has been the centre of attraction for many phytochemists throughout the world, especially in Asia. Cassia plants are a known source of seed gums which are usually galactomannans having close structural resemblance to many of the commercial seed gums, such as guar and locust bean gums, and are considered as non-conventional renewable reservoirs for the galactomannan seed gums. Thus, properties of Cassia seed gums in general can be tailored by chemical modification whereupon they can be exploited as useful dye flocculants and heavy metal adsorbents depending upon their solubility in water. Though galactomannans from Cassia seeds are nonionic polysaccharides, their adsorption performance is comparable with that of chitin and chitosan, and superior to other polysaccharides.

Gum Arabica is a natural plant gum that exudates a carbohydrate type and is an electroactive biopolymer. Gum Arabica and its complexes have potential applications in developing ionic devices such as batteries, sensors, bio-sensors, and other electronic applications, in addition to solar material, energy storage material and nanoscience. Biopolymers obtained from bacteria are rapidly emerging because they are biodegradable and available in abundance. Simple methods are being developed to grow and harvest the polymers to exploit them for numerous industrial and biomedical applications. Electronic structures and conduction properties of biopolymers are also discussed in Part III.

Part IV includes applications of various biopolymers such as seed coating to protect against biotic stress, biosorbent for the organic pollutant, pharmaceutical technology, drug delivery, and gene therapy.

Discussions in this book regarding the very important issues and topics related to biopolymers should be useful to those in the scientific community such as,
scientists, academicians, research scholars, polymer engineers and specialists in other industries. The book also acts as a support for undergraduate and postgraduate students in the institutes of polymer and technology and other technical institutes. We hope it will be an exceptional book with important contributions from well-known experts from all over the world.

Both Editors would like to express their gratitude for all the excellent contributions made by the contributors to this book. We would also like to thank all who helped in the editorial work as well.

Susheel Kalia
Luc Avérous
April 2011
List of Contributors

Sabrine Alila is Associate Professor in the Department of Chemistry of the University of Sfax, Tunisia. Her research topic is concerned with surface chemical modification of cellulose fibres in order to enhance their absorption capacity toward dissolved organic pollutants, including pesticides and herbicides.

Vinita Arora is presently Assistant Professor and Research Scholar in the Department of Chemistry, University of Delhi, India. She is a MSc (Chemistry) Gold Medalist from Delhi University and her research interests include theoretical designing of novel electrically conducting polymers and biopolymers.

Marjorie S. Austero is a MS Food Science/PhD candidate in the Materials Science and Engineering Department at Drexel University, USA. She is currently working with the Natural Polymers and Photonics Groups and her current research is focused on biopolymer materials for use in filtration and active food packaging systems.

A.K. Bakhshi is presently Head, Chemistry Department, Delhi University, where he has held the prestigious Sir Shankar Lal Chair of Chemistry since 1996. A double gold medalist, Dr. Bakhshi did his post-doctoral training in Germany and Japan. He is the author/coauthor of more than 140 research and education articles, five monographs and one patent.

Antonio J. F. Carvalho received his BSc in Chemistry and PhD in Materials Science from University of São Paulo. He worked at the Pirelli Corporation for 10 years but later moved to a position at the Federal University of São Carlos and then to University of São Paulo. His research interests include reactive extrusion, polymers from renewable resources, and surface chemistry.

Cécile Courgneau received her MS in chemical science from National Institute of Applied Science of Rouen in 2007 and her PhD in macromolecular science from AgroParisTech, in 2011. Her research is focused on the crystallinity and the gas and organic compound transport properties of polylactide.

Dipaloy Datta is a Lecturer in Chemical Engineering at the Birla Institute of Technology in India. His research interests includes separation in biotechnology, polymer technology, liquid-liquid equilibrium and, modeling & simulation.
Tereza Dekova is an Assistant Professor of Genetics at Sofia University, Bulgaria. Her interests include genetics, proteomics, cytogenetics and genomics in plants. Dr. Dekova is the author of the 25 scientific articles.

Sandra Domenek is an Associate Professor at the Graduate School AgroParisTech, Paris, France. She holds an MS in Chemical Engineering from the Technical University of Graz, Austria and a PhD in Biotechnology from SupAgro Montpellier. Her research focuses on the relationship between transport properties in polymers and microstructure applied on biobased thermoplastics.

Violette Ducruet is a Senior Scientist at the National Institute for Agricultural Research (INRA), in Massy, France. In 1981, she earned her PhD in Food Science. Since 1991, she works on mass transfer between food and petrochemical packaging material implying food safety and sensorial impacts. She is involved in the characterization of the structure/barrier properties relationship of biobased polymers.

István Erös is Emeritus Professor from the Institute of Pharmaceutical Technology, University of Szeged in Hungary. He has authored more than 250 English language journal articles as well as authored or edited 7 books.

Keith J. Fahnestock is a MS student in the Materials Science and Engineering Department at Drexel University.

Sutapa Ghosh has a PhD in Chemistry and works as a scientist in the Indian Institute of Chemical Technology, Hyderabad, India. She has expertise on biopolymers for environmental applications.

Sevdalin Georgiev received his PhD and DSc in Genetics from Institute of Genetics from the Sofia University, Bulgaria where is now a Professor of Genetics. His research interests includes genetics and genomics in plants.

Rathna Gundloori has a PhD in Chemistry and works as a scientist in the National Chemical Laboratory, Pune, India. Her research interests are in biopolymers for biomedical and environmental applications.

Eva Hrabarová works at the Institute of Chemistry, Slovak Academy of Sciences in Bratislava, Slovakia. Her research interests focus on the study of preparation of cellulose derivatives, characterization of pectins/pectates, hyaluronan degradation, isolation and characterization of recombinant proteins such as GFP.

B. S. Kaith is Professor & Head of the Department of Chemistry at the National Institute of Technology, Jalandhar, India. He has more than 80 research papers in peer-reviewed international journals and 160 research papers in the proceedings of the international and national conferences.

Susheel Kalia is Assistant Professor in the Department of Chemistry, Bahra University, Shimla Hills, India. He received his PhD from PTU Jalandhar and has 33 research papers to his credit in international journals along with 50 publications in proceedings of national & international conferences.
Pramendra Kumar is an Assistant Professor in the Chemistry Department at M.J.P. Rohilkhand University, Bareilly. He obtained his Master of Science from C.C.S. University, Meerut and Master of Engineering from Delhi College of Engineering. His research interests include modification of polysaccharides, synthesis of multifunctional nano materials and synthesis of nano bio-composites for their various applications e.g. water remediation, enzyme immobilization and other adsorbent applications.

Sushil Kumar is an Assistant Professor in the Chemical Engineering Department at the Birla Institute of Technology, India. He earlier worked with the Central Institute of Plastic Engineering and Technology (CIPET), Lucknow, INDIA. His research areas include process intensification, polymer technology & biopolymers, separation processes in biotechnology and modeling & simulation. He has 34 research publications (11 journals and 23 conferences) to his credit.

Patit P. Kundu is Professor in the Department of Polymer Science & Technology at Calcutta University, India. He obtained his PhD in 1997 from IIT, Kharagpur, India. He has 67 research papers to his credit in international journals along with ten papers in national/international conferences, contributed 2 book chapters, and one patent. His research interest centers on the fields of synthesis and characterization of oil based rubber and nano-composites, microbial fuel cell, direct methanol fuel cell, microbial biodegradation of waste polyolefin film, tissue engineering and gene therapy.

Thomas Kurian is a Professor of Polymer Technology at the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, India. Dr. Kurian received his PhD in Rubber Technology from IIT Kharagpur.

N.M.Mathew retired as Director of the Rubber Research Institute of India in October 2006. He has published more than 100 papers and edited four books on rubber.

Hemant Mittal and Jaspreet Kaur Bhatia are research scholars in the Department of Chemistry, National Institute of Technology, Jalandhar, India.

P. L.Nayak is an eminent polymer scientist and is now the Chairman of P.L.Nayak Research Foundation, Cuttack, India. He possesses both PhD and DSc Degrees in Polymer Science and Technology. He has done extensive research work on biopolymers, polymers for biomedical applications, nanomedicine, nanobio-technology, controlled drug delivery and conducting polymers. About 80 of his students have been awarded a PhD Degree. He has published more than 400 peer reviewed research papers in international journals in various fields of Polymer Science and Technology.

Sanjay Kumar Nayak is the Professor & Chair of Laboratory for Advanced Research in Polymeric Materials (LARPM), an exclusive R&D wing of the Central Institute of Plastics Engineering & Technology (CIPET), an Academic
Institution under the Dept. of Chemicals & Petrochemicals, Indian Ministry of Chemicals & Fertilizers. Prof Nayak has been heading the operations of 15 CIPET centres, situated at different locations in India, over the past 4 years. He has 24 years of research experience in the areas of polymer composites, nanocomposites, blends & alloys, recycling technologies & biopolymers. Prof Nayak has delivered over 300 presentations at national & international conferences, published over 150 research papers and has been awarded 5 patents.

S.N. Lavanya completed her MSc in Botany and MPhil in Seed Technology from the University of Mysore, India and is currently working as a research fellow in the UGC sponsored project. Her research areas include lipid transfer proteins in plant defense, induced resistance in plants, biological control and isolation of biomolecules from plants and microbes.

Smita Mohanty is working as a Scientist at Laboratory for Advanced Research in Polymeric Materials (LARPM). Dr. Mohanty’s research interests include biopolymers, blend nanocomposites and natural fiber based composites. She has 8 years of research experience and has 50 research publications and 5 patents to her credit. She has guided 15 Masters Thesis and 2 doctoral students.

Sagar Pal is an Assistant Professor in the Department of Applied Chemistry, Indian School of Mines, Dhanbad, India. Previously he was Lecturer at Birla Institute of Technology and has worked as and R&D Scientist at Hindustan Gum & Chemicals, Ltd. in Bhiwani. His research interests are in the field of synthesis and applications of polymeric biomaterials.

Nikhil Prakash is a Lecturer in the Chemical Engineering Department at the Birla Institute of Technology, India. His research areas include polymer science and technology, kinetics of polymers and modeling & Simulation.

Niranjan Raj is working as Assistant Professor in the Department of Studies in Biotechnology, University of Mysore. He is the recipient of Paul Neergaard Gold Medal for his work in seed technology. He has more than 10 years of teaching and research experience and has published more than 35 research articles in international and national journals.

Betina Ramos graduated in Pharmacy at the Univeridade Federal de Santa Catarina, Brazil and earned her PhD in Chemistry from Université Bordeaux, France. She is the Technical Director and head of the Department of Research, Development and Innovation at the Nanovetores company which is involved with Encapsulated High Technology. She has published 16 articles, written and translated many book chapters as well as being the inventor of 5 patents.

Debasish Sahoo is a senior lecturer in the Institute of Nanobiotechnology, Cuttack, India. He has an MSc in Biotechnology and has carried out extensive research work on biomedical applications of chitosan. He recently submitted his PhD thesis to the faculty of Biotechnology, Utkal University.
Boufi Sami is Professor at the Department of Chemistry of the University of Sfax, Tunisia. His research activities include chemical modification of cellulose and carbohydrate materials, the synthesis of functional polymer for colloidal chemistry, and the exploitation of chemically modified cellulose fibres as reusable adsorbent for dissolved organic pollutants.

Aloke Sarkar gained her PhD at the University of Calcutta. She joined the Bijoy Krishna Girls'College in 1982 and is currently Associate Professor of Physics at Jadavpur University, Kolkata. Her research interests include nanomaterials, quantum mechanics, spintronics, and bio-materials.

Kishor Sarkar is Senior Research Fellow in the Department of Polymer Science & Technology at Calcutta University, India. He obtained B. Tech. and M. Tech. degrees in Polymer Science & Technology from University of Calcutta, India in 2006 and 2008, respectively. His research interest centers on the fields of synthesis and characterization of PAMAM dendrimer, chitosan and chitosan derivatives for their application in gene therapy and waste water treatment.

Caroline L. Schauer received her BS in Chemistry from Beloit College and PhD in Chemistry from SUNY at Stony Brook. She is an Associate Professor in the Department of MSE at Drexel University and has 21 publications and 2 patents in the field of polysaccharides (out of 31 total publications).

J. Schiller is currently group leader at Leipzig University (Biophysics). His research focus is on (phospho)lipids and polysaccharides and their structural investigation by using NMR, mass spectrometry and chromatographic techniques. Dr. Schiller is the author of about 150 journal papers, reviews and contributions to books. He has about 1000 citations.

Gautam Sen received his PhD from Birla Institute of Technology, India, where he is now an Assistant Professor. His current research includes development of graft copolymer based smart materials and their futuristic applications.

Ashoke Sharon received his PhD from CDRI, Lucknow, India and then moved to Drug Discovery Group at the University of Georgia, USA for postdoctoral research on design and synthesis of new chemical entity as antiviral candidate. In 2009, he returned to India to join Birla Institute of Technology as an Assistant Professor. His current research includes in-silico simulation, molecular modeling and synthesis of nucleosides/non-nucleosides analogs towards drug discovery.

H. Shekar Shetty is leading the research work on Biology and Control of Plant Diseases at the Department of Studies in Biotechnology, University of Mysore, India. Prof. Shetty is a Fellow of Indian Academy of Sciences (FASc,), Fellow of National Academy of Agricultural Sciences (FNAAS) and Fellow of National Academy of Sciences (FNASC). He has won many national and international prestigious awards including the International Seed Health Award by the Danish Seed Health Center in 2006. He has 338 research publications in national and international journals and has guided 40 research students for PhD.
Vandana Singh is working as Associate Professor at Department of Chemistry, University of Allahabad, Allahabad, India. She joined the Chemistry Department as Lecturer in 1994. Her research interests are polysaccharides, polymers and polymer composites. Currently she is working on the biomimetic synthesis and applications of silica hybrids. She has over 70 international journal publications to her credit. She is Associate editor of Advanced Materials Letters, VBRI Press.

Dr. Šoltés has been employed for over 30 years at Academic Research Institutes in Bratislava, Slovakia. His research related to the polysaccharides, which started over two decades ago, resulted in patenting a novel approach “Clathrate complexes formed by hyaluronic acid derivatives and use thereof as pharmaceuticals”. His current research interests are focused on the studies of hyaluronan oxidative damage and the regulation of this process. Dr. Šoltés is the sole distinguished representative of Slovakia in the International Society for Hyaluronan Sciences. In 2007 he was named Scientist of the Year of the Slovak Republic.

J. Sudisha is working as a Scientist in the Department of Studies in Biotechnology, University of Mysore, India. He has published more than 30 research articles in reputed international and national journals and has several merits and awards to his credit including the Young Scientist award from Association of Microbiologists of India.

N. Volpi is Associate Professor in Biochemistry at the University of Modena & Reggio Emilia, Italy where he teaches biological chemistry. He has published 4 books, 130 scientific papers, 80 communications to congress and two books as the editor. His main interest is the study of complex carbohydrate macromolecules named proteoglycans and glycosaminoglycans.

Mohsineen Wazir is currently working as an Assistant Professor in Zakir Husain College, University of Delhi and is also pursuing research from the Department of Chemistry, University of Delhi. She received the UGC Research Fellowship in Science for Meritorious Students in March 2008 and the CSIR Junior Research Fellowship in June 2008. Her research interests include the development of robust optimization algorithms for the designing and theoretical investigation of biopolymers and conducting polymers.
PART 1
POLYSACCHARIDES
This page intentionally left blank