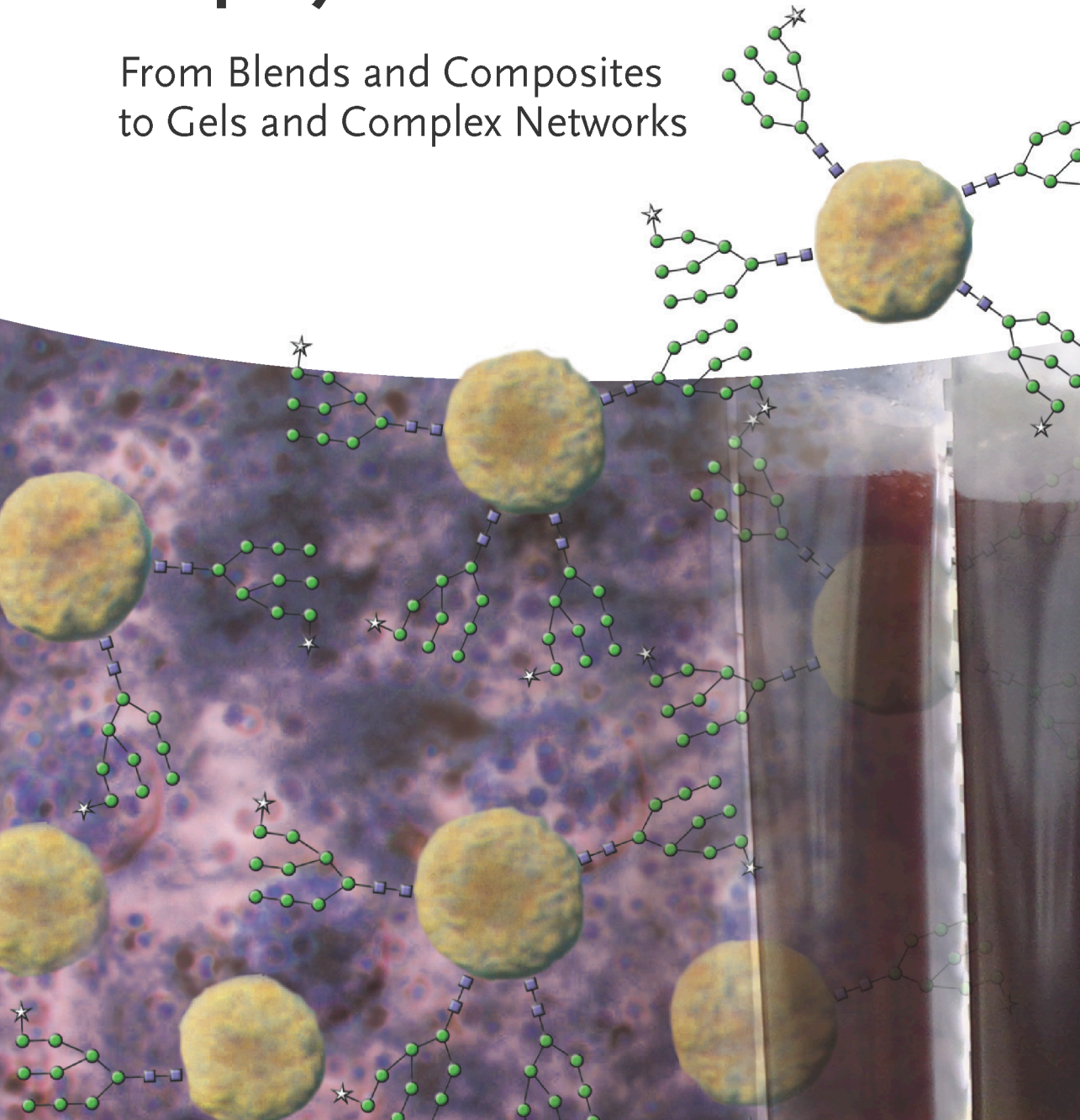


S. Thomas, D. Durand,
C. Chassenieux, and P. Jyotishkumar

Handbook of Biopolymer-Based Materials

From Blends and Composites
to Gels and Complex Networks



Edited by
Sabu Thomas,
Dominique Durand,
Christophe Chassenieux, and
P. Jyotishkumar

Handbook of
Biopolymer-Based Materials

Related Titles

Lendlein, A., Sisson, A. (Eds.)

**Handbook of Biodegradable
Polymers**
**Synthesis, Characterization and
Applications**

2011

Hardcover

ISBN: 978-3-527-32441-5

Kalia, S., Avérous, L.

Biopolymers
Biomedical and Environmental
Applications Series: Wiley-Scrivener

2012

Hardcover

ISBN: 978-0-470-63923-8

Mittal, V. (Ed.)

Renewable Polymers
Synthesis, Processing, and Technology

2012

Hardcover

ISBN: 978-0-470-93877-5

McDermott, A. (Ed.)

Solid State NMR Studies of
Biopolymers

2010

Hardcover

ISBN: 978-0-470-72122-3

Loos, K. (Ed.)

Biocatalysis in Polymer
Chemistry

2011

Hardcover

ISBN: 978-3-527-32618-1

*Edited by Sabu Thomas, Dominique Durand,
Christophe Chassenieux, and P. Jyotishkumar*

Handbook of Biopolymer-Based Materials

From Blends and Composites to Gels and Complex Networks



**WILEY-
VCH**

WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Prof. Dr. Sabu Thomas

Mahatma Gandhi University
Centre for Nanosc.a. Nanotech.
Priyadarshini Hills P.O.
Kottayam, Kerala 686-560
India

Prof. Dominique Durand

LUNAM Université du Maine
IMMM UMR CNRS 6283
Dept. Polymères, Colloïdes, Interfaces
1, Avenue Olivier Messiaen
72085 Le Mans cedex 9
France

Prof. Christophe Chassenieux

LUNAM Université du Maine
IMMM UMR CNRS 6283
Dept. Polymères, Colloïdes, Interfaces
1, Avenue Olivier-Messiaen
72085 Le Mans cedex 9
France

Dr. P. Jyotishkumar

INSPIRE Faculty
Department of Polymer Science and
Rubber Technology
Cochin University of Science and
Technology, Kochi-682022

All books published by **Wiley-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

©2013 Wiley-VCH Verlag GmbH & Co. KGaA,
Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-32884-0

ePDF ISBN: 978-3-527-65248-8

ePub ISBN: 978-3-527-65247-1

mobi ISBN: 978-3-527-65246-4

oBook ISBN: 978-3-527-65245-7

Cover Design Grafik-Design Schulz, Fußgönheim

Typesetting Thomson Digital, Noida, India

Printing and Binding Markono Print Media Pte Ltd,
Singapore

Contents

Foreword XXIII

List of Contributors XXV

1	Biopolymers: State of the Art, New Challenges, and Opportunities	1
	<i>Christophe Chassenieux, Dominique Durand, Parameswaranpillai Jyotishkumar, and Sabu Thomas</i>	
1.1	Introduction	1
1.2	Biopolymers: A Niche For Fundamental Research in Soft Matter Physics	3
1.3	Biopolymers: An Endless Source of Applications	4
1.4	Topics Covered by the Book	5
1.5	Conclusions	5
	References	6
2	General Overview of Biopolymers: Structure, Properties, and Applications	7
	<i>Charles Winkworth-Smith and Tim J. Foster</i>	
2.1	Introduction	7
2.2	Plant Cell Wall Polysaccharides	11
2.2.1	Cellulose	11
2.2.1.1	Cellulose Extraction	12
2.2.1.2	Nanocellulose	13
2.2.1.3	Microfibrillated Cellulose	14
2.2.1.4	Cellulose Nanowhiskers	14
2.2.2	Hemicelluloses	15
2.2.2.1	Galactomannans	15
2.2.2.2	Konjac Glucomannan	19
2.2.2.3	Xylan	19
2.2.2.4	Xyloglucan	20
2.2.3	Pectins	21
2.3	Biocomposites	23
2.3.1	Natural Fiber Composites	23

2.3.2	Cellulose Composites	25
2.3.3	Cellulose–Polymer Interactions	26
2.3.4	Semi-Solid Composites	27
2.4	Future Outlook	28
	References	29
3	Biopolymers from Plants	37
	<i>Maria J. Sabater, Tania Ródenas, and Antonio Heredia</i>	
3.1	Introduction	37
3.2	Lipid and Phenolic Biopolymers	38
3.2.1	The Biopolymer Cutin	38
3.2.1.1	Cutin Monomers: Biosynthesis and Physicochemical Characteristics	39
3.2.1.2	Molecular Architecture of Cutin	40
3.2.1.3	Cutin Biosynthesis	41
3.2.2	Lignin	42
3.2.2.1	Monomer Precursors and Chemical Reactivity	42
3.2.2.2	Lignin Biosynthesis	43
3.2.3	Suberin	45
3.2.3.1	Chemical Composition	45
3.2.3.2	Biosynthesis and Fine Structure	47
3.3	Carbohydrate Biopolymers: Polysaccharides	48
3.3.1	Structural Polysaccharides	49
3.3.1.1	Cellulose	49
3.3.1.2	Hemicellulose	54
3.3.1.3	Pectin	57
3.3.2	Storage Polysaccharides	59
3.3.2.1	Starch	59
3.3.2.2	Fructans: Inulin	63
3.3.3	Other: Gums (Guar Gum, Gum Arabic, Gum Karaya, Gum Tragacanth, and Locust Bean Gum)	66
3.4	Isoprene Biopolymers: Natural Rubber	67
3.4.1	<i>cis</i> -Polyisoprene	67
3.4.1.1	Occurrence	67
3.4.1.2	Composition, Structure, and Properties	67
3.4.1.3	<i>cis</i> -1,4-Polyisoprene Biosynthesis	68
3.4.1.4	Applications	73
3.4.2	<i>trans</i> -Polyisoprene	73
3.5	Concluding Remarks	74
	References	75
4	Bacterial Biopolymers and Genetically Engineered Biopolymers for Gel Systems Application	87
	<i>Deepti Singh and Ashok Kumar</i>	
4.1	Introduction	87
4.1.1	Nucleic Acid Biopolymers: Central Dogma	89

4.2	Microbial Polysaccharides as Biopolymers	90
4.2.1	Synthesis and Applications	90
4.3	Microbial Biopolymers as Drug Delivery Vehicle	92
4.3.1	ϵ -Poly-L-Lysine (ϵ -PL) and Its Applications	92
4.3.2	Polyhydroxyalkanoates and Its Applications	92
4.4	Polyanhydrides	93
4.5	Recombinant Protein Polymer Production	94
4.6	Recombinant Genetically Engineered Biopolymer: Elastin	95
4.7	Collagen as an Ideal Biopolymer	97
4.7.1	Microbial Recombinant Collagens: Production in <i>Pichia Pastoris</i>	97
4.8	Biopolymers for Gel System	99
4.9	Hydrogels of Biopolymers for Regenerative Medicine	99
4.9.1	Polysaccharide Hydrogels	99
4.9.2	Cellulose-Derived Biopolymers-Based Hydrogels	100
4.9.3	Protein Biopolymers-Based Hydrogels	100
4.10	Supermacroporous Cryogel Matrix from Biopolymers	100
4.10.1	Protein Cryogel	101
4.11	Biopolymers Impact on Environment	102
4.12	Conclusion	103
	References	104
5	Biopolymers from Animals	109
	<i>Khaleelulla Saheb Shaik and Bernard Moussian</i>	
5.1	Introduction	109
5.2	Chitin and Hyaluronic Acid in the Living World	110
5.3	Milestones in Chitin History	110
5.4	From Trehalose to Chitin	112
5.5	Chitin Synthase	115
5.6	Regulation of Chitin Synthesis in Fungi	117
5.7	Organization of Chitin in the Fungal Cell Wall	118
5.8	Organization of Chitin in the Arthropod Cuticle	119
5.9	Chitin-Organizing Factors	123
5.10	Secretion and Cuticle Formation	126
5.11	Transcriptional Regulation of Cuticle Production	128
5.12	Chitin Synthesis Inhibitors	130
5.13	Noncuticular Chitin in Insects	131
5.14	Chitin as a Structural Element	133
5.15	Application of Chitin	134
5.16	Conclusion	135
	References	135
6	Polymeric Blends with Biopolymers	143
	<i>Hero Jan Heeres, Frank van Maastrigt, and Francesco Picchioni</i>	
6.1	Introduction	143
6.2	Starch-Based Blends	146

6.2.1	Polymer Selection for Starch Blending	147
6.2.2	Starch Structure	150
6.2.3	Uncompatibilized Blends	152
6.2.4	Compatibilization	155
6.2.5	Composites	157
6.3	Blends with Chitosan (One Amino Group Too Much . . .)	158
6.4	Future Perspectives	161
6.4.1	Biopolymer Plasticization	161
6.4.2	Blend Morphology and Compatibilization	162
6.4.3	Blend Processing: Technological Aspects	163
	References	164
7	Macro-, Micro-, and Nanocomposites Based on Biodegradable Polymers	173
	<i>Luc Avérous and Eric Pollet</i>	
7.1	Introduction	173
7.2	Biodegradable Polymers	174
7.2.1	Classification	174
7.2.2	Agro-Polymers: The Case of Starch	175
7.2.2.1	Native Starch Structure	175
7.2.2.2	Plasticized Starch	176
7.2.3	Biodegradable Polyesters	177
7.2.3.1	Polyesters Based on Agro-Resources	177
7.2.3.2	Petroleum-Based Polyesters	179
7.3	Biocomposites	181
7.3.1	Generalities	181
7.3.2	The Case of Biocomposites Based on Agro-Polymers	181
7.3.2.1	Cellulose Fiber Reinforcement	181
7.3.2.2	Lignin and Mineral Fillers	182
7.3.3	The Case of Biocomposites Based on Biopolyesters	182
7.3.3.1	Generalities	182
7.3.3.2	The Case of Biocomposites Based on Aromatic Copolyesters	183
7.4	Nanobiocomposites	186
7.4.1	Generalities	186
7.4.2	Nanobiocomposites Based on Agro-Polymers (Starch)	187
7.4.2.1	Whisker-Based Nanobiocomposites	190
7.4.2.2	Starch Nanocrystal-Based Nanobiocomposites	190
7.4.2.3	Nanoclay-Based Nanobiocomposites	190
7.4.3	Nanobiocomposites Based on Biopolyesters	193
7.4.3.1	Poly(lactic acid)-Based Nanobiocomposites	193
7.4.3.2	Polyhydroxyalkanoate-Based Nanobiocomposites	194
7.4.3.3	Polycaprolactone-Based Nanobiocomposites	195
7.4.3.4	Biodegradable Aliphatic Copolyester-Based Nanobiocomposites	197
7.4.3.5	Aromatic Copolyester-Based Nanobiocomposites	199
	References	200

8	IPNs Derived from Biopolymers	211
	<i>Fernando G. Torres, Omar Paul Troncoso, and Carlos Torres</i>	
8.1	Introduction	211
8.2	Types of IPNs	212
8.3	IPNs Derived from Biopolymers	214
8.3.1	Alginate	215
8.3.2	Agarose	215
8.3.3	Chitosan	215
8.3.4	Starch	216
8.3.5	Dextran	217
8.3.6	Gum Arabic	217
8.3.7	Fibrinogen	217
8.3.8	Collagen and Gelatin	217
8.3.9	Cellulose and Cellulose Derivatives	218
8.3.10	Polyhydroxyalkanoates	218
8.3.11	Lactide-Derived Polymers	219
8.4	Manufacture of IPNs	220
8.4.1	Casting–Evaporation Processing	220
8.4.2	Emulsification Cross-Linking Technique	220
8.4.3	Miniemulsion/Inverse Miniemulsion Technique	221
8.4.4	Freeze Drying Technique	222
8.5	Characterization of IPNs	222
8.5.1	Morphological and Structural Characterization	222
8.5.2	FTIR Spectroscopy	223
8.5.3	Mechanical Characterization	224
8.5.4	Rheological Characterization	225
8.5.5	Swelling Behavior Characterization	225
8.5.6	Thermal Characterization	226
8.6	Applications of IPNs	226
8.6.1	Drug Delivery Applications	226
8.6.2	Scaffolds for Tissue Engineering	227
8.6.3	Other Biomedical Applications	227
8.6.4	Antibacterial Applications	228
8.6.5	Sensor, Actuators, and Artificial Muscle Applications	228
8.7	Conclusions	229
	References	229
9	Associating Biopolymer Systems and Hyaluronate Biomaterials	235
	<i>Deborah Blanchard and Rachel Auzély-Velty</i>	
9.1	Introduction	235
9.2	Synthesis and Self-Association of Hydrophobically Modified Derivatives of Chitosan and Hyaluronic Acid in Aqueous Solution	237
9.2.1	General Aspects of Association in Amphiphilic Polyelectrolytes	237
9.2.2	Synthesis and Behavior in Aqueous Solution of Hydrophobically Modified Water-Soluble Derivatives of Chitosan	239

9.2.3	Synthesis and Behavior in Aqueous Solution of Hydrophobically Modified Water-Soluble Derivatives of Hyaluronic Acid	242
9.3	Design of Novel Biomaterials Based on Chemically Modified Derivatives of Hyaluronic Acid	248
9.3.1	Nanoassemblies Based on Amphiphilic Hyaluronic Acid	249
9.3.2	Hydrogels for Cell Biology and Tissue Engineering	254
9.3.2.1	Strategies for the Cross-Linking of HA to Obtain Scaffolds for Cells	254
9.3.2.2	Engineering Biological Functionality in Hyaluronic Acid-Based Scaffolds	260
9.3.2.3	Patterning of Hyaluronic Acid	261
9.4	Conclusions	271
	References	271
10	Polymer Gels from Biopolymers	279
	<i>Esra Alveroglu, Ali Gelir, and Yasar Yilmaz</i>	
10.1	Introduction	279
10.2	Experimental Methods	279
10.3	Polymerization and Gelation Kinetics	281
10.3.1	Fluoroprobe–Polymer Interactions	283
10.3.2	Real-Time Monitoring of Monomer Conversion	286
10.4	Sol–Gel Transition and Universality Discussion	287
10.5	Imprinting the Gels	292
10.6	Heterogeneity of Hydrogels	301
10.6.1	Effect of Ion Doping on Swelling Properties and Network Structure of Hydrogels	301
10.6.2	Current Measurements for Searching the Internal Morphology of the Gels	302
10.7	Ionic p-Type and n-Type Semiconducting Gels	303
10.7.1	Electrical Properties of Ionic p-Type and n-Type Semiconducting Gels	304
10.7.2	Polymeric Gel Diodes with Ionic Charge Carriers	305
10.8	Conclusions	307
	References	308
11	Conformation and Rheology of Microbial Exopolysaccharides	317
	<i>Jacques Desbrieres</i>	
11.1	Introduction	317
11.2	Conformation of Polysaccharides	318
11.3	Secondary Solid-State Structures for Microbial Polysaccharides	318
11.3.1	No Secondary Solid-State Structure	319
11.3.2	Single-Chain Conformation	319
11.3.3	Simple or/and Double Helices	321
11.3.4	Double Helix	323
11.3.5	Triple Helix	323

11.4	Conformation in Solution: Solution Properties and Applications	325
11.4.1	Dextran and Pullulan	325
11.4.2	Hyaluronan	326
11.4.3	Xanthan	331
11.4.4	Succinoglycan	334
11.5	Gelling Properties in the Presence of Salts	336
11.5.1	$\beta(1\rightarrow4)$ -D-Glucuronan	336
11.5.2	Polysaccharide 1644	337
11.5.3	Gellan and Similar Polysaccharides	337
11.5.4	$\beta(1\rightarrow3)$ -D-Glucans	341
11.5.5	YAS 34	342
11.6	Conclusions	345
	References	345
12	Sulfated Polysaccharides in the Cell Wall of Red Microalgae	351
	<i>Shoshana (Malis) Arad and Oshrat Levy-Ontman</i>	
12.1	Introduction	351
12.2	Sulfated Polysaccharides from Red Microalgae – General Overview	352
12.3	Sulfated Polysaccharides of Red Microalgal Cell Walls: Chemical Aspects	354
12.4	Proteins in the Cell Wall of Red Microalgae	355
12.5	Rheology of Red Microalgal Polysaccharide Solutions	356
12.6	Modifications of the Sulfated Polysaccharides	359
12.7	Red Microalgal Sulfated Polysaccharide Bioactivities	362
	References	365
13	Dielectric Spectroscopy and Thermally Stimulated Current Analysis of Biopolymer Systems	371
	<i>Valérie Samouillan, Jany Dandurand, and Colette Lacabanne</i>	
13.1	Introduction	371
13.2	Theory and Principle of Dielectric Analyses	372
13.2.1	Theoretical Background	372
13.2.1.1	Polarization Mechanisms in Materials	372
13.2.1.2	Orientation Polarization	373
13.2.2	Dynamic Dielectric Spectroscopy	376
13.2.2.1	General Principle	376
13.2.2.2	DDS Relaxation Map	377
13.2.2.3	Analysis of DDS Responses	378
13.2.3	Thermally Stimulated Currents	379
13.2.3.1	General Principle	379
13.2.3.2	Complex TSC Thermograms and Experimental Decomposition	380
13.2.4	Relaxation Time	382
13.3	Characterization of Biopolymers	383
13.3.1	Native Biopolymers	383
13.3.2	Role OH Hydration in Biopolymers Dynamics	389

13.3.2.1	Soluble Biopolymers	389
13.3.2.2	Fibrillar Proteins	390
13.3.3	Biological Systems and Biomaterials	395
13.4	Conclusion	398
	References	398
14	Solid-State NMR Spectroscopy of Biopolymers	403
	<i>Garrick F. Taylor, Phedra Marius, Chris Ford, and Philip T.F. Williamson</i>	
14.1	Introduction	403
14.2	NMR of Biological Polymers	404
14.3	Methods for the Study of Biological Polymers	405
14.3.1	Static Powder Samples	406
14.3.2	Oriented Fibers	407
14.3.3	Magic Angle Spinning	408
14.4	Solid-State NMR Experiments Employed for the Analysis of Biopolymers	409
14.4.1	Cross-Polarization	409
14.4.2	Heteronuclear Decoupling	411
14.4.3	Correlation Spectroscopy of Unoriented Samples	412
14.4.4	Correlation Spectroscopy of Oriented Samples	414
14.4.5	Magic Angle Spinning Dipolar Recoupling/Correlation Spectroscopy	415
14.4.6	Homonuclear Dipolar Recoupling Methods	415
14.4.7	Heteronuclear Dipolar Recoupling Methods	418
14.4.8	Analysis of Dynamics in Biopolymers	420
14.5	Application of Solid-State NMR to Biopolymers	422
14.5.1	Silk	422
14.5.2	Structural Studies of Silks Derived from Silkworm	423
14.5.3	Structural Studies of Silks Derived from Spiders	425
14.5.4	Collagen	428
14.5.5	Elastin	432
14.6	Conclusions	436
	References	436
15	EPR Spectroscopy of Biopolymers	443
	<i>Janez Štrancar and Vanja Kokol</i>	
15.1	Introduction	443
15.2	Theoretical Background	445
15.3	Biopolymers	451
15.3.1	Biopolymers Structure and Molecular Motions Determination	451
15.3.2	Biopolymers Degradation Dynamic Study	453
15.3.2.1	Thermal Degradation	453
15.3.2.2	Radiolytic and Photolytic Irradiated Degradation	453
15.3.2.3	Radical Degradation Pathways of Polymers Due to Involved Redox Reactions of Transition Metal Ions	458

- 15.3.3 Determination of Antioxidant Activity of Biopolymers 460
- 15.3.4 Penetration of Small Molecules through Biopolymer Structures 461
- 15.3.5 Biopolymers Functionalization, Polymerization, and/or Cross-Linking 462
- 15.3.6 Biopolymer Surface/Interface Interactions 462
- 15.3.7 Biopolymer Blends Morphology and Temperature-Dependent Behavior 463
- 15.3.8 Biocatalytic Oxidation/Reduction of Biopolymers 465
- 15.4 Conclusion 466
- References 467

16 X-Ray Photoelectron Spectroscopy: A Tool for Studying Biopolymers 473

Ana Maria Botelho do Rego, Ana Maria Ferraria, Manuel Rei Vilar, and Sami Boufi

- 16.1 Introduction 473
- 16.2 XPS Basics 474
 - 16.2.1 Qualitative Aspects 475
 - 16.2.1.1 Binding Energy and Chemical Shift 475
 - 16.2.1.2 Charge Shifts and Auger Parameter 478
 - 16.2.2 Quantitative Aspects 480
 - 16.2.2.1 Atomic Relative Amounts 480
 - 16.2.2.2 Heterogeneities in Depth 481
- 16.2.3 Degradation Induced by X-Ray 483
- 16.3 Cellulose 483
 - 16.3.1 Ultrathin Cellulose Films: A Good Tool for Cellulose Surface Studies 484
 - 16.3.2 Adsorption of a Phthalocyanine on Ultrathin Cellulose Films 485
 - 16.3.3 Activation of Cellulose Film with Isocyanate Derivatives 488
 - 16.3.4 Activation of Cellulose with Imidazole Derivatives 492
 - 16.3.4.1 Surface Grafting of Hemin on Cellulose Films 492
 - 16.3.4.2 Growth of Metallic Nanoparticles on Cellulose Surface 496
 - 16.3.4.3 Controlled Surface Modification of Cellulose Fibers by Amino Derivatives 499
- 16.3.5 Other Works 506
- 16.4 Starch 507
 - 16.4.1 Ability of XPS to Characterize Native Starch 508
 - 16.4.2 Starch Functionalization 508
- 16.5 Chitin and Chitosan 509
 - 16.5.1 Chitin 510
 - 16.5.2 Chitosan 511
- 16.6 Gums 511
 - 16.6.1 Ability of XPS to Characterize Natural Gums 512
 - 16.6.2 Adsorbed Metals and Nanoparticles on Natural Gums 512
- 16.7 Complementary Techniques 513

16.7.1	Infrared Spectroscopy	513
16.7.1.1	Activation of Cellulose Film with Isocyanate Derivatives	513
16.7.1.2	Activation of Cellulose with Imidazole Derivatives: Functionalization with Hemin	517
16.7.1.3	New Hybrid Films Based on Cellulose and Hydroxygallium Phthalocyanine	518
16.7.1.4	Hybrid Systems of Silver Nanoparticles Generated on Cellulose Surfaces	519
16.7.2	Atomic Force Microscopy	521
16.7.2.1	Hydroxygallium Phthalocyanine Physisorbed on Cellulose Films Studied by AFM	522
16.7.2.2	Silver Nanoparticles on Cellulosic Films Studied by AFM	524
16.8	Conclusions	525
	References	526
17	Light-Scattering Studies of Biopolymer Systems	533
	<i>Taco Nicolai and Dominique Durand</i>	
17.1	Introduction	533
17.2	Static Scattering	534
17.2.1	Theoretical Background	534
17.2.2	Applications of Static Scattering Methods to Study Particular Structures and Processes	539
17.2.2.1	Dilute Systems	539
17.2.2.2	Undiluted Systems	543
17.3	Dynamic Light Scattering	545
17.3.1	Theoretical Background	545
17.3.2	Applications of Dynamic Scattering Methods to Study Particular Structures and Processes	548
17.4	Cross-Correlation Dynamic Light Scattering	552
17.4.1	Theoretical Background	553
17.4.2	Applications of Cross-Correlation Dynamic Light Scattering	553
17.5	Turbidimetry	556
17.5.1	Theoretical Background	556
17.5.2	Applications of Turbidimetry	557
17.6	Diffusive Wave Spectroscopy	558
17.6.1	Theoretical Background	558
17.6.2	Applications of Diffusive Wave Spectroscopy	560
17.7	Micro Rheology Using DLS and DWS	561
17.8	Conclusion	563
	References	563
18	X-Ray Scattering and Diffraction of Biopolymers	567
	<i>Yoshiharu Nishiyama and Marli Miriam de Souza Lima</i>	
18.1	Basics	567
18.1.1	Interaction of X-Ray with Electron	567

18.1.2	Structure Factor and Scattered Intensity	568
18.1.3	Diffraction	569
18.1.4	Model System for Small-Angle X-Ray Scattering (SAXS)	570
18.1.5	Explicit Model	572
18.2	Practical Consideration	573
18.2.1	Line- or Point-Focused Beam	573
18.2.2	Monochromator and Filters	573
18.2.3	Choice of Wavelength	573
18.2.4	Beam Size	574
18.3	Examples	574
18.3.1	Molecular Conformation	574
18.3.2	Polydisperse Particles	575
18.3.3	Molecular Shape from Fiber Diffraction	576
18.3.4	Precise Crystallographic Coordinates from Fiber Diffraction or Single Crystal Diffraction	577
18.3.5	Microfocus Capacity and Beam Damage	578
18.4	Conclusions	580
	References	580

19 Large-Scale Structural Characterization of Biopolymer Systems by Small-Angle Neutron Scattering 583

Ferenc Horkay

19.1	Introduction	583
19.2	Basic Principles of SANS	584
19.2.1	Advantages of Using SANS	584
19.2.2	Physical Background	585
19.2.3	Scattering Contrast	587
19.2.4	Form Factor	588
19.2.5	Structure Factor	588
19.2.6	Zero Average Contrast Method	590
19.3	Experimental Examples	591
19.3.1	Similarities between Synthetic and Biopolymer Solutions	591
19.4	Proteins	593
19.4.1	Protein Folding	593
19.4.2	Protein–Water Interaction	594
19.5	Polynucleic Acids (DNA and RNA)	595
19.5.1	Ionic Interactions in DNA Solution	595
19.5.2	DNA Folding	596
19.5.3	Crowding Effects in DNA	598
19.5.4	Crowding and RNA Folding	599
19.6	Polysaccharide-Based Biopolymers	600
19.6.1	Diversity of Polysaccharides in Nature	600
19.6.2	Chondroitin Sulfate	601
19.6.3	Hyaluronic Acid	603

19.6.4 Aggrecon Assemblies 604

19.7 Summary 607

References 608

20 Microscopy of Biopolymer Systems 611

Changmin Hu and Wenguo Cui

20.1 Introduction 611

20.2 Emerging Techniques in Biopolymer Microscopy 612

20.2.1 Optical Microscopy 612

20.2.2 Scanning Electron Microscopy 614

20.2.3 Transmission Electron Microscopy 616

20.2.4 Cryo Transmission Electron Microscopy 617

20.2.5 Atomic Force Microscopy 619

20.2.6 Scanning Tunneling Microscope 621

20.2.7 Laser Scanning Confocal Microscope 623

20.3 Microstructure and Application of Biopolymers 625

20.3.1 Microstructure of Biopolymers 625

20.3.2 Microspheres 626

20.3.3 Hydrogels 630

20.3.3.1 Structure of Hydrogels 630

20.3.3.2 Applications of Hydrogels 630

20.3.4 Fibers 632

20.3.4.1 Structure of Fibers 632

20.3.4.2 Self-Assembly Fibers 632

20.3.4.3 Phase Separation in Fiber Formation 633

20.3.4.4 Electrospinning Fibers 635

20.3.5 Scaffolds 636

20.3.5.1 Structure of Porous Scaffolds 636

20.3.5.2 Sponge-Like Porous Scaffolds 636

20.3.5.3 Collagen-Like Nanofibrous Scaffolds 637

20.3.6 Membranes 637

20.4 Biopolymeric Microstructure for Medical Applications 638

20.5 Summary 640

References 641

21 Rheo-optical Characterization of Biopolymer Systems 645

Dagang Liu, Rakesh Kumar, Donglin Tian, Fei Lu, and Mindong Chen

21.1 Introduction 645

21.2 Mechanism and Equipment of Rheo-optics 646

21.2.1 Polarimetry 646

21.2.1.1 Theoretical Background 646

21.2.1.2 Experimental Setup 647

21.2.2 Light Scattering (Raman) 648

21.2.2.1 Mechanism and Applications 648

21.2.2.2 Experimental Setup 650

21.2.3	Rheo-optical Fourier Transform Infrared Spectroscopy	651
21.3	Rheo-optical Applications for Biopolymers	652
21.3.1	Stress	652
21.3.2	Flow Birefringence	656
21.3.2.1	Proteins	656
21.3.2.2	Xanthan Gum Solution	657
21.3.2.3	Collagens	657
21.3.2.4	Wormlike Micelles	658
21.3.2.5	Polysaccharides	659
21.3.3	Orientation (Liquid Crystal)	660
21.3.3.1	Method for Determination of Orientation	660
21.3.3.2	Birefringent Characterization of Fiber Orientation Degree	661
21.3.3.3	Applications	661
21.3.4	Size of Phase or Particle	664
21.3.4.1	Particle Characterization Method	667
21.3.4.2	Rheo-optical Properties	667
21.4	Conclusions	668
	References	669
22	Rheological Behavior of Biopolymer Systems	673
	<i>Tao Feng and Ran Ye</i>	
22.1	Introduction	673
22.2	Rheological Behavior of Polysaccharide Systems	674
22.2.1	Structure of Polysaccharide regarding Rheological Properties	674
22.2.2	Mathematical Modeling of Linear Viscoelastic Properties	676
22.2.3	Rheological Behavior and Modeling of Polysaccharide Systems	677
22.3	Rheological Behavior of Protein Systems	685
22.3.1	Rheological Behavior of Milk Proteins	685
22.3.2	Rheological Behavior of Soy Proteins	688
22.3.3	Rheological Behavior of Meat Proteins	689
22.4	Rheological Behavior of Mixture Systems	690
22.4.1	Rheological Properties of the Mixtures of Milk Proteins and Polysaccharides	690
22.4.2	Rheological Properties of the Mixtures of Soy Proteins and Other Proteins	693
22.5	Conclusions	694
	References	694
23	Physical Gels of Biopolymers: Structure, Rheological and Gelation Properties	699
	<i>Camille Michon</i>	
23.1	Introduction	699
23.2	Gel Organization at Different Scales	700
23.3	Sol–Gel Transition in Polymer Gels: Determination and Applications	703

- 23.3.1 Definition of the Sol–Gel Transition 703
- 23.3.2 Different Techniques to Follow the Gel Formation 704
- 23.3.3 Classical Methods for Determining the Gel Point 705
- 23.3.3.1 Determining the Gel Point Using $G'(\omega)$ and $G''(\omega)$ Spectra 706
- 23.3.4 The Method of “tan δ Crossing” Applied to the Study of Mixed Gels 707
- 23.4 Gel and Sol–Gel Transition Applications 710
- 23.4.1 Uses of Gel to Trap Scattered Elements 710
- 23.4.2 Mechanical Reversibility of Physical Gels and Applications 711
- 23.4.3 Foams Containing Gelatin. How to Choose the Whipping Temperature 712
- 23.5 Conclusion 714
- References 715

- 24 Interfacial Properties of Biopolymers, Emulsions, and Emulsifiers 717**
Adamantini Paraskevopoulou and Vassilis Kiosseoglou
- 24.1 Introduction 717
- 24.2 Surface-Active Polysaccharides 720
- 24.3 Biopolymer Blends in Emulsions 724
- 24.3.1 Incompatible Protein–Polysaccharide Blends 724
- 24.3.2 Associative Protein–Polysaccharide Interactions 726
- 24.3.2.1 Physical Protein–Polysaccharide Complexes 726
- 24.3.2.2 Covalent Protein–Polysaccharide Conjugates 730
- 24.4 Concluding Remarks 734
- References 736

- 25 Modeling and Simulation of Biopolymer Systems 741**
Denis Bouyer
- 25.1 Introduction 741
- 25.2 Why Modeling (and Simulating)? 741
- 25.2.1 Describing the Mechanisms Involved in the Fabrication of Biopolymer Matrices 741
- 25.2.2 Discriminating the Elementary Phenomena 742
- 25.2.3 Developing a Predictive Tool 742
- 25.2.4 Opening New Perspectives 742
- 25.3 What Modeling (Transfer, Transport, Chemical Reaction, etc.)? 743
- 25.4 Which Validation for a Model? 744
- 25.5 Methodology 745
- 25.5.1 Description of the Geometry 745
- 25.5.2 Definition of the Initial Assumptions 746
- 25.5.3 Modeling the Thermodynamics 747
- 25.5.4 Mass Balance Equation 747
- 25.5.5 Coupling between Mass and Heat Transfer 748
- 25.5.5.1 Definition of the Biot Number 748

25.5.5.2	Lumped Parameter Approach	749
25.5.5.3	Solving the Heat Equation	749
25.5.6	Definition of the Initial and Boundary Conditions	749
25.5.6.1	Initial Conditions for Mass and Heat Transfer	749
25.5.6.2	Boundary Conditions for Mass Transfer	750
25.5.6.3	Boundary Conditions for Heat Transfer	750
25.5.7	Solving the Boundary Displacement	750
25.5.8	Mass and Heat Transfer Coefficients	751
25.5.8.1	Free Convection	751
25.5.8.2	Forced Convection	753
25.5.9	Numerical Simulation	753
25.6	Application to Biopolymer Systems	754
25.6.1	Elaboration of Chitin Hydrogels Using Nonsolvent Vapors	754
25.6.1.1	Nature of Chitin and Chitosan Biopolymers	754
25.6.1.2	Preparation of Chitin Matrices	754
25.6.1.3	Modeling Approach for the Elaboration of Chitin Hydrogel	755
25.6.1.4	Main Results and Applications	756
25.6.2	Elaboration of Chitosan Hydrogels by Ammonia Penetration and Chemical Reaction	760
25.6.2.1	Preparation of Chitosan Solutions	761
25.6.2.2	Elementary Phenomena Involved in the Vapor Gelation Process	761
25.6.2.3	Experimental Procedure for Following the Gelation Front	761
25.6.2.4	Equation System Including the Coupling between Transport and Chemical Reaction	762
25.6.2.5	Main Results and Applications	764
25.7	Conclusions	772
	Nomenclature	772
	References	773
26	Aging and Biodegradation of Biocomposites	777
	<i>Siji K. Mary, Prasanth Kumar Sasidharan Pillai, Deepa Bhanumathy Amma, Laly A. Pothen, and Sabu Thomas</i>	
26.1	Introduction	777
26.1.1	Aging of Biopolymer Systems	780
26.1.2	Aging Tests	781
26.1.2.1	Environmental Aging Test	781
26.1.2.2	Artificial Aging Test	781
26.1.2.3	Accelerated Aging Tests	781
26.1.3	Effects of Aging and Moisture on Mechanical Properties	782
26.2	Biodegradation of Biopolymers	785
26.2.1	Biodegradation Behavior	786
26.3	Recycling of Biopolymer-Embedded Biocomposites	790
26.4	Future Vision	795
	References	795

27	Biopolymers for Health, Food, and Cosmetic Applications	801
	<i>Robin Augustine, Rajakumari Rajendran, Uroš Cvelbar, Miran Mozetič, and Anne George</i>	
27.1	Introduction	801
27.2	Biopolymers for Health Applications	802
27.2.1	Introduction	802
27.2.2	Biodegradable Polymers	802
27.2.3	Considerations for Selection of Polymers	803
27.2.4	Proteins and Poly(Amino Acids): Enzymatically Degradable Polymers as Biomaterials	803
27.2.4.1	Collagen	803
27.2.4.2	Natural Poly(Amino Acids)	805
27.2.4.3	Elastin	805
27.2.4.4	Fibrin	805
27.2.5	Polysaccharides of Human Origin	806
27.2.5.1	Hyaluronic Acid	806
27.2.5.2	Chondroitin Sulfate	806
27.2.6	Polysaccharides of Nonhuman Origin	807
27.2.6.1	Chitin and Chitosan	807
27.2.6.2	Alginic Acid	807
27.2.6.3	Xanthan Gum	808
27.2.6.4	Gum Arabic	808
27.2.6.5	Starch	809
27.2.6.6	Cellulose	809
27.2.6.7	Pectin	810
27.2.6.8	Carrageenan	810
27.2.7	Polymers with Hydrolyzable Backbone	810
27.2.7.1	Poly(α -Esters)	810
27.2.7.2	Polyglycolide	813
27.2.7.3	Poly lactides	813
27.2.7.4	Poly(Lactide-co-Glycolide)	813
27.2.7.5	Polycaprolactone	814
27.2.7.6	Polydioxanone	814
27.2.7.7	Poly(3-Hydroxyalkanoates)(PHA)s	814
27.2.7.8	Poly(Ester Amide)	815
27.2.7.9	Poly(Orthoesters) (POE)	816
27.2.7.10	Polyanhydrides	816
27.2.7.11	Poly Propylenefumarate	816
27.2.7.12	Poly(Alkyl Cyanoacrylates)	817
27.2.7.13	Polyphosphazenes	817
27.2.7.14	Polyphosphoester	817
27.2.8	Conclusions	818
27.3	Biopolymers for Food Applications	819
27.3.1	Introduction	819
27.3.2	Chitin and Chitosan	819

27.3.3	Dextran	819
27.3.4	Xanthan	821
27.3.5	Bacterial Cellulose	822
27.3.6	Gellan	823
27.3.7	Curdlan	823
27.3.8	Pullulan	824
27.3.9	Starch	825
27.3.10	Alginic Acid	825
27.3.11	Gelatin	825
27.3.12	Cyclodextrins	826
27.3.13	Carrageenan	826
27.3.14	Conclusions	826
27.4	Biopolymers for Cosmetic Applications	827
27.4.1	General Ingredients of Cosmetic Products	828
27.4.2	Cosmeceuticals	828
27.4.3	Biopolymers in Cosmetic Preparations	829
27.4.3.1	Proteins in Cosmetics	829
27.4.3.2	Polysaccharides in Cosmetics	836
27.4.4	Conclusions	843
	References	844
	Index	851

Foreword

Our industrialized world is driven in large part by petroleum. It is an important source of energy and materials, and many of the products that we depend upon for day-to-day living are derived from it. However, the cost of oil and gas has increased dramatically over the past decade and this upward spiral is expected to continue due to increased demand, finite quantities, and unreliable supply chains. Beyond the monetary cost, our petroleum-based economy comes at a significant environmental price that cannot be sustained. As a consequence, research scientists, university professors, university students, technology developers in industry, and government policy makers focus their interest in the future prospects for a world less dependent on fossil fuels, taking steps to reduce greenhouse gas emissions, and efficiently addressing the significant challenges associated with plastic wastes in the global environment. It is now widely recognized that more cost-effective and environmentally benign alternatives to petroleum and the products derived from it will be required in order to realize a future with a sustainable economy and environment. Since you have this book in your hands, chances are that you are one of these actors. The bio-derived polymers discussed in this book and their applications provide part of the solution to these problems.

This book examines the current state of the art, new challenges, opportunities, and applications in the field of biopolymers. It is organized in two volumes morphology, structure, and properties (Chapters 1–12), and characterization and applications (Chapters 13–27). This book summarizes in an edited format and in a comprehensive manner many of the recent technical research accomplishments in the area of biopolymers and their blends, composites, IPNs, and gels from macro- to nanoscale. The handpicked selection of topics and expert contributors make this survey of biopolymers an outstanding resource reference for anyone involved in the field of eco-friendly biomaterials for advanced technologies. It surveys processing–morphology–property relationship of biopolymers, their blends, composites, and gels. The influence of experimental conditions and preparation techniques (processing) on the generation of micro- and nanomorphologies and the dependence of these morphologies on the properties of the biopolymer systems are discussed in detail. The application of various theoretical models for the prediction of the morphologies of these systems is discussed. This book also illustrates the use of biopolymers in health, medicine, food, and cosmetics.

There are already a number of fine texts that comprehensively cover the subject of biopolymers in great detail, but the content of this book is unique. For the first time, a book deals with processing, morphology, dynamics, structure, and properties of various biopolymers and their multiphase systems. It covers an up-to-date record on the major findings and observations in the field of biopolymers.

Grenoble, Institute of Technology
February 26, 2013

Alain Dufresne

List of Contributors

Esra Alveroglu

Istanbul Technical University
Department of Physics
Maslak
34469 Istanbul
Turkey

Shoshana (Malis) Arad

Ben-Gurion University of the Negev
Department of Biotechnology
Engineering
POB 653 Beer-Sheva 84105
Israel

Robin Augustine

Mahatma Gandhi University
Centre for Nanoscience and
Nanotechnology
Priyadarshini Hills
Kottayam 686560
Kerala
India

Rachel Auzély-Velty

Université Joseph Fourier
Centre de Recherches sur les
Macromolécules Végétales
(CERMAV-CNRS)
601 rue de la Chimie
38041 Grenoble
France

Luc Avérous

Université de Strasbourg
BioTeam/ICPEES-ECPM, UMR 7515
25 rue Becquerel
67087 Strasbourg Cedex 2
France

Deepa Bhanumathy Amma

Bishop Moore College
Department of Chemistry
Mavelikara 690110
Kerala
India

Deborah Blanchard

Université Joseph Fourier
Centre de Recherches sur les
Macromolécules Végétales
(CERMAV-CNRS)
601 rue de la Chimie
38041 Grenoble
France

Ana Maria Botelho do Rego

Technical University of Lisbon
Institute of Nanoscience and
Nanotechnology
Centro de Química-Física Molecular
Av. Rovisco Pais
1049-001 Lisboa
Portugal

Sami Boufi

University of Sfax
Faculté des Sciences de Sfax
Laboratoire des Sciences des
Matériaux et Environnement
BP 1171-3000 Sfax
Tunisia

Denis Bouyer

Université de Montpellier
Institut Européen des Membranes
2, Place Eugene Bataillon
34967 Montpellier
Cedex 2
France

Christophe Chassenieux

LUNAM Université du Maine
IMMM UMR CNRS 6283
Dept. Polymères, Colloïdes,
Interfaces
1 Avenue Olivier Messiaen
72085 Le Mans Cedex 9
France

Mindong Chen

Nanjing University of Information
Science & Technology
Department of Chemistry
Nanjing 210044
China

Wenguo Cui

The First Affiliated Hospital of
Soochow University
Department of Orthopedics
188 Shizi Street
Suzhou, Jiangsu 215006
China

and

Soochow University
Orthopedic Institute
708 Renmin Road
Suzhou, Jiangsu 215007
China

Uroš Cvelbar

Jožef Stefan Institute
F4 Plasma Laboratory
Jamova 39
1000 Ljubljana
Slovenia

Jany Dandurand

Université Paul Sabatier
CIRIMAT UMR CNRS 5085
Physique des Polymères 3R1B2
118 route de Narbonne
31062 Toulouse cedex 02
France

Jacques Desbrieres

Université de Pau et des Pays de
l'Adour
IPREM
Helioparc Pau Pyrenees
2 Avenue P. Angot
64053 Pau Cedex 09
France

Marli Miriam de Souza Lima

Universidade Estadual de Maringa
Pharmacy Departement LAFITEC
Av. Colombo, 5790 - Zona 07
CEP 87020-900 Maringa
Parana, Brasil

Dominique Durand

LUNAM Université du Maine
IMMM UMR CNRS 6283
Dept. Polymères, Colloïdes,
Interfaces
1 Avenue Olivier Messiaen
72085 Le Mans Cedex 9
France

Tao Feng

Shanghai Institute of Technology
 Department of Food Science and
 Technology
 School of Perfume and Aroma
 Technology
 120 Caobao Road
 Shanghai 200235
 China

Ana Maria Ferraria

Technical University of Lisbon
 Institute of Nanoscience and
 Nanotechnology
 Centro de Química-Física Molecular
 Av. Rovisco Pais
 1049-001 Lisboa
 Portugal

Chris Ford

University of Southampton
 School of Biological Sciences
 Highfield Campus
 Southampton SO17 1BJ
 UK

Tim J. Foster

University of Nottingham
 School of Biosciences
 Division of Food Sciences
 Sutton Bonington Campus
 Loughborough
 Leicestershire LE12 5RD
 UK

Ali Gelir

Istanbul Technical University
 Department of Physics
 Maslak
 34469 Istanbul
 Turkey

Anne George

Medical College Kottayam
 Department of Anatomy
 Gandhinagar
 Kottayam 686008
 Kerala
 India

and

Center of Excellence for Polymer
 Materials and Technologies
 Tehnoloski Park 24
 1000 Ljubljana
 Slovenia

Hero Jan Heeres

University of Groningen
 Department of Chemical
 Engineering
 Nijenborgh 4
 9747 Groningen
 The Netherlands

Antonio Heredia

Facultad de Ciencias
 Departamento de Biología Molecular
 y Bioquímica
 Campus de Teatinos, s/n
 29071 Málaga
 Spain

Ferenc Horkay

National Institute of Child Health
 and Human Development NICHD
 13 South Dr Room 3W16, MSC 5772
 Bethesda Md 20892-5772
 USA

Changmin Hu

Shanghai Jiao Tong University
 School of Biomedical Engineering
 and Med-X Research Institute
 1954 Hua Shan Road
 Shanghai 200030
 China

Parameswaranpillai Jyotishkumar

INSPIRE Faculty
Department of Polymer Science and
Rubber Technology
Cochin University of Science and
Technology, Kochi-682022

Vassilis Kiosseoglou

Aristotle University of Thessaloniki
School of Chemistry
Laboratory of Food Chemistry and
Technology
54124 Thessaloniki
Greece

Vanja Kokol

University of Maribor
Faculty of Mechanical Engineering
Institute for Engineering Materials
and Design
Smetanova ul. 17
2000 Maribor
Slovenia

Ashok Kumar

Indian Institute of Technology
Kanpur
Department of Biological Sciences
and Bioengineering
Kanpur 208016
Uttar Pradesh
India

Rakesh Kumar

Birla Institute of Technology, Mesra.
Patna Campus
Department of Applied Chemistry
P.O. - B. V. College, Patna - 800014,
Bihar
India

Colette Lacabanne

Université Paul Sabatier
CIRIMAT UMR CNRS 5085
Physique des Polymères 3R1B2
118 route de Narbonne
31062 Toulouse cedex 02
France

Oshrat Levy-Ontman

Sami Shamoon College of
Engineering
Department of Chemical
Engineering
Beer-Sheva 84100
POB 950
Israel

Dagang Liu

Nanjing University of Information
Science & Technology
Department of Chemistry
Nanjing 210044
Ningliu Rd 219
China

Fei Lu

Nanjing University of Information
Science & Technology
Department of Chemistry
Nanjing 210044
China

Phedra Marius

University of Southampton
School of Biological Sciences
Highfield Campus
Southampton SO17 1BJ
UK

Siji K. Mary

Bishop Moore College
Department of Chemistry
Mavelikara 690110
Kerala
India