

Contents

Introduction *xiii*

1	The Surface of Polymers	<i>1</i>
	<i>Rosica Mincheva and Jean-Marie Ravez</i>	
1.1	Introduction	1
1.2	The Surface of Polymers	2
1.2.1	Definition of a Polymer Surface	2
1.2.2	Factors Determining a Polymer Surface	3
1.2.2.1	Internal Factors	3
1.2.2.2	External Factors	4
1.2.3	The Polymer Surface at a Microscopic Level	11
1.3	Properties of Polymer Surfaces at Interfaces	12
1.3.1	Surface Wettability	13
1.3.2	Surface Thermal Properties	15
1.3.2.1	Surface T_g	15
1.3.2.2	Surface Crystallization	17
1.4	Experimental Methods for Investigating Polymer Surfaces at Interfaces	21
1.5	Conclusions	21
	References	21

Part I Gas Phase Methods 31

2	Surface Treatment of Polymers by Plasma	<i>33</i>
	<i>Pieter Cools, Laura Astoreca, Parinaz Saadat Esbah Tabaei, Monica Thukkaram, Herbert De Smet, Rino Morent, and Nathalie De Geyter</i>	
2.1	Plasma: An Introduction	33
2.1.1	Definition	33
2.1.2	Thermal Versus Nonthermal Plasma	34
2.1.3	The Formation of Nonthermal Plasma	35
2.1.4	Plasma Generation and Operating Conditions	37

2.1.4.1	Different Methods of Plasma Generation	37
2.1.4.2	DC Discharges	38
2.1.4.3	DC Pulsed Discharges	38
2.1.4.4	RF and MW Discharges	38
2.1.4.5	Dielectric Barrier Discharge (DBD)	39
2.1.4.6	Atmospheric Pressure Plasma Jet (APPJ)	40
2.1.4.7	Gliding Arc	41
2.1.5	Nonthermal Plasma for Polymer Surface Treatment	41
2.2	Applications of Plasma Surface Activation of Polymers	43
2.2.1	Adhesion Improvement	43
2.2.2	Packaging and Textile Applications	47
2.2.2.1	Printability Enhancement	47
2.2.2.2	Dyeability Improvement	47
2.2.2.3	Mass Transfer Changes	49
2.2.3	Biomedical Applications	50
2.2.3.1	Inert Synthetic Polymers	50
2.2.3.2	Biodegradable Polymers	53
2.3	Plasma Grafting	56
2.4	Hydrophobic Recovery	59
2.5	Conclusion	61
	References	61

3 A Joint Mechanistic Description of Plasma Polymers Synthesized at Low and Atmospheric Pressure 67
Damien Thiry, François Reniers, and Rony Snyders

3.1	Introduction	67
3.2	Plasma Polymerization	69
3.2.1	Plasma Fundamentals	70
3.2.2	Growth Mechanism	72
3.3	Probing the Plasma Chemistry	83
3.3.1	Optical Emission Spectroscopy	84
3.3.2	Mass Spectrometry	87
3.4	Conclusions	96
	References	97

4 Organic Surface Functionalization by Initiated CVD (iCVD) 107
Karen K. Gleason

4.1	Introduction	107
4.2	Mechanistic Principles of iCVD	108
4.3	Functional, Surface Reactive, and Responsive Organic Films Prepared by iCVD	113
4.4	Interfacial Engineering with iCVD: Adhesion and Grafting	127
4.5	Reactors for Synthesizing Organic Films by iCVD	128
4.6	Summary	129
	References	130

5	Atomic Layer Deposition and Vapor Phase Infiltration	135
	<i>Mark D. Losego and Qing Peng</i>	
5.1	Atomic Layer Deposition Versus Vapor Phase Infiltration	135
5.2	Atomic Layer Deposition (ALD) on Polymers	138
5.2.1	Chemical Mechanisms of ALD	138
5.2.2	ALD on Polymers with Dense –OH Groups: Cellulose and Poly(vinyl alcohol)	140
5.2.3	ALD onto “Unreactive” Polymer Substrates	141
5.2.4	Applications of ALD Coated Polymers	143
5.2.4.1	ALD Coated Cotton Fibers	143
5.2.4.2	Applications for ALD Coatings on Other Polymers	144
5.3	Vapor Phase Infiltration of Polymers	145
5.3.1	Processing Thermodynamics and Kinetics of VPI	145
5.3.1.1	Thermodynamics of Vapor-Phase Precursor Sorption into Polymers	145
5.3.1.2	Kinetics of Precursor Diffusion During VPI	147
5.3.1.3	VPI Processes Incorporating Both Penetrant Diffusion and Reaction	148
5.3.1.4	Measuring the Thermodynamics and Kinetics of a VPI Process	149
5.3.2	Applications of Vapor Phase Infiltrated Polymers	150
5.3.2.1	Altering Mechanical Performance	150
5.3.2.2	Contrasting Agent for Multi-phase Polymer Imaging	152
5.3.2.3	Improved Chemical Resistance	152
5.3.2.4	Patterning for Microsystems	153
5.3.2.5	Vapor Diffusion Barriers	154
5.3.2.6	Conducting Polymers and Hybrid Photovoltaic Cells	154
5.3.2.7	Other Application Spaces	155
5.4	Summary and Future Outlook for ALD and VPI on Polymers	156
	References	156

Part II UV and Related Methods 161

6	Photoinduced Functionalization on Polymer Surfaces	163
	<i>Kazuhiko Ishihara</i>	
6.1	Introduction	163
6.2	Improving the Surface Properties of Polymeric Materials by Photoirradiation	165
6.3	Photoreaction of Polymers with Other Polymers	166
6.3.1	Photoinduced Chemical Reaction Between Polymers	166
6.3.2	Photoinduced Grafting at the Polymer Surface	168
6.3.3	Preparation of High-functionality Surface by Photoinduced Graft Polymerization	169
6.3.4	Application of Photoinduced Grafting Process to Artificial Organs	172
6.4	Self-initiated Photoinduced Graft Polymerization	174
6.4.1	Poly(ether ketone) as Photoinitiator for Graft Polymerization	174

6.4.2	Effects of Inorganic Salts on Photoinduced Graft Polymerization in an Aqueous System	178
6.5	Conclusion and Future Perspective	180
	References	181
7	γ-Rays and Ions Irradiation	185
	<i>Alejandro Ramos-Ballesteros, Victor H. Pino-Ramos, Felipe López-Saucedo, Guadalupe G. Flores-Rojas, and Emilio Bucio</i>	
7.1	γ -Rays and Ions Irradiation	185
7.2	Ionizing Radiation Sources	186
7.3	γ -Ray-Induced Modifications	186
7.3.1	Grafting Modifications	186
7.3.1.1	Radiation-induced Grafting Methods	188
7.3.1.2	Ionic Grafting	192
7.3.1.3	RAFT-graft Polymerization	193
7.3.1.4	Applications	194
7.3.2	Cross-linking	197
7.3.2.1	γ -Ray Cross-linking Modifications	199
7.3.2.2	Cross-linking with Additives	200
7.3.2.3	Industrial Applications	201
7.4	Heavy Ion-Induced Modifications	202
7.4.1	Polymers	204
7.5	Conclusions	205
	Acknowledgments	206
	References	206

Part III Chemical Methods 211

8	Functionalization of Polymers by Hydrolysis, Aminolysis, Reduction, Oxidation, and Some Related Reactions	213
	<i>Dardan Hetemi and Jean Pinson</i>	
8.1	Hydrolysis and Aminolysis	213
8.1.1	PLA and Polyesters	213
8.1.2	Hydrolysis	214
8.1.3	Aminolysis	214
8.1.4	PCL	215
8.1.5	PET	216
8.1.6	PMMA	216
8.1.7	Cellulose	217
8.2	Chemical Reduction	220
8.2.1	PEEK	220
8.2.2	PET	225
8.2.3	PMMA	227
8.2.4	PC	227
8.2.5	PTFE	229

8.3	Chemical Oxidation	231
8.4	Non-covalent Surface Modification	234
8.5	Conclusion	235
	References	236
9	Functionalization of Polymers by Reaction of Radicals, Nitrenes, and Carbenes	<i>241</i>
	<i>Jean Pinson</i>	
9.1	Functionalization of Polymers by Reaction of Radicals	241
9.1.1	Peroxides as Radical Initiators	241
9.1.2	Hydrogen Peroxides as Radical Initiator	244
9.1.3	Persulfates as Radical Initiators	246
9.1.4	Oxygen as Radical Initiator	248
9.1.5	Azo Compounds as Radical Initiator	249
9.1.6	Diazonium Salts as Radical Initiator	250
9.1.6.1	Polypyrrole	251
9.1.6.2	Polyaniline	251
9.1.6.3	Poly(3,4-ethylenedioxythiophene)–Poly(styrenesulfonate) (PEDOT:PSS)	253
9.1.6.4	Polymethylmethacrylate (PMMA)	254
9.1.6.5	Polypropylene (PP)	255
9.1.6.6	Polyvinyl Chloride	255
9.1.6.7	Cyclic Olefin Copolymers (COC)	256
9.1.6.8	Polyetheretherketone (PEEK)	256
9.1.6.9	PET (Polyethylene Terephthalate)	257
9.1.6.10	Polysulfone Membranes	258
9.1.6.11	Cation Exchange Membranes	258
9.1.6.12	Fluoro Polymers	259
9.1.6.13	Natural Polymers	260
9.1.7	Alkyl Halides as Radical Initiator	260
9.2	Surface Modification of Polymers with Carbenes and Nitrenes	260
9.2.1	Carbenes	261
9.2.2	Nitrenes	264
9.3	Conclusion	267
	References	268
10	Surface Modification of Polymeric Substrates with Photo- and Sonochemically Designed Macromolecular Grafts	<i>273</i>
	<i>Fatima Mousli, Youssef Snoussi, Ahmed M. Khalil, Khouloud Jlassi, Ahmed Mekki, and Mohamed M. Chehimi</i>	
10.1	Introduction	273
10.1.1	Context	273
10.1.2	Scope of the Chapter	274
10.2	Surface-confined Radical Photopolymerization of Insulating Vinylic and Other Monomers	274
10.2.1	Type I and Type II Photoinitiation Systems	275

10.2.2	Simultaneous Photoinduced Electron Transfer and Free Radical Polymerization Confined to Surfaces	282
10.2.3	Surface-initiated Photoiniferter	284
10.2.4	"Brushing Up from Anywhere" Using Polydopamine Thin Adhesive Coatings	284
10.2.5	Recent Trends in Surface-confined Photopolymerization (CRP)	287
10.3	Surface-confined Photopolymerization of Conjugated Monomers	289
10.3.1	Polypyrrole	290
10.3.1.1	Mechanisms of Photopolymerization of Pyrrole	290
10.3.1.2	Substrates for in Situ Photoinduced Polymerization of Pyrrole and Potential Applications	291
10.3.2	Polyaniline	294
10.3.2.1	Mechanisms of Photopolymerization of Aniline	294
10.3.2.2	Substrates for in Situ Photoinduced Polymerization of Aniline	298
10.4	Surface-confined Sonochemical Polymerization of Conjugated and Vinylidic Monomers	298
10.4.1	Insights into Sonochemistry: Origin of the Phenomenon and Mechanism of Polymer Synthesis	298
10.4.2	Ultrasound-assisted Polymerization or Polymer Deposition over Organic Polymeric Substrates	303
10.4.2.1	Sonopolymerization	303
10.4.2.2	Ultrasonic Spray	303
10.4.3	Sonopolymerization over Miscellaneous Types of Surface: Inorganic Polymeric Substrates	305
10.5	Conclusion	306
	Acknowledgments	307
	References	307

Part IV Applications 317

11	Surface Modification of Nanoparticles: Methods and Applications	319
	<i>Gopikrishna Moku, Vijayagopal Raman Gopalsamuthiram, Thomas R. Hoye, and Jayanth Panyam</i>	
11.1	Introduction	319
11.2	Polymers Used in the Preparation of Nanoparticles	320
11.3	Common Biodegradable Polymers for Nanoparticle Fabrication	320
11.3.1	Albumin	320
11.3.2	Alginate	320
11.3.2.1	Chitosan	321
11.3.3	Gelatin	322
11.3.4	Poly(lactide- <i>co</i> -glycolide) (PLGA) and Polylactide (PLA)	322
11.3.5	Poly- ϵ -caprolactone (PCL)	323

11.4	Fabrication of Nanoparticles	323
11.5	Linker Chemistry for Attaching Ligands on Polymeric Nanoparticles	324
11.5.1	Hydrazone Bond Formation	327
11.5.2	Non-covalent Attachment	328
11.6	Surface-functionalized Polymeric Nanoparticles for Drug Delivery Applications	328
11.6.1	Polysaccharides	329
11.6.2	Lipids	329
11.6.3	Aptamers	332
11.6.4	Antibodies	332
11.6.5	Peptides	333
11.6.5.1	Polyethylene Glycol (PEG)	334
11.7	Characterization of Surface-modified Nanoparticles	336
11.7.1	Particle Size	336
11.7.2	Dynamic Light Scattering (DLS)	337
11.7.3	Scanning Electron Microscopy (SEM)	337
11.7.4	Transmission Electron Microscopy (TEM)	339
11.7.5	Surface Charge	339
11.7.6	Surface Hydrophobicity	340
11.7.7	Fourier Transform IR (FTIR) Spectroscopy	341
11.8	Summary/Conclusion	342
	References	342
12	Surface Modification of Polymers for Food Science	347
	<i>Valentina Siracusa</i>	
12.1	Introduction	347
12.2	Physical and Chemical Methods	348
12.2.1	Gas Phase and Radiation	349
12.2.1.1	Gas Phase	349
12.2.1.2	Radiation	350
12.2.2	Liquid and Bulk Phase Methods	352
12.2.2.1	Adsorption Methods	352
12.2.2.2	Desorption Method	352
12.2.3	Interfacial Adhesion of Polymers	353
12.2.4	Grafting and Polymerization	354
12.3	Mechanical Method	354
12.4	Biological Method	354
12.5	Surface Modification of Polymer for Food Packaging	355
12.5.1	Applications	355
12.5.1.1	Surface Sterilization	355
12.5.1.2	Printing	355
12.5.1.3	Mass Transfer	356
12.5.2	Polymers	356
12.6	Conclusion	358
	References	359

13	Surface Modification of Water Purification Membranes	363
	<i>Anthony Szymczyk, Bart van der Bruggen, and Mathias Ulbricht</i>	
13.1	Introduction	363
13.2	Irradiation-Based Direct Polymer Modification	365
13.2.1	Plasma Treatment	365
13.2.2	UV Irradiation	366
13.2.3	Irradiation with High Energy Sources	368
13.3	Coatings	369
13.3.1	Coatings from Gas Phase	369
13.3.2	Coatings from Wet Phase	371
13.4	Grafting Methods	378
13.4.1	Grafting-to	378
13.4.2	Grafting-from	381
13.4.2.1	Plasma-Induced Graft Polymerization	381
13.4.2.2	UV-Induced Grafting	383
13.4.2.3	Grafting Induced by High Energy Radiations	385
13.4.2.4	Grafting Initiated by Chemical/Electrochemical Means	385
13.4.3	Controlled Grafting-from	389
13.5	Conclusion	392
	References	394
14	Surface Modification of Polymer Substrates for Biomedical Applications	399
	<i>P. Slepčka, N. Slepčková Kasálková, Z. Kolská, and V. Švorčík</i>	
14.1	Introduction	399
14.2	Plasma Treatment	400
14.3	Laser Modification	411
14.3.1	Interaction with Cells	411
14.3.2	Sensor Construction	412
14.4	Conclusion	416
	Acknowledgments	417
	References	417