Contents

1 Introduction 1

References 5

2 Classification of Electrochemically Active Polymers 7
2.1 Redox Polymers 7
2.1.1 Redox Polymers Where the Redox Group Is Incorporated into the Chain (Condensation Redox Polymers, Organic Redox Polymers) 8
2.1.2 Redox Polymers with Pendant Redox Groups 10
2.1.3 Ion-Exchange Polymers Containing Electrostatically Bound Redox Centers 13
2.2 Electronically Conducting Polymers (Intrinsically Conducting Polymers—ICPs) 14
2.2.1 Polyaniline (PANI) and PANI Derivatives 15
2.2.2 Poly(Diphenylamine) (PDPA) 18
2.2.3 Poly(o-Phenylenediamine) (PPD) 21
2.2.4 Poly(2-Aminodiphenylamine) (P2ADPA) 21
2.2.5 Polypyrrole (PP) and PP Derivatives 22
2.2.6 Polythiophene (PT) and PT Derivatives 23
2.2.7 Poly(3,4-Ethylenedioxythiophene) (PEDOT) and Its Derivatives 26
2.2.8 Polyphenazine (PPh) and Poly(1-Hydroxyphenazine) (PPhOH) 27
2.2.9 Poly(Acridine Red) (PAR) 29
2.2.10 Poly(Neutral Red) (PNR) 30
2.2.11 Poly(Phenosafranin) (PPhS) 30
2.2.12 Polycarbazoles (PCz) 31
2.2.13 Poly(Methylene Blue) (PMB) and Other Polythiazines 32

2.2.14 Poly(o-Aminophenol) (POAP) 33
2.2.15 Polyfluorene (PF) and Poly(9-Fluorenone) (PFO) 34
2.2.16 Polyluminol (PL) 34
2.2.17 Polyrhodanine (PRh) 35
2.2.18 Polyflavins (PFl) 35
2.2.19 Poly(5-Carboxyindole), Poly(5-Fluorindole) and Polymelatonin 36
2.2.20 Poly(New Fuchsin) (PnF) 37
2.2.21 Poly(p-Phenylene) (PPP) and Poly(Phenylenevinylene) (PPPV) 38
2.2.22 Polytriphenylamine (PTPA) and Poly(4-Vinyl-Triphenylamine) (PVTPA) 39
2.3 Electronically Conducting Polymers with Built-In or Pendant Redox Functionalities 40
2.3.1 Poly(5-Amino-1,4-Naphthoquinone) (PANQ) 40
2.3.2 Poly(5-Amino-1-Naphthol) 41
2.3.3 Poly(4-Ferrocenylmethylidene-4H-Cyclopenta-[2,1-b;3,4-b′]-Dithiophene) 41
2.3.4 Fullerene-Functionalized Poly(Terthiophenes) (PTTh–BB) . 42
2.3.5 Poly[Iron(4-(2-Pyrrol-1-Ylethyl)-4′-Methyl-2,2′-Bipyridine)$_3^{2+}$] 43
2.3.6 Polypyrrole Functionalized by Ru(bpy)$(CO)_2$ 43
2.3.7 Poly[Bis(3,4-Ethylene-Dioxythiophene)-(4,4′-Dinonyl-2,2′-Bithiazole)] (PENBTE) 44
2.3.8 Poly(Tetraphenylporphyrins) 44
2.3.9 Poly[4,4′(5′)-Bis(3,4-Ethylenedioxy)Thien-2-Yl] Tetrathiafulvalene (PEDOT–TTF) and Poly{3-[7-Oxa-8-(4-Tetrathiafulvalenyl)Octyl]-2,2′-Bithiophene} (PT–TTF) 45
2.4 Copolymers 46
2.4.1 Poly(Aniline-co-Diaminodiphenyl Sulfone) 46
2.4.2 Poly(Aniline-co-2/3-amino or 2,5-Diamino Benzenesulfonic Acid) 47
2.4.3 Poly(Aniline-co-o-Aminophenol) 47
2.4.4 Poly(m-Toluidine-co-o-Phenylenediamine) 47
2.4.5 Other Copolymers 47
2.5 Composite Materials 48

References 49

3 Methods of Investigation 67
3.1 Electrochemical Methods 68
3.1.1 Cyclic Voltammetry 68
3.1.2 Chronoamperometry and Chronocoulometry 71

3.1.3 Electrochemical Impedance Spectroscopy (EIS) 72
3.2 In Situ Combinations of Electrochemistry with Other Techniques . . 88
3.2.1 Electrochemical Quartz Crystal Microbalance (EQCM) 88
3.2.2 Radiotracer Techniques 96
3.2.3 Probe Beam Deflection Technique (PBD) 99
3.2.4 Ellipsometry 101
3.2.5 Spectroelectrochemistry 101
3.2.6 Scanning Probe Techniques 104
3.2.7 Conductivity Measurements 109
3.3 Other Techniques Used in the Field of Conducting Polymers 110
3.3.1 Scanning Electron Microscopy (SEM) 110
3.3.2 X-Ray Photoelectron Spectroscopy (XPS) 111
3.3.3 X-Ray Diffraction (XRD) and Absorption 111
3.3.4 Electrospray Ionization Mass Spectrometry (ES–MS) 111

References 113

4 Chemical and Electrochemical Syntheses of Conducting Polymers . . . 123

References 145

5 Thermodynamic Considerations 149
5.1 Neutral Polymer in Contact with an Electrolyte Solution 150
5.2 Charged Polymer in Contact with an Electrolyte Solution 154
5.2.1 Nonosmotic Membrane Equilibrium 154
5.2.2 Osmotic Membrane Equilibrium and Electrochemical and Mechanical Equilibria 156
5.3 Dimerization, Disproportionation and Ion Association Equilibria Within the Polymer Phase 164

References 167

6 Redox Transformations and Transport Processes 169
6.1 Electron Transport 172
6.1.1 Electron Exchange Reaction 172
6.1.2 Electronic Conductivity 178
6.2 Ion Transport 188
6.3 Coupling of Electron and Ionic Charge Transport 195
6.4 Other Transport Processes 198
6.4.1 Solvent Transport 199
6.4.2 Dynamics of Polymeric Motion 199
6.5 Effect of Film Structure and Morphology 201
6.5.1 Thickness 202

6.5.2 Synthesis Conditions and Nature of the Electrolyte 202
6.5.3 Effect of Electrolyte Concentration and Temperature 205
6.6 Relaxation and Hysteresis Phenomena 208
6.7 Measurements of the Rate of Charge Transport 217

References 219

7 Applications of Conducting Polymers 225
7.1 Material Properties of Conducting Polymers 225
7.2 Applications of Conducting Polymers in Various Fields of Technologies 227
7.2.1 Thin-Film Deposition and Microstructuring of Conducting Materials (Antistatic Coatings, Microwave Absorption, Microelectronics) 227
7.2.2 Electroluminescent and Electrochromic Devices 229
7.2.3 Membranes and Ion Exchanger 235
7.2.4 Corrosion Protection 236
7.2.5 Sensors 237
7.2.6 Materials for Energy Technologies 246
7.2.7 Artificial Muscles 248
7.2.8 Electrocatalysis 250

References 255

8 Historical Background (Or: There Is Nothing New Under the Sun) . . 265

References 269

About the Author 271

About the Editor 273

Name Index 275

Subject Index 277