

# Contents

## Introduction

xxi

## Chapter 1 Chemically Driven Artificial Molecular Machines

*J.D. Crowley, E.R. Kay and D.A. Leigh*

1.1	Design Principles for Molecular-Level Motors and Machines	1
1.1.1	The Effects of Scale	2
1.1.2	Machines that Operate at Low Reynolds Number	3
1.1.3	Lessons to Learn from Biological Motors and Machines	3
1.2	Controlling Motion in Covalently Bonded Molecular Systems	4
1.2.1	Controlling Conformational Changes	4
1.2.2	Controlling Configurational Changes	9
1.3	Controlling Motion in Mechanically Bonded Molecular Systems	12
1.3.1	Basic Features	13
1.3.2	Translational Molecular Switches: Stimuli-Responsive Molecular Shuttles	13
1.3.3	Controlling Rotational Motion in Catenanes	24
1.4	From Laboratory to Technology: Towards Useful Molecular Machines	29
1.4.1	The Current Challenges: Constraining, Communicating, Correlating	30
1.4.2	Reporting Controlled Motion in Solution	32
1.4.3	Reporting Controlled Motion on Surfaces, in Solids and Other Condensed Phases	32
1.5	Summary and Outlook	38
	References	40

## Chapter 2 Photochemically Controlled Molecular Devices and Machines

*V. Balzani, G. Bergamini, P. Ceroni, A. Credi and  
M. Venturi*

2.1	Introduction	48
2.2	Molecular-level Devices for Processing Light Signals	50
2.2.1	Wires	50
2.2.2	Switching Devices	51
2.2.3	Plug/socket Systems	52
2.2.4	Molecular Extension Cables	53
2.2.5	Antenna Systems for Light Harvesting	53
2.2.6	Molecular Lenses Capable of Tuning the Colour of Light	56
2.2.7	Fluorescent Sensors with Signal Amplification	56
2.2.8	Dendrimers for a Multiple Use of Light Signals	59
2.2.9	Logic Gates	62
2.3	Light-driven Molecular Machines	65
2.3.1	Dethreading/rethreading of Pseudorotaxanes	65
2.3.2	A Sunlight-Powered Nanomotor	66
2.4	Conclusions	69
	Acknowledgements	70
	References	70

## Chapter 3 Transition-Metal Complex-Based Molecular Machines

*B. Champin, U. Létinois-Halbes and J.-P. Sauvage*

3.1	Introduction	76
3.2	Molecular Motions Driven by a Chemical Reaction	77
3.2.1	Use of a Chemical Reaction to Induce the Contraction/Stretching Process of a Muscle-like Rotaxane Dimer	77
3.2.2	Intramolecular Complexation/Decomplexation Processes as a Means to Make an Intermittent Degenerate Molecular Shuttle	78
3.2.3	Molecular Machines Based on Metal-ion Translocation	82
3.3	Electrochemically Induced Motions	83
3.3.1	Transition-metal-complexed Catenanes and Rotaxanes	83
3.3.2	Other Related Noninterlocking Systems	89
3.4	Light-fuelled Molecular Machines	91
3.4.1	Photoinduced Decoordination and Thermal Recoordination of a Ring in a Ruthenium(II)- containing 2catenane	91

3.4.2 A Photochemically Driven Molecular-level Abacus	92
3.5 Conclusion and Prospective	96
Acknowledgments	96
References	97

#### **Chapter 4 Chemomechanical Polymers**

*H.-J. Schneider and K. Kato*

4.1 Introduction	100
4.2 Chemomechanical Polymers Triggered by pH	101
4.3 Particle-size Effects and Kinetics	107
4.4 Water Uptake and Release	108
4.5 Concentration Profiles	110
4.6 Cooperativity and Logical Gate Functions	111
4.7 Selectivity with Organic Effector Molecules	114
4.8 Ternary Complex Formation for Amino Acids and Peptides as Effectors	117
4.9 Selectivity by Covalent Interactions/Glucose-triggered Size Changes	118
4.10 Conclusions	119
References	120

#### **Chapter 5 Ionic Polymer Metal Nanocomposites as Intelligent Materials and Artificial Muscles**

*M. Shahinpoor*

5.1 Summary	126
5.2 Introduction	127
5.3 Three-dimensional Fabrication of IPMNCs	128
5.4 Manufacturing Methodologies	128
5.5 Manufacturing Steps	129
5.6 Electrically Induced Robotic Actuation	130
5.7 Distributed Nanosensing and Transduction	132
5.8 Modeling and Simulation	136
5.9 Smart-Product Development	138
5.10 Medical, Engineering and Industrial Applications	139
References	140

#### **Chapter 6 Artificial Muscles, Sensing and Multifunctionality**

*T.F. Otero*

6.1 Introduction	142
6.2 Materials	143

6.3	Electrochemical Behaviour of Conducting Polymers in Aqueous Solution	143
6.4	Nonstoichiometric, Soft, and Wet Materials	147
6.5	Electrochemical Properties	149
6.5.1	Electrochemomechanical Properties	150
6.5.2	Electrochromic Properties	150
6.5.3	Charge Storage	150
6.5.4	Porosity	150
6.5.5	Electron/Chemical Transduction	151
6.5.6	Unparalleled Simultaneous Sensing Possibilities	151
6.6	Multifunctional and Biomimicking Properties	151
6.7	Natural Muscles	152
6.8	Devices based on the Electrochemical Properties of Conducting Polymers	153
6.8.1	Artificial Muscles	153
6.8.2	Other Electrochemically based Properties and Devices: Electrochromic Devices	170
6.8.3	Batteries	172
6.8.4	Membranes and Electron/Ion (or Electron/Chemical) Transducers	174
6.9	Theoretical Models	174
6.9.1	Elastic Models	177
6.9.2	Electrochemical Models	177
6.9.3	Relaxation Models	178
6.9.4	Molecular Dynamics Treatment	179
6.10	Final Remarks	179
	References	182

## **Chapter 7 Electrochemically Controllable Polyacrylonitrile-Derived Artificial Muscle as an Intelligent Material**

*K.J. Kim and K. Choe*

7.1	Polyacrylonitrile in General	191
7.2	Force-Strain Behaviour of Modified PAN	194
7.3	Actuation Properties of Modified PAN	194
7.3.1	Length-change Characteristics of Modified PAN: Effect of pH Variation	194
7.3.2	Generative Force Characteristics: pH-driven and/or Electrically Driven PAN Actuator	194
7.3.3	Generative Force Characteristics: Effect of Different Anions	196
7.3.4	Generative Force Characteristics: Effect of Acidity	197
7.4	Performance of PAN Bundle Artificial Muscle	198

7.4.1	Electric-current Effect on Force Generation	199
7.4.2	Work Performance	201
7.5	Summary of Performance Capability of PAN Artificial Muscle	201
	References	203

## Chapter 8 Unimolecular Electronic Devices

*R.M. Metzger*

8.1	Introduction	205
8.2	Donors and Acceptors; HOMOs and LUMOs	206
8.3	Contacts	207
8.4	Two-probe, Three-probe and Four-probe Electrical Measurements	209
8.5	Resistors	210
8.6	Rectifiers or Diodes	212
8.7	Switches	221
8.8	Capacitors	221
8.9	Future Flash Memories	222
8.10	Field Effect Transistors	222
8.11	Negative Differential Resistance Devices	222
8.12	Coulomb-blockade Device and Single-electron Transistor	222
8.13	Future Unimolecular Amplifiers	223
8.14	Future Organic Interconnects	223
	Acknowledgements	223
	References	223

## Chapter 9 Piezoelectric Ceramics as Intelligent Multifunctional Materials

*A. Yousefi-Koma*

9.1	Introduction	231
9.2	Piezoelectricity	232
9.3	Piezoelectric Ceramics	232
9.4	Piezoelectric Ceramic Actuators	233
9.5	Modeling	235
	9.5.1 Sensors	239
	9.5.2 Actuators	242
9.6	Applications	242
	9.6.1 Vibration/Acoustic Control	243
	9.6.2 Rotor-blade Flap	245
	9.6.3 Adaptive Structural Shape Control	246
	9.6.4 Structural Health Monitoring	246
	9.6.5 Compact Hybrid Actuators	247

9.7 Commercial Products	247
References	252
<b>Chapter 10 Ferroelectric Relaxor Polymers as Intelligent Soft Actuators and Artificial Muscles</b>	
<i>Q. M. Zhang, B. Chu and Z.-Y. Cheng</i>	
10.1 Introduction	256
10.2 High-energy Electron-irradiated Copolymer (HEEIP)	258
10.2.1 Microstructures of HEEIP	258
10.2.2 Electromechanical Responses of HEEIP	262
10.3 Electrostrictive Responses and Relaxor Ferroelectric Behaviour in P(VDF-TrFE)-based Terpolymers	266
10.3.1 The Electromechanical Response in P(VDF-TrFE)-based Terpolymers	266
10.3.2 The Microstructure and Ferroelectric Relaxor Behaviour of P(VDF-TrFE-CFE) Terpolymers	268
10.4 Performance of Microelectromechanical Devices	273
10.5 Summary	278
Acknowledgement	279
References	279
<b>Chapter 11 Magnetic Polymeric Gels as Intelligent Artificial Muscles</b>	
<i>M. Zrinyi</i>	
11.1 Introduction	282
11.2 Ferrogel as a New Type of Responsive Gel	283
11.3 Interpretation of the Abrupt Shape Transition	288
11.4 Nonhomogeneous Deformation of Ferrogels	290
11.5 Muscle-like Contraction Mimicked by Ferrogels	294
11.6 Control of Pseudomuscular Contraction	295
11.7 Future Aspects	299
Acknowledgements	299
References	299
<b>Chapter 12 Intelligent Materials: Shape-Memory Polymers</b>	
<i>M. Behl, R. Langer and A. Lendlein</i>	
12.1 Introduction	301
12.2 Thermally Induced Shape-memory Polymers	303
12.2.1 General Concept and Characterisation of Shape-memory Effect	303

12.2.2	Thermoplastic Shape-memory Polymers	304
12.2.3	Covalently Crosslinked Shape-memory Polymers	306
12.2.4	Composites from Shape-memory Polymers and Particles	308
12.2.5	Indirect Actuation of Thermally Induced Shape-memory Effect in Polymers	308
12.3	Light-induced Shape-memory Polymers	311
12.4	Multifunctional Polymers with Shape-memory Effect	312
12.5	Conclusion and Outlook	313
	References	314

## Chapter 13 Shape-Memory Alloys as Multifunctional Materials

*L. McDonald Schetky*

13.1	Introduction to Shape-memory Alloys	317
13.2	Shape-memory Alloy Applications	320
13.2.1	Couplings	320
13.2.2	Seals	321
13.2.3	Electrical Connectors	322
13.2.4	Virtual Two-way Actuation Using One-way NiTi Shape-memory Alloys	323
13.2.5	Nonbiased Safety Devices	324
13.2.6	Thermal Interrupter	325
13.2.7	Eyeglass Frames	326
13.2.8	Cellular-phone Antennas	327
13.2.9	Home Appliances	327
13.3	Medical Applications	327
13.3.1	Orthodontics and Dental Procedures	328
13.3.2	Superelastic Medical Devices	328
13.3.3	Cardiovascular Stents	329
13.4	Engineering Applications	331
13.4.1	Adaptive Structures	331
13.4.2	Structural Damping	333
13.4.3	High-force Devices	334
13.4.4	Jet-engine and Other Aeronautical Applications	334
13.5	Thin-film and Porous Devices	336
	References	338

## Chapter 14 Magnetorheological Materials and their Applications

*X. Wang and F. Gordaninejad*

14.1	Introduction	339
14.2	Historical Perspective	340
14.3	Magnetorheological Materials	341

14.3.1	Magnetorheological Fluids	341
14.3.2	Magnetorheological Elastomers	344
14.3.3	Rheological Behaviour of MR Fluids	348
14.3.4	Models for Shear-yield Stress	351
14.3.5	Field-induced Microstructures	353
14.3.6	Rheometry of MR Fluids	354
14.3.7	Effects of Surface Roughness	357
14.4	Magnetorheological Fluid Devices	363
14.4.1	Magnetorheological Fluid Dampers	363
14.4.2	Modeling of Magnetorheological-Fluid Dampers	365
14.4.3	Effect of Temperature	369
14.4.4	Other Applications	373
14.5	Summary	376
	Acknowledgements	376
	References	376

## **Chapter 15 Metal Hydrides as Intelligent Materials and Artificial Muscles**

*K.J. Kim, G. Lloyd and M. Shahinpoor*

15.1	Metal Hydrides in General	386
15.2	Metal-hydride-actuation Principle	387
15.2.1	Modeling	390
15.2.2	Experiments	393
15.3	Summary	394
	References	394

## **Chapter 16 Dielectric Elastomer Actuators as Intelligent Materials for Actuation, Sensing and Generation**

*G. Kofod and R. Kornbluh*

16.1	Introduction	396
16.2	Actuation Basics	397
16.3	Pre-stress Bias	399
16.4	Compliant Electrodes	400
16.4.1	Percolating Conductive Particle Networks	400
16.4.2	Structured Metal Electrodes	400
16.5	Theory and Modeling	401
16.6	Actuator Design: Geometry and Structure	405
16.7	Applications	406
16.7.1	Artificial Muscles for Biomimetic Robots	409
16.7.2	Linear Actuators for Industrial Applications	411
16.7.3	Diaphragm Actuators for Pumps and Arrays	411
16.7.4	Enhanced-thickness Mode Arrays	412



16.7.5	Framed Actuator for Optics	414
16.7.6	Sensors	415
16.7.7	Generators	416
16.8	Implementation Challenges for Dielectric Elastomers	417
16.9	The Future: Materials Development for New Elastomers	418
16.9.1	Improving Elastic Properties	419
16.9.2	Improving Dielectric Properties	420
16.9.3	Improving Breakdown Properties	420
16.10	Conclusion	421
	References	421

## **Chapter 17 Azobenzene Polymers as Photomechanical and Multifunctional Smart Materials**

*K.G. Yager and C.J. Barrett*

17.1	Introduction	424
17.2	Azobenzenes	425
17.3	Azobenzene Systems	427
17.4	Photoswitchable Azo Materials	430
17.5	Photoresponsive Azo Materials	432
17.5.1	Photo-orientation	432
17.5.2	Surface Properties	434
17.6	Photodeformable Azo Materials	434
17.6.1	Surface Mass Transport	434
17.6.2	Photomechanical Effects	437
17.7	Conclusion	437
	References	438

## **Chapter 18 Intelligent Chitosan-based Hydrogels as Multifunctional Materials**

*A.F.T. Mak and S. Sun*

18.1	Introduction	447
18.2	Characteristics of Chitosan	448
18.2.1	Physical and Chemical Properties of Chitosan	448
18.2.2	Biological Properties of Chitosan	449
18.2.3	Solvent and Solubility	449
18.3	Intelligent Properties	450
18.3.1	pH Sensitivity	450
18.3.2	Ionic Strength Sensitivity	452
18.3.3	Organic Effectors Sensitivity	453
18.3.4	Electrosensitivity	453
18.3.5	Thermosensitivity	455

18.4	Chitosan-based Intelligent Materials	456
18.4.1	pH-Responsive Hydrogels	456
18.4.2	Thermoresponsive and Dual Stimuli-responsive Polymers	456
18.4.3	Magnetic Chitosan Microsphere	457
18.4.4	Electrical Responsive Polymers	458
18.5	Biomedical Applications	458
18.5.1	Drug-delivery and Drug-release Systems	458
18.5.2	Injectable Gels for Tissue Engineering	460
18.5.3	Artificial Actuators and Muscles	460
18.6	Conclusions	461
	References	461

## **Chapter 19 Polymer-Protein Complexation and its Application as ATP-driven Gel Machine**

*R. Kawamura, A. Kakugo, Y. Osada and J.P. Gong*

19.1	Introduction	464
19.2	Actin Gel formed from Polymer-Actin Complexes	465
19.3	Polymorphism of Actin Complexes	467
19.4	Oriented Myosin Gel Formed under Shear Flow	469
19.5	Motility Assay of F-actin on Oriented Myosin Gel	470
19.6	Motility Assay of Polymer-Actin Complex Gel	471
19.7	Polarity of the Actin in Complexes	472
19.8	Conclusions	474
	References	475

## **Chapter 20 Intelligent Composite Materials Having Capabilities of Sensing, Health Monitoring, Actuation, Self-Repair and Multifunctionality**

*H. Asanuma*

20.1	Introduction	478
20.2	A New Route to Develop Intelligent Composite Materials	479
20.3	Composite Materials Fabricated by the New Route	481
20.4	A New Category of Composite Materials Having Liquid Phases for Self-repair and Other Capabilities	485
20.5	Summary and Outlook	489
	References	490

**Chapter 21 Overview of Liquid-crystal Elastomers, Magnetic Shape-memory Materials, Fullerenes, Carbon Nanotubes, Nonionic Smart Polymers and Electrorheological Fluids as Other Intelligent and Multifunctional Materials**

*M. Shahinpoor and H.-J. Schneider*

21.1	Liquid-crystal Elastomers as Multifunctional Materials	491
21.2	Magnetic Shape-memory (MSM) Materials	493
21.2.1	MSM Alloy Actuators	496
21.2.2	Sensing and Multifunctionality Properties of MSM Materials	496
21.3	Fullerenes and Carbon Nanotubes as Multifunctional Intelligent Materials	497
21.4	Nonionic Polymer Gels/EAPs	500
21.5	Electrorheological (ER) Fluids as Multifunctional Smart Materials	500
21.5.1	Other Applications of ER Fluids	501
	References	501

**Chapter 22 Overview on Biogenic and Bioinspired Intelligent Materials—from DNA-based Devices to Biochips and Drug-delivery Systems**

*H.-J. Schneider*

22.1	Introduction	506
22.2	Biological Materials: Nucleic Acids as an Example	507
22.3	Biosensors and Biochips	508
22.4	Intelligent Bionanoparticles	509
22.5	Nanobiosensors	511
22.6	Drug-delivery and Related Systems	512
	References	517

**Subject Index**