

Contents

Preface *xiii*

Part I Mechanically Responsive Crystals 1

- 1 Photomechanical Behavior of Photochromic Diarylethene Crystals 3**
Seiya Kobatake and Daichi Kitagawa
 - 1.1 Introduction 3
 - 1.2 Crystal Deformation Exhibiting Expansion/Contraction upon Photoirradiation 6
 - 1.3 Photoresponsive Bending 7
 - 1.4 Dependence of Bending Behavior on Irradiation Wavelength 11
 - 1.5 Photomechanical Work of Diarylethene Crystals That Exhibit Bending 13
 - 1.6 New Types of Photomechanical Motion 15
 - 1.7 Photosalient Effect 20
 - 1.8 Summary 22
 - References 23
- 2 Photomechanical Crystals Made from Anthracene Derivatives 29**
Fei Tong, Christopher J. Bardeen, and Rabih O. Al-Kaysi
 - 2.1 Introduction 29
 - 2.2 Elements of Photomechanical Molecular Crystals 30
 - 2.3 The Advantage of Using Anthracene Derivatives in Photomechanical Crystals 33
 - 2.4 Types of Anthracene Photomechanical Crystals 34
 - 2.4.1 NR-Type Anthracene Derivatives 34
 - 2.4.1.1 9-Anthracene Carboxylate Ester Derivatives 34
 - 2.4.1.2 9-Methylanthracene 36
 - 2.4.1.3 9-Cyanoanthracene, 9-Anthraldehyde, and 9,10-Dinitroanthracene 37
 - 2.4.1.4 Conjugated Anthracene Derivatives with Trans-to-Cis Photochemistry 38
 - 2.4.2 T-Type Photomechanical Crystals Based on Reversible $4\pi + 4\pi$ Photodimerization 39

2.4.3	P-Type Anthracene Derivatives	44
2.5	Synthesis of Anthracene Derivatives	46
2.6	Future Direction and Outlook	47
2.6.1	Modeling Reaction Dynamics in Molecular Crystals	47
2.6.2	New Anthracene Derivatives and Crystal Shapes	48
2.6.3	Interfacing Photomechanical Molecular Crystals with Other Materials	49
2.7	Conclusion	50
	Acknowledgments	50
	References	50
3	Mechanically Responsive Crystals by Light and Heat	57
	<i>Hideko Koshima, Takuya Taniguchi, and Toru Asahi</i>	
3.1	Introduction	57
3.2	Photomechanical Bending of Crystals by Photoreactions	59
3.2.1	Azobenzene	59
3.2.1.1	Bending	59
3.2.1.2	Twisted Bending	61
3.2.2	Salicylideneaniline and Analogues	61
3.2.2.1	Bending and the Mechanism	63
3.2.2.2	Comparison of Chiral and Racemic Crystals	64
3.2.3	Fulgide	64
3.2.4	Carbonyl Compounds	66
3.3	Locomotion of Crystals by Thermal Phase Transition	67
3.3.1	Inchworm-Like Walking	70
3.3.2	Fast Rolling Locomotion	71
3.4	Diversification of Mechanical Motion by Photo-triggered Phase Transition	72
3.4.1	Discovery and the Mechanism of Photo-triggered Phase Transition	72
3.4.2	Stepwise Bending	75
3.5	Why Crystals?	75
3.6	Summary and Outlook	77
	References	77
4	Crawling Motion of Crystals on Solid Surfaces by Photo-induced Reversible Crystal-to-Melt Phase Transition	83
	<i>Yasuo Norikane and Koichiro Saito</i>	
4.1	Introduction	83
4.2	Isomerization of Azobenzene	84
4.3	Phase Transitions in Liquid Crystals (Liquid-Crystal-to-Isotropic)	86
4.4	Phase Transitions in Crystal Phase (Crystal-to-Melt)	87
4.4.1	Characteristics of the Crystal-to-Melt Phase Transition	87
4.4.2	Potential Applications of Crystal-to-Melt Transition	89
4.4.3	Mechanical Motions Derived from the Crystal-to-Liquid Phase Transition	92
4.5	Photo-induced Crawling Motion of Azobenzene Crystals	94
4.5.1	Discovery of the Crawling Motion of Crystal on Solid Surface	94

4.5.2	Characteristics of the Crawling Motion of Crystals	95
4.5.3	Mechanism of the Crawling Motion	98
4.5.4	Crawling Motion of Azobenzene Crystals	98
4.6	Conclusion	98
	References	99
5	Bending, Jumping, and Self-Healing Crystals	105
	<i>Panče Naumov, Stanislav Chizhik, Patrick Commins, and Elena Boldyreva</i>	
5.1	Bending Crystals	105
5.1.1	General Mechanism of Crystal Bending	105
5.1.2	Kinetic Model of the Transformation	108
5.1.3	Mechanical Response of a Crystal to Irradiation	112
5.1.4	A Case Study, Linkage Isomerization of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}(\text{NO}_3)$	116
5.1.5	Concluding Remarks	117
5.2	Salient Crystals	118
5.2.1	Salient Effects	118
5.2.2	Mechanism of the Thermosalient Transition	120
5.2.3	Thermal Signature of the Thermosalient Effect	123
5.2.4	Directionality of Motion	124
5.2.5	Effect of Intermolecular Interactions	125
5.2.6	Effect of Crystal Habit	127
5.2.7	Photosalient and Mechanosalient Effects	128
5.2.8	Applications of the Salient Effects	130
5.3	Self-healing Crystals	131
	References	133
6	Shape Memory Molecular Crystals	139
	<i>Satoshi Takamizawa</i>	
	Introduction	139
6.1	Discovery of Organosuperelasticity	141
6.2	Twinning Organosuperelasticity	149
6.3	Organosuperplasticity Through Multilayered Sliding	156
6.4	Twinning Ferroelasticity	158
6.5	Summary	173
	References	173

Part II Mechanically Responsive Polymers and Composites 177

7	Mechanical Polymeric Materials Based on Cyclodextrins as Artificial Muscles	179
	<i>Akira Harada, Yoshinori Takashima, Akihito Hashidzume, and Hiroyasu Yamaguchi</i>	
7.1	Introduction	179
7.2	Artificial Muscle Regulated by Cross-Linking Density	180
7.2.1	A Host–Guest Gel with αCD and Azo	180

7.2.2	Photo-Responsive Volume Change of α CD-Azo Gels	181
7.2.3	Photo-Responsive Property of α CD-Azo Gels	184
7.3	Artificial Muscle Regulated by Sliding Motion	187
7.3.1	Preparation of a Topological Hydrogel (α CD-Azo Hydrogel)	188
7.3.2	Mechanical and Photo-Responsive Properties of the α CD-Azo Hydrogel	188
7.3.3	UV and Vis Light-Responsive Actuation of the α CD-Azo Xerogel	192
7.4	An Artificial Molecular Actuator with a [c2]Daisy Chain ([c2]AzoCD ₂)	192
7.4.1	Photo-Responsive Actuation of the [c2]AzoCD ₂ Hydrogel	194
7.4.2	Photo-Responsive Actuation of the [c2]AzoCD ₂ Xerogel	196
7.5	Supramolecular Materials Consisting of CD and Sti	199
7.5.1	(α CD-Sti) ₂ Hydrogel	199
7.5.2	(α CD-Sti) ₂ Dry Gel	202
7.6	Concluding Remarks	204
	References	205
8	Cross-Linked Liquid-Crystalline Polymers as Photomobile Materials	209
	<i>Toru Ube and Tomiki Ikeda</i>	
	Introduction	209
8.1	Structures and Functions of Photomobile Materials Based on LCPs	211
8.1.1	Polysiloxanes	211
8.1.2	Polyacrylates	213
8.1.3	Polyacrylate Elastomers Prepared from LC Macromers	218
8.1.4	Systems with Multiple Polymer Components	218
8.1.5	Composites	220
8.1.6	Linear Polymers	222
8.1.7	Rearrangeable Network with Dynamic Covalent Bonds	224
8.2	Summary	226
	References	226
9	Photomechanical Liquid Crystal Polymers and Bioinspired Soft Actuators	233
	<i>Chongyu Zhu, Lang Qin, Yao Lu, Jiahao Sun, and Yanlei Yu</i>	
9.1	Background	233
9.2	Actuation Principles	234
9.2.1	Photochemical Phase Transition	235
9.2.2	Weigert Effect	237
9.2.3	Photothermal Effect	239
9.3	Bioinspired Actuators and Their Applications	242
9.3.1	Soft Actuators Driven by Photothermal Effect	243
9.3.2	Photoinduced Actuation of Soft Actuators	245
9.4	Conclusion	251
	References	253

10	Organic–Inorganic Hybrid Materials with Photomechanical Functions	257
	<i>Sufang Guo and Atsushi Shimojima</i>	
10.1	Introduction	257
10.2	Azobenzene as Organic Components	258
10.3	Siloxane-Based Organic–Inorganic Hybrids	258
10.4	Photoresponsive Azobenzene–Siloxane Hybrid Materials	261
10.4.1	Nanostructural Control by Self-Assembly Processes	261
10.4.2	Lamellar Siloxane-Based Hybrids with Pendant Azobenzene Groups	262
10.4.3	Lamellar Siloxane-Based Hybrids with Bridging Azobenzene Groups	264
10.4.4	Photo-Induced Bending of Azobenzene–Siloxane Hybrid Film	265
10.4.5	Control of the Arrangement of Azobenzene Groups	268
10.5	Other Azobenzene–Inorganic Hybrids	270
10.5.1	Intercalation Compounds	270
10.5.2	Hybridization with Carbon-Based Materials	270
10.6	Summary and Outlook	272
	References	272
 11	 Multi-responsive Polymer Actuators by Thermo-reversible Chemistry	 277
	<i>Antoniya Toncheva, Loïc Blanc, Pierre Lambert, Philippe Dubois, and Jean-Marie Raquez</i>	
11.1	Introduction	277
11.2	Covalent Adaptive Networks	279
11.2.1	Associative CANs	279
11.2.2	Dissociative CANs	280
11.3	Thermo-reversible Chemistry	280
11.4	DA Reactions for Thermo-reversible Networks	282
11.4.1	Basic Definitions	282
11.4.2	DA Reactions for Polymer Synthesis	282
11.4.3	DA Reactions for Thermo-reversible Polymer Network	283
11.4.3.1	Self-healing Materials	283
11.4.3.2	Hydrogels	287
11.5	Soft Actuators	289
11.6	DA-based SMPs for Soft Robotics Application	292
11.7	On the Road to 3D Printing	293
11.8	Perspectives and Challenges	295
	Acknowledgments	298
	References	298
 12	 Mechanochromic Polymers as Stress-sensing Soft Materials	 307
	<i>Daisuke Aoki and Hideyuki Otsuka</i>	
12.1	Introduction	307
12.2	Classification of Mechanochromic Polymers	307

- 12.3 Mechanochromophores Based on Dynamic Covalent Chemistry 309
- 12.4 Mechanochromic Polymers Based on Dynamic Covalent Chemistry 310
- 12.4.1 Polystyrenes with Mechanochromophores at the Center of the Polymer Chain 310
- 12.4.2 Polyurethane Elastomers with Mechanophores in the Repeating Units 310
- 12.4.3 Mechanochromic Elastomers Based on Polymer–Inorganic Composites with Dynamic Covalent Mechanochromophores 312
- 12.5 Mechanochromic Polymers Exhibiting Mechanofluorescence 315
- 12.6 Rainbow Mechanochromism Based on Three Radical-type Mechanochromophores 316
- 12.7 Multicolor Mechanochromism Based on Radical-type Mechanochromophores 318
- 12.8 Foresight 321
- References 323

Part III Application of Mechanically Responsive Materials to Soft Robots 327

- 13 Soft Microrobots Based on Photoresponsive Materials 329**
Stefano Palagi
- 13.1 Soft Robotics at the Micro Scale 329
- 13.2 LCEs for Microrobotics 330
- 13.2.1 Thermal Response of LCEs 330
- 13.2.2 Photothermal Actuation of LCEs 331
- 13.3 Light-Controlled Soft Microrobots 335
- 13.3.1 Structured Light 337
- 13.3.2 Controlled Actuation 338
- 13.3.2.1 Role of Control Parameters 338
- 13.3.3 *Swimming* Microrobots 341
- 13.4 Outlook 344
- References 344
- 14 4D Printing: An Enabling Technology for Soft Robotics 347**
Carlos Sánchez-Somolinos
- 14.1 Introduction 347
- 14.2 3D Printing Techniques 348
- 14.2.1 Material Extrusion-Based Techniques 349
- 14.2.2 Vat Photopolymerization Techniques 350
- 14.3 4D Printing of Responsive Materials 352
- 14.3.1 Shape Memory Polymers 352
- 14.3.2 Hydrogels 355
- 14.3.3 Liquid Crystalline Elastomers 356
- 14.4 4D Printing Toward Soft Robotics 358

14.5	Conclusions	359
	Acknowledgments	360
	References	360
15	Self-growing Adaptable Soft Robots	363
	<i>Barbara Mazzolai, Alessio Mondini, Emanuela Del Dottore, and Ali Sadeghi</i>	
15.1	Introduction	363
15.2	Evolution of Growing Robots	365
15.3	Mechanisms for Adaptive Growth in Plants	367
15.4	Plant-Inspired Growing Mechanisms for Robotics	369
15.4.1	Challenges in Underground Exploration	369
15.4.2	The “Evolution” of Plantoids	369
15.4.3	Sloughing Mechanism	371
15.4.4	First Growing Mechanism	371
15.4.5	Artificial Roots with Soft Spring-Based Actuators	373
15.4.6	Growing Robots via Embedded 3D Printing	375
15.4.6.1	Deposition Strategies	376
15.5	Adaptive Strategies in Plant for Robot Behavior	379
15.5.1	A Plant-Inspired Kinematics Model	380
15.5.2	Plant-Inspired Behavioral Control	382
15.5.3	Circumnutation Movements in Natural and Artificial Roots	385
15.6	Applications and Perspective	387
	Acknowledgments	388
	References	388
16	Biohybrid Robot Powered by Muscle Tissues	395
	<i>Yuya Morimoto and Shoji Takeuchi</i>	
16.1	Introduction	395
16.2	Muscle Usable in Biohybrid Robots	396
16.2.1	Cardiomyocyte and Cardiac Muscle Tissue	397
16.2.2	Skeletal Muscle Fiber and Skeletal Muscle Tissue	398
16.2.3	Cell and Tissue Other Than Mammals	399
16.3	Actuation of Biohybrid Robots Powered by Muscle	400
16.3.1	Biohybrid Robot with a Single Muscle Cell	401
16.3.2	Biohybrid Robot with Monolayer of Muscle Cells	402
16.3.3	Biohybrid Robot with Muscle Tissues	406
16.4	Summary and Future Directions	410
	References	411
	Index	417