

Contents

Preface *XIII*

List of Contributors *XVII*

Part One Synthesis 1

1	Microgels and Their Synthesis: An Introduction	3
	<i>Robert Pelton and Todd Hoare</i>	
1.1	Introduction	3
1.1.1	Defining Microgels	3
1.1.1.1	The Generic Microgel: Structure and Characterization	4
1.1.2	Microgels Are Special	6
1.1.3	The Microgel Landscape	7
1.2	Microgel Synthesis	8
1.2.1	Introduction	8
1.2.2	Approach 1: Microgels Formed by Homogeneous Nucleation	10
1.2.2.1	Emulsion Polymerization and Surfactant-Free Emulsion Polymerization	11
1.2.2.2	Homogeneous Nucleation of Microgels from Linear Polymers	14
1.2.2.3	Core–Shell Microgels	14
1.2.3	Approach 2: Microgels from Emulsification	15
1.2.4	Approach 3: Microgels by Polymer Complexation	16
1.2.5	Exotic Microgels	18
1.2.6	Summary	19
1.3	Particle Derivatization	19
1.3.1	Chemical Coupling to Microgels	19
1.3.2	Microgel Decross-Linking	19
1.3.3	Charged Microgels from Nonionic Precursors	20
1.3.4	Nanoparticle-Filled Gels	21
1.4	Microgel Purification and Storage	22
1.4.1	Microgel Characterization	22
1.5	Conclusions	25
	References	25

Microgel Suspensions: Fundamentals and Applications

Edited by Alberto Fernandez-Nieves, Hans M. Wyss, Johan Mattsson, and David A. Weitz

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

ISBN: 978-3-527-32158-2

2	Polymerization Kinetics of Microgel Particles	33
	<i>Abdelhamid Elaissari and Ali Reza Mahdavian</i>	
2.1	Introduction	33
2.2	Polymerization Processes	36
2.3	Kinetics of Polymerization Reaction	37
2.3.1	The Influence of Initiators	39
2.3.2	The Effect of the Cross-Linking Agent	41
2.3.3	The Effect of Functional Monomers	42
2.3.4	Kinetic Aspects of Microgel Formation	45
2.4	Conclusions	49
	References	49
3	New Functional Microgels from Microfluidics	53
	<i>Jin-Woong Kim and Liang-Yin Chu</i>	
3.1	Introduction	53
3.2	Monodisperse Thermosensitive Microgels Fabricated in a PDMS Microfluidic Chip	54
3.3	Monodisperse Thermosensitive Microgels Fabricated in a Capillary Microfluidic Device	57
3.4	Monodisperse Thermosensitive Microgels with Tunable Volume-Phase Transition Kinetics	62
3.5	Monodisperse Thermosensitive Microgels with Core-Shell Structures Containing Functional Materials	63
3.6	Monodisperse Thermosensitive Microgels with Multiphase Complex Structures	65
3.7	Conclusions	68
	References	68
Part Two	Physical Properties of Microgel Particles	71
4	Swelling Thermodynamics of Microgel Particles	73
	<i>Benjamin Sierra-Martin, Juan Jose Lietor-Santos, Antonio Fernandez-Barbero, Toan T. Nguyen, and Alberto Fernandez-Nieves</i>	
4.1	Introduction	73
4.2	Swelling Thermodynamics	76
4.2.1	Polymer/Solvent Mixing	76
4.2.2	Rubber Elasticity	79
4.2.3	Ionic Effects	81
4.2.3.1	Ideal Gas Contribution	81
4.2.3.2	Electrostatic Energy of a Homogeneously Charged Microgel	83
4.2.3.3	Contribution from Counterion Correlations	84
4.2.3.4	Effect of a Slightly Inhomogeneous Fixed-Charge Distribution	86
4.2.4	Equilibrium: Equation of State	88
4.3	Theory Versus Experiment	94
4.3.1	Role of Flory Solubility Parameter	94

4.3.2	Influence of Cross-Linking Density	97
4.3.3	Effect of Charge Density	98
4.3.4	Salt Effects	100
4.3.5	Effect of Added Polymer	102
4.3.6	Cononsolvency: Swelling in Solvent Mixtures	104
4.3.7	Surfactant Effects	106
4.4	Additional Aspects	108
4.4.1	Elastic Moduli	108
4.4.2	Brief Remarks on Swelling Kinetics	108
4.5	Summary	110
	References	113
5	Determination of Microgel Structure by Small-Angle Neutron Scattering	117
	<i>Walter Richtering, Ingo Berndt, and Jan Skov Pedersen</i>	
5.1	Introduction	117
5.2	Form Factor of Microgels	118
5.3	Core–Shell Particles	129
5.2	Summary	131
	References	131
6	Interactions and Colloid Stability of Microgel Particles	133
	<i>Brian Vincent and Brian Saunders</i>	
6.1	Theoretical Background	133
6.1.1	Introduction	133
6.1.2	Van der Waals Interactions	136
6.1.3	Electrostatic Interactions	137
6.1.4	Depletion Interactions	139
6.1.5	Criteria for Dispersion Stability	140
6.2	Experimental Studies	141
6.2.1	Temperature- and Electrolyte-Induced Aggregation	141
6.2.2	Depletion-Induced Aggregation	151
6.2.3	Heteroaggregation	153
6.2.4	Probing Interactions between Microgel Particles	154
	References	160
Part Three Phase Behavior and Dynamics of Microgel Suspensions		163
7	Structure and Thermodynamics of Ionic Microgels	165
	<i>Christos N. Likos</i>	
7.1	Introduction	165
7.2	Effective Interparticle Potentials	167
7.3	The Fluid Phase of Ionic Microgels	174
7.4	Genetic Algorithms for the Crystal Structures	178
7.5	Phase Behavior	182

7.6	Summary and Concluding Remarks	189
	References	191
8	Elasticity of Soft Particles and Colloids Near the Jamming Threshold	195
	<i>Matthieu Wyart</i>	
8.1	Introduction	195
8.2	Structure and Mechanical Stability	196
8.3	Elastic Moduli	199
8.3.1	Force Balance and Contact Deformation Operators	199
8.3.2	Energy Expansion and Virtual Force Field	200
8.3.3	Elastic Moduli	202
8.4	Summary and Conclusion	204
	References	205
9	Crystallization of Microgel Spheres	207
	<i>Zhibing Hu</i>	207
9.1	Introduction	207
9.2	Synthesis and Characterization of PNIPAM Microgels	208
9.3	Phase Behavior of Dispersions of PNIPAM Microgels at Room Temperature	210
9.3.1	Characterization of Different Phases Using UV-Visible Spectroscopy	212
9.4	Temperature- and Polymer Concentration-Dependent Phases of the PNIPAM Microgel Dispersions	213
9.5	Theoretical Investigation of Phase Behavior	215
9.6	Phase Diagram in Terms of Volume Fraction	217
9.7	The Interparticle Potential	219
9.8	Annealing and Aging Effects	220
9.9	Kinetics of Crystallization	222
9.10	Crystallization Along a Single Direction	224
9.11	Summary and Outlook	225
	References	226
10	Melting and Geometric Frustration in Temperature-Sensitive Colloids	229
	<i>Ahmed M. Alsayed, Yilong Han, and Arjun G. Yodh</i>	
10.1	Introduction	229
10.2	The Experimental System	232
10.2.1	Synthesis of NIPA Microgel Particles	232
10.2.2	Microscopy and Temperature Control	235
10.2.3	Characterization: Dynamic Light Scattering	238
10.2.4	Characterization: Video Microscopy Measurement of Interparticle Potentials	240
10.3	“First” Melting in Bulk (3D) Colloidal Crystals	242

10.3.1	Background	242
10.3.2	Sample Preparation and Imaging	244
10.3.3	Positional Fluctuations and the Lindemann Parameter	246
10.3.4	Bulk Melting	247
10.3.5	“First” Melting Near Grain Boundaries	248
10.3.6	“First” Melting Near Dislocations	250
10.3.7	Positional and Angular Fluctuations Near Defects	251
10.3.8	Summary	253
10.4	Melting in Two Dimensions: The Hexatic Phase	254
10.4.1	Theoretical Background	254
10.4.2	Experimental Background	257
10.4.3	2D Samples	258
10.4.4	Data Analysis	259
10.4.5	The Hexatic Phase and Other Features of the Phase Diagram	264
10.4.6	The Order of the Phase Transitions	265
10.4.7	Summary	265
10.5	Geometric Frustration in Colloidal “Antiferromagnets”	266
10.5.1	Background	266
10.5.2	The Experimental System	269
10.5.3	Antiferromagnetic Order	270
10.5.4	Stripes and the Zigzagging Ground State	270
10.5.5	Dynamics	271
10.5.6	Summary	273
10.6	Future	273
	References	274

Part Four Mechanical Properties 283

11	Yielding, Flow, and Slip in Microgel Suspensions: From Microstructure to Macroscopic Rheology	285
	<i>Michel Cloitre</i>	
11.1	Introduction	285
11.2	Advanced Techniques for Microgel Rheology	286
11.2.1	Macroscopic Shear Rheology	286
11.2.2	DWS-Based Microrheology	288
11.2.3	Real Space Particle-Tracking Techniques	290
11.3	Near-Equilibrium Properties and Linear Rheology of Microgel Suspensions	291
11.3.1	Dilute Regime and Paste Formation	291
11.3.2	Linear Viscoelasticity of Microgel Pastes	293
11.3.3	Elastic Properties of Concentrated Microgel Pastes	294
11.4	Yielding, Flow, and Aging	297
11.4.1	Yielding	297
11.4.2	Flow of Microgel Pastes	299
11.4.3	Slow Dynamics and Aging of Microgel Pastes	301

11.5	Slip and Flow of Microgel Suspensions Near Confining Surfaces	303
11.5.1	Wall Slip	303
11.5.2	Direct Measurements of Slip Velocity	304
11.5.3	Elastohydrodynamic Lubrication as the Origin of Wall Slip	306
11.6	Outlook	307
	References	307
12	Mechanics of Single Microgel Particles	311
	<i>Hans M. Wyss, Johan Mattsson, Thomas Franke, Alberto Fernandez-Nieves, and David A. Weitz</i>	
12.1	Compressive Measurements by Variation of the Osmotic Pressure	312
12.2	Capillary Micromechanics: Full Mechanical Behavior of a Single Microgel Particle	315
12.3	Discussion: Effects of Particle Softness on Suspension Rheology	322
12.4	Microgels as Model Glasses: Soft Particles Make Strong Glasses	323
12.5	Analogy to Emulsions and Foams	324
	References	324
13	Rheology of Industrially Relevant Microgels	327
	<i>Jason R. Stokes</i>	
13.1	Introduction	327
13.2	Flow Behavior	328
13.2.1	Influence of Phase Volume and Concentration	329
13.2.2	Shear Rheology of Concentrated Microgel Suspensions	332
13.2.3	Linear Viscoelasticity of Concentrated Microgel Suspensions	335
13.3	Microgel Suspension Rheology in Applications	338
13.3.1	Coating Formulations	339
13.3.2	Biomedical, Pharmaceutical, Personal Care, and Cosmetic Products	342
13.3.3	Biopolymer Microgels for Food and Other Applications	345
13.3.3.1	Starch Microgels	345
13.3.3.2	Biopolymer Microgels and Particle Anisotropy	347
13.4	Outlook	350
	References	351
Part Five	Applications	355
14	Exploiting the Optical Properties of Microgels and Hydrogels as Microlenses and Photonic Crystals in Sensing Applications	357
	<i>L. Andrew Lyon, Grant R. Hendrickson, Zhiyong Meng, and Ashlee N. St. John Iyer</i>	
14.1	Introduction	357
14.2	Responsive Microgel and Hydrogel-Based Lenses	358
14.3	Photonic Crystals	362
14.4	Other Responsive Systems	368

14.5	Summary	372
	References	372
15	Microgels in Drug Delivery	375
	<i>Martin Malmsten</i>	
15.1	Introduction	375
15.2	Polymer Gels	376
15.3	Polymer Microgels	378
15.3.1	Temperature Triggering of Microgels	380
15.3.2	Electrostatic Triggering of Microgels	382
15.3.3	Triggering of Microgels by Specific Metabolites	385
15.3.4	Microgel Triggering by External Fields	385
15.3.5	Microgel Triggering by Degradation	389
15.4	Polymer Microcapsules	393
15.4.1	Microcapsule Triggering	395
15.5	Swelling, Loading, and Release Kinetics	399
15.6	Outlook	402
	References	403
16	Microgels for Oil Recovery	407
	<i>Yuxing Ben, Ian Robb, Peng Tonmukayakul, and Qiang Wang</i>	
16.1	Introduction	407
16.2	Microgels Used in Oil Recovery	410
16.2.1	Guar	410
16.2.1.1	Gel Formation	411
16.2.2	Rheology of Guar Gels and its Relation to Proppant Transport	415
16.2.2.1	Proppant Transport	416
16.2.3	Xanthan	416
16.2.4	Gels for Gravel Packing	418
16.2.5	Gels for Fluid Loss Control	419
16.2.6	Gels for Pills	420
16.3	Concluding Remarks	421
	References	421
17	Applications of Biopolymer Microgels	423
	<i>Eugene Pashkovski</i>	
17.1	Introduction	423
17.2	Origin, Production, and Molecular Properties of Xanthan Gum	425
17.3	Characterization of Xanthan and CMC Microgels	429
17.4	Rheology of Silica Suspensions in Xanthan Microgel Pastes	436
17.5	Aging of Concentrated Xanthan Suspensions	442
17.6	Conclusions	446
	References	447
	Index	451

