Contents

Preface *xiii*

1 Synthesis of Hairy Nanoparticles *1*
Zongyu Wang, Jiajun Yan, Michael R. Bockstaller, and Krzysztof Matyjaszewski
1.1 Introduction to Grafting Chemistry *1*
1.2 Surface Functionalization of Nanoparticles *2*
1.2.1 Surface Modification by Chemical Treatment *2*
1.2.2 Surface Modification by Plasma Treatment *8*
1.2.3 Synthesis of Functionalized Nanoparticles Through Initiator-Containing Precursors *8*
1.3 Synthesis of Hairy Nanoparticles *9*
1.3.1 Surface-Initiated Polymerization/The "Grafting-from" Approach *9*
1.3.1.1 SI-Free Radical Polymerization *10*
1.3.1.2 SI-ATRP *10*
1.3.1.3 SI-RAFT *17*
1.3.1.4 Other Polymerization Techniques *19*
1.3.2 The "Grafting-onto" Approach *21*
1.3.2.1 Conventional "Grafting-onto" Approach *21*
1.3.2.2 Ligand Exchange *23*
1.3.3 Template Synthesis *24*
1.3.3.1 Block Copolymer and Its Derivative Templates *24*
1.3.3.2 Star/Bottlebrush Polymer Templates *25*
1.4 The Role of "Architecture" in Hairy Nanoparticles *25*
1.4.1 Conformation of Hairy Nanoparticles *26*
1.4.2 Bimodal Hairy Nanoparticles *31*
1.5 Conclusion *32*
Acknowledgment *34*
References *34*

2 Hairy Nanoparticles via Self-assembled Linear Block Copolymers *49*
Zhen Zhang, Yi Shi, and Yongming Chen
2.1 Introduction *49*
2.2 Hairy NPs via Bulk Microphase Separation of Block Copolymers *50*
2.2.1 Bulk Microphase Separation of Diblock Copolymers *50*
2.2.1.1 Theoretical Research *51*
2.2.1.2 Experimental Study *52*
2.2.1.3 Effect Factors *53*
2.2.2 Bulk Microphase Separation of Triblock Copolymers *54*
2.2.3 Preparation of Hairy NPs with Different Shapes *55*
2.2.3.1 Diblock Copolymers with PTEPM or PGMA Components *56*
2.2.3.2 Diblock Copolymers Containing PS *56*
2.2.3.3 Triblock Copolymer System with PS Components *59*
2.3 Hairy NPs via the Self-assembly of Block Copolymer in Solution *61*
2.3.1 Morphology of Block Copolymers Assembly *62*
2.3.1.1 Spherical Micelles *62*
2.3.1.2 Rod-Like Micelles *63*
2.3.1.3 Bilayer Structure *63*
2.3.1.4 New Morphologies *64*
2.3.2 Preparation of Hairy Copolymer NPs *65*
2.3.3 Major Factors Influencing the Morphology of Hairy NPs *65*
2.3.3.1 Block Copolymer Composition *65*
2.3.3.2 Block Copolymer Concentration *66*
2.3.3.3 The Nature of the Solvent *66*
2.3.3.4 Additives *67*
2.3.3.5 Other Factors *68*
2.4 Summary *69*
References *69*

3 Hairy Nanoparticles via Unimolecular Block Copolymer Nanoreactors *73*
Wenjie Zhang and Xinchang Pang
3.1 Background *73*
3.2 Synthesis and Properties of Block Copolymer Unimolecular Micelles *75*
3.2.1 Properties of Unimolecular Block Copolymer Micelles *75*
3.2.2 Synthesis and Features of Star-Liked Block Copolymers *77*
3.2.2.1 Synthesis of Star-Liked Block Copolymers via Core-First Method *77*
3.2.2.2 Synthesis of Star-Liked Block Copolymers via Arm-First Method *83*
3.2.3 Synthesis of Bottle Brush-Liked Block Copolymer *84*
3.3 Synthesis of Monodispersed Nanoparticles via Block Copolymer Unimolecular Micelles Nanoreactors *88*
3.3.1 Star-Like Block Copolymers as Unimolecular Nanoreactors *88*

3.3.1.1 Plain Nanoparticles *88*
3.3.1.2 Core@Shell Nanoparticles *94*
3.3.1.3 Hollow Nanoparticles *97*
3.3.1.4 Nanoring *99*
3.3.1.5 Colloidal Nanoparticles Assemblies *102*
3.3.2 Cylindrical Polymer Brushes as Unimolecular Nanoreactors *104*
3.4 Application of Polymer-Capped Nanoparticles *111*
3.4.1 Solar Energy Conversion *112*
3.4.2 Light-Emitting Diodes *113*
3.4.3 Lithium-Ion Batteries *114*
3.4.4 Catalysis *115*
3.5 Conclusions and Perspectives *117*
3.5.1 Conclusion *117*
3.5.2 Perspectives *117*
References *119*

4 Environmentally Responsive Hairy Inorganic Particles *123*
Caleb A. Bohannon, Ning Wang, and Bin Zhao
4.1 Introduction *123*
4.2 Environmentally Responsive Well-defined Binary Mixed Homopolymer Brush-grafted Silica Particles *126*
4.2.1 Introduction to Mixed Polymer Brushes *126*
4.2.2 Mixed Polymer Brushes Grafted on Particles *129*
4.2.3 Synthesis of Well-defined Binary Mixed Homopolymer Brushes on Silica Particles *130*
4.2.4 Responsive Properties of Binary Mixed Homopolymer Brush-grafted Silica Particles *134*
4.3 Thermoresponsive Polymer Brush-grafted Silica Particles *141*
4.3.1 Synthesis and Thermally Induced LCST Transition of Thermoresponsive Polymer Brushes Grafted on Silica Particles *141*
4.3.2 Thermally Induced Phase Transfer of Thermoresponsive Hairy Particles Between Two Immiscible Liquid Phases *144*
4.3.2.1 Thermally Induced Phase Transfer of Thermoresponsive Hairy Particles Between Water and Immiscible Organic Solvents *144*
4.3.2.2 Thermally induced Phase Transfer of Thermoresponsive Hairy Particles Between Water and a Hydrophobic Ionic Liquid *146*
4.3.3 Thermoreversible Gelation of Thermoresponsive Diblock Copolymer Brush-grafted Silica Nanoparticles in Water *150*
4.3.4 Thermoresponsive Polymer Brush-grafted Nanoparticles for Enhancing Gelation of Thermoresponsive Linear ABC Triblock Copolymers in Water *156*
4.4 Summary and Outlook *160*
Acknowledgements *161*
References *161*

5 Self-Assembly of Hairy Nanoparticles with Polymeric Grafts *167*
Xiaoxue Shen, Huibin He, and Zhihong Nie
5.1 Introduction *167*
5.2 Self-Assembly of PGNPs into Colloidal Molecules *168*
5.2.1 Precisely Defined Assembly of Patchy NPs *168*
5.2.1.1 Isotropic NPs *169*
5.2.1.2 Anisotropic NPs *171*
5.2.2 Polymer-Guided Assembly of NPs *172*
5.3 Self-Assembly of PGNPs Into One-Dimensional (1-D) Structures *175*
5.3.1 Self-Assembly of PGNPs in Solution Guided by Various Molecular Interactions *176*
5.3.1.1 Self-Assembly Driven by Neutralization Reaction *176*
5.3.1.2 Self-Assembly Driven by Hydrophobic Interaction *178*
5.3.1.3 Self-Assembly Driven by Dipolar Interaction *180*
5.3.2 Templated Self-Assembly of PGNPs into 1-D Structures *182*
5.3.2.1 Hard Template-Assisted Assembly of PGNPs *182*
5.3.2.2 Self-Assembly of PGNPs Assisted by Soft Templates *184*
5.3.3 The Self-Assembly of 1-D Structures in Polymer Films *187*
5.4 Self-Assembly of PGNPs into 2-D Structures *190*
5.4.1 Templated Self-Assembly of PGNPs into 2-D Structures *190*
5.4.1.1 Self-Assembly Using BCPs as Templates *190*
5.4.1.2 Hard Template-Assisted Self-Assembly *193*
5.4.2 Interfacial Assembly *193*
5.4.3 2-D Assemblies Within Thin Film *197*
5.4.3.1 PGNPs/Homopolymer System *197*
5.4.3.2 Self-Assembly of Single-Component Neat PGNPs *199*
5.4.3.3 Self-Assembly of Binary PGNPs Blends *201*
5.5 Self-Assembly of PGNPs into 3-D Structures *202*
5.5.1 Self-Assembly of PGNPs into Clusters *202*
5.5.2 Self-Assembly of PGNPs into Vesicles *206*
5.5.2.1 Self-Assembly of Hydrophilic Homopolymer-Grafted NPs *206*
5.5.2.2 Self-Assembly of Mixed Homopolymer-Grafted NPs (M-PGNPs) *206*
5.5.2.3 Self-Assembly of BCP-Grafted NPs (B-PGNPs) *209*
5.5.2.4 Co-Assembly of Binary B-PGNPs or B-PGNPs/BCPs *210*
5.5.3 Self-Assembly of PGNPs into 3-D Superlattices and Crystals *212*
5.5.3.1 Superlattices and Crystals Assembled in Solution *212*
5.5.3.2 Binary Superlattice Assembled at Interfaces *214*
5.6 Representative Applications of Assembled PGNPs *215*
5.6.1 Biological Applications: Imaging, Therapy, and Drug Delivery *215*
5.6.1.1 Assemblies of Plasmonic PGNPs *216*
5.6.1.2 Assemblies of Magnetic PGNPs *216*
5.6.1.3 Assemblies of Plasmonic-Magnetic PGNPs *217*
5.6.2 Dielectric Materials *218*
5.7 Summary and Outlook *219*
References *220*

6 Interfacial Property of Hairy Nanoparticles *227*
Yilan Ye and Zhenzhong Yang
6.1 Introduction *227*
6.2 Hairy NPs as Interfacial Building Blocks *228*
6.2.1 Conformation of Grafted Polymers in Good Solvents *228*
6.2.2 Patchy and Janus Geometry in Selective Solvents *230*
6.2.3 Interfacial Activity as Colloids *233*
6.3 Hairy NPs Assembly at Various Interfaces *235*
6.3.1 Dispersion in Polymer Nanocomposites *235*
6.3.2 Anisotropic Assembly *237*
6.3.3 Liquid–Liquid Interfaces *240*
6.3.4 Air–Solid Surfaces *243*
6.3.5 Air–Liquid Surfaces *244*
6.4 Interfacial Entropy *246*
6.5 Interfacial Jamming *248*
6.5.1 Electrostatic Assembly *248*
6.5.2 Host–Guest Molecular Recognition *251*
6.6 Single-Chain NPs at Interfaces *251*
6.6.1 Efficient Synthesis *251*
6.6.1.1 Electrostatic-Mediated Intramolecular Crosslinking Toward Large-Scale Synthesis of SCNPs *252*
6.6.1.2 Grafting Single-Chain at NPs *255*
6.6.2 Interfacial Applications *256*
References *258*

7 Hairy Hollow Nanoparticles *261*
Huiqi Zhang
7.1 Introduction *261*
7.2 Overview of the Progress in the Design and Synthesis of Hairy Hollow NPs *262*
7.2.1 Synthetic Strategies for Hairy Hollow Polymer NPs *262*
7.2.1.1 Sacrificial Template Method *263*
7.2.1.2 Self-Assembly (of Block Copolymers) Method *282*
7.2.1.3 Single-Molecule Templating (of Core–Shell Bottlebrush Polymers) Method *288*
7.2.2 Synthetic Strategies for Hairy Hollow Inorganic NPs *293*
7.2.2.1 Direct Grafting of Polymer Brushes onto Hollow Inorganic NPs *293*
7.2.2.2 Sacrificial Template Strategy Combined with Sol–Gel Chemistry and Polymer Brush-Grafting Methods *296*
7.2.3 Synthetic Strategies for Hairy Hollow Organic/Inorganic Hybrid NPs *302*
7.2.3.1 Direct Deposition of Polymer Layers onto Hollow Inorganic NPs by SI-Polymerizations *302*
7.2.3.2 Self-Assembly Method *302*
7.2.3.3 Single-Molecule Templating Method *304*

7.2.3.4 Sacrificial Template Method Combined with Polymer Brush Nanoreactors *305*
7.3 Conclusions and Perspectives *306*
Acknowledgment *308*
References *308*

8 Self-Assembly of Binary Mixed Homopolymer Brush-Grafted Silica Nanoparticles *313*
Bin Zhao, Ping Tang, Phoebe L. Stewart, Rong-Ming Ho, Christopher Y. Li, and Lei Zhu
8.1 Introduction *313*
8.2 Computer Simulations of the Self-Assembled Morphology of MBNPs *315*
8.3 Self-Assembled Morphologies of Well-Defined Binary Mixed Homopolymer Brushes Grafted on Silica NPs *318*
8.3.1 Synthesis of Well-Defined Binary Mixed Homopolymer Brush-Grafted Silica NPs *318*
8.3.2 Lateral Microphase Separation of Nearly Symmetric P*t*BA/PS MBNPs *319*
8.3.3 Effect of Chain Length Disparity on the Self-Assembled Morphology of P*t*BA/PS MBNPs *320*
8.3.4 Effect of Overall Grafting Density on Morphology of P*t*BA/PS MBNPs *324*
8.3.5 Effect of Molecular Weight on Morphology of Symmetric MBNPs *327*
8.3.6 Effect of Core Particle Size on Morphology of P*t*BA/PS MBNPs *332*
8.3.7 3D Morphologies of P*t*BA/PS MBNPs by Cryo-TEM and Electron Tomography *335*
8.4 Self-Assembled Morphology in Solvents and Homopolymer Matrices *339*
8.4.1 Self-Assembly of MBNPs in Good and Selective Solvents *339*
8.4.2 Self-Assembly of MBNPs in Homopolymer Matrices with Different Molecular Weights *341*
8.5 Conclusions and Future Work *346*
Acknowledgment *346*
References *347*

9 Hairy Plasmonic Nanoparticles *351*
Christian Rossner, Tobias A.F. König, and Andreas Fery
9.1 Introduction *351*
9.2 Plasmonic Properties of Isolated NPs and Energy Transfer to Adjacent Hairy Environment *354*
9.2.1 Plasmonic Principles of Hairy NPs *354*
9.2.2 Energy Transfer to Adjacent Hairy Environment *358*
9.2.2.1 Hairy NPs for Photothermal Heating *358*
9.2.2.2 Hairy NPs Conjugated with Photoactive Entities *360*

9.2.2.3 Hairy NPs Conjugated with Acceptors *361*
9.3 Plasmonic Coupling Scenarios of Hairy Plasmonic NPs *362*
9.3.1 Supercolloidal Structures in Solution *362*
9.3.2 Hairy NPs Linked to Surface and Self-assembly *366*
9.4 Summary and Outlook Discussions *368*
Acknowledgments *370*
References *370*

10 Hairy Metal Nanoparticles for Catalysis: Polymer Ligand-Mediated Catalysis *375*
Zichao Wei and Jie He
10.1 Nanocatalysis Mediated by Surface Ligands *375*
10.1.1 Surface Ligands as an Important Component for Nanocatalysis *375*
10.1.2 Polymers as Better Ligands for NPs *377*
10.2 Catalysis Mediated by PGNPs with Thiol-Terminated Polymers *380*
10.3 Catalysis Mediated by PGNPs with NHC-Terminated Polymers *387*
10.4 Other PGNP Nanocatalysts *393*
10.5 Conclusion and Outlook *396*
References *397*

11 Hairy Inorganic Nanoparticles for Oil Lubrication *401*
Michael T. Kelly and Bin Zhao
11.1 Introduction *401*
11.1.1 Oil Lubrication *401*
11.1.2 Nanoparticles as Oil Lubricant Additives for Friction and Wear Reduction *402*
11.1.3 Polymer Brush-Grafted Nanoparticles: Definition and Synthesis *404*
11.2 Oil-Soluble Poly(lauryl methacrylate) Brush-Grafted Metal Oxide NPs as Lubricant Additives *406*
11.2.1 Synthesis, Dispersibility, and Stability in PAO of Poly(lauryl methacrylate) Brush-Grafted Silica and Titania NPs *406*
11.2.2 Lubrication Properties of Poly(lauryl methacrylate) Brush-Grafted Silica and Titania NPs in PAO *410*
11.3 Effects of Alkyl Pendant Groups on Oil Dispersibility, Stability, and Lubrication Property of Poly(alkyl methacrylate) Brush-Grafted Silica Nanoparticles *413*
11.3.1 Synthesis of Poly(alkyl methacrylate) Brush-Grafted, 23-nm Silica NPs *413*
11.3.2 Dispersibility and Stability of 23-nm Silica NPs Grafted with Poly(alkyl methacrylate) Brushes with Various Pendant Groups in PAO-4 *414*
11.3.3 Effect of Alkyl Side Chains of Poly(alkyl methacrylate) Brushes on Lubrication Performance of 23-nm Hairy Silica NPs as Additives for PAO-4 *416*
11.4 Improved Lubrication Performance by Combining Oil-Soluble Hairy Silica Nanoparticles and an Ionic Liquid as Additives for PAO-4 *420*

11.4.1 Preparation of PAO-4 Lubricants with Various Amounts of PLMA Hairy Silica NPs and [P8888][DEHP] and Stability of Hairy Silica NPs in the Presence of [P8888][DEHP] *421*
11.4.2 Lubrication Performances of PAO-4 Lubricants with the Addition of HNP, IL, and HNP + IL at Various Mass Ratios *422*
11.4.3 SEM–EDS and XPS Analysis of Wear Scars Formed on Iron Flats from Tribological Tests *424*
11.5 Upper Critical Solution Temperature (UCST)-Type Thermoresponsive Poly(alkyl methacrylate)s in PAO-4 *426*
11.5.1 Synthesis of Poly(alkyl methacrylate)s with Various Alkyl Pendant Groups by RAFT Polymerization and Their Thermoresponsive Properties in PAO-4 *428*
11.5.2 UCST-Type Thermoresponsive ABA Triblock Copolymers as Gelators for PAO-4 *429*
11.6 Summary *432*
Acknowledgments *433*
References *433*

Index *437*