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I am submitting herewith a dissertation written by Jonathan Michael Horton entitled “Synthesis and Temperature-Induced Phase Transfer Behavior of Thermosensitive Hairy Particles between Aqueous Solution and a Hydrophobic Ionic Liquid.” I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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**Synthesis and Temperature-Induced Phase Transfer
Behavior of Thermosensitive Hairy Particles between
Aqueous Solution and a Hydrophobic Ionic Liquid**

A Dissertation

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Jonathan Michael Horton

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Abstract

This dissertation presents the synthesis of a family of thermosensitive polymer brush-grafted silica particles and the study of their thermally induced phase transfer behavior between water and a hydrophobic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]). The hairy particles were prepared by surface-initiated atom transfer radical polymerization.

Chapter 1 describes the synthesis and phase transfer behavior of a series of 205 nm silica particles grafted with thermosensitive polymers of methoxyoligo(ethylene glycol) methacrylates. The hairy particles with sufficiently high lower critical solution temperatures underwent reversible and quantitative transfer between water and [EMIM][TFSA] in response to temperature changes. The transfer temperature (T_{tr}) of hairy particles from water to [EMIM][TFSA] upon heating was a linear function of the cloud point (CP) of corresponding free polymer in [EMIM][TFSA]-saturated water. Chapter 2 presents the synthesis and study of thermo- and pH-sensitive hairy particles. A small amount of carboxylic acid groups was incorporated into the thermosensitive polymer brushes. The T_{tr} of hairy particles from water to [EMIM][TFSA] increased with increasing the pH of the aqueous phase. By exploiting the tunability of T_{tr} , we demonstrated pH-driven reversible transfer of hairy particles at a constant temperature and multiple transfer processes by controlling both temperature and pH. Chapter 3 describes a study of the effect of silica core size on phase transfer of thermosensitive hairy particles. The transfer temperatures of thermosensitive polymer brush-grafted 67 nm nanoparticles were higher by 1-3 °C than those of thermosensitive hairy particles with

silica core sizes of ~ 200 nm. They also moved faster by 1.8 times from water to [EMIM][TFSA] than larger hairy particles.

Chapter 4 presents the synthesis of a series of mixed poly(*tert*-butyl acrylate) (PtBA)/polystyrene (PS) brushes from Y-initiator-functionalized 67 nm silica nanoparticles. Transmission electron microscopy studies showed that with the increase of PS M_n from below to above that of PtBA, the morphology of mixed brushes evolved from isolated PS nanodomains, to truncated wedge-shaped nanostructures, and two-layered structures. A notable feature of the morphology of mixed brushes on 67 nm nanoparticles is the truncated wedge-shaped nanostructures. A summary of this dissertation research and future work are provided in Chapter 5.

Table of Contents

Chapter 1. Synthesis of Thermosensitive Hairy Particles and Their Thermally Induced Phase Transfer Behavior between Water and a Hydrophobic Ionic Liquid	1
Abstract.....	2
1.1 Introduction.....	4
1.2 Experimental Section.....	8
1.2.1 Materials	8
1.2.2 Characterization	9
1.2.3 Synthesis of Bare Silica Particles	10
1.2.4 Synthesis of ATRP-Initiator-Functionalized Silica Particles	10
1.2.5 Synthesis of Thermosensitive Polymer Brush-Grafted Silica Particles.....	11
1.2.6 Determination of Cloud Points of Free Polymers in Water	13
1.2.7 Reversible Transfer of Thermosensitive Polymer Brush-Grafted Silica Particles between Water and [EMIM][TFSA] Induced by Temperature Changes.....	13
1.2.8 Determination of Transfer Temperature of Thermosensitive Hairy Particles from Water to [EMIM][TFSA] upon Heating	15
1.3 Results and Discussion	16
1.3.1 Synthesis of Thermosensitive Polymer Brush-Grafted Silica Particles.....	16
1.3.2 Cloud Points of Free Polymers in Water	19
1.3.3 Thermo-Induced Phase Transfer of LMW PEGMMA Brush-Grafted Silica Particles.....	21

1.3.4	Determination of Phase Transfer Temperature of LMW PPEGMMA Hairy Particles from Water to [EMIM][TFSA] Phase upon Heating	23
1.3.5	Thermo-Induced Phase Transfer of HMW PPEGMMA Brush-Grafted Silica Particles.....	29
1.3.6	Temperature Change-Induced Phase Transfer of Other Thermosensitive Hairy Particles Between Water and [EMIM][TFSA] and Effect of LCST on Particle Transfer Temperature	31
1.4	Conclusions.....	37
	References.....	40
	Appendix A.....	43
Chapter 2. Synthesis of Thermo- and pH-Sensitive Hairy Particles and Their Stimuli-Induced Reversible Transfer Behavior between Water and a Hydrophobic Ionic Liquid		63
	Abstract.....	64
2.1	Introduction.....	66
2.2	Experimental Part.....	71
2.2.1	Materials	71
2.2.2	Characterization	72
2.2.3	Synthesis of Poly(methoxytri(ethylene glycol) methacrylate- <i>co-t</i> -butyl methacrylate) Brush-Grafted Silica Particles.....	73
2.2.4	Removal of <i>tert</i> -Butyl Groups of P(TEGMMA- <i>co-t</i> BMA) Brushes Grafted on Silica Particles and of Free Copolymer P(TEGMMA- <i>co-t</i> BMA) by CF ₃ COOH	74

2.2.5	Determination of Cloud Points of P(TEGMMA- <i>co</i> -MAA) in Aqueous Solutions in the Absence and Presence of Ionic Liquid	75
2.2.6	Thermally Induced Reversible Transfer of P(TEGMMA- <i>co</i> -MAA) Brush-Grafted Silica Particles between Water and [EMIM][TFSA] at pH Values of 2.99, 5.00, and 7.02	76
2.2.7	Determination of Transfer Temperature of P(TEGMMA- <i>co</i> -MAA) Hairy Particles from Aqueous to [EMIM][TFSA] Phase at Various pH Values upon Heating.....	77
2.2.8	Reversible Transport of Thermo- and pH-Sensitive P(TEGMMA- <i>co</i> -MAA) Hairy Particles at a Constant Temperature by Altering the pH.....	78
2.2.9	Multiple Transfer Processes of Thermo- and pH-Sensitive Hairy Particles between Aqueous and [EMIM][TFSA] Phases by Controlling both pH and Temperature	79
2.3	Results and Discussion	80
2.3.1	Synthesis of Thermo- and pH-Sensitive P(TEGMMA- <i>co</i> -MAA) Brush-Grafted Silica Particles	80
2.3.2	Thermosensitive Property of Free Polymer P(TEGMMA- <i>co</i> -MAA): pH Dependence of Cloud Point of P(TEGMMA- <i>co</i> -MAA) in Water and [EMIM][TFSA]-Saturated Water	84
2.3.3	Thermo-Induced Reversible Transfer of P(TEGMMA- <i>co</i> -MAA) Hairy Particles between Aqueous and [EMIM][TFSA] Phases at pH Values of 2.99, 5.00, and 7.02.....	87

2.3.4	Phase Transfer Temperatures of Thermo- and pH-Sensitive Hairy Particles from Aqueous to [EMIM][TFSA] Phase at Various pH Values upon Heating.....	88
2.3.5	pH-Driven Transfer of Thermo- and pH-Sensitive Hairy Particles at a Constant Temperature.....	94
2.3.6	Multiple Transport Processes of Thermo- and pH-Sensitive P(TEGMMA- <i>co</i> -MAA) Hairy Particles between Aqueous and [EMIM][TFSA] Layers by Controlling Both pH and Temperature	95
2.4	Conclusions.....	99
	References.....	101
	Appendix B.....	105
 Chapter 3. Synthesis of Thermosensitive Polymer Brushes on Sub-100 nm Silica Nanoparticles and Their Thermally Induced Phase Transfer Behavior between Water and a Hydrophobic Ionic Liquid		
	Abstract.....	113
3.1	Introduction.....	114
3.2	Experimental Part.....	120
3.2.1	Materials	120
3.2.2	Characterization	121
3.2.3	Synthesis of Themosensitive Polymer Brushes Grafted on 67 nm Silica Particles.....	121
3.2.3.1	Synthesis of {[(2-Bromo-2-methylpropionyl)oxy]propyl} triethoxysilane Functionalized Silica Particles	121

3.2.3.2	Synthesis of Poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) Brushes Grafted on 67 nm Silica Nanoparticles by Surface-Initiated Atom Transfer Radical Polymerization	123
3.2.3.3	Synthesis of Poly(methoxypoly(ethylene glycol) methacrylate) (PPEGMMA) Brushes Grafted on 67 nm Silica Nanoparticles by Surface-Initiated Atom Transfer Radical Polymerization	124
3.2.4	Synthesis of Thermosensitive Polymer Brushes Grafted on 215 nm Silica Particles.....	125
3.2.4.1	Synthesis of 215 nm Silica Particles	125
3.2.4.2	Hydrosilylation and Immobilization of 6-(Chlorodimethylsilyl)hexyl 2-Bromo-2-methylpropanoate on 215 nm Silica Particles.....	126
3.2.4.3	Surface-Initiated Atom Transfer Radical Polymerization of Methoxypoly(ethylene glycol) Methacrylate (PEGMMA) from 215 nm Silica Particles.....	127
3.2.5	Synthesis of Polymer Brushes Grafted on 27 nm Silica Nanoparticles...	128
3.2.5.1	Synthesis of 27 nm Silica Nanoparticles by <i>L</i> -Lysine Mediated Condensation.....	128
3.2.5.2	Surface Functionalization of 27 nm Silica Nanoparticles with {[2-Bromo-2-methylpropionyl)oxy]propyl}triethoxysilane	128
3.2.5.3	Synthesis of Poly(<i>tert</i> -butyl acrylate) Brushes Grafted on 27 nm Silica Nanoparticles	129
3.2.5.4	Cleavage of Grafted PtBA from 27 nm Silica Nanoparticles for SEC Analysis.....	130

3.2.6	Reversible Transfer of Thermosensitive Polymer Brush-Grafted Silica Particles between Water and [EMIM][TFSA] Induced by Temperature Changes.....	130
3.2.7	Determination of Transfer Temperature of Thermosensitive Hairy Particles from Water to [EMIM][TFSA] upon Heating.	131
3.2.8	Kinetics Study of Phase Transfer of Thermosensitive Hairy Particles from Water to [EMIM][TFSA] at a Temperature 15 °C above the Transfer Temperature.	132
3.3	Results and Discussion	134
3.3.1	Synthesis of ATRP-Initiator Functionalized Silica Particles with Average Diameters of 67 nm, 215 nm, and 27 nm.....	134
3.3.2	Synthesis of Polymer Brushes Grafted on Silica Particles with Different Sizes	136
3.3.3	Temperature-Induced Reversible Phase Transfer of Thermosensitive Polymer Brush-Grafted Silica Particles with Different Sized Silica Cores.	147
3.3.4	Determination of Phase Transfer Temperatures of Thermosensitive Polymer Brush-Grafted Silica Particles with Different Sized Silica Cores	150
3.3.5	Kinetics Study of Phase Transfer of Thermosensitive PEGMMA-Grafted Silica Particles from the Water Phase to the Ionic Liquid Phase at $T = T_{tr} + 15\text{ }^{\circ}\text{C}$	159
3.4	Conclusions.....	164

References	168
Chapter 4. Synthesis and Phase Morphology of Well-Defined Mixed Homopolymer Brushes Grafted on 67 nm Silica Nanoparticles	171
Abstract	172
4.1. Introduction	173
4.2 Experimental	175
4.2.1 Materials	175
4.2.2 Characterization	177
4.2.3 Synthesis of Y-initiator-Functionalized 67 nm Silica Nanoparticles (Y- Initiator Nanoparticles)	178
4.2.3.1 Isolation and Solvent Exchange of 67 nm Silica Nanoparticles	178
4.2.3.2 Hydrosilylation of 2-[4-(But-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl -1'-piperidinyloxy)ethyl 2-Bromo-2-methylpropanoate	178
4.2.3.3 Immobilization of 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(4- (4-(triethoxysilyl)butyl)phenyl)ethyl 2-bromo-2-methylpropanoate (Y-Silane) onto 67 nm Silica Nanoparticles (Y-Initiator Nanoparticles)	179
4.2.4 Synthesis of PtBA Brushes from Y-Initiator-Functionalized 67 nm Silica Nanoparticles by Atom Transfer Radical Polymerizaiton of <i>tert</i> -Butyl Acrylate	179
4.2.5 Synthesis of Mixed PtBA/PS Polymer Brushes with PtBA $M_{n,SEC}$ of 22.2 kDa and Various PS Molecular Weights by Surface-Initiated NMRP of Styrene from PtBA Brush-Grafted 67 nm Silica Nanoparticles	180

4.2.6	Transmission Electron Microscopy (TEM) Study of Mixed PtBA/PS Brushes Grafted on 67 nm Silica Nanoparticles	181
4.3	Results and discussion	182
4.3.1	Synthesis of Y-initiator-Functionalized 67 nm Silica Nanoparticles.....	182
4.3.2	Synthesis of Mixed PtBA/PS Brushes with a Fixed PtBA $M_{n,SEC}$ and Various PS Molecular Weights from Y-Initiator-Functionalized 67 nm Silica Nanoparticles by Sequential ATRP and NMRP	182
4.3.3	TEM Study of Phase Morphologies of Mixed PtBA/PS Brush Grafted on 67 nm Silica Particles	1900
4.4	Conclusion	197
	References	200
Chapter 5.	Summary and Outlook	204
5.1.	Summary	204
5.2	Future Work	208
	References	208
	Vita.....	210

List of Tables

1.1	Characterization Data for Six Thermosensitive Polymer Brush-Grafted Particle Samples and the Corresponding Free Polymers	20
1.2	Cloud Points of Free Thermosensitive Polymers in Pure Water and in the [EMIM][TFSA]-Saturated Water in the Presence of a Separate [EMIM][TFSA] Phase at a Concentration of 0.5 wt%	22
1.3	Transfer Temperature (T_{tr}), Standard Enthalpy Change ΔH° and Standard Entropy Change ΔS° Calculated from the Plot of $\ln K$ versus $1/T$ for Five Thermosensitive Polymer Brush-Grafted Particle Samples	36
3.1	Characterization Data for five Thermosensitive Polymer Brush-Grafted Particle Samples Synthesized from Initiator Particles and their Corresponding Free Polymers as well as Two Thermosensitive Hairy Particle Samples from Chapter 1	143
3.2	Standard Enthalpy Changes ΔH° and Standard Entropy Changes ΔS° Calculated from Plots of $\ln K$ vs. $1/T$ and Transfer Temperature (T_{tr}) for Five Thermosensitive Hairy Particle Samples and Two Particle Samples from Chapter 1	158
4.1	Molecular Weight Characteristics of Mixed <i>Pt</i> BA/PS Brushes with a Fixed <i>Pt</i> BA $M_{n, SEC}$ of 22.2 kDa and Different PS Molecular Weight Grafted on 67 nm Silica Particles and the Corresponding Free Polymers	189

List of Schemes

1.1	Synthesis of Thermosensitive Polymer Brush-Grafted Silica Particles by Surface-Initiated ATRP and Molecular Structures of PEGMMA, TEGMMA, and DEGMMA.....	7
2.1	Synthesis of Thermo- and pH-sensitive Poly(methoxytri(ethylene glycol) methacrylate- <i>co</i> -methacrylic acid) Brush-Grafted Silica Particles by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) and Subsequent Treatment with CF ₃ COOH	69
2.2	Schematic Illustration of Thermo- and pH-Triggered Transfer of Hairy Particles between Aqueous Solution and a Hydrophobic Ionic Liquid.....	70
3.1	Synthesis of Thermoresponsive Polymer Brush Grafted on Silica Nanoparticles with an Average Size of 67 nm by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP)	117
3.2	Synthesis of Thermoresponsive PPEGMMA Brushes Grafted on 215 nm Silica Particles by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP).....	118
3.3	Synthesis of Polymer Brushes Grafted on 27 nm Silica Nanoparticles by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP)	119
4.1	Schematic Illustration of the Synthesis of Mixed PtBA/PS Brush Grafted on 67 nm Silica Nanoparticles by Sequential Atom Transfer Radical Polymerization and Nitroxide Mediated Radical Polymerization	176

List of Figures

- 1.1 (A) Thermogravimetric analysis (TGA) of (i) bare silica particles, (ii) initiator particle-I, and (iii) PEGMMA brush-grafted silica particles with PEGMMA $M_{n,SEC}$ of 23 kDa. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C. (B) Size exclusion chromatography trace of free polymer PEGMMA formed from the free initiator in the synthesis of lower molecular weight PEGMMA brush-grafted particles.....17
- 1.2 Pictures of the water-[EMIM][TFSA] biphasic system that contained LMW PEGMMA brush-grafted silica particles at (a) 22 and (b) 80 °C in the 4th cycle and at (c) 22 and (d) 80 °C in the 5th cycle. In each group of pictures, the left one shows the picture of the vial with no laser; the central and right ones show the vial with a laser beam passing through the top water layer and bottom ionic liquid layer, respectively.24
- 1.3 Plot of normalized absorbance (A/A_{max}) of LMW PEGMMA hairy particles in the aqueous phase (solid square) and the ionic liquid phase (solid circle) versus temperature. A and A_{max} represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range 26
- 1.4 Plot of natural logarithm of equilibrium constant of LMW PEGMMA brush-grafted silica particles ($K = [\text{particle}]_{IL}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.98628

- 1.5 (A) Plot of normalized absorbance ($A/A_{\max}$) of HMW PPEGMMA hairy particles in water (solid square) and [EMIM][TFSA] (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range. (B) Plot of natural logarithm of equilibrium constant of HMW PPEGMMA brush-grafted silica particles ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.99330
- 1.6 (A) Plot of normalized absorbance ($A/A_{\max}$) of P(PEGMMA-*co*-TEGMMA)-82 hairy particles in water (solid black square) and [EMIM][TFSA] (solid circle) versus temperature in thermo-induced transport experiments. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range, respectively. (B) Plot of natural logarithm of equilibrium constant ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature for P(PEGMMA-*co*-TEGMMA)-82 hairy particles, respectively. The solid line in the plot is a linear fit with a correlation coefficient R shown in the plot..... 33
- 1.7 (A) Plot of normalized absorbance ($A/A_{\max}$) of P(PEGMMA-*co*-TEGMMA)-74 hairy particles in water (solid black square) and [EMIM][TFSA] (solid circle) versus temperature in thermo-induced transport experiments. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range, respectively. (B) Plot of natural logarithm of equilibrium constant ($K =$

	[particle] _{IL} /[particle] _{water}) versus the inverse of absolute temperature for P(PEGMMA- <i>co</i> -TEGMMA)-74 hairy particles, respectively. The solid line in the plot is a linear fit with a correlation coefficient R shown in the plot.....	34
1.8	(A) Plot of normalized absorbance ($A/A_{\max}$) of PTEGMMA) hairy particles in water (solid black square) and [EMIM][TFSA] (solid circle) versus temperature in thermo-induced transport experiments. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range, respectively. (B) Plot of natural logarithm of equilibrium constant ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature for PTEGMMA) hairy particles, respectively. The solid line in the plot is a linear fit with a correlation coefficient R shown in the plot.	35
1.9	Transfer Temperature of thermosensitive polymer brush-grafted particles from water to the [EMIM][TFSA] phase versus cloud point of thermosensitive free polymer in the [EMIM][TFSA]-saturated water. The solid line is a linear fit with R value of 0.997	38
A.1	Size exclusion chromatography analysis of free polymer PPEGMMA formed from the free initiator, ethyl 2-bromoisobutyrate, in the synthesis of HMW PPEGMMA brushes from initiator particle-II by surface-initiated ATRP of PEGMMA. The $M_{n,\text{SEC}}$ and polydispersity index of the free PPEGMMA were 40 kDa and 1.08, respectively	45

A.2	Thermogravimetric analysis of (a) bare silica particles, (b) initiator particles-II and (c) HMW PPEGMMA hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C	46
A.3	Size exclusion chromatography analysis of the polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of P(TEGMMA- <i>co</i> -PEGMMA)-82 brushes from initiator particle-II by surface-initiated ATRP of a mixture of PPEGMMA and TEGMMA with a molar ratio of 70 : 30. The $M_{n,SEC}$ and polydispersity index of the free copolymer were 29 kDa and 1.12, respectively	47
A.4	Thermogravimetric analysis of (a) bare silica particles, (b) initiator particles-II, and (c) P(TEGMMA- <i>co</i> -PEGMMA)-82 hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C	48
A.5	Size exclusion chromatography analysis of the polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of P(TEGMMA- <i>co</i> -PEGMMA)-74 brushes from initiator particle-I by surface-initiated ATRP of a mixture of PPEGMMA and TEGMMA with a molar ratio of 40:60. The $M_{n,SEC}$ and polydispersity index of the free copolymer were 23 kDa and 1.12, respectively	49
A.6	Thermogravimetric analysis (TGA) of (a) bare silica particles, (b) initiator particles-I and (c) P(TEGMMA- <i>co</i> -PEGMMA)-74 hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C	50
A.7	SEC analysis of free PTEGMMA formed from free initiator in the synthesis of PTEGMMA brush-grafted particles	51

A.8	Themogravimetric analysis of (a) bare silica particles, (b) initiator particles-II, and (c) PTEGMMA hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.....	52
A.9	SEC analysis of PDEGMMA formed from free initiator in the synthesis of PDEGMMA brush-Grafted silica particles.....	53
A.10	Themogravimetric analysis of (a) bare silica particles, (b) initiator particle-II, and (c) PDEGMMA hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.....	54
A.11	The absorbance of the dispersion of HMW PPEGMMA brush-grafted silica particles in [EMIM][TFSA]-saturated water at the wavelength of 500 nm versus particle concentration. The absorbances were recorded from a UV-vis spectrometer at room temperature	56
A.12	The absorbance of the dispersion of HMW PPEGMMA brush-grafted silica particles in the water-saturated [EMIM][TFSA] at the wavelength of 500 nm versus particle concentration. The absorbances were recorded from a UV-vis spectrometer at room temperature	58
2.1	Thermogravimetric analysis (TGA) of (A) bare silica particles, (B) initiator-functionalized silica particles, (C) poly(methoxytri(ethylene glycol) methacrylate- <i>co-tert</i> -butyl methacrylate) (P(TEGMMA- <i>co-t</i> BMA)) brush-grafted silica particles, and (D) poly(TEGMMA- <i>co</i> -methacrylic acid) (P(TEGMMA- <i>co</i> -MAA)) brush-grafted silica particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.....	81

- 2.2 (A) Size exclusion chromatography (SEC) trace of free polymer P(TEGMMA-*co*-*t*BMA) formed from the free initiator in the synthesis of P(TEGMMA-*co*-*t*BMA) brush-grafted particles and ^1H NMR spectra of free polymer P(TEGMMA-*co*-*t*BMA) before (B) and after (C) the removal of *tert*-butyl groups using trifluoroacetic acid83
- 2.3 Plot of cloud point of P(TEGMMA-*co*-MAA) in aqueous solution without [EMIM][TFSA] (solid circle) and in [EMIM][TFSA]-saturated aqueous solution (solid square) at a concentration of 0.1 wt % versus pH. The black curve is a 3rd order polynomial fit to the cloud points of the polymer in [EMIM][TFSA]-saturated aqueous solution ($y = 20.7 + 24.5x - 7.85x^2 + 0.91x^3$, $R = 0.997$, where y = cloud point and x = pH). The red curve is a 3rd order polynomial fit to the cloud points of the polymer in aqueous solutions in the absence of [EMIM][TFSA] ($y = 34.34 + 9.67x - 3.81x^2 + 0.53x^3$, $R = 0.998$, where y = cloud point and x = pH). The inset shows the difference between the cloud points of 0.1 wt % aqueous solutions of P(TEGMMA-*co*-MAA) in the absence and presence of [EMIM][TFSA], calculated from the fit equations, as a function of pH85
- 2.4 Pictures of three aqueous-[EMIM][TFSA] biphasic systems that contained thermo- and pH-sensitive P(TEGMMA-*co*-MAA) brush-grafted silica particles with a concentration of 1.0 mg/mL in the initial state at 22 °C (A), 80 °C after stirring for 2 h (B), 10 °C after stirring for 4 h (C), and 80 °C after stirring for 2 h (D). The pH values of aqueous layers in three vials from left to right were 2.99, 5.00, and 7.02, respectively. The pictures were taken when a laser beam from a laser pointer passed

	through the bottom ionic liquid layers. More pictures can be found in the Appendix B.....	89
2.5	Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA- <i>co</i> -MAA) hairy particles in the aqueous phase with pH of (A) 3.05, (B) 5.09, (C) 6.08, (D) 6.52, and (E) 7.07 (solid square) and in the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range.....	91
2.6	Plots of (A) transfer temperature (T_{tr}) of P(TEGMMA- <i>co</i> -MAA) hairy particles and cloud point of free polymer P(TEGMMA- <i>co</i> -MAA) in [EMIM][TFSA]-saturated water versus pH, and (B) transfer temperature (T_{tr}) of P(TEGMMA- <i>co</i> -MAA) hairy particles versus cloud point of free polymer P(TEGMMA- <i>co</i> -MAA) in [EMIM][TFSA]-saturated water. The cloud points of P(TEGMMA- <i>co</i> -MAA) presented here were calculated from the fit equation shown in the caption of Figure 2.3. The straight line in (B) is a linear fit with $R = 0.998$ ($y = 2.332 + 0.579x$, where y is T_{tr} and x is cloud point)	93
2.7	Transfer of thermo- and pH-sensitive P(TEGMMA- <i>co</i> -MAA) hairy particles driven by changing the pH of the aqueous layer between 3.0 and 7.0. (A) The start point of the experiment at which the pH of the aqueous layer was 3.02; (B) after the system was stirred at 40 °C for 4 h; (C) after the pH of the aqueous layer was changed to 7.03 and the mixture was stirred at 40 °C for 4 h; (D) after the pH was adjusted to 3.00 and the system was stirred at 40 °C for 4 h; (E) after the pH was changed to 6.98 and the system was stirred overnight at 40 °C. In each group of pictures, the	

	left one shows the vial without a laser beam; the central and right pictures show the vial with a laser beam passing through the top and bottom layer, respectively	96
2.8	Normalized absorbances ($A/A_{\max}$) of P(TEGMMA- <i>co</i> -MAA) hairy particles in the aqueous layer (solid square) and the ionic liquid phase (solid circle) at sampling points corresponding to those in Figure 7. A and $A_{\max}$ represent the absorbance under a given condition at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm.....	97
2.9	Multiple transfer processes of thermo- and pH-sensitive P(TEGMMA- <i>co</i> -MAA) hairy particles between aqueous and [EMIM][TFSA] phases under different conditions by controlling both temperature and pH	98
B.1	Pictures of three water-[EMIM][TFSA] biphasic systems that contained thermo- and pH-sensitive P(TEGMMA- <i>co</i> -MAA) brush-grafted silica particles with a concentration of 1.0 mg/mL in the initial state at 22 °C (A), 80 °C after stirring for 2 h (B), 10 °C after stirring for 4 h (C), and 80 °C after stirring for 2 h (D). The pH values of aqueous layers in three vials from left to right were 2.99, 5.00, and 7.02, respectively.	106
B.2	Pictures of three water-[EMIM][TFSA] biphasic systems that contained thermo- and pH-sensitive P(TEGMMA- <i>co</i> -MAA) brush-grafted silica particles with a concentration of 1.0 mg/mL in the initial state at 22 °C (A), 80 °C after stirring for 2 h (B), 10 °C after stirring for 4 h (C), and 80 °C after stirring for 2 h (D). The pH values of aqueous layers in three vials from left to right were 2.99, 5.00, and 7.02,	

respectively. The pictures were taken when a laser beam from a laser pointer passed through the top aqueous layer107

- B.3 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous phase with pH of 3.91 (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range108
- B.4 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous phase with pH of 4.43 (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range109
- B.5 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous phase with pH of 5.01 (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range110
- B.6 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous phase with pH of 5.54 (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range111

3.1	(A) Thermogravimetric analysis of (i) 67 nm bare silica nanoparticles and (ii) ATRP-initiator-functionalized 67 nm silica nanoparticles (IP-67-I). (B) Thermogravimetric analysis of (iii) 215 nm bare silica particles and (iv) ATRP-initiator-functionalized 215 nm silica particles (IP-215)	135
3.2	(A) Size exclusion chromatograph traces of poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) free polymers formed from free initiator ethyl 2-bromoisobutyrate at 30, 60, 120, 180, 240, and 300 min in the synthesis of PTEGMMA brushes (PTEGMMA-67) from ATRP-initiator-functionalized 67 nm silica nanoparticles (IP-67-I). Polymerization conditions: [EBiB] ₀ : [CuBr] ₀ : [CuBr ₂] ₀ : [PMDETA] ₀ : [TEGMMA] ₀ = [1]:[1.3]:[0.7]:[1.3]:[489], 50 °C. (B) Thermogravimetric analysis of (i) 67 nm bare silica particles, (ii) ATRP-initiator-functionalized silica nanoparticles (IP-67-I), and (iii) PTEGMMA brush-grafted 67 nm silica nanoparticles made from IP-67-I	137
3.3	(A) Size exclusion chromatography trace of PPEGMMA free polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of PPEGMMA brush-grafted silica nanoparticles (PPEGMMA-67-I) from initiator particles IP-67-I. $M_{n,SEC}$ = 21.1 kDa and PDI = 1.14. Polymerization condition: [EBiB] ₀ : [CuBr] ₀ : [CuBr ₂] ₀ : [PMDETA] ₀ : [PEGMMA] ₀ = [1]:[1.3]:[0.7]:[1.4]:[445], 60 °C. (B) Thermogravimetric analysis of (i) 67 nm bare silica particles, (ii) ATRP-initiator-functionalized silica nanoparticles (IP-67-I), and (iii) PPEGMMA brush-grafted 67 nm silica nanoparticles (PPEGMMA-67-I) synthesized from IP-67-I with PPEGMMA $M_{n,SEC}$ of 21.1 kDa	139

- 3.4 (A) Size exclusion chromatography trace of PPEGMMA free polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of PPEGMMA brush-grafted silica nanoparticles (PPEGMMA-67-II) from initiator particles IP-67-II. $M_{n,SEC} = 22.0$ kDa and $PDI = 1.19$. Polymerization condition: $[EBiB]_0:[CuBr]_0:[CuBr_2]_0:[PMDETA]_0:[PEGMMA]_0 = [1]:[1.4]:[0.9]:[1.5]:[439]$, 65 °C. (B) Thermogravimetric analysis of (i) 67 nm bare silica particles, (ii) ATRP-initiator-functionalized silica nanoparticles (IP-67-II), and (iii) PPEGMMA brush-grafted 67 nm silica nanoparticles (PPEGMMA-67-II) synthesized from IP-67-II with PPEGMMA $M_{n,SEC}$ of 22.0 kDa140
- 3.5 (A) Size exclusion chromatography trace of PPEGMMA free polymer formed from free initiator 2-ethyl 2-bromoisobutyrate in the synthesis of PPEGMMA brush-grafted silica nanoparticles (PPEGMMA-67-III) from initiator particles IP-67-III. $M_{n,SEC} = 21.2$ kDa and $PDI = 1.20$. Polymerization condition: $[EBiB]_0:[CuBr]_0:[CuBr_2]_0:[PMDETA]_0:[PEGMMA]_0 = [1]:[1.3]:[0.8]:[1.3]:[442]$, 65 °C. (B) Thermogravimetric analysis of (i) 67 nm bare silica particles, (ii) ATRP-initiator-functionalized silica nanoparticles (IP-67-III), and (iii) PPEGMMA brush-grafted 67 nm silica nanoparticles (PPEGMMA-67-III) synthesized from IP-67-III with PPEGMMA $M_{n,SEC}$ of 21.2 kDa141
- 3.6 (A) Size exclusion chromatography trace of PPEGMMA free polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of PPEGMMA brush-grafted silica particles from initiator particles IP-215. $M_{n,SEC} = 23.0$ kDa and $PDI = 1.17$. Polymerization condition: $[EBiB]_0:[CuBr]_0:[CuBr_2]_0:[PMDETA]_0:[PEGMMA]_0 = [1]:[1.3]:[0.4]:[1.4]:[602]$, 60 °C. (B) Thermogravimetric analysis of (i) 215 nm

	bare silica particles, (ii) ATRP-initiator-functionalized silica particles (IP-215), and (iii) PPEGMMA brush-grafted 215 nm silica particles synthesized from IP-215 with PPEGMMA $M_{n,SEC}$ of 23.0 kDa	142
3.7	(A) Thermogravimetric analysis of (i) ATRP-initiator-functionalized 27 nm silica nanoparticles (IP-27), and (ii) PtBA brush-grafted 27 nm silica nanoparticles synthesized from IP-27. ATRP condition for the synthesis of PtBA brushes: $[EBiB]_0:[CuBr]_0:[CuBr_2]_0:[PMDETA]_0:[tBA]_0 = [1]:[1.2]:[0.3]:[1.2]:[511]$, 75 °C. (b) Size exclusion chromatography trace of PtBA cleaved from PtBA brush-grafted silica nanoparticles by the use of aqueous hydrofluoric acid. $M_{n,SEC} = 11.0$ kDa, PDI = 1.20	145
3.8	Top-view, bright field TEM micrographs of poly(<i>tert</i> -butyl acrylate) brush-grafted 27 nm silica nanoparticles synthesized by surface-initiated atom transfer radical polymerization (ATRP) from ATRP-initiator-functionalized 27 nm silica nanoparticles.	146
3.9	Pictures of a water-[EMIM][TFSA] biphasic system that contained PPEGMMA brush-grafted silica nanoparticles (PPEGMMA-67-I) at (a) 10 and (b) 80 °C in the 1 st cycle and at (c) 10 and (d) 80 °C in the 2 nd cycle. In each group of pictures, the left one shows the picture of the vial with no laser; the central and right ones show the vial with a laser beam passing through the top (water) layer and bottom (ionic liquid) layer, respectively.....	148
3.10	Pictures of a water-[EMIM][TFSA] biphasic system that contained PPEGMMA brush-grafted 215 nm silica particles (PPEGMMA-215) at (a) 10 and (b) 80 °C in the 9 th cycle and at (c) 10 and (d) 80 °C in the 10 th cycle. In each group of pictures,	

the left one shows the picture of the vial with no laser; the central and right ones show the vial with a laser beam passing through the top (water) layer and bottom (ionic liquid) layer, respectively149

3.11 (A) Plots of normalized absorbance ($A/A_{\max}$) of PEGMMA brush-grafted 67 nm silica nanoparticles (PEGMMA-67-I, solid symbols) and PEGMMA brush-grafted 205 nm silica particles (PEGMMA-205, hollow symbols) in the aqueous phase (square symbol) and the ionic liquid phase (circle symbol) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range. (B) Plot of natural logarithm of equilibrium constant of PEGMMA-67-I ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.991151

3.12 (A) Plot of normalized absorbance ($A/A_{\max}$) of PEGMMA brush-grafted 215 nm silica particles (PEGMMA-215) in the aqueous phase (square square) and in the ionic liquid phase (solid circle) versus temperature. (B) Plot of natural logarithm of equilibrium constant of PEGMMA-215 ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.999153

3.13 (A) Plot of normalized absorbance ($A/A_{\max}$) of PEGMMA brush-grafted 67 nm silica particles (PEGMMA-67-II) synthesized from initiator particles IP-67-II in the aqueous phase (square square) and the ionic liquid phase (solid circle) versus temperature. (B) Plot of natural logarithm of equilibrium constant of PEGMMA-

- 67-II ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.942154
- 3.14 (A) Plot of normalized absorbance (A/A_{max}) of PPEGMMA brush-grafted 67 nm silica particles (PPEGMMA-67-III) synthesized from initiator particles IP-67-III in the aqueous phase (square square) and the ionic liquid phase (solid circle) versus temperature. (B) Plot of natural logarithm of equilibrium constant of PPEGMMA-67-III ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.984155
- 3.15 (A) Plots of normalized absorbance (A/A_{max}) of PTEGMMA brush-grafted 67 nm silica nanoparticles (PTEGMMA-67, solid symbols) and PTEGMMA brush-grafted 205 nm silica particles (PTEGMMA-205, hollow symbols) in the aqueous phase (square symbol) and the ionic liquid phase (circle symbol) versus temperature. A and A_{max} represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range. (B) Plot of natural logarithm of equilibrium constant of PTEGMMA-67 ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.996156
- 3.16 Normalized absorbance (A/A_{max}) of PPEGMMA brush-grafted 67 nm silica particles (PPEGMMA-67-I) in the aqueous layer (solid square) and in the ionic liquid layer (solid circle) as a function of time. A and A_{max} represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength

of 500 nm. The data were obtained from a kinetics study of transfer of PPEMMA-67-I from water to [EMIM][TFSA] at 60 °C	160
3.17 Normalized absorbance ($A/A_{\max}$) of PPEGMMA brush-grafted 67 nm silica particles (PPEGMMA-67-II) in the aqueous layer (solid square) and in the ionic liquid layer (solid circle) as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm. The data were obtained from a kinetics study of transfer of PPEMMA-67-II from water to [EMIM][TFSA] at 60 °C.....	161
3.18 Normalized absorbance ($A/A_{\max}$) of PPEGMMA brush-grafted 205 nm silica particles (PPEGMMA-205) in the aqueous layer (solid square) and in the ionic liquid layer (solid circle) as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm. The data were obtained from a kinetics study of transfer of PPEMMA-205 from water to [EMIM][TFSA] at 57 °C	162
3.19 Normalized absorbance ($A/A_{\max}$) of PPEGMMA brush-grafted 215 nm silica particles (PPEGMMA-215) in the aqueous layer (solid square) and in the ionic liquid layer (solid circle) as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm. The data were obtained from a kinetics study of transfer of PPEMMA-215 from water to [EMIM][TFSA] at 57 °C	163
3.20 Normalized absorbance ($A/A_{\max}$) of PPEGMMA-67-I (solid square), PPEGMMA-67-II (solid circle), PPEGMMA-205 (solid triangle), and PPEGMMA-215 (solid diamond) from the aqueous layer as a function of time. A and $A_{\max}$ represent the	

	absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm.....	165
3.21	Normalized absorbance ($A/A_{\max}$) of PPEGMMA-67-I (solid square), PPEGMMA-67-II (solid circle), PPEGMMA-205 (solid triangle), and PPEGMMA-215 (solid diamond) from the ionic liquid layer as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm.....	166
4.1	Thermogravimetric analysis (TGA) of (a) bare nanoparticles, (b) Y-initiator-functionalized silica nanoparticles, (c) PtBA brush-grafted nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa, (d) mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 11.0 kDa (MB-1), (e) mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 18.7 kDa (MB-2), (f) mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 23.4 kDa (MB-3), (g) mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 29.5 kDa (MB-4), (h) mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 31.7 kDa (MB-5).....	183
4.2	Size exclusion chromatography (SEC) trace of the PtBA formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of PtBA brush-grafted silica nanoparticles by surface-initiated ATRP of t BA from Y-initiator nanoparticles. $M_{n,SEC} = 22.2$ kDa and PDI = 1.19.....	185
4.3	Size exclusion chromatography traces of five free polymers formed from the free initiator STEMPO in the synthesis of mixed PtBA/PS brush-grafted silica	

	nanoparticles by NMRP of styrene from the <i>Pt</i> BA brush-grafted silica nanoparticles with <i>Pt</i> BA $M_{n,SEC}$ of 22.2 kDa and PDI of 1.19.....	187
4.4	The amount of grafted polymers in the mixed <i>Pt</i> BA/PS brush-grafted silica particles synthesized from Y-initiator nanoparticles relative to the silica residue at 800 °C versus polystyrene molecular weight.....	188
4.5	Representative top-view, bright field TEM micrographs of mixed <i>Pt</i> BA/PS brush-grafted silica nanoparticles with <i>Pt</i> BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 11.0 kDa (MB-1).....	191
4.6	Representative top-view, bright field TEM micrographs of mixed <i>Pt</i> BA/PS brush-grafted silica nanoparticles with <i>Pt</i> BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 18.7 kDa (MB-2).....	192
4.7	Representative top-view, bright field TEM micrographs of mixed <i>Pt</i> BA/PS brush-grafted silica nanoparticles with <i>Pt</i> BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 23.4 kDa (MB-3).....	193
4.8	Representative top-view, bright field TEM micrographs of mixed <i>Pt</i> BA/PS brush-grafted silica nanoparticles with <i>Pt</i> BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 29.5 kDa (MB-4).....	194
4.9	Representative top-view, bright field TEM micrographs of mixed <i>Pt</i> BA/PS brush-grafted silica nanoparticles with <i>Pt</i> BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 31.7 kDa (MB-5).....	195
4.10	STEM dark field image of mixed <i>Pt</i> BA/PS brush-grafted silica nanoparticles with <i>Pt</i> BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 23.4 kDa (MB-3). In this dark field TEM image, the PS domains are light and the <i>Pt</i> BA domains are dark.....	196

4.11 Enlarged TEM image of mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 24.0 kDa and PS $M_{n,SEC}$ of 23.4 kDa (MB-3). The truncated wedge-shaped nanodomain is marked with an arrow.....	198
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List of Abbreviations

$A/A_{\max}$: Normalized absorbance value

ATRP: Atom transfer radical polymerization

*t*BA: *tert*-butyl acrylate

*t*BMA: *tert*-butyl methacrylate

[BMIM][PF₆]: 1-butyl-3-methylimidazolium hexafluorophosphate

CP: Cloud Point

DP: Degree of polymerization

EBiB: Ethyl 2-bromoisobutyrate

[EMIM][TFSA]: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide

ΔH° : Standard enthalpy change

¹H NMR: Proton nuclear magnetic resonance spectroscopy

Hairy Particles: Polymer brush-grafted particles

HMW: Higher molecular weight

kDa: kilodaltons

LCST: Lower critical solution temperature

ln*K*: Natural log of the equilibrium constant

LMW: Lower molecular weight

MB: Mixed brush sample

M_n : Number average molecular weight

P*t*BA: Poly(*tert*-butyl acrylate)

P*t*BMA: Poly(*tert*-butyl methacrylate)

PDEGMMA: Poly(methoxydi(ethylene glycol) methacrylate)

PEO: Poly(ethylene oxide)

PMAA: Poly(methacrylic acid)

PMDETA: *N, N, N', N', N''*-pentamethyldiethylenetriamine

PNIPAM: Poly(*N*-isopropylacrylamide)

PTEGMMA: Poly(methoxytri(ethylene glycol) methacrylate)

PPEGMMA: Poly(methoxypoly(ethylene glycol) methacrylate) average $M_n \sim 475$

PS: Polystyrene

R_g : Radius of gyration

R_{RMS} : Root-mean-square end-to-end distance

ΔS° : Standard entropy change

SEC: Size exclusion chromatography

STEM: Scanning transmission electron microscopy

STEMPO: 1-Phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane

TEM: Transmission electron microscopy

TEOS: Tetraethoxysilane

TGA: Thermogravimetric analysis

THF: Tetrahydrofuran

T_{tr} : Transfer Temperature

UV-vis: Ultraviolet-visible spectrometry

Y-initiator: 2-[4-(But-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethyl 2-bromo-2-methylpropanoate

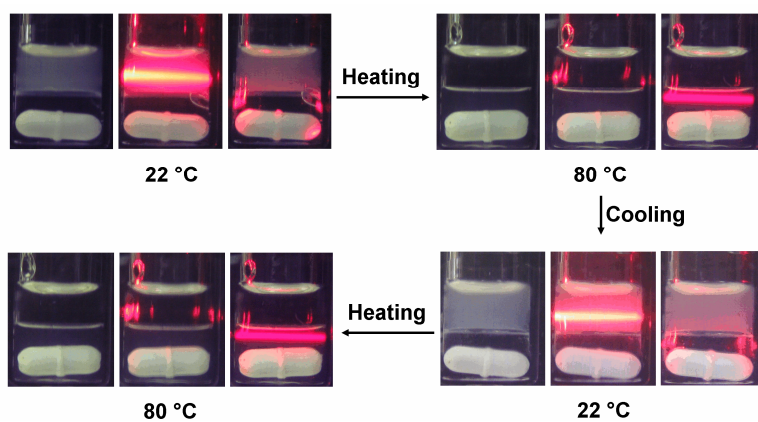
Y-silane: 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(4-(4-(triethoxysilyl)butyl)phenyl)ethyl 2-bromo-2-methylpropanoate

**Chapter 1. Synthesis of Thermosensitive Hairy Particles and Their
Thermally Induced Phase Transfer Behavior between Water and a
Hydrophobic Ionic Liquid**

Abstract

This chapter presents the synthesis of a series of thermosensitive polymer brush-grafted particles and their temperature-induced phase transfer behavior between water and a hydrophobic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]). Six samples were made by surface-initiated atom transfer radical polymerization: silica particles grafted with poly(methoxypoly(ethylene glycol) methacrylate) (PPEGMMA) with two different molecular weights, poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA), poly(methoxydi(ethylene glycol) methacrylate) (PDEGMMA), and two copolymers of PEGMMA and TEGMMA with different compositions (P(PEGMMA-*co*-TEGMMA)-82 and P(PEGMMA-*co*-TEGMMA)-74). The cloud points of free PPEGMMA with $M_{n,SEC}$ of 23 kDa and 40 kDa, P(PEGMMA-*co*-TEGMMA)-82, P(PEGMMA-*co*-TEGMMA)-74, and PTEGMMA in [EMIM][TFSA]-saturated water were 95, 94, 80, 72, and 43 °C, respectively. PDEGMMA was not soluble in the ionic liquid-saturated water. PPEGMMA brush-grafted particles moved spontaneously and completely from water to the [EMIM][TFSA] phase upon heating at 80 °C. When cooled to 22 °C, all particles returned to the water layer. From UV-vis absorbance measurements, the transfer temperature (T_{tr}) of PPEGMMA-grafted particles from water to the ionic liquid was 42 °C. Thermodynamic analysis showed that the particle transfer was an entropically driven process. P(PEGMMA-*co*-TEGMMA)-82, P(PEGMMA-*co*-TEGMMA)-74, and PTEGMMA brush-grafted particles also underwent reversible and quantitative transfer between the two phases upon heating at 70 °C and cooling at 0 °C; their transfer temperatures from water to [EMIM][TFSA] were 36, 30, and 16 °C, respectively. T_{tr} was

a linear function of the cloud point of the corresponding free polymer in ionic liquid-saturated water. In contrast, PDEGMMA-grafted particles moved spontaneously to the ionic liquid layer upon heating, but did not return to water even after prolonged stirring at 0 °C.



1.1 Introduction

Efficient transport of substances (molecules, supramolecular assemblies, particles, etc.) across interfaces between immiscible liquid phases is of great importance to many applications, including phase transfer catalysis, separation, and targeted delivery of drugs and biomolecules.¹⁻⁶ Often, the transfer involves protection-deprotection or modification of structures and properties of substances, especially when the two immiscible phases have very different polarities and the partition coefficient of the substance does not favor the transfer. While one-way transport processes are widely employed, there is growing interest to develop strategies for reversible and quantitative transfer of substances between two immiscible liquid phases. One can envision significant implications, for example, for the development of new recyclable catalysts.¹⁻³ An appealing strategy that is being intensively pursued is the use of external stimuli to induce the transfer.^{1-3,6-20} For example, Desset and Cole-Hamilton recently reported that a rhodium catalyst could be triggered to move back and forth between aqueous and organic phases by bubbling with and removal of CO₂, which greatly simplified the process for recycling and reusing the catalyst.³ In a similar spirit, Liu and Wang attached a light-responsive spiropyran moiety to a ruthenium catalyst and demonstrated that the catalyst can be induced to transport between two immiscible organic phases by light.⁷

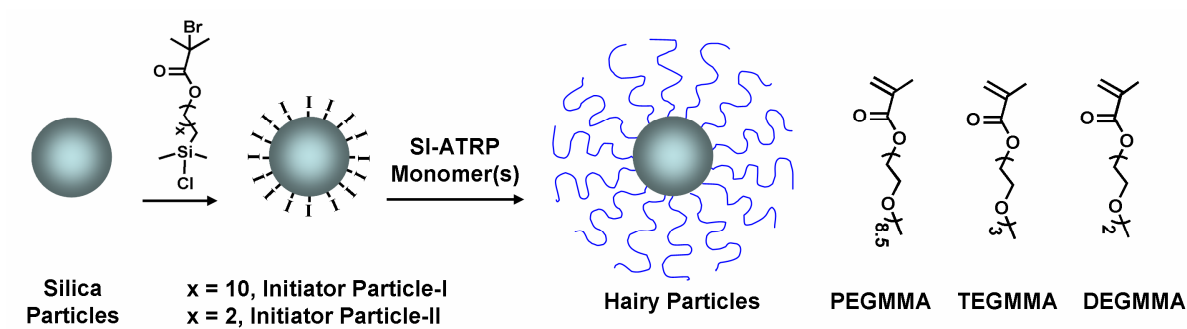
We are especially interested in environmentally responsive polymer brush-grafted particles (“hairy” particles) and block copolymer micelles.^{9-14,21} Hairy particles that can undergo structural or conformational changes in response to external triggers are an intriguing class of responsive hybrid materials.²¹⁻²³ These particles can be made by growing stimuli-sensitive polymer brushes from initiator-functionalized particles via

surface-initiated polymerization or by grafting pre-formed polymers onto the particle surface.²¹⁻²⁷ We and other groups recently reported that thermosensitive polymer brush-grafted particles can undergo spontaneous transfer between aqueous and organic phases upon temperature changes.^{10,17,18} For the water/ethyl acetate biphasic system, the thermo-induced transfer was reversible and quantitative and could be repeated for many times.¹⁰ Note that thermosensitive water-soluble polymers undergo reversible phase transitions in water at a temperature called the lower critical solution temperature (LCST). Besides temperature, other external stimuli were also employed to induce the transport of hairy particles between water and organic solvents. Wu et al. synthesized spiropyran-containing polymer brushes on silica colloids by surface-initiated atom transfer radical polymerization (ATRP) and demonstrated light-induced phase transfer of particles between water and toluene.¹⁹ Cheng et al. recently reported the pH-induced transport of gold nanoparticles that were grafted with mixed PEO and poly(*N,N*-diethylaminoethyl methacrylate) brushes in a biphasic system of water and chloroform.²⁰

Ionic liquids are molten salts with melting points below room temperature.²⁸ They are a promising class of “green” solvents that possess many attractive features, including extremely low vapor pressure, widely tunable solvation ability, and excellent thermal and chemical stability. Ionic liquids are now being intensively explored as media for reactions and separation and as components for advanced materials (e.g., ion gels).²⁸ Lodge et al. recently reported a series of block copolymer micelle shuttles that can transfer back and forth between water and an immiscible hydrophobic ionic liquid upon temperature changes.¹¹⁻¹⁴ Micelles with poly(ethylene oxide) (PEO) coronas reside preferentially in water at room temperature and move spontaneously to an immiscible hydrophobic ionic

liquid (e.g., 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆])) at elevated temperatures. Upon cooling, the micelles transfer back to the water phase.^{9,11} Further analysis showed that the micelle shuttle was driven by the change of relative affinity of PEO corona to the two solvents caused by the LCST behavior of PEO in water.¹² By taking advantage of the LCST behavior in water and the upper critical solution temperature behavior in an ionic liquid of poly(*N*-isopropylacrylamide) (PNIPAM), a micellization-transfer-demicellization shuttle of PEO-*b*-PNIPAM was demonstrated,¹³ allowing encapsulation, transfer, and release to be accomplished in one system by changing temperature. A pH triggered transfer of block copolymer micelles between water and organic phases was also reported.¹⁵

In the present work, we synthesized a set of thermosensitive hairy particles from initiator-functionalized silica particles by surface-initiated ATRP (Scheme 1.1) and systematically investigated their thermo-induced phase transfer behavior between water and a common hydrophobic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]). [EMIM][TFSA] was chosen in this study because it was previously reported that PEO-*b*-poly(1,2-butadiene) micelles can be reversibly transferred between this ionic liquid and water upon temperature changes.¹² Three monomers, poly(ethylene glycol) methyl ether methacrylate (or methoxypoly(ethylene glycol) methacrylate, PEGMMA), methoxytri(ethylene glycol) methacrylate (TEGMMA), and methoxydi(ethylene glycol) methacrylate (DEGMMA), and their mixtures were used in the synthesis of hairy particles (Scheme 1.1). The cloud points of poly(PEGMMA) (PPEGMMA), poly(TEGMMA) (PTEGMMA), and



Scheme 1.1 Synthesis of Thermosensitive Polymer Brush-Grafted Silica Particles by Surface-Initiated ATRP and Molecular Structures of PEGMMA, TEGMMA, and DEGMMA.

poly(DEGMMA) (PDEGMMA) in water are ≥ 90 , 52, and 26 °C, respectively.^{29,30} These polymers belong to a new class of thermosensitive water-soluble polymers with a short oligo(ethylene glycol) pendant from each repeat unit.²⁹⁻³¹ We found that when the LCST in water is sufficiently high, the hairy particles underwent thermo-induced reversible and quantitative phase transfer between water and [EMIM][TfSA] and that there was a linear correlation between the cloud point of free polymer and the transfer temperature. The results from this study could provide a basis for the future design of novel recyclable phase transfer catalysts for water/ionic liquid biphasic systems.

1.2 Experimental Section

1.2.1 Materials

Hydrogen hexachloroplatinate (IV) hydrate (ACS reagent grade) and CuBr₂ (anhydrous, 99%) were purchased from Acros and used as received. Chlorodimethylsilane (98%) was obtained from Alfa Aesar and stored in a refrigerator. Platinum-divinyltetramethyldisiloxane complex in xylene (2.1~2.4% Pt concentration in xylene) was purchased from Gelest, Inc. Tetrahydrofuran (THF) was distilled from sodium and benzophenone and used immediately for the dispersion of bare silica particles that were dried in high vacuum. CuBr (98%, Aldrich) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol and diethyl ether. After being dried in vacuum, the purified CuBr was stored in a desiccator. *N*, *N*, *N'*, *N'*, *N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and ethyl 2-bromoisobutyrate (98%, Aldrich) were dried with calcium hydride, distilled under reduced pressure, and stored in a desiccator. Methoxydi(ethylene glycol) methacrylate (DEGMMA, 95%,

Aldrich) was stirred in the presence of CaH_2 , distilled under vacuum, and stored in a refrigerator prior to use. Poly(ethylene glycol) methyl ether methacrylate (or methoxypoly(ethylene glycol) methacrylate, PEGMMA, average $M_n = 475$, Aldrich) was passed through a basic alumina column to remove the inhibitor. Methoxytri(ethylene glycol) methacrylate (TEGMMA) was synthesized according to the procedure reported previously.²² [EMIM][TFSA] was prepared via a synthetic route described in the literature.³² The clear and colorless liquid was dried in a vacuum oven at $\sim 60^\circ\text{C}$ for 3 days prior to use. 10-Undecen-1-yl 2-bromo-2-methylpropionate and allyl 2-bromo-2-methylpropionate were synthesized according to the literature procedures and their molecular structures were confirmed by ^1H NMR spectroscopy.^{22,33,34} All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

1.2.2 Characterization

Size exclusion chromatography (SEC) was carried out at ambient temperature using PL-GPC 20 (an integrated SEC system from Polymer Laboratories, Inc.) with a refractive index detector, one PLgel 5 μm guard column (50×7.5 mm), and two PLgel 5 μm mixed-C columns (each 300×7.5 mm, linear range of molecular weight from 200 to 2,000,000 according to Polymer Laboratories, Inc.). The data were processed using CirrusTM GPC/SEC software (Polymer Laboratories, Inc.). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Polystyrene standards (Polymer Laboratories, Inc.) were used for calibration. ^1H NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer and the residual solvent proton signal was used as the internal standard.

Thermogravimetric analysis was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C using TA Q-series Q50.

1.2.3 Synthesis of Bare Silica Particles

Ammonium hydroxide (25% in water, 14.024 g) and tetraethoxysilane (TEOS, 7.801 g) were each dissolved in ethanol (each 10 mL). The two solutions were added into a 500 mL flask that contained 155 mL ethanol under vigorous stirring. The concentrations of NH_3 , TEOS, and water in the solution were 0.51, 0.19, and 2.96 M, respectively. The mixture was stirred vigorously at room temperature for 4 h. The particles were then isolated by centrifugation (Eppendorf 5804 centrifuge, 6000 rpm, 15 min), re-dispersed in ethanol, and centrifuged again. This washing process was repeated with ethanol one more time, water four times, and ethanol again. The silica particles were then dried with a stream of air. The average size of the particles was 205 nm, determined by dynamic light scattering.

1.2.4 Synthesis of ATRP-Initiator-Functionalized Silica Particles

Two batches of ATRP-initiator-functionalized silica particles were prepared from the aforementioned bare silica particles using two different initiator precursors: undec-10-enyl 2-bromo-2-methylpropanoate (the corresponding initiator-functionalized silica particles are designated as initiator particle-**I**) and allyl 2-bromo-2-methylpropanoate (the initiator particles are designated as initiator particle-**II**). Described below is the procedure for the preparation of initiator particle-**I**. A similar procedure was employed for the synthesis of initiator particle-**II**.³⁵

10-Undecen-1-yl 2-bromo-2-methylpropionate (202.4 mg, 0.634 mmol) was added into a 25 mL two-necked round bottom flask and dried at room temperature under high

vacuum for 30 min. Chlorodimethylsilane (2.0 mL, 16.6 mmol) was injected via a syringe into the flask under nitrogen atmosphere, followed by the addition of Pt complex in xylenes (25 μ L). The mixture was stirred at room temperature under nitrogen atmosphere and the reaction was monitored by ^1H NMR spectroscopy. Once the reaction proceeded to completion, excess chlorodimethylsilane was removed by vacuum and the product was dissolved in anhydrous THF (2.0 mL). The solution was transferred via a syringe under nitrogen into the flask that contained a dispersion of bare silica particles (802 mg) in anhydrous THF (10 mL). The bare silica particles were dried at 110 $^{\circ}\text{C}$ under high vacuum for 7 h before the dispersion in anhydrous THF was made by stirring and ultrasonication. The flask was then placed in a 70 $^{\circ}\text{C}$ oil bath and the reaction mixture was stirred for 39 h under nitrogen atmosphere. The particles were isolated by centrifugation, re-dispersed in THF, and isolated again. This process was repeated an additional four times. The initiator-functionalized particles were dried with a stream of air flow.

1.2.5 Synthesis of Thermosensitive Polymer Brush-Grafted Silica Particles

Described below is a procedure for the preparation of PPEGMMA brush-grafted silica particles with PPEGMMA $M_{n,\text{SEC}}$ of 23 kDa from initiator particle-**I**. Similar procedures were used for the synthesis of other thermosensitive polymer brushes on silica particles, including PPEGMMA brushes with $M_{n,\text{SEC}}$ of 40 kDa, PTEGMMA brushes, PDEGMMA brushes, and two poly(PEGMMA-*co*-TEGMMA) (P(PEGMMA-*co*-TEGMMA)) copolymer brush samples with different molar ratios of PEGMMA to TEGMMA units.

CuBr (5.7 mg, 40 μ mol), CuBr₂ (4.4 mg, 20 μ mol), and the ATRP-initiator-functionalized silica particles (initiator particle-I, 95.8 mg) were added into a two-necked flask and were dried under high vacuum at 45 °C for 4 h. The initiator particles were then dispersed in anisole (12 mL) by ultrasonication. Poly(ethylene glycol) methyl ether methacrylate (11.967 g, 25.2 mmol) and free initiator ethyl 2-bromoisobutyrate (7.6 mg, 39 μ mol) were injected into the flask. After the mixture was degassed by three freeze-pump-thaw cycles, *N,N,N',N',N''*-pentamethyldiethylenetriamine (6.9 mg, 40 μ mol) was added via a microsyringe at the thawing point of the mixture. A sample was taken immediately for ¹H NMR spectroscopy analysis. The flask was then placed in an oil bath with a preset temperature of 70 °C. The polymerization was monitored by ¹H NMR spectroscopy analysis. After the reaction proceeded for 361 min, the flask was removed from the oil bath and opened to air; the mixture was diluted with THF (20 mL). The particles were isolated by centrifugation (Eppendorf 5804, 8000 rpm, 15 min) and the supernatant liquid was passed through a short column of silica gel (bottom)/activated basic aluminum oxide (top) (2/1, v/v). The polymer was then precipitated in hexanes twice and dissolved in THF. The purified free polymer was analyzed by SEC relative to polystyrene standards. The $M_{n,SEC}$ and polydispersity index (PDI) were 23 kDa and 1.12, respectively. The particles were re-dispersed in THF and isolated by centrifugation. This purification process was repeated an additional four times. The polymer brush-grafted silica particles were then dried by a stream of air flow. A small portion of the particles was transferred into a 25 mL two-necked flask and dried under high vacuum at 45 °C for 6 h for thermogravimetric analysis. The remaining particles were re-dispersed and stored in THF. The degree of polymerization (DP) of the free copolymer was calculated from

the monomer conversion and the monomer-to-free initiator molar ratio. The peaks located at 4.25 and 4.04 ppm, which were from $-CH_2OOC-$ of monomer PEGMMA and the polymer, respectively, were used as internal standards. The final monomer conversion was calculated from the integrals of the peaks at 5.52 ppm ($CHH=C-$ from monomer PEGMMA) at $t = 0$ min and 361 min. The DP was 128.

1.2.6 Determination of Cloud Points of Free Polymers in Water

The cloud points in water of thermosensitive polymers, which were formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of thermosensitive hairy particles, were measured as follows. Aqueous solutions of thermosensitive polymers with a concentration of 0.5 wt% were made in 3.7 mL vials using deionized water. The vials were placed in an oil bath and the temperature was gradually increased. At each temperature, the polymer solutions were allowed to equilibrate for 5 min. The cloud point was recorded when the polymer solution turned cloudy. We reported previously that this method gave cloud points consistent with those measured by turbidimetry using a UV-vis spectrometer.³¹ For the cloud points of thermosensitive polymers in [EMIM][TFSA]-saturated water, the polymer solutions were made by using the water that was saturated with [EMIM][TFSA] at room temperature, and a small drop of [EMIM][TFSA] was added as a separate ionic liquid phase. The cloud points were then determined in the same way as for the solutions made from pure water.

1.2.7 Reversible Transfer of Thermosensitive Polymer Brush-Grafted Silica Particles between Water and [EMIM][TFSA] Induced by Temperature Changes

Described below is a typical procedure for thermally-induced reversible transport of PPEGMMA brush-grafted particles (PPEGMMA $M_{n,SEC} = 23$ kDa) between water and

[EMIM][TFSA] by changing temperature back and forth from 22 to 80 °C. Similar procedures were employed for transfer of other thermosensitive hairy particles between aqueous and ionic liquid phases.

The PPEGMMA hairy particles (1.9 mg, PPEGMMA $M_{n,SEC} = 23$ kDa) were dispersed in water (1.893 g) in a 20 mL scintillation vial. Part of the dispersion (1.801 g) was then carefully transferred into a 3.7 mL vial that contained [EMIM][TFSA] (2.740 g, 1.80 mL) at ambient temperature (22 °C). The vial was placed into an 80 °C oil bath and the system was stirred at a stirring rate of 500 rpm. In another 3.7 mL vial, water and [EMIM][TFSA] of equal volumes were stirred at the same stirring rate and temperature and for the same amount of time as for the biphasic system that contained PPEGMMA particles. After 210 min, the two biphasic systems were allowed to stand still for 30 min and an aliquot (0.4 mL) was taken from the water layer from each vial. The aliquots were diluted to 1.0 mL with pure water. The vials were then removed from the oil bath and the mixtures were stirred at ambient temperature (22 °C) at 100 rpm for 210 min. An aliquot (0.4 mL) was taken from the ionic liquid layer from each vial after the systems were allowed to stand still without stirring for 30 min. The aliquots were diluted to 1.0 mL with pure ionic liquid [EMIM][TFSA]. Aliquots taken from the vial that did not contain particles were used as references for the measurement of absorbances of the corresponding samples taken from the biphasic system for the particle transport experiment. This cycle was repeated once more and samples were taken for UV-vis spectrometry measurements to ensure that the transport was complete in both heating and cooling processes. Afterwards, the heating and cooling cycle was repeated an additional eight times.

1.2.8 Determination of Transfer Temperature of Thermosensitive Hairy Particles from Water to [EMIM][TFSA] upon Heating

Described below is a typical procedure for the determination by UV-vis absorbance measurements of the transfer temperature of PPEGMMA brush-grafted silica particles (PPEGMMA $M_{n,SEC} = 23$ kDa) from water to ionic liquid [EMIM][TFSA] upon heating. Similar procedures were employed to study the thermo-induced phase transfer of other thermosensitive hairy particles. The PPEGMMA hairy particles (8.8 mg) were dispersed in water that was saturated with the ionic liquid overnight at room temperature (8.803 g) in a 20 mL scintillation vial. The particle dispersion was then carefully transferred into a 30 mL vial that contained [EMIM][TFSA] (12.161 g, 7.98 mL). The 30 mL vial with an inner diameter of 2.7 cm was custom-made and equipped with a Teflon valve that could be opened to allow the insertion of a needle to take samples. The biphasic system was stirred with a magnetic stir bar (dimension 4.5×12 mm) at a stirring rate of 500 rpm at room temperature (22 °C). After stirring for at least 12 h, the system was allowed to stand still for 30 min at the same temperature; an aliquot (0.4 mL) was taken from each layer and diluted to 0.6 mL with the corresponding pure liquid for UV-vis absorbance measurement. The temperature was then increased to 31 °C and the aforementioned process was repeated. The same procedure was applied for other temperatures (38, 40, 42, 43, 44, 45, 46, 48, and 55 °C).

In another vial, water and [EMIM][TFSA] of equal volumes were stirred at the same stirring rate and temperature and for the same amount of time as for the biphasic system that contained PPEGMMA particles. At each temperature, an aliquot (0.6 mL) was taken from each layer after the system was allowed to stand still without stirring for 30 min and

was diluted to 0.9 mL with the corresponding pure liquid. These aliquots were used as references for the measurement of absorbances of the corresponding samples taken at the same temperature from the biphasic system that contained hairy particles. The absorbance of the diluted dispersion at the wavelength of 500 nm was recorded at room temperature using a UV-visible spectrometer.

1.3 Results and Discussion

1.3.1 Synthesis of Thermosensitive Polymer Brush-Grafted Silica Particles

We synthesized a series of hairy particles grafted with thermosensitive water-soluble polymers of different LCSTs by surface-initiated ATRP.²¹⁻²³ The bare silica particles were prepared by the Stöber process, which is known to produce spherical particles with a relatively narrow size distribution,³⁶ and had an average diameter of 205 nm. The bare particles were surface-functionalized with either 11-(2-bromo-2-methyl)propionyloxyundecyldimethylchlorosilane (the corresponding initiator-coated particles were designated as initiator particle-**I**) or 3-(2-bromo-2-methyl)propionyloxypropyldimethylchlorosilane (the corresponding initiator-functionalized particles were designated as initiator particle-**II**, see Scheme 1.1). Thermogravimetric analysis (TGA) showed that the weight retention difference at 800 °C was 3.5 wt% for bare particles and initiator particle-**I** and 2.0 wt% for bare particles and initiator particle-**II**,³⁷ when the weight percentage difference at 100 °C between bare particles and corresponding initiator particles was taken into consideration (Figure 1.1A). These values are comparable to those reported in the literature.^{22,23}

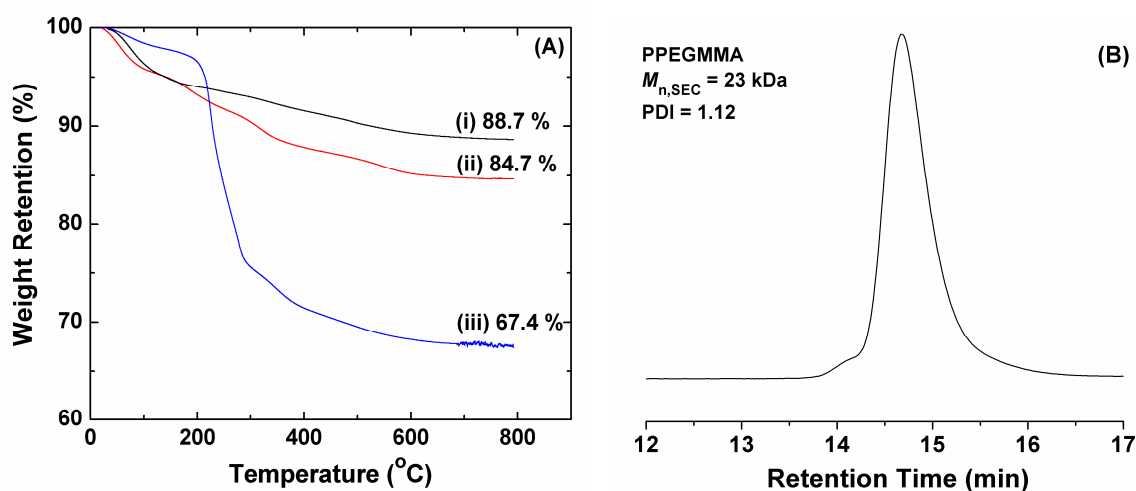


Figure 1.1 (A) Themogravimetric analysis (TGA) of (i) bare silica particles, (ii) initiator particle-I, and (iii) PPEGMMA brush-grafted silica particles with PPEGMMA $M_{n,SEC}$ of 23 kDa. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C. (B) Size exclusion chromatography trace of free polymer PPEGMMA formed from the free initiator in the synthesis of lower molecular weight PPEGMMA brush-grafted particles.

The initiator particles were then used to make thermosensitive polymer brush-grafted particles by surface-initiated ATRP. A free initiator, ethyl 2-bromoisobutyrate (EBiB), was added into the reaction mixture to facilitate the control of surface-initiated polymerization.^{22,23} It also allowed the progress of polymerization to be monitored by ¹H NMR spectroscopy for the monomer conversion and size exclusion chromatography (SEC) analysis of the molecular weight of the free polymer formed from EBiB. We previously confirmed that the molecular weight and molecular weight distribution of polymer brushes synthesized by surface-initiated “living”/controlled radical polymerization are essentially identical to those of the free polymer formed from the free initiator.²³ By using PEGMMA, TEGMMA, DEGMMA, and two mixtures of PEGMMA and TEGMMA with different molar ratios (70 : 30 and 40 : 60), six polymer brush samples, including two PPEGMMA samples with different molecular weights, were synthesized.

For the lower molecular weight (LMW) PPEGMMA sample, TGA showed that the weight retention at 800 °C was 67.4% (Figure 1.1A), much lower than that of the initiator particles (84.7%). From SEC analysis (Figure 1.1B), the $M_{n,SEC}$ and the polydispersity index of the free polymer were 23 kDa and 1.12, respectively, indicating that the polymerization was well controlled. The monomer conversion was determined from ¹H NMR spectra of the samples taken at 0 min and at the end of the polymerization. Assuming that the initiator efficiency was 100%, the degree of polymerization (DP) of the free polymer was 128. By using the size of bare silica particles, TGA data, and the DP of the free polymer, the grafting density of the LMW PPEGMMA brush-grafted particles was found to be 0.24 chains/nm². The TGA and SEC data of other hairy particles and

free polymers are included in the Supporting Information. For the copolymer P(PEGMMA-*co*-TEGMMA)-84 sample that was synthesized from the mixture of PEGMMA and TEGMMA with a molar ratio of 70:30, ^1H NMR spectroscopy analysis showed that the molar ratio of PEGMMA to TEGMMA units in the copolymer was 59:41, which was reasonably close to the feed ratio. For the copolymer P(PEGMMA-*co*-TEGMMA)-74 sample, the molar ratio of PEGMMA to TEGMMA units in the free copolymer was 40 : 60, essentially the same as the feed ratio of two monomers. The characterization results of all hairy particles and corresponding free polymers are summarized in Table 1. Except the higher molecular weight (HMW) PPEGMMA brushes, the DPs of the polymers in these samples were close to each other. The grafting densities of these polymer brushes were also similar, in the range of 0.23 to 0.29 chains/nm². Note that our group previously reported the synthesis of similar PDEGMMA and PTEGMMA brush-grafted silica particles and their characterization by TGA, electron microscopy, and dynamic light scattering.²² The grafting densities were comparable to the values in Table 1.1.

1.3.2 Cloud Points of Free Polymers in Water

The cloud points of free polymers in pure water at a concentration of 0.5 wt% were determined by visual examination. This method was previously found to give results essentially identical to those measured by turbidimetry.³¹ The cloud points of PPEGMMA with $M_{n,SEC}$ of 23 kDa, PPEGMMA with $M_{n,SEC}$ of 40 kDa, PTEGMMA ($M_{n,SEC}$ = 31 kDa), and PDEGMMA ($M_{n,SEC}$ = 18 kDa) in pure water were 98, 98, 52, and 25 °C, respectively, very close to or the same as those reported in the literature.^{22,29,30} The two copolymers, P(PEGMMA-*co*-TEGMMA)-82 and P(PEGMMA-*co*-TEGMMA)-74,

Table 1.1 Characterization Data for Six Thermosensitive Polymer Brush-Grafted Particle Samples and the Corresponding Free Polymers.

Hairy Particles	Initiator Particles	Free Polymer $M_{n,SEC}$ PDI, DP ^a	Grafting density (chains/nm ²) ^b
LMW PPEGMMA ^c	Initiator Particle-I ^d	23 kDa, 1.12, 128	0.24
HMW PPEGMMA ^c	Initiator Particle-II ^d	40 kDa, 1.08, 218	0.23
P(PEGMMA- <i>co</i> -TEGMMA)-82 ^e	Initiator Particle-II	29 kDa, 1.12, 154	0.26
P(PEGMMA- <i>co</i> -TEGMMA)-74 ^f	Initiator Particle-I	23 kDa, 1.12, 141	0.25
PTEGMMA	Initiator Particle-II	31 kDa, 1.16, 190	0.26
PDEGMMA	Initiator Particle-II	18 kDa, 1.14, 152	0.29

^a The values of $M_{n,SEC}$ and polydispersity index (PDI) were determined by size exclusion chromatography using polystyrene calibration. The degree of polymerization (DP) was calculated from the monomer conversion and the initial monomer-to-initiator ratio, assuming that the initiator efficiency is 100%.

^b The grafting densities were calculated by using the DPs of free polymers, TGA data, and the size of bare silica particles. The calculation of the grafting density of LMW PPEGMMA brushes can be found in the Supporting Information.

^c LMW and HMW stand for lower and higher molecular weight, respectively.

^d Initiator particle-I and -II were prepared by surface functionalization of bare silica particles using 11-(2-bromo-2-methyl)propionyloxyundecyldimethylchlorosilane and 3-(2-bromo-2-methyl)propionyloxypropyldimethylchlorosilane, respectively.

^e The sample was synthesized from the copolymerization of the mixture of PEGMMA and TEGMMA with a molar ratio of 70 : 30; ¹H NMR spectroscopy analysis showed that the molar ratio of PEGMMA to TEGMMA units in the copolymer was 59 : 41.

^f The sample was obtained from the copolymerization of a mixture of PPEGMMA and TEGMMA with a molar ratio of 40:60. ¹H NMR spectroscopy showed that the molar ratio of PEGMMA to TEGMMA units in the copolymer was 40 : 60.

exhibited LCST phase transitions at 82 and 74 °C, respectively; the higher the PPEGMMA content, the higher the cloud point, which is reasonable. Since the particle transport experiments involved two phases and it is known that the presence of an organic or inorganic additive could affect the cloud point of a thermosensitive polymer in water,²² we also measured the cloud points of 0.5 wt% aqueous solutions of free polymers, made by using the [EMIM][TFSA]-saturated water, in the presence of a separate [EMIM][TFSA] phase (a small drop of [EMIM][TFSA]). The results are summarized in Table 1.2. In general, the presence of [EMIM][TFSA] decreased the cloud points of free polymers in water, with the largest drops observed for the aqueous solutions of PTEGMMA and PDEGMMA. While the LCST of PTEGMMA in the presence of a separate [EMIM][TFSA] phase was 9 °C lower than that in pure water, the aqueous solution of PDEGMMA in the presence of the ionic liquid was cloudy even in an ice/water bath, indicating that any cloud point would lie below 0 °C.³⁸

1.3.3 Thermo-Induced Phase Transfer of LMW PPEGMMA Brush-Grafted Silica Particles

We first studied the phase transfer behavior of LMW PPEGMMA hairy particles (PPEGMMA $M_{n,SEC} = 23$ kDa) between water and [EMIM][TFSA] in response to temperature changes. The sample was dispersed in water at room temperature by ultrasonication (particle concentration: 1.0 mg/mL). Upon heating at 80 °C, the particles were found to spontaneously cross the interface of two layers and move into the [EMIM][TFSA] phase. From UV-vis analysis, the absorbance of the sample taken from the water layer after heating at 80 °C for 210 min was essentially 0 (≤ 0.001) at the wavelength of 500 nm (water from the biphasic system that did not contain hairy particles

Table 1.2 Cloud Points of Free Thermosensitive Polymers in Pure Water and in the [EMIM][TFSA]-Saturated Water in the Presence of a Separate [EMIM][TFSA] Phase at a Concentration of 0.5 wt%.

Free Polymer	Cloud Point (°C, in pure water)	Cloud Point (°C, in [EMIM]-saturated water)
LMW PEGMMA	98	95
HMW PEGMMA	98	94
P(PEGMMA- <i>co</i> -TEGMMA)-82	82	80
P(PEGMMA- <i>co</i> -TEGMMA)-74	74	72
PTEGMMA	52	43
PDEGMMA	25	NA

after stirring at the same temperature for the same amount of time was used as reference, see Experimental Part). This observation indicated that the particle transfer was complete.³⁹ The particles spontaneously moved back to the water phase when the system was removed from the oil bath and stirred at room temperature. The transport was again quantitative, as evidenced by the virtually zero absorbance of the sample taken from the ionic liquid phase after stirring at room temperature for 210 min. The spontaneous phase transfer of PPEGMMA hairy particles upon heating at 80 °C and cooling at 22 °C can be repeated for at least 10 times. Figure 1.2 shows pictures of the biphasic system in the 4th and 5th cycle. Very strong scattering was observed from the aqueous layer at 22 °C and the ionic liquid layer at 80 °C when a laser beam passed through the layer, while another layer showed no scattering. This is consistent with the quantitative analysis results using UV-vis spectrometry. Therefore, we conclude that the PPEGMMA hairy particles can undergo spontaneous, quantitative, and reversible phase transfer between two immiscible phases upon temperature changes. A control experiment, conducted using bare silica particles under the same conditions as for PPEGMMA hairy particles, showed that the bare particles stayed in the water layer at both ambient temperature and 80 °C after stirring for 19 and 6 h, respectively.³⁵ This confirmed that the thermo-induced phase transfer of PPEGMMA hairy particles was a consequence of the grafted PPEGMMA brushes.

1.3.4 Determination of Phase Transfer Temperature of LMW PPEGMMA Hairy Particles from Water to [EMIM][TFSA] Phase upon Heating

We further determined the transfer temperature (T_{tr}) of LMW PPEGMMA brush-grafted silica particles from water to the ionic liquid phase upon increasing temperature.

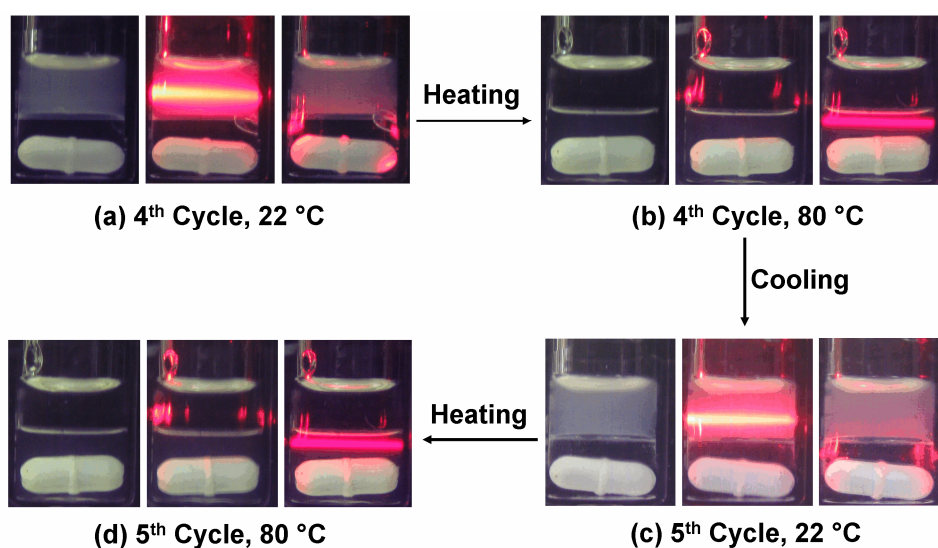


Figure 1.2 Pictures of the water-[EMIM][TFSA] biphasic system that contained LMW PPEGMMA brush-grafted silica particles at (a) 22 and (b) 80 °C in the 4th cycle and at (c) 22 and (d) 80 °C in the 5th cycle. In each group of pictures, the left one shows the picture of the vial with no laser; the central and right ones show the vial with a laser beam passing through the top water layer and bottom ionic liquid layer, respectively.

An aqueous dispersion of hairy particles with a concentration of 1.0 mg/mL was carefully added on top of [EMIM][TFSA] in a custom-made vial. The vial was then placed in an oil bath and the mixture was stirred with a magnetic bar at a stirring rate of 500 rpm. At a given temperature, the system was equilibrated for at least 12 h and then allowed to stand still without stirring for 30 min. An aliquot (0.4 mL) was taken from each layer and diluted to 0.6 mL with the corresponding pure liquid for UV-vis absorbance measurements. In another vial, water and [EMIM][TFSA] of equal volumes in the absence of hairy particles were stirred at the same stirring rate and temperature and for the same amount of time. The water and ionic liquid from this vial were used as references in the measurements of absorbances of samples from the transport experiment by UV-vis spectrometry.

We confirmed that Beer's law at a wavelength of 500 nm can be applied to the dispersions of hairy particles in both water and ionic liquid in the studied concentration range from 0.667 mg/mL (after dilution of aliquots) to 0.0334 mg/mL.³⁷ Figure 1.3 shows the ratio of the absorbance at a given temperature to the maximum absorbance for both water and ionic liquid layers versus temperature. Note that the normalized absorbance $A/A_{\max}$ is proportional to the normalized particle concentration ($[\text{particle}]/[\text{particle}]_{\max}$). As can be clearly seen from Figure 1.3, the particles began to move to the ionic liquid phase at 40 °C and the transport was complete at ~ 46 °C. Taking 50 % particle concentration change as the transfer temperature gives $T_{\text{tr}} = 42$ °C. Compared with the poly(1,2-butadiene)-*b*-PEO micelle shuttle, the transfer temperature of PPEGMMA hairy particles is ~ 11 °C lower.¹² One likely reason for this observation is that the cloud point

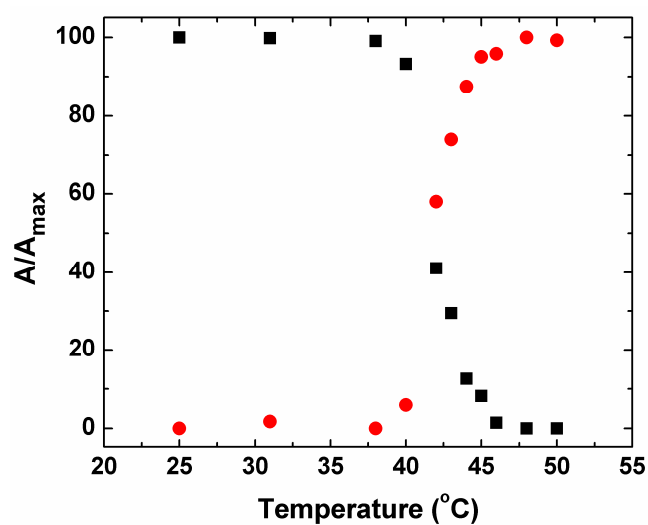


Figure 1.3 Plot of normalized absorbance ($A/A_{\max}$) of LMW PPEGMMA hairy particles in the aqueous phase (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range.

of PPEGMMA in water (98 °C in pure water and 95 °C in the [EMIM][TFSA]-saturated water) is lower than that of PEO (> 100 °C in pure water).

By using the normalized particle concentrations in water and [EMIM][TFSA], the equilibrium constant K ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) at each temperature in the transition zone was calculated and a plot of $\ln K$ versus the inverse of absolute temperature ($1/T$) was made (Figure 1.4). The standard enthalpy change ΔH° and standard entropy change ΔS° for the transfer of thermosensitive hairy particles from water to the ionic liquid phase can be calculated from the plot of $\ln K$ versus $1/T$ and the following relations: $\Delta G^\circ = -RT\ln K$, $\Delta H^\circ = -R[\partial \ln K / \partial (1/T)]_p$, and $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$, in which R is the gas constant, T is absolute temperature, and $\partial \ln K / \partial (1/T)$ is the slope of the plot of $\ln K$ versus $1/T$ (Figure 1.4). The calculated values of ΔH° and ΔS° are $8.9 \times 10^2 \text{ kJmol}^{-1}$ and $2.8 \times 10^3 \text{ JK}^{-1}\text{mol}^{-1}$, respectively, for the temperature range of 40 to 46 °C.

As mentioned earlier, PPEGMMA is a thermosensitive water-soluble polymer exhibiting an LCST transition in pure water at a temperature of 98 °C. We confirmed that it did not undergo any noticeable phase transition in [EMIM][TFSA] up to 100 °C. We also tested the stability of the LMW PPEGMMA brush-grafted particles in water and in [EMIM][TFSA] at 80 °C; no visible changes were observed after three days. Thus, the transfer of PPEGMMA particles is triggered by the increasingly unfavorable interaction of polymer brushes with water with the increase of temperature. The positive ΔH° suggests that the interaction of PPEGMMA brushes with water is more energetically favorable than with the ionic liquid, which is understandable because of the strong hydrogen bonding formation between pendant ethylene glycol units and water.



Figure 1.4 Plot of natural logarithm of equilibrium constant of LMW PEGMMA brush-grafted silica particles ($K = [\text{particle}]_{\text{II}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.986.

In addition, the cloud point of LMW PPEGMMA in [EMIM][TFSA]-saturated water was 95 °C, far above the transfer temperature of PPEGMMA hairy particles (42 °C). The positive entropy change ΔS° indicates that the transfer is an entropically driven process. The dissolution in water of thermosensitive polymers with an oligo(ethylene glycol) pendant from each repeat unit has been explained by a negative ΔH° value, caused by the formation of hydrogen bonding with water, and also a negative ΔS° value, resulting from the formation of more ordered, structured water around polymer chains.²⁹⁻³¹ Although some studies also suggested the possible formation of hydrogen bonds between PEO derivatives and the imidazolium ring,^{12,40} it is reasonable that the hydrogen bonding of PPEGMMA and [EMIM][TFSA], if it exists, is much weaker than that with water. Thus, with the particles moving from water to [EMIM][TFSA], the structured water around polymer chains was disrupted and the entropy of the whole system increased. Although the process was closely related to the LCST transition of PPEGMMA in water, the transfer temperature was significantly below the cloud point of PPEGMMA in water. We speculate that the transfer temperature is determined by the interplay of enthalpy and entropy changes of the interactions of polymer brushes with water and the ionic liquid or the changes of relative affinity of PPEGMMA to water and [EMIM][TFSA].

1.3.5 Thermo-Induced Phase Transfer of HMW PPEGMMA Brush-Grafted Silica Particles

To study if the molecular weight of PPEGMMA brushes affects T_{tr} , we synthesized a high molecular weight PPEGMMA brush-grafted particle sample ($M_{n,SEC} = 40$ kDa) and determined the transfer temperature. Figure 1.5 shows the normalized absorbance versus temperature for both water and ionic liquid phases. The transfer temperature was found to

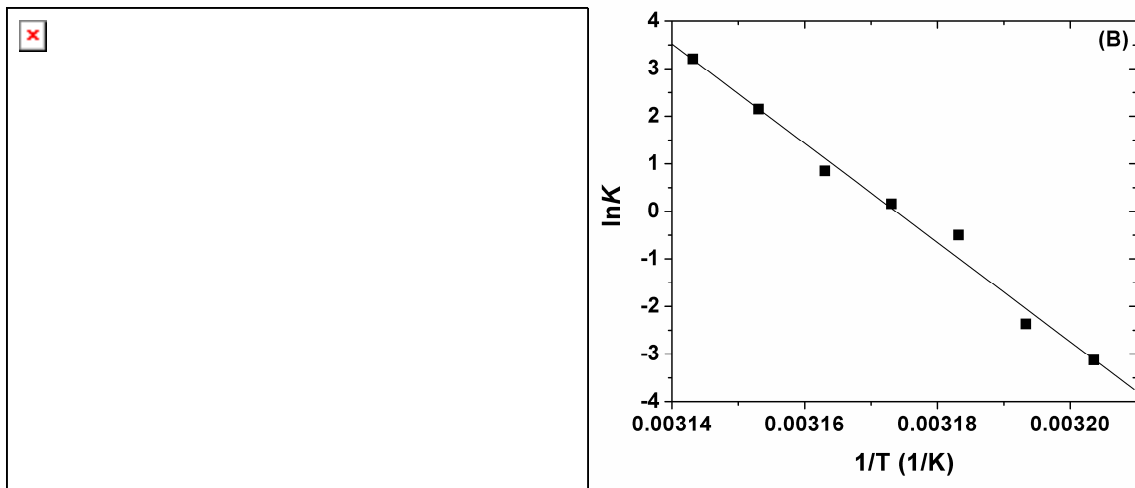


Figure 1.5 (A) Plot of normalized absorbance ($A/A_{\max}$) of HMW PEGMMA hairy particles in water (solid square) and [EMIM][TFSA] (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range. (B) Plot of natural logarithm of equilibrium constant of HMW PEGMMA brush-grafted silica particles ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.993.

be essentially the same as that of the LMW PPEGMMA particles, which indicates that the molecular weight of PPEGMMA brushes had little effect on T_{tr} . Moreover, the values of ΔH° and ΔS° for the transfer of HMW PPEGMMA particles in the temperature range of 39 to 45 °C were 8.7×10^2 kJ/mol and 2.8×10^3 JK⁻¹mol⁻¹, respectively, which are essentially identical to those for the LMW PPEGMMA particles.

1.3.6 Temperature Change-Induced Phase Transfer of Other Thermosensitive Hairy Particles Between Water and [EMIM][TFSA] and Effect of LCST on Particle Transfer Temperature

To study whether and how thermosensitive properties of polymers affect the phase transfer behavior of hairy particles, we synthesized a series of particles grafted with thermosensitive polymers of different LCSTs in water. Their DPs and grafting densities were comparable (Table 1.1). The cloud point in pure water decreased progressively from 98 °C for free PPEGMMA, to 82 °C for copolymer P(PEGMMA-*co*-TEGMMA)-82, to 74 °C for copolymer P(PEGMMA-*co*-TEGMMA)-74, to 52 °C for PTEGMMA, and 25 °C for PDEGMMA. We found that the hairy particles grafted with P(PEGMMA-*co*-TEGMMA)-82, P(PEGMMA-*co*-TEGMMA)-74, and PTEGMMA spontaneously transferred from water to the ionic liquid phase upon heating at 70 °C and returned to the aqueous phase upon cooling at 0 °C in an ice/water bath. From the UV-vis absorbances of the samples taken from the vial using the liquids from the control experiment as reference, both heating and cooling-induced transfer of particles was complete (absorbances of the aqueous phase at 70 °C and the [EMIM][TFSA] phase at 0 °C $\leq$ 0.002).³⁵ Just like PPEGMMA hairy particles, the transport of the particles can be repeated many times by heating at 70 °C and cooling in an ice/water bath. In contrast,

PDEGMMA brush-grafted particles behaved differently. Upon heating at 70 °C for 210 min, the particles completely moved to the ionic liquid phase. However, no particles were found to transfer back to the aqueous phase at 0 °C even after stirring for 330 min. This is consistent with the observation that the cloud point of PDEGMMA in water at a concentration of 0.5 wt% in the presence of a separate ionic liquid phase was < 0 °C (the solution was cloudy in an ice/water bath). The results from the attempted transport experiment suggested that the PDEGMMA hairy particles preferred to stay in the ionic liquid phase even at 0 °C.

Using the same procedure as for the PPEGMMA hairy particles, we determined the transfer temperatures of silica particles grafted with P(PEGMMA-*co*-TEGMMA)-82, P(PEGMMA-*co*-TEGMMA)-74, and PTEGMMA brushes from water to the ionic liquid phase upon increasing temperature. The results from UV-vis measurements are summarized in Figures 1.6A, 1.7A, and 1.8A. Clearly, the transfer temperature decreased with the decrease of cloud point of free polymer in water, from 36 °C for P(PEGMMA-*co*-TEGMMA)-82 brush-grafted particles, to 30 °C for P(PEGMMA-*co*-TEGMMA)-74 brush-grafted particles, and 16 °C for PTEGMMA hairy particles. As with the PPEGMMA brush-grafted silica particles, the transfer temperatures of three types of thermosensitive hairy particles were much lower than the cloud points of free polymers in ionic liquid-saturated water. The values of ΔH° and ΔS° , obtained from Figure 1.6B, 1.7B, and 1.8B, and the transfer temperatures are summarized in Table 1.3. For PPEGMMA and copolymer brush-grafted particles, the values of ΔH° are very similar, and the value of ΔS° appears to increase with the decrease of transfer temperature, which might be related to the fact that the structured water is more ordered around polymer

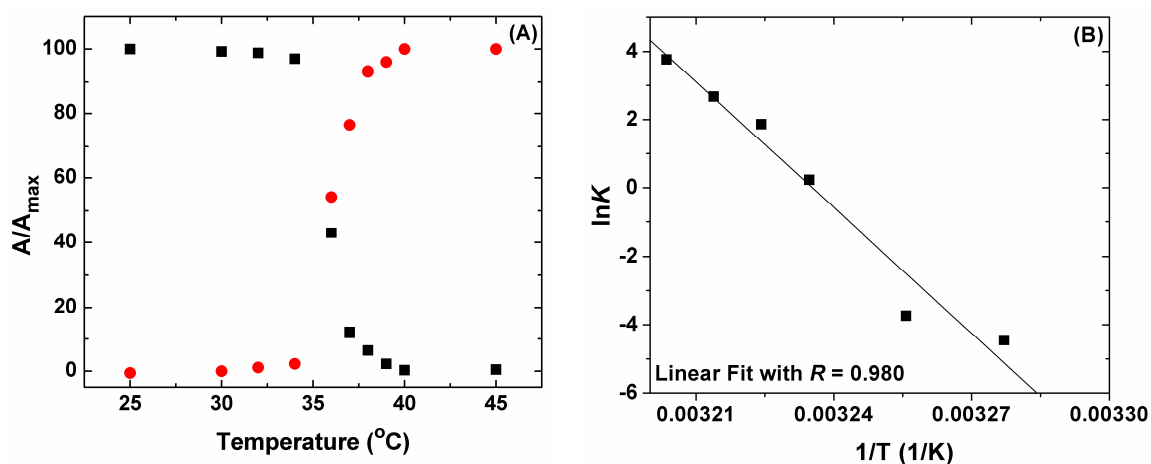


Figure 1.6 (A) Plot of normalized absorbance ($A/A_{\max}$) of P(PEGMMA-*co*-TEGMMA)-82 hairy particles in water (solid black square) and [EMIM][TFSA] (solid circle) versus temperature in thermo-induced transport experiments. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range, respectively. (B) Plot of natural logarithm of equilibrium constant ($K = [\text{particle}]_{\text{II}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature for P(PEGMMA-*co*-TEGMMA)-82 hairy particles, respectively. The solid line in the plot is a linear fit with a correlation coefficient R shown in the plot.

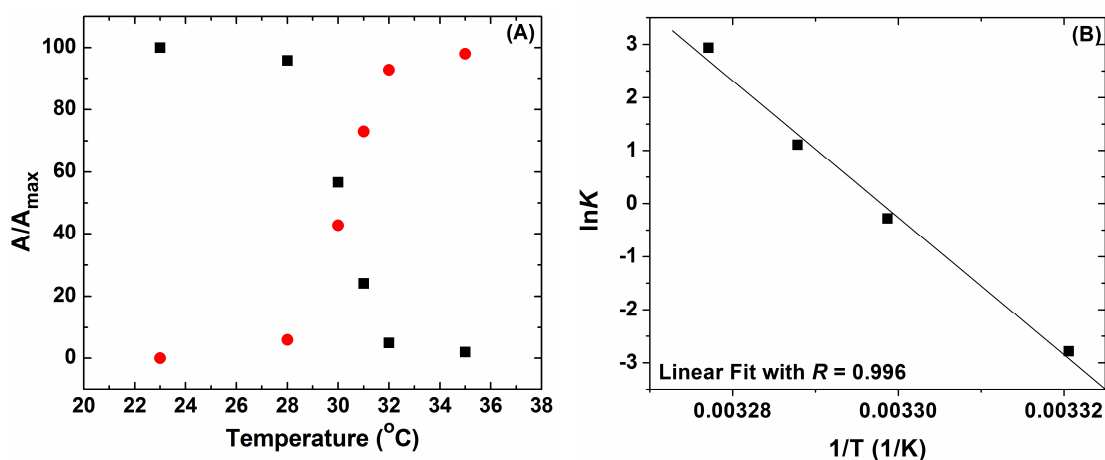


Figure 1.7 (A) Plot of normalized absorbance ($A/A_{\max}$) of P(PEGMMA-*co*-TEGMMA)-74 hairy particles in water (solid black square) and [EMIM][TFSA] (solid circle) versus temperature in thermo-induced transport experiments. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range, respectively. (B) Plot of natural logarithm of equilibrium constant ($K = [\text{particle}]_{\text{II}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature for P(PEGMMA-*co*-TEGMMA)-74 hairy particles, respectively. The solid line in the plot is a linear fit with a correlation coefficient R shown in the plot.

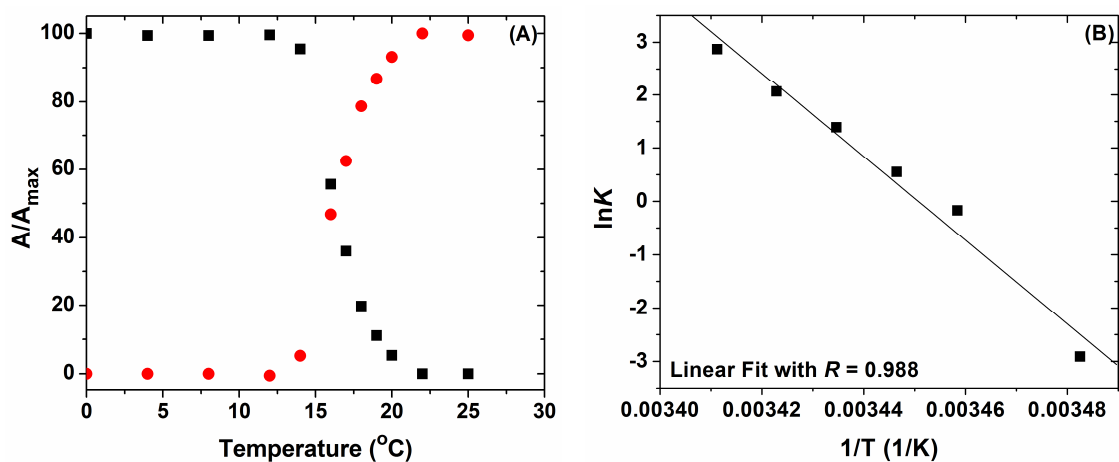


Figure 1.8 (A) Plot of normalized absorbance ($A/A_{\max}$) of PTEGMMA) hairy particles in water (solid black square) and [EMIM][TFSA] (solid circle) versus temperature in thermo-induced transport experiments. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range, respectively. (B) Plot of natural logarithm of equilibrium constant ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature for PTEGMMA) hairy particles, respectively. The solid line in the plot is a linear fit with a correlation coefficient R shown in the plot.

Table 1.3 Transfer Temperature (T_{tr}), Standard Enthalpy Change ΔH° and Standard Entropy Change ΔS° Calculated from the Plot of $\ln K$ versus $1/T$ for Five Thermosensitive Polymer Brush-Grafted Particle Samples.

Hairy Particles	T_{tr} ($^\circ\text{C}$)	ΔH° (kJmol^{-1})	ΔS° ($\text{JK}^{-1}\text{mol}^{-1}$)
LMW PEGMMA	42	8.9×10^2	2.8×10^3
HMW PEGMMA	42	8.7×10^2	2.8×10^3
P(PEGMMA- <i>co</i> -TEGMMA)-82	36	1.0×10^3	3.3×10^3
P(PEGMMA- <i>co</i> -TEGMMA)-74	30	1.0×10^3	3.5×10^3
PTEGMMA	16	6.5×10^2	2.3×10^3

chains at lower temperatures. Compared with other thermosensitive hairy particles, the values of ΔH° and ΔS° for PTEGMMA particles were slightly lower, which is reflected in the broader transition zone.

Figure 1.9 shows the plot of transfer temperature of thermosensitive hairy particles from water to the ionic liquid phase versus the cloud point of free copolymer in [EMIM][TFSA]-saturated water. A nearly linear relationship was observed (linear fit $R = 0.997$) and showed that if the cloud point is lower than 12 °C, the transfer temperature would be below 0 °C. This is consistent with our observation that the cloud point of PDEGMMA in the ionic liquid-saturated water was below 0 °C (if there was a cloud point) and PDEGMMA hairy particles easily moved to the ionic liquid phase upon heating but did not return to the aqueous phase at 0 °C.

1.4 Conclusions

By using surface-initiated ATRP, we synthesized a series of thermosensitive hairy particles with comparable grafting densities but different thermosensitive properties.⁴¹ These included LMW PPEGMMA ($M_{n,SEC} = 23$ kDa), HMW PPEGMMA ($M_{n,SEC} = 40$ kDa), P(PEGMMA-*co*-TEGMMA)-82, P(PEGMMA-*co*-TEGMMA)-74, PTEGMMA, and PDEGMMA brush-grafted silica particles. The LMW PPEGMMA hairy particles were found to undergo spontaneous, quantitative, and reversible phase transfer between water and ionic liquid [EMIM][TFSA] upon heating at 80 °C and cooling at 22 °C. The transfer temperature was 42 °C, determined by absorbance measurements of both water and ionic liquid phases using UV-vis spectrometry. The molecular weight of polymer brushes had a negligible effect on T_{tr} . From the equilibrium distributions of hairy

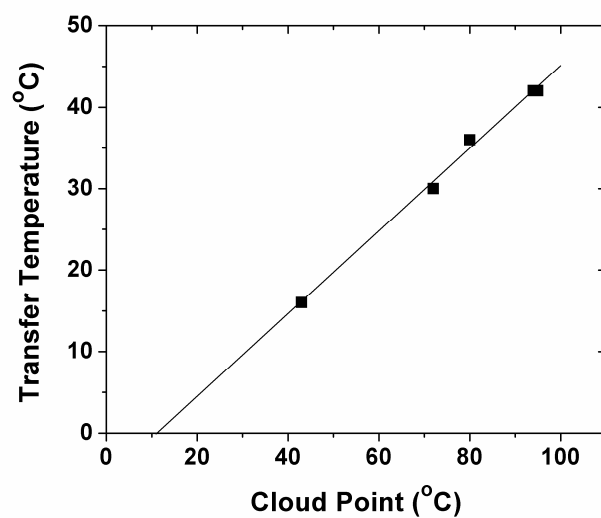


Figure 1.9 Transfer Temperature of thermosensitive polymer brush-grafted particles from water to the [EMIM][TFSA] phase versus cloud point of thermosensitive free polymer in the [EMIM][TFSA]-saturated water. The solid line is a linear fit with R value of 0.997.

particles in the two phases, we calculated the standard enthalpy and entropy changes for the particles transferring from water to the ionic liquid. Positive values of ΔH° and ΔS° indicated that the transfer of hairy particles was an entropically driven process and was governed by the LCST of thermosensitive polymers in water. Particles grafted with P(PEGMMA-*co*-TEGMMA)-82, P(PEGMMA-*co*-TEGMMA)-74, and PTEGMMA brushes could also undergo reversible and quantitative transfer between the two phases upon heating at 70 °C and cooling at 0 °C. The transfer temperatures of these particles were determined and a linear relationship was observed between transfer temperature of hairy particles and cloud point of corresponding free polymer in the ionic liquid-saturated water. Since the cloud point can be continuously tuned by copolymerization of two or more different monomers, the results reported in this Chapter can help us to design thermally-driven particle or micelle shuttles between water and ionic liquid phases with desired transfer temperatures. Although silica particles were used in the present work, we believe that other inorganic or metal particles grafted with appropriate thermosensitive polymer brushes can also be induced to transfer between water and [EMIM][TFSA] upon temperature changes.

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38. We also made aqueous solutions of PDEGMMA with concentrations of 0.1 wt% and 0.05 wt% using the [EMIM][TFSA]-saturated water, the solutions were still cloudy.
39. The absorbance of an aqueous solution of LMW PPEGMMA hairy particles at a concentration of 0.667 mg/mL was 0.429, which was > 400 times higher than that of the sample from the particle transfer experiment.
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Appendix A

for

**Chapter 1. Synthesis of Thermosensitive Hairy Particles and Their
Thermally Induced Phase Transfer Behavior between Water and a
Hydrophobic Ionic Liquid**

A.1 Synthesis of Initiator particle-II

Allyl 2-bromo-2-methylpropanoate (217.7 mg, 731 μmol) was added into a 25 mL two-necked round bottom flask and dried at room temperature in vacuum for 30 min. Chlorodimethylsilane (2.4 mL, 18.6 mmol) was injected via a syringe into the flask under nitrogen atmosphere, followed by the addition of Pt complex in xylenes (25 μL). The mixture was stirred at room temperature under nitrogen atmosphere and the reaction was monitored by ^1H NMR spectroscopy analysis. Because the reaction proceeded slowly, additional catalyst (22.1 mg of a solution of hydrogen hexachloroplatinate hydrochloride (28.6 mg) in a mixture of diethyl ether (0.1 mL) and ethanol (0.1 mL)) was added. Once the reaction was complete, excess chlorodimethylsilane was removed by vacuum. The product was dissolved in anhydrous THF (2.0 mL) and added into a flask that contained a dispersion of dried bare silica particles (801 mg) in anhydrous THF (5 mL). The bare silica particles were dried at 110 $^{\circ}\text{C}$ under high vacuum for 11 h before the dispersion in THF was made by stirring and ultrasonication. The flask was placed in a 70 $^{\circ}\text{C}$ oil bath and the mixture was stirred under nitrogen atmosphere for 60 h. The particles were then isolated by centrifugation, re-dispersed in THF, and isolated again. This process was repeated for additional four times. The particles were then dried with a stream of air flow.

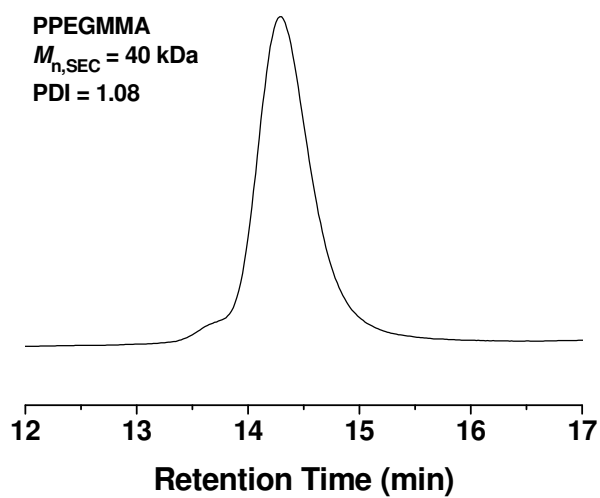


Figure A.1 Size exclusion chromatography analysis of free polymer PPEGMMA formed from the free initiator, ethyl 2-bromoisobutyrate, in the synthesis of HMW PPEGMMA brushes from initiator particle-**II** by surface-initiated ATRP of PEGMMA. The $M_{n,SEC}$ and polydispersity index of the free PPEGMMA were 40 kDa and 1.08, respectively.

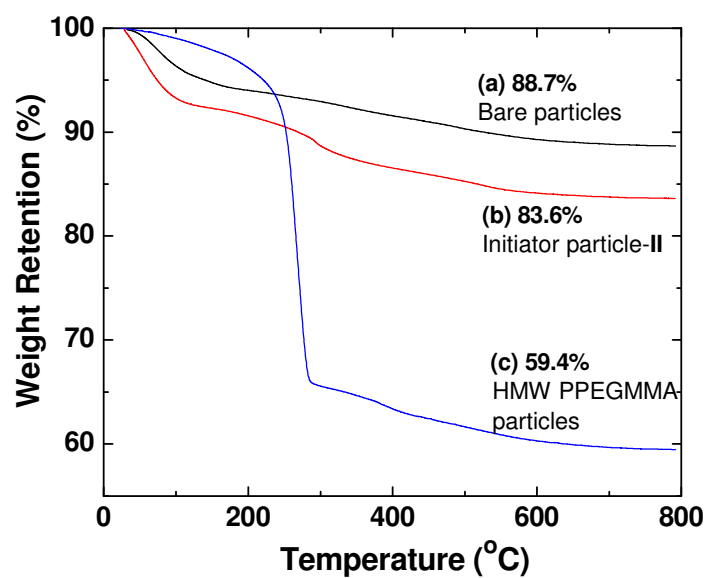


Figure A.2 Thermogravimetric analysis of (a) bare silica particles, (b) initiator particles-II and (c) HMW PEGMMA hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.

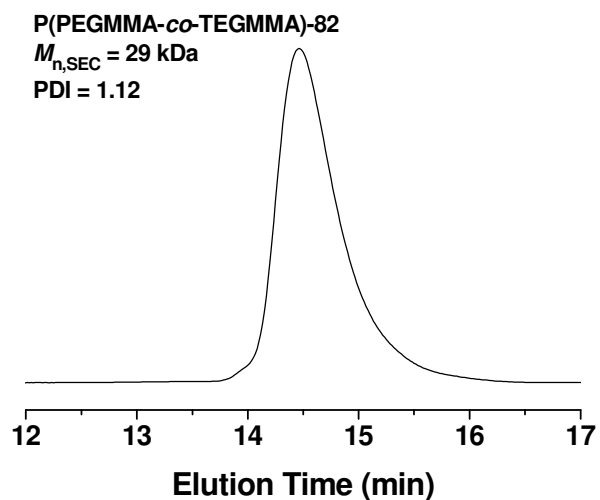


Figure A.3 Size exclusion chromatography analysis of the polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of P(TEGMMA-co-PEGMMA)-82 brushes from initiator particle-**II** by surface-initiated ATRP of a mixture of PPEGMMA and TEGMMA with a molar ratio of 70 : 30. The $M_{n,SEC}$ and polydispersity index of the free copolymer were 29 kDa and 1.12, respectively.

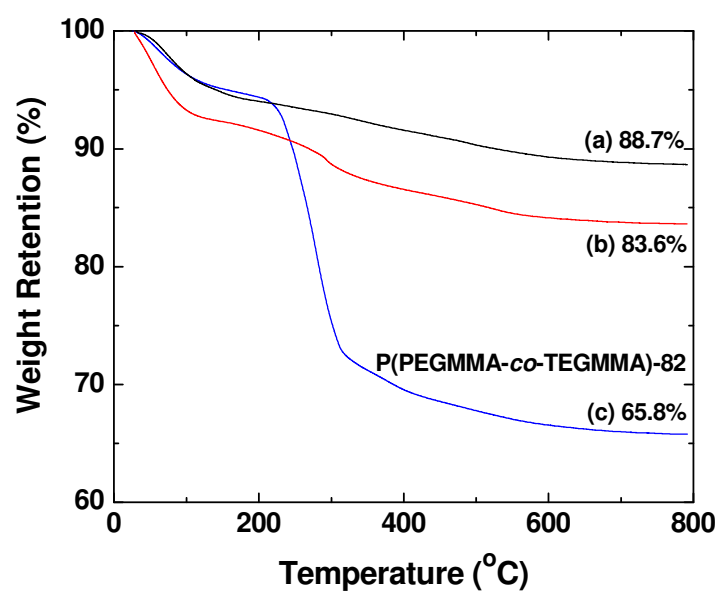


Figure A.4 Thermogravimetric analysis of (a) bare silica particles, (b) initiator particles-II, and (c) P(TEGMMA-co-PEGMMA)-82 hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.

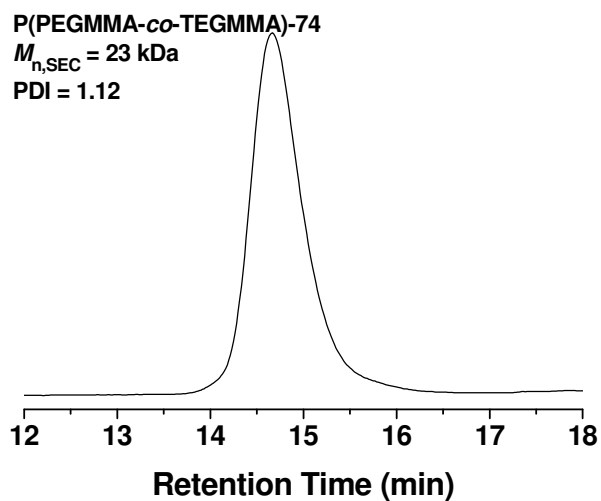


Figure A.5 Size exclusion chromatography analysis of the polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of P(TEGMMA-co-PEGMMA)-74 brushes from initiator particle-I by surface-initiated ATRP of a mixture of PPEGMMA and TEGMMA with a molar ratio of 40:60. The $M_{n,SEC}$ and polydispersity index of the free copolymer were 23 kDa and 1.12, respectively.

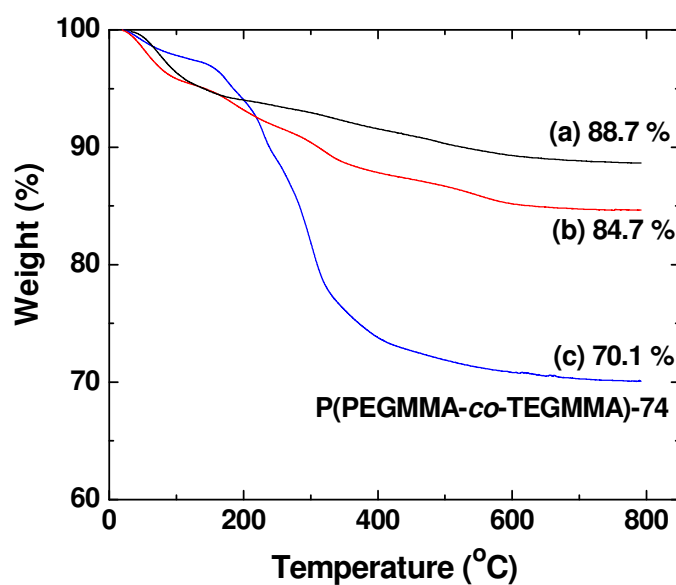


Figure A.6 Thermogravimetric analysis (TGA) of (a) bare silica particles, (b) initiator particles-I and (c) P(TEGMMA-co-PEGMMA)-74 hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.

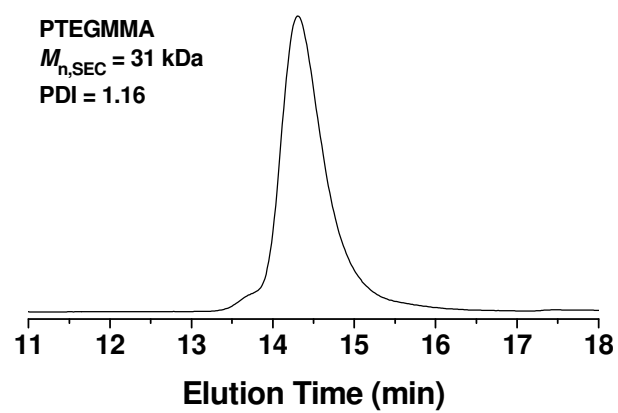


Figure A.7 SEC analysis of free PTEGMMA formed from free initiator in the synthesis of PTEGMMA brush-grafted particles.

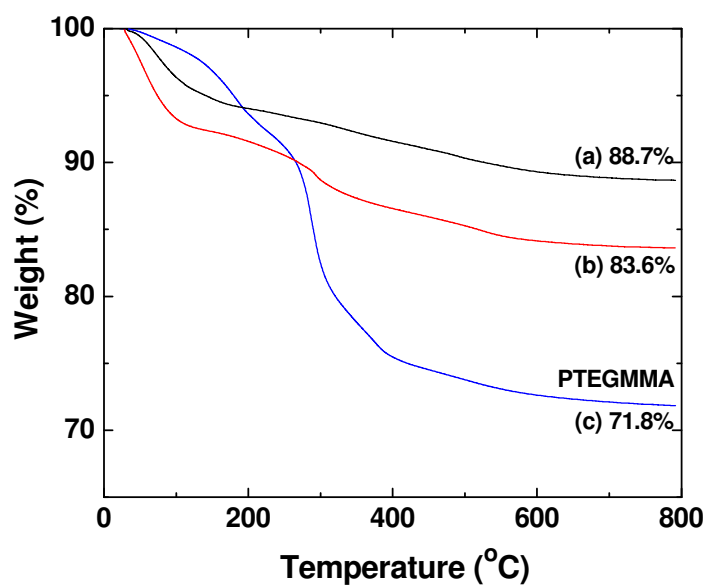


Figure A.8 Thermogravimetric analysis of (a) bare silica particles, (b) initiator particles-II and (c) PTEGMMA hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.

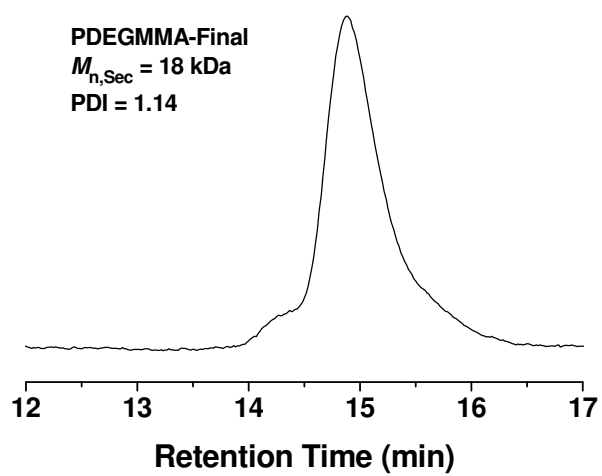


Figure A.9 SEC analysis of PDEGMMA formed from free initiator in the synthesis of PDEGMMA brush-Grafted silica particles.

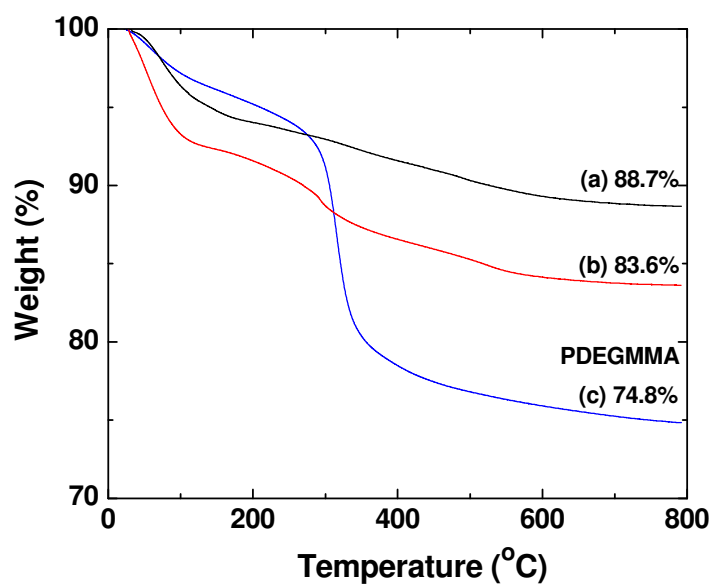


Figure A.10 Thermogravimetric analysis of (a) bare silica particles, (b) initiator particle-II and (c) PDEGMMA hairy particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.

A.2 Calibration Curve of Absorbance of HMW PEGMMA Brush-Grafted Silica Particles versus Particle Concentration in Ionic Liquid-Saturated Water.

HMW PEGMMA hairy particles (1.76 mg) was dispersed in water that was saturated with [EMIM][TFSA] at room temperature (2.640 g) in a vial by ultrasonication. The absorbance of this dispersion at the wavelength of 500 nm was measured at room temperature by a UV-vis spectrometer (Thermo scientific evolution 600 UV-Vis spectrophotometer) using [EMIM][TFSA]-saturated water as reference. The dispersion was then diluted with the ionic-liquid saturated water to various concentrations and the absorbances at the wavelength of 500 nm were measured. Figure A.11 shows the plot of absorbance versus particle concentration. A linear relationship was obtained with linear fit coefficient $R = 0.99994$, indicating that Beer's law can be applied to the dispersions of hairy particles in water.

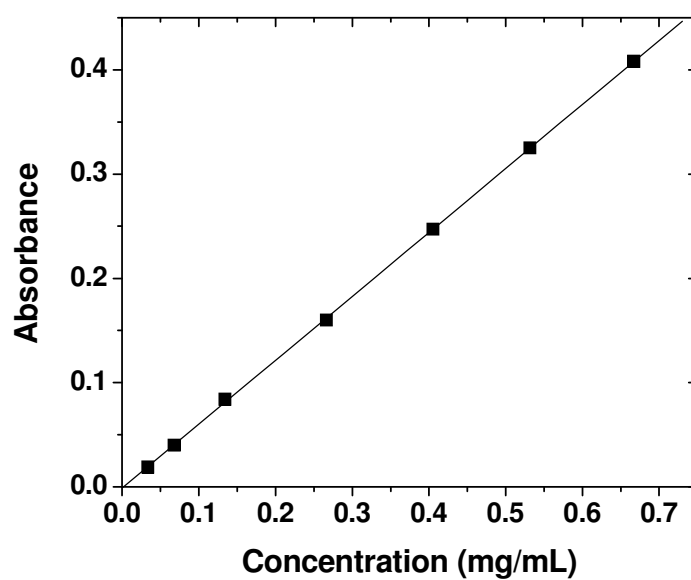


Figure A.11 The absorbance of the dispersion of HMW PPEGMMA brush-grafted silica particles in [EMIM][TFSA]-saturated water at the wavelength of 500 nm versus particle concentration. The absorbances were recorded from a UV-vis spectrometer at room temperature.

A.3 Calibration Curve of Absorbance of HMW PEGMMA Brush-Grafted Silica Particles versus Particle Concentration in Water-Saturated Ionic Liquid [EMIM][TFSA].

HMW PEGMMA hairy particles (1.37 mg) was dispersed in [EMIM][TFSA] that was saturated with water at room temperature (3.1256 g, 2.056 mL) in a vial by ultrasonication. The absorbance of the dispersion at the wavelength of 500 nm was measured at room temperature by a UV-vis spectrometer (Thermo scientific evolution 600 UV-Vis spectrophotometer) using water-saturated [EMIM][TFSA] as reference. The dispersion was then diluted with the water-saturated ionic liquid to various concentrations and the absorbances at the wavelength of 500 nm were measured. Figure A.12 shows the plot of absorbance versus particle concentration in the ionic liquid. A linear relationship was obtained with a linear fit a coefficient $R = 0.9999$, indicating that Beer's law can be applied to the dispersions of hairy particles in ionic liquid [EMIM][TFSA].

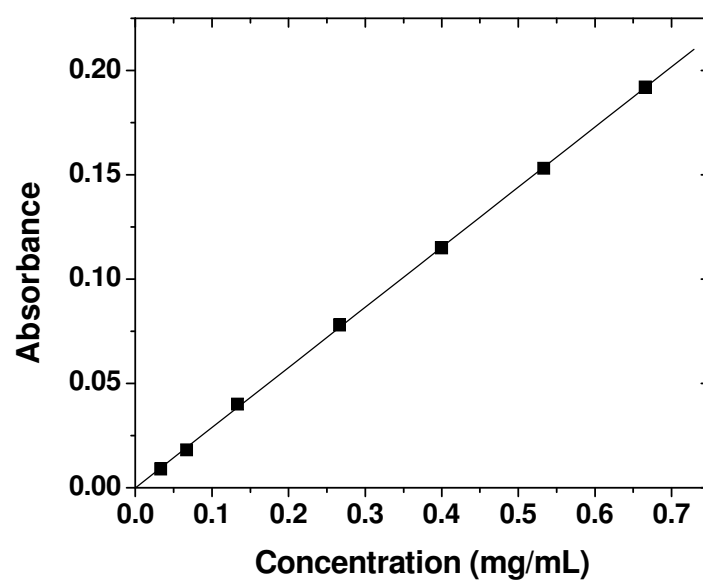


Figure A.12 The absorbance of the dispersion of HMW PPEGMMA brush-grafted silica particles in the water-saturated [EMIM][TFSA] at the wavelength of 500 nm versus particle concentration. The absorbances were recorded from a UV-vis spectrometer at room temperature.

A.4 Thermo-Induced Spontaneous and Reversible Transfer of P(PEGMMA-*co*-TEGMMA)-82 Brush-Grafted Silica Particles between Water and [EMIM][TFSA] upon Heating at 70 °C and Cooling at 0 °C.

The P(PEGMMA-*co*-TEGMMA)-82 hairy particles (2.87 mg) were dispersed in water (2.870 g) in a 20 mL scintillation vial. Part of the dispersion (1.795 g) was then carefully transferred into a 3.7 mL vial that contained [EMIM][TFSA] (2.744 g, 1.80 mL). The vial was placed into a 70 °C oil bath and the system was stirred at a stirring rate of 500 rpm. In another 3.7 mL vial, water and [EMI][TFSA] of equal volumes were stirred at the same stirring rate and temperature for the same amount of time as for the biphasic system that contained the hairy particles. After stirring at 70 °C for 210 min with a stirring rate of 500 rpm, an aliquot (0.4 mL) was taken from the water layer from both vials after the mixture was allowed to stand without stirring for 30 min and diluted to 0.6 mL with pure water. The vials were then removed from the oil bath and the mixtures were stirred at 0 °C in an ice bath with a stirring rate of 100 rpm for 210 min. An aliquot (0.4 mL) was then taken from the ionic liquid layer from each vial after the mixture was allowed to stand for 30 min without stirring and diluted to 0.6 mL with pure [EMIM][TFSA]. The aliquots taken from the vial that did not contain any particles were used as references for the measurement of absorbances for the corresponding samples taken from the biphasic system for the particle transport experiment. This cycle was repeated once more and samples were taken. UV-vis measurements showed that the absorbances of the samples from both layers at the wavelength of 500 nm was ≤ 0.002 , indicating that the transport was complete in both heating and cooling processes.

A.5 Thermo-Induced Spontaneous and Reversible Transfer of P(PEGMMA-*co*-TEGMMA)-74 Brush-Grafted Silica Particles between Water and [EMIM][TFSA] upon Heating at 70 °C and Cooling at 0 °C.

The P(PEGMMA-*co*-TEGMMA)-74 brush-grafted silica particles (2.05 mg) were dispersed in water (2.0503 g) in a 20 mL scintillation vial. Part of the dispersion (1.804 g) was then carefully transferred into a 3.7 mL vial that contained [EMIM][TFSA] (2.745 g, 1.80 mL). The vial was placed into a 70 °C oil bath and the system was stirred at a stirring rate of 500 rpm. In another 3.7 mL vial, water and [EMIM][TFSA] of equal volumes were stirred at the same stirring rate and temperature for the same amount of time as for the biphasic system that contained the hairy particles. After stirring for 210 min, the two systems were allowed to stand still without stirring for 30 min and an aliquot (0.4 mL) was taken from the water layer from both vials and diluted to 0.6 mL with pure water. The vials were then removed from the oil bath and the mixtures were stirred at 0 °C in an ice bath with a stirring rate of 100 rpm for 210 min. An aliquot (0.4 mL) was then taken from the ionic liquid layer from each vial after the mixture was allowed to stand for 30 min without stirring and diluted to 0.6 mL with pure [EMI][TFSA]. The aliquots taken from the vial that did not contain any particles were used as references for the measurements of absorbances for the corresponding samples taken from the biphasic system for the particle transport experiment. This cycle was repeated once more and samples were taken. UV-vis measurements showed that the absorbances of the samples from both layers at the wavelength of 500 nm was ≤ 0.001 , indicating that the transport was complete in both heating and cooling processes.

A.6 Thermo-Induced Spontaneous and Reversible Transfer of PTEGMMA Brush-Grafted Silica Particles between Water and [EMIM][TFSA] upon Heating at 70 °C and Cooling at 0 °C.

The PTEGMMA hairy particles (10.3 mg) were dispersed in water (10.321 g) in a 20 mL scintillation vial. Part of the dispersion (1.802 g) was then carefully transferred into a 3.7 mL vial that contained [EMIM][TFSA] (2.739 g, 1.80 mL). The vial was placed into a 70 °C oil bath and the system was stirred at a stirring rate of 500 rpm. In another 3.7 mL vial, water and [EMIM][TFSA] of equal volumes were stirred at the same stirring rate and temperature for the same amount of time as for the biphasic system that contained the hairy particles. After stirring at 70 °C for 210 min, an aliquot (0.4 mL) was taken from the water layer from both vials after the mixture was allowed to stand without stirring for 30 min and diluted to 0.6 mL with pure water. The vials were then removed from the oil bath and the mixtures were stirred at 0 °C in an ice bath with a stirring rate of 100 rpm for 330 min. An aliquot (0.4 mL) was then taken from the ionic liquid layer from each vial after the mixture was allowed to stand for 30 min without stirring and diluted to 0.6 mL with pure [EMIM][TFSA]. The aliquots taken from the vial that did not contain any particles were used as a reference for the measurement of absorbances for the corresponding samples taken from the biphasic system for the particle transport experiment. This cycle was repeated once more and samples were taken. UV-vis measurements showed that the absorbances of the samples from both layers at the wavelength of 500 nm was ≤ 0.002 , indicating that the transport was complete in both heating and cooling processes.

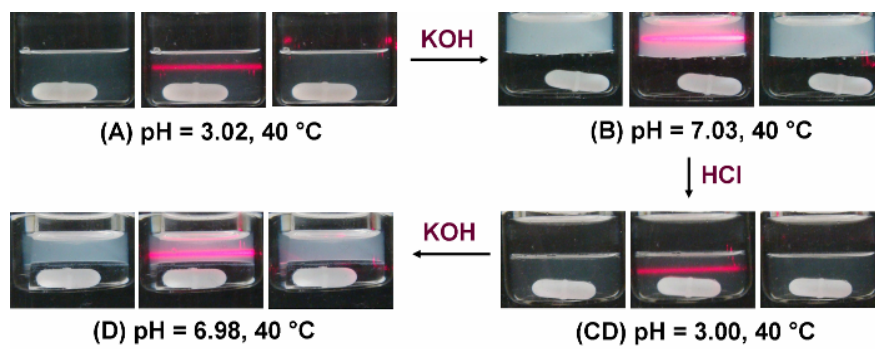
A.7 Thermo-Induced Phase Transfer behavior of PDEGMMA Brush-Grafted Silica Particles between Water and [EMIM][TFSA] upon Heating at 70 °C and Cooling at 0 °C.

The PDEGMMA hairy particles (1.85 mg) were dispersed in water (1.851 g) in a 20 mL scintillation vial. Part of the dispersion (1.801 g) was then carefully transferred into a 3.7 mL vial that contained [EMIM][TFSA] (2.743 g, 1.80 mL). The vial was placed into a 70 °C oil bath and the system was stirred at a stirring rate of 500 rpm. In another 3.7 mL vial, water and [EMIM][TFSA] of equal volumes were stirred at the same stirring rate and temperature for the same amount of time as for the biphasic system that contained the hairy particles. After stirring at 70 °C for 210 min, an aliquot (0.4 mL) was taken from the water layer from both vials after the mixture was allowed to stand without stirring for 30 min and diluted to 0.6 mL with pure water. The aliquot taken from the vial that did not contain any particles were used as a reference for the measurement of absorbances for the corresponding sample taken from the biphasic system for the particle transport experiment. The UV-vis measurement of the aliquot showed that the absorbance of the aqueous layer was essentially zero (0.001), indicating that the particles completely transferred to the ionic layer upon heating. The vials were then removed from the oil bath and the mixtures were stirred at 0 °C in an ice bath with a stirring rate of 100 rpm for 330 min. An aliquot (0.4 mL) was then taken from the water layer from each vial after the mixture was allowed to stand for 30 min without stirring and diluted to 0.6 mL with pure water. From the UV-vis measurement, the absorbance of the water layer was essentially zero (0.001), indicating that no PDEGMMA hairy particles moved to the water layer even after stirring in an ice/water bath for 330 min.

**Chapter 2. Synthesis of Thermo- and pH-Sensitive Hairy Particles and
Their Stimuli-Induced Reversible Transfer Behavior between Water
and a Hydrophobic Ionic Liquid**

Abstract

This Chapter describes the synthesis of thermo- and pH-sensitive polymer brush-grafted silica particles (hairy particles) and the study of their phase transfer behavior between water and a hydrophobic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]), in response to temperature and pH changes. The hairy particles were made by surface-initiated atom transfer radical polymerization of methoxytri(ethylene glycol) methacrylate (TEGMMA) and *tert*-butyl methacrylate with a molar ratio of 100 : 11 in the presence of a free initiator and subsequent removal of *tert*-butyl groups. The cloud points (CPs) of poly(TEGMMA-*co*-methacrylic acid), obtained after the treatment of the free polymer with trifluoroacetic acid, in both water and [EMIM][TFSA]-saturated water increased with the increase of pH and can be tuned over a wide temperature range. The hairy particles moved spontaneously from the aqueous phase to [EMIM][TFSA] phase upon heating at 80 °C and returned to the aqueous layer upon cooling at 10 °C. This process can be repeated many times regardless of whether the pH of the aqueous phase was 2.99, 5.00, or 7.02. UV-vis absorbance measurements showed that the transfer temperature (T_{tr}) of hairy particles from water to [EMIM][TFSA] increased with the increase of the pH of the aqueous phase. A linear relationship was observed between T_{tr} of hairy particles and the CP of the corresponding free polymer. By taking advantage of the tunability of T_{tr} of hairy particles, we demonstrated pH-driven reversible transfer of hairy particles at a fixed temperature by changing the pH of the aqueous phase and multiple phase transfer processes by controlling both temperature and pH.



2.1 Introduction

The ability to efficiently transport substances (molecules, supramolecular assemblies, particles, etc.) across interfaces between immiscible liquid phases is of critical importance to many applications, including separation and purification, catalysis, and targeted delivery of drugs and biomolecules.¹⁻⁹ While one-way transport processes are widely employed, there is a growing interest in reversible and quantitative transfer of substances. Such processes hold promise, for example, for developing next generation recyclable catalysts.¹⁻⁶ An appealing strategy that is being intensively pursued is to tag target substances with stimulus-responsive groups or polymers and apply external stimuli to reversibly modify their affinities to two immiscible liquids.^{1-6,9-22} Consequently, the partition coefficient of the substance in two phases is altered, resulting in spontaneous phase transfer. For example, Liu and Wang attached a light-responsive spiropyran moiety to a ruthenium catalyst and demonstrated that the catalyst could be induced to transfer between two immiscible organic phases by light.³ Desset and Cole-Hamilton reported a rhodium catalyst that could be triggered to move back and forth between aqueous and organic phases by bubbling with and removal of CO₂.⁴ Such methods can greatly simplify the process for recycling and reuse of catalysts.¹⁻⁶

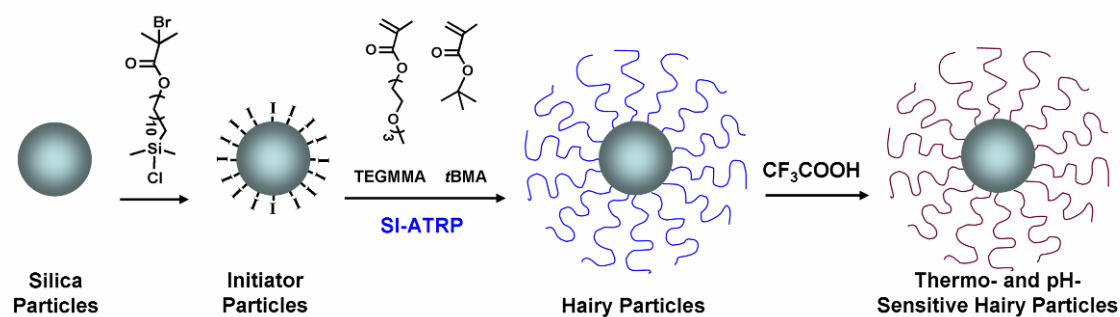
Polymer brush-grafted particles (“hairy” particles), especially those that can undergo structural or conformational changes in response to external stimuli, are an intriguing class of hybrid materials.¹⁰⁻¹³ These particles can be made by growing polymer chains from initiator-functionalized particles via surface-initiated polymerization or by grafting pre-formed polymers onto the particle surface.¹⁰⁻¹⁷ Using surface-initiated atom transfer radical polymerization (ATRP), we previously synthesized a series of well-defined

thermosensitive hairy particles.^{11,12} When the lower critical solution temperature (LCST) of polymer brushes was sufficiently high, the hairy particles were found to undergo spontaneous transfer between water and ethyl acetate or 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]), a common hydrophobic ionic liquid, upon temperature changes.¹² The transfer was reversible and quantitative and could be repeated many times. For the water/[EMIM][TFSA] biphasic system, a linear relationship was observed between transfer temperature (T_{tr}) of hairy particles and the cloud point (CP) of the corresponding free polymer in ionic liquid-saturated water.^{12b} The thermo-induced transfer of polymer brush-grafted gold nanoparticles between water and toluene was reported by Wang et al.¹⁵ Besides temperature, other stimuli, such as light and pH changes, were also employed to induce the transport of hairy particles between water and organic solvents.^{16,17} Notably, Wu et al. synthesized spiropyran-containing polymer brushes on silica colloids by surface-initiated ATRP and demonstrated light-induced phase transfer of hairy particles between water and toluene.¹⁶ Cheng et al. reported the pH-induced transport of gold nanoparticles that were grafted with mixed PEO and poly(*N,N*-diethylaminoethyl methacrylate) brushes in a biphasic system of water and chloroform.¹⁷

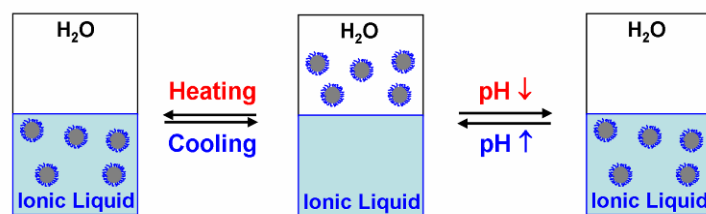
Responsive block copolymer micelles are another class of materials that can reversibly transfer between two immiscible liquid phases upon application of external stimuli.¹⁸⁻²² Lodge et al. reported a series of temperature-driven block polymer micelle shuttles that exhibited an ability to move back and forth between water and immiscible hydrophobic ionic liquid phases upon temperature changes.^{18,19} Micelles with poly(ethylene oxide) (PEO) coronas were found to reside in water at room temperature

and move spontaneously to an immiscible hydrophobic ionic liquid (e.g., 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆])) upon heating. When the temperature was decreased, the micelles returned to the water phase. Similar to thermosensitive hairy particles,¹² micelle shuttles were driven by the change of relative affinity of PEO corona to the two solvents caused by the LCST behavior of PEO in water.^{19c} More recently, Bai and Lodge reported polymersomes of poly(butadiene)-*b*-PEO with ionic liquid interiors dispersed in water; these block copolymer vesicles can be reversibly transported between water and [EMIM][TFSA] by changing temperature.²⁰ It should be noted here that Schubert and coworkers recently reported thermoreversible transfer of poly(2-nonyl-2-oxazoline-*b*-2-ethyl-2-oxazoline) block copolymer micelles between a hydrophobic ionic liquid and water.²¹

In this work, we synthesized thermo- and pH-sensitive hydrophilic polymer brush-grafted silica particles and demonstrated that the transfer of such hairy particles between water and [EMIM][TFSA] phases can be triggered by either temperature or pH changes or both (Schemes 2.1 and 2.2). The hybrid particles were made by surface-initiated ATRP of methoxytri(ethylene glycol) methacrylate (TEGMMA) and *tert*-butyl methacrylate (*t*BMA) with a molar ratio of 100 : 11 in the presence of a free initiator and subsequent removal of *tert*-butyl groups by CF₃COOH (Scheme 1). Poly(TEGMMA) (PTEGMMA) is a thermosensitive water-soluble polymer with an LCST of 52 °C in water,^{11,12,23} which belongs to a new class of thermosensitive polymers with a short oligo(ethylene glycol) pendant from each repeat unit.^{24,25} The incorporation of a small amount of weak acid into a thermosensitive water-soluble polymer allows the LCST to be readily and reversibly tuned over a wide temperature range by changing the solution pH,²⁶ making it possible to



Scheme 2.1 Synthesis of Thermo- and pH-sensitive Poly(methoxytri(ethylene glycol) methacrylate-*co*-methacrylic acid) Brush-Grafted Silica Particles by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) and Subsequent Treatment with CF₃COOH.



Scheme 2.2 Schematic Illustration of Thermo- and pH-Triggered Transfer of Hairy Particles between Aqueous Solution and a Hydrophobic Ionic Liquid.

actively control the T_{tr} of hairy particles via an external means. The T_{tr} of poly(TEGMMA-*co*-methacrylic acid) (P(TEGMMA-*co*-MAA) brush-grafted particles is found to increase with the increase of pH of the aqueous phase and exhibits a trend similar to that of CP of free polymer P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water. We demonstrated the pH-driven transfer of hairy particles between water and [EMIM][TFSA] at a fixed temperature by changing the pH and multiple phase transfer processes by controlling both temperature and pH. The results from this study could provide a basis for future design of novel stimuli-responsive recyclable phase transfer catalysts based on water/ionic liquid biphasic systems with tunable transfer temperatures.

2.2 Experimental Part

2.2.1 Materials

Chlorodimethylsilane (98%, Alfa Aesar) was stored in a refrigerator and used as received. Platinum-divinyltetramethyldisiloxane complex in xylene (2.1~2.4% Pt concentration in xylene) was purchased from Gelest, Inc. Tetrahydrofuran (THF) was dried over sodium and benzophenone, distilled, and used immediately for the dispersion of bare silica particles that were dried in high vacuum. CuBr (98%, Aldrich) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol and diethyl ether. The purified CuBr was dried in vacuum and stored in a desiccator. *N, N, N', N', N''*-pentamethyldiethylenetriamine (99%, Aldrich) and ethyl 2-bromoisobutyrate (98%, Aldrich) were dried with calcium hydride, distilled under reduced pressure, and stored in a desiccator. *tert*-Butyl methacrylate (*t*BMA, 98%, Aldrich) was stirred in the presence of

CaH₂, distilled under vacuum, and stored in a refrigerator prior to use. Methoxytri(ethylene glycol) methacrylate (TEGMMA) was synthesized according to the procedure reported previously.¹¹ [EMIM][TfSA] was prepared via a synthetic route described in the literature.²⁷ The clear and colorless liquid was dried in a vacuum oven at 60 °C for 3 days prior to use. 10-Undecen-1-yl 2-bromo-2-methylpropionate was synthesized according to a literature procedure;^{11,12} the molecular structure was confirmed by ¹H NMR spectroscopy. All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

2.2.2 Characterization

Size exclusion chromatography (SEC) was carried out at ambient temperature using PL-GPC 20 (an integrated SEC system from Polymer Laboratories, Inc.) with a refractive index detector, one PLgel 5 µm guard column (50 × 7.5 mm), and two PLgel 5 µm mixed-C columns (each 300 × 7.5 mm, linear range of molecular weight from 200 to 2 000 000 according to Polymer Laboratories, Inc.). The data were processed using CirrusTM GPC/SEC software (Polymer Laboratories, Inc.). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Polystyrene standards (Polymer Laboratories, Inc.) were used for calibration. ¹H NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer and the residual solvent proton signal was used as internal standard. Thermogravimetric analysis of particles was performed in air from room temperature to 800 °C at a heating rate of 20 °C/min using TA Q-series Q50. pH measurements were carried out with a pH meter (Accumet AB15 pH meter from Fisher Scientific, calibrated with pH = 4.01, 7.00, and 10.01 standard buffer solutions).

2.2.3 Synthesis of Poly(methoxytri(ethylene glycol) methacrylate-*co-t*-butyl methacrylate) Brush-Grafted Silica Particles.

The ATRP-initiator-functionalized silica particles (initiator particles) were prepared by immobilizing 11-(2-bromo-2-methyl)propionyloxyundecyldimethyl-chlorosilane, synthesized by the reaction of 10-undecen-1-yl 2-bromo-2-methylpropionate with chlorodimethylsilane, onto the surface of bare silica particles via a procedure described previously.^{11,12} The average size of bare silica particles was 180 nm, determined by dynamic light scattering.

CuBr (10.0 mg, 70 μ mol) and the initiator particles (235.0 mg) were placed into a two-necked flask and dried under high vacuum at 50 °C for 4 h. The initiator particles were then dispersed in anisole (10 mL) by ultrasonication. Methoxytri(ethylene glycol) methacrylate (TEGMMA, 10.000 g, 43.1 mmol), *tert*-butyl methacrylate (*t*BMA, 0.682 g, 4.8 mmol), and free initiator ethyl 2-bromoisobutyrate (10.5 mg, 54 μ mol) were added into the flask. After the mixture was degassed by three freeze-pump-thaw cycles, *N,N,N',N',N''*-pentamethyldiethylenetriamine (12.1 mg, 70 μ mol) was added via a microsyringe at the thawing point of the mixture. A sample was taken immediately for ¹H NMR spectroscopy analysis. The flask was then placed in an oil bath with a preset temperature of 60 °C. The polymerization was monitored by ¹H NMR spectroscopy. After the reaction proceeded for 75 min, the flask was removed from the oil bath and opened to air; the mixture was diluted with THF (20 mL). The particles were isolated by centrifugation (Eppendorf 5804, 10000 rpm, 15 min) and the supernatant liquid was passed through a short column of silica gel (bottom)/activated basic aluminum oxide (top) (2/1, v/v). The polymer was then precipitated in hexanes twice and dissolved in

THF. The purified free polymer was analyzed by SEC relative to polystyrene standards. The $M_{n,SEC}$ and polydispersity index (PDI) were 29 kDa and 1.09, respectively. The polymer brush-grafted particles were re-dispersed in THF and isolated by centrifugation. This purification process was repeated an additional four times. The hairy particles were then dried by a stream of air flow. A small portion of the particles was transferred into a 25 mL two-necked flask and dried under high vacuum at 50 °C for 8 h for thermogravimetric analysis. The remaining particles were re-dispersed and stored in THF. The degree of polymerization (DP) of the free copolymer P(TEGMMA-*co*-*t*BMA) was calculated from the monomer-to-free initiator molar ratio and the monomer conversion. The peaks located at 4.31 and 4.09 ppm, which were from -COOCH₂- of TEGMMA and the polymer, respectively, were used as internal standard (the sum of the integrals was a constant throughout the polymerization). The final monomer conversion was calculated from the integrals of the peaks at 5.7-5.4 ppm (CHH=C- from TEGMMA and *t*BMA) at $t = 0$ min and 75 min. The calculated DP was 210.

2.2.4 Removal of *tert*-Butyl Groups of P(TEGMMA-*co*-*t*BMA) Brushes Grafted on Silica Particles and of Free Copolymer P(TEGMMA-*co*-*t*BMA) by CF₃COOH

P(TEGMMA-*co*-*t*BMA) brush-grafted silica particles (264.1 mg) and dry dichloromethane (5.19 g) were added into a flask, followed by the addition of trifluoroacetic acid (3.004 g). After the reaction mixture was stirred at ambient temperature for four days, the volatiles were removed by a rotary evaporator. The particles were isolated by centrifugation (10000 rpm for 15 min), dispersed in dichloromethane, and separated again. This process was repeated an additional three times. The free polymer P(TEGMMA-*co*-*t*BMA), formed from free initiator ethyl 2-

bromoisobutyrate in the synthesis of P(TEGMMA-*co*-*t*BMA) hairy particles, was subjected to the similar condition to remove *tert*-butyl groups. The resultant polymer P(TEGMMA-*co*-MAA) was precipitated four times in a mixture of hexanes and diethyl ether (10/4, v/v). The purified polymer was then dried under vacuum.

2.2.5 Determination of Cloud Points of P(TEGMMA-*co*-MAA) in Aqueous Solutions in the Absence and Presence of Ionic Liquid

The cloud points of P(TEGMMA-*co*-MAA) in aqueous solutions and [EMIM][TFSA]-saturated aqueous solutions with various pH values were measured by visual examination as detailed below. An aqueous solution of P(TEGMMA-*co*-MAA) with a concentration of 0.1 wt % was made in a small vial using deionized water and the pH value was measured with a pH meter. The vial was placed in an oil bath and the temperature was raised gradually. At each temperature, the polymer solution was allowed to equilibrate for at least 5 min. When the solution turned cloudy, the temperature was recorded as the cloud point. We previously reported that this method gave cloud points essentially the same as those measured by turbidimetry using a UV-vis spectrometer.²⁸ After the solution was cooled to room temperature, the pH was adjusted by adding a 0.05 N aqueous KOH solution or a 0.05 N aqueous HCl solution and the cloud point of the polymer solution was determined. For the cloud points of P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated aqueous solutions, the polymer solution with a concentration of 0.1 wt % was made by using water that was saturated with [EMIM][TFSA] at room temperature overnight, and a small drop of [EMIM][TFSA] was placed as a separate ionic liquid phase at the bottom of the vial. The cloud points of P(TEGMMA-*co*-MAA)

in [EMIM][TFSA]-saturated aqueous solutions at various pH values were determined in the same way as for the solution made from water without [EMIM][TFSA].

2.2.6 Thermally Induced Reversible Transfer of P(TEGMMA-*co*-MAA) Brush-Grafted Silica Particles between Water and [EMIM][TFSA] at pH Values of 2.99, 5.00, and 7.02

Described below is a typical procedure for thermally induced reversible transport of P(TEGMMA-*co*-MAA) hairy particles between [EMIM][TFSA] and aqueous solutions with pH values of 2.99, 5.00, and 7.02 by cycling temperature between 10 to 80 °C.

The P(TEGMMA-*co*-MAA) hairy particles (4.76 mg) were dispersed in water that was saturated with [EMIM][TFSA] at room temperature overnight (4.77 g) in a 20 mL scintillation vial. The dispersion was transferred into three small vials; each vial had 1.5 g of the particle dispersion. The pH values of the three samples were adjusted to 2.99, 5.00, and 7.02. Each aqueous dispersion was then carefully transferred to a 3.7 mL vial that contained [EMIM][TFSA] (1.5 mL). The vials were placed into an 80 °C oil bath and the systems were stirred at a stirring rate of 400 rpm for 2 h. The aqueous layers exhibited virtually no scattering when a laser from a laser pointer passed through it. Pictures of vials were taken by a digital camera. The vials were then removed from the oil bath and placed in a 10 °C water bath. The systems were stirred at 400 rpm for 4 h. There was essentially no scattering when a laser passed through the ionic liquid layer, while the aqueous layer became cloudy. Pictures were again taken using a digital camera. This heating and cooling cycle was repeated for a total of 10 times.

2.2.7 Determination of Transfer Temperature of P(TEGMMA-*co*-MAA) Hairy Particles from Aqueous to [EMIM][TFSA] Phase at Various pH Values upon Heating

Described below is a typical procedure for the determination by UV-vis absorbance measurements of the transfer temperature (T_{tr}) of P(TEGMMA-*co*-MAA) hairy particles from water with pH of 3.05 to [EMIM][TFSA] upon gradual heating. Similar procedures were employed to study the thermally induced phase transfer of P(TEGMMA-*co*-MAA) hairy particles from water with other pH values to [EMIM][TFSA]. The particles (20.4 mg) were dispersed in water that was saturated with [EMIM][TFSA] at room temperature overnight (20.401 g) in a 20 mL scintillation vial. A portion of this dispersion (9.002 g) was taken and its pH value was adjusted to 3.05 using 0.05 N aqueous HCl. The particle dispersion was then carefully transferred into a 20 mL vial that contained [EMIM][TFSA] (13.680 g, 9.00 mL). The 20 mL vial with an inner diameter of 2.7 cm was custom-made and equipped with a Teflon valve that could be opened to allow the insertion of a needle to take samples. The biphasic system was stirred with a magnetic stir bar (dimension 4.5×12 mm) at a stirring rate of 400 rpm at 5 °C. After stirring for at least 12 h, the system was allowed to stand still for 30 min at the same temperature; an aliquot (0.4 mL) was taken from each layer and diluted to 0.6 mL with the corresponding pure liquid for UV-vis absorbance measurement. The temperature was then increased to 8 °C and the aforementioned process was repeated. The same procedure was applied for other temperatures (10, 16, 25, 28, 31, 34, and 37 °C).

In another vial, water and [EMIM][TFSA] of equal volumes were stirred at the same stirring rate and temperature and for the same amount of time as for the biphasic system

that contained P(TEGMMA-*co*-MAA) hairy particles. At each temperature, an aliquot (0.4 mL) was taken from each layer after the system was allowed to stand still for 30 min and was diluted to 0.6 mL with the corresponding pure liquid. These aliquots were used as references for the measurement of absorbances of the corresponding samples taken at the same temperature from the biphasic system that contained P(TEGMMA-*co*-MAA) hairy particles. The absorbances of the diluted dispersions at the wavelength of 500 nm were recorded at room temperature using a UV-visible spectrometer.

2.2.8 Reversible Transport of Thermo- and pH-Sensitive P(TEGMMA-*co*-MAA) Hairy Particles at a Constant Temperature by Altering the pH

A dispersion of P(TEGMMA-*co*-MAA) hairy particles in [EMIM][TFSA]-saturated water with a concentration of 1.0 mg/mL (3.51 g) was transferred into a glass vial, which was then placed into an oil bath with a preset temperature of 40 °C. After the dispersion was equilibrated at this temperature for 25 min, the pH of the aqueous dispersion was adjusted to 3.02 using 0.05 N aqueous HCl. [EMIM][TFSA] (5.33 g) was added into a separate 7.6 mL glass vial with an inner diameter of 1.7 cm. This vial was placed into the same oil bath (40 °C) and allowed to equilibrate for the same amount of time as for the particle dispersion. The aqueous dispersion of hairy particles was then carefully transferred into the vial that contained the ionic liquid. The biphasic system was stirred with a magnetic stir bar (dimension 4.5 × 12 mm) at a stirring rate of 350 rpm. After 4 h, an aliquot (0.4 mL) was taken from each layer and diluted with the corresponding pure liquid to 0.6 mL for UV-vis absorbance analysis. The pH of the aqueous phase was then adjusted to 7.03 using 0.05 N KOH. After 4 h, an aliquot was withdrawn from each layer again. The pH of the aqueous layer was then changed to 3.00; the cycle was repeated

additional one time and samples were taken for quantitative analysis of particle transfer using UV-vis spectrometry. The references used in the UV-vis absorbance measurements were prepared in the same manner as described in the preceding section.

2.2.9 Multiple Transfer Processes of Thermo- and pH-Sensitive Hairy Particles between Aqueous and [EMIM][TFSA] Phases by Controlling both pH and Temperature

A dispersion of P(TEGMMA-*co*-MAA) hairy particles in [EMIM][TFSA]-saturated water with a concentration of 1.0 mg/mL (3.751 g) was added into a glass vial and its pH value was adjusted to 3.01 by using 0.05 N HCl. The particle dispersion was then carefully transferred into a 7.6 mL vial that contained [EMIM][TFSA] (5.704 g, 3.75 mL). After the biphasic system was stirred with a magnetic stir bar (dimension 4.5×12 mm) at a stirring rate of 400 rpm at 5 °C for 2 h, the system was allowed to stand still for 30 min at the same temperature and an aliquot (0.4 mL) was withdrawn from each layer and diluted to 0.6 mL with the corresponding pure liquid for UV-vis absorbance measurement. The temperature was then increased to 40 °C and the mixture was stirred for 1 h. The aforementioned sample withdrawing process was repeated. The pH of the aqueous layer was then changed to 7.03 and the biphasic system was stirred for 5 h, followed by taking a sample from each layer for UV-Vis spectrometry analysis. The vial was then heated to 85 °C. After the mixture was stirred for 6 h, an aliquot was withdrawn from each layer. Finally, the vial was allowed to cool to room temperature overnight and samples were withdrawn. The references used in the UV-vis absorbance measurements were prepared in the same manner as described in the experimental procedure for the determination of T_{tr} of hairy particles.

2.3 Results and Discussion

2.3.1 Synthesis of Thermo- and pH-Sensitive P(TEGMMA-*co*-MAA) Brush-Grafted Silica Particles

Thermo- and pH-sensitive P(TEGMMA-*co*-MAA) brushes were prepared by surface-initiated ATRP of a mixture of TEGMMA and *t*BMA with a molar ratio of 100 : 11 from the initiator-functionalized silica particles and subsequent removal of *tert*-butyl groups using trifluoroacetic acid (TFA). The bare silica particles with an average size of 180 nm were made by the Stöber process, which is known to produce spherical silica particles with a relatively narrow size distribution.²⁹ The bare particles were surface-functionalized with 11-(2-bromo-2-methyl)propionyloxyundecyldimethylchlorosilane, an ATRP initiator-terminated monochlorosilane, via a known procedure described in previous publications.^{11,12} Thermogravimetric analysis (TGA) showed that the weight retention difference between bare particles and initiator particles at 800 °C was 3.3 wt%, when the weight percentage difference at 100 °C between two TGA curves was taken into consideration (Figure 2.1). This value is comparable to those reported in the literature.^{11,12}

The surface-initiated ATRP of TEGMMA and *t*BMA from initiator particles was carried out in anisole at 60 °C in the presence of a free initiator, ethyl 2-bromoisobutyrate (EBiB). The addition of EBiB facilitated the control of surface-initiated polymerization, and also allowed the polymerization to be monitored by ¹H NMR spectroscopy or size exclusion chromatography (SEC).¹⁰⁻¹² The polymerization was stopped after 75 min. The particles were isolated by centrifugation and the free polymer P(TEGMMA-*co*-*t*BMA), formed from free initiator EBiB, was purified by repetitive precipitation in hexanes. The

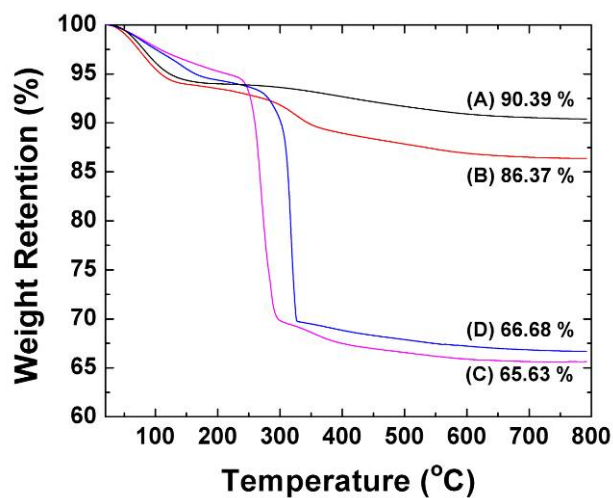


Figure 2.1 Thermogravimetric analysis (TGA) of (A) bare silica particles, (B) initiator-functionalized silica particles, (C) poly(methoxytri(ethylene glycol) methacrylate-*co*-*tert*-butyl methacrylate) (P(TEGMMA-*co*-*t*BMA)) brush-grafted silica particles, and (D) poly(TEGMMA-*co*-methacrylic acid) (P(TEGMMA-*co*-MAA)) brush-grafted silica particles. TGA was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C.

DP of P(TEGMMA-*co*-*t*BMA) was 210, calculated from the monomer conversion and the monomer-to-initiator ratio under the assumption that the initiator efficiency was 100 %. Figure 2.2A shows the SEC curve of the free polymer; the $M_{n,SEC}$ and polydispersity index (PDI) were 29 kDa and 1.09, respectively (based on polystyrene standards). The relatively narrow molecular distribution suggested that the polymerization was well controlled. It has been reported by many researchers that the molecular weight and molecular weight distribution of polymer brushes grown on particles by “living”/controlled radical polymerization are essentially identical to those of the free polymer formed from the added free initiator.^{14a,30,31}

The *tert*-butyl groups of hairy particles and free polymer P(TEGMMA-*co*-*t*BMA) were removed by treatment with TFA, which is known not to affect other ester groups.³² Figure 2.2B and C shows the ¹H NMR spectra of P(TEGMMA-*co*-*t*BMA) before and after the reaction with TFA; the *tert*-butyl peak located at 1.39 ppm disappeared while other peaks remained the same. The molar ratio of TEGMMA to *t*BMA units in the copolymer were determined from the ¹H NMR spectra using the integral values of the peaks at 4.09 ppm (COOCH₂CH₂ of TEGMMA units) and the peak located at 1.39 ppm (COOC(CH₃)₃ of *t*BMA units, excluding the integral value of the small broad peak shown in the ¹H NMR spectrum of P(TEGMMA-*co*-MAA).³³ The molar ratio of TEGMMA to *t*BMA units in the copolymer was found to be 100 to 10.5, which was very close to the molar ratio of two monomers in the polymerization mixture (100 : 11).

TGA showed that the weight retention of P(TEGMMA-*co*-*t*BMA) hairy particles at 800 °C was 65.6 %. After the cleavage of *tert*-butyl groups, the weight retention changed to 66.7 %, which was essentially the same as the calculated value of 66.3 %. By using the

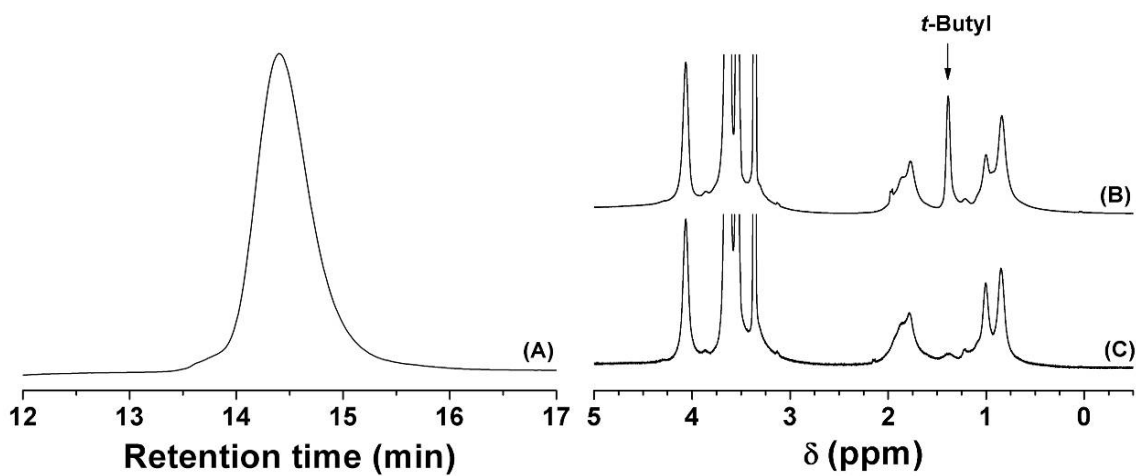


Figure 2.2 (A) Size exclusion chromatography (SEC) trace of free polymer P(TEGMMA-*co*-*t*BMA) formed from the free initiator in the synthesis of P(TEGMMA-*co*-*t*BMA) brush-grafted particles and ¹H NMR spectra of free polymer P(TEGMMA-*co*-*t*BMA) before (B) and after (C) the removal of *tert*-butyl groups using trifluoroacetic acid.

size of bare silica particles, TGA data, and the DP of the free copolymer, the grafting density of P(TEGMMA-*co*-*t*BMA) brushes on silica particles was calculated to be 0.31 chains/nm².

2.3.2 Thermosensitive Property of Free Polymer P(TEGMMA-*co*-MAA): pH Dependence of Cloud Point of P(TEGMMA-*co*-MAA) in Water and [EMIM][TFSA]-Saturated Water

The cloud point (CP) of a thermosensitive water-soluble polymer that contains a small amount of weak acid is known to depend on solution pH.²⁶ With the increase of pH, the weak acid ionizes, making the polymer chain more soluble and thus raising the LCST of the polymer in water. To study the pH dependence of CP of P(TEGMMA-*co*-MAA), an aqueous solution of the polymer with a concentration of 0.1 wt % was prepared and the CP was determined by visual examination. We previously showed that this simple method gave results essentially identical to those from turbidimetry using a UV-vis spectrometer.²⁸ The pH of the solution was then adjusted and the CP was recorded. This process was repeated until a total of 8 pH values were examined. The results are summarized in Figure 2.3. As expected, the CP increased with the increase of pH, from 43 °C at pH = 3.01 to 83 °C at pH = 6.53. The increase was initially slow, but became stronger when the pH value was above 5.0. This is consistent with our group's previous observation in the study of cloud points of poly(methoxydi(ethylene glycol) methacrylate-*co*-methacrylic acid) (P(DEGMMA-*co*-MAA) in aqueous solutions. The pK_a value of carboxylic acid in P(DEGMMA-*co*-MAA) was found to be 5.6 by titration.³³

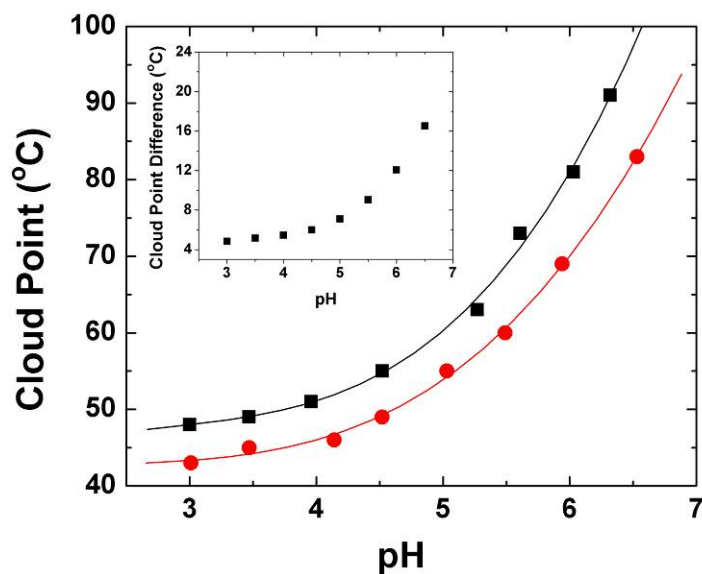


Figure 2.3 Plot of cloud point of P(TEGMMA-*co*-MAA) in aqueous solution without [EMIM][TFSA] (solid circle) and in [EMIM][TFSA]-saturated aqueous solution (solid square) at a concentration of 0.1 wt % versus pH. The black curve is a 3rd order polynomial fit to the cloud points of the polymer in [EMIM][TFSA]-saturated aqueous solution ($y = 20.7 + 24.5x - 7.85x^2 + 0.91x^3$, $R = 0.997$, where y = cloud point and x = pH). The red curve is a 3rd order polynomial fit to the cloud points of the polymer in aqueous solutions in the absence of [EMIM][TFSA] ($y = 34.34 + 9.67x - 3.81x^2 + 0.53x^3$, $R = 0.998$, where y = cloud point and x = pH). The inset shows the difference between the cloud points of 0.1 wt % aqueous solutions of P(TEGMMA-*co*-MAA) in the absence and presence of [EMIM][TFSA], calculated from the fit equations, as a function of pH.

The CP of a thermosensitive polymer in water can be affected by various additives.³⁴ Since [EMIM][TFSA] was used in the particle transfer experiments and two liquids were mutually saturated, we also measured the CPs of P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water in the presence of a small drop of [EMIM][TFSA] at various pH values. Surprisingly, the CP of P(TEGMMA-*co*-MAA) in water in the presence of [EMIM][TFSA] was higher than that in the absence of [EMIM][TFSA] at all tested pH values (Figure 2.3). Nevertheless, the trend of CP was the same as that in the absence of [EMIM][TFSA]. To look into the extent to which [EMIM][TFSA] affected the CP of P(TEGMMA-*co*-MAA) at different pH values, we performed a polynomial fit to each set of data. From the fit equations, we calculated the difference between CPs of P(TEGMMA-*co*-MAA) in the absence and presence of the ionic liquid at various pH values. The results are shown in the inset of Figure 2.3. Interestingly, the trend of the cloud point difference was similar to that of CP of P(TEGMMA-*co*-MAA) with respect to pH. It increased with the increase of pH; the CP difference was only ~ 5 °C at pH = 3.0 but became more than 16 °C at pH = 6.5, suggesting that the increased difference at a higher pH value was related to the increased degree of ionization of carboxylic acid groups.

We previously observed that the CPs of poly(alkoxyoligo(ethylene glycol) methacrylate)s in [EMIM][TFSA]-saturated water were lower than those in pure water.^{12b} Thus, the higher CP of P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water was caused by the incorporation of carboxylic acid groups into the polymer chain. The salt effects on LCSTs of thermosensitive water-soluble polymers have been reported and in general are related to the Hofmeister series.^{35,36} Zhang et al. recently carried out a

systematic study on the effects of Hofmeister anions on the LCST of poly(*N*-isopropylacrylamide) and found that the observed effects could be explained by three interactions of the ions with the polymer and its water of hydration.³⁶ First, the anions can polarize an adjacent water molecule that is involved in hydrogen bonding with the amide group. Second, the anions can interfere with the hydrophobic hydration of the macromolecule by increasing surface tension of the cavity surrounding the backbone and the isopropyl side chains. Third, the anions may bind directly to the polyamide. The first and second of these effects lead to the salting-out of the polymer and thus lowering of the LCST. The third effect results in the salting-in of the polymer and an increase in CP. Our observation appears to be in line with the third scenario, i.e., the elevated CP of P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water was likely caused by the direct binding of [EMIM]⁺ cations to the carboxylic acid groups, most probably, the ionized carboxylic acid groups (COO⁻), of the polymer. This speculation is supported by the fact that the difference between CPs of P(TEGMMA-*co*-MAA) in aqueous solutions in the presence and absence of [EMIM][TFSA] increased with the increase of pH with a greater increase observed at pH > pK_a.

2.3.3 Thermo-Induced Reversible Transfer of P(TEGMMA-*co*-MAA) Hairy Particles between Aqueous and [EMIM][TFSA] Phases at pH Values of 2.99, 5.00, and 7.02

We first examined whether or not P(TEGMMA-*co*-MAA) hairy particles can be transported between aqueous and [EMIM][TFSA] phases at three different pH values, 2.99, 5.00, and 7.02, upon temperature changes. Note that from the fit equation the CPs of P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated aqueous solutions at pH values

of 3.0, 5.0, and 7.0 are 48, 61, and > 100 °C, respectively. Three aqueous dispersions of P(TEGMMA-*co*-MAA) hairy particles with a concentration of 1.0 mg/mL were made using [EMIM][TFSA]-saturated water and their pH values were adjusted to 2.99, 5.00, and 7.02, respectively using either 0.05 N HCl or 0.05 N KOH. The aqueous dispersions were transferred into three vials that contained equal volumes of [EMIM][TFSA] (Figure 2.4A). The vials were then placed into an 80 °C oil bath, and the systems were stirred with a magnetic stir bar at a stirring rate of 400 rpm. After 2 h, the aqueous layers in all three vials became clear and exhibited virtually no scattering when a laser from a laser pointer passed through them, while the ionic liquid layers turned slightly cloudy (Figure 2.4B). The vials were then removed from the 80 °C oil bath and placed into a 10 °C water bath. After stirring at a stirring rate of 400 rpm for 4 h, the ionic liquid layers in all three vials turned clear and the aqueous phases became cloudy as in the initial state (Figure 2.4C), indicating that the hairy particles moved from the bottom [EMIM][TFSA] layer to the top aqueous layer. This process can be repeated at least 10 times. Figure 4D shows the picture of three vials after the hairy particles were transferred to the bottom layer upon heating at 80 °C.

2.3.4 Phase Transfer Temperatures of Thermo- and pH-Sensitive Hairy Particles from Aqueous to [EMIM][TFSA] Phase at Various pH Values upon Heating

To investigate how the phase transfer behavior of P(TEGMMA-*co*-MAA) hairy particles from water to [EMIM][TFSA] was affected by the pH of the aqueous layer, we measured the transfer temperatures of hairy particles at pH values ranging from 3.05 to 7.07 by gradual heating. For each pH, a dispersion of hairy particles in [EMIM][TFSA]-saturated water with a concentration of 1.0 mg/mL was prepared and the pH was adjusted

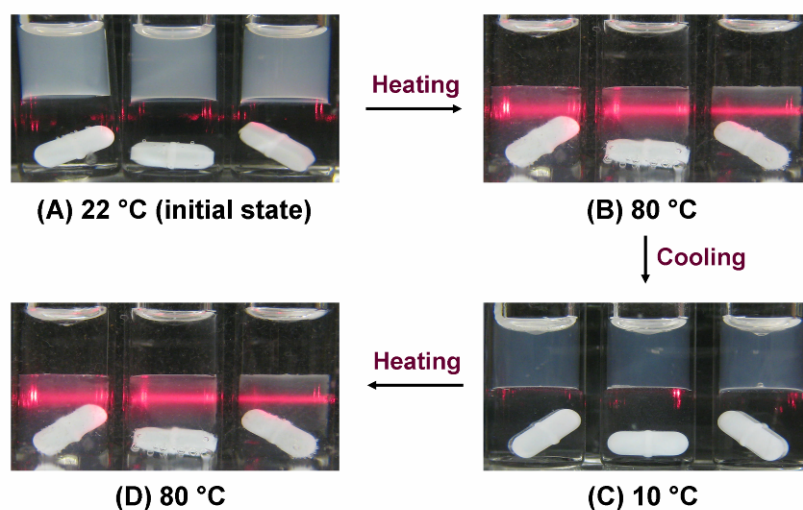


Figure 2.4 Pictures of three aqueous-[EMIM][TFSA] biphasic systems that contained thermo- and pH-sensitive P(TEGMMA-*co*-MAA) brush-grafted silica particles with a concentration of 1.0 mg/mL in the initial state at 22 °C (A), 80 °C after stirring for 2 h (B), 10 °C after stirring for 4 h (C), and 80 °C after stirring for 2 h (D). The pH values of aqueous layers in three vials from left to right were 2.99, 5.00, and 7.02, respectively. The pictures were taken when a laser beam from a laser pointer passed through the bottom ionic liquid layers. More pictures can be found in the Appendix B.

to a desired value. The dispersion was carefully added on top of [EMIM][TFSA] in a custom-made vial. The vial was then placed in a water or an oil bath with a preset temperature and the mixture was stirred with a magnetic bar at a stirring rate of 400 rpm. At a given temperature, the system was equilibrated for at least 12 h and then allowed to stand still for 30 min. An aliquot (0.4 mL) was taken from each layer and diluted to 0.6 mL with the corresponding pure liquid for UV-vis absorbance measurement.

Figure 2.5 shows the ratio of the absorbance at a given temperature to the maximum absorbance versus temperature for both aqueous and ionic liquid layers at five selected pH values. The data for additional four pH values are included in the Appendix B. We previously confirmed that the Beer's law at the wavelength of 500 nm can be applied to the dispersions of hairy particles in both water and ionic liquid in the studied concentration range from 0.667 mg/mL (after dilution of aliquots) to 0.0334 mg/mL.^{12b} Therefore, the normalized absorbance $A/A_{\max}$ is proportional to the normalized particle concentration ($[\text{particle}]/[\text{particle}]_{\max}$). By examining the five plots in Figure 5, one can easily discern that the T_{tr} of hairy particles from aqueous to [EMIM][TFSA] phase upon heating was dependent on the pH of the aqueous layer; the greater the pH, the higher the T_{tr} . However, compared with the thermally induced transfer of silica particles grafted with thermosensitive poly(methoxyoligo(ethylene glycol) methacrylate) brushes that did not contain carboxylic acid groups,^{12b} the transitions of the transfer of P(TEGMMA-*co*-MAA) hairy particles were noticeably broader, especially at lower pH values. With the increase of pH, the transition appeared to become narrower, similar to those of poly(methoxyoligo(ethylene glycol) methacrylate) brush-grafted particles.^{12b} The broader transitions at low pH values were likely caused by the decreased solubility of

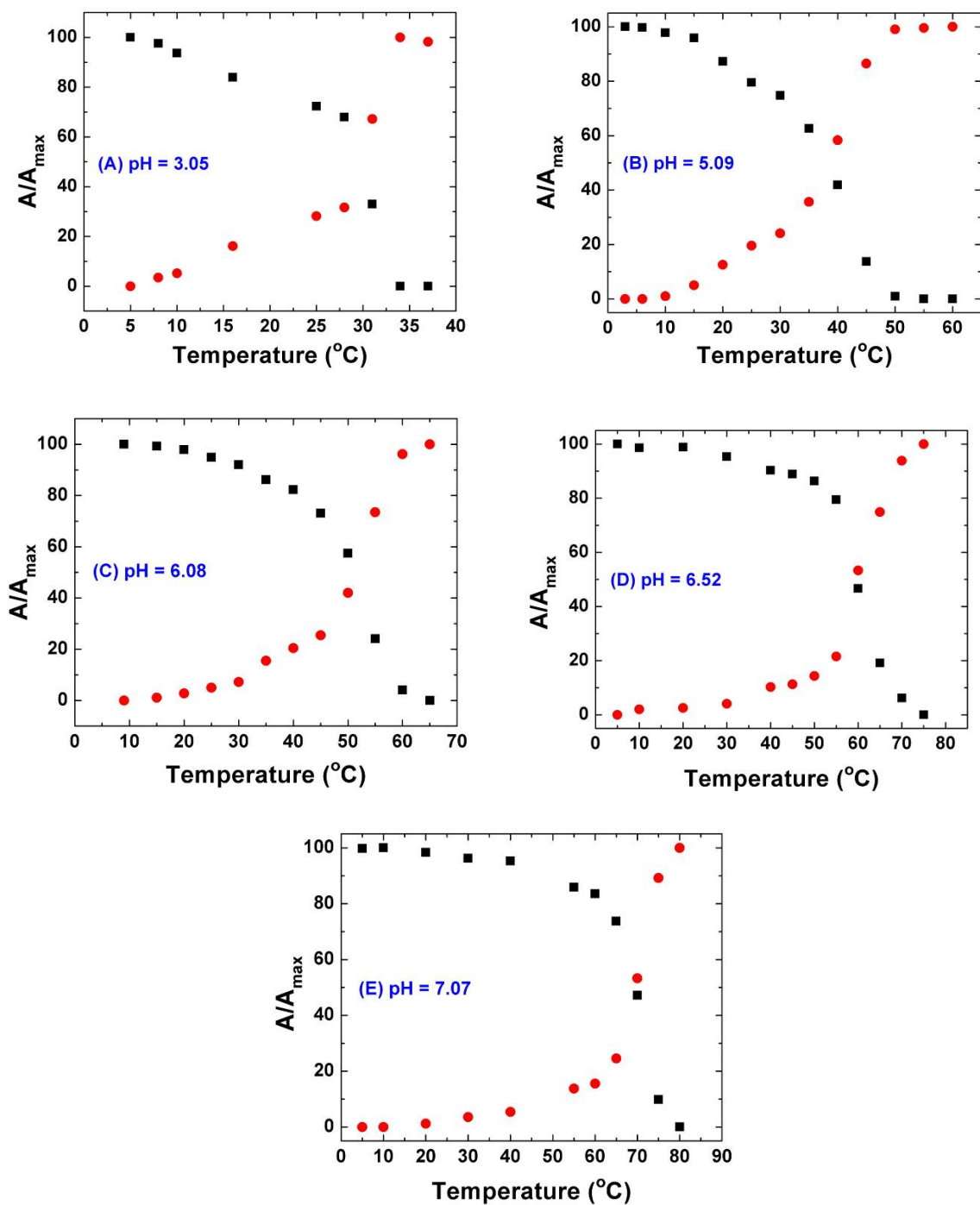


Figure 2.5 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-co-MAA) hairy particles in the aqueous phase with pH of (A) 3.05, (B) 5.09, (C) 6.08, (D) 6.52, and (E) 7.07 (solid square) and in the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range.

P(TEGMMA-*co*-MAA) (and thus hairy particles) in the aqueous phase due to the hydrogen bonding interactions between MAA and neighboring TEGMMA units. The formation of complexes of poly(MAA) and poly(ethylene oxide) at acidic pH via hydrogen bonds has long been known.³⁷

If the temperature at which the particle concentration changed by 50 % is taken as the T_{tr} , the T_{tr} was 29.5 °C at pH = 3.05, 38.1 °C at pH = 5.09, 51.1 °C at pH = 6.08, 59.5 °C at pH = 6.52, and 69.4 °C at pH = 7.07. Figure 2.6A shows the plots of T_{tr} of hairy particles and CP of P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water, calculated from the fit equation, versus pH. A striking feature of the figure is that the T_{tr} of hairy particles exhibited a trend similar to that of CP of P(TEGMMA-*co*-MAA) with respect to pH, though there was an offset. Figure 2.6B shows the plot of T_{tr} of hairy particles versus CP of P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water at various pH values. A nearly linear relationship was observed (linear fit $R = 0.998$), consistent with our previous observations in the study of a set of silica particles grafted with thermosensitive polymers with different LCSTs in water.^{12b}

As can be seen from Figure 2.6, the T_{tr} of hairy particles at a specific pH was significantly lower, by at least 18 °C, than the CP of free polymer P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water at the same pH. Our previous studies showed that the transfer of thermosensitive hairy particles from water to [EMIM][TFSA] was an entropically driven process; thermodynamic analysis indicated that both ΔH° and ΔS° were positive.^{12b} The dissolution of thermosensitive polymers with an oligo(ethylene glycol) pendant from each repeat unit in water at temperatures below LCSTs is associated with the formation of more ordered, structured water around the hydrophobic moieties of

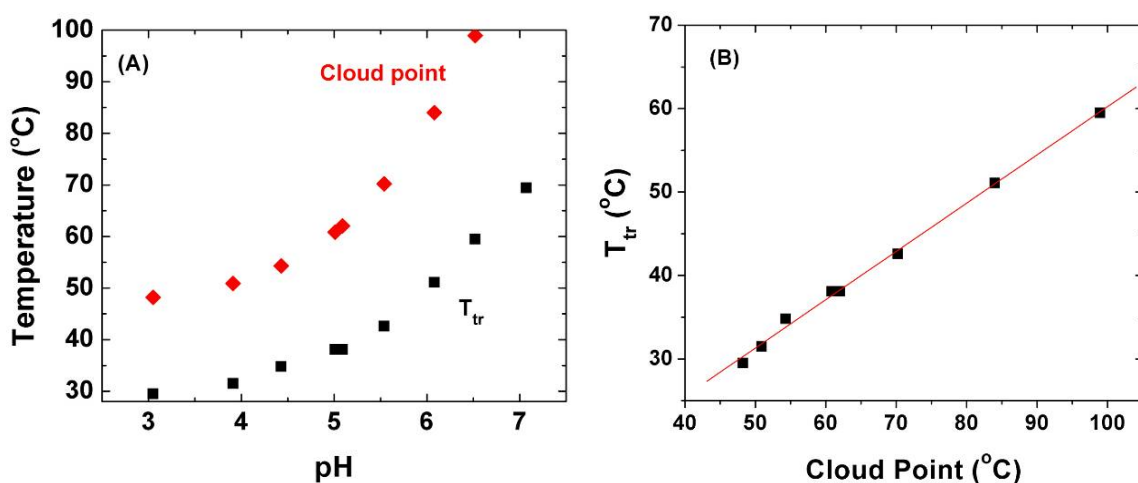


Figure 2.6 Plots of (A) transfer temperature (T_{tr}) of P(TEGMMA-*co*-MAA) hairy particles and cloud point of free polymer P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water versus pH, and (B) transfer temperature (T_{tr}) of P(TEGMMA-*co*-MAA) hairy particles versus cloud point of free polymer P(TEGMMA-*co*-MAA) in [EMIM][TFSA]-saturated water. The cloud points of P(TEGMMA-*co*-MAA) presented here were calculated from the fit equation shown in the caption of **Figure 2.3**. The straight line in (B) is a linear fit with $R = 0.998$ ($y = 2.332 + 0.579x$, where y is T_{tr} and x is cloud point).

polymer chains, which results in a negative ΔS° value.^{24,25} Thus, when the thermosensitive hairy particles moved from the aqueous to [EMIM][TFSA] phase, the structured water around polymer chains was disrupted and the entropy of the whole system increased. Although the particle transfer process was closely related to the LCST behavior of thermosensitive polymer P(TEGMMA-*co*-MAA) in water, the transfer temperature was not the same as the cloud point. We speculate that the transfer temperature is determined by the interplay of enthalpy and entropy changes of the interactions of polymer brushes with water and the ionic liquid or the changes of relative affinity of polymer brushes to water and [EMIM][TFSA].

2.3.5 pH-Driven Transfer of Thermo- and pH-Sensitive Hairy Particles at a Constant Temperature

As shown in Figure 2.6A, the T_{tr} of P(TEGMMA-*co*-MAA) hairy particles was 29.5 °C at pH 3.05. When the pH value was raised to 7.07, the T_{tr} increased to 69.4 °C. The significant difference in the transfer temperatures of P(TEGMMA-*co*-MAA) hairy particles at low and high pH values provides an opportunity to drive particles to transfer between two phases at a constant temperature by changing the pH value of the aqueous layer. To demonstrate this possibility, we selected a temperature of 40 °C, which was between 29.5 and 69.4 °C. A dispersion of P(TEGMMA-*co*-MAA) hairy particles in [EMIM][TFSA]-saturated water with a concentration of 1.0 mg/mL was made. After the equilibration in a 40 °C oil bath for 25 min and the adjustment of the pH to 3.02, the aqueous dispersion was transferred into a vial that contained an equal volume of [EMIM][TFSA] in the same 40 °C oil bath. After stirring at 40 °C for 4 h, the aqueous layer became clear and there was essentially no scattering when a laser from a laser

pointer passed through it (Figure 2.7). From UV-vis absorbance measurements, $\geq 98\%$ of hairy particles were transferred from the aqueous to the ionic liquid layer (Figure 2.8). The pH of the aqueous phase was then adjusted to 7.03. The hairy particles moved spontaneously back to the aqueous phase with $\sim 2\%$ of particles staying in [EMIM][TFSA] after 4 h from UV-vis absorbance analysis. This process was further repeated and in each transfer at least 96% of particles migrated to another phase (Figures 2.7 and 2.8). The quantitative results were consistent with those shown in Figure 2.5; all particles resided in the ionic liquid phase at 40 °C when the pH of the aqueous phase was 3.05 (Figure 2.5A) and $\sim 95\%$ of particles was located in water at the same temperature when the pH was 7.07 (Figure 2.5E). The pH-driven, nearly complete transfer of hairy particles at a fixed temperature demonstrated the unique capability of this type of thermo- and pH-sensitive polymer brush-grafted silica particles.

2.3.6 Multiple Transport Processes of Thermo- and pH-Sensitive P(TEGMMA-*co*-MAA) Hairy Particles between Aqueous and [EMIM][TFSA] Layers by Controlling Both pH and Temperature

We further demonstrated that thermo- and pH-sensitive P(TEGMMA-*co*-MAA) hairy particles can be transported back and forth between water and [EMIM][TFSA] phases under different conditions by controlling both temperature and pH. A 1.0 mg/mL aqueous dispersion of P(TEGMMA-*co*-MAA) hairy particles with pH of 3.01 was carefully placed on top of an equal volume of [EMIM][TFSA] in a glass vial (Figure 2.9A). The system remained unchanged after stirring in a 5 °C water bath for 2 h (Figure 2.9B). The temperature was then raised to 40 °C and the mixture was stirred for 1 h. As can be seen from Figure 2.9C, the particles moved to the ionic liquid layer; the aqueous layer

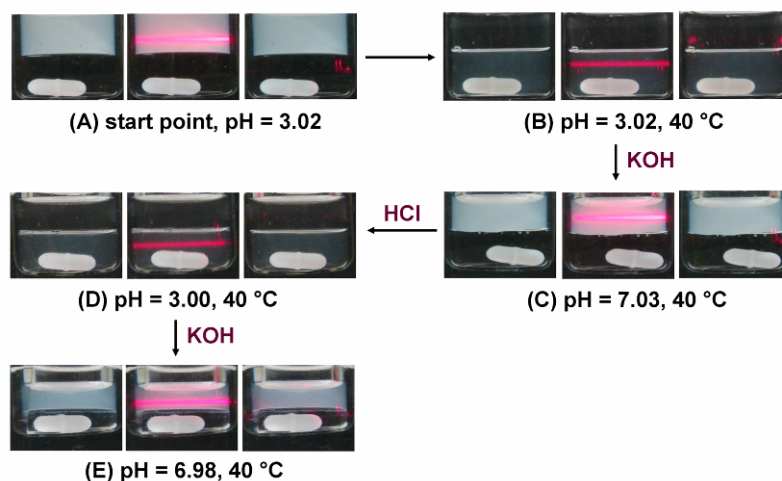


Figure 2.7 Transfer of thermo- and pH-sensitive P(TEGMMA-*co*-MAA) hairy particles driven by changing the pH of the aqueous layer between 3.0 and 7.0. (A) The start point of the experiment at which the pH of the aqueous layer was 3.02; (B) after the system was stirred at 40 °C for 4 h; (C) after the pH of the aqueous layer was changed to 7.03 and the mixture was stirred at 40 °C for 4 h; (D) after the pH was adjusted to 3.00 and the system was stirred at 40 °C for 4 h; (E) after the pH was changed to 6.98 and the system was stirred overnight at 40 °C. In each group of pictures, the left one shows the vial without a laser beam; the central and right pictures show the vial with a laser beam passing through the top and bottom layer, respectively.

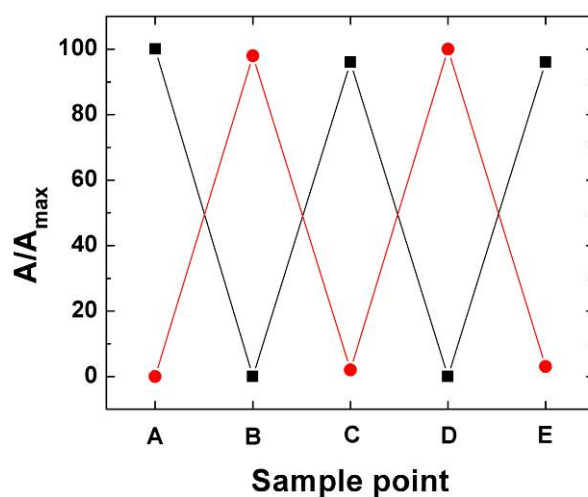


Figure 2.8 Normalized absorbances ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous layer (solid square) and the ionic liquid phase (solid circle) at sampling points corresponding to those in Figure 7. A and $A_{\max}$ represent the absorbance under a given condition at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm.

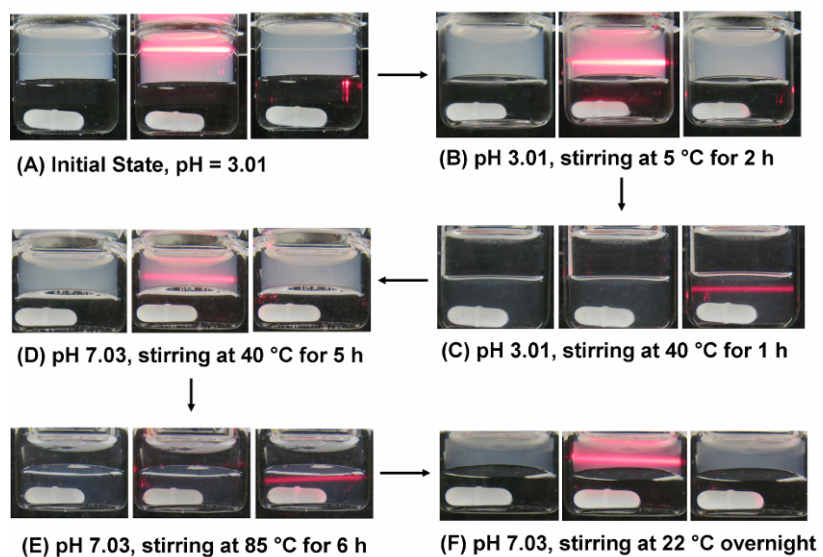


Figure 2.9 Multiple transfer processes of thermo- and pH-sensitive P(TEGMMA-*co*-MAA) hairy particles between aqueous and [EMIM][TFSA] phases under different conditions by controlling both temperature and pH.

exhibited almost no scattering when a laser beam passed through it. We then changed the pH of the aqueous phase to 7.03; the particles migrated to the top layer (Figure 9D). Increasing the temperature from 40 to 85 °C induced the transfer of hairy particles to the bottom layer (Figure 9E). After the temperature was lowered to room temperature and the mixture was stirred overnight, the particles were found in the aqueous layer. Quantitative analysis using UV-vis absorbance measurements indicated that $\geq 96\%$ of particles moved to another phase in each transfer. This experiment demonstrated the unique advantage of the design of thermo- and pH-sensitive hairy particles by the incorporation of a small amount of carboxylic acid groups into thermosensitive polymer brushes.

2.4 Conclusions

Thermo- and pH-sensitive P(TEGMMA-*co*-MAA) brush-grafted silica particles were prepared by surface-initiated ATRP of TEGMMA and *t*BMA with a molar ratio of 100 : 11 in the presence of a free initiator and subsequent treatment with TFA to remove the *tert*-butyl groups.³⁸ To study the pH-dependence of CP of the corresponding untethered polymer P(TEGMMA-*co*-MAA) in water, we treated P(TEGMMA-*co*-*t*BMA), the free polymer formed from the free initiator in the synthesis of P(TEGMMA-*co*-*t*BMA) hairy particles, with TFA, yielding thermo- and pH-sensitive P(TEGMMA-*co*-MAA). The CP of P(TEGMMA-*co*-MAA) in both aqueous solutions and [EMIM][TFSA]-saturated aqueous solutions increased with the increase of pH. At a specific pH, the CP of P(TEGMMA-*co*-MAA) in water in the presence of [EMIM][TFSA] was higher than that in the absence of [EMIM][TFSA] by at least 4 °C, which was presumably caused by the interaction between [EMIM]⁺ cations and the ionized carboxylic acid groups in the

polymer brushes. The hairy particles can be reversibly transported between water and [EMIM][TFSA] upon heating at 80 °C and cooling at 10 °C at pH values of 2.99, 5.00, and 7.02. From UV-vis absorbance measurements, the T_{tr} of P(TEGMMA-*co*-MAA) hairy particles from water to [EMIM][TFSA] upon heating increased with the increase of the pH of the aqueous layer, from 29.5 °C at pH = 3.05 to 69.4 °C at pH = 7.07. The plot of T_{tr} versus pH exhibited a similar trend to that of CP of P(TEGMMA-*co*-MAA). Moreover, a linear relationship was observed between the T_{tr} of hairy particles and the CP of the corresponding free polymer. By taking advantage of the tunable transfer temperature of hairy particles, we demonstrated reversible transfer of hairy particles at a fixed temperature, 40 °C, by changing the pH of the aqueous layer, and multiple phase transfer processes of hairy particles under different conditions by controlling both temperature and pH, evidencing the unique feature of these thermo- and pH-sensitive hairy particles. The ability to tune the T_{tr} of hairy particles over a wide temperature range allows for a greater degree of flexibility in the design of thermosensitive hairy particles for potential applications, for example, in the development of new stimuli-responsive phase transfer catalysts.

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38. The work presented in this Chapter has been published in *Langmuir* as an article (*Langmuir* **2011**, *27*, 11324-11334). <http://pubs.acs.org/doi/abs/10.1021/la2031818>

Appendix B

for

**Chapter 2. Synthesis of Thermo- and pH-Sensitive Hairy Particles and
Their Stimuli-Induced Reversible Transfer Behavior between Water
and a Hydrophobic Ionic Liquid**

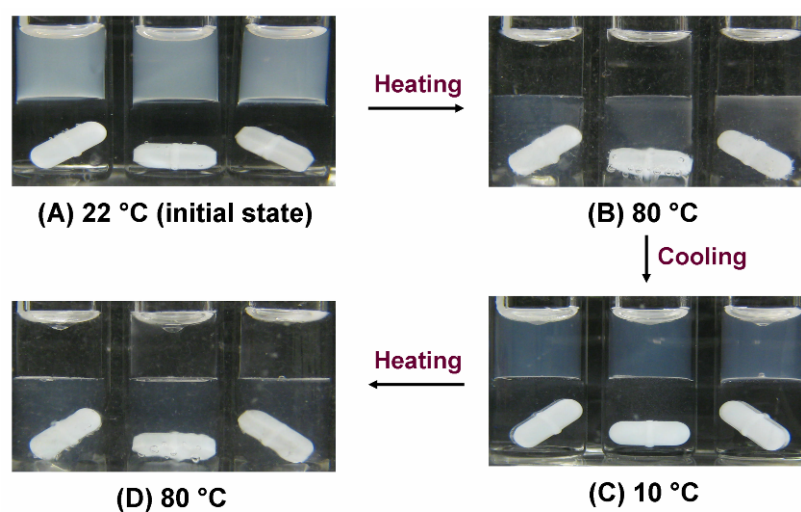


Figure B.1 Pictures of three water-[EMIM][TFSA] biphasic systems that contained thermo- and pH-sensitive P(TEGMMA-co-MAA) brush-grafted silica particles with a concentration of 1.0 mg/mL in the initial state at 22 °C (A), 80 °C after stirring for 2 h (B), 10 °C after stirring for 4 h (C), and 80 °C after stirring for 2 h (D). The pH values of aqueous layers in three vials from left to right were 2.99, 5.00, and 7.02, respectively. The pictures were taken using a digital camera.

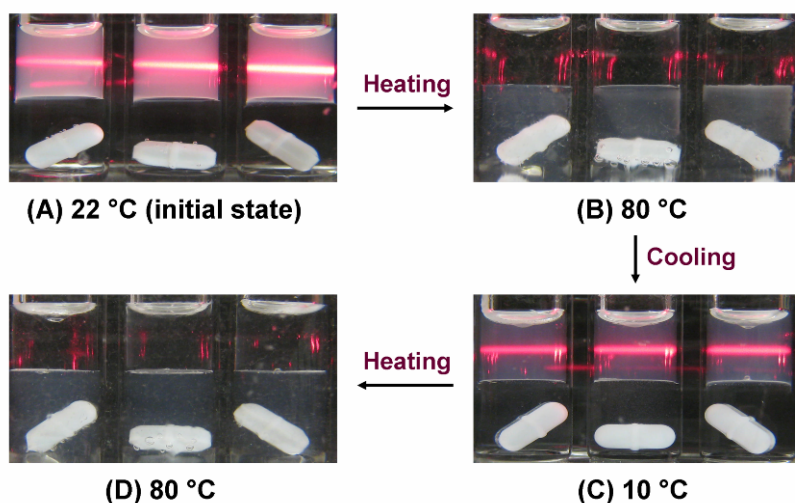


Figure B.2 Pictures of three water-[EMIM][TFSA] biphasic systems that contained thermo- and pH-sensitive P(TEGMMA-*co*-MAA) brush-grafted silica particles with a concentration of 1.0 mg/mL in the initial state at 22 °C (A), 80 °C after stirring for 2 h (B), 10 °C after stirring for 4 h (C), and 80 °C after stirring for 2 h (D). The pH values of aqueous layers in three vials from left to right were 2.99, 5.00, and 7.02, respectively. The pictures were taken when a laser beam from a laser pointer passed through the top aqueous layer.

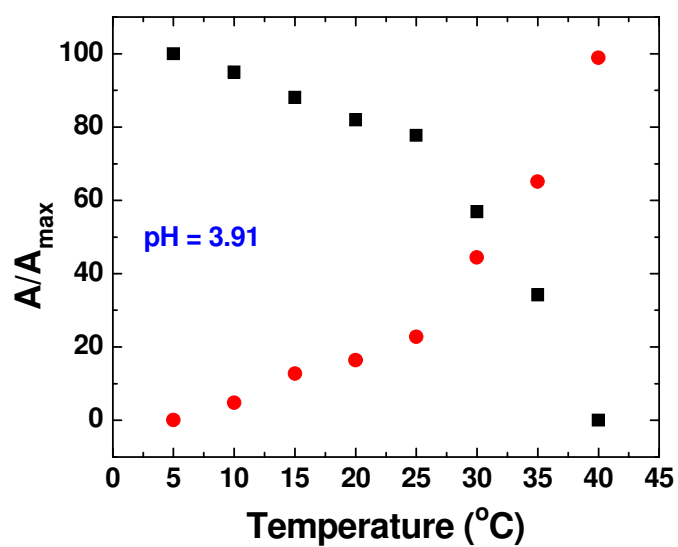


Figure B.3 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous phase with pH of 3.91 (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range.

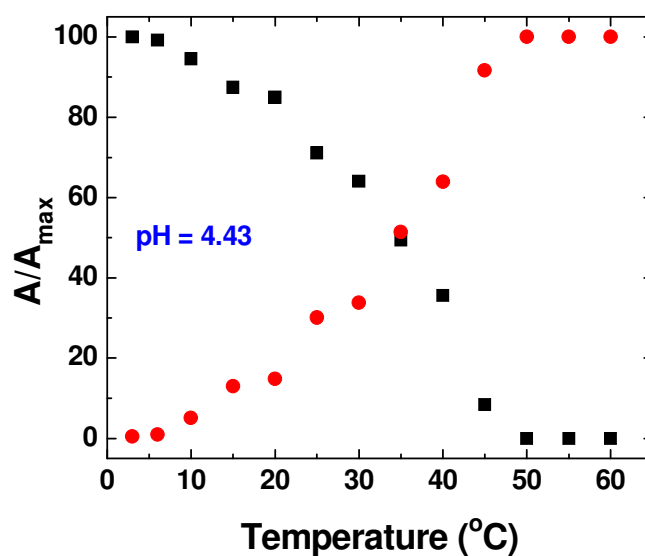


Figure B.4 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous phase with pH of 4.43 (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range.

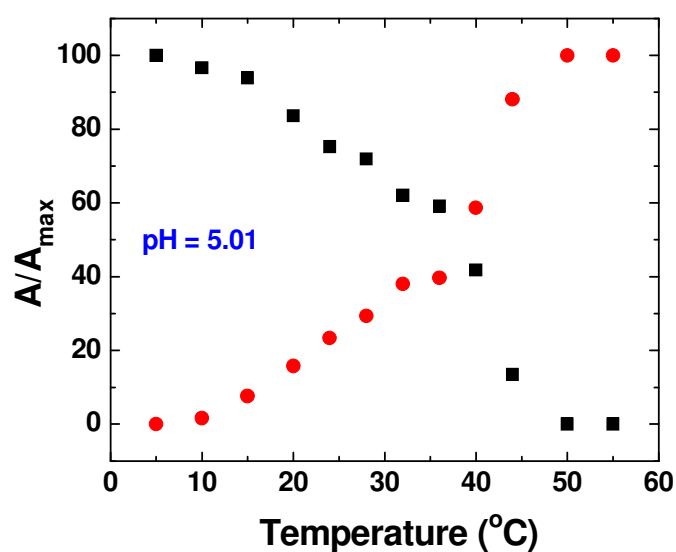


Figure B.5 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous phase with pH of 5.01 (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range.

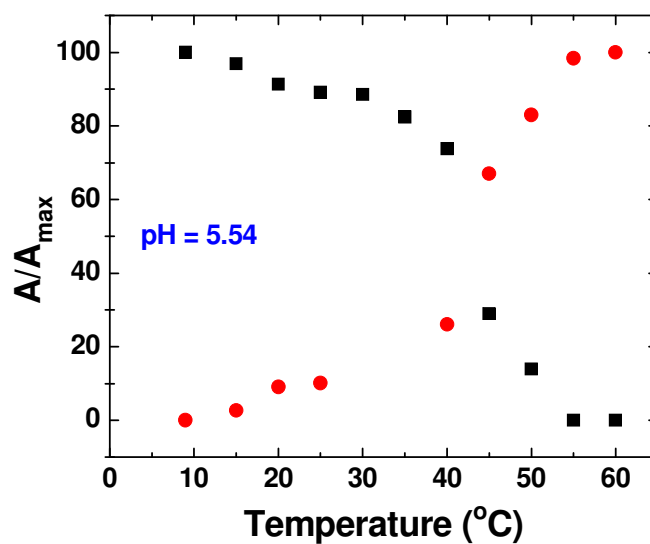
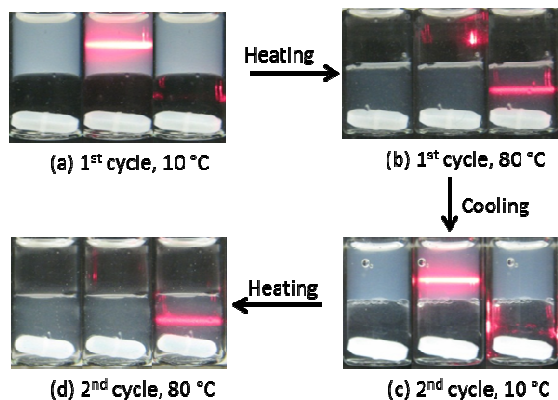


Figure B.6 Plot of normalized absorbance ($A/A_{\max}$) of P(TEGMMA-*co*-MAA) hairy particles in the aqueous phase with pH of 5.54 (solid square) and the ionic liquid phase (solid circle) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range.

**Chapter 3. Synthesis of Thermosensitive Polymer Brushes on Sub-100
nm Silica Nanoparticles and Their Thermally Induced Phase Transfer
Behavior between Water and a Hydrophobic Ionic Liquid**

Abstract

Using surface-initiated atom transfer radical polymerization, we synthesized a series of thermosensitive polymer brush-grafted silica particles from 67 nm silica nanoparticles functionalized with a triethoxysilane-terminated ATRP initiator and poly(*tert*-butyl acrylate) brushes from 27 nm silica nanoparticles. The thermosensitive hairy nanoparticles can undergo reversible transfer between water and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]), a common hydrophobic ionic liquid, upon heating at 80 °C and cooling at 10 °C. The transfer temperatures of thermosensitive polymer brush-grafted 67 nm silica nanoparticles were found to be higher by 1-3 °C than those of thermosensitive polymer brush-grafted silica particles with silica core sizes of 205 and 215 nm. Thermodynamic analysis showed that both standard enthalpy and entropy changes for the transfer of hairy nanoparticles from water to [EMIM][TFSA] were positive, indicating that the particle transfer was entropically driven. Kinetics studies showed that thermosensitive polymer brush-grafted 67 nm silica nanoparticles moved faster (by 1.8 times) from the aqueous phase to the ionic liquid phase than thermosensitive polymer brush-grafted 205 and 215 nm silica particles at temperatures 15 °C above the respective transfer temperatures.



3.1 Introduction

Efficient transfer of substances (small molecules, macromolecules, particles, etc.) across boundaries between immiscible phases is critical to a wide variety of applications, including separation, catalysis, and transport across biological membranes.¹⁻¹⁰ Although one way transfer of materials from one phase to another immiscible phase has been widely used, it may not be suitable for some applications as it often involves protection-deprotection or other structural modifications to induce the transfer.⁷ Recently, there has been a growing interest to develop methods for reversible transfer of substances between immiscible liquids at a quantitative or a nearly quantitative level. Such methods could be used, for example, to develop next generation recyclable catalysts. An appealing strategy to induce reversible transfer is to introduce stimulus-responsive groups or polymers to the systems and apply external stimuli to reversibly modify their affinities to two immiscible liquids, allowing a simple and active control over their locations.^{1-6,9-22} For example, Liu and Wang prepared a ruthenium catalyst that contained a light-responsive spiropyran moiety and showed that the catalyst can be triggered to transfer between two immiscible organic phases by light.³ Desset and Cole-Hamilton reported a recyclable rhodium catalyst that can be induced to move back and forth between aqueous and organic phases by bubbling with and removal of CO₂.⁴

Environmentally responsive polymer brush-grafted particles (“hairy” particles), which can undergo spontaneous structural or conformational changes in response to environmental variations, are an intriguing class of nanostructured materials with potential applications in many areas.²³⁻²⁵ The core of such hairy particles can be inorganic, metal, or polymeric nanoparticles. The polymer brushes can be made by

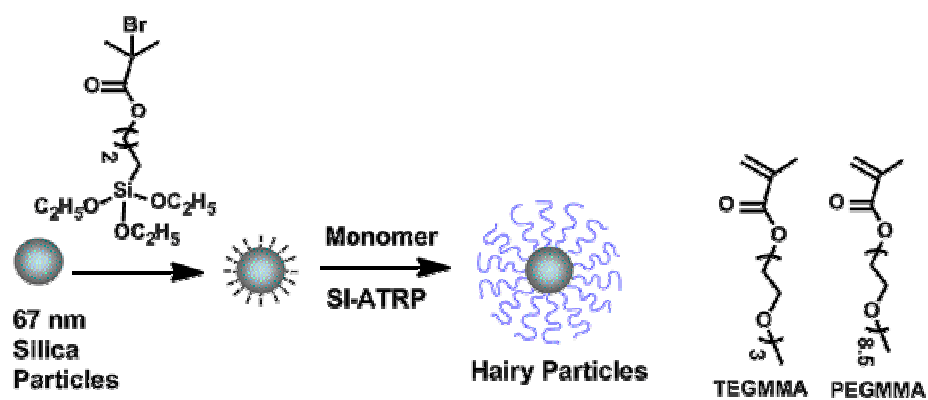
grafting preformed polymers to the surface of core particles or growing from initiator-functionalized particles.²³ Using surface-initiated atom transfer radical polymerization (SI-ATRP), our group previously synthesized a series of thermosensitive polymer brushes on silica particles with a typical average size of ~ 200 nm.^{12,24a,26,27} When the lower critical solution temperature (LCST) of polymer brushes was sufficiently high, the hairy particles can undergo thermally induced spontaneous, reversible and quantitative transfer between water and ethyl acetate or 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]), a common hydrophobic ionic liquid.^{12,26} By introducing a small amount of weak carboxylic acid groups into thermosensitive polymer brushes, we showed that the particle transfer between an aqueous solution and [EMIM][TFSA] can be induced by either temperature or pH changes or both.²⁷

When the particle size is reduced to tens of nanometers, new properties are likely to emerge as can be seen from the progress in the field of inorganic and metal nanoparticles.²⁸ We reasoned that if the diameter of the silica core of our thermosensitive hairy particles is reduced to sub-100 nm, the hairy nanoparticles might transfer faster than bigger hairy particles between water and [EMIM][TFSA] and might be more stable against aggregation because of higher polymer contents in the hybrid nanoparticles. However, particles with a size of tens of nanometers are known to tend to form aggregates, making it very challenging to handle them during the reactions. For example, the surface functionalization process that we previously used for particles of ~ 200 nm, drying at 110 °C under high vacuum for at least 6 h and then dispersing in THF followed by the functionalization with a monochlorosilane, cannot be applied to silica

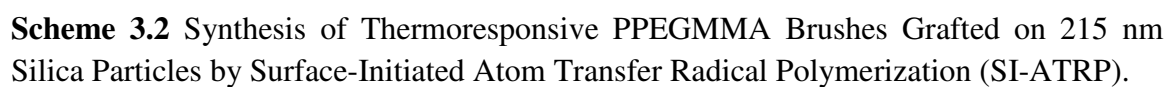
nanoparticles. This is because once the nanoparticles are dried at high temperatures in vacuo, they cannot be re-dispersed in THF. Therefore, new methods must be developed.

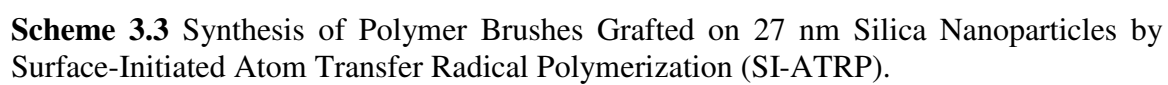
There have been a number of reports in the literature on the growth of polymer brushes from nanoparticles.^{29,30} For example, Pyun et al. directly functionalized silica nanoparticles that were dispersed in methyl isobutyl ketone with an ATRP-initiator-terminated monochlorosilane.²⁹ Polymer brushes were successfully synthesized from these nanoparticles. More recently, Ohno et al. developed a method to fix a triethoxysilane-terminated ATRP initiator onto 15 nm silica nanoparticles that were made by a lysine-mediated synthesis process and grew polymer brushes by surface-initiated ATRP.³⁰ The ATRP initiator was immobilized onto the silica nanoparticles through an ammonia-catalyzed hydrolysis/condensation process.

In the present work, we used a method similar to that reported by Ohno et al.³¹ to immobilize an ATRP initiator onto the surface of 67 nm silica nanoparticles and grew poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) and poly(methoxypoly(ethylene glycol) methacrylate) (PPEGMMA) brushes by SI-ATRP (Scheme 3.1). The thermally induced phase transfer behavior of these hairy nanoparticles between water and [EMIM][TFSA] was studied. For comparison, we also synthesized PPEGMMA brushes on 215 nm silica particles (Scheme 3.2). The synthesis of polymer brushes from 27 nm silica nanoparticles, made by the lysine-mediated process, was also attempted (Scheme 3.3). We examined the effects of particle size on reversibility, thermodynamics, and kinetics of temperature-induced phase transfer of thermosensitive hairy particles between water and [EMIM][TFSA]. With a reduction in the size of silica particles, there is an increase in transfer temperature and transfer rate of hairy particles.



Scheme 3.1 Synthesis of Thermoresponsive Polymer Brush Grafted on Silica Nanoparticles with an Average Size of 67 nm by Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP).





3.2 Experimental Part

3.2.1 Materials

CuBr₂ (anhydrous, 99%) was purchased from Acros and used as received. Triethoxysilane (95%) was obtained from Acros and stored in a refrigerator prior to use. Platinum-divinyltetramethyldisiloxane complex in xylene (2.1~2.4% Pt concentration in xylene) was purchased from Gelest, Inc. Tetrahydrofuran (THF) was distilled from sodium and benzophenone and used immediately for the dispersion of bare silica particles that were dried in high vacuum. CuBr (98%, Aldrich) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol and diethyl ether. After being dried in vacuum, the purified CuBr was stored in a desiccator. *N, N, N', N', N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and ethyl 2-bromoisobutyrate (98%, Aldrich) were dried with calcium hydride, distilled under reduced pressure, and stored in a desiccator. Poly(ethylene glycol) methyl ether methacrylate (or methoxypoly(ethylene glycol) methacrylate, PEGMMA, average $M_n = 475$, Aldrich) was passed through a basic alumina column to remove the inhibitor and dried under high vacuum prior to use. Methoxytri(ethylene glycol) methacrylate (TEGMMA) was synthesized according to the procedure reported previously.²⁶ 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]) was prepared via a synthetic route described in the literature.³² The clear and colorless liquid was dried in a vacuum oven at 60 °C for 3 days prior to use. Allyl 2-bromo-2-methylpropanoate and hex-5-en-1-yl 2-bromo-2-methylpropanoate were synthesized according to the literature procedures.^{26,30} Snowtex-ST-OL (a 20 wt% aqueous dispersion of silica nanoparticles with a size of 40-50 nm from the manufacturer) was kindly provided by

Nissan Chemical USA. All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

3.2.2 Characterization

Size exclusion chromatography (SEC) was carried out at ambient temperature using PL-GPC 20 (an integrated SEC system from Polymer Laboratories, Inc.) with a refractive index detector, one PLgel 5 μ m guard column (50 $\times$ 7.5 mm), and two PLgel 5 μ m mixed-C columns (each 300 $\times$ 7.5 mm, linear range of molecular weight from 200 to 2,000,000 according to Polymer Laboratories, Inc.). The data were processed using Cirrus GPC/SEC software (Polymer Laboratories, Inc.). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Polystyrene standards (Polymer Laboratories, Inc.) were employed for calibration. ^1H NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer. Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ from room temperature to 800 $^{\circ}\text{C}$ using TA Q-series Q50. Transmission electron microscopy micrographs were acquired using a FEI Tecnai T12 at an accelerating voltage of 100 kV. UV-Vis measurements were taken on a Thermo-Scientific Evolution 600 UV-Vis spectrophotometer.

3.2.3 Synthesis of Themosensitive Polymer Brushes Grafted on 67 nm Silica Particles

3.2.3.1 Synthesis of $\{[(2\text{-Bromo-2-methylpropionyl)oxy}]\text{propyl}\}$ triethoxysilane Functionalized Silica Particles

Snotex-ST-OL from Nissan chemical USA was an aqueous dispersion. The silica nanoparticles were isolated by centrifugation (Eppendorf 5804, 11000 rpm, 25 min) and re-dispersed in ethanol via ultrasonication. The nanoparticles were separated again by

centrifugation and re-dispersed in ethanol. This process was repeated an additional two times. A small portion of the dispersion was taken out, weighed, and dried under high vacuum to determine the mass percent of silica nanoparticles in the dispersion. The average size of the nanoparticles was 67 nm, measured from TEM micrographs using software Nano Measurer 1.2.

A typical procedure for the immobilization of $\{[(2\text{-bromo-2-methylpropionyl})\text{oxy}]\text{propyl}\}$ triethoxysilane, a triethoxysilane-terminated ATRP initiator, onto the surface of 67 nm silica nanoparticles is detailed as follows. Allyl 2-bromo-2-methylpropanoate (0.312 g, 1.51 mmol) was added into a 25 mL two-necked flask and dried at room temperature in vacuum for 1 h. Triethoxysilane (2.0 mL, 10.8 mmol) was injected into the flask using a disposable syringe under N_2 atmosphere, followed by addition of the platinum-divinyltetramethyldisiloxane complex in xylene (30 μL). The mixture was stirred at 30 $^{\circ}\text{C}$ under nitrogen atmosphere, and the hydrosilylation reaction was monitored by ^1H NMR spectroscopy. Once the reaction was complete, excess triethoxysilane was removed by vacuum at 40 $^{\circ}\text{C}$ and the product was used directly for the functionalization of silica nanoparticles.

In another round bottom flask, bare silica nanoparticles (500 mg) were dispersed in ethanol (30 mL) by ultrasonication. A solution of ammonium hydroxide (25% in water, 2.75 g) in ethanol (12 mL) was added into the nanoparticle dispersion. After the mixture was stirred at 40 $^{\circ}\text{C}$ for 2 h, a solution of $\{[(2\text{-bromo-2-methylpropionyl})\text{oxy}]\text{-propyl}\}$ triethoxysilane, freshly prepared from 0.312 g of allyl 2-bromo-2-methylpropanoate, in ethanol (3 mL) was added dropwise into the dispersion. After the mixture was stirred at 40 $^{\circ}\text{C}$ for 22.5 h, the nanoparticles were isolated by centrifugation,

redispersed in ethanol, and centrifuged again. This washing process was repeated with ethanol again and then THF three times, followed by drying with a stream of air flow to yield ATRP-initiator-functionalized silica nanoparticles designated as IP-67-I (492 mg). Initiator particles IP-67-II and -III were synthesized by using similar procedures.

3.2.3.2 Synthesis of Poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) Brushes Grafted on 67 nm Silica Nanoparticles by Surface-Initiated Atom Transfer Radical Polymerization

CuBr (13.1 mg, 91 μ mol), CuBr₂ (10.6 mg, 47 μ mol), and initiator nanoparticles IP-67-I (24.9 mg) were added into a two-necked flask and dried under high vacuum at room temperature for 3 h. The initiator nanoparticles were then dispersed in anisole (12.053 g) by ultrasonication. Methoxytri(ethylene glycol) methacrylate (TEGMMA, 8.057 g, 34.7 mmol) and free initiator ethyl 2-bromoisobutyrate (13.8 mg, 71 μ mol) were added into the flask. After the mixture was degassed by three freeze-pump-thaw cycles, *N,N,N',N',N''*-pentamethyldiethylenetriamine (15.4 mg, 89 μ mol) was added via a microsyringe at the thawing point of the mixture. A sample was taken immediately for ¹H NMR spectroscopy analysis. The flask was then placed in an oil bath with a preset temperature of 50 °C. The polymerization was monitored by ¹H NMR spectroscopy. After the reaction proceeded for 5 h, the flask was removed from the oil bath and opened to air; the mixture was diluted with THF (20 mL). The nanoparticles were isolated by centrifugation (Eppendorf 5804, 11000 rpm, 25 min) and the supernatant liquid was passed through a short column of silica gel (bottom)/activated basic aluminum oxide (top) (2/1, v/v). The free polymer was analyzed by SEC relative to polystyrene standards. The $M_{n,SEC}$ and polydispersity index (PDI) were 26.6 kDa and 1.11, respectively. The

polymer brush-grafted particles, designated as PTEGMMA-67, were re-dispersed in THF and isolated by centrifugation. This purification process was repeated an additional four times. The polymer content of hairy particles was determined by thermogravimetric analysis (TGA). The monomer conversion was calculated from the integrals of the peaks at 5.57 ppm ($\text{CHH}=\text{C}$ - from monomer) at 0 min and 5 h by using the peaks located at 4.29 and 4.08 ppm, which were from $-\text{CH}_2\text{OOC}-$ of monomer and the polymer, respectively, as the internal standard. The degree of polymerization (DP) of the free polymer PTEGMMA was calculated from the monomer-to-free initiator molar ratio and the monomer conversion. Assuming a 100% initiator efficiency, the calculated DP of PTEGMMA was 184. The grafting density of PTEGMMA brushes on nanoparticles was 0.24 chains/nm^2 , which was calculated using the DP of PTEGMMA and the TGA data.

3.2.3.3 Synthesis of Poly(methoxypoly(ethylene glycol) methacrylate) (PPEGMMA) Brushes Grafted on 67 nm Silica Nanoparticles by Surface-Initiated Atom Transfer Radical Polymerization

CuBr (13.1 mg, 91 μmol), CuBr₂ (10.6 mg, 47 μmol), and initiator particles IP-67-I (26.4 mg) were placed into a two-necked flask and dried under high vacuum at room temperature for 3 h. The initiator particles were then dispersed in anisole (15.036 g) by ultrasonication. Methoxypoly(ethylene glycol) methacrylate (PEGMMA, average $M_n = 475$, 15.014 g, 31.6 mmol) and free initiator ethyl 2-bromoisobutyrate (13.9 mg, 71 μmol) were added into the flask. After the mixture was degassed by three freeze-pump-thaw cycles, N,N,N',N',N'' -pentamethyldiethylenetriamine (16.6 mg, 96 μmol) was added via a microsyringe at the thawing point of the mixture. A sample was taken immediately for ^1H NMR spectroscopy analysis. The flask was then placed in an oil bath with a preset

temperature of 60 °C. The polymerization was monitored by ^1H NMR spectroscopy. After the reaction proceeded for 5 h, the flask was removed from the oil bath and opened to air; the mixture was diluted with THF (20 mL). The nanoparticles were isolated by centrifugation (Eppendorf 5804, 11000 rpm, 30 min) and the supernatant liquid was passed through a short column of silica gel (bottom)/activated basic aluminum oxide (top) (2/1, v/v). The free polymer was analyzed by SEC relative to polystyrene standards. The $M_{n,\text{SEC}}$ and PDI were 21.1 kDa and 1.14, respectively. The polymer brush-grafted particles were re-dispersed in THF and isolated by centrifugation. This purification process was repeated an additional four times. The hairy nanoparticles are designated as PPEGMMA-IP-I. A small portion of hairy nanoparticles was dried under high vacuum at 45 °C for at least 5 h and analyzed by TGA for the polymer content. The DP of free polymer PPEGMMA was 133, calculated from the monomer-to-free initiator molar ratio and the monomer conversion assuming a 100% initiator efficiency. The grafting density of PPEGMMA brushes on silica nanoparticles was 0.19 chains/nm², calculated by using the DP of PPEGMMA and TGA data. The surface-initiated polymerizations of PPEGMMA from IP-67-II and -III and the characterizations of the resultant hairy particles were carried out in a similar manner.

3.2.4 Synthesis of Thermosensitive Polymer Brushes Grafted on 215 nm Silica Particles

3.2.4.1 Synthesis of 215 nm Silica Particles

Ammonium hydroxide (25% in water, 13.988 g) and tetraethoxysilane (TEOS, 7.01 g) were dissolved separately in ethanol (each 10 mL). The two solutions were added to a 500 mL round bottom flask that contained 180 mL ethanol under vigorous stirring. The

concentrations of NH_3 , TEOS, and water in the solution were 0.455, 0.153, and 2.658 M, respectively. The mixture was stirred vigorously at room temperature for 4 h. The particles were then isolated by centrifugation (Eppendorf 5804 centrifuge, 8000 rpm, 15 min), re-dispersed in ethanol, and centrifuged again. This washing process was repeated with water three times and ethanol two times. The particles were then dried with a stream of air flow. The average size of the silica particles in THF, measured by dynamic light scattering, was 215 nm.

3.2.4.2 Hydrosilylation and Immobilization of 6-(Chlorodimethylsilyl)hexyl 2-Bromo-2-methylpropanoate on 215 nm Silica Particles

Hex-5-en-1-yl 2-bromo-2-methylpropanoate (252 mg, 1.01 mmol) was added into a 25 mL two-necked round bottom flask and dried at room temperature under high vacuum for 30 min. Chlorodimethylsilane (2.0 mL, 18 mmol) was injected via a disposable syringe into the flask under nitrogen atmosphere, followed by the addition of Pt complex in xylenes (30 μL). The mixture was stirred under nitrogen at room temperature, and the progress of the hydrosilylation reaction was monitored by ^1H NMR spectroscopy. Once the reaction proceeded to completion, excess chlorodimethylsilane was removed by vacuum. The product 6-(chlorodimethylsilyl)hexyl 2-bromo-2-methylpropanoate was then dissolved in anhydrous THF (2.0 mL) for the functionalization of silica particles.

Bare silica particles (1.004 g) were dried at 110 $^\circ\text{C}$ under high vacuum overnight. The particles were then dispersed in anhydrous THF (10 mL) by ultrasonication and stirring. The solution of 6-(chlorodimethylsilyl)hexyl 2-bromo-2-methylpropanoate in THF was added into the particle dispersion using a syringe. The flask was placed in a 70 $^\circ\text{C}$ oil bath and the reaction mixture was stirred under nitrogen atmosphere for 48 h. The

particles were then isolated by centrifugation (8000 rpm, 15 min), re-dispersed in THF, and isolated again. This process was repeated an additional four times before. The obtained initiator particles, designated as IP-215, were dried in a stream of air flow.

3.2.4.3 Surface-Initiated Atom Transfer Radical Polymerization of Methoxypoly(ethylene glycol) Methacrylate (PEGMMA) from 215 nm Silica Particles

CuBr (7.8 mg, 54 μmol), CuBr₂ (3.8 mg, 17 μmol), and initiator particles IP-215 (68.3 mg) were placed into a two-necked flask and dried under high vacuum at room temperature for 3 h. The initiator particles were then dispersed in anisole (12 mL) by ultrasonication. Methoxypoly(ethylene glycol) methacrylate (PEGMMA, average $M_n = 475$, 12.000 g, 25.3 mmol) and free initiator ethyl 2-bromoisobutyrate (8.2 mg, 42 μmol) were added into the flask. After the mixture was degassed by three freeze-pump-thaw cycles, *N,N,N',N',N''*-pentamethyldiethylenetriamine (10.1 mg, 58 μmol) was added via a microsyringe at the thawing point of the mixture. A sample was taken immediately for ¹H NMR spectroscopy analysis. The flask was then placed in a 60 °C oil bath. The polymerization was monitored by ¹H NMR spectroscopy. After the reaction proceeded for 90 min, the flask was removed from the oil bath and opened to air; the mixture was diluted with THF (20 mL). The particles were isolated by centrifugation (Eppendorf 5804, 11000 rpm, 30 min) and the supernatant liquid was passed through a short column of silica gel (bottom)/activated basic aluminum oxide (top) (2/1, v/v). The free polymer was analyzed by SEC relative to polystyrene standards. The $M_{n,\text{SEC}}$ and PDI were 23.0 kDa and 1.17, respectively. The polymer brush-grafted particles were re-dispersed in THF and isolated by centrifugation. This purification process was repeated an additional

four times. The obtained hairy particles are designated as PPEGMMA-215. A small portion of hairy particles was dried at 45 °C under high vacuum for at least 5 h and analyzed by TGA. The DP of the free polymer PPEGMMA was 135, calculated from the molar ratio of monomer to free initiator and the monomer conversion. The grafting density of PPEGMMA brushes on silica particles was 0.40 chains/nm², which was calculated by using the DP of PPEGMMA and TGA results of hairy particles and IP-215.

3.2.5 Synthesis of Polymer Brushes Grafted on 27 nm Silica Nanoparticles

3.2.5.1 Synthesis of 27 nm Silica Nanoparticles by *L*-Lysine Mediated Condensation

Water (139 g) and octane (7.312 g) were heated at 60 °C in a 250 mL three-necked round bottom flask equipped with a condenser for 15 min. To this heated mixture were added *L*-lysine (0.149 g), TEOS (10.395 g), and a single drop of ammonium hydroxide. The mixture was stirred vigorously at this temperature for 20 h. It was then heated to 100 °C and allowed to stand still for 24 h. The system was cooled to room temperature; the organic and aqueous phases were separated from one another. The aqueous phase was dialyzed against DI water for 4 days. DLS measurements showed that the average size of silica nanoparticles was 27 nm after the dialysis. The nanoparticle dispersion was transferred to a 250 mL round bottom flask, and ethylene glycol (35.004 g, 564 mmol) was added. The mixture was rotovapped at 55 °C for 1 h and then placed under high vacuum to remove volatiles. The remaining mixture was dispersed in ethanol (20 mL).

3.2.5.2 Surface Functionalization of 27 nm Silica Nanoparticles with [(2-Bromo-2-methylpropionyl)oxy]propyl}triethoxysilane

Allyl 2-bromo-2-methylpropanoate (4.019 g, 19 mmol) was added into a 25 mL two-necked flask and dried at room temperature under vacuum for 1 h. Triethoxysilane (10.0

g, 60.9 mmol) was injected into the flask via a syringe under N₂ atmosphere, followed by addition of the platinum-divinyltetramethyldisiloxane complex in xylene (50 µL). The mixture was stirred at 30 °C under nitrogen atmosphere and the hydrosilylation reaction was monitored by ¹H NMR spectroscopy. Once the reaction was complete, excess triethoxysilane was removed by vacuum at 45 °C and a portion of the product (1.63 g) was used directly for surface functionalization of 27 nm silica nanoparticles. A portion of the nanoparticle dispersion in ethanol (4 mL) was added to a 100 mL round bottom flask that contained a solution of triethylamine (1.56 g, 15.4 mmol) in ethanol (46 mL). After the mixture was sonicated and stirred for 1 h, {[2-bromo-2-methylpropionyl)oxy]propyl}triethoxysilane (1.63 g) was added. The reaction mixture was then stirred at room temperature for 2 days. After the mixture was concentrated under high vacuum, it was dispersed in acetone (10 mL) and precipitated in hexanes (200 mL). The supernatant liquid was poured off, and the nanoparticles were re-dispersed in acetone. This process was repeated an additional two times. After the third precipitation, a portion of the nanoparticle dispersion (7.996 g) was added to dimethyl formamide (5.006 g). The volatile compounds were then removed by high vacuum to yield ATRP-initiator-functionalized silica nanoparticles (IP-27) dispersed in DMF.

3.2.5.3 Synthesis of Poly(*tert*-butyl acrylate) Brushes Grafted on 27 nm Silica Nanoparticles

CuBr (24.2 mg, 169 µmol), CuBr₂ (8.4 mg, 38 µmol), *N,N*-dimethylformamide (DMF, 9 mL), and a dispersion of 64 mg of initiator particles IP-27 in DMF (1.64 g) were added into a two-necked flask. The mixture was ultrasonicated using a ultrasonic water bath. *tert*-Butyl acrylate (9.226 g, 72.0 mmol) and free initiator ethyl 2-bromoisobutyrate

(26.5 mg, 141 μmol) were added into the flask. After the mixture was degassed by three freeze-pump-thaw cycles, *N,N,N',N',N''*-pentamethyldiethylenetriamine (29.4 mg, 169 μmol) was added by a microsyringe at the thawing point of the mixture. A sample was taken immediately for ^1H NMR spectroscopy analysis. The flask was then placed in an oil bath with a preset temperature of 75 $^{\circ}\text{C}$. The polymerization was monitored by ^1H NMR spectroscopy. After the polymerization proceeded for 8 h, the flask was removed from the oil bath and opened to air; the mixture was diluted with THF (20 mL). The nanoparticles were isolated by centrifugation (Beckman L8-M ultracentrifuge, 30,000 rpm, 60 min). The isolated nanoparticles were then redispersed in THF by ultrasonication and centrifuged again. This washing cycle was repeated for a total of three times.

3.2.5.4 Cleavage of Grafted PtBA from 27 nm Silica Nanoparticles for SEC Analysis

PtBA brush-grafted silica nanoparticles (6 mg) were dispersed in toluene (2 mL) by ultrasonication and stirring. The nanoparticle dispersion was then transferred to a small plastic container, followed by the addition of an aqueous solution of hydrofluoric acid (48-51%, 0.2 mL). The mixture was stirred at room temperature for 225 min, and then neutralized with a saturated calcium hydroxide solution. The cleaved polymer was extracted from the mixture with toluene three times, and the combined organic layer was dried with anhydrous sodium sulfate. The solution was then filtered and the solvent was removed. The obtained polymer was analyzed by SEC; $M_{n,\text{SEC}} = 11.0$ kDa, PDI = 1.20.

3.2.6 Reversible Transfer of Thermosensitive Polymer Brush-Grafted Silica Particles between Water and [EMIM][TFSA] Induced by Temperature Changes.

Described below is a typical procedure for the thermally induced reversible transfer of PPEGMMA brush-grafted 67 nm silica nanoparticles (PPEGMMA-67-I, $M_{n,\text{SEC}} = 21.1$

kDa) between water and [EMIM][TFSA] by changing temperature back and forth between 10 and 80 °C. Similar procedures were employed for transfer of other thermosensitive hairy particles between aqueous and ionic liquid phases.

The PEGMMA brush-grafted 67 nm silica nanoparticles (PEGMMA-67-I, 1.6 mg, PEGMMA $M_{n,SEC} = 21.1$ kDa) were dispersed in water (1.599 g) in a 20 mL scintillation vial. The dispersion was then carefully transferred into a 3.7 mL vial that contained [EMIM][TFSA] (2.432 g, 1.60 mL) at ambient temperature (22 °C). The vial was then placed into an oil bath with a preset temperature of 80 °C. The system was stirred at a stirring rate of 500 rpm for 180 min. The transfer of the hairy nanoparticles from water to the ionic liquid phase at this time was complete. The vial was then removed from the oil bath and the mixture was stirred at 10 °C at 500 rpm for 240 min. The heating and cooling cycle was repeated for a total of ten times.

3.2.7 Determination of Transfer Temperature of Thermosensitive Hairy Particles from Water to [EMIM][TFSA] upon Heating.

The determination of transfer temperature of PEGMMA brush-grafted 67 nm silica nanoparticles (PEGMMA-67-I, PEGMMA $M_{n,SEC} = 21.1$ kDa) from water to [EMIM][TFSA] upon heating is detailed below. The transfer temperatures of other hairy particles from water to the ionic liquid phase were measured using similar procedures.

The PEGMMA brush-grafted silica nanoparticles (PEGMMA-67-I, 8.1 mg) were dispersed in water that was saturated with [EMIM][TFSA] at room temperature overnight (8.102 g) in a 20 mL scintillation vial. The aqueous nanoparticle dispersion was then carefully transferred into a 20 mL vial that contained [EMIM][TFSA] (12.162 g, 8.00 mL). The 20 mL vial with an inner diameter of 2.7 cm was custom-made and equipped

with a valve that can be opened to allow the insertion of a needle to take samples. The biphasic system was stirred with a magnetic stir bar (dimension 4.5×12 mm) at a stirring rate of 500 rpm at 25 °C. After stirring for at least 12 h, the system was allowed to stand still for 30 min at the same temperature; an aliquot (0.4 mL) was taken from each layer and diluted to 0.6 mL with the corresponding pure liquid for UV-vis absorbance measurement. The temperature was then increased to 30 °C and the aforementioned process was repeated. The same procedure was applied for other temperatures (35, 40, 43, 45, 46, 47, 50, and 55 °C).

In another vial, water and [EMIM][TFSA] of equal volumes were stirred at the same stirring rate and temperature and for the same amount of time as for the biphasic system that contained hairy nanoparticles PPEGMMA-67-I. At each temperature, an aliquot (0.4 mL) was taken from each layer after the system was allowed to stand still without stirring for 30 min and was diluted to 0.6 mL with the corresponding pure liquid. These liquids were used as references for the measurements of absorbances of the corresponding samples taken at the same temperature from the biphasic system that contained hairy nanoparticles. The absorbances of the diluted dispersions at the wavelength of 500 nm were recorded at room temperature using a UV-visible spectrometer.

3.2.8 Kinetics Study of Phase Transfer of Thermosensitive Hairy Particles from Water to [EMIM][TFSA] at a Temperature 15 °C above the Transfer Temperature.

The kinetics study of phase transfer of thermosensitive PPEGMMA brush-grafted 67 nm silica nanoparticles from water to [EMIM][TFSA] upon heating is detailed as follows. Similar procedures were used for kinetics studies of thermally induced phase transfer of other thermosensitive hairy particles.

The PPEGMMA brush-grafted 67 nm silica nanoparticles (PPEGMMA-67-I, PPEGMMA $M_{n,SEC} = 21.1$ kDa, 8.0 mg) were dispersed in water that was saturated with [EMIM][TFSA] overnight at room temperature (8.004 g) in a 20 mL scintillation vial. The hairy nanoparticle dispersion was then carefully transferred into a 20 mL vial that contained [EMIM][TFSA] (12.129 g, 7.98 mL). The 20 mL vial with an inner diameter of 2.7 cm was custom-made and equipped with a valve that can be opened to allow the insertion of a needle to take samples. The vial was then placed into an oil bath with a preset temperature of 60 °C ($t = 0$ min), and the biphasic system was stirred with a magnetic stir bar (dimension 4.5×12 mm) at a stirring rate of 500 rpm. After $t = 20$ min, an aliquot (0.4 mL) was taken from each layer and diluted to 0.6 mL with the corresponding pure liquid for UV-Vis absorbance measurement. Samples were withdrawn from the system at various time intervals ($t = 35, 50, 70, 90, 110, 130,$ and 150 min) until there was no scattering observed from the water layer.

In another vial, water and [EMIM][TFSA] of equal volumes were stirred at the same stirring rate and temperature and for the same amount of time as for the biphasic system that contained hairy nanoparticles PPEGMMA-67-I. An aliquot (0.4 mL) was taken from each layer at the same time interval as for the sample from the vial containing the hairy particle dispersion, and diluted to 0.6 mL with the corresponding pure liquid. These aliquots were used as references for the measurement of absorbances of the corresponding samples taken at the same time interval from the biphasic system that contained hairy particles. The absorbances of the diluted dispersions at the wavelength of 500 nm were recorded at room temperature using a UV-visible spectrometer.

3.3 Results and Discussion

3.3.1 Synthesis of ATRP-Initiator Functionalized Silica Particles with Average Diameters of 67 nm, 215 nm, and 27 nm

It is known that sub-100 nm silica nanoparticles cannot be readily dispersed in THF or ethanol once dried at elevated temperatures under high vacuum. Therefore, a different method was used in this work to immobilize an ATRP initiator onto the sub-100 nm silica particles. The 67 nm silica nanoparticles, provided by Nissan Chemical USA, were functionalized with a triethoxysilane-terminated ATRP initiator, $\{[(2\text{-bromo-2-methylpropionyl})\text{oxy}]\text{propyl}\}\text{triethoxysilane}$, via an ammonia-catalyzed hydrolysis and condensation process in ethanol. This method, first reported by Ohno et al.,³¹ does not require the drying of bare silica nanoparticles in high vacuum at elevated temperatures. Their results suggested that a uniform initiator layer was formed on the surface of silica particles. Three batches of ATRP-initiator-functionalized 67 nm silica nanoparticles were made using similar conditions and are designated as IP-67-I, IP-67-II, and IP-67-III. Figure 3.1A shows the TGA data of IP-67-I and bare silica nanoparticles. A difference of 4.14 % in the weight retentions at 800 °C was observed.

The silica particles with an average size of 215 nm were synthesized by the Stöber process, which is known to produce silica particles with a relatively narrow size distribution.³³ These silica particles were functionalized with a monochlorosilane-terminated ATRP initiator, 6-(chlorodimethylsilyl)hexyl 2-bromo-2-methylpropanoate. The obtained initiator particles are designated as IP-215. TGA analysis showed that there was a difference of 3.78 % in the weight retentions of IP-215 and bare silica particles at 800 °C (Figure 3.1B) when the difference in the weight retentions between initiator

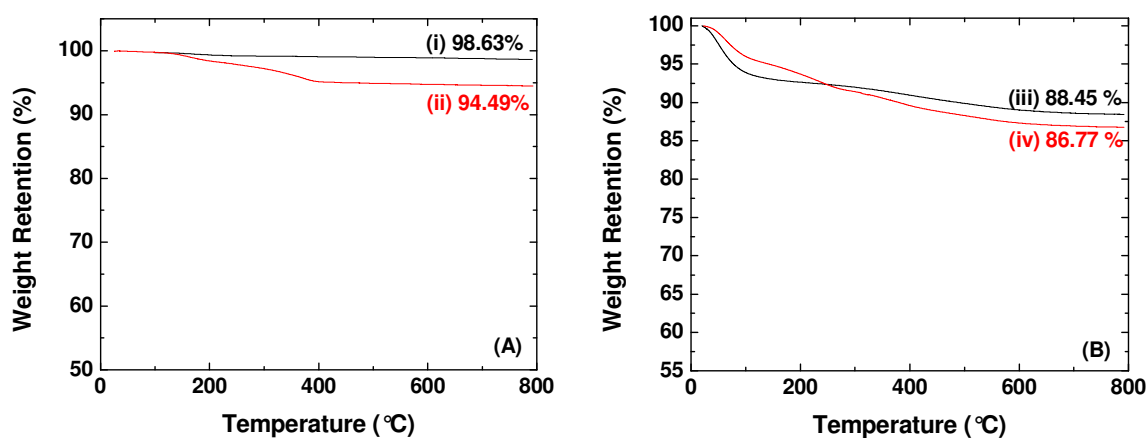


Figure 3.1 (A) Thermogravimetric analysis of (i) 67 nm bare silica nanoparticles and (ii) ATRP-initiator-functionalized 67 nm silica nanoparticles (IP-67-I). (B) Thermogravimetric analysis of (iii) 215 nm bare silica particles and (iv) ATRP-initiator-functionalized 215 nm silica particles (IP-215).

particles and bare particles at 100 °C is taken into consideration. This result is comparable with our previously reported results.^{26,27} We also synthesized 27 nm silica nanoparticles through a lysine-mediated process³⁴ and functionalized them with 3-(triethoxysilyl)propyl 2-bromo-2-methylpropanoate, a triethoxysilane-terminated ATRP initiator.³⁰ The resultant initiator nanoparticles are designated as IP-27.

3.3.2 Synthesis of Polymer Brushes Grafted on Silica Particles with Different Sizes

A series of thermosensitive polymer brushes, either poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) or poly(methoxypoly(ethylene glycol) methacrylate) (PPEGMMA) brushes, were grown from the ATRP-initiator-functionalized 67 nm silica nanoparticles by surface-initiated atom transfer radical polymerizations. The polymerizations were carried out in anisole using CuBr/CuBr₂/*N,N,N',N',N''*-pentamethyldiethylenetriamine as catalyst in the presence of a free initiator, ethyl 2-bromoisobutyrate (EBiB). The addition of EBiB not only enabled the surface-initiated polymerization to be better controlled but also allowed for the progress of the polymerization to be readily monitored by size exclusion chromatography and ¹H NMR spectroscopy. Our group's previous work showed that the molecular weight of the grafted polymer was essentially identical to that of the free polymer formed from the free initiator during a controlled/"living" radical polymerization.

Figure 3.2A shows the SEC traces of free PTEGMMA at different polymerization times in the synthesis of thermosensitive PTEGMMA brush-grafted 67 nm silica nanoparticles (PTEGMMA-67). Clearly, the peak shifted to the high molecular weight side with the increase of time. The $M_{n,SEC}$ increased from 4.0 kDa at 30 min to 9.1 kDa at 60 min, to 16.1 kDa at 120 min, 19.6 kDa at 180 min, 24.6 kDa at 240 min, and 26.6 kDa

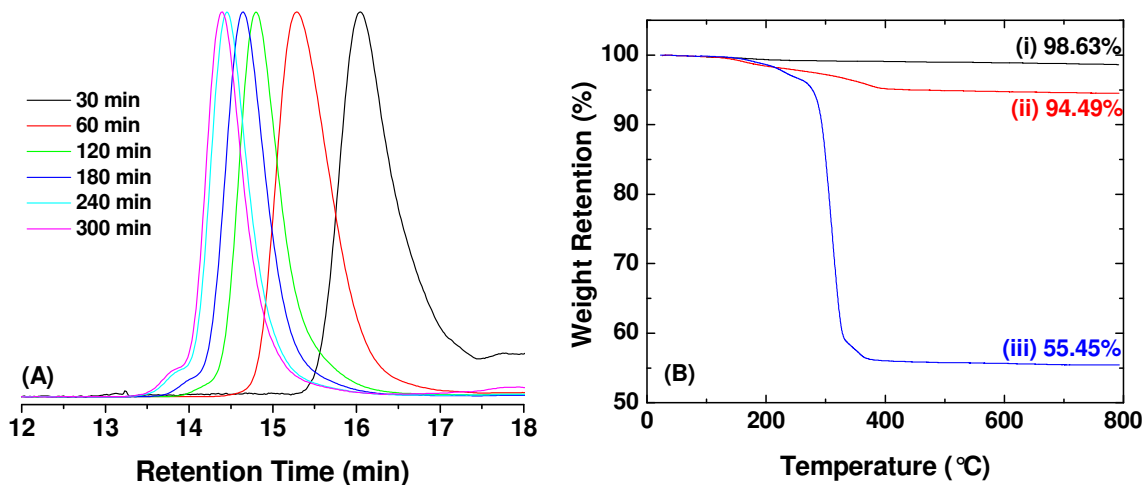


Figure 3.2 (A) Size exclusion chromatograph traces of poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) free polymers formed from free initiator ethyl 2-bromoisobutyrate at 30, 60, 120, 180, 240, and 300 min in the synthesis of PTEGMMA brushes (PTEGMMA-67) from ATRP-initiator-functionalized 67 nm silica nanoparticles (IP-67-I). Polymerization condition: $[\text{EBiB}]_0:[\text{CuBr}]_0:[\text{CuBr}_2]_0:[\text{PMDETA}]_0:[\text{TEGMMA}]_0 = [1]:[1.3]:[0.7]:[1.3]:[489]$, 50 °C. (B) Thermogravimetric analysis of (i) 67 nm bare silica particles, (ii) ATRP-initiator-functionalized silica nanoparticles (IP-67-I), and (iii) PTEGMMA brush-grafted 67 nm silica nanoparticles made from IP-67-I.

at 300 min, and the PDI gradually decreased from 1.15 at 30 min to 1.11 at 300 min. All these indicated that the polymerization was controlled. For this particular polymerization, the reaction was stopped at 300 min. The $M_{n,SEC}$ and PDI of the final polymer were 26.6 kDa and 1.11, respectively. The monomer conversion was calculated from the 1H NMR spectra at 0 and 300 min. The degree of polymerization (DP) of PTEGMMA was 184, calculated by using the monomer-to-free initiator ratio and the monomer conversion. Figure 3.2B shows the TGA data of the obtained PTEGMMA brush-grafted 67 nm silica nanoparticles (PTEGMMA-67); the weight retention at 800 °C was 55.45 %, much lower than that of IP-67-I at 800 °C, suggesting that PTEGMMA brushes were successfully grown on the surface of silica nanoparticles. By using the TGA data and the DP of PTEGMMA and assuming that the density of silica nanoparticles is 2.07 g/mL, we calculated the grafting density of PTEGMMA brushes on the 67 nm silica nanoparticles. It was 0.24 chains/nm², similar to those of thermosensitive hairy particles presented in Chapters 1 and 2.

A total of four thermosensitive hairy particle samples were made from 67 nm silica nanoparticles (PTEGMMA-67-I, PPEGMMA-67-I, PPEGMMA-II, and PPEGMMA-III) and one PPEGMMA brush-grafted silica particle sample was synthesized from the ATRP-initiator-functionalized 215 nm silica particles (PPEGMMA-215). The SEC traces of free polymers and TGA data of hairy particles and corresponding bare and initiator particles are shown in Figures 3.3, 3.4, 3.5, and 3.6. The characterization data are summarized in Table 3.1. Also included in Table 3.1 are two hairy particle samples synthesized from 205 nm particles that were functionalized with an ATRP initiator from the work described in Chapter 1 (PTEGMMA-205 and PPEGMMA-205).

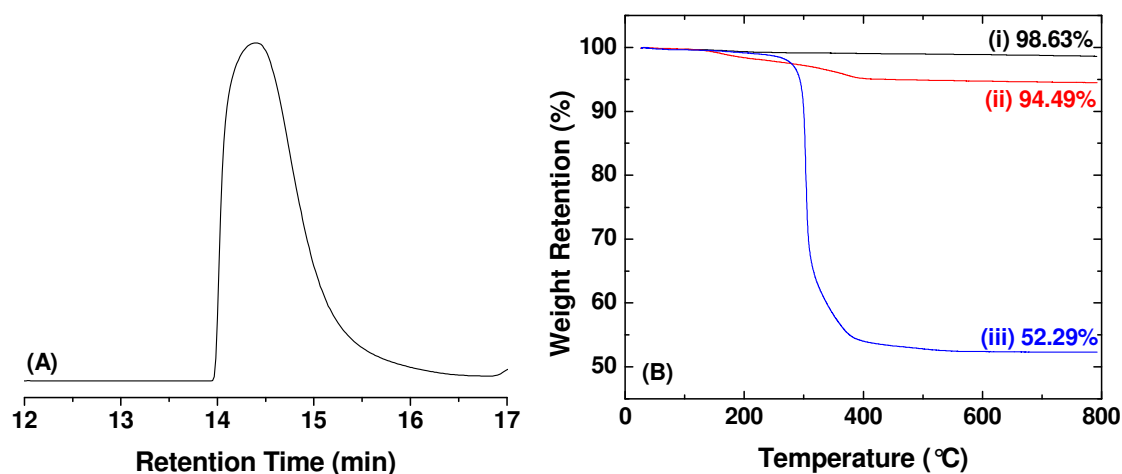


Figure 3.3 (A) Size exclusion chromatography trace of PPEGMMA free polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of PPEGMMA brush-grafted silica nanoparticles (PPEGMMA-67-I) from initiator particles IP-67-I. $M_{n,SEC} = 21.1$ kDa and $PDI = 1.14$. Polymerization condition: $[EBiB]_0:[CuBr]_0:[CuBr_2]_0:[PMDETA]_0:[PEGMMA]_0 = [1]:[1.3]:[0.7]:[1.4]:[445]$, 60 °C. (B) Thermogravimetric analysis of (i) 67 nm bare silica particles, (ii) ATRP-initiator-functionalized silica nanoparticles (IP-67-I), and (iii) PPEGMMA brush-grafted 67 nm silica nanoparticles (PPEGMMA-67-I) synthesized from IP-67-I with PPEGMMA $M_{n,SEC}$ of 21.1 kDa.

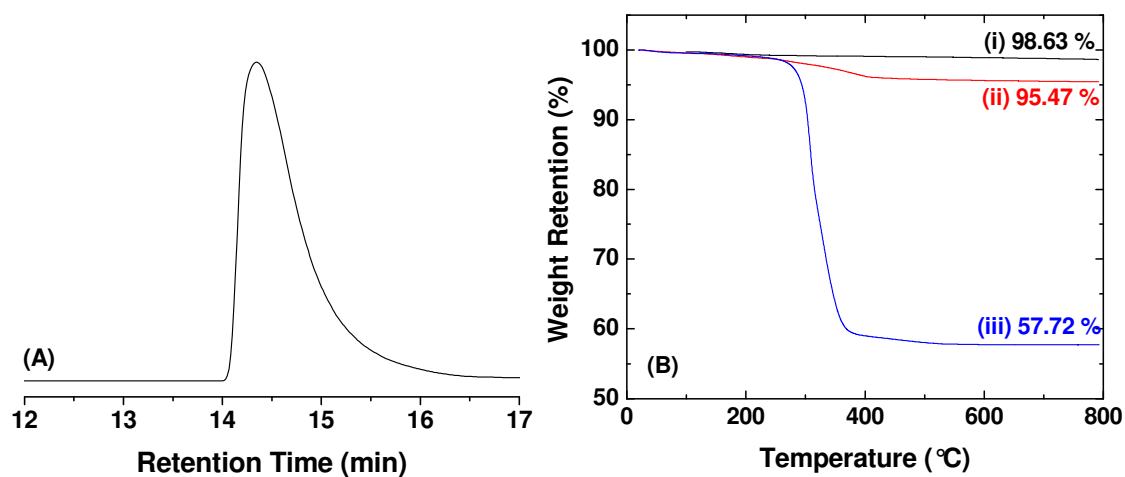


Figure 3.4 (A) Size exclusion chromatography trace of PPEGMMA free polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of PPEGMMA brush-grafted silica nanoparticles (PPEGMMA-67-II) from initiator particles IP-67-II. $M_{n,SEC} = 22.0$ kDa and $PDI = 1.19$. Polymerization condition: $[EBiB]_0:[CuBr]_0:[CuBr_2]_0:[PMDETA]_0:[PEGMMA]_0 = [1]:[1.4]:[0.9]:[1.5]:[439]$, 65 °C. (B) Thermogravimetric analysis of (i) 67 nm bare silica particles, (ii) ATRP-initiator-functionalized silica nanoparticles (IP-67-II), and (iii) PPEGMMA brush-grafted 67 nm silica nanoparticles (PPEGMMA-67-II) synthesized from IP-67-II with PPEGMMA $M_{n,SEC}$ of 22.0 kDa.

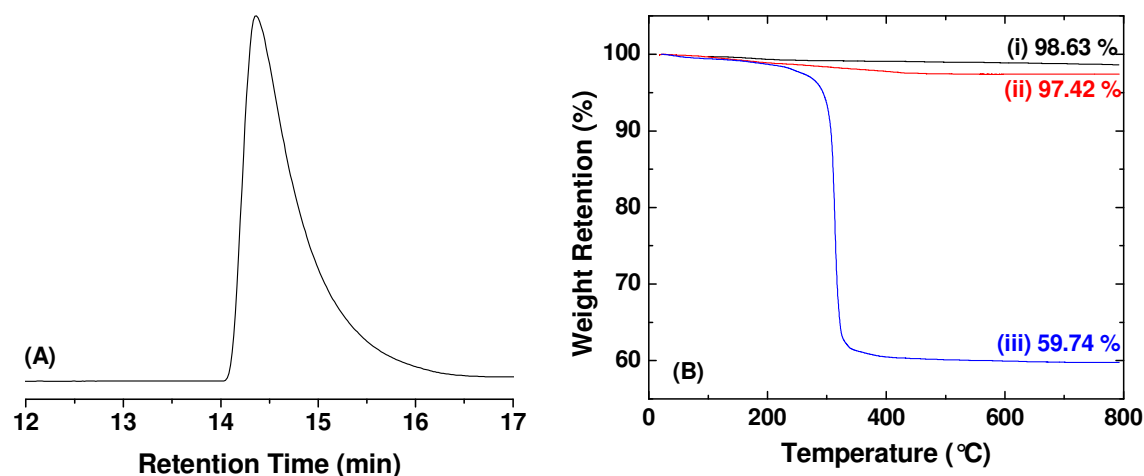


Figure 3.5 (A) Size exclusion chromatography trace of PPEGMMA free polymer formed from free initiator 2-ethyl 2-bromoisobutyrate in the synthesis of PPEGMMA brush-grafted silica nanoparticles (PPEGMMA-67-III) from initiator particles IP-67-III. $M_{n,SEC} = 21.2$ kDa and $PDI = 1.20$. Polymerization condition: $[EBiB]_0:[CuBr]_0:[CuBr_2]_0:[PMDETA]_0:[PEGMMA]_0 = [1]:[1.3]:[0.8]:[1.3]:[442]$, $65^\circ C$. (B) Thermogravimetric analysis of (i) 67 nm bare silica particles, (ii) ATRP-initiator-functionalized silica nanoparticles (IP-67-III), and (iii) PPEGMMA brush-grafted 67 nm silica nanoparticles (PPEGMMA-67-III) synthesized from IP-67-III with PPEGMMA $M_{n,SEC}$ of 21.2 kDa.

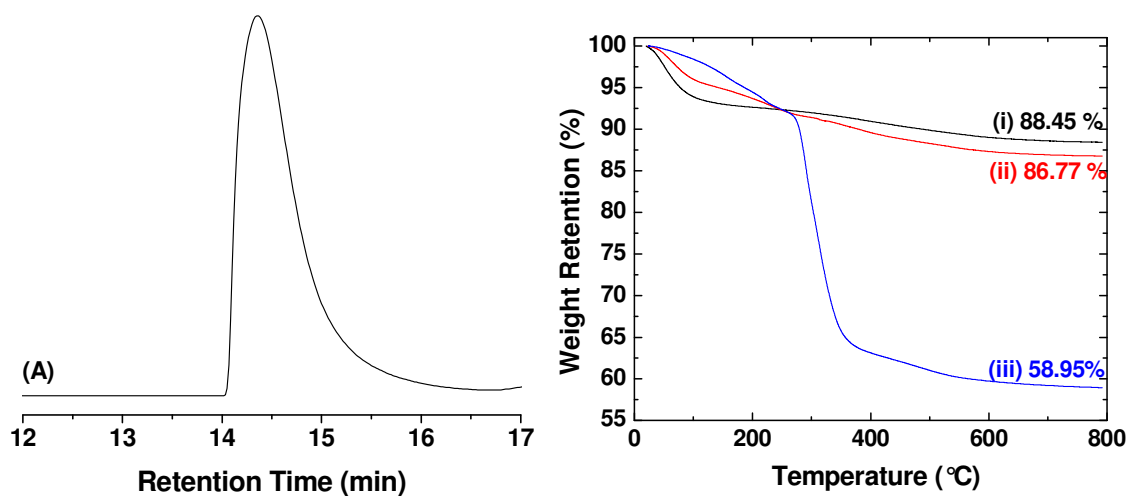


Figure 3.6 (A) Size exclusion chromatography trace of PPEGMMA free polymer formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of PPEGMMA brush-grafted silica particles from initiator particles IP-215. $M_{n,SEC} = 23.0$ kDa and PDI = 1.17. Polymerization condition: $[EBiB]_0:[CuBr]_0:[CuBr_2]_0:[PMDTA]_0:[PEGMMA]_0 = [1]:[1.3]:[0.4]:[1.4]:[602]$, 60 °C. (B) Thermogravimetric analysis of (i) 215 nm bare silica particles, (ii) ATRP-initiator-functionalized silica particles (IP-215), and (iii) PPEGMMA brush-grafted 215 nm silica particles synthesized from IP-215 with PPEGMMA $M_{n,SEC}$ of 23.0 kDa.

Table 3.1 Characterization Data for five Thermosensitive Polymer Brush-Grafted Particle Samples Synthesized from Initiator Particles and their Corresponding Free Polymers as well as Two Thermosensitive Hairy Particle Samples from Chapter 1.

Thermosensitive Hairy Particles	Initiator Particles	Average Size of Bare Particles	Free Polymer ^g $M_{n,SEC}$, PDI, DP	Grafting Density (Chains/nm ²) ^h
PTEGMMA-67 ^a	IP-67-I	67 nm	26.6 kDa, 1.11, 184	0.24
PPEGMMA-67-I ^b	IP-67-I	67 nm	21.1 kDa, 1.14, 133	0.19
PPEGMMA-67-II ^c	IP-67-II	67 nm	22.0 kDa, 1.19, 138	0.14
PPEGMMA-67-III ^d	IP-67-III	67 nm	21.2 kDa, 1.20, 131	0.14
PPEGMMA-215 ^e	IP-215	215 nm	23.0 kDa, 1.17, 135	0.40
PTEGMMA-205 ^f	NA	205 nm	31.0 kDa, 1.16, 190	0.26
PPEGMMA-205 ^f	NA	205 nm	23.0 kDa, 1.12, 128	0.24

^a SEC of free polymer and TGA data are presented in Figure 3.2; ^b SEC of free polymer and TGA data are presented in Figure 3.3; ^c SEC of free polymer and TGA data are presented in Figure 3.4; ^d SEC of free polymer and TGA data are presented in Figure 3.5; ^e SEC of free polymer and TGA data are presented in Figure 3.6; ^f Samples are from the work described in Chapter 1; ^g $M_{n,SEC}$ and PDI were obtained from SEC using polystyrene calibration. The DPs were calculated by using the monomer-to-free initiator molar ratio and monomer conversion. ^h The grafting density for each sample was calculated by using the DP of free polymer and TGA data.

The synthesis of polymer brushes from 27 nm silica nanoparticles functionalized with an ATRP initiator was attempted. We first tested the atom transfer radical polymerization

of *tert*-butyl acrylate (*t*BA), which was carried out in anisole at 75 °C using CuBr/CuBr₂/*N,N,N',N',N''*-pentamethyldiethylenetriamine as catalyst in the presence of a free initiator, ethyl 2-bromoisobutyrate (EBiB). After the reaction proceeded for 8 h, the nanoparticles were isolated by centrifugation and repeatedly washed with THF. TGA analysis showed that the weight retention at 800 °C was 50.93 %, significantly lower than that of the ATRP initiator-functionalized 27 nm silica nanoparticles (IP-27) at the same temperature (77.24 %, see Figure 3.7A), indicating that *Pt*BA was successfully grown from the surface of initiator particles IP-27. This was further confirmed by TEM studies; the *Pt*BA brushes can be clearly seen from TEM micrographs (Figure 3.8). HF was then used to etch the *Pt*BA brush-grafted 27 nm silica particles. The cleaved *Pt*BA was analyzed by SEC; the $M_{n,SEC}$ and PDI were 11.0 kDa and 1.20, respectively (Figure 3.7B). Although SEC and TGA analysis showed that *Pt*BA can be grown from 27 nm silica nanoparticles, attempted synthesis of thermosensitive polymer brushes from the same batch of 27 nm initiator nanoparticles (IP-27) was not successful. No reactions were observed in the repeatedly attempted atom transfer radical polymerizations regardless of how the reaction conditions were varied. The reason was unclear. It appeared that there was some kind of inhibitor present in the initiator particle dispersion. More effort is needed to purify the initiator-functionalized 27 nm silica nanoparticles and to grow thermosensitive polymer brushes from silica nanoparticles of this size.

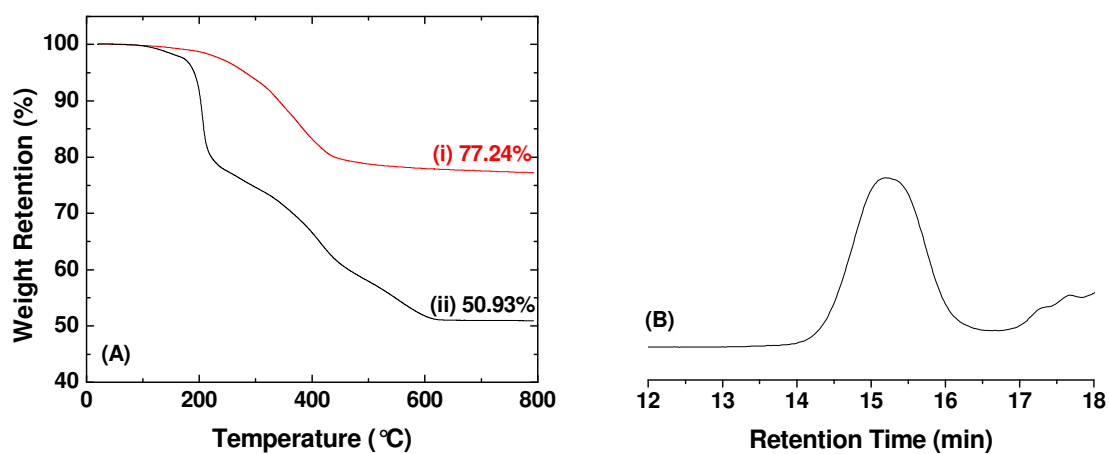


Figure 3.7 (A) Thermogravimetric analysis of (i) ATRP-initiator-functionalized 27 nm silica nanoparticles (IP-27), and (ii) PtBA brush-grafted 27 nm silica nanoparticles synthesized from IP-27. ATRP condition for the synthesis of PtBA brushes: $[\text{EBiB}]_0:[\text{CuBr}]_0:[\text{CuBr}_2]_0:[\text{PMDETA}]_0:[t\text{BA}]_0 = [1]:[1.2]:[0.3]:[1.2]:[511]$, 75 °C. (b) Size exclusion chromatography trace of PtBA cleaved from PtBA brush-grafted silica nanoparticles by the use of aqueous hydrofluoric acid. $M_{n,\text{SEC}} = 11.0$ kDa, PDI = 1.20.

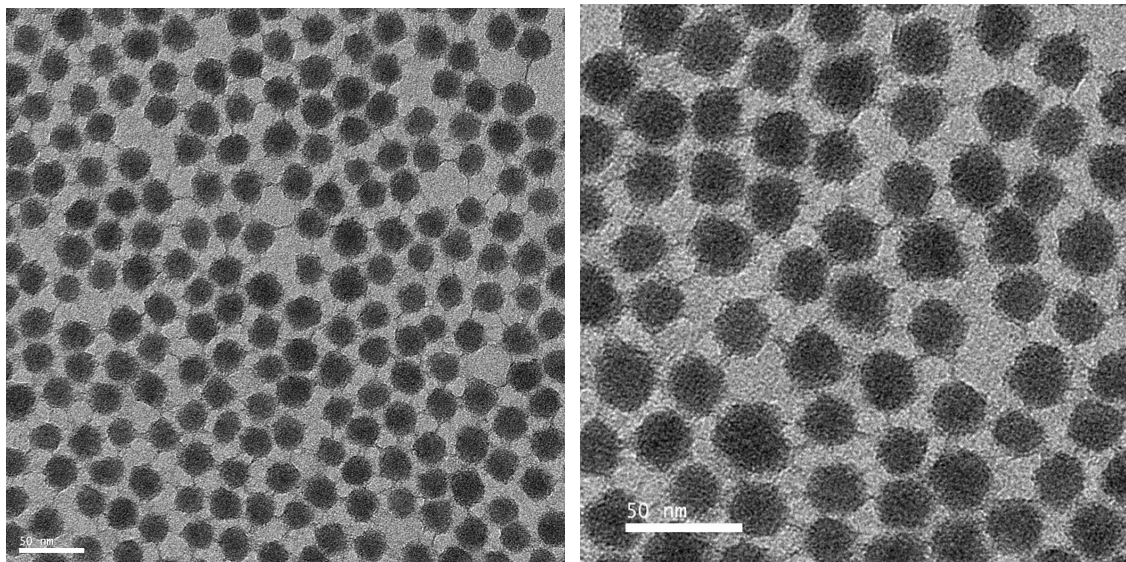


Figure 3.8 Top-view, bright field TEM micrographs of poly(*tert*-butyl acrylate) brush-grafted 27 nm silica nanoparticles synthesized by surface-initiated atom transfer radical polymerization (ATRP) from ATRP-initiator-functionalized 27 nm silica nanoparticles.

3.3.3 Temperature-Induced Reversible Phase Transfer of Thermosensitive Polymer Brush-Grafted Silica Particles with Different Sized Silica Cores.

We previously showed that 205 nm silica particles grafted with PEGMMA brushes can undergo quantitative and reversible transfer between water and a hydrophobic ionic liquid, [EMIM][TFSA], in response to changes in temperature for at least 10 times.²⁶ To study the phase transfer property of PEGMMA brush-grafted 67 nm silica nanoparticles, we first examined their reversible phase transfer behavior. PEGMMA-67-I hairy particles were dispersed in [EMIM][TFSA]-saturated deionized water at a concentration of 1.0 mg/mL. The hairy nanoparticle dispersion was then carefully added onto an equal volume of water-saturated [EMIM][TFSA] in a glass vial. The vial was placed in a 80 °C oil bath. After stirring at a stirring rate of 500 rpm for 3 h, the aqueous layer became clear and there was no scattering when a laser passed through it. Meanwhile, strong scattering was observed from the ionic liquid layer when a laser was applied, indicating that the transfer from water to [EMIM][TFSA] was complete. The vial was then removed from the oil bath and placed in a 10 °C water bath. The nanoparticles gradually moved back to the water layer and the transfer was complete in 4 h. The quantitative and reversible transfer induced by heating at 80 °C and cooling at 10 °C can be repeated at least 10 times. Figure 3.9 shows the pictures of the system at 10 and 80 °C in the 1st and 2nd cycles. For comparison, we also conducted reversible transfer of 215 nm silica particles grafted with PEGMMA brushes (PEGMMA-215) by heating at 80 °C and cooling at 10 °C and the pictures of the system in the 9th and 10th cycles are shown in Figure 3.10. Thus, qualitatively, the phase transfer behaviors of 67 and 215 nm silica particles grafted with PEGMMA brushes are very similar.

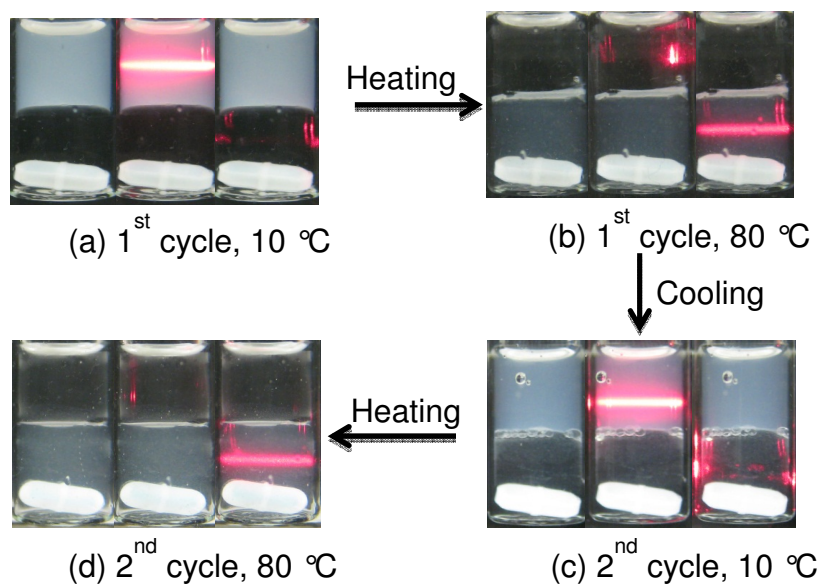


Figure 3.9 Pictures of a water-[EMIM][TFSA] biphasic system that contained PPEGMMA brush-grafted silica nanoparticles (PPEGMMA-67-I) at (a) 10 and (b) 80 °C in the 1st cycle and at (c) 10 and (d) 80 °C in the 2nd cycle. In each group of pictures, the left one shows the picture of the vial with no laser; the central and right ones show the vial with a laser beam passing through the top (water) layer and bottom (ionic liquid) layer, respectively.

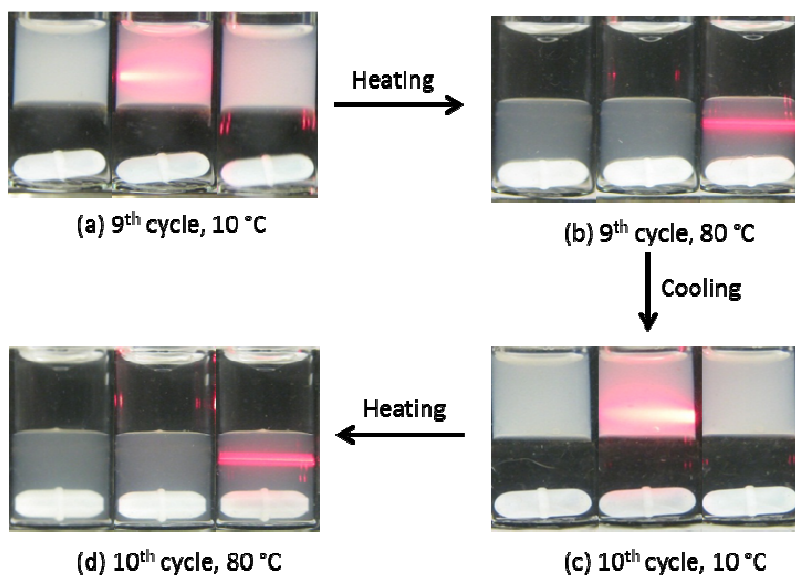


Figure 3.10 Pictures of a water-[EMIM][TFSA] biphasic system that contained PPEGMMA brush-grafted 215 nm silica particles (PPEGMMA-215) at (a) 10 and (b) 80 °C in the 9th cycle and at (c) 10 and (d) 80 °C in the 10th cycle. In each group of pictures, the left one shows the picture of the vial with no laser; the central and right ones show the vial with a laser beam passing through the top (water) layer and bottom (ionic liquid) layer, respectively.

3.3.4 Determination of Phase Transfer Temperatures of Thermosensitive Polymer Brush-Grafted Silica Particles with Different Sized Silica Cores

We then investigated if the transfer temperature (T_{tr}) of thermosensitive hairy particles from water to [EMIM][TFSA] upon heating is affected by the size of silica core particles. The transfer temperatures were determined by UV-vis measurements.^{26,27} For each particle sample, a dispersion in water with a concentration of 1.0 mg/mL was made and carefully added into a custom-made vial that contained an equal volume of [EMIM][TFSA]. The vial was equipped with a valve that allowed for samples to be taken from the system via a syringe. The vial was then placed into an oil bath with a preset temperature and the biphasic system was magnetically stirred at a constant rate of 500 rpm. The system was equilibrated at the selected temperature for at least 12 h and then allowed to stand still for 30 min. An aliquot (0.4 mL) was taken from each phase and dilute to 0.6 mL with the corresponding pure solvent for the UV-vis measurement. In another vial, water and [EMIM][TFSA] of equal volumes without hairy particles were stirred at the same stirring rate and temperature and for the same amount of time. The water and ionic liquid from this vial were used as references in the measurement of absorbances of samples from the particle transfer experiment by UV-vis spectrometry. The temperature of the oil bath was then increased and the process of taking samples was repeated at selected temperatures after equilibration for at least 12 h. We previously showed that Beer's law at a wavelength of 500 nm can be applied to the dispersions of hairy particles in both water and ionic liquid.²⁶

Figure 3.11A shows the plot of normalized absorbance, the ratio of the absorbance at a given temperature (A) to the maximum absorbance (A_{max}), versus temperature for

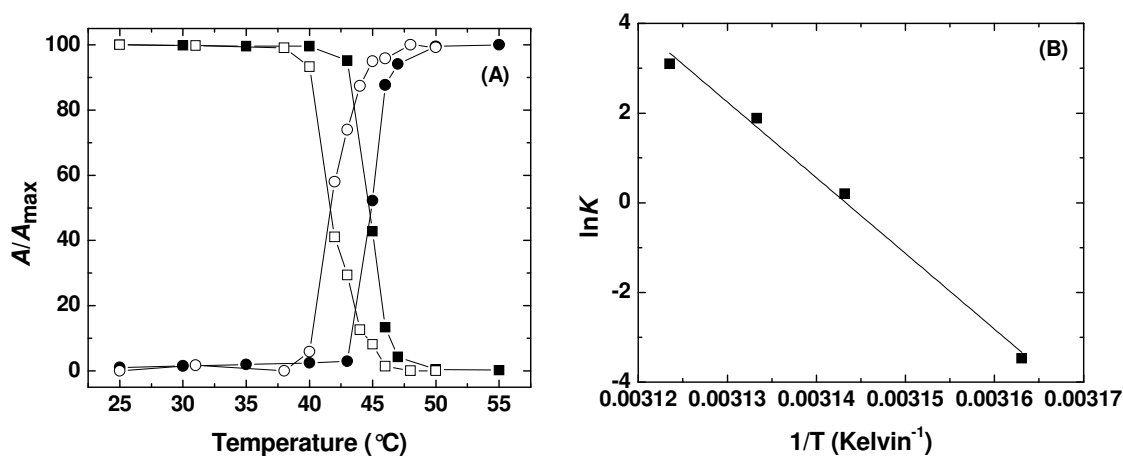


Figure 3.11 (A) Plots of normalized absorbance ($A/A_{\max}$) of PEGMMA brush-grafted 67 nm silica nanoparticles (PEGMMA-67-I, solid symbols) and PEGMMA brush-grafted 205 nm silica particles (PEGMMA-205, hollow symbols) in the aqueous phase (square symbol) and the ionic liquid phase (circle symbol) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range. (B) Plot of natural logarithm of equilibrium constant of PEGMMA-67-I ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.991.

samples taken from both aqueous and ionic liquids in the experiment of the determination of T_{tr} of PPEGMMA-67-I. Note that the normalized absorbance A/A_{max} is proportional to the normalized particle concentration ($[particle]/[particle]_{max}$). For comparison, we also include the data for PPEGMMA-205 from Chapter 1. As can be seen from Figure 3.11A, the PPEGMMA-67-I began to move from the aqueous layer to the [EMIM][TFSA] phase at 43 °C and the transfer was complete at 50 °C. If the temperature at which 50 % of particles are transferred is taken as the transfer temperature, then the T_{tr} is 45 °C, which is higher by 3 °C than that of PPEGMMA brush-grafted 205 nm silica particles (PPEGMMA-205). To further confirm this observation, we determined the transfer temperature of newly synthesized PPEGMMA brush-grafted 215 nm silica particles (PPEGMMA-215). The data are shown in Figure 3.12A. The phase transfer behavior of PPEGMMA-215 is very similar to that of PPEGMMA-205; the T_{tr} of PPEGMMA is 42 °C, same as that of PPEGMMA-205. Note that the grafting density of PPEGMMA-215 is 0.40 chains/nm², slightly higher than that of PPEGMMA-205 (0.24 chains/nm²), suggesting that the grafting density of thermosensitive brushes has a negligible effect on the transfer behavior. Thus, the observed difference in the transfer temperatures of PPEGMMA-67-I and PPEGMMA-205 is very likely caused by the different sizes of silica core particles.

We also quantitatively studied the phase transfer behavior of other thermosensitive hairy particles (PPEGMMA-67-II, PPEGMMA-67-III, and PTEGMMA-67) by UV-vis measurements. The results are presented in Figures 3.13A, 3.14A, and 3.15A. The transfer temperatures of PPEGMMA-67-II and -III are 44 and 44.5 °C, respectively, which are very close to that of PPEGMMA-67-I and appreciably higher than that of

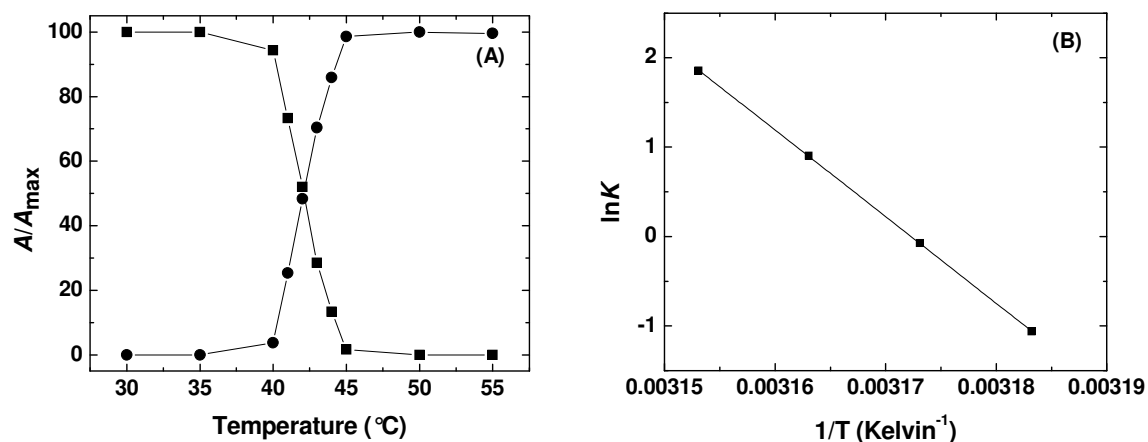


Figure 3.12 (A) Plot of normalized absorbance ($A/A_{\max}$) of PEGMMA brush-grafted 215 nm silica particles (PEGMMA-215) in the aqueous phase (square square) and in the ionic liquid phase (solid circle) versus temperature. (B) Plot of natural logarithm of equilibrium constant of PEGMMA-215 ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.999.

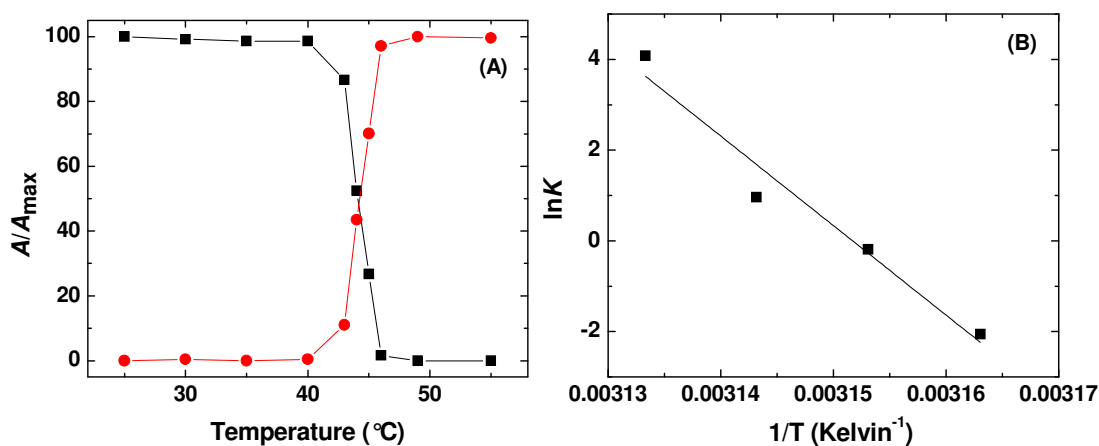


Figure 3.13 (A) Plot of normalized absorbance ($A/A_{\max}$) of PEGMMA brush-grafted 67 nm silica particles (PEGMMA-67-II) synthesized from initiator particles IP-67-II in the aqueous phase (square square) and the ionic liquid phase (solid circle) versus temperature. (B) Plot of natural logarithm of equilibrium constant of PEGMMA-67-II ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.942.

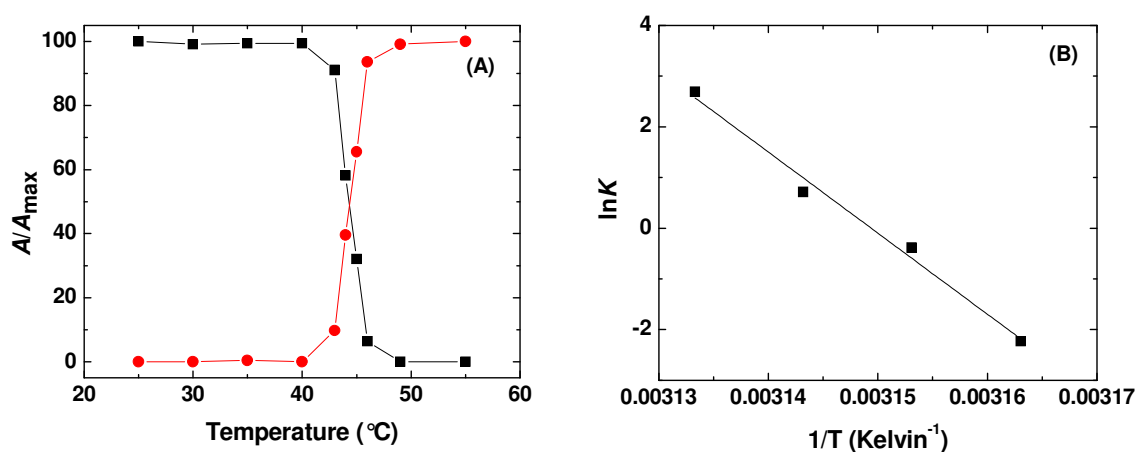


Figure 3.14 (A) Plot of normalized absorbance ($A/A_{\max}$) of PEGMMA brush-grafted 67 nm silica particles (PEGMMA-67-III) synthesized from initiator particles IP-67-III in the aqueous phase (square square) and the ionic liquid phase (solid circle) versus temperature. (B) Plot of natural logarithm of equilibrium constant of PEGMMA-67-III ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.984.

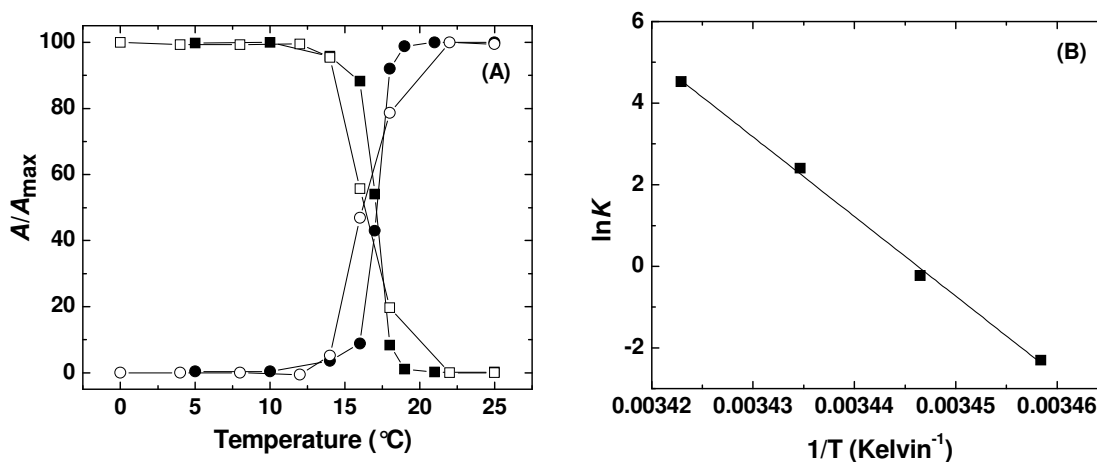


Figure 3.15 (A) Plots of normalized absorbance ($A/A_{\max}$) of PTEGMMA brush-grafted 67 nm silica nanoparticles (PTEGMMA-67, solid symbols) and PTEGMMA brush-grafted 205 nm silica particles (PTEGMMA-205, hollow symbols) in the aqueous phase (square symbol) and the ionic liquid phase (circle symbol) versus temperature. A and $A_{\max}$ represent the absorbance at a given temperature at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm in the studied temperature range. (B) Plot of natural logarithm of equilibrium constant of PTEGMMA-67 ($K = [\text{particle}]_{\text{IL}}/[\text{particle}]_{\text{water}}$) versus the inverse of absolute temperature. The solid line is a linear fit with a correlation coefficient (R) of 0.996.

PPEGMMA-205 and -215 particles. The T_{tr} of PTEGMMA-67 is 17 °C (Figure 3.15A). Although it is only 1 °C higher than that of PTEGMMA-205, the difference between two particle samples is clear (see Figure 3.15A). In summary, the transfer temperatures of small hairy particles are slightly higher than those of bigger hairy particles; the smaller hairy hybrid particles appear to have a higher affinity to water than to [EMIM][TFSA], likely because of the polymer contents.

For each hairy particle sample, we calculated the equilibrium constant K ($K = [\text{particle}]_{II}/[\text{particle}]_{\text{water}}$) at each temperature in the transition zone by using the normalized particle concentrations in water and [EMIM][TFSA]. The plots of $\ln K$ versus the inverse of absolute temperature ($1/T$) are shown in Figures 3.11B, 3.12B, 3.13B, 3.14B, and 3.15B. The standard enthalpy change ΔH° and entropy change ΔS° for the transfer of thermosensitive particles from water to [EMIM][TFSA] can be calculated from the plot of $\ln K$ versus $1/T$ and the following relations: $\Delta G^\circ = -RT \ln K$, $\Delta H^\circ = -R[\partial \ln K / \partial (1/T)]_p$, and $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$, in which R is the gas constant and $\partial \ln K / \partial (1/T)$ is the slope of the plot of $\ln K$ versus $1/T$. The calculated values of ΔH° and ΔS° are shown in Table 3.2 for the temperature range in the transition zone for each of particle samples. The values of ΔH° and ΔS° are positive for all hairy particle samples.

The positive values of ΔH° suggest that the interaction of PPEGMMA brushes with water is more energetically favorable than with the ionic liquid regardless of the size of silica particles. Given the strong ability of the pendant oligo(ethylene glycol) units to hydrogen bond with water, the positive values of ΔH° are understandable. The positive values of ΔS° indicates that the transfer of thermosensitive hairy particles from water to [EMIM][TFSA] is an entropically driven process as discussed in Chapters 1 and 2. With

Table 3.2 Standard Enthalpy Changes ΔH° and Standard Entropy Changes ΔS° Calculated from Plots of $\ln K$ vs. $1/T$ and Transfer Temperature (T_{tr}) for Five Thermosensitive Hairy Particle Samples and Two Particle Samples from Chapter 1.

Particle Sample	T_{tr} (°C)	ΔH° (kJmol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)
PTEGMMA-67	17	$1.6 \pm 0.3 \times 10^3$	$5.6 \pm 1.0 \times 10^3$
PTEGMMA-205 ^a	16	$6.5 \pm 0.1 \times 10^2$	$2.3 \pm 0.3 \times 10^3$
PPEGMMA-67-I	45	$1.4 \pm 0.2 \times 10^3$	$4.4 \pm 0.7 \times 10^3$
PPEGMMA-67-II	44	$1.6 \pm 0.2 \times 10^3$	$4.9 \pm 0.5 \times 10^3$
PPEGMMA-67-III	44.5	$1.3 \pm 0.3 \times 10^3$	$4.2 \pm 1.0 \times 10^3$
PPEGMMA-205 ^a	42	$8.9 \pm 0.2 \times 10^2$	$2.8 \pm 0.4 \times 10^3$
PPEGMMA-215	42	$8.1 \pm 0.2 \times 10^2$	$2.6 \pm 0.6 \times 10^3$

^a Particle samples are from Chapter 1.

The formulas used in the determination of the error for the thermodynamic values were from Xue et al.³⁶

the particles moving from water to [EMIM][TFSA], the structured water around polymer chains was disrupted, making the entropy of the whole system higher. The values of ΔH° and ΔS° for the transfer of thermosensitive polymer brush-grafted 67 nm silica nanoparticles from water to [EMIM][TFSA] are slightly higher than but still comparable to those for larger particles.

3.3.5 Kinetics Study of Phase Transfer of Thermosensitive PEGMMA-Grafted Silica Particles from the Water Phase to the Ionic Liquid Phase at $T = T_{tr} + 15\text{ }^\circ\text{C}$

We further studied the kinetics of thermally induced phase transfer of hairy particles from water to [EMIM][TFSA] to examine if the size of silica core particles affects the transfer rate. Four particle samples (PEGMMA-67-I, PEGMMA-67-II, PEGMMA-205, and PEGMMA-215) were used. The kinetics study for each particle sample was conducted at a temperature 15 °C above the transfer temperature (60 °C for 67 nm particles and 57 °C for 205 and 215 nm particles), which allows the transfer of hairy particles to be completed in a reasonable amount of time. As for the determination of transfer temperatures, the particle sample was dispersed in [EMIM][TFSA]-saturated water at a concentration of 1.0 mg/mL. The dispersion was carefully added into a vial that contained an equal volume of [EMIM][TFSA]. The system was then placed in an oil bath with a preset temperature ($= T_{tr} + 15\text{ }^\circ\text{C}$) and was magnetically stirred at a stirring rate of 500 rpm. Samples were taken from both layers at various time intervals and diluted with the corresponding pure liquids for UV-vis spectrometry measurements. Note that during the transfer process, no visible aggregates were observed in the aqueous layer.

Figures 3.16-3.19 show the plots of normalized absorbances of hairy particles from both layers versus time. As can be seen from these figures, the transfer of particles began

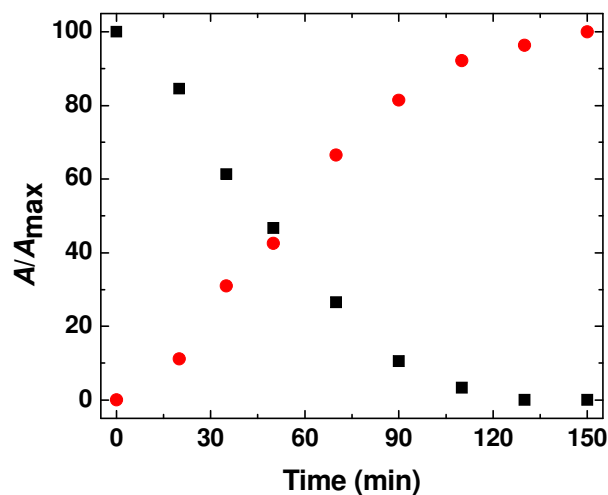


Figure 3.16 Normalized absorbance ($A/A_{\max}$) of PPEGMMA brush-grafted 67 nm silica particles (PPEGMMA-67-I) in the aqueous layer (solid square) and in the ionic liquid layer (solid circle) as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm. The data were obtained from a kinetics study of transfer of PPEGMMA-67-I from water to [EMIM][TfSA] at 60 °C.

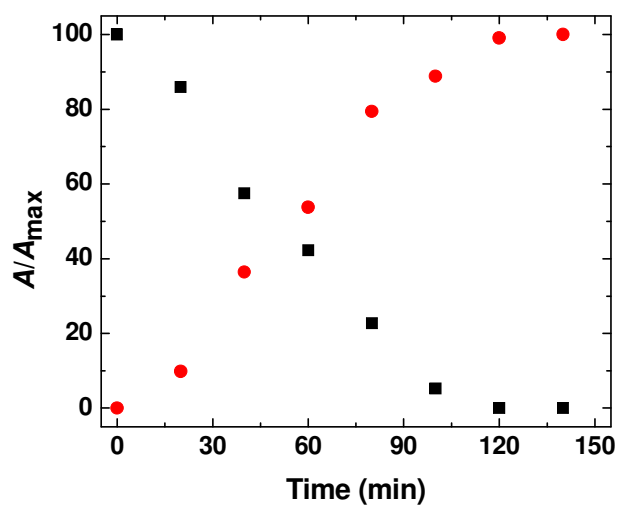


Figure 3.17 Normalized absorbance ($A/A_{\max}$) of PPEGMMA brush-grafted 67 nm silica particles (PPEGMMA-67-II) in the aqueous layer (solid square) and in the ionic liquid layer (solid circle) as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm. The data were obtained from a kinetics study of transfer of PPEGMMA-67-II from water to [EMIM][TFSA] at 60 °C.

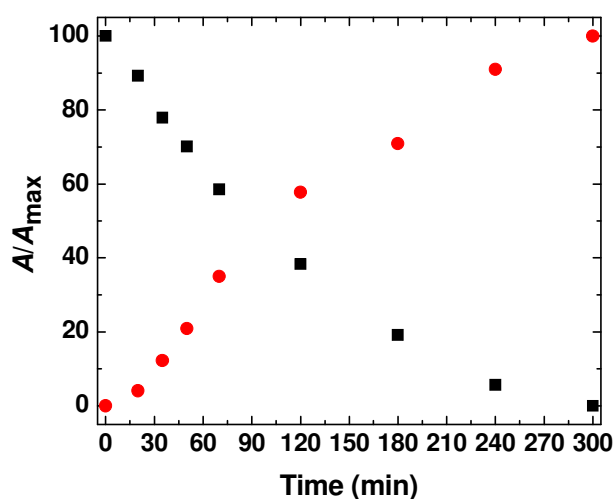


Figure 3.18 Normalized absorbance ($A/A_{\max}$) of PPEGMMA brush-grafted 205 nm silica particles (PPEGMMA-205) in the aqueous layer (solid square) and in the ionic liquid layer (solid circle) as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm. The data were obtained from a kinetics study of transfer of PPEGMMA-205 from water to [EMIM][TFSA] at 57 °C.

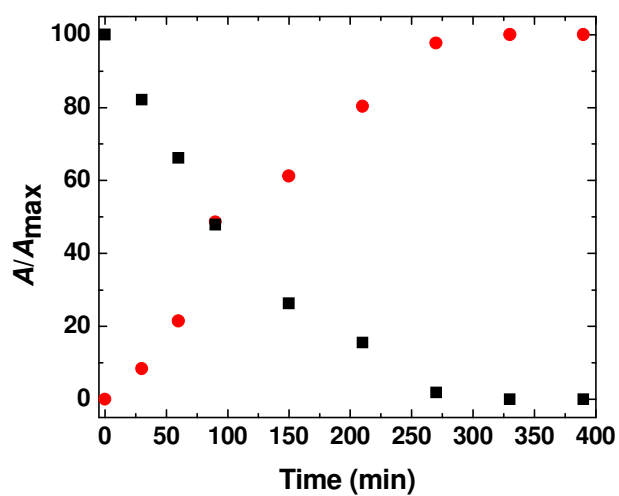


Figure 3.19 Normalized absorbance ($A/A_{\max}$) of PPEGMMA brush-grafted 215 nm silica particles (PPEGMMA-215) in the aqueous layer (solid square) and in the ionic liquid layer (solid circle) as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm. The data were obtained from a kinetics study of transfer of PPEGMMA-215 from water to [EMIM][TFSA] at 57 °C.

immediately after the vial was placed into the pre-heated oil bath. For both PPEGMMA-67-I and -II samples, the transfer was complete in ~ 2 h. The time for 50 % of particles to move to the ionic liquid phase ($t_{1/2}$) was ~ 50 min for both samples. In contrast, the transfer of PPEGMMA-205 and 215 samples were much slower; it was not complete until 5 h after the experiment was started. The $t_{1/2}$ was ~ 90 min for both PPEGMMA-205 and -215 particles. The difference between small and bigger hairy particles can be better appreciated from Figures 3.20 (normalized absorbance of the aqueous phase versus time for four samples and 3.21 (normalized absorbance of the ionic liquid phase versus time). The curves of two small particle samples almost overlap, so do the two big particle samples, implying that the transfer behavior is likely mainly determined by the size of the silica core particles.

3.4 Conclusions

Using surface-initiated ATRP, we synthesized a series of thermosensitive polymer brush-grafted silica particles from 67 nm silica nanoparticles functionalized with a triethoxysilane-terminated ATRP initiator and poly(*tert*-butyl acrylate) from 27 nm silica nanoparticles. The thermosensitive hairy nanoparticles can undergo reversible phase transfer between water and [EMIM][TFSA] upon heating at 80 °C and cooling at 10 °C. The transfer temperatures of thermosensitive polymer brush-grafted 67 nm silica nanoparticles were found to be higher by 1-3 °C than those of thermosensitive polymer brush-grafted silica particles with sizes of 205 and 215 nm. The change in the transfer temperature was more pronounced for PPEGMMA brush-grafted hairy particles (2-3 °C) than that of the PTEGMMA brush-grafted hairy particles (1 °C). Thermodynamics

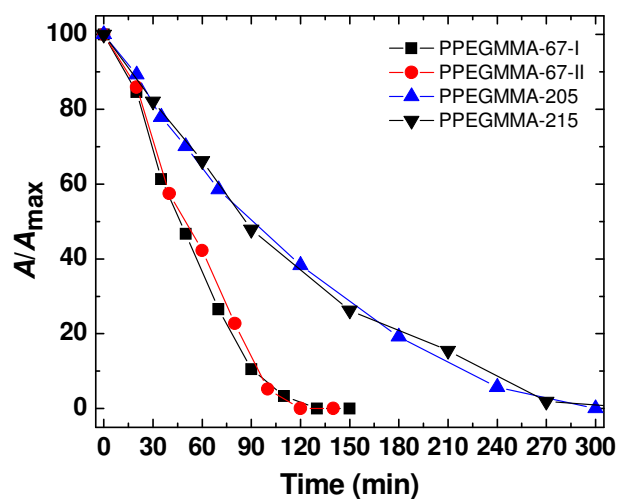


Figure 3.20 Normalized absorbance ($A/A_{\max}$) of PPEGMMA-67-I (solid square), PPEGMMA-67-II (solid circle), PPEGMMA-205 (solid triangle), and PPEGMMA-215 (solid diamond) from the aqueous layer as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm.

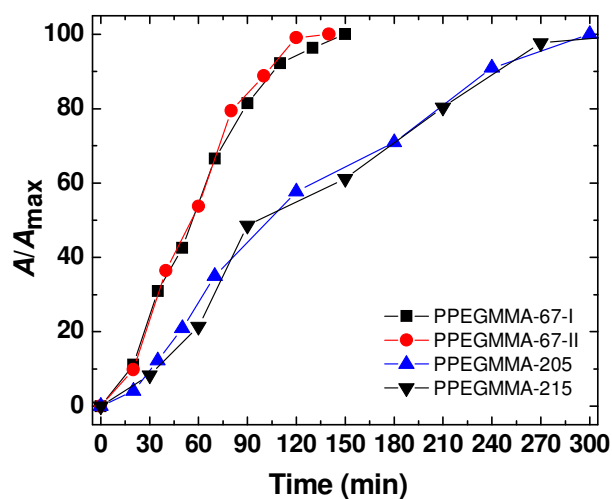


Figure 3.21 Normalized absorbance ($A/A_{\max}$) of PPEGMMA-67-I (solid square), PPEGMMA-67-II (solid circle), PPEGMMA-205 (solid triangle), and PPEGMMA-215 (solid diamond) from the ionic liquid layer as a function of time. A and $A_{\max}$ represent the absorbance at a given time at the wavelength of 500 nm and the maximum absorbance at the wavelength of 500 nm.

analysis showed that both standard enthalpy and entropy changes for the transfer of hairy nanoparticles from water to [EMIM][TFSA] are positive, indicating that the particle transfer was entropically driven. Kinetics studies showed that the smaller thermosensitive hairy particles moved faster (by 1.8 times) from the aqueous phase to the ionic liquid phase than the bigger thermosensitive hairy particles at temperatures 15 °C above the respective transfer temperatures. The results from this work suggest that the transfer temperature and kinetics of thermosensitive hairy particles are affected by the size of silica cores.

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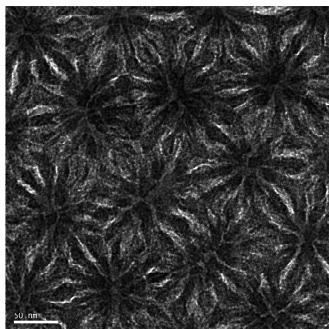
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Chapter 4. Synthesis and Phase Morphology of Well-Defined Mixed Homopolymer Brushes Grafted on 67 nm Silica Nanoparticles

Abstract

The work presented in this Chapter represents our first step toward the synthesis well-defined mixed homopolymer brushes grafted on sub-100 nm silica nanoparticles and the study of the effect of substrate curvature on phase morphology of mixed brushes. We synthesized a series of mixed *Pt*BA/PS brushes with a constant *Pt*BA M_n and various PS molecular weights from 67 nm Y-initiator-functionalized silica nanoparticles by sequential ATRP and NMRP. The triethoxysilane-terminated Y-initiator was immobilized onto the surface of 67 nm silica nanoparticles via a hydrolysis/condensation process. The free polymers formed from the added free initiators in the polymerization mixtures were analyzed by size exclusion chromatography. The polymer brush-grafted silica nanoparticles were characterized by thermogravimetric analysis. Transmission electron microscopy studies showed that with the increase of PS molecular weight from below to above that of *Pt*BA the morphology of mixed brushes evolved from isolated PS nanodomains buried inside the *Pt*BA matrix, to stripe-like nanostructures, and two-layered nanostructures in which the laterally phase separated bottom layer was covered with longer PS chains. Compared with the mixed brushes grafted on 172 nm silica particles, a notable feature of the morphology of mixed *Pt*BA/PS brushes grafted on 67 nm silica nanoparticles is the formation of pronounced wedge-shaped nanostructures, which we believe is caused by a greater substrate curvature.



4.1 Introduction

Binary mixed homopolymer brushes are composed of two chemically distinct homopolymers each grafted by one end via a covalent bond in a random or alternate fashion on a solid substrate.¹⁻¹⁰ These brushes have shown great potential in a variety of applications due to their intriguing responsive properties, which stem from their ability to undergo spontaneous and reversible chain reorganization in response to environmental variations. Depending on environmental conditions, mixed brushes can self-assemble into various nanostructures driven by the minimization of the free energy of the system. These nanostructures are fully reversible because of the covalent grafting of polymer chains on the substrate.³ The responsive properties of mixed brushes have been intensively studied since Sidorenko et al. reported the first synthesis of mixed polystyrene (PS)/poly(2-vinyl pyridine) on silicon wafers.⁸⁻¹⁰

Our group has been interested in the fundamental understanding of how two grafted polymer chains phase separate from each other and how various parameters affect the morphology of mixed brushes.^{10,11} Marko and Witten theoretically studied whether symmetric mixed homopolymer brushes undergo lateral microphase separation, forming a “rippled” morphology, or vertical phase separation, producing a “layered” nanostructure under equilibrium melt conditions.¹ They predicted that the “rippled” nanostructure should appear.¹ Further theoretical and computer simulation studies by other researchers have shown many interesting nanostructures through the tuning of chain lengths, chemical compositions, and grafting densities of two tethered polymers as well as environmental conditions.^{2a,b,4-7} In particular, when the polymer chains are grafted on nanoparticles, the morphology of mixed brushes could be influenced by the substrate

curvature. One can image that the polymer chains are less stretched and crowded at the exterior of the brush layer than at the interior close to the grafting sites. Using computer simulations, Roan⁶ and Wang et al.⁷ studied the self-assembly of mixed brushes on nanospheres with sizes similar to those of polymer chains. The morphology of mixed brushes evolves from layered to various ordered polyhedral and rippled nanostructures with the change of relative grafting densities or relative chain lengths of two polymers.^{6, 7}

There have been few reports in the literature on the synthesis and phase morphology of mixed homopolymer brushes grafted on (nano)particles because of the challenges in the preparation of well-defined mixed brushes.^{11,12} Our group has developed a unique strategy to synthesize well-defined mixed homopolymer brushes from asymmetric difunctional initiator (Y-initiator)-functionalized silica wafers and silica particles by sequential atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMRP). For the mixed poly(*tert*-butyl acrylate) (PtBA)/PS brushes grown from 172 nm silica particles that were functionalized with a monochlorosilane-terminated Y-initiator,^{11c} with the increase of PS M_n from below to above the M_n of PtBA, the morphology evolved from isolated, nearly spherical PS nanodomains in the PtBA matrix, to short PS cylinders, to nearly bicontinuous nanostructures, and a two-layered nanostructure composed of a laterally microphase-separated bottom layer and a thin PS top layer. By using a triethoxysilane-terminated Y-initiator to functionalize 172 nm silica particles, a series of high density mixed PtBA/PS brush-grafted particle samples were prepared.^{11d} The sizes of the nanostructures formed from phase separation of high density mixed brushes were found to be significantly smaller than those of mixed brushes grown from monochlorosilane-terminated Y-initiator-functionalized silica particles.

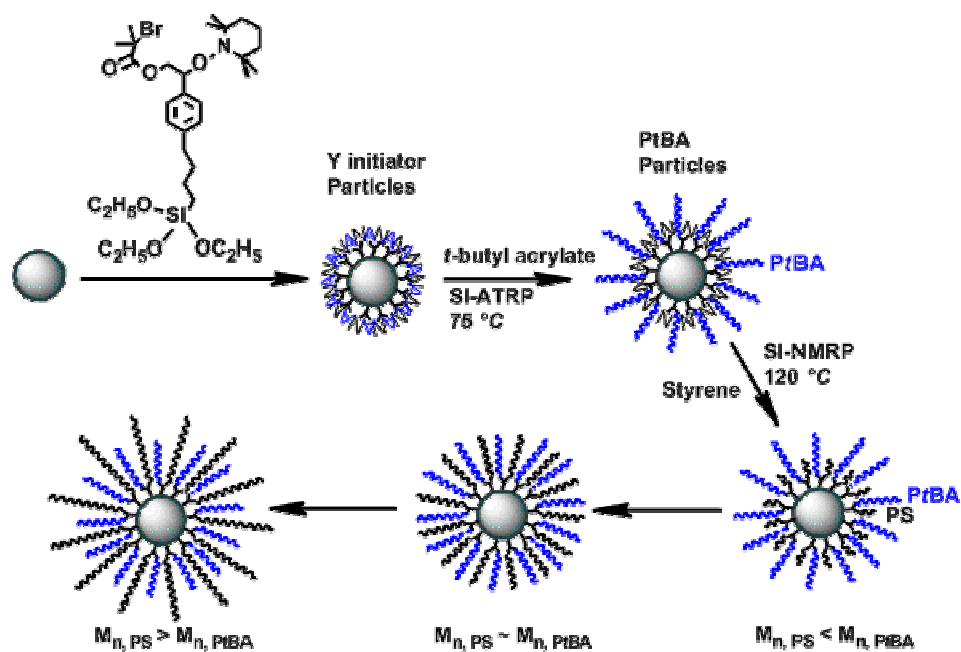
The work presented in this Chapter represents our first step toward the synthesis of well-defined mixed brushes on sub-100 nm silica nanoparticles and the study of the effect of substrate curvature on phase morphology of mixed brushes. The synthesis of polymer brushes on nanoparticles is more challenging than growing polymer brushes from bigger particles because of the known tendency of nanoparticles to form aggregates. For example, silica nanoparticles, once dried at elevated temperatures under vacuum, can no longer be dispersed in common organic solvents. Therefore, the method previously used to functionalize silica particles with a monochlorosilane-terminated Y-initiator is not applicable to sub-100 nm silica nanoparticles because it requires the drying of particles at 110 °C in vacuum.^{11c}

In the present work, we functionalized 67 nm silica nanoparticles with a triethoxysilane-terminated Y-initiator through a hydrolysis/condensation process. This method does not require drying of silica nanoparticles at elevated temperature under high vacuum.¹³ Mixed PtBA/PS brushes with various molecular weights for the two polymers were then grown from the surface of Y-initiator-modified silica nanoparticles by the established synthetic protocol from our laboratory (Scheme 4.1).^{10f} The morphologies of the obtained mixed brush samples were studied by transmission electron microscopy.

4.2 Experimental

4.2.1 Materials

Triethoxysilane (95%) was obtained from Acros Organic and stored in a refrigerator prior to use. Platinum-divinyltetramethyldisiloxane complex in xylene (2.1~2.4% Pt concentration in xylene) was purchased from Gelest, Inc. and stored in a desiccator. CuBr



Scheme 4.1 Schematic Illustration of the Synthesis of Mixed *Pt*BA/PS Brush Grafted on 67 nm Silica Nanoparticles by Sequential Atom Transfer Radical Polymerization and Nitroxide Mediated Radical Polymerization.

(98%, Aldrich) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol and diethyl ether. After being dried in vacuum, the purified CuBr was stored in a desiccator. *N, N, N', N', N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and ethyl 2-bromoisobutyrate (98%, Aldrich) were dried with calcium hydride, distilled under reduced pressure, and stored in a desiccator. Styrene (99%, Aldrich) and *tert*-butyl acrylate (99%, Aldrich) were dried overnight with calcium hydride, distilled under reduced pressure, and stored in a refrigerator prior to use. 1-Phenyl-1-(2',2',6',6'-tetramethyl-1'-piperodinyloxy)ethane (STEMPO) was synthesized according to a procedure from the literature.¹⁴ 2-[4-(But-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethyl 2-bromo-2-methylpropanoate (Y-silane precursor) was synthesized as previously reported.^{10f} Snowtex-ST-OL (manufacturer's estimated size 40-50 nm) was received from Nissan chemical USA in a 20 wt% aqueous dispersion. All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

4.2.2 Characterization

Size exclusion chromatography (SEC) was carried out at ambient temperature using PL-GPC 20 (an integrated SEC system from Polymer Laboratories, Inc.) with a refractive index detector, one PLgel 5 μ m guard column (50 $\times$ 7.5 mm), and two PLgel 5 μ m mixed-C columns (each 300 $\times$ 7.5 mm, linear range of molecular weight from 200 to 2,000,000 according to Polymer Laboratories, Inc.). The data were processed using CirrusTM GPC/SEC software (Polymer Laboratories, Inc.). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Polystyrene standards (Polymer Laboratories, Inc.) were used for calibration. ¹H NMR spectra were recorded on a Varian Mercury 300 NMR

spectrometer and the residual solvent proton signal was used as the internal standard. Thermogravimetric analysis was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C using TA Q-series Q50. A FEI Tecnai T12 at accelerating voltage of 100 kV with a CCD camera was used to acquire TEM images. A Zeiss LIBRA 200FE with an accelerating voltage of 200 kV was used to take dark field STEM images.

4.2.3 Synthesis of Y-initiator-Functionalized 67 nm Silica Nanoparticles (Y-Initiator Nanoparticles)

4.2.3.1 Isolation and Solvent Exchange of 67 nm Silica Nanoparticles

Snowtex-ST-OL (spherical silica nanoparticles, manufacturer's estimated size = 40-50 nm) was provided by Nissan Chemical USA in a 20 wt% aqueous dispersion. The nanoparticles were isolated by centrifugation (Eppendorf 5804, 11000 rpm, 25 min), and then dispersed in ethanol by ultrasonication. The nanoparticles were separated and dispersed in ethanol again. This process was repeated an additional two times. A dispersion of silica nanoparticles in ethanol was obtained. A small portion of this dispersion was then dried under high vacuum to determine the concentration of the silica nanoparticles in the dispersion.

4.2.3.2 Hydrosilylation of 2-[4-(But-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethyl 2-Bromo-2-methylpropanoate

2-[4-(But-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethyl 2-bromo-2-methylpropanoate (Y-silane precursor, 0.447 g, 930 µmol) was added into a 25 mL two-necked flask and dried at room temperature in vacuum for 1 h. Triethoxysilane (3.0 mL, 16.3 mmol) was injected into the flask via a syringe under N₂ atmosphere, followed by

addition of the platinum-divinyltetramethyldisiloxane complex in xylene (30 μ L). The mixture was stirred at 30 $^{\circ}$ C under nitrogen atmosphere and the hydrosilylation reaction was monitored by ^1H NMR spectroscopy analysis. Once the reaction was complete, excess triethoxysilane was removed by vacuum at 40 $^{\circ}$ C and the product was used in the next step to functionalize silica nanoparticles.

4.2.3.3 Immobilization of 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(4-(4-(triethoxysilyl)butyl)phenyl)ethyl 2-bromo-2-methylpropanoate (Y-Silane) onto 67 nm Silica Nanoparticles (Y-Initiator Nanoparticles)

Bare silica nanoparticles with an average diameter of 67 nm (399 mg) were dispersed in ethanol (27 mL) by ultrasonication. A solution of ammonium hydroxide (25% in water, 3.648 g) in EtOH (14 mL) was added into the nanoparticle dispersion. After the mixture was stirred at 40 $^{\circ}$ C for 3 h, a solution of the triethoxysilane-terminated Y-initiator, freshly prepared from 0.447 g of Y-silane precursor in ethanol (3 mL) was added dropwise into the dispersion. After the mixture was stirred at 40 $^{\circ}$ C for 18 h, the nanoparticles were isolated by centrifugation, redispersed in ethanol, and centrifuged again. This washing process was repeated with ethanol again and then THF three times, followed by drying with a stream of air flow to yield dry Y-initiator-functionalized silica nanoparticles (Y-Initiator Nanoparticles, 439 mg).

4.2.4 Synthesis of PtBA Brushes from Y-Initiator-Functionalized 67 nm Silica Nanoparticles by Atom Transfer Radical Polymerization of *tert*-Butyl Acrylate

CuBr (15.2 mg, 106 μ mol) and Y-initiator-functionalized silica nanoparticles (200 mg) were placed into a two-necked flask and dried under high vacuum at room temperature overnight. The initiator nanoparticles were then dispersed in anisole (3 mL)

by ultrasonication. *tert*-Butyl acrylate (8.002 g, 62.4 mmol) and free initiator ethyl 2-bromoisobutyrate (14.3 mg, 73.3 μ mol) were added into the flask. After the mixture was degassed by three freeze-pump-thaw cycles, *N,N,N',N',N''*-pentamethyldiethylenetriamine (16.0 mg, 92.3 μ mol) was added via a microsyringe at the thawing point of the mixture. A sample was taken immediately for ^1H NMR spectroscopy analysis. The flask was then placed in an oil bath with a preset temperature of 75 °C. The polymerization was monitored by ^1H NMR spectroscopy. After the reaction proceeded for 10.5 h, the flask was removed from the oil bath and opened to air; the mixture was diluted with THF (20 mL). The nanoparticles were isolated by centrifugation (Eppendorf 5804, 11000 rpm, 20 min) and the supernatant liquid was passed through a short column of silica gel (bottom)/activated basic aluminum oxide (top) (2/1, v/v). The free polymer was analyzed by SEC relative to polystyrene standards. The $M_{n,\text{SEC}}$ and polydispersity index (PDI) were 22.2 kDa and 1.19, respectively. The polymer brush-grafted particles were re-dispersed in THF and isolated by centrifugation. This purification process was repeated an additional four times. The hairy particles were then dried by a stream of air flow. A small portion of the particles was transferred into a 25 mL two-necked flask and dried under high vacuum at 45 °C for 3 h for thermogravimetric analysis.

4.2.5 Synthesis of Mixed PtBA/PS Polymer Brushes with PtBA $M_{n,\text{SEC}}$ of 22.2 kDa and Various PS Molecular Weights by Surface-Initiated NMRP of Styrene from PtBA Brush-Grafted 67 nm Silica Nanoparticles

The PtBA brush-grafted 67 nm silica nanoparticles (PtBA $M_{n,\text{SEC}}$ = 22.2 kDa, 250 mg) were dispersed in anisole (9.148 g) in a 50 mL two-necked flask using an ultrasonic water bath. To this dispersion were added STEMPO (40.0 mg, 153 μ mol) and styrene

(13.722 g, 132 mmol). The mixture was degassed by three freeze-pump-thaw cycles. The flask was placed into a 120 °C oil bath and the polymerization was monitored by SEC analysis. Samples were taken from the reaction mixture using a degassed syringe and diluted with THF when the molecular weight of the free polystyrene formed from free initiator STEMPO reached desired values. The mixed PtBA/PS brush-grafted particles were separated from the free polymer by centrifugation, re-dispersed in THF, and centrifuged again (11,000 rpm 30 min). For each sample, this washing process was repeated four times to remove the physically adsorbed polymer. The particles were then dried with a stream of nitrogen. The molecular weights of free polymers were measured by SEC using polystyrene calibration.

4.2.6 Transmission Electron Microscopy (TEM) Study of Mixed PtBA/PS Brushes Grafted on 67 nm Silica Nanoparticles

Mixed PtBA/PS brush-grafted 67 nm silica nanoparticles were dispersed in chloroform, a nonselective good solvent for both PtBA and PS, by ultrasonication. The concentration of hairy nanoparticles was 0.5 mg/mL. Three drops of the nanoparticle dispersion were drop cast onto carbon-coated TEM copper grids. The samples were then annealed with chloroform vapor in a closed container at room temperature for at least 3 h, followed by staining with ruthenium tetroxide vapor at room temperature for 20 min. The TEM experiments were performed on a FEI Tecnai T12 at an accelerating voltage of 100 kV or a Zeiss LIBRA 200FE at an accelerating voltage of 200 kV.

4.3 Results and discussion

4.3.1 Synthesis of Y-initiator-Functionalized 67 nm Silica Nanoparticles

The Y-initiator functionalized silica nanoparticles were prepared by immobilizing a triethoxysilane-terminated Y-initiator (Y-silane) onto 67 nm silica nanoparticles via an ammonia-catalyzed hydrolysis and condensation process.^{11d,13} This method is preferred over the use of monochlorosilane-terminated Y-initiator because the 67 nm silica nanoparticles cannot be re-dispersed in common organic solvents once dried at elevated temperature under high vacuum. The Y-silane, 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(4-(4-(triethoxysilyl)butyl)phenyl)ethyl 2-bromo-2-methylpropanoate, was synthesized by the hydrosilylation of 2-[4-(but-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethyl 2-bromo-2-methylpropanoate with triethoxysilane using a platinum complex as catalyst.^{11d} The immobilization of the Y-initiator on the surface of silica nanoparticles was conducted at 40 °C for 18 h. The Y-initiator-functionalized silica nanoparticles were then isolated by centrifugation and repeatedly washed with ethanol and THF. Thermogravimetric analysis (TGA) of Y-initiator-functionalized silica nanoparticles shows a clear difference in the weight retention at 800 °C compared with the bare silica nanoparticles, 7.83 wt% (Figure 4.1), indicating that the immobilization of the Y-initiator onto the surface of silica particles was successful.

4.3.2 Synthesis of Mixed PtBA/PS Brushes with a Fixed PtBA $M_{n,SEC}$ and Various PS Molecular Weights from Y-Initiator-Functionalized 67 nm Silica Nanoparticles by Sequential ATRP and NMRP

The growth of PtBA brushes from Y-initiator-functionalized 67 nm silica nanoparticles was achieved using surface-initiated ATRP of *tert*-butyl acrylate at 75 °C

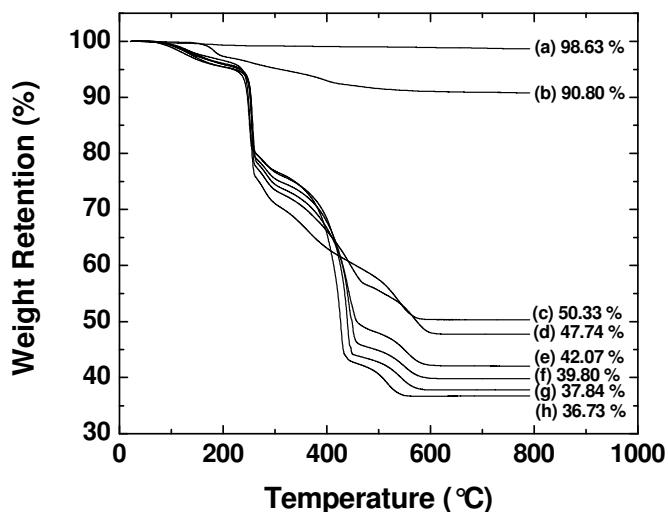


Figure 4.1 Thermogravimetric analysis (TGA) of (a) bare nanoparticles, (b) Y-initiator-functionalized silica nanoparticles, (c) *Pt*BA brush-grafted nanoparticles with *Pt*BA $M_{n,SEC}$ of 22.2 kDa, (d) mixed *Pt*BA/PS brush-grafted silica nanoparticles with *Pt*BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 11.0 kDa (MB-1), (e) mixed *Pt*BA/PS brush-grafted silica nanoparticles with *Pt*BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 18.7 kDa (MB-2), (f) mixed *Pt*BA/PS brush-grafted silica nanoparticles with *Pt*BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 23.4 kDa (MB-3), (g) mixed *Pt*BA/PS brush-grafted silica nanoparticles with *Pt*BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 29.5 kDa (MB-4), (h) mixed *Pt*BA/PS brush-grafted silica nanoparticles with *Pt*BA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 31.7 kDa (MB-5).

using CuBr/*N,N,N',N',N''*-pentamethyldiethylenetriamine as the catalytic system and ethyl 2-bromoisobutyrate (EBiB) as the free initiator. EBiB was added into the polymerization system to facilitate the control of the surface-initiated polymerization and allow to the progress of polymerization to be monitored by ¹H NMR spectroscopy and size exclusion chromatography. The TEMPO portion of the Y-initiator has been shown to remain stable under this ATRP condition.^{10f} The polymerization of *t*BA was stopped when the $M_{n,SEC}$ of the free polymer reached 22.2 kDa (Figure 4.2).

TGA shows that the weight retentions of *Pt*BA brush-grafted silica nanoparticles synthesized from Y-initiator nanoparticles at 800 °C is 50.33 wt% (see Figure 4.1). It has been shown that the molecular weights and molecular weight distributions of the free polymers and the grafted polymer brushes synthesized by “living”/controlled radical polymerization are essentially identical.^{10f,15} By using the TGA data, the molecular weight from SEC analysis, and the nanoparticle size (67 nm, measured from TEM micrographs), and assuming that silica nanoparticles have the same density as bulk SiO₂, i.e., 2.07 g/cm³, the grafting density of *Pt*BA brushes grown from Y-initiator nanoparticles is 0.54 chains/nm². Note that we previously observed that the molecular weight of *Pt*BA obtained from SEC analysis relative to PS standards was essentially the same as that calculated from the monomer-to-initiator molar ratio and the monomer conversion determined by ¹H NMR spectroscopy.¹¹

Mixed *Pt*BA/PS brush-grafted silica nanoparticles were obtained after the surface-initiated NMRP of styrene from *Pt*BA brush-grafted silica nanoparticles. As for the surface-initiated ATRP of *t*BA, a free initiator, 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperodiny-loxy)ethane (STEMPO), was added into the polymerization mixture. The

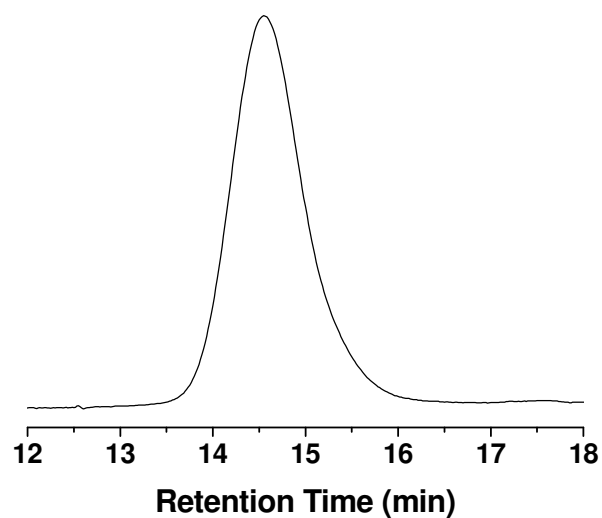


Figure 4.2 Size exclusion chromatography (SEC) trace of the *Pt*BA formed from free initiator ethyl 2-bromoisobutyrate in the synthesis of *Pt*BA brush-grafted silica nanoparticles by surface-initiated ATRP of *t*BA from Y-initiator nanoparticles. $M_{n,SEC} = 22.2$ kDa and PDI = 1.19.

NMRP was carried out at 120 °C and monitored by SEC. Samples were taken from the polymerization mixture at different polymerization times, yielding samples with different PS molecular weights. Five mixed *Pt*BA/PS brush-grafted particle samples with different PS molecular weights were obtained and are designated as MB-1 to -5. The free polymers were analyzed by SEC to determine their molecular weights and molecular weight distributions (Figure 4.3). The hairy particles were repeatedly washed, dried under high vacuum, and analyzed by TGA. The TGA data are shown in Figure 4.1.

From Figure 4.3, one can see that the M_n of PS increased smoothly with the increase of polymerization time, and the PDI decreased gradually, indicating that the NMRP was a controlled process. As expected, the weight retention of mixed *Pt*BA/PS brush-grafted particles decreased with the increase of PS M_n (Figure 4.1). Figure 4.4 shows the plot of the relative amount of grafted polymers versus PS M_n for mixed *Pt*BA/PS brush-grafted 67 nm nanoparticles. A nearly relationship was observed, suggesting that the surface-initiated NMRP was also a “living” process. The grafting density of PS in each mixed brush sample was calculated by using the particle size (67 nm), molecular weight of PS, and the TGA data and taking into consideration the difference in weight retentions of initiator particles and hairy particles. The results are summarized in Table 4.1. Using the Flory characteristic ratio for polystyrene from the literature,¹⁶ we calculated the root-mean-squared end-to-end distances and the radii of gyration for PS free polymers in the unperturbed state.¹⁵ We were unable to find the Flory characteristic ratio of *Pt*BA from the literature. Therefore, the value of PS (9.5) was used to estimate the unperturbed size of *Pt*BA. These values are significantly larger than the distance between grafted chains, confirming that the grafted polymers are in the brush regime.^{11c}

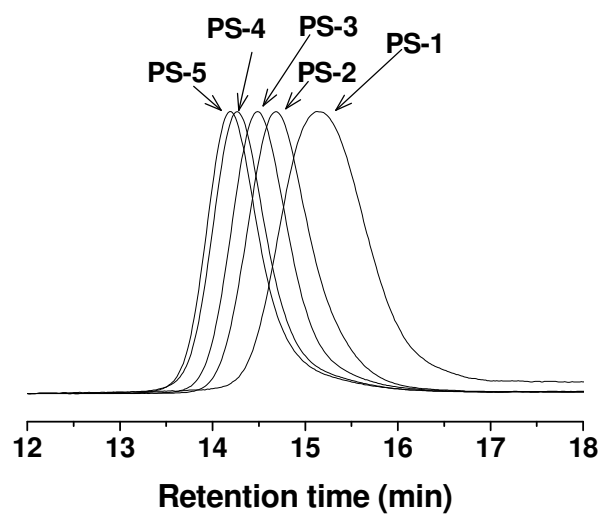


Figure 4.3 Size exclusion chromatography traces of five free polymers formed from the free initiator STEMPO in the synthesis of mixed *Pt*BA/PS brush-grafted silica nanoparticles by NMRP of styrene from the *Pt*BA brush-grafted silica nanoparticles with *Pt*BA $M_{n,SEC}$ of 22.2 kDa and PDI of 1.19.

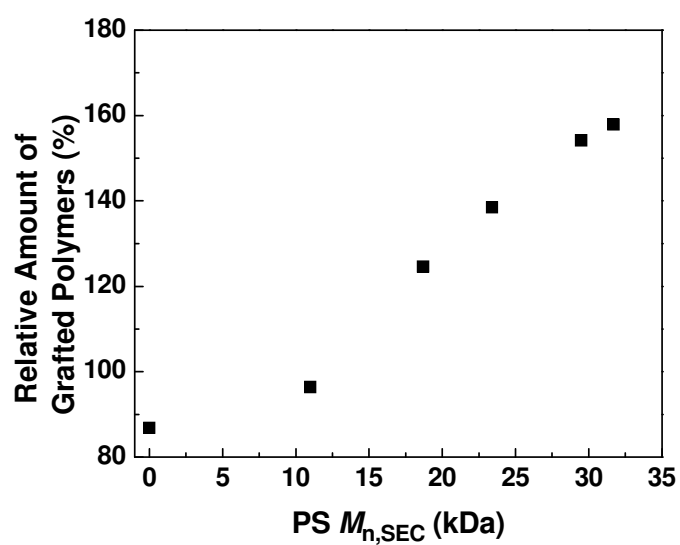


Figure 4.4 The amount of grafted polymers in the mixed *Pt*BA/PS brush-grafted silica particles synthesized from Y-initiator nanoparticles relative to the silica residue at 800 °C versus polystyrene molecular weight.

Table 4.1 Molecular Weight Characteristics of Mixed PtBA/PS Brushes with a Fixed PtBA $M_{n, SEC}$ of 22.2 kDa and Different PS Molecular Weight Grafted on 67 nm Silica Particles and the Corresponding Free Polymers.

Mixed PtBA/PS Brush-Grafted Silica Nanoparticles ^a	$M_{n, SEC}$ (kDa), PDI, and DP of PS ^b	DP _{PS} /DP _{PtBA}	σ_{PtBA} and σ_{total} (chains/nm ²) ^c	$\langle R_{RMS} \rangle$ and $\langle R_g \rangle$ (nm) ^d
MB-1	11.0, 1.24, 106	0.61	0.12, 0.66	6.9, 2.8
MB-2	18.7, 1.18, 180	1.04	0.28, 0.82	9.0, 3.7
MB-3	23.4, 1.17, 225	1.30	0.31, 0.85	10.1, 4.1
MB-4	29.5, 1.17, 284	1.64	0.31, 0.85	11.3, 4.6
MB-5	31.7, 1.16, 305	1.76	0.31, 0.85	11.7, 4.8

^a Mixed PtBA/PS brush-grafted silica nanoparticles were obtained by surface-initiated NMRP of styrene from PtBA brush-grafted silica nanoparticles with PtBA $M_{n, SEC}$ of 22.2 kDa and PDI of 1.19. The DP of PtBA was 173, calculated from SEC analysis of the free polymer using PS standards. The grafting density of PtBA was 0.54 chains/nm². ^b The DP of five PS samples were calculated by using the molecular weights determined by SEC analysis of the free polymers using PS standards. ^c The grafting density was calculated by using the size (67 nm) and density (2.07 g/cm³) of the silica nanoparticles, the DP of polymer, and the TGA data corrected for the difference in the weight retentions at 100 °C between hairy particles and initiator particles. ^d $\langle R_{rms} \rangle$ was calculated by using the formula $\sqrt{C_{\infty} * n * l^2}$, where C_{∞} is the characteristic ratio for the polymer, n is the number of bonds in the polymer backbone, and l is the bond length.¹⁶ $\langle R_g \rangle$ was calculated from $\langle R_g \rangle = \sqrt{\frac{\langle R_{RMS} \rangle^2}{6}}$. The C_{∞} value of PtBA was unavailable from the literature. We used the value of PS (9.5) to calculate the $\langle R_{rms} \rangle$ and $\langle R_g \rangle$ of PtBA, which were 8.8 and 3.6 nm, respectively.

4.3.3 TEM Study of Phase Morphologies of Mixed PtBA/PS Brush Grafted on 67 nm Silica Particles

For TEM study, the mixed PtBA/PS brush-grafted nanoparticle samples were dispersed in chloroform, a nonselective good solvent for both PtBA and PS, and drop cast onto 400 mesh carbon-coated TEM grids. The TEM samples were then annealed with CHCl_3 vapor in a closed container for at least 3 h, followed by staining with RuO_4 vapor at room temperature for 20 min. RuO_4 selectively stained PS, making PS nanodomains appear dark in the TEM micrographs, while the PtBA microdomains remains relatively light.¹¹ Figures 4.5 – 4.9 shows representative TEM micrographs of mixed PtBA/PS brush-grafted silica particle samples MB-1, -2, -3, -4, and -5, respectively. A cursory examination of these figures reveals a clear change in the phase morphology of mixed PtBA/PS brushes with the increase of PS molecular weight from below to above PtBA molecular weight. For MB-1 in which the PS M_n (11.0 kDa) is significantly lower than that of PtBA, polystyrene chains self-assembled into an isolated nanodomains with a typical size of 10 nm buried inside the PtBA matrix (Figure 4.5). With the increase of PS M_n to 18.7 kDa, which is close to the PtBA M_n (22.2 kDa), the mixed brushes underwent lateral microphase separation, forming nearly truncated wedge-shaped nanostructures except in the center of nanoparticles where nearly spherical nanodomains can still be seen (Figure 4.6). MB-3, in which PS M_n was increased to 23.4 kDa, exhibited morphology similar to that of MB-2 (Figure 4.7). Figure 4.10 shows a dark field TEM micrograph in which the PS nanodomains are bright and PtBA nanodomains are dark. For MB-4 and -5, the molecular weights of PS were higher than that of PtBA. One can see that the interstitial space among silica nanoparticles becomes darker and weak dark rings can be

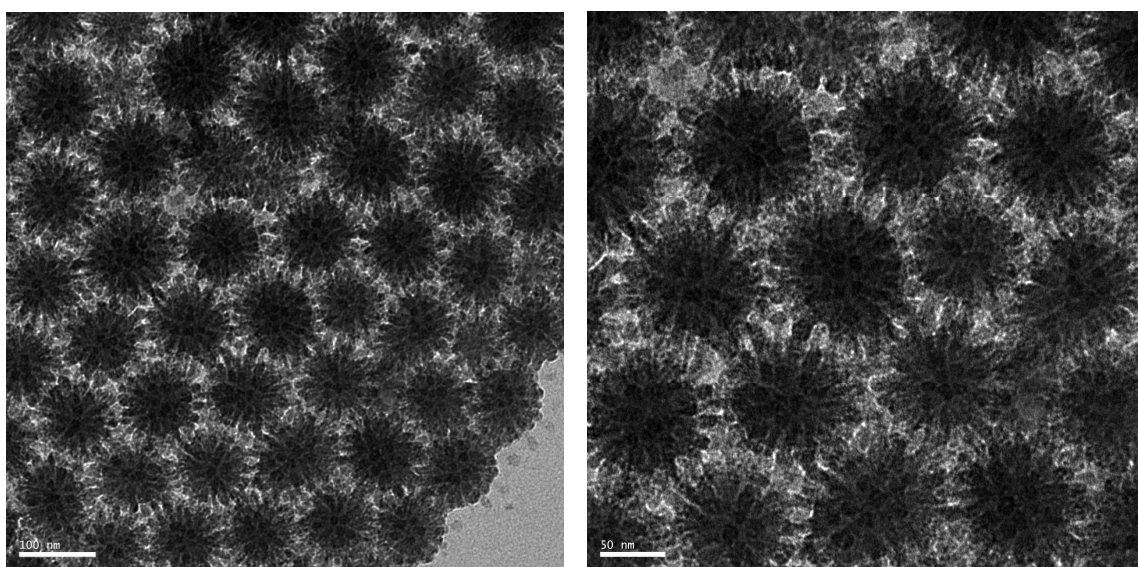


Figure 4.5 Representative top-view, bright field TEM micrographs of mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 11.0 kDa (MB-1).

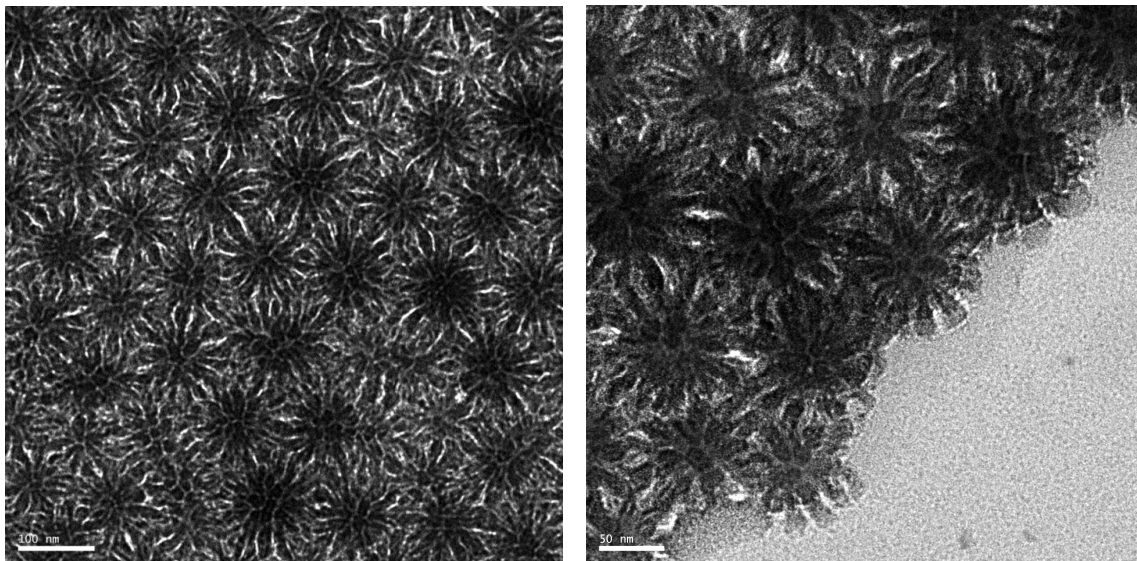


Figure 4.6 Representative top-view, bright field TEM micrographs of mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 18.7 kDa (MB-2).

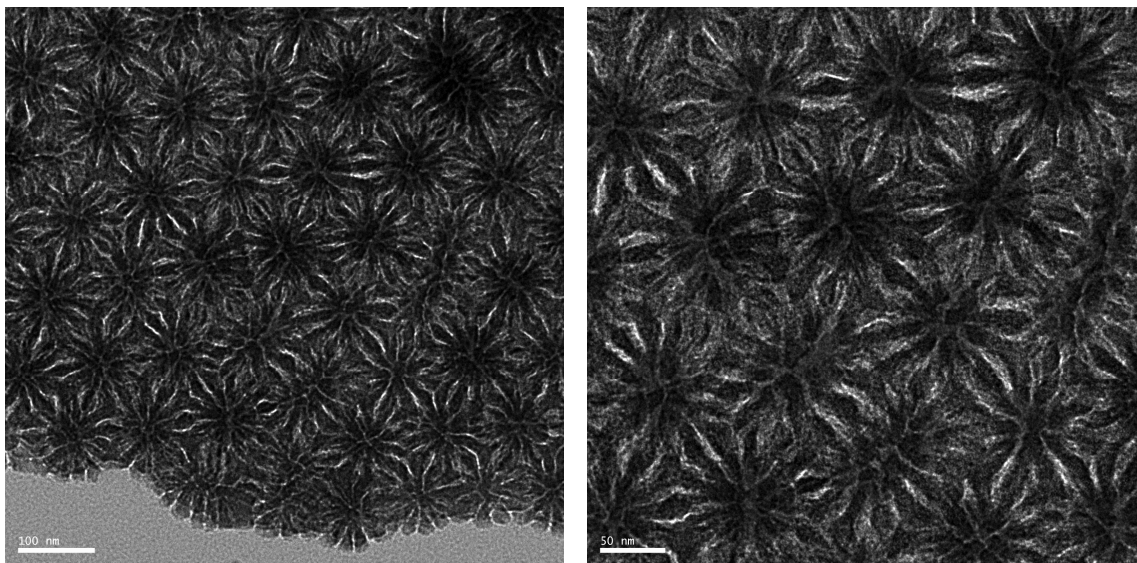


Figure 4.7 Representative top-view, bright field TEM micrographs of mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 23.4 kDa (MB-3).

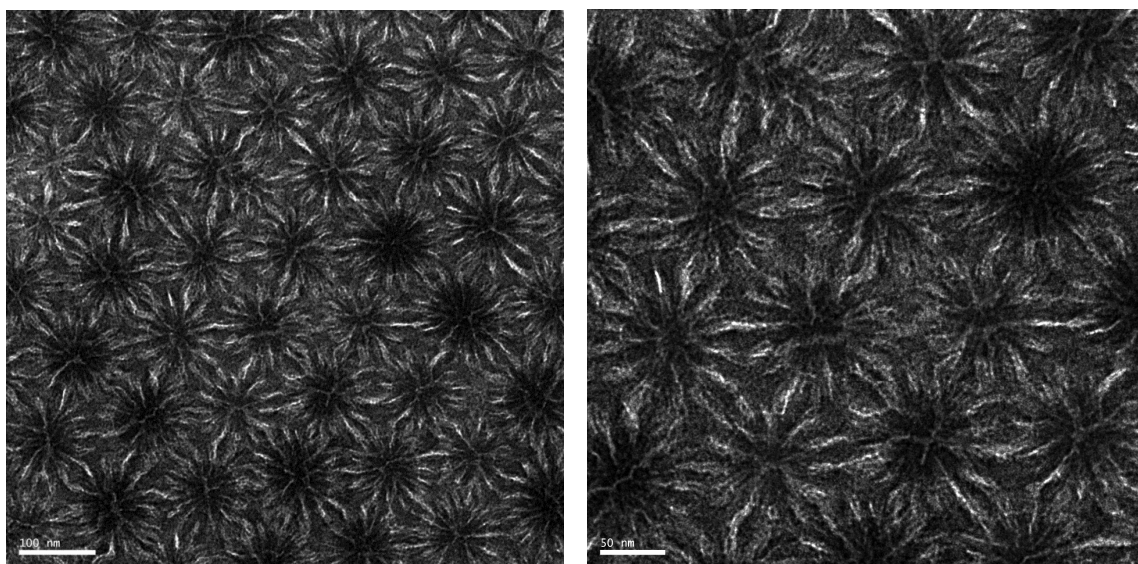


Figure 4.8 Representative top-view, bright field TEM micrographs of mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 29.5 kDa (MB-4).

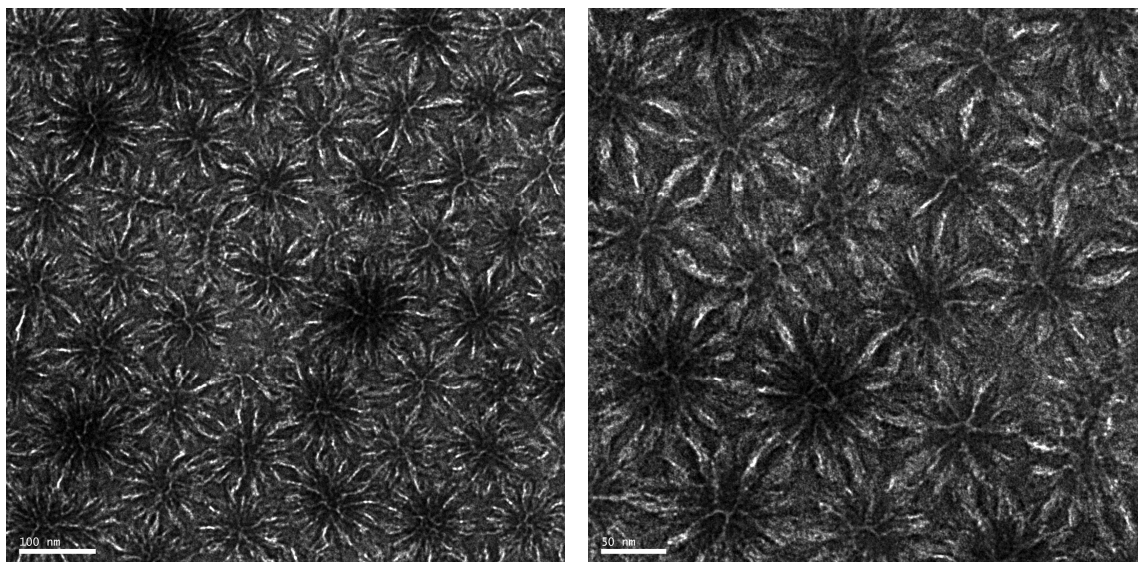


Figure 4.9 Representative top-view, bright field TEM micrographs of mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 31.7 kDa (MB-5).

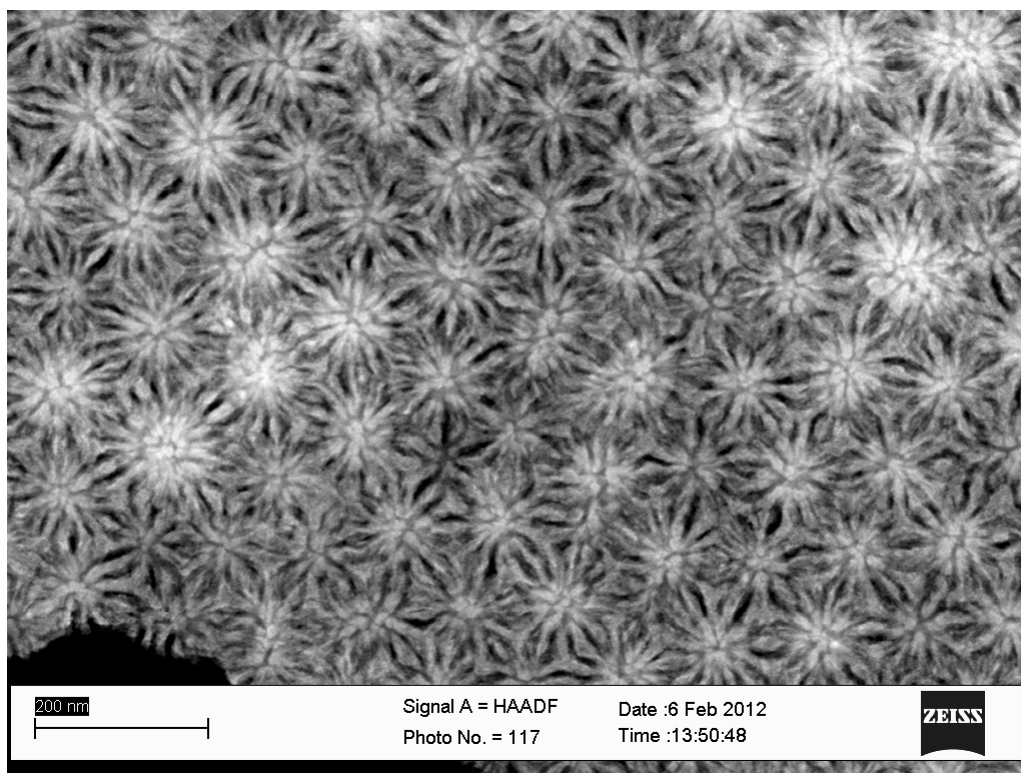


Figure 4.10 STEM dark field image of mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 22.2 kDa and PS $M_{n,SEC}$ of 23.4 kDa (MB-3). In this dark field TEM image, the PS domains are light and the PtBA domains are dark.

seen in the TEM images of both MB-4 and -5, which apparently is a result of the increased PS chain lengths (Figures 4.8 and 9). These observations suggest that mixed brushes in samples MB-4 and -5 self-assembled into a two-layer nanostructure in which the laterally phase separated bottom layer was covered by longer PS chains.

While the self-assembled nanostructures of mixed brushes on 67 nm silica nanoparticles and the morphological evolution with the increase of PS molecular weight are similar to those of mixed brushes grafted on 172 nm silica nanoparticles,^{11c} one notable exception is the shape of nanodomains in the mixed brush samples in which PS molecular weight is close to that of *PtBA*. The PS nanodomains in Figures 4.6-9 are truncated wedges, i.e., the nanodomains are smaller in size at the interior close to the grafting sites but become larger when moving away from the surface. We believe that this is caused by the substrate curvature; more space becomes available for polymer segments to pack with the increase of distance from the surface of silica nanoparticles. This can be better seen in Figure 4.11 for the sample MB-3 (*PtBA* $M_{n,SEC}$ = 22.2 kDa and PS $M_{n,SEC}$ = 23.4 kDa). At the sample-vacuum interface, the typical truncated wedge-shaped nanodomains are marked with an arrow; the length of the highlighted truncated wedge-shaped microdomain is 27.4 nm, and the width is 6.9 nm at the particle surface and 24.5 nm at the sample-vacuum interface.

4.4 Conclusion

A series of mixed *PtBA*/PS brushes with a constant *PtBA* M_n and various PS molecular weights were synthesized from 67 nm Y-initiator-functionalized silica nanoparticles by sequential ATRP and NMRP. The Y-initiator-functionalized silica

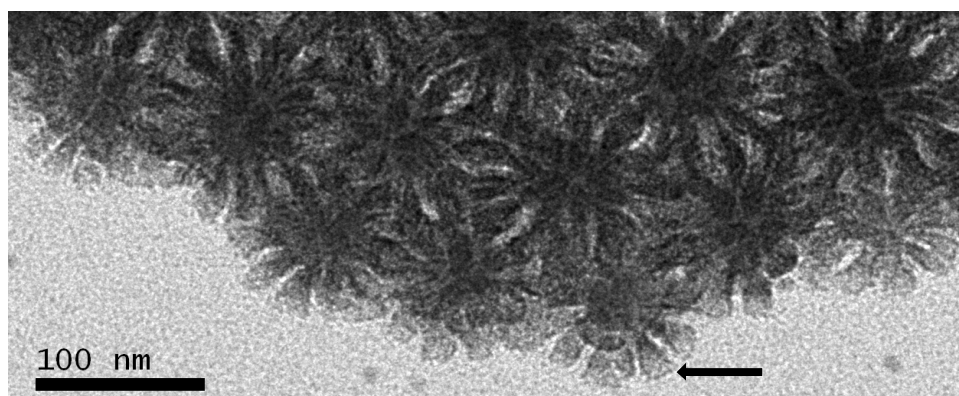


Figure 4.11 Enlarged TEM image of mixed PtBA/PS brush-grafted silica nanoparticles with PtBA $M_{n,SEC}$ of 24.0 kDa and PS $M_{n,SEC}$ of 23.4 kDa (MB-3). The wedge-shaped nanodomain is marked with an arrow.

nanoparticles were prepared by the immobilization of a triethoxysilane-terminated Y-initiator via a hydrolysis/condensation process. The hairy particles were characterized by TGA and the free polymers were analyzed by SEC. TEM studies showed that with the increase of PS M_n from below to above that of PtBA the phase morphology of mixed brushes evolved from the isolated PS nanodomains in the PtBA matrix, to truncated wedge-shaped nanostructures, and a two-layered nanostructure in which the laterally microphase separated bottom layer was covered with longer PS chains. Compared with the mixed brushes grafted on 172 nm silica particles, a notable feature of the phase morphology of mixed PtBA/PS brushes grafted on 67 nm silica nanoparticles is the formation of truncated wedge-shaped nanostructures, which we believe is caused by the effect of the substrate curvature.

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Chapter 5. Summary and Outlook

5.1 Summary

In this dissertation work, a family of thermosensitive polymer brush-grafted silica particles (“hairy” particles) was synthesized by surface-initiated atom transfer radical

polymerization of methacrylate monomers featuring oligo(ethylene glycol) pendant groups of various lengths. Incorporation of a small amount of pH-responsive methacrylic acid groups into thermosensitive polymer brushes yielded doubly responsive hairy particles. When the lower critical solution temperature (LCST) was sufficiently high, the hairy particles can undergo quantitative and reversible phase transfer between an aqueous phase and a hydrophobic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIM][TFSA]).^{1,2} Reducing the size of the silica core of thermosensitive hairy particles from ~ 200 nm to 67 nm raised the transfer temperature slightly and nearly doubled the rate of the particle transfer from water to [EMIM][TFSA].

A series of thermosensitive hairy particles was synthesized by surface-initiated ATRP from 205 nm silica particles.¹ The thermosensitive polymers included homopolymers of methoxydi(ethylene glycol) methacrylate (DEGMMA), methoxytri(ethylene glycol) methacrylate (TEGMMA), and methoxypoly(ethylene glycol) methacrylate (PEGMMA, $M_n = 475$ g/mol), and two random copolymers of TEGMMA and PEGMMA with different compositions. These thermosensitive hairy particles, except the particles grafted with PDEGMMA, were found to undergo spontaneous, quantitative, and reversible phase transfer between water and [EMIM][TFSA] in response to temperature changes. The transfer temperatures of thermosensitive hairy particles from water to [EMIM][TFSA] upon heating were determined by absorbance measurements of both water and ionic liquid phases using UV-vis spectrometry. From the equilibrium distributions of hairy particles in the two phases, the standard enthalpy and entropy changes for the particles transferring from water to the ionic liquid were calculated. Both ΔH° and ΔS° were

positive, which indicated that the transfer of hairy particles was an entropically driven process. A linear relationship between the transfer temperature of hairy particles and the cloud point of the corresponding free polymers in ionic liquid-saturated water was observed.

We then demonstrated that the transfer of thermosensitive hairy particles between aqueous and [EMIM][TFSA] phases can be induced by either temperature or pH changes or both.² In Chapter 2, thermo- and pH-sensitive hairy particles were prepared from ATRP-initiator-functionalized 180 nm silica particles by surface-initiated copolymerization of TEGMMA and *tert*-butyl methacrylate (*t*-BMA) and subsequent removal of *tert*-butyl groups. The cloud point of poly(TEGMMA-*co*-methacrylic acid) in both pure water and [EMIM][TFSA]-saturated water increased with the increase of pH. The hairy particles moved spontaneously from the aqueous phase to [EMIM][TFSA] phase upon heating at 80 °C and returned to the aqueous layer upon cooling at 10 °C, regardless of whether the pH of the aqueous phase was 2.99, 5.00, or 7.02. From UV-vis absorbance measurements, the transfer temperature of hairy particles from water to [EMIM][TFSA] increased with the increase of the pH of the aqueous phase. A linear relationship was observed between T_{tr} of hairy particles and the cloud point of the corresponding free polymer. By taking advantage of the tunable transfer temperature of doubly responsive hairy particles, we demonstrated the reversible transfer of hairy particles at 40 °C by changing the pH of the aqueous layer and multiple phase transfer processes by controlling both temperature and pH.

We further studied whether the size of silica core of thermosensitive hairy particles affects the thermally induced phase transfer behavior of hairy particles between water and

[EMIM][TFSA]. Silica nanoparticles with an average size of 67 nm were functionalized with a triethoxysilane-terminated ATRP initiator via a hydrolysis/condensation process. The initiator particles were then used to grow PPEGMMA brushes by surface-initiated ATRP. The obtained thermosensitive hairy nanoparticles can undergo reversible and quantitative phase transfer between water and [EMIM][TFSA] upon heating at 80 °C and cooling at 10 °C. The transfer temperatures of thermosensitive polymer brush-grafted 67 nm silica nanoparticles were found to be higher by 1-3 °C than those of thermosensitive polymer brush-grafted silica particles with silica core sizes of 205 and 215 nm. Kinetics studies showed that thermosensitive polymer brush-grafted 67 nm silica nanoparticles transferred faster, by 1.8 times, from water to the ionic liquid phase than thermosensitive polymer brush-grafted 205 and 215 nm silica particles at temperatures 15 °C above the respective transfer temperatures.

In a separate effort toward the study of the effect of substrate curvature on phase morphology of mixed homopolymer brushes, we synthesized a series of well-defined mixed poly(*t*-butyl acrylate) (PtBA) and polystyrene (PS) brushes with a constant PtBA M_n and various PS molecular weights from Y-initiator-functionalized 67 nm silica nanoparticles by sequential ATRP and NMRP. The free polymers formed from free initiators in the synthesis of hairy particles were analyzed by SEC; the hairy particles were characterized by TGA. TEM studies showed that with the increase of PS M_n from below to above that of PtBA, the morphology of mixed brushes evolved from isolated PS nanodomains, to truncated wedge-shaped nanostructures, and two-layered nanostructures in which the laterally phase separated bottom layer was covered with longer PS chains. Compared with the mixed brushes grafted on larger silica particles,³⁻⁵ a notable feature of

the morphology of mixed PtBA/PS brushes grafted on 67 nm silica nanoparticles is the formation of truncated wedge-shaped nanostructures,⁶ which likely is caused by the effect of the substrate curvature.

5.2 Future Work

As shown in Chapter 3, the size of silica core of hairy particles does affect the thermally induced phase transfer behavior of hairy particles between water and [EMIM][TFSA]. A logical next step is to explore the synthesis of thermosensitive polymer brushes on even smaller silica nanoparticles, for example, 20 nm, and to study their phase transfer behavior. Reducing the size of silica core particles may continue to increase the transfer rate of hairy nanoparticles between water and the ionic liquid phase. Thermosensitive hairy nanoparticles with a smaller silica core might also be more stable against aggregation in aqueous buffer solutions. Incorporation of a catalyst into the polymer brushes could produce a catalyst system that can shuttle back and forth between aqueous solutions and [EMIM][TFSA] in response to temperature changes. This type of catalyst system may prove valuable in reducing the amount of catalyst needed since it can be recycled between batches.

The phase morphology of mixed brushes is intriguing. From TEM studies of mixed PtBA/PS brushes grafted on 67 nm silica nanoparticles, we saw interesting wedge-shaped nanostructures. More effort is definitely needed to synthesize mixed brushes on smaller silica nanoparticles and to elucidate the effect of substrate curvature on the self-assembly of mixed brushes and mixed brush-grafted silica nanoparticles. Intriguing nanostructures are expected to emerge when the size of polymer chains begins to approach that of the silica nanoparticle core as shown in the computer simulations reported in the literature.

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Vita

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