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I am submitting here with a dissertation written by Dejin Li entitled "Synthesis, Characterization, and Applications of Responsive Polymer Brush-Grafted Particles." 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, Characterization, and Applications
of Responsive Polymer Brush-Grafted
Particles

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Abstract

In this dissertation, I present the synthesis, characterization, and applications of responsive polymer brush-grafted silica/crosslinked polymeric particles. The polymer brush-grafted particles were synthesized by surface-initiated "living"/controlled radical polymerizations from initiator-functionalized particles in the presence of free initiators. Two types of core particles were used in my research. One was silica particles, which were synthesized by Stöber method. The other one was crosslinked PrBA particles, which were prepared by seeded emulsion polymerization. The responsive properties of the grafted polymer brushes were characterized with $^1$H NMR and Dynamic Light Scattering.
## Contents

**Chapter 1. Thermosensitive Hairy Hybrid Particles Synthesized by Surface-Initiated Atom Transfer Radical Polymerization** ................................................................. 1

1.1 Introduction ............................................................................................................ 2

1.2 Experimental Section ............................................................................................. 5

1.2.1 Materials .......................................................................................................... 5

1.2.2 Characterization .............................................................................................. 6

1.2.3 Synthesis of Silica Particles .............................................................................. 7

1.2.4 Synthesis of (11-(2-Bromo-2-methyl)propionyloxy)undecyldimethylchlorosilane and Immobilization of Initiator on Silica Particles ............... 8

1.2.5 Synthesis of Methoxytri(ethylene glycol) Methacrylate (TEGMMA) ......... 9

1.2.6 Synthesis of Benzyl 2-Bromoisobutyrate (BBiB) ........................................... 10

1.2.7 Surface-Initiated ATRPs of DEGMMA and TEGMMA ............................... 10

1.3 Results and Discussion ........................................................................................ 12

1.3.1 Synthesis of ATRP-Initiator-Functionalized Silica Particles ......................... 12

1.3.2 Synthesis of Thermosensitive Polymer Brushes on Silica Particles by Surface-Initiated Atom Transfer Radical Polymerization ................. 14

1.3.3 Thermoresponsive Properties of Poly(methoxydi(ethylene glycol) methacrylate) and Poly(methoxytri(ethylene glycol) methacrylate) in Water ........................................................................................................... 21

1.3.4 Thermoresponsive Properties of PDEGMMA and PTEGMMA Brush-Grafted Particles ............................................................................................................. 25

1.4 Conclusions .......................................................................................................... 30
## Chapter 2. Temperature-Induced Transport of Thermosensitive Hairy Hybrid Particles between Aqueous and Organic Phases

2.1 Introduction

2.2 Experimental Section

2.2.1 Materials

2.2.2 Characterization

2.2.3 Quantitative Study of Transport of PTEGMMA Brush-Grafted Silica Particles from Aqueous to Organic Phases by Heating at 60 °C

2.2.4 Quantitative Study of Transport of PTEGMMA Particles from Organic to Aqueous Phases by Cooling in an Ice/Water Bath

2.2.5 Transport of Free Poly(methoxytri(ethylene glycol) methacrylate) from EA-Saturated Water to Water-Saturated EA by Heating at 60 °C

2.2.6 Transport of Free Poly(methoxytri(ethylene glycol) methacrylate) from Water-Saturated EA to EA-Saturated Water by Cooling in an Ice/Water Bath

2.2.7 Reversible Transport of PTEGMMA Particles between Aqueous and Ethyl Acetate Phases Induced by Temperature Changes

2.3 Results

2.3.1 Synthesis and Characterization of Thermosensitive PTEGMMA Brushes on Silica Particles

2.3.2 Thermosensitive Properties of Free PTEGMMA in Pure Water and Ethyl Acetate-Saturated Water
Chapter 3. Thermosensitive Water-Dispersible Hairy Particle-Supported Pd Nanoparticles for Catalysis of Hydrogenation in Aqueous/Organic Biphasic System

3.1 Introduction ........................................................................................................... 89

3.2 Experiments .......................................................................................................... 91

3.2.1 Materials ......................................................................................................... 91

3.2.2 Characterizations ........................................................................................... 93

3.2.3 Synthesis of 2-(2-Bromo-2-methylpropionyloxy)ethyl Acrylate (Inimer) ........................................................................................................... 94

3.2.4 Synthesis of Poly(tert-butyl acrylate) (PrBA) Seed Latex Particles ......... 94

3.2.5 Synthesis of Initiator-Functionalized Core-Shell Crosslinked PrBA Particles ........................................................................................................... 95

3.2.6 Synthesis of PTEGMMA Brush-Grafted PrBA Particles ......................... 96

3.2.7 Removal of t-Butyl Group of PrBA in PTEGMMA Brush-Grafted PrBA Particles ........................................................................................................... 97

3.2.8 Synthesis of PTEGMMA Hairy Particle-Supported Pd Nanoparticles .... 98

3.2.9 General Procedure for Hydrogenation of Styrene in Aqueous Biphasic System ........................................................................................................... 98

3.3 Results and Discussion ...................................................................................... 99

3.3.1 Synthesis of Initiator-Functionalized Core-Shell Crosslinked PrBA Particles ........................................................................................................... 99

3.3.2 Synthesis of PTEGMMA Brush-Grafted PrBA Particles by Surface-Initiated ATRP .............................................................................................. 100
Chapter 4. Environmentally Responsive "Hairy" Particles: Mixed Homopolymer Brushes on Silica Particles Synthesized by Living Radical Polymerization Techniques

4.1 Introduction

4.2 Experimental Part

4.2.1 Materials

4.2.2 Characterization

4.2.3 Synthesis of Silica Particles

4.2.4 Synthesis of 1

4.2.5 Synthesis of 2

4.2.6 Synthesis of 3

4.2.7 Synthesis of 2-{4-[4'-{(Chlorodimethylsilyl)butyl}phenyl]-2-(2",2",6",6"-tetramethyl-1-piperidinyl)oxy)ethyl 2-Bromo-2-methylpropionate (Y-Silane)
4.2.8 Immobilization of Y-Initiator on Silica Particles ........................................133
4.2.9 Surface-Initiated ATRP of t-BA..............................................................133
4.2.10 Cleavage of the Grafted PrBA from Particles ........................................134
4.2.11 Dehalogenation of PrBA Particles .........................................................135
4.2.12 NMRP of Styrene from Dehalogenated PrBA Particles .........................135
4.2.13 Cleavage of the Grafted Polymers from PrBA/PS Particles ....................136
4.2.14 Hydrolysis of the Polymer Mixture Cleaved from PrBA/PS Particles ....136
4.2.15 Hydrolysis of PrBA by Use of Iodotrimethylsilane ..................................137
4.2.16 Synthesis of Mixed PAA/PS Particles from PrBA/PS Particles .............137
4.2.17 Tyndall Scattering Experiments ...........................................................137

4.3 Results and Discussion ..................................................................................138
4.3.1 Synthesis of Y-Initiator-Functionalized Silica Particles .........................138
4.3.2 Synthesis of PrBA Brushes from Y-Initiator Particles .........................144
4.3.3 Characterization of Free Polymers Formed in the Solution from the Free
    Initiator .......................................................................................................145
4.3.4 Characterization of PrBA Brush-Grafted Particles ..................................147
4.3.5 The Molecular Weight and Grafting Density of PrBA Brushes on Silica
    Particles ......................................................................................................155
4.3.6 NMRP of Styrene from Dehalogenated PrBA Particles .......................157
4.3.7 The Molecular Weight and Molecular Weight Distribution of the Grafted
    PS ...............................................................................................................160
4.3.8 Preparation of Amphiphilic Mixed PAA/PS Particles from Mixed
PrBA/PS Particles and Their Responsive Properties in Selective
Solvents........................................................................................................163

4.4 Conclusions.............................................................................................168

References....................................................................................................168

Vita.............................................................................................................175
List of Tables

2.1 Characterization Data for PTEGMMA Particle-I and –II and Corresponding Free Polymers..........................................................45
2.2 Viscosities of Ethyl Acetate at Various Temperatures from the Literature and Calculation by Use of Arrhenius Equation.................................48
2.3 Refractive Indices of Ethyl Acetate at Various Temperatures..................48
2.4 Cloud Points of PTEGMMA (Mₐ = 24,500 g/mol, 0.5 wt %) in Pure Water and Ethyl Acetate (EA)-Saturated Water..............................................50
2.5 Effect of Toluene on the Cloud Point of PTEGMMA in Water................53
2.6 Effect of 1-Butanol on the Cloud Point of PTEGMMA in Water..............53
2.7 Transmittance/Absorbances of the Dispersions of PTEGMMA Brush-Grafted Silica Particles in Different Solvents...........................................61
3.1 The Yields of Hydrogenation of Styrene in a Water/Octane Biphasic System Using PTEGMMA Hairy Particle-Supported Pd Nanoparticles as Catalyst at 25 °C in five Consecutive Cycles.................................................111
3.2 Initial Reaction Rate Constants of Hydrogenation of Styrene in a Water/Octane Biphasic System Using Thermosensitive Hairy Particle-Supported Pd Nanoparticles as Catalyst at Different Temperatures..............................................115
4.1 Number-Average Molecular Weights of PtBA-1, PtBA-2, and PtBA-3 Obtained from the Conversion, ¹H NMR, and GPC Analysis.............................150
4.2 The Calculated and Observed Diameters of PtBA, PtBA/PS, and PAA/PS Particles.....................................................................................164
List of Figures

1.1 Scanning electron microscopy images of (a) bare particle-1, (b) initiator-functionalized particles (initiator particle-1) prepared from bare particle-1, (c) poly(methoxydi(ethylene glycol) methacrylate) brush-grafted particles synthesized from initiator particle-1, (d) bare particle-2, (e) initiator-functionalized particles (initiator particle-2) prepared from bare particle-2, and (f) poly(methoxytri(ethylene glycol) methacrylate) brush-grafted particles synthesized from initiator particle-2. Scale bar: 200 nm……………………………………….13

1.2 Thermogravimetric analysis (TGA) of (a) bare particle-1, (b) bare particle-2, (c) initiator-functionalized particles (initiator particle-1) prepared from bare particle-1, (d) initiator-functionalized particles (initiator particle-2) prepared from bare particle-2, (e) poly(methoxydi(ethylene glycol) methacrylate) brush-grafted particles synthesized from initiator particle-1, and (f) poly(methoxytri(ethylene glycol) methacrylate) brush-grafted particles synthesized from initiator particle-2. TGA was performed in air at a heating rate of 20 °C/min……………………………………………………………………15

1.3 (a) Relationship between ln([M]o/[M]) and reaction time for the polymerization of methoxydi(ethylene glycol) methacrylate (DEGMA) at 40 °C in THF. The ratios of [DEGMA]o : [benzyl 2-bromoisobutyrate]o : [CuBr]o : [N, N', N', N'′-pentamethyldiethylenetriamine]o were 489 : 1 : 0.90 : 1.94. (b) Number-average molecular weight obtained from gel permeation chromatography relative to polystyrene standards (M_n,GPC, ▲) and polydispersity index (▼) versus monomer conversion……………………………………….17
1.4 Gel permeation chromatography analysis of the polymers obtained from the polymerization of methoxytri(ethylene glycol) methacrylate (TEGMMA) in THF at 40 °C. \([\text{TEGMMA}]_o : [\text{benzyl 2-bromoisobutyrate}]_o : [\text{CuBr}]_o : [N, N, N', N', N''-pentamethyldiethylenetriamine]_o\) were 543 : 1 : 0.94 : 1.99. Number average molecular weight (\(M_{n,GPC}, ▲\)) and polydispersity index (▼) were based on polystyrene calibration……………………………………………………………………………….20

1.5 Optical transmittance of aqueous solutions of PDEGMMA (▲) and PTEGMMA (▼) at wavelength of 500 nm versus temperature during the course of heating. At each temperature, the solutions were equilibrated for 20 min. The concentrations for both solutions were 0.5 wt %. The number average molecular weights of PDEGMMA and PTEGMMA obtained from GPC analysis relative to polystyrene standards were 19,900 and 27,500 g/mol, respectively……………………………………………………………………………………………22

1.6 \(^1\text{H NMR spectra of (a) PDEGMMA free polymer (0.5 wt %) and (b) PDEGMMA brush-grafted particles (2.0 wt %) in D}_2\text{O at various temperatures. The number average molecular weight of free PDEGMMA obtained from gel permeation chromatography analysis relative to polystyrene standards was 19,900 g/mol…………………………………………………………………………………23

1.7 \(^1\text{H NMR spectra of (a) PTEGMMA free polymer (0.5 wt %) and (b) PTEGMMA brush-grafted particles (2.0 wt %) in D}_2\text{O at various temperatures. The number average molecular weight of free PTEGMMA determined from gel permeation chromatography analysis relative to polystyrene standards was 27,500 g/mol…………………………………………………………………………………24

xiii
1.8 Average hydrodynamic diameters of PDEGMMA-particles (■) and bare particle-1 (▼) in the temperature range of 15 to 33 °C measured by dynamic light scattering. The concentrations of the particles in the dispersions were 0.05 mg/mL………………………………………………………………………….27

1.9 Average hydrodynamic diameters of PTEGMMA-particles (■) and bare particle-2 (▼) in the temperature range of 35 to 55°C measured by dynamic light scattering. The concentrations of the particles in the dispersions were 0.05 mg/mL………………………………………………………………………….28

2.1 Hydrodynamic diameter of poly(methoxytri(ethylene glycol) methacrylate) brush-grafted silica nanoparticles (PTEGMMA particle-II) in pure ethyl acetate as a function of temperature. The concentration of PTEGMMA particles in ethyl acetate is 0.5 mg/mL. The hydrodynamic sizes of the hairy particles were measured by dynamic light scattering using the viscosities and refractive indices in Table 2.2 and 2.3…………………………………………………...……46

2.2 1H-NMR spectroscopy study of the saturation of D2O by ethyl acetate at room temperature under the condition of stirring (a) and no stirring (b). The intensity of the methyl peak from CH3CH2- of ethyl acetate was monitored using the deuterated solvent residue peak as reference………………………………………49

2.3 Optical transmittances of aqueous solutions of poly(methoxytri(ethylene glycol) methacrylate) (Mn,GPC = 24,500 g/mol, PDI = 1.09) in pure water (▲, 0.5 wt %) and in water that was saturated with ethyl acetate at 40 °C, 0.5 wt %) as a function of temperature. The transmittances were recorded at wavelength of 500 nm by use of a UV-visible spectrometer…………………………………………………….52
2.4 Optical images of (a) the initial state of aqueous (bottom) and ethyl acetate (upper) layers and (b) the final state after stirring at 60 °C for 24 h. The poly(methoxytri(ethylene glycol) methacrylate) brush-grafted silica particles were initially dispersed in pure water in an ice/water bath (concentration: 1.0 mg/mL)...

2.5 Optical images of (a) the initial state of aqueous (bottom) and ethyl acetate (upper) layers at 60 °C and (b) the final state after stirring in an ice/water bath for 20 h (to avoid water condensing on the outer wall, the vial was placed in a room temperature oil bath and the picture was taken immediately). The poly(methoxytri(ethylene glycol) methacrylate) brush-grafted silica particles were initially dispersed in pure ethyl acetate at 63 °C (concentration: 1.0 mg/mL) and the dispersion was transferred into a 20 mL scintillation vial that contained an equal volume of water...

2.6 Relative absorbance \( \frac{A_i}{A_o} \) of the aqueous dispersion of PTEGMMA brush-grafted particles versus the relative concentration \( \frac{C_i}{C_o} \). \( A_i \) and \( A_0 \) represent the absorbances of sample \( i \) with a concentration of \( C_i \) and the original sample (concentration \( C_o = 1.0 \) mg/mL), respectively. The samples with various concentrations were prepared by diluting the original dispersion with pure water. Transmittances were recorded at wavelength of 500 nm by use of a UV-visible spectrometry...

2.7 Relative concentration \( \frac{C_i}{C_o} \) of PTEGMMA brush-grafted particles in the aqueous layer versus time in the experiment of transporting particles from originally pure water to originally pure ethyl acetate phases by heating at 60 °C
under the condition of (a) stirring at 300 rpm (●) and (b) no stirring (◦). $C_t$ and $C_o$ are the concentrations of the particles in the aqueous layer at time $t$ and 0, respectively. PTEGMMA particles were originally dispersed in water (1.0 mg/mL) in an ice/water bath.

2.8 Relative concentration $C_t/C_o$ of PTEGMMA brush-grafted particles in the ethyl acetate layer versus time in the experiment of transporting particles from ethyl acetate to H$_2$O phases by cooling in an ice/water bath under the condition of (a) stirring at 400 rpm (●) and (b) no stirring (◦). $C_t$ and $C_o$ are the concentrations of the particles in the ethyl acetate layer at time $t$ and 0, respectively. PTEGMMA particles were originally dispersed in ethyl acetate (1.0 mg/mL) at 63 °C.

2.9 Optical image of the aqueous (bottom) and ethyl acetate (upper) layers at time $t$ = 3 min after the vial was placed in a 60 °C oil bath. The streams of particles can be seen in the upper layer.

2.10 Relative concentration $C_t/C_o$ of PTEGMMA brush-grafted particles in the aqueous layer versus time in the experiment of transporting particles from ethyl acetate-saturated water to water-saturated ethyl acetate phase by heating at 60 °C under the condition of (a) stirring at 300 rpm (●) and (b) no stirring (◦). $C_t$ and $C_o$ are the concentrations of the particles in the aqueous layer at time $t$ and 0, respectively. PTEGMMA particles were originally dispersed in ethyl acetate-saturated water (1.0 mg/mL) in an ice/water bath.

2.11 Relative concentration $C_t/C_o$ of PTEGMMA brush-grafted nanoparticles in the aqueous layer versus time in the experiment of transporting particles from EA-saturated water to water-saturated EA phase by heating at 60 °C under the
condition of stirring at 300 rpm. \( C_t \) and \( C_0 \) are the concentrations of the particles in the aqueous layer at time \( t \) and 0, respectively. PTEGMMA particles were originally dispersed in EA-saturated water ((a) 5.0 mg/mL and (b) 0.3 mg/mL) in an ice/water bath. Different batch of bare particles and initiator-functionalized silica particles were used. The weight retentions of bare particles, initiator-functionalized silica particles and PTEGMMA grafted particles (PTEGMMA particle-III) at 800 °C from thermogravimetric analysis (TGA) were 87.1, 85.2 % and 62.7 %, respectively. The \( M_{n,GPC} \) of free PTEGMMA was 37,100 g/mol and the polydispersity index was 1.08.

2.12 Relative concentration \( C_t/C_0 \) of PTEGMMA brush-grafted particles in the ethyl acetate layer versus time in the experiment of transporting particles from water-saturated ethyl acetate to ethyl acetate-saturated water phase by cooling in an ice/water bath under the condition of (a) stirring at 400 rpm (■) and (b) no stirring (●). \( C_t \) and \( C_0 \) are the concentrations of the particles in the ethyl acetate layer at time \( t \) and 0, respectively. PTEGMMA particles were originally dispersed in water-saturated ethyl acetate (1.0 mg/mL) at 63 °C.

2.13 Relative concentration \( C_t/C_0 \) of PTEGMMA brush-grafted nanoparticles (PTEGMMA particle-III) in the EA layer versus time in the experiment of transporting particles from water-saturated EA to EA-saturated water phase by cooling in an ice/water bath under the condition of stirring at 400 rpm. \( C_t \) and \( C_0 \) are the concentrations of the particles in the EA layer at time \( t \) and 0, respectively. PTEGMMA particles were originally dispersed in water-saturated EA ((a) 5.0 mg/mL and (b) 0.3 mg/mL) at 63°C.
2.14 Relative concentration $C_t/C_0$ of PTEGMMA brush-grafted particles in the ethyl acetate layer versus time in the experiment of transporting particles from water-saturated ethyl acetate to ethyl acetate-saturated water phase by cooling in an ice/water bath under the condition of stirring at 400 rpm. $C_t$ and $C_0$ are the concentrations of the particles in the ethyl acetate layer at time $t$ and 0, respectively. The particles were originally dispersed in ethyl acetate-saturated water (1.0 mg/mL) at 0 °C. After being heated at 60 °C with stirring at 300 rpm for 2 h, the vial was placed in an ice/water bath.

2.15 Optical images of aqueous and ethyl acetate layers after 7th cooling in an ice/water bath (a); 7th heating in an 60 °C oil bath (b); 8th cooling (c); 8th heating (d); 9th cooling (e); and 9th heating (f). The PTEGMMA brush-grafted particles were originally dispersed in water-saturated ethyl acetate at 63 °C (concentration: 1.0 mg/mL, PTEGMMA particle-I).

2.16 Attempted transport of bare particles from ethyl acetate-saturated water to ethyl acetate phase upon heating at 60 °C under the condition of stirring at 300 rpm. Bare particles were initially dispersed in ethyl acetate-saturated water in an ice/water bath (concentration: 1.0 mg/mL). The vial was then placed in a 60 °C oil bath. Optical images of aqueous and ethyl acetate layers in the initial state in the 60 °C oil bath (a); after 10 min (b); and after 369 min (c).

2.17 Optical transmittance versus time of (a) pure water (▲) and ethyl acetate-saturated water (▼, saturated at 21 °C) at 60 °C; (b) pure ethyl acetate (●) and water-saturated ethyl acetate (■, saturated at 60 °C) at 15 °C. In (a), a quartz cell that contained pure water (or water that was saturated with ethyl acetate at
21 °C) was placed in the cell holder with a preset temperature of 60 °C and the transmittance was recorded immediately at wavelength of 500 nm. In (b), a quartz cell that contained pure ethyl acetate (or ethyl acetate that was saturated with water at 60 °C) was placed in the cell holder with a preset temperature of 15 °C and the transmittance was recorded immediately at 500 nm.

2.18 Dynamic light scattering study of the droplets formed in the aqueous layer after the glass tube that contained mutually saturated ethyl acetate and water (saturated at 21 °C, both layers were 1.5 cm high) was placed in the sample holder with a preset temperature of 60 °C. (a) 0 min and (b) 3 min.

3.1 ¹H NMR spectra of (a) poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) brush-grafted PrBA particles and (b) free PTEGMMA. D₂O was used as solvent.

3.2 ¹H NMR spectra of (a) poly(t-butyl acrylate) (PtBA in CDCl₃) and (b) poly(acrylic acid) (PAA, obtained from hydrolysis of PrBA with CF₃COOH as catalyst, D₂O was used as solvent).

3.3 ¹H NMR spectra of (a) PTEGMMA and (b) PTEGMMA after treatment under the conditions used for hydrolysis of PrBA. CDCl₃ was used as solvent.

3.4 Thermogravimetric analysis (TGA) of PTEGMMA brush-grafted crosslinked poly(acrylic acid) particles and Pd nanoparticle-embedded hairy particles. The Pd content in the hairy particles was 9.5 wt %. TGA was performed in air at a heating rate of 20 °C/min.
3.5 A typical transmission electron microscopy (TEM) micrograph of Pd nanoparticle-loaded, thermosensitive PTEGMMMA brush-grafted PAA particles.................................................................106

3.6 Average hydrodynamic diameters of (■) PTEGMMMA brush-grafted PtBA particles and (○) Pd nanoparticle-embedded PTEGMMMA brush-grafted PAA particles as a function of temperature. The concentrations of hairy particles in water were 0.01 mg/mL. At each temperature, at least eight measurements were mad to give an average hydrodynamic diameter.................................108

3.7 Kinetics of hydrogenation of styrene in a water/octane biphasic system using thermosensitive hairy particle-supported Pd nanoparticles as catalyst at 20 °C (▲), 25 °C (●), 34.5 °C (▼) and 42 °C (■).................................................................113

3.8 lnk versus 1/T for the hydrogenation of styrene in a water/octane biphasic system using thermosensitive hairy particle-supported Pd nanoparticles as catalyst. k is the initial reaction rate constant at a specific temperature, obtained by linear regression fitting of the data points below 40 % conversions........115

4.1 Scanning electron microscopy images of (a) bare silica particles, (b) Y-initiator particles, (c) poly(tert-butyl acrylate) particles, (d) dehalogenated poly(tert-butyl acrylate) particles, (e) poly(tert-butyl acrylate)/polystyrene particles, and (f) poly(acrylic acid)/polystyrene particles. Scale bars: 200 nm.........................139

4.2 ¹H NMR spectrum of Y-silane.................................................................141

4.3 IR spectra of (a) bare particles, (b) Y-initiator particles, (c) poly(tert-butyl acrylate) particles, (d) poly(tert-butyl acrylate)/PS particles, and (e) poly(acrylic acid)/PS particles.........................................................142

xx
4.4 Thermogravimetric analysis (TGA) of (a) bare particles, (b) Y-initiator particles, (c) PtBA-particle-1 obtained at the monomer conversion of 14.1%, (d) PtBA-particle-2 obtained at the monomer conversion of 24.6%, (e) PtBA-particle-3 obtained after the polymerization was stopped at the monomer conversion of 38.0%, (f) PAA/PS particles, and (g) PtBA/PS particles. TGA was performed in air at a heating rate of 20 °C/min.

4.5 $^1$H NMR spectra of the polymerization mixture at $t = 0$ (a) and 30 min (b)...

4.6 Relationship between $\ln([M]_0/[M])$ versus time for the ATRP of tBA at 75 °C. The ratios of $[M]_0$:[free EBiB]:[CuBr]:[CuBr$_2$]:[PMDETA]$_o$ were 553:1:1.07:0.033: 1.05.

4.7 GPC curves of PtBA-1, PtBA-2, and PtBA-3.

4.8 $^1$H NMR spectrum of free PtBA-1 taken at the reaction time $t = 547$ min.

4.9 $^1$H NMR spectrum of free PtBA-2 taken from the mixture at reaction time $t = 1053$ minutes.

4.10 $^1$H NMR spectrum of free PtBA-3 (corresponding to PtBA-particle-3) obtained at the reaction time $t = 1805$ minutes.

4.11 $^1$H NMR spectra of (a) PtBA-particle-3 and (b) mixed PtBA/PS particles dispersed in CDCl$_3$.

4.12 The mass percent of the grafted PtBA relative to the mass of the residual silica at 800 °C corrected from Y-initiator particles versus the degree of polymerization of free polymers calculated on the basis of the monomer conversion. (■) Degree of polymerization calculated by use of the ratio of monomer to total initiator; (●) degree of polymerization obtained by use of the
ratio of monomer to the free initiator. Relative mass increase) \[ \frac{(1 - W_{pp})/W_{pp} - (1 - W_{ip})/W_{ip}}{W_{pp}} \times 100 \], where \( W_{pp} \) and \( W_{ip} \) represent the percent weight retention at 800 °C of PrBA particles and Y-initiator particles, respectively.

4.13 \(^1\)H NMR spectrum of cleaved PrBA.

4.14 GPC curves of the free (―) and cleaved polymers (⁎⁎⁎): (a) the PrBA cleaved from PrBA-particle-3; (b) free PrBA-3; (c) the polymer mixture cleaved from mixed PrBA/PS particles; (d) cleaved PS; and (e) free PS.

4.15 Relationship between ln([M]_o/[M]) versus time for the NMRP of styrene at 120 °C. \([M]_o:[\text{Free initiator PTEMPO}] = 644:1\).

4.16 \(^1\)H NMR spectrum of PrBA/PS cleaved from the silica particles.

4.17 \(^1\)H NMR spectrum of PS obtained from cyclohexane extract.

4.18 \(^1\)H NMR spectra of (a) free poly(\(t\)-butyl acrylate) in CDCl\(_3\) and (b) poly(acrylic acid) in D\(_2\)O obtained from hydrolysis of poly(\(t\)-butyl acrylate) with iodonitromethane.

4.19 Tyndall light scattering experiment shows the stable suspensions of PAA particles in CH\(_3\)OH but not in CHCl\(_3\), PS particles in CHCl\(_3\) but not in CH\(_3\)OH, mixed PAA/PS particles in both CHCl\(_3\) and CH\(_3\)OH.

4.20 \(^1\)H NMR spectra of PAA/PS particles dispersed in (a) CDCl\(_3\), (b) DMF-\(_d_7\), and (c) CD\(_3\)OD. A drop of DMF-\(_d_7\) was added into the particles prior to CDCl\(_3\) and CD\(_3\)OD to increase the concentration of the dispersed particles.

4.21 \(^1\)H NMR spectra of (a) PAA free polymer dissolved in DMD-\(_d_7\) and (b) PAA/PS particles dispersed in DMD-\(_d_7\).
Chapter 1. Thermosensitive Hairy Hybrid Particles

Synthesized by Surface-Initiated Atom Transfer

Radical Polymerization
1.1 Introduction

Hybrid particles composed of an inorganic core and an organic polymer shell have attracted growing interest due to the intriguing properties associated with the core (optical, magnetic, mechanical properties, etc.) and the desired properties of polymers (processability, compatibility to the environment, etc.).\textsuperscript{1,2} If the shell is composed of polymer chains that are densely tethered by one end via a covalent bond to the surface of core particle, hairy particles are obtained as polymer chains are forced to stretch away from the grafting sites forming polymer brushes.\textsuperscript{1-5} Generally, there are two approaches to chemically attach polymer chains to a surface: (1) the “grafting to” method, in which the end-functionalized polymers react with an appropriate surface;\textsuperscript{6} (2) the “grafting from” method, in which polymer chains are grown from initiator-terminated self-assembled monolayers (SAMs).\textsuperscript{1-3,7} Using the grafting from approach, Prucker and Rühe described in their seminal papers the growth of polystyrene from high-surface-area silica gels that were functionalized with an azo monolayer.\textsuperscript{7,8} Compared to conventional polymerizations, “living”/controlled processes are advantageous as they can provide control on molecular weight, molecular weight distribution, polymer architecture, and end functionality. A variety of “living”/controlled radical polymerization techniques including atom transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization (NMRP), and reversible radical addition-fragmentation chain transfer process, and living anionic polymerization have been used by a number of research groups to synthesize polymer brushes on silica particles,\textsuperscript{9-26} gold particles,\textsuperscript{27} quantum dots,\textsuperscript{28,29} and magnetic particles.\textsuperscript{30,31}
By use of stimuli-responsive polymers or polymeric systems, one can prepare environmentally responsive hairy hybrid particles, which are attractive building blocks for design and fabrication of smart nanostructured materials. Up to date, there are only a few reports on stimuli-responsive hairy particles and in most cases poly(N-isopropylacrylamide) (PNIPAm), one of the most studied thermosensitive polymers, was used. Tenhu et al. prepared PNIPAm-grafted gold particles using both “grafting to” and “grafting from” (RAFT) methods and found from microcalorimetric measurements that PNIPAm brushes exhibited two phase transitions. Zhu et al. synthesized gold particles that were stabilized by thiol-terminated PNIPAm. The solution of hybrid particles underwent a clear-to-opaque transition when the temperature was increased from 25 to 30 °C. Poly(2-(N-morpholino)ethyl methacrylate brushes were grown on silica particles by Perruchot et al. using aqueous ATRP. The particles were found to begin aggregation at around 34 °C, which corresponded approximately to the cloud point of this polymer in water. PNIPAm brushes were also synthesized from functionalized anionic polystyrene latex particles by Kizhakkedathu et al. Very recently, Kim et al. reported the preparation of gold nanoparticle/PNIPAm hybrids via surface-initiated ATRP and Liu et al. fabricated hybrid particles with PNIPAm chains in the corona layer through a self-assembling approach.

In this work, we used surface-initiated ATRP from silica particles to synthesize thermoresponsive hairy particles (Scheme 1.1) and studied the thermo-induced phase transitions. It has been shown recently that the introduction of a short oligo(ethylene glycol) chain to the polymer backbone as pendant group yields thermosensitive water-soluble polymers and the cloud point (or lower critical solution temperature,
Scheme 1.1. Synthesis of Thermosensitive Hairy Hybrid Particles.
LCST) can be tuned by the side chain length and end group.\textsuperscript{45-47} Using a living anionic polymerization technique, Han et al. synthesized poly(methoxydi(ethylene glycol) methacrylate) (PDEGMMA) and poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA).\textsuperscript{45} The cloud points of PDEGMMA and PTEGMMA were around 26 °C and 52 °C, respectively. In this work, DEG MMA and TEGMMA were used and the thermoresponsive properties of the polymers and polymer brushes on particles were characterized by turbidimetry, variable temperature \textsuperscript{1}H NMR spectroscopy, and dynamic light scattering.

1.2 Experimental Section

1.2.1 Materials

Methoxydi(ethylene glycol) methacrylate (95%, Aldrich) was distilled over CaH\textsubscript{2}. CuBr (98%, Aldrich) was purified according to the procedure described in the literature\textsuperscript{48} and stored in a desiccator. Tetrahydrofuran (THF) was distilled from sodium and benzophenone and stored in a solvent storage bottle. Tetraethoxysilane (98%) and ammonium hydroxide (25% in water) were purchased from Acros and used as received. Chlorodimethylsilane (98%), 2-bromoisobutyryl bromide (98%), 10-undecen-1-ol (98%), methacryloyl chloride (97%), and tri(ethylene glycol) monomethyl ether (95%) were obtained from Aldrich and used as received. Platinum-divinyl tetramethyldisiloxane complex in xylene (2.1–2.4% Pt concentration in xylene) was purchased from Gelest Inc.
1.2.2 Characterization

Gel permeation chromatography (GPC) was carried out at room temperature using PL-GPC 20 (an integrated GPC 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). The data were processed using Cirrus™ GPC/SEC software (Polymer Laboratories). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Standard monodisperse polystyrenes (Polymer Laboratories) were used for calibration. The $^1$H (300 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded on a Varian Mercury 300 NMR spectrometer and the residual solvent proton signal was used as the internal standard. Electron ionization mass spectroscopy was performed on a ZAB-EQ (VG-Analytical; Manchester, UK) in the Mass Spectroscopy Center in the Chemistry Department at the University of Tennessee at Knoxville. Variable temperature $^1$H NMR (400 MHz) spectra were recorded on a thermoregulated Bruker Avance 400 using solutions of polymers (0.5 wt %) or dispersions of polymer brush-grafted particles (2.0 wt %) in D$_2$O (99.9 D atom %). An acquisition of 32 scans (for polymer solutions) or 300 scans (for polymer brush-grafted particles) was performed with an acquisition time of 4 s per scan, a pulse of 10 μs and a recycle delay of 1 s. At each temperature, the solutions or dispersions were equilibrated for 20 min. IR spectra were recorded on a BOMEM MB-Series Fourier transform infrared instrument. The samples were prepared by adding several drops of a solution of the compound in chloroform on a NaCl plate and drying in vacuum at room temperature for 10 min.

Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C using TA Q-series Q50. Scanning electron
microscopy (SEM) images were acquired on a LEO 1525 scanning electron microscope. The SEM samples were prepared by adding a few drops of a dilute dispersion on a clean silicon wafer and allowing the solvent to evaporate in air. Dynamic light scattering (DLS) measurements were conducted with a Brookhaven Instruments BI-200SM goniometer (633 nm) and a BI-9000AT digital correlator. The time correlation functions were analyzed with a Laplace inversion program (CONTIN). Aqueous dispersions of particles were filtered through Millipore membranes (0.45 μm PTFE filters for bare particles and 1.0 μm Nylon filters for polymer brush-grafted particles). For each temperature, the dispersions were equilibrated for 30 min. Multiple measurements were made to give an average hydrodynamic diameter. Optical transmittances of aqueous polymer solutions (0.5 wt %) at various temperatures were recorded at wavelength of 500 nm with a UV-visible spectrometer (Biomate 5 from Thermospectronic). The sample cell was thermostated with an external water bath of a Fisher Scientific Isotemp refrigerated circulator. At each temperature, the solutions were equilibrated for 20 min.

1.2.3 Synthesis of Silica Particles

Ammonium hydroxide (30.72 g, 25% in water) and ethanol (320 mL) were added into a 1000 mL two-necked flask that was placed in a 43 °C oil bath, followed by injection of a solution of tetraethoxysilane (TEOS) (3.52 g, 16.9 mmol) in ethanol (5 mL) at a rate of 9.3 mL/min using a syringe pump. The concentrations of NH₃, H₂O, and TEOS in the solution were 0.603 M, 4.13 M, 0.0465 M, respectively. The mixture was stirred vigorously for 310 min. The particles were isolated by centrifugation (Eppendorf 5804, 8500 rpm, 35 min), redispersed in ethanol, and centrifugated again. This washing process
was repeated with ethanol one more time, water three times, and ethanol again. The particles were dried with a stream of air flow (1.07 g).

### 1.2.4 Synthesis of (11-(2-Bromo-2-methyl)propionyloxy)undecyl(dimethylchlorosilane and Immobilization of Initiator on Silica Particles

10-Undecen-1-yl 2-bromo-2-methylpropionate was synthesized according to the procedure reported in the literature.\(^4\)\(^8\) \(^1\)H NMR (CDCl\(_3\)): \(\delta\) (ppm) 1.26-1.34 (m, 12H, \(\text{CH}_2(\text{CH}_2)_6\text{CH}_2\text{CH}_2\text{O}\)), 1.65 (m, 2H, \(\text{CH}_2\text{CH}_2\text{O}\)), 1.90 (s, 6H, \(\text{CH}_3\)), 2.01 (q, 2H, =CH\(\text{CH}_2\)), 4.13 (t, 2H, \(\text{CH}_2\text{O}\)), 4.92 (m, 2H, \(\text{CH}_2\text{=CH-}\)), 5.79 (m, 1H, \(\text{CH}_2\text{=CH-}\)); \(^1\)\(^3\)C NMR (CDCl\(_3\)): \(\delta\) (ppm) 25.74, (\(\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\)), 28.30 (\(\text{CH}_2\text{CH}_2\text{O}\)), 28.87 (\(\text{CH}_3(\text{CH}_2)_3\text{O}\)), 29.03, 29.10, 29.32, 29.37 (\(\text{CH}_2\)), 30.75 (\(\text{CH}_3\)), 33.75 (\(\text{CH}_2\text{CH}_2\text{CH}=\)), 55.92 (\(\text{C(CH}_3)_2\text{Br}\)), 66.09 (\(\text{CH}_2\text{CH}_2\text{OOC}\)), 114.10 (\(\text{CH}_2\text{=CH-}\)), 139.12 (\(\text{CH}_2\text{=CH-}\)), 171.68 (C=O).

Chlorodimethylsilane (4.0 mL) was injected via a disposable syringe into a 25 mL two-necked flask containing 10-undecen-1-yl 2-bromo-2-methylpropionate (0.464 g, 1.45 mmol) under nitrogen atmosphere, followed by addition of platinum-divinyltetramethyldisiloxane complex in xylene (14 \(\mu\)L). The reaction was monitored by \(^1\)H NMR spectroscopy. After the reaction was complete, excess chlorodimethylsilane was removed by vacuum and the product was used directly without further purification. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) (ppm) 0.37 (s, 6H, \(\text{Si(CH}_3)_2\)), 0.78 (t, 2H, \(\text{CH}_2\text{Si}\)), 1.25-1.38 (m, 16H, \(\text{CH}_2(\text{CH}_2)_8\text{CH}_2\text{CH}_2\text{O}\)), 1.65 (m, 2H, \(\text{CH}_2\text{CH}_2\text{O}\)), 1.91 (s, 6H, \(\text{C(CH}_3)_2\text{Br}\)), 4.14 (t, 2H, \(\text{CH}_2\text{O}\)); \(^1\)\(^3\)C NMR (CDCl\(_3\)): \(\delta\) (ppm) 1.65 (\(\text{Si(CH}_3)_2\)), 18.95 (\(\text{CH}_2\text{Si}\)), 22.95 (\(\text{CH}_2\text{CH}_2\text{Si}\)), 25.76 (\(\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\)), 28.31 (\(\text{CH}_2\text{CH}_2\text{O}\)), 29.15, 29.21, 29.43, 29.51 (\(\text{CH}_2\)), 30.76
(C(\text{CH}_3)\text{H}_2), 32.94 (\text{CH}_2\text{CH}_2\text{SiH}_3), 55.99 (\text{C}(\text{CH}_3)\text{H}_2\text{Br}), 66.14 (\text{CH}_2\text{CH}_2\text{OOC}), 171.73 (\text{C}=\text{O}).

The product was dissolved in dry THF (8 mL) and the solution was transferred via a syringe to a flask that contained a dispersion of bare silica particles (1.05 g) in dry THF (10 mL). The bare silica particles were dried in vacuum at 110 °C for 5 h before dispersed in THF. The mixture was stirred at 70 °C under N\textsubscript{2} atmosphere for 67 h. The particles were isolated by centrifugation, redispersed in THF, and centrifuged again. This washing process was repeated four times, followed by drying with a stream of air to yield dry particles (0.90 g).

1.2.5 Synthesis of Methoxytris(ethylene glycol) Methacrylate (TEGM-MA)

A solution of methacryloyl chloride (22.05 g, 0.211 mol) in diethyl ether (40 mL) was added dropwise to a mixture of tri(ethylene glycol) monomethyl ether (41.06 g, 0.250 mol), triethylamine (60.0 mL, 0.43 mol), and diethyl ether (160 mL) in an ice/water bath under nitrogen atmosphere. The mixture was stirred at room temperature overnight and was filtered to remove the precipitate. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexanes/ethyl acetate = 1/2, v/v). The product was then distilled in vacuum (b.p. 90 °C/0.09 mm Hg) with addition of a small amount of catechol as inhibitor. A colorless liquid was obtained (34.25 g, 70.0%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \textit{\delta} (ppm) 1.88 (s, 3H, CH\text{H}_3), 3.31 (s, 3H, CH\text{H}_3), 3.48 (t, 2H, CH\text{H}_2OCH\text{H}_3), 3.57-3.63 (m, 6H, OCH\text{H}_2CH\text{H}_2OCH\text{H}_2CH\text{H}_2OCH\text{H}_2CH\text{H}_2OCH\text{H}_3), 3.68 (m, 2H, COOCH\text{H}_2CH\text{H}_2), 4.23 (t, 2H, COOCH\text{H}_2), 5.51 (s, 1H, CH\text{H}\text{H}=\text{C}), 6.06 (s, 1H, CH\text{H}H=\text{C}); \textsuperscript{13}C NMR (CDCl\textsubscript{3}): \textit{\delta} (ppm) 18.20 (CH\text{H}_3C), 58.91
(CH₃O), 63.75, 68.99, 70.45, 70.49, 71.78 (CH₂), 125.62 (CH₂=C), 135.99 (C(CH₃)=CH₂), 167.21 (C=O). IR (cm⁻¹): 2880 (CH₂, ether), 1719 (C=O), 1637 (CH₂=C-), 1454 (CH₃ and CH₂), 1170 and 1117 (C-O-C).

1.2.6 Synthesis of Benzyl 2-Bromoisobutyrate (BBiB)

Benzyl alcohol (1.01 g, 9.34 mmol), methylene chloride (20 mL), and triethylamine (2.90 g, 28.7 mmol) were added into a three-necked flask, which was then placed in an ice/water bath. A solution of 2-bromo-2-methylpropionyl bromide (8.02 g, 34.9 mmol) in methylene chloride (20 mL) was added dropwise under nitrogen atmosphere. After being stirred at room temperature for 14 h, the reaction mixture was washed with an aqueous solution of ammonium chloride (40 mL × 4). The organic layer was isolated and dried over anhydrous sodium sulfate. After removal of solvent using a rotavapor, the crude product was purified by silica column chromatography (hexanes/ethyl acetate = 4/1, v/v) to give a colorless liquid (1.05 g, 43.8%). ¹H NMR (CDCl₃): δ (ppm) 1.97 (s, 6H, 2CH₃), 5.23 (s, 2H, CH₂), 7.39-7.41 (m, 5H, aromatic); ¹³C NMR (CDCl₃): δ (ppm) 30.66 (CH₃), 55.59 (C(CH₃)₂Br), 67.43 (CH₂O), 127.78, 128.22, 128.48, 135.31 (aromatic), 171.32 (C=O). IR (cm⁻¹): 3034 (aromatic C-H), 2975 and 2933 (CH₃), 1737 (C=O), 1498 (aromatic C=C), 1458 (CH₃ and CH₂), 1009 (C-Br). MS (EI) m/z: 256.01.

1.2.7 Surface-Initiated ATRPs of DEGMMA and TEGMMA

A typical procedure for surface-initiated ATRP of DEGMMA was described below. A similar procedure was used for the synthesis of PTEGMMA brushes on silica particles. The particles functionalized with the ATRP initiator (0.169 g) were added into a two-necked flask that contained CuBr (9.2 mg, 64 µmol), and were dried in vacuum at 35
°C for 18 h. DEGMA (6.55 g, 34.8 mmol) and free initiator BBiB (18.3 mg, 71.2 µmol) were added into the flask. The particles were dispersed by ultrasonication, followed by injection of dry THF (6.1 mL). After the mixture was degassed by three freeze-pump-thaw cycles, \(N, N, N', N', N''\)-pentamethyldiethylenetriamine (PMDETA) (24.0 mg, 138 µmol) was added via a microsyringe at the thawing point of the mixture. The flask was then placed in an oil bath with a preset temperature of 40 °C. After the polymerization proceeded for 139 min, the flask was removed from the oil bath and opened to air. The mixture was diluted with THF (15 mL). The particles were isolated by centrifugation (Eppendorf 5804, 8000 rpm, 15 min), and the supernatant was passed through a short column of activated neutral aluminum oxide (top)/silica gel (bottom) (1/2, v/v) three times. The particles were dispersed in THF and separated by centrifugation. Methanol was used to disperse the particles and several drops of an ammonia solution (25% in water) were added into the dispersion, followed by centrifugation. This process was repeated one more time. The particles were then redispersed in CH\(_3\)OH, allowed to stand overnight (the precipitate was removed), and isolated by centrifugation. A portion of the particles was dried in vacuum at 40 °C for 5 h for thermogravimetric analysis. The rest of the particles were washed with water twice for use in the experiments of variable temperature \(^1\)H NMR spectroscopy and dynamic light scattering. The free polymer formed in the solution was precipitated in hexanes and analyzed by GPC relative to polystyrene standards. \(M_{n,GPC} = 19,900\) g/mol, polydispersity index (PDI) = 1.14.
1.3 Results and Discussion

1.3.1 Synthesis of ATRP-Initiator-Functionalized Silica Particles

Bare silica particles were prepared using the Stöber process, which involves the hydrolysis and condensation of tetraethoxysilane (TEOS) in an ammonia/ethanol solution. This process is known to produce spherical silica particles with a relatively uniform size distribution, and the size of the particles can be controlled by the initial concentrations of the reactants and the addition rate of TEOS. In this study, two batches of silica particles with average diameters of 135 nm (bare particle-1) and 133 nm (bare particle-2), measured from scanning electron microscopy (SEM) images (Figure 1.1a and 1.1d, respectively), were used to prepare thermosensitive hairy particles by surface-initiated ATRPs of methoxydi(ethylene glycol) methacrylate (DEGMMA) and methoxytri(ethylene glycol) methacrylate (TEGMMA), respectively. An ATRP-initiator-terminated monolayer was deposited on the surface of the particles via the reaction between the surface silanol groups and the Si-Cl of an initiator-terminated organosilane. Although denser SAMs can be obtained by use of organotrichlorosilanes, the reaction process is complex and crosslinked polymeric species formed in the solution might precipitate on the surface. To avoid this issue, an initiator-terminated monochlorosilane, (11-(2-bromo-2-methyl)propionyloxy)undecyldimethylchlorosilane, was synthesized and used.

Bare silica particles were dried in vacuum (~ 30 millitorr) at 110 °C for 5 h, and were dispersed in dry THF by ultrasonication. The surface immobilization reactions were carried out under N₂ atmosphere at 70 °C. The particles were then separated by centrifugation and repeatedly washed with solvents, followed by drying with a stream of
**Figure 1.1.** Scanning electron microscopy images of (a) bare particle-1, (b) initiator-functionalized particles (initiator particle-1) prepared from bare particle-1, (c) poly(methoxydi(ethylene glycol) methacrylate) brush-grafted particles synthesized from initiator particle-1, (d) bare particle-2, (e) initiator-functionalized particles (initiator particle-2) prepared from bare particle-2, (f) poly(methoxytri(ethylene glycol) methacrylate) brush-grafted particles synthesized from initiator particle-2. Scale bar: 200 nm.
The initiator-functionalized particles can be easily dispersed in common organic solvents (THF, toluene, CH$_3$OH, etc.) but not in water. From SEM images (Figure 1.1b and e), the average diameters of the initiator-functionalized particles were essentially the same as those of bare particles (initiator-functionalized particles prepared from bare particle-1 and -2 were designated as initiator particle-1 and -2, respectively). Thermogravimetric analysis (TGA), which was performed in air at a heating rate of 20 °C/min, showed that there was a difference of 3.2% in the weight retentions at 800 °C between the initiator particles and the corresponding bare particles (Figure 1.2). Calculations show that the initiator density on the particle surface is ~0.34 nm$^2$/initiator for both initiator particle-1 and -2. This value is consistent with those reported in the literature.$^{11,12}$

1.3.2 Synthesis of Thermosensitive Polymer Brushes on Silica Particles by Surface-Initiated Atom Transfer Radical Polymerization

Poly(DEGMMA) (PDEGMMA) and poly(TEGMMA) (PTEGMMA) are thermosensitive water-soluble polymers that have been reported to undergo phase transitions from a soluble to an insoluble state in water at 26 and 52 °C, respectively.$^{45}$ Although living anionic polymerizations of DEGMMA and TEGMMA were achieved by Han et al.$^{45}$, controlled/“living” free radical polymerizations of these two monomers have not been reported in the literature. Note that ATRPs of oligo(ethylene glycol) methacrylate (OEGMMA) have been conducted by several research groups.$^{53-55}$ However, the monomer is a mixture of oligo(ethylene glycol) esters with a distribution of side chain lengths and it has been reported by Stöver et al. that the polymer does not exhibit a LCST transition.$^{54}$ To achieve controlled radical polymerizations of DEGMMA and TEGMMA,
Figure 1.2. Thermogravimetric analysis (TGA) of (a) bare particle-1, (b) bare particle-2, (c) initiator-functionalized particles (initiator particle-1) prepared from bare particle-1, (d) initiator-functionalized particles (initiator particle-2) prepared from bare particle-2, (e) poly(methoxydi(ethylene glycol) methacrylate) brush-grafted particles synthesized from initiator particle-1, (f) poly(methoxytri(ethylene glycol) methacrylate) brush-grafted particles synthesized from initiator particle-2. TGA was performed in air at a heating rate of 20 °C/min.
an effort was made to optimize the reaction conditions. Various solvents including anisole, THF, dimethylsulfoxide, water, CH₃OH, and H₂O/CH₃OH (1:1, v/v) were used as polymerization medium, and ligands such as tetramethylethylenediamine, \(N,N',N''\)-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyl-triethylenetetramine, 2,2'-bipyridine, and 4,4'-di-5-nonyl-2,2'-bipyridine were examined in combination with CuBr or CuCl as catalytic system. We found that when CuBr and PMDETA were used as catalyst and ethyl 2-bromoisobutyrate (or benzyl 2-bromoisobutyrate (BB₂B)) as initiator, the polymerizations of DEGMMA and TEGMMA in THF were close to the controlled process but still not an ideal process (see the kinetics analysis in Figure 1.3 and the discussion). In this work, we used this condition to grow PDEGMMA and PTEGMMA brushes on silica particles.

Initiator particle-1 and -2 were used to grow PDEGMMA and PTEGMMA brushes, respectively. Surface-initiated ATRP of DEGMMA or TEGMMA was carried out at 40 °C in THF with CuBr/PMDETA as catalyst in the presence of a free initiator BB₂B. For DEGMMA, the ratios of \([M]_o : [BB₂B]_o : [CuBr]_o : [PMDETA]_o\) were 489 : 1 : 0.90 : 1.94. For TEGMMA, the ratios were 543 : 1 : 0.94 : 1.99. Since the polymerizations of DEGMMA and TEGMMA were fast, a slightly different procedure from that for the growth of PtBA brushes was used to ensure that the surface-initiated and solution polymerizations begin simultaneously. The initiator particles were dispersed in a mixture of monomer, THF, and free initiator BB₂B. A sample was taken for \(^1\)H NMR spectroscopy analysis. After the reaction mixture was degassed by three freeze-pump-thaw cycles, PMDETA was injected via a microsyringe at the thawing point of the mixture. The flask was then placed in an oil bath with a preset temperature of 40 °C. The
Figure 1.3. (a) Relationship between \(\ln([M]_o/[M])\) and reaction time for the polymerization of methoxydi(ethylene glycol) methacrylate (DEGMA) at 40 °C in THF. The ratios of \([\text{DEGMA}]_o : [\text{benzyl 2-bromoisobutyrate}]_o : [\text{CuBr}]_o : [N, N', N', N''-pentamethyldiethylenetriamine]_o\) were 489 : 1 : 0.90 : 1.94. (b) Number-average molecular weight obtained from gel permeation chromatography relative to polystyrene standards (\(M_{n,GPC}, \triangle\)) and polydispersity index (\(\triangledown\)) versus monomer conversion.
color of the reaction mixture gradually changed from light blue to yellow. In this procedure, the initiator particles and free initiator were mixed prior to the addition of ligand, allowing the radicals on the surface and in the solution to form and propagate at the same time.

The polymerizations were monitored by $^1$H NMR spectroscopy using the integrals of the peaks located at 4.12-4.39 ppm and 3.93-4.12 ppm, which were from -CH$_2$OOC- of the monomer and polymer, respectively. The polymers formed in the solutions were also analyzed by gel permeation chromatography (GPC) relative to polystyrene standards. After desired conversions were reached, the polymerizations were stopped by opening the flasks to air and the particles were isolated by centrifugation. As described in the literature,$^{42}$ the free initiator efficiency can be quantified by $^1$H NMR spectroscopy. Since the methylene peaks of ethyl 2-bromoisobutyrate overlap with those of the monomer and polymer, a new initiator, BB$^i$B, was used as free initiator. The methylene peak from the benzyl group of BB$^i$B completely shifted from 5.14 to 4.99 ppm after the reaction started, suggesting an initiator efficiency of 100%.

Figure 1.3 shows the kinetics plot and GPC results for the polymerization of DEGMMA. Although a linear relationship between $\ln([M]_o/[M])$ and reaction time was not observed, the molecular weight of the polymer obtained from GPC analysis increased linearly with monomer conversion and the polydispersity index decreased progressively from 1.19 to 1.14. The number-average molecular weight ($M_n$) of the final polymer was 19,900 g/mol. An ideal controlled radical process means a linear relationship between $\ln([M]_o/[M])$ and polymerization time, a linear increase of polymer molecular weight with monomer conversion, and narrow molecular weight distributions. If we assume that
the polymerization is an ideal controlled process, the degree of polymerization (DP) of PDEGMMA calculated on the basis of monomer-to-initiator ratio and the monomer conversion is 152. Considering that the initiator efficiency was quantitative from $^1$H NMR spectroscopy analysis and the polymer molecular weight increased linearly with monomer conversion, this assumption should be plausible. For the ATRP of TEGMMA, similar results were obtained (Figure 1.4 shows the GPC results). The M$_{n,GPC}$ of the final polymer is 27,500 g/mol and the polydispersity index is 1.13. The calculated DP is 193.

PDEGMMA brush-grafted silica particles (PDEGMMA-particles) and PTEGMMA-grafted particles (PTEGMMA-particles) were characterized by TGA and SEM. The weight retentions of PDEGMMA-particles and PTEGMMA-particles at 800°C were 69.1 % (Figure 1.2e) and 67.9 % (Figure 1.2f), respectively, in comparison to 87.7 % (Figure 1.2c) and 86.8 % (Figure 1.2d) for the corresponding initiator particles. From SEM images, the average size of PDEGMMA-particles is 155 nm (Figure 1.1c), 20 nm greater than that of corresponding bare particles (bare particle-1). For PTEGMMA-particles, the size increased from 133 nm to 156 nm (Figure 1.1f). It has been confirmed that the molecular weight and molecular weight distribution of the grafted polymers are essentially identical to those of the free polymers formed from the free initiators in the solution.$^{13,22,42}$ If the DPs calculated from the monomer conversions are used along with the TGA data and the size of bare particles from SEM, the grafting densities of PDEGMMA and PTEGMMA brushes can be calculated and the results are 3.6 nm$^2$/PDEGMMA chain and 5.6 nm$^2$/PTEGMMA chain. These values are reasonably lower than that of PrBA brushes on silica particles (2.5 nm$^2$/PrBA chain$^{42}$), which was reported in the literature as the size of monomer unit increases in the order of $t$BA,
Figure 1.4. Gel permeation chromatography analysis of the polymers obtained from the polymerization of methoxytri(ethylene glycol) methacrylate (TEGMMA) in THF at 40 °C. 

\([\text{TEGMMA}]_0 : [\text{benzyl 2-bromoisobutyrate}]_0 : [\text{CuBr}]_0 : [N, N', N', N''-pentamethyl-diethylenetriamine]_0\) were 543 : 1 : 0.94 : 1.99. Number average molecular weight (\(M_{n,GPC}\), ▲) and polydispersity index (▼) were based on polystyrene calibration.
DEGMMA, and TEGMMA. Considering the thickness and grafting density of the polymer chains on the surface of silica particles, we can conclude that the grafted polymers are in the brush regime.

1.3.3 Thermoresponsive Properties of Poly(methoxydi(ethylene glycol) methacrylate) and Poly(methoxytri(ethylene glycol) methacrylate) in Water

This work was intended to study and compare the phase transitions of thermosensitive polymer brushes and corresponding free polymers in water. Thus, the thermoresponsive properties of free PDEGMMA and PTEGMMA obtained from the polymerizations were studied first by turbidimetry and variable temperature $^1$H NMR spectroscopy, although their LCSTs in water have been reported before. Aqueous solutions of PDEGMMA ($M_{n,\text{GPC}} = 19,900 \text{ g/mol}$) and PTEGMMA ($M_{n,\text{GPC}} = 27,500 \text{ g/mol}$) with a concentration of 0.5 wt % were made and their optical transmittances at wavelength of 500 nm were recorded as a function of temperature by use of a UV-visible spectrometer. At each temperature, the solutions were equilibrated for 20 min. The results are shown in Figure 1.5. The solution of PDEGMMA was transparent at 24 °C and suddenly became cloudy at 25 °C during the course of heating. The cloud point of PTEGMMA in water was 48 °C, slightly lower than the value reported in the literature. Apparently, the higher LCST of PTEGMMA is due to the longer side chain of oligo(ethylene glycol). From this figure, one can find that the transition from a soluble to an insoluble state was sharp (< 2 °C) for both polymers.

The LCST transitions of the two polymers in water were also studied by variable temperature $^1$H NMR spectroscopy. Figures 1.6(a) and 1.7(a) show the $^1$H NMR spectra
Figure 1.5. Optical transmittance of aqueous solutions of PDEGMMA (▲) and PTEGMMA (▼) at wavelength of 500 nm versus temperature during the course of heating. At each temperature, the solutions were equilibrated for 20 min. The concentrations for both solutions were 0.5 wt %. The number average molecular weights of PDEGMMA and PTEGMMA obtained from GPC analysis relative to polystyrene standards were 19,900 and 27,500 g/mol, respectively.
Figure 1.6. $^1$H NMR spectra of (a) PDEGMMA free polymer (0.5 wt %) and (b) PDEGMMA brush-grafted particles (2.0 wt %) in D$_2$O at various temperatures. The number average molecular weight of free PDEGMMA obtained from gel permeation chromatography analysis relative to polystyrene standards was 19,900 g/mol.
Figure 1.7. $^1$H NMR spectra of (a) PTEGMMMA free polymer (0.5 wt %) and (b) PTEGMMMA brush-grafted particles (2.0 wt %) in D$_2$O at various temperatures. The number average molecular weight of free PTEGMMMA determined from gel permeation chromatography analysis relative to polystyrene standards was 27,500 g/mol.
of 0.5 wt % solutions of PDEGMMA and PTEGMMA in D$_2$O at various temperatures, respectively. The height and position of water peak were used as references. For PDEGMMA, at temperatures from 15 to 25 °C, the peaks from polymer backbone and methoxydi(ethylene glycol) group were visible and sharp, indicating a high mobility of polymer molecules in water. When the temperature was raised to 30 °C, the peaks from the polymer backbone almost disappeared and the peaks from the side chain became broadened, suggesting that the transition occurred between 25 and 30 °C, consistent with turbidimetry study. For PTEGMMA, when the temperature was increased from 45 to 50 °C, the peaks from the polymer backbone decreased noticeably, implying that the polymer underwent a transition from a soluble to an insoluble state somewhere between 45 and 50 °C. The fact that the peaks from PTEGMMA backbone were more visible than those of PDEGMMA in $^1$H NMR spectra at temperatures above LCSTs indicated that the hydrophilicity of PTEGMMA was still high after LCST transition.

1.3.4 Thermoresponsive Properties of PDEGMMA and PTEGMMA Brush-Grafted Particles

The thermoresponsive properties of PDEGMMA-particles and PTEGMMA-particles were studied by variable temperature $^1$H NMR spectroscopy and dynamic light scattering. Figures 1.6(b) and 1.7(b) show the $^1$H NMR spectra of PDEGMMA-particles and PTEGMMA-particles in D$_2$O (2.0 wt %) at various temperatures, respectively. The peaks of the grafted polymers are much broader than those of corresponding free polymers due to the reduced chain mobilities from covalent immobilization. Moreover, because of the longer side chain of methoxytri(ethylene glycol) group, the $^1$H NMR peaks of PTEGMMA-particles are more discernible than those of the grafted PDEGMMA chains.
For PDEGMMA-particles, with the increase of temperature from 15 °C to 30 °C, the peak located in the range of 0 – 1 ppm, which was from the methyl group of -CHCCH₃, disappeared at ~ 25 °C, indicating that the phase transition occurred. This transition can also be observed from the changes of the two peaks at 3 – 4 ppm. At 30 °C, the two peaks that were discernable at 15 °C and 20 °C merged into one peak. For PTEGMMA-particles, all peaks were visible at temperatures from 35 °C to 60 °C (Figure 1.7b). Although the transition was not very noticeable, the difference for the peak at 2 ppm (-CH₂- of backbone) between 45 and 55 °C can be appreciated and the peak located at 4.2 ppm, which was from -COOCH₂-, gradually decreased when the temperature was increased from 45 to 55 °C. These observations suggest that the phase transitions of the grafted polymer chains are not as sharp as free polymers but occur over a broader temperature range.

The thermo-induced phase transitions of PDEGMMA- and PTEGMMA-particles were further investigated by variable temperature dynamic light scattering (DLS) and the results are presented in Figures 1.8 and 1.9. The aqueous dispersions of bare particle-1 and PDEGMMA-particles with concentrations of 0.05 mg/mL were gradually heated from 15 to 33 °C. For PTEGMMA-particles and corresponding bare particle-2, the dispersions were gradually heated from 35 to 55 °C. At each temperature, the dispersions were equilibrated for 30 min. The average hydrodynamic diameters of bare particle-1 and -2 at room temperature were 163 nm and 161 nm, respectively. No significant changes in the hydrodynamic diameter were observed for both bare particle-1 and -2. However, the sizes of the bare particles were bigger than those obtained from SEM images (135 nm for bare particle-1 and 133 nm for bare particle-2). These discrepancies might come from
Figure 1.8. Average hydrodynamic diameters of PDEGMA-particles (■) and bare particle-1 (▼) in the temperature range of 15 to 33 °C measured by dynamic light scattering. The concentrations of the particles in the dispersions were 0.05 mg/mL.
Figure 1.9. Average hydrodynamic diameters of PTEGMMA-particles (■) and bare particle-2 (▼) in the temperature range of 35 to 55°C measured by dynamic light scattering. The concentrations of the particles in the dispersions were 0.05 mg/mL.
the slight swelling of the bare particles in water. Similar observations were reported recently by Ohno et al.26

The hydrodynamic size of PDEGMMA-particles in the temperature range from 15 to 21 °C was around 203 nm, 40 nm bigger than that of bare particle-1. Therefore, the thickness of PDEGMMA brushes in water was 20 nm, which was twice that in the dry state, suggesting that the polymer chains were highly stretched in water. When the temperature was raised from 21 to 25 °C, the hydrodynamic diameter decreased from 203 nm to 192 nm, consistent with the observations in variable temperature ¹H NMR spectroscopy analysis (Figure 1.6b). No appreciable change in the size was observed at temperatures above 25 °C. The transition began at ~ 21 °C, 4 °C lower than that of the free polymer in water, and occurred over a broader temperature range from 21 to 25 °C.

For PTEGMMA particles, the hydrodynamic size was ~ 200 nm in the temperature range of 35 to 42 °C. The thickness of PTEGMMA brushes in water was ~ 20 nm, similar to that of PDEGMMA brushes, though the DP of PTEGMMA was 193, higher than that of PDEGMMA (DP = 152). A lower grafting density of PTEGMMA (5.6 nm²/chain) compared with PDEGMMA brushes (3.6 nm²/chain) would be responsible for this observation. The hydrodynamic size decreased over a wide temperature range from 42 (200 nm) to 52 °C (189 nm) (Figure 1.9), much broader than the transition of free PTEGMMA in water. These results are consistent with the observations by Kizhakkedathu et al. on PNIPAm brushes on PS latex particles.39 In the DLS experiments, we did not observe the aggregation of particles at temperatures above the transition points, presumably due to the low concentrations. The optical transmittances of an aqueous dispersion of PDEGMMA-particles with a concentration of 0.05 mg/mL at various
temperatures were recorded at wavelength of 500 nm by use of a UV-vis spectrometer. No appreciable changes in the transmittance were observed when the temperature was gradually increased from 20 to 32 °C.

Because of the relatively high grafting densities of PDEGMMA and PTEGMMA chains on the particles, the interactions among the neighboring polymer chains might play a role in the transitions. Interchain interactions make the collapse of the grafted polymers weaker than that of a free polymer chain in a dilute solution as the interchain contacts reduce water-monomer interactions. The broader transitions of polymer brushes on the particles might be also related to the different degrees of freedom of segments along the grafted polymer chains. The lower onset temperatures in the transitions can be understood because the concentration of the polymer chains in the brush layer is higher than that of polymer solutions used in the turbidimetry study. A lower transition temperature is usually observed for a solution with a higher concentration.

1.4 Conclusions

We have synthesized thermosensitive PDEGMMA brush- and PTEGMMA brush-grafted particles by surface-initiated ATRPs from initiator-functionalized silica particles. A free initiator, BBiB, was added into the polymerization mixtures to control the polymerizations. Although a linear relationship between \( \ln([M]_0/[M]) \) and reaction time was not observed in the kinetics analysis of the polymerizations of DEGMMA and TEGMMA, the number average molecular weight increased linearly with monomer conversion and the polydispersity index decreased progressively. The cloud points of free PDEGMMA and PTEGMMA in water were \( \sim 25 \, ^\circ\text{C} \) and \( \sim 48 \, ^\circ\text{C} \), respectively, from
turbidimetry study. Variable temperature $^1$H NMR spectroscopy and dynamic light scattering studies indicated that the thermo-induced phase transitions of polymer brushes on silica particles began at a lower temperature compared to the free polymers in water, and continued over a broader temperature range (4 – 10 °C). The weak transitions of polymer brushes might be due to the interchain interactions in the brush layer. These thermosensitive hairy particles may find applications as building blocks for environmentally responsive nanostructured materials.

References


40. Kim, D. J.; Kang, S. M.; Kong, B.; Kim, W.-J.; Paik, H.-J.; Choi, H.; Choi, I. S.


34
Chapter 2. Temperature-Induced Transport of Thermosensitive Hairy Hybrid Particles between Aqueous and Organic Phases
2.1 Introduction

Hairy hybrid particles,\(^1\)\(^-\)\(^3\) composed of an inorganic/metal core and a layer of polymer chains that are densely tethered by one end on the core surface (i.e., polymer brushes),\(^4\)\(^-\)\(^6\) are an interesting class of nanostructured materials. These nano-objects exhibit desired properties of both inorganic/metal particles (optical, magnetic, catalytic, mechanical properties, etc.) and polymer brushes (environmental compatibility, responsiveness, etc.), and thus have potential applications in biotechnology (e.g., magnetic resonance imaging probes),\(^7\)\(^,\)\(^8\) colloidal crystals,\(^9\) and sensors.\(^10\)

Generally, there are two approaches to covalently attach polymer chains to a solid surface: (1) grafting end-functionalized polymers to the surface (“grafting to”);\(^11\) (2) growing polymer chains from initiator-functionalized self-assembled monolayers (“grafting from”).\(^1\)\(^-\)\(^3\),\(^6\) The latter has been proven as an effective method to synthesize high density polymer brushes on planar and curved substrates. Since Prucker and Rühe reported in their seminal papers the growth of polystyrene brushes from azo-monolayer-functionalized silica gels by conventional free radical polymerization,\(^12\)\(^,\)\(^13\) a variety of polymerization methods, especially “living”/controlled radical polymerization techniques (atom transfer radical polymerization (ATRP), nitroxide-mediated radical polymerization, and reversible addition-fragmentation chain transfer process (RAFT)), have been used by a number of research groups to synthesize polymer brushes with high grafting densities on various particles including silica,\(^14\)\(^-\)\(^31\) gold,\(^32\) quantum dots,\(^33\)\(^-\)\(^34\) and magnetic particles\(^8\)\(^,\)\(^35\).

We are especially interested in environmentally responsive hairy hybrid particles.\(^36\),\(^37\) The densely tethered polymer chains on these particles can respond to environmental
changes such as solvents, temperature, pH, etc., exhibiting different chain conformations/
structures and thus different surface physical and chemical properties. Up to date, there are only a few examples of environmentally responsive hairy particles and, in most cases, thermosensitive hairy particles.\textsuperscript{10,20,36-48} For instances, Tenhu et al. prepared poly(N-isopropylacrylamide) (PNIPAm) brushes on gold particles using both “grafting to” and “grafting from” (RAFT) methods, and observed from microcalorimetric measurements that PNIPAm brushes exhibited two phase transitions.\textsuperscript{38-40} The same group also reported thermally responsive amphiphilic gold nanoparticles grafted with a mixture of PNIPAm and polystyrene.\textsuperscript{41,42} Zhu et al. found that the aqueous solution of gold particles that were stabilized by thiol-terminated PNIPAm underwent a clear-to-opaque transition when the temperature was increased from 25 to 30 °C.\textsuperscript{10} Thermoresponsive poly(2-(N-morpholino)ethyl methacrylate) brushes were grown on silica particles by Perruchot et al. using aqueous ATRP.\textsuperscript{20} The hairy particles began aggregation at \( \sim 34 \) °C, which corresponded approximately to the cloud point of this polymer in water. PNIPAm brushes were also grown from functionalized anionic polystyrene latex particles by Kizhakkedathu et al. by surface-initiated ATRP.\textsuperscript{43} Very recently, Zhang et al. prepared poly(N,N-dimethylaminoethyl methacrylate) brushes on colloidal particles.\textsuperscript{45} These hairy particles can respond to both pH and temperature changes, exhibiting different hydrodynamic sizes under different environmental conditions. Liu et al. fabricated hybrid nanoparticles with PNIPAm chains in the corona layer through a self-assembling approach\textsuperscript{46} and double hydrophilic block copolymer monolayer protected hybrid gold nanoparticles via “grafting to” method.\textsuperscript{47}
In previous chapter, we synthesized thermosensitive poly(methoxydi(ethylene glycol) methacrylate) (PDEGMMA) and poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) brushes on silica particles by surface-initiated ATRP in the presence of a free initiator. The LCST (lower critical solution temperature) transitions of these polymer brushes began at a lower temperature and continued over a broader range compared with the free polymers in water. These results are consistent with those reported from other researchers.\textsuperscript{40,42} In this work, we explore the possibility of transporting PTEGMMA brush-grafted silica particles between aqueous and organic phases by exploiting the thermo-induced transitions of PTEGMMA brushes between hydrated and dehydrated states. It was found that the particles were quantitatively, reversibly transported between water and ethyl acetate phases upon temperature changes and the transport rates were enhanced by use of pre-mutually saturated solvents. UV-vis spectrometry was employed to determine the concentration change of the particles in the original dispersion upon heating or cooling.

\textbf{2.2 Experimental Section}

\textbf{2.2.1 Materials}

Tetrahydrofuran (THF) was distilled from sodium and benzophenone and stored in a solvent storage bottle. Ethyl acetate (HPLC grade), water (HPLC grade), and toluene (certified ACS grade) were purchased from either Acros or Fisher and used as received. PTEGMMA brush-grafted silica particles (PTEGMMA particles) were synthesized from silica particles that were functionalized with a monolayer of (11-(2-bromo-2-methyl) propionyloxy)undecyldimethyl chlorosilane by surface-initiated ATRP in THF with addition of a free initiator, benzyl 2-bromoisobutyrate. Detailed procedures can be found
in the previous chapter and the characterization data are presented in the section of Results. PTEGMMA brush-grafted particles were stored in methanol dispersion. Prior to the transport study, the particles were isolated by centrifugation, dried in vacuum for 2 h, dispersed in water or organic solvents, and used immediately for transport experiments.

### 2.2.2 Characterization

Gel permeation chromatography (GPC) was carried out at room temperature using PL-GPC 20 (an integrated GPC 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). The data were processed using Cirrus GPC/SEC software (Polymer Laboratories). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Standard polystyrenes (Polymer Laboratories) were used for calibration. Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C using TA Q-series Q50. The cloud points of PTEGMMA in pure water and ethyl acetate-saturated water were measured by two methods. The first one used UV-vis spectrometry. The optical transmittances of aqueous polymer solutions (0.5 wt %) at various temperatures were recorded at wavelength of 500 nm with a UV-visible spectrometer (Biomate 5 from Thermospectronic). The sample cell was thermostated with an external water bath of a Fisher Scientific Isotemp refrigerated circulator. At each temperature, the solutions were equilibrated for 20 min. In the second method, the polymer solutions were transferred into a 3.5 mL vial and then placed in the water bath of a Fisher Scientific Isotemp refrigerated circulator. The temperature was increased at a step of 1 °C. At each temperature, the polymer solutions were allowed to equilibrate with the water bath for 5 min. The cloud point was recorded when the
polymer solution turned cloudy. The difference between the cloud points determined by these two methods was within one degree. The absorbances/transmittances of the dispersions of PTEGMMA brush-grafted particles were recorded at wavelength of 500 nm in the ambient conditions. Optical images were taken with Canon PowerShot A95 digital camera. Dynamic light scattering measurements were conducted with a Brookhaven Instruments BI-200SM goniometer (633nm) and a BI-9000AT digital correlator. The time correlation functions were analyzed with a Laplace inversion program (CONTIN). The dispersion of PTEGMMA particles in water or ethyl acetate (concentration: 0.5 mg/mL) was filtered through Milipore membranes (1.0 μm Nylon filters). At each temperature, the dispersion was equilibrated for 30 min. Multiple measurements were made to give an average hydrodynamic diameter.

2.2.3 Quantitative Study of Transport of PTEGMMA Brush-Grafted Silica Particles from Aqueous to Organic Phases by Heating at 60 °C

Described below is the study of transport of PTEGMMA particles from ethyl acetate (EA)-saturated water to water-saturated EA by heating at 60 °C. Similar procedures were used for other transport studies of particles from aqueous to organic phases with or without stirring. Mutually saturated water and EA used in this experiment were prepared by vigorously stirring the two liquid layers in an ice/water bath for 1 h. In an ice/water bath, PTEGMMA particles (7.7 mg) were dispersed in EA-saturated water (7.7 mL) in a 30 mL vial equipped with a glass valve that can be opened to allow insertion of a needle to take samples. A portion of the dispersion (0.4 mL) was taken out with a syringe and diluted to 0.8 mL with pure water. The transmittance of the diluted dispersion was recorded at room temperature at wavelength of 500 nm using a UV-visible spectrometer.
Water-saturated EA (7.3 mL) was carefully added into the vial that contained the aqueous dispersion of PTEGMMA particles. The vial was then placed in an oil bath with a preset temperature of 60 °C and the liquids were stirred by a magnetic bar at 300 rpm. Samples (0.4 mL) were taken from the aqueous dispersion at various time intervals and diluted to 0.8 mL with pure water for absorbance/transmittance measurements. The experiment was stopped when the aqueous layer became completely clear.

2.2.4 Quantitative Study of Transport of PTEGMMA Particles from Organic to Aqueous Phases by Cooling in an Ice/Water Bath

Described below is the study of transport of PTEGMMA particles from water-saturated EA to EA-saturated water upon cooling in an ice/water bath. Similar procedures were used for other transport studies of particles from an organic to an aqueous phase in an ice/water bath with or without stirring. Mutually saturated water and EA used in this experiment were prepared by vigorously stirring the two liquid layers at 60 °C for 1 h. At 63 °C, PTEGMMA particles (7.3 mg) were dispersed in water-saturated EA (7.3 mL). A portion of the dispersion (0.4 mL) was taken out and diluted to 0.8 mL with pure EA. The transmittance of the diluted dispersion was recorded at room temperature at wavelength of 500 nm with a UV-visible spectrometer. The remaining dispersion was carefully transferred into a 30 mL vial that contained EA-saturated water (6.9 mL). The vial equipped with a glass valve was placed in an ice/water bath and the liquids were stirred by a magnetic bar at 300 rpm. Portions of the organic dispersion (0.4 mL/each) were taken out at various time intervals and diluted to 0.8 mL with pure EA for absorbance/transmittance measurements. The experiment was stopped when the EA layer became completely clear.
2.2.5 Transport of Free Poly(methoxytri(ethylene glycol) methacrylate) from EA-Saturated Water to Water-Saturated EA by Heating at 60 °C

Mutually saturated water and EA used in this experiment were prepared by vigorously stirring the two liquid layers in an ice/water bath for 1 h. PTEGMMA (25.7 mg, M_{n,GPC} = 37,100 g/mol, PDI = 1.08) was dissolved in EA-saturated water (5.2 mL) in a 20 mL scintillation vial in an ice/water bath, followed by addition of water-saturated EA (5.2 mL). The vial was placed in a 60 °C oil bath and the liquids were stirred at 300 rpm. After 90 min, the EA layer was carefully taken out with a syringe. After removal of EA, the polymer was dried in vacuum at 50 °C till a constant weight. 19.9 mg of polymer was obtained, which indicated that 77.4 % PTEGMMA was transported to the EA layer in 90 min.

2.2.6 Transport of Free Poly(methoxytri(ethylene glycol) methacrylate) from Water-Saturated EA to EA-Saturated Water by Cooling in an Ice/Water Bath

Mutually saturated water and EA used in this experiment were prepared by vigorously stirring the two liquid layers at 60 °C for 1 h. PTEGMMA (26.5 mg, M_{n,GPC} = 37,100 g/mol, PDI = 1.08) was dissolved in water-saturated EA (5.3 mL) at 60 °C. The solution was added into a 20 mL scintillation vial which contained EA-saturated water (5.3 mL). The vial was then placed in an ice/water bath and the liquids were stirred at 400 rpm. After 173 min, the EA layer was carefully taken out with a syringe. EA was removed and the residue was dried in vacuum at 50 °C till a constant weight (2.1 mg), which indicated that 92.1 wt % PTEGMMA was transported to the aqueous layer.
2.2.7 Reversible Transport of PTEGMMA Particles between Aqueous and Ethyl Acetate Phases Induced by Temperature Changes

In this experiment, mutually saturated water and EA were prepared by stirring the two liquid layers at 60 ºC for 1 h. At 63 ºC, PTEGMMA particles (6.3 mg) were dispersed in water-saturated EA (6.3 mL). The dispersion was carefully transferred into a 20 mL scintillation vial that contained EA-saturated water (6.3 mL) and a magnetic stirring bar. The vial was kept at 60 ºC and a picture was taken. The vial was then placed in an ice/water bath and the liquids were stirred at 900 rpm. After 2 h, the stirring speed was decreased to 400 rpm and the stirring continued for 1 h. The vial was then placed in an oil bath with a preset temperature of 60 ºC and a picture was taken immediately. The liquids were stirred at 300 rpm in the oil bath for 30 min and a picture was taken. The vial was placed in an ice/water bath again to transport the particles from the EA to the water phase. This cooling-heating cycle was repeated for additional nine times and pictures were taken after the particles were transported from one phase to another.

2.3 Results

2.3.1 Synthesis and Characterization of Thermosensitive PTEGMMA Brushes on Silica Particles

Polymers, including poly(vinyl ether), polymethacrylates, polystyrenes, and polyacrylates, with a short oligo(ethylene glycol) pendant group from each repeating unit exhibit a LCST transition from a hydrated to a dehydrated state in water. The cloud point can be easily tuned by varying the length and end group of the pendant oligo(ethylene glycol) and the type of polymer backbone. In Chapter 1, the synthesis
of PTEGMMA brushes on silica particles by surface-initiated ATRP in the presence of a free initiator, benzyl 2-bromoisobutyrate, in THF at 40 °C has been discussed. The polymer formed in the solution from the free initiator had a narrow molecular weight distribution ($M_w/M_n = 1.13$) and exhibited a cloud point of 48 °C in water (0.5 wt %), which was close to the LCST (52 °C) of the same polymer synthesized from a living anionic polymerization. It has been confirmed by several research groups that the molecular weight and molecular weight distribution of the grafted polymer chains are essentially identical to those of the free polymer formed from the free initiator in the solution. Dynamic light scattering (DLS) studies showed that the hydrodynamic size of the PTEGMMA brush-grafted particles (PTEGMMA particles) decreased over a broad temperature range from 42 °C to 52 °C in water.

In this work, the PTEGMMA particles were prepared from initiator-functionalized silica particles by use of the same method. Silica particles with a diameter of 141 nm, measured by DLS in water, were used for the deposition of a monolayer of (11-(2-bromo-2-methyl)propionyloxy)undecyltrimethyl chlorosilane and the growth of PTEGMMA brushes by ATRP. The characterization data of these PTEGMMA particles and the free polymers are summarized in Table 2.1. DLS study showed that the average hydrodynamic diameters of PTEGMMA particle-II in pure water and pure EA at 25 °C were 202 and 204 nm, respectively. The size of PTEGMMA particle-II in pure EA increased slightly from 204 nm at 25 °C to 209 nm at 60 °C, suggesting that EA is a good solvent for PTEGMMA at both low and high temperatures (Figure 2.1).

The viscosities of EA at different temperatures were calculated by use of Arrhenius equation: $\mu(T) = \mu_0 \exp(E/RT)$, where $\mu_0$ is a constant, $E$ is the activation energy, R is
Table 2.1. Characterization Data for PTEGMMA Particle-I and –II and Corresponding Free Polymers.

<table>
<thead>
<tr>
<th>Particles</th>
<th>TGA</th>
<th>$M_n$GPC $^c$</th>
<th>PDI $^d$</th>
<th>DP $^e$</th>
<th>Grafting Density $^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTEGMMA Particle-1 $^a$</td>
<td>56.8 % $^b$</td>
<td>29,300</td>
<td>1.07</td>
<td>223</td>
<td>3.13 nm$^2$/chain</td>
</tr>
<tr>
<td>PTEGMMA Particle-2 $^a$</td>
<td>61.0 % $^b$</td>
<td>24,500</td>
<td>1.09</td>
<td>178</td>
<td>3.24 nm$^2$/chain</td>
</tr>
</tbody>
</table>

$^a$ PTEGMMA particle–I and –II were synthesized from the same batch of initiator-functionalized silica particles. $^b$ The weight retentions of bare particles and initiator-functionalized silica particles at 800 °C from thermogravimetric analysis (TGA) were 87.5 and 83.1 %, respectively, for PTEGMMA partie–I and –II. $^c$ The values of $M_n$ of the free polymers formed from the free initiator were obtained from GPC analysis using PS standards. $^d$ PDI: polydispersity index, obtained from GPC analysis with PS as standards. $^e$ DP: degree of polymerization, calculated from the monomer conversion and the ratio of monomer to free initiator. The monomer conversion was determined by $^1$H NMR spectroscopy using the integrals of the peaks located at 4.12-4.39 ppm and 3.93-4.12 ppm, which were from –CH$_2$OOC– of the monomer and polymer, respectively. $^f$ The grafting density of PTEGMMA brushes was calculated by use of the size of bare particles, TGA data, and the DP from monomer conversion.
Figure 2.1. Hydrodynamic diameter of poly(methoxytri(ethylene glycol) methacrylate) brush-grafted silica nanoparticles (PTEGMMA particle-II) in pure ethyl acetate as a function of temperature. The concentration of PTEGMMA particles in ethyl acetate is 0.5 mg/mL. The hydrodynamic sizes of the hairy particles were measured by dynamic light scattering using the viscosities and refractive indices in Table 2.2 and 2.3.
gas constant, and \( T \) is temperature (K). Based on the viscosities of EA at 25 °C (\( \mu = 0.423 \) cP) and 50 °C (\( \mu = 0.325 \) cP) from the literature,\(^{55}\) the values of \( E \) and \( \mu_0 \) are calculated and they are 8458 J and 0.01395 cP, respectively. The viscosities of EA at various temperatures are included in Table 2.2. The refractive indices of ethyl acetate at different temperatures were calculated from the equation, \( RI(T_2) = RI(T_1) - (T_2 - T_1) \times 0.00045 \) (Table 2.3). This equation could be derived from the data in the literature.\(^{56}\) We did not find the refractive index of ethyl acetate at wavelength of 633 nm at 25 °C from the literature but used the refractive index at wavelength of 589.3 nm.\(^{56}\)

### 2.3.2 Thermosensitive Properties of Free PTEGMMA in Pure Water and Ethyl Acetate-Saturated Water

This work is intended to study whether the thermo-induced transitions of polymer brushes between hydrated and dehydrated states can be exploited to transport the hairy particles between aqueous and organic phases. Since the organic phase is involved in the transport experiments and it is known that the cloud points of thermosensitive polymers in water can be affected by various additives (organic solvents, salts, etc.),\(^{57}\) we first studied whether and how the presence of ethyl acetate (EA), which was used as the main organic phase in the transport experiments, changes the LCST transition temperatures of PTEGMMA. From the literature, the solubility of EA in water decreases with the increase of temperature.\(^{58}\) EA-saturated water was prepared by vigorously stirring the two liquids at a specific temperature for 1 h and was used to measure the cloud point of PTEGMMA. We found from \(^1\)H NMR spectroscopy analysis that D\(_2\)O is saturated by EA after vigorous stirring for 30 min. Without stirring, it takes two days to reach saturation (Figure 2.2). Table 2.4 shows the cloud points of PTEGMMA (\( M_{n,GPC} = 24,500 \) g/mol) in
Table 2.2. Viscosities of Ethyl Acetate at Various Temperatures from the Literature and Calculation by Use of Arrhenius Equation.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>25</th>
<th>35</th>
<th>40</th>
<th>45</th>
<th>50</th>
<th>55</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ(viscosity) (cP)</td>
<td>0.423</td>
<td>0.378</td>
<td>0.358</td>
<td>0.341</td>
<td>0.325</td>
<td>0.309</td>
<td>0.295</td>
</tr>
</tbody>
</table>

Table 2.3. Refractive Indices of Ethyl Acetate at Various Temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>25</th>
<th>35</th>
<th>40</th>
<th>45</th>
<th>50</th>
<th>55</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive Index</td>
<td>1.370</td>
<td>1.366</td>
<td>1.363</td>
<td>1.361</td>
<td>1.359</td>
<td>1.357</td>
<td>1.354</td>
</tr>
</tbody>
</table>
Figure 2.2. $^1$H-NMR spectroscopy study of the saturation of D$_2$O by ethyl acetate at room temperature under the condition of stirring (a) and no stirring (b). The intensity of the methyl peak from CH$_3$CH$_2$- of ethyl acetate was monitored using the deuterated solvent residue peak as reference.
Table 2.4. Cloud Points of PTEGMMA ($M_n = 24,500$ g/mol, 0.5 wt %) in Pure Water and Ethyl Acetate (EA)-Saturated Water.

<table>
<thead>
<tr>
<th>Temperature at which H$_2$O saturated with EA ($^\circ$C) $^a$</th>
<th>EA Conc. (%) $^b$</th>
<th>Cloud Point ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>7.8</td>
<td>23.5</td>
</tr>
<tr>
<td>30</td>
<td>6.8</td>
<td>29.5</td>
</tr>
<tr>
<td>40</td>
<td>6.3</td>
<td>31</td>
</tr>
<tr>
<td>50</td>
<td>6.2</td>
<td>34</td>
</tr>
<tr>
<td>60</td>
<td>6.1</td>
<td>35.5</td>
</tr>
<tr>
<td>Pure water</td>
<td>0</td>
<td>48</td>
</tr>
</tbody>
</table>

$^a$ EA-saturated water was prepared by stirring the two liquids at the specified temperature for 1 h. $^b$ The concentration of ethyl acetate was obtained from Ref. 58.
pure water and EA-saturated water. In pure water, this polymer underwent a phase transition at 48 °C (Figure 2.3). With the increase of the EA content in water, the LCST of PTEGMMA decreases. For example, the cloud point of this polymer is 31 °C when the EA concentration in water is 6.3 % (Figure 2.3). In Chapter 1, the thermo-induced transition of PTEGMMA brushes on silica particles from a hydrated to a dehydrated state in pure water has been discussed. It began at a lower temperature (42 °C) and continued over a range of ~ 10 °C. The LCST behavior of PTEGMMA brushes in EA-saturated water is expected to be similar. We also studied the effects of toluene and 1-butanol, which were also used as organic phases in the transport experiments, on the LCST of PTEGMMA. While the cloud point of PTEGMMA in toluene-saturated water changes slightly (2-3 °C lower than in pure water), it decreases significantly in 1-butanol-saturated water (to 26 °C and below) (Table 2.5 and 2.6).

2.3.3 Transport of PTEGMMA Particles between Water and Ethyl Acetate Phases

We found that the PTEGMMA particles that were originally dispersed in pure water in a 20 mL scintillation vial in an ice/water bath spontaneously migrated into the EA phase upon heating at 60 °C under the stirring condition (Figure 2.4). After 24 h, no Tyndall light scattering was observed when a laser from a laser pointer passed through the aqueous phase in Figure 2.4(b), indicating a complete transport. Similarly, the PTEGMMA particles that were originally dispersed in pure EA at 63 °C were transported to aqueous layer upon cooling in an ice/water bath under stirring condition (Figure 2.5).
Figure 2.3. Optical transmittances of aqueous solutions of poly(methoxytri(ethylene glycol) methacrylate) \((M_n,GPC = 24,500 \text{ g/mol}, \text{PDI} = 1.09)\) in pure water \((\uparrow, 0.5 \text{ wt} \%)\) and in water that was saturated with ethyl acetate at 40 °C \((\downarrow, 0.5 \text{ wt} \%)\) as a function of temperature. The transmittances were recorded at wavelength of 500 nm by use of a UV-visible spectrometer.
Table 2.5. Effect of Toluene on the Cloud Point of PTEGMMA in Water.

<table>
<thead>
<tr>
<th>Saturation temperature (°C) a</th>
<th>20</th>
<th>35</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloud point (°C)</td>
<td>43</td>
<td>42</td>
<td>42</td>
</tr>
</tbody>
</table>

a The temperature at which water and toluene were vigorously stirred for at least 1 h.

---

Table 2.6. Effect of 1-Butanol on the Cloud Point of PTEGMMA in Water.

<table>
<thead>
<tr>
<th>Saturation temperature (°C) a</th>
<th>20</th>
<th>35</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloud point (°C)</td>
<td>19.5</td>
<td>25</td>
<td>26</td>
</tr>
</tbody>
</table>

a The temperature at which water and 1-butanol were vigorously stirred for at least 1 h.
Figure 2.4. Optical images of (a) the initial state of aqueous (bottom) and ethyl acetate (upper) layers and (b) the final state after stirring at 60 °C for 24 h. The poly(methoxytri(ethylene glycol) methacrylate) brush-grafted silica particles (PTEGMMMA particle-II) were initially dispersed in pure water in an ice/water bath (concentration: 1.0 mg/mL).
Figure 2.5. Optical images of (a) the initial state of aqueous (bottom) and ethyl acetate (upper) layers at 60 °C and (b) the final state after stirring in an ice/water bath for 20 h (to avoid water condensing on the outer wall, the vial was placed in a room temperature oil bath and the picture was taken immediately). The poly(methoxytri(ethylene glycol) methacrylate) brush-grafted silica particles (PTEGMMA particle-II) were initially dispersed in pure ethyl acetate at 63 °C (concentration: 1.0 mg/mL) and the dispersion was transferred into a 20 mL scintillation vial that contained an equal volume of water.
To quantitatively study the thermo-induced transport of PTEGMMA brush-grafted particles between water and ethyl acetate phases by use of UV-visible spectrometry, it is necessary to verify whether the Beer’s law can be applied to the dispersion of particles.

The Beer’s Law is expressed as \( A = \varepsilon bc \), where \( A \) is the absorbance, \( \varepsilon \) is the absorptivity, \( b \) is the path length of the quartz cell, and \( c \) is the concentration.

A series of aqueous dispersions of PTEGMMA brush-grafted silica particles (PTEGMMA particle-II) were prepared by diluting a dispersion (1.0 mg/mL) to various concentrations. The absorbances at wavelength of 500 nm were recorded at room temperature by use of a UV-visible spectrometer. The results are shown in Figure 2.6. A very good linear relationship was observed between the ratio \( A_i/A_o \) and the concentration ratio \( C_i/C_o \), where \( A_i \) and \( A_o \) are the absorbances of particle dispersions with concentrations of \( C_i \) and \( C_o \) (1.0 mg/mL), respectively, at wavelength of 500 nm. A linear fitting gives \( A_i/A_o = 1.001 \times C_i/C_o \), a correlation coefficient (R) of 0.9998, and a standard deviation of 0.0092 (Figure 2.6). This proves that the Beer’s Law can be used to determine the concentration change of the nanoparticle’s dispersion.

In each transport experiment, portions of the dispersion (0.4 mL/each) were taken at various time intervals from the layer in which the particles were originally dispersed, and were diluted with the corresponding solvent to 0.8 mL for UV-vis measurements. From the Beer’s Law, \( A_i/A_o \) is proportional to \( C_i/C_o \), where \( A_i \) and \( A_o \) are the absorbances and \( C_i \) and \( C_o \) are the concentrations of the particles in the original phase at time t and 0, respectively. Thus the change of the relative concentration \( C_i/C_o \) versus time t can be obtained from UV-vis spectrometry measurements.
Figure 2.6. Relative absorbance ($A_i/A_o$) of the aqueous dispersion of PTEGMMMA brush-grafted particles versus the relative concentration ($C_i/C_o$). $A_i$ and $A_o$ represent the absorbances of sample $i$ with a concentration of $C_i$ and the original sample (concentration $C_o = 1.0$ mg/mL), respectively. The samples with various concentrations were prepared by diluting the original dispersion with pure water. Transmittances were recorded at wavelength of 500 nm by use of a UV-visible spectrometry.
2.3.4 Quantitative Study of Transport of PTEGMMA Particles from Originally Pure Water to Originally Pure Ethyl Acetate upon Heating at 60 °C with/without Stirring

The hairy particles (PTEGMMA particle-I) were dispersed in pure water (1.0 mg/mL) in an ice/water bath, and an equal volume of pure EA was placed on top of the aqueous dispersion in a vial equipped with a glass valve, which can be opened to allow the insertion of a syringe needle to take samples. The vial was then placed in a 60 °C oil bath. Two experiments were conducted, one with stirring at 300 rpm and another one without stirring. Figure 2.7 shows the relative concentrations of the particles in the aqueous layers as a function of time. Under the stirring condition, more than 90 % particles were transferred into the EA layer after 435 min and the aqueous phase became clear. After 665 min, the absorbance was essentially the same as water, indicating that the particles were completely transported into the EA layer. We noticed that the $C_t/C_o$ was slightly > 100 % (102 % at 66 min) in the beginning. We initially suspected that this might be due to the diffusion of EA into the water layer, and the effect of the presence of the second solvent on the transmittance/absorbance of the dispersion of PTEGMMA particles was then studied by use of a UV-visible spectrometer. Water and ethyl acetate were mutually saturated in an ice/water bath and at 60 °C. PTEGMMA brush-grafted silica particles (PTEGMMA particle-II) were originally dispersed in either pure water or pure ethyl acetate (concentration: 1.0 mg/mL). The dispersions (each 0.8 mL) were diluted with relevant mutually saturated solvents (0.8 mL) from different temperatures and the transmittances were measured at room temperature at wavelength of 500 nm with a UV-
Figure 2.7. Relative concentration $C_t/C_0$ of PTEGMMA brush-grafted particles in the aqueous layer versus time in the experiment of transporting particles from originally pure water to originally pure ethyl acetate phases by heating at 60 °C under the condition of (a) stirring at 300 rpm (●) and (b) no stirring (●). $C_t$ and $C_0$ are the concentrations of the particles in the aqueous layer at time $t$ and 0, respectively. PTEGMMA particles were originally dispersed in water (1.0 mg/mL) in an ice/water bath.
visible spectrometer. The results are summarized in Table 2.7 and showed that EA had little effect on the absorbance of the aqueous dispersion of PTEGMMA particles.

Without stirring, the aqueous layer became clear after 460 min and no noticeable Tyndall light scattering was observed when a laser from a laser pointer passed through the aqueous phase. However, only a small amount of the particles was transported to the EA layer. Most of them precipitated in the bottom of the vial. Without stirring, the particles had limited opportunities to reach the interface of the two liquids and the transport from H₂O to EA was restricted. Under the stirring conditions, the precipitation was effectively prevented and no particles were observed in the bottom of the vial. Clearly, the particles had better chances to interact with the interface and migrated into the EA layer. It should be noted that the PTEGMMA particles do not precipitate in either pure water above the LCST transition or in pure EA.

2.3.5 Quantitative Study of Transport of PTEGMMA Particles from Originally Pure Ethyl Acetate to Pure Water by Cooling in an Ice/Water Bath with/without Stirring

The particles were dispersed in pure EA at 63 °C (concentration: 1.0 mg/mL). The dispersion was carefully transferred into a vial that contained an equal volume of water, which was then placed in an ice/water bath. Similarly, two experiments were conducted, one with stirring at 400 rpm and another one without stirring. Figure 2.8 shows the concentration change of the particles with time. Interestingly, the EA layer initially became cloudier than the original dispersion under the stirring condition and then
Table 2.7. Transmittance/Absorbances of the Dispersions of PTEGMMA Brush-Grafted Silica Particles in Different Solvents.

<table>
<thead>
<tr>
<th>Diluting solvent</th>
<th>Original</th>
<th>Aqueous dispersion</th>
<th>Dispersion in ethyl acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation Temp</td>
<td>0 °C</td>
<td>60 °C</td>
<td>0 °C</td>
</tr>
<tr>
<td>Transmittance</td>
<td>57.80 %</td>
<td>57.85 %</td>
<td>72.48 %</td>
</tr>
<tr>
<td>Absorbance</td>
<td>0.2355</td>
<td>0.2351</td>
<td>0.1390</td>
</tr>
</tbody>
</table>
Figure 2.8. Relative concentration $C_t/C_o$ of PTEGMMA brush-grafted particles in the ethyl acetate layer versus time in the experiment of transporting particles from ethyl acetate to H$_2$O phases by cooling in an ice/water bath under the condition of (a) stirring at 400 rpm (●) and (b) no stirring (●). $C_t$ and $C_o$ are the concentrations of the particles in the ethyl acetate layer at time t and 0, respectively. PTEGMMA particles were originally dispersed in ethyl acetate (1.0 mg/mL) at 63 °C.
gradually changed to clear. After 1310 min, the particles were completely transported to the aqueous phase. Compare Figures 2.7(a) and 2.8(a), one can find that the transfer of particles from EA to H₂O was slower than that in the opposite direction. It took 732 min to transport 88 % particles in the cooling process, while only ~ 350 min was needed by heating at 60 °C.

In the stationary state, the concentration change of the particles in the EA layer was faster than that under the stirring condition (Figure 2.8b). In 360 min, the concentration decreased more than 95 %, while under the stirring condition the change of the concentration was only 88 % even after 732 min. This unusually fast decrease was due to the precipitation of the PTEG MMA particles onto the interface. In the experiment, we observed a thin film of particles at the interface of H₂O and EA. While the EA layer became nearly clear, the aqueous phase was not as cloud as expected. Eventually, the particles were completely dispersed in H₂O.

2.3.6 Quantitative Study of Transport of PTEG MMA Particles from Ethyl Acetate-Saturated Water to Water-Saturated Ethyl Acetate by Heating at 60 °C with/without Stirring

We found that the transport of PTEG MMA particles between the two phases was much faster when mutually saturated H₂O and EA were used. For the transport of particles from water to EA, the two liquids were mutually saturated by stirring them vigorously in an ice/water bath for 1 h and the EA-saturated water was used to disperse the particles. Because the solubility of EA in water decreases with the increase of temperature and the two liquids are saturated in the ice/water bath, EA will phase separate out from water when the dispersion is warmed to room temperature, which will
affect the absorbance/transmittance measurements. This problem can be effectively avoided by diluting the sample taken from the aqueous dispersion (0.4 mL) with pure water (0.4 mL). After an equal volume of water-saturated EA was added, the vial was placed in a 60 °C oil bath. The aqueous layer became extremely cloud immediately. Several minutes later, streams of particles were observed in the EA layer (Figure 2.9). Figure 2.10 shows the relative concentrations of the particles in the aqueous layers versus time under the conditions of stirring at 300 rpm and no stirring. No particles were observed to precipitate during the experiment. It can be clearly seen from Figure 2.10a that in 10 min more than 90 % particles were transported from the aqueous to the EA layer. After 90 min, the transfer was complete. Compared with the experiment using originally pure water and EA (95% transported at t = 435 min in Figure 2.7a), pre-mutual saturation of solvents makes the transport of particles more than 40 times faster. Without stirring, the transfer of particles was slower (91 % particles transported at t = 43 min, Figure 2.10b), but it is still much faster than using pure water and EA under the stirring condition (Figure 2.7a). The PTEGMMA particles were also quantitatively transported from EA-saturated water to EA layer upon heating at 60 °C in about 2 h when the dispersions of the particles with higher (5.0 mg/mL) and lower concentration (0.3 mg/mL) were used (Figure 2.11). For comparison, we also studied the temperature-induced transport of free PTEGMMA polymer (5 mg/mL) by use of mutually-saturated water and ethyl acetate. We found that the transport of free polymer was slower than that of thermosensitive hairy particles. For heating at 60 °C, 77.4% of PTEGMMA was transported to the EA phase after 90 min, while > 99% of PTEGMMA particles were transported in 90 min (Figure 2.10a).
Figure 2.9. Optical image of the aqueous (bottom) and ethyl acetate (upper) layers at time $t = 3$ min after the vial was placed in a $60^\circ$C oil bath. The streams of particles can be seen in the upper layer.

Figure 2.10. Relative concentration $C_t/C_o$ of PTEGMMA brush-grafted particles in the aqueous layer versus time in the experiment of transporting particles from ethyl acetate-saturated water to water-saturated ethyl acetate phase by heating at $60^\circ$C under the condition of (a) stirring at 300 rpm (■) and (b) no stirring (●). $C_t$ and $C_o$ are the concentrations of the particles in the aqueous layer at time $t$ and 0, respectively. PTEGMMA particles were originally dispersed in ethyl acetate-saturated water (1.0 mg/mL) in an ice/water bath.
Figure 2.11. Relative concentration $C_t/C_o$ of PTEGMMA brush-grafted nanoparticles in the aqueous layer versus time in the experiment of transporting particles from EA-saturated water to water-saturated EA phase by heating at 60 °C under the condition of stirring at 300 rpm. $C_t$ and $C_o$ are the concentrations of the particles in the aqueous layer at time $t$ and 0, respectively. PTEGMMA particles were originally dispersed in EA-saturated water ((a) 5.0 mg/mL and (b) 0.3 mg/mL) in an ice/water bath. Different batch of bare particles and initiator-functionalized silica particles were used. The weight retentions of bare particles, initiator-functionalized silica particles and PTEGMMA grafted particles (PTEGMMA particle-III) at 800 °C from thermogravimetric analysis (TGA) were 87.1, 85.2 % and 62.7 %, respectively. The $M_n$ GPC of free PTEGMMA was 37,100 g/mol and the polydispersity index was 1.08.
2.3.7 Quantitative Study of Transport of PTEGMMA Particles from Water-Saturated Ethyl Acetate to Ethyl Acetate-Saturated Water Layers upon Cooling in an Ice/Water Bath with/without Stirring

In this experiment, water and EA were mutually saturated by stirring them vigorously at 60 °C for 1 h, and the water-saturated EA was used to disperse the particles (PTEGMMA particle-I) at 63 °C. The vial that contained the particle dispersion and an equal volume of EA-saturated water was placed immediately in an ice/water bath. Figure 2.12 shows the relative concentration of particles versus time. Under the stirring condition, the transport was very fast in the beginning. In 15 min, 73 % particles were transferred to the water layer. Note that it took 575 min to reach a similar percentage when pure water and ethyl acetate were used (Figure 2.8a). After 173 min, the particles were completely transferred to the aqueous phase. The PTEGMMA particles were also quantitatively transported from water-saturated EA to water layer upon cooling in an ice/water bath in about 3 h when the dispersions of the particles with higher (5.0 mg/mL) and lower concentration (0.3 mg/mL) were used (Figure 2.13). The transport of free PTEGMMA from water-saturated EA to water layer upon cooling in an ice/water bath was also slower than the transport of hairy particles. After the same period of time (173 min), only 92.1 wt % of free PTEGMMA was transported. By comparing Figures 2.10a and 2.12a, one can find that the transport by cooling was slower than that by heating, although the stirring rate was higher (400 vs 300 rpm). Under the stationary condition, the transfer of particles was much slower than that with stirring. A complete transport of particles took more than 1200 min. Apparently, stirring facilitated the transfer of the particles into the aqueous layer. We could not compare Figures 2.8b and 2.12b because
Figure 2.12. Relative concentration $C_t/C_0$ of PTEGMMA brush-grafted particles in the ethyl acetate layer versus time in the experiment of transporting particles from water-saturated ethyl acetate to ethyl acetate-saturated water phase by cooling in an ice/water bath under the condition of (a) stirring at 400 rpm (●) and (b) no stirring (●). $C_t$ and $C_0$ are the concentrations of the particles in the ethyl acetate layer at time $t$ and 0, respectively. PTEGMMA particles were originally dispersed in water-saturated ethyl acetate (1.0 mg/mL) at 63 °C.
Figure 2.13. Relative concentration $C_t/C_o$ of PTEGMMA brush-grafted nanoparticles (PTEGMMA particle-III) in the EA layer versus time in the experiment of transporting particles from water-saturated EA to EA-saturated water phase by cooling in an ice/water bath under the condition of stirring at 400 rpm. $C_t$ and $C_o$ are the concentrations of the particles in the EA layer at time $t$ and 0, respectively. PTEGMMA particles were originally dispersed in water-saturated EA ((a) 5.0 mg/mL and (b) 0.3 mg/mL) at 63°C.
the particles precipitated at the interface of the two liquids when pure water and EA were used. No particles were observed at the interface when mutually saturated solvents were used under the stationary conditions.

In a separate experiment, the PTEGMMA particles were first dispersed in EA-saturated water in an ice/water bath and were then transported to the EA phase by heating at 60 °C under the stirring condition. After the particles completely migrated into the EA layer, the vial was placed into an ice/water bath and the liquids were stirred at 400 rpm. Figure 2.14 shows the relative concentration of the particles in the EA phase versus time. The transport was much slower than that shown in Figure 2.12a, where the particles were originally dispersed in water-saturated EA. Only 58 % particles were transported at 278 min in comparison with 73 % at 15 min in Figure 2.12a. However, it was still faster than the transport using originally pure water and EA under the stirring condition (47 % transported at 371 min, Figure 2.8a). We could not give a clear explanation for this.

The hairy particles can be transported reversibly between the two phases for at least 10 times. Figure 2.15 shows the pictures of the vial from the seventh cooling to the ninth heating in a reversible transport experiment. We estimated that >95% of the PTEGMMA particles were transported in each process. In general, the transport of particles from water to EA upon heating at 60 °C was faster than the reverse process by cooling in the ice/water bath. After the tenth heating, the vial was allowed to cool down to room temperature spontaneously. Under the stationary condition, no particle transport from the EA to the aqueous layer was observed even after 42 h. This indicates that PTEGMMA particles have a better affinity to EA than to water at room temperature. From Table 2.4, the cloud point of PTEGMMA in EA-saturated water is around room temperature.
Figure 2.14. Relative concentration $C_t/C_0$ of PTEGMA brush-grafted particles in the ethyl acetate layer versus time in the experiment of transporting particles from water-saturated ethyl acetate to ethyl acetate-saturated water phase by cooling in an ice/water bath under the condition of stirring at 400 rpm. $C_t$ and $C_0$ are the concentrations of the particles in the ethyl acetate layer at time $t$ and 0, respectively. The particles were originally dispersed in ethyl acetate-saturated water (1.0 mg/mL) at 0 °C. After being heated at 60 °C with stirring at 300 rpm for 2 h, the vial was placed in an ice/water bath.
Figure 2.15. Optical images of aqueous and ethyl acetate layers after 7th cooling in an ice/water bath (a); 7th heating in an 60 °C oil bath (b); 8th cooling (c); 8th heating (d); 9th cooling (e); and 9th heating (f). The PTEGMMA brush-grafted particles were originally dispersed in water-saturated ethyl acetate at 63 °C (concentration: 1.0 mg/mL, PTEGMMA particle-I).
2.3.8 Transport of PTEGMMA Particles in Other Water/Organic Solvent Systems

The transport of PTEGMMA particles was also studied in the mutually saturated 1-BuOH/H₂O system. Similar to the cooling experiment using mutually saturated water and EA, the particles (PTEGMMA particle-II) were dispersed in 1-BuOH that was saturated with water at 63 °C. Under the stirring condition in an ice/water bath, the particles were quantitatively transported to the aqueous phase in 300 min. Using the same condition for the transport of particles from H₂O to EA, we found that only 60 % particles were transferred to the 1-BuOH layer even after stirring at 300 rpm for 24 h at 60 °C. For water/toluene system, the particles were quantitatively transported from toluene to water upon cooling in an ice/water bath, but no noticeable particles were observed to transport from H₂O to toluene by heating at 60 °C.

2.4 Discussion

2.4.1 Transport of Hairy Particles between Aqueous and Organic Phases

If hairy particles can be quantitatively, reversibly transported between an aqueous and an organic phase by use of an external stimulus, one can imagine many potential applications, e.g., delivery of substances, phase transfer catalysis, etc. In this work, we exploit the thermo-induced, reversible transitions of thermosensitive polymer brushes between hydrated and dehydrated states to transport thermosensitive hairy particles between aqueous and organic phases. Above the LCST, polymer chains are dehydrated in water, and thus the affinity of the polymer brush-grafted particles to water decreases. Under this condition, if the affinity of the particles to the organic phase is better than
water, the particles may transfer to the organic phase. We observed that the PTEGMMA particles were 100% transferred from water to the EA layer at 60 °C under the stirring condition. Note that from Table 2.4 the cloud point of PTEGMMA in water decreases significantly in the presence of EA. At 60 °C, PTEGMMA brushes are highly dehydrated, even if the transition zone of the brushes is broader than that of free polymers. Under the similar conditions, the PTEGMMA particles were partially transported to the 1-butanol layer and no particles to the toluene layer. We believe that the affinities of PTEGMMA particles to water and 1-butanol at 60 °C are comparable, and the affinity of PTEGMMA particles to water is better than to toluene despite that the polymer brushes are dehydrated above the LCST. We are not able to make quantitative comparisons because a quantitative discussion of the affinities of a specific polymer to various solvents would involve the Flory-Huggins interaction parameter $\chi$ and the change of $\chi$ with temperature.

To transport the hairy particles from an organic to an aqueous phase, we need to choose a temperature at which the particles exhibit a better affinity to water than to the organic solvent. Because the cloud point of PTEGMMA in water decreases significantly in the presence of EA (29.5 °C if water is saturated with EA at 30 °C), we conducted the transport experiments in an ice/water bath. Our results showed that the PTEGMMA particles that were originally dispersed in EA, 1-butanol, and toluene were completely transported to the aqueous layer under this condition.

To further look into how the affinities of particles to the two liquids affect the transport, we carried out a control experiment by use of bare silica particles. Bare particles have a very good affinity to water due to the hydrogen bonding between water
molecules and the silanol groups on the particles. Bare particles can also be well dispersed in EA. One can imagine that the bare particles would have a better affinity to water at both 0 and 60 °C. We found that the bare particles that were originally dispersed in water-saturated EA at 60 °C were efficiently transported into the aqueous layer upon cooling in an ice/water bath under the stirring condition. From UV-vis spectrometry measurements, more than 90% particles migrated into the aqueous layer after 77 min and the transport was complete after 360 min. For the attempted transport of bare particles from water to EA, the particles were dispersed in EA-saturated water at 0 °C. The vial that contained the dispersion and an equal volume of water-saturated EA was then placed in a 60 °C oil bath. After stirring at 300 rpm for 10 min, the bare particles were found to aggregate at the interface of water, EA, and the inner wall of the vial (Figure 2.16). Interestingly, the particles were completely re-dispersed in the aqueous layer with continuous stirring. No particles were transported to the EA layer. Apparently, the bare particles prefer to stay in contact with water due to the higher affinity to water.

In summary, to transport particles from one phase to another, a condition should be chosen under which the particles have a stronger affinity to the second phase than to the first phase. Although the transport of PTEGMMA particles from water to toluene upon heating at 60 °C in our experiment was not successful, we believe that it is possible for hairy particles to reversibly, quantitatively migrate between H₂O and toluene phases if a “right” thermosensitive polymer is used.
Figure 2.16. Attempted transport of bare particles from ethyl acetate-saturated water to ethyl acetate phase upon heating at 60 °C under the condition of stirring at 300 rpm. Bare particles were initially dispersed in ethyl acetate-saturated water in an ice/water bath (concentration: 1.0 mg/mL). The vial was then placed in a 60 °C oil bath. Optical images of aqueous and ethyl acetate layers in the initial state in the 60 °C oil bath (a); after 10 min (b); and after 369 min (c).
2.4.2 Why are the Transport Rates of PTEGMMA Particles Higher When Pre-Mutually Saturated Water and Ethyl Acetate are used?

We observed that the transport rates of particles between the two phases were higher when pre-mutually saturated water and EA were used (Figures 2.10 and 2.12). As mentioned earlier, the solubility of EA in water decreases gradually from 9.71 % to 6.06 % when the temperature is raised from 0 to 60 °C. On the other hand, the solubility of water in EA decreases from 4.23 % to 2.13 % when the temperature changes from 60 to 0 °C. Thus, the aqueous layer that is saturated with EA in an ice/water bath undergoes a phase separation when the vial is placed in a 60 °C oil bath. Similarly, the EA layer that is saturated with water at 60 °C phase separates when it is cooled in an ice/water bath. Using UV-vis spectrometry, we monitored the phase separation at 60 °C of water that was pre-saturated with EA at 21 °C and the phase separation at 15 °C of ethyl acetate that was pre-saturated with water at 60 °C. The results are summarized in Figure 2.17. The phase separation of both saturated solvents decreased the transmittance dramatically. For EA-saturated water, the transmittance was < 10 % and increased quickly (Figure 2.17a). No transmittance change was observed for pure water. Dynamic light scattering was employed to study the phase separation of ethyl acetate-saturated water. Ethyl acetate and water were mutually saturated at 21 °C. Ethyl acetate-saturated water was filtered into a borosilicate glass tube with an inner diameter of 7.5 mm (1.5 cm high) followed by addition of water-saturated ethyl acetate (1.5 cm high). The glass tube was placed in the sample holder with a preset temperature of 60 °C. Droplets of several hundreds of nanometers (average hydrodynamic size $D_h = 205$ nm) were formed immediately (Figure 2.18a). Droplets were not stable, and no signal was detected after 3 min (Figure 2.18b).
Figure 2.17. Optical transmittance versus time of (a) pure water (▲) and ethyl acetate-saturated water (▼, saturated at 21 °C) at 60 °C; (b) pure ethyl acetate (●) and water-saturated ethyl acetate (■, saturated at 60 °C) at 15 °C. In (a), a quartz cell that contained pure water (or water that was saturated with ethyl acetate at 21 °C) was placed in the cell holder with a preset temperature of 60 °C and the transmittance was recorded immediately at wavelength of 500 nm. In (b), a quartz cell that contained pure ethyl acetate (or ethyl acetate that was saturated with water at 60 °C) was placed in the cell holder with a preset temperature of 15 °C and the transmittance was recorded immediately at 500 nm.
Figure 2.18. Dynamic light scattering study of the droplets formed in the aqueous layer after the glass tube that contained mutually saturated ethyl acetate and water (saturated at 21 °C, both layers were 1.5 cm high) was placed in the sample holder with a preset temperature of 60 °C. (a) 0 min and (b) 3 min.
For the phase separation at 15 °C of EA that was saturated with water at 60 °C, the increase of transmittance was slower (Figure 17b). It took a longer time for the EA layer to become clear, and this might be the reason for the slower transport by cooling than by heating (Figures 2.11a and 2.10a).

Phase separation of presaturated solvents results in the formation of EA droplets in the aqueous layer at 60 °C and water droplets in the EA phase at 0 °C, greatly increasing the interfacial areas. The small droplets coalesce forming bigger droplets and move to another phase due to the density difference. These solvent phase separation processes provide good opportunities to the particles to transport from one phase to another as the particles have a tendency to adsorb at the interface of two liquids.59-62

At 60 °C, the surface-tethered PTEGMMA chains are highly dehydrated in water, resulting in a better affinity of the particles to EA than to water. These dehydrated hairy particles are adsorbed to the interface of the EA droplets formed from the phase separation, and are very likely located on the concave side of the interface (Scheme 2.1). When the EA droplets move to the upper layer (EA has a lower density than water), the particles are transported along with them to the EA phase. Consequently, the transport rate is greatly increased. This explanation is supported by the observations of streams of PTEGMMA particles in Figure 2.9 and the aggregation of bare particles in Figure 16b. In the experiment shown in Figure 2.16, the bare particles are adsorbed to the interface of EA droplets and are very likely located on the convex side of the interface because of their strong affinity to water. When the EA droplets move to the interface of the two layers and merge with the EA layer, the bare particles are still located on the water side.
Scheme 2.1. Schematic Illustration of Transport of Thermosensitive PTEGMMA Brush-Grafted Particles between Water and Ethyl Acetate Phases Facilitated by the Solvent Phase Separation upon Heating and Cooling.
and thus aggregate at the interface. With continuous stirring, these aggregated bare particles are eventually re-dispersed in water.

At 0 °C, the PTEGMMA chains are hydrated and the particles have a better affinity to water than to EA. The hairy particles are adsorbed to the interface of the water droplets in the EA phase and are very likely located on the concave side, and then transferred to the aqueous layer along with the water droplets (Scheme 2.1). Because the phase separation of water-saturated EA is slower than that of EA-saturated water (Figure 17), the transport of PTEGMMA particles is slower by cooling in an ice/water bath than by heating at 60 °C.

2.5 Conclusions

Thermosensitive PTEGMMA brush-grafted particles were prepared by surface-initiated ATRP from initiator-functionalized silica particles. The cloud point of PTEGMMA in water was found to decrease significantly in the presence of EA. By stirring and heating at 60 °C, the PTEGMMA particles that were originally dispersed in water were quantitatively transported to the EA layer. Upon cooling in an ice/water bath, the particles migrated from the EA to the water phase. These temperature-induced transport processes were accelerated by using pre-mutually saturated water and EA. Pre-saturated solvents undergo phase separation when the temperature changes, resulting in the formation of droplets, which increases the interfacial area and facilitates the transfer of particles. The reversible transport of PTEGMMA particles between H2O and EA phases can be repeated consecutively at least ten times. The PTEGMMA particles can also be quantitatively transported from 1-butanol and toluene to water by cooling in an ice/water bath. However, upon heating at 60 °C, the particles were only partially transported from
water to 1-butanol and no particles migrated into toluene. To quantitatively, reversibly transport the particles between aqueous and organic phases, it is speculated that the affinity changes of the particles to the two solvents upon environmental condition variations must be high enough. This thermo-induced transport of hairy particles may be used in the development of new phase transfer catalysts.

References


Chapter 3. Thermosensitive Water-Dispersible Hairy Particle-Supported Pd Nanoparticles for Catalysis of Hydrogenation in Aqueous/Organic Biphasic System
3.1 Introduction

Hairy particles,\textsuperscript{1,2} composed of an inorganic, metal, or polymeric core and a layer of polymer chains that are densely grafted by one end via a covalent bond (i.e., polymer brushes\textsuperscript{3-5}) on the core, have attracted growing interest in recent years. The structures and properties of both core and brush layer can be tailored for various applications, e.g., biocompatible magnetic imaging probes,\textsuperscript{6} sensing materials,\textsuperscript{7} new colloidal crystals,\textsuperscript{8} and catalysts.\textsuperscript{9} These particles are now commonly prepared from initiator-functionalized particles via surface-initiated living/controlled polymerizations,\textsuperscript{1-4,8-20} especially living radical polymerizations, which have been shown to produce polymer brushes with predetermined molecular weights, narrow polydispersities, and controlled architectures.

Environmentally responsive hairy particles are intriguing; the covalently grafted polymer chains undergo spontaneous changes in response to environmental variations, rendering hairy particles different properties under different conditions.\textsuperscript{21-35} Moreover, the changes in chain conformations/structures of polymer brushes may produce an effect on the properties of core particles. A number of papers have been published recently on the hairy particles that can respond to the changes in temperature,\textsuperscript{21-29} pH,\textsuperscript{30} light,\textsuperscript{31,32} and solvents.\textsuperscript{33-35} We previously synthesized thermosensitive poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) brushes on silica particles via surface-initiated atom transfer radical polymerization (ATRP) and found that the hairy particles can be reversibly and quantitatively transported between water and ethyl acetate phases upon heating at 60 °C and cooling in an ice/water bath.\textsuperscript{28,29} Interestingly, these thermosensitive hairy particles cannot be transported to toluene or other hydrocarbon solvents by heating, although they readily moved from toluene to water upon cooling in an ice/water bath. These
observations have led us to explore the applications of thermoresponsive hairy particles in catalysis. In this chapter, the use of PTEGMA brush-grafted polymeric particles as carrier for Pd nanoparticles for catalysis of hydrogenation of styrene in a water/octane biphasic system was discussed.

Metal particles with sizes in the range of several to tens of nanometers exhibit very high surface-to-volume ratios, which make them ideal candidates for application as catalysts. To prevent their pronounced tendency to aggregate, various polymers, including dendrimers, hyperbranched polymers, multiarm star copolymers, block copolymer micelles, crosslinked latex particles, and microgels, have been used to stabilize metal particles. In most cases studied so far, the polymer matrix acts only as a stabilizer. Very recently, there have been several reports on the use of stimuli-responsive polymers as supports for metal particles to regulate their catalytic activities. For example, Lu et al. used thermosensitive core-shell particles as carrier for Ag particles and observed that the catalytic activity of Ag particles was modulated by the temperature-induced volume phase transition of crosslinked poly(N-isopropyl acrylamide) shell layer of the carrier particles.

Due to the increased economic and environmental concerns, there has been a growing interest in the use of biphasic systems with metal catalysts for hydrogenation reactions. Biphasic reaction systems, consisting of two immiscible liquid phases, either water/hydrocarbon, or water/ionic liquid, or hydrocarbon/ionic liquid, allow easy separation of products and catalysts and reuse of catalysts. For example, Vasylyev et al. prepared the alkylated branched polyethyleneimine-stabilized Pd nanoparticles, which were found to be an effective aqueous biphasic catalyst for hydrogenation of alkenes.
To the best of our knowledge, reactions in biphasic systems catalyzed by stimuli-responsive polymer-supported metal particles have not been reported.

In the present work, we synthesized Pd nanoparticles in the core of thermosensitive PTEGMMA brush-grafted polymeric particles and used them for catalysis of aqueous biphasic hydrogenation of styrene. Initiator-functionalized core-shell crosslinked poly(t-butyl acrylate) (PtBA) particles were prepared by seeded emulsion polymerization,24 followed by surface-initiated ATRP to grow PTEGMMA brushes (Scheme 3.1). After removal of t-butyl groups of PtBA, Pd^{2+} ions were introduced into the core of hairy particles and reduced to Pd nanoparticles with ethanol at 70 °C. The supported Pd was found to be an efficient catalyst for aqueous biphasic hydrogenation of styrene (Scheme 3.2) and the catalytic activity was modulated by the thermo-induced phase transition of PTEGMMA brushes.

3.2 Experiments

3.2.1 Materials

CuBr (98%, Aldrich) was purified according to the procedure described in the literature and stored in a desiccator. Tetrahydrofuran (THF) was distilled from sodium and benzophenone and stored in a solvent storage bottle. Styrene (99%, Aldrich) and tert-butyl acrylate (t-BA, 99%, Aldrich) were distilled over CaH₂ under reduced pressure and stored in a refrigerator prior to use. N, N, N', N', N"-pentamethyldiethylenetriamine (PMDETA) was distilled under reduced pressure and stored in a desiccator. Di(ethylene glycol) bisacrylate (DEGBA, tech., 75 %, Aldrich) was passed through a short alumina column to remove the inhibitor. The synthesis of methoxytri(ethylene glycol)
**Scheme 3.1** Preparation of Water-Dispersible Thermosensitive Hairy Particle-Supported Pd Nanoparticles.

**Scheme 3.2** Thermosensitive Hairy Particle-Supported Pd Nanoparticles as Catalyst for Aqueous Biphsic Hydrogenation of Hydrophobic Alkene.
methacrylate (TEGMMA) and benzyl 2-bromoisobutyrate (BBiB) was discussed in chapter 1. All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

### 3.2.2 Characterizations

The $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer and the residual solvent proton signal was used as the internal standard. Gel permeation chromatography (GPC) was carried out at ambient temperature using PL-GPC 20 (an integrated GPC system from Polymer Laboratories Inc) with a refractive index detector, one PLgel 5 $\mu$m guard column (50 × 7.5 mm), and two PLgel 5 $\mu$m mixed-C columns (each 300 × 7.5 mm). The data were processed using Cirrus™ GPC/SEC software (Polymer Laboratories). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Standard monodisperse polystyrenes (Polymer Laboratories, USA) were used for calibration. Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 °C/min from room temperature to 700 °C using TA Q-series Q50. Transmission electron microscopy (TEM) experiments were performed on a Hitachi H-80 transmission electron microscope. The TEM samples were prepared by drop casting dilute aqueous dispersion on carbon-coated copper grids and measured at an accelerating voltage of 75 kV. GC-MS was conducted on a Hewlett Packard HP 6890 Series GC system with a Hewlett Packard 5973 Mass Selective Detector. Dynamic light scattering (DLS) measurements were conducted with a Brookhaven Instruments BI-200SM goniometer (633 nm) and a BI-9000AT digital correlator, a temperature controller, and a solid-state laser (model 25-LHP-928-249, $\lambda = 633$ nm) at a scattering angle of 90°. The intensity-intensity time correlation functions were analyzed with a Laplace inversion
program (CONTIN). The particle dispersions were filtered through Millipore membranes (1.0 µm Nylon filters). At each temperature, the particle dispersions were equilibrated for 30 min. Multiple measurements were made to give an average hydrodynamic diameter.

### 3.2.3 Synthesis of 2-(2-Bromo-2-methylpropionyloxy)ethyl Acrylate (Inimer)

A solution of 2-bromo-2-methylpropionyl bromide (3.09 g, 13.4 mmol) in CH₂Cl₂ (5 mL) was added dropwise into the solution of 2-hydroxyethyl acrylate (2.41 g, 20.8 mmol) and triethylamine (1.59 g, 15.7 mmol) in CH₂Cl₂ (20 mL) in an ice water bath. After stirring the mixture at room temperature overnight, the precipitate was removed by filtration. The filtrate was washed with water and the aqueous phase was extracted with diethyl ether (50 mL × 2). The organic phases were combined and dried over anhydrous sodium sulfate. The solvents were removed by a rotavapor, and purification by silica gel column chromatography using ethyl acetate/hexanes (1/2, v/v) as eluent gave the desired product (2.93 g, 11.1 mmol, yield: 82.5 %). ¹H NMR (CDCl₃): δ (ppm) 1.87 (s, 6 H, 2 CH₃), 4.36 (s, 4 H, 2 CH₂O), 5.81 (dd, 1 H, CHH=CH), 6.07 (dd, 1H, CH=CHH), 6.37 (dd, 1 H, CHH=CH). ¹³C NMR (CDCl₃): δ (ppm) 30.55 (2 CH₃C), 55.27 (C(CH₃)₂), 61.63, 63.39 (CH₂-CH₂), 127.84 (CH=CH₂), 131.34 (CH₂=CH), 165.64 (CH₂=CH-C=O), 171.33 (Br-C-C=O). Mass (DART) ([M+NH₄]⁺): 282.04, 284.03

### 3.2.4 Synthesis of Poly(tert-butyl acrylate) (PrBA) Seed Latex Particles

*tert*-Butyl acrylate (5.49 g, 42.8 mmol), di(ethylene glycol) bisacrylate (0.27 g, 0.95 mmol), sodium dodecyl sulfate (0.30 g, 1.0 mmol) and water (100 mL) were added into a 250 mL three-necked flask. After the mixture was bubbled with nitrogen for 30 min,
potassium persulfate (50.5 mg, 0.187 mmol) was added. The flask was placed in an oil bath with a preset temperature of 60 °C. After the reaction mixture was stirred at 350 rpm for 2 h, the flask was removed from the oil bath. A portion of the emulsion (13 mL) was used directly for the seeded emulsion polymerization to synthesize initiator-functionalized core-shell PtBA particles. Dynamic light scattering measurements showed that the hydrodynamic diameter of PtBA seed particles was 96 ± 3.0 nm in water and 124 ± 4.5 nm in methanol.

3.2.5 Synthesis of Initiator-Functionalized Core-Shell Crosslinked PtBA Particles

Initiator-functionalized core-shell crosslinked PtBA particles (initiator particles) were prepared by seeded emulsion polymerization. A typical procedure is described as following. The dispersion of PtBA particles in water (13 mL) was added into a 100 mL three-necked flask, which contained t-BA (0.334 g, 2.61 mmol), 2-(2′-bromo-2′-methyl-propionyloxy)ethyl acrylate (inimer, 0.302 g, 1.14 mmol) and di(ethylene glycol) bisacrylate (35.4 mg, 0.165 mol). The mixture was bubbled with nitrogen for 30 min, followed by the addition of potassium persulfate (6.4 mg, 0.024 mmol). After the polymerization mixture was stirred at 350 rpm at 60 °C for 10 h, the flask was removed from the oil bath. The dispersion was added into methanol (20 mL) and the initiator particles were separated with a centrifuge (6000 rpm, 10 min). The separated particles were redispersed in methanol (100 mL) and purified by dialysis against methanol. During the dialysis process, the solvent was changed frequently. After the removal of methanol with a rotavapor, the particles were dispersed in THF, precipitated in hexanes, and separated with a centrifuge (6000 rpm, 10 min). The obtained solid was redispersed in
freshly dried THF. The particle concentration, determined by gravimetric analysis, was 17.8 mg particles per g dispersion in THF. DLS study showed that the average hydrodynamic diameter of initiator particles in water was 111 nm. After purification, the diameter of the particles in methanol was 141 nm.

### 3.2.6 Synthesis of PTEGMMA Brush-Grafted PrBA Particles

The dispersion of initiator particles in THF (20.01 g, containing 0.356 g initiator particles) was added into the flask, which contained CuBr (40.0 mg, 0.279 mmol) and benzyl 2-bromoisobutyrate (75.4 mg, 0.293 mmol), followed by the addition of TEGMMA (21.60 g, 93.1 mmol). After the mixture was degassed by one freeze-pump-thaw cycle, PMDETA (91.6 mg, 0.529 mmol) was injected into the flask. The mixture was further degassed by two freeze-pump-thaw cycles. The flask was then placed in a 40 °C oil bath. After 220 min, the flask was removed from the oil bath and the reaction mixture was opened to air. The polymerization mixture was diluted with THF (40 mL) and precipitated in hexanes. The monomer conversion, determined by 1H NMR spectroscopy analysis, was 45.4%.

The particles were separated from free polymer PTEGMMA by repetitive fractionation as described below. The mixture of free polymer and PTEGMMA brush-grafted particles was dissolved/dispersed in THF (150 mL), followed by gradual addition of hexanes (175 mL). The obtained precipitate was redispersed in THF (150 mL), and hexanes (150 mL) was added. The precipitate was then redispersed in THF (150 mL), and kept in a stationary state overnight. After the removal of trace amount of green precipitate, hexanes (140 mL) was gradually added into the dispersion. The precipitated particles were isolated and redispersed in THF (150 mL). DLS studies showed that the
hydrodynamic diameter of the PTEGMMA brush-grafted particles in water was 262 ± 3.5 nm at 25 °C.

The solution of free polymer PTEGMMA in THF was passed through a short Al₂O₃/silica gel (1/2, v/v) column with THF as eluent to remove the copper catalyst. The polymer solution was concentrated and precipitated in a mixture of hexanes and THF (10:1, v/v, 330 mL). The obtained polymer was redissolved in THF (30 mL), and precipitated in hexanes (300 mL) again. GPC results (PS calibration): $M_{n,GPC} = 19,400$ g/mol, $M_{w,GPC} = 21,400$ g/mol, polydispersity index (PDI) = 1.10.

### 3.2.7 Removal of t-Butyl Group of PtBA in PTEGMMA Brush-Grafted PtBA Particles

The dispersion of PTEGMMA brush-grafted PtBA particles in THF (100 mL) was added into hexanes (100 mL). The precipitated particles were collected and dried with a stream of nitrogen. The hairy particles (1.8 g) were dispersed in methylene chloride (140 mL) in a 250 mL three-necked flask. The flask was then placed in an ice/water bath and CF₃COOH (5.0 mL, 0.067 mol) was injected. After being stirred at room temperature for 22 h, the reaction mixture was poured into hexanes (300 mL). The hairy particles were redispersed in THF (50 mL) and precipitated in hexanes (200 mL). This purification process was repeated one additional time. The obtained product was dried with a stream of air flow. A portion of the particles (~1.5 g) was dispersed in deionized water (150 mL). The particle dispersion (130 mL) was dialyzed against water (MWCO of dialysis tubing: 100000) for 3 days and water was changed frequently. After dialysis, the total volume of the particle dispersion was 116 mL. DLS studies showed that the hydrodynamic diameter
of PTEGMMA brush-grafted poly(acrylic acid) PAA particles in water was at 25 °C 284 ± 7.5 nm.

3.2.8 Synthesis of PTEGMMA Hairy Particle-Supported Pd Nanoparticles

The dispersion of PTEGMMA brush-grafted PAA particles in water (100 mL) (containing ~ 1.1 g of hairy particles) was diluted to 200 mL with water. Palladium (II) acetate (172 mg, 0.766 mmol) was dissolved in THF (3 mL), diluted with water (10 mL), and added into the dispersion of particles. After being stirred at room temperature for 24 h, the mixture was dialyzed against water for 36 h to remove free Pd²⁺. The obtained dispersion (180 mL) was added into a flask that contained ethanol (60 mL). The flask was then placed in a 70 °C oil bath. After the reaction mixture was stirred at 300 rpm for 12 h, the flask was removed from the oil bath and the volatile solvents were evaporated by a rotavapor at 50 °C. A trace amount of precipitate was observed and removed by filtration. The particle dispersion was dialyzed against water for 36 h and water was changed frequently. Deionized water was added to dilute the particle dispersion to the concentration of 2.25 mg particles/g dispersion (the concentration was determined by gravimetric analysis). The average hydrodynamic diameter of the obtained particles in water at 25 °C was 299 nm.

3.2.9 General Procedure for Hydrogenation of Styrene in Aqueous Biphasic System

A general procedure for hydrogenation of styrene in a biphasic system consisting of water and octane is described below. The dispersion of Pd nanoparticle-embedded
PTEGMMA hairy particles in water (4.0 g, containing 9.0 mg particles, 0.86 mg (0.0081 mmol) of Pd nanoparticles) was added into a 50 mL three-necked flask and bubbled with H₂ for 1 h and then N₂ for 30 min. Styrene and octane were bubbled with nitrogen for 30 min. A solution of degassed styrene (0.166 g, 1.59 mmol) in degassed octane (4.0 mL) was added into the flask. The reaction mixture was stirred at 1000 rpm under 1 atm H₂ at a specific temperature. The reaction was monitored by GC-MS.

3.3 Results and Discussion

3.3.1 Synthesis of Initiator-Functionalized Core-Shell Crosslinked PtBA Particles

This work is intended to explore the use of thermosensitive polymer brush-grafted polymeric particles as carrier for catalytic Pd nanoparticles and exploit the temperature-induced phase transition of polymer brushes to modulate the catalytic activity of supported Pd in an aqueous/organic biphasic hydrogenation reaction. Pd nanoparticles were chosen as catalyst because of the facile synthesis and the widespread applications in many important organic reactions. We first prepared initiator-functionalized core-shell crosslinked PtBA particles (initiator particles) by seeded emulsion polymerization and then grew thermosensitive PTEGMMA brushes from the particles by surface-initiated ATRP (Scheme 3.1). Initiator particles were synthesized by a two-step emulsion polymerization. The seed PtBA particles were prepared by conventional emulsion polymerization at 60 °C using di(ethylene glycol) bisacrylate as crosslinker, sodium dodecyl sulfate as surfactant, and potassium persulfate as water-soluble initiator. From DLS measurements, the average hydrodynamic diameter of
PtBA particles was 96 nm in water and 124 nm in methanol. Methanol is a good solvent for PtBA swelling the crosslinked PtBA particles. The particles were then used as seeds in the second-step emulsion polymerization to incorporate 2-(2′-bromo-2′-methyl-propionyloxy)ethyl acrylate, which was an inimer (initiator and monomer) containing an ATRP initiator, into the thin shell layer. DLS study showed that the average hydrodynamic size of particles in water increased to 111 nm, which was 15 nm larger than that of seed particles. The initiator particles were precipitated in a mixture of methanol and water, redispersed in methanol, and purified by dialysis against methanol. The average hydrodynamic diameter of initiator particles in methanol was 141 nm. The initiator particles were then isolated, dispersed in dry THF, and used for the synthesis of thermosensitive PTEGMMA brush-grafted PtBA particles.

3.3.2 Synthesis of PTEGMMA Brush-Grafted PtBA Particles by Surface-Initiated ATRP

PTEGMMA brushes were grown from the initiator particles by surface-initiated ATRP, which was conducted in THF at 40 °C in the presence of a free initiator, benzyl 2-bromoisobutyrate, using CuBr/PMDETA as catalyst. The polymerization was stopped by opening the flask to air and diluting the reaction mixture with THF after 220 min. The monomer conversion was 45.4 %, determined by ¹H NMR spectroscopy analysis using the integrals of the peaks located at 4.12 – 4.39 ppm and 3.93 – 4.12 ppm, which were from –CH₂OOC- of the monomer and polymer, respectively. Based on the monomer conversion and the molar ratio of monomer to free initiator, the calculated degree of polymerization (DP) of PTEGMMA was 144. The PTEGMMA brush-grafted PtBA particles were separated from free polymer by repetitive fractionation using THF as a
good solvent and hexanes as a poor solvent. The THF solution of the free polymer was passed through a short Al₂O₃/SiO₂ (1/2, v/v) column to remove the copper catalyst. The free polymer was further purified by precipitation in hexanes and then analyzed by GPC and ¹H NMR spectroscopy. The number average and weight average molecular weights from GPC analysis (Mₙ,GPC and Mₘ,GPC) using polystyrene standards were 19,400 and 21,400 g/mol, respectively. The narrow molecular weight distribution (PDI = 1.10) indicated that the polymerization was a controlled process.

Figure 3.1 shows the ¹H NMR spectra of free PTEGMMA and PTEGMMA brush-grafted P(BA) particles in D₂O. All peaks of PTEGMMA in the hairy particles including the peaks from polymer backbone are discernible in the ¹H NMR spectrum but slightly broader than those of free PTEGMMA, which is attributed to the reduced mobility of polymer chains because of one end being fixed on the core particle. DLS studies showed that the hydrodynamic diameter of PTEGMMA brush-grafted particles was 262 ± 3.5 nm in water at 25 °C, which was 151 nm larger than the size of the initiator particles (111 nm). Considering the DP of PTEGMMA (DP = 144) obtained from the monomer conversion, this size increase was larger than expected. Possible reasons include: (1) the polymerization took place not only from the surface of the initiator particles but also inside the shell layer that contained initiator groups; (2) DLS measurements gave the hydrodynamic size of particles, i.e., the longer polymer chains played a more important role in determining the hydrodynamic size. Nevertheless, we can speculate that the grafting density of polymer brushes on the particles is very high, making the grafted polymer chains highly extended.
Figure 3.1. $^1$H NMR spectra of (a) poly(methoxytri(ethylene glycol) methacrylate) (PTEGMMA) brush-grafted PBA particles and (b) free PTEGMMA. D$_2$O was used as solvent.
3.3.3 Synthesis of PTEGMMA Brush-Grafted Crosslinked PAA Particles

PTEGMMA brush-grafted crosslinked PAA particles were synthesized from PTEGMMA brush-grafted PrBA particles by removal of t-butyl group of PrBA using trifluoroacetic acid as catalyst. It has been reported that CF₃COOH can hydrolyze the t-butyl group of an ester without affecting other types of esters. The hydrolysis reaction was carried out in CH₂Cl₂ at room temperature for 22 h using excess CF₃COOH. After the reaction, the hairy particles were purified by repetitive dispersion in THF and precipitation in hexanes, followed by dispersion in deionized water and dialysis against water for three days to remove CF₃COOH and other possible organic molecules. DLS studies showed that the average hydrodynamic diameter of PTEGMMA brush-grafted crosslinked PAA particles in water at 25 °C was 284 nm. The hydrodynamic size increased by 22 nm after hydrolysis, which is attributed to the swelling of crosslinked PAA core by water. Control experiments showed that while more than 98% of t-butyl groups of a linear PrBA was removed under the similar conditions, no changes were observed in the ¹H NMR spectrum of PTEGMMA after treatment with CF₃COOH (Figure 3.2 and 3.3), indicating that PTEGMMA was stable against CF₃COOH, consistent with the report in the literature for other types of ester groups.

3.3.4 Synthesis of Pd Nanoparticles inside PTEGMMA Brush-Grafted PAA Particles

Pd²⁺ cations were loaded into the PTEGMMA brush-grafted crosslinked PAA particles through ion exchange. Palladium acetate was first dissolved in a small amount of THF and diluted with water. The solution was then added into the aqueous dispersion
Figure 3.2. $^1$H NMR spectra of (a) poly($t$-butyl acrylate) (PtBA in CDCl$_3$) and (b) poly(acrylic acid) (PAA, obtained from hydrolysis of PtBA with CF$_3$COOH as catalyst, D$_2$O was used as solvent).

Figure 3.3. $^1$H NMR spectra of (a) PTEGMMA and (b) PTEGMMA after treatment under the conditions used for hydrolysis of PtBA. CDCl$_3$ was used as solvent.
of PTEGMMA brush-grafted PAA particles. The mixture was stirred at room temperature for 24 h and then dialyzed against water to remove free Pd$^{2+}$ ions. Pd nanoparticles were synthesized by reduction of Pd$^{2+}$ ions with ethanol $^{45,69}$ ($v_{\text{ethanol}}/v_{\text{water}}$, 1:3) at 70 °C for 12 h. The color changed from slight yellow to brown, indicating the formation of Pd nanoparticles. Ethanol was then evaporated by the use of a rotavapor at 50 °C. A trace amount of precipitate was observed and removed by filtration. After the dispersion was dialyzed against water at room temperature for 36 h, no ethanol was detected from $^1$H NMR spectroscopy analysis. The concentration of hairy particles in the aqueous dispersion, measured by gravimetric analysis, was 2.25 mg hairy particles/g dispersion. The Pd content in the hairy particles was determined by thermogravimetric analysis in air (Figure 3.4). The lowest weight retention was 9.8 % at 366 °C. The weight retention then gradually increased to 10.6 %, likely due to the oxidation of Pd nanoparticles in air. The lowest weight retention of PTEGMMA brush-grafted crosslinked PAA particles was found to be 0.3 % at 520 °C. The difference between the lowest retentions of two samples (9.5 wt %) was taken as the content of Pd nanoparticles in the hairy particles. Figure 3.5 shows a typical transmission electron microscopy (TEM) micrograph. Most of Pd nanoparticles were located in the core of hairy particles, but there were some Pd nanoparticles in the brush layer, which is likely due to the coordination of Pd$^{2+}$ cations with methoxytri(ethylene glycol) pendant of PTEGMMA. The calculated size of Pd nanoparticles was 8.6 ± 3.0 nm.

### 3.3.5 Thermosensitive Properties of Hairy Particles

One goal of this work is to exploit the thermo-induced phase transitions of polymer brushes between hydrated and dehydrated states to regulate the catalytic activity of Pd
Figure 3.4. Thermogravimetric analysis (TGA) of PTEGMA brush-grafted crosslinked poly(acrylic acid) particles and Pd nanoparticle-embedded hairy particles. The Pd content in the hairy particles was 9.5 wt %. TGA was performed in air at a heating rate of 20 °C/min.

Figure 3.5. A typical transmission electron microscopy (TEM) micrograph of Pd nanoparticle-loaded, thermosensitive PTEGMA brush-grafted PAA particles.
nanoparticles in an aqueous biphasic hydrogenation reaction. Therefore, we first studied the thermosensitive properties of PTEGMMA brush-grafted PtBA particles, PTEGMMA brush-grafted PAA particles, and Pd nanoparticle-loaded PTEGMMA brush-grafted PAA particles in dilute aqueous dispersions by variable temperature DLS. Note that the cloud point of PTEGMMA in water at a concentration of 0.5 wt % is 48 °C and the transition zone is narrow (≤ 2 °C) (Chapter 1). Figure 3.6 shows the hydrodynamic sizes of PTEGMMA brush-grafted PtBA particles and Pd nanoparticle-embedded hairy particles as a function of temperature. The aqueous dispersions of particles with concentrations of 0.01 mg/mL were gradually heated from 25 °C. At each temperature, the dispersions were equilibrated for 30 min prior to data recording. The average hydrodynamic diameter of PTEGMMA brush-grafted PtBA particles was 262 nm at 25 °C and remained constant in the temperature range of 25 to 40 °C. Above 40 °C, the hairy particles began to shrink; the size decreased to 243 nm at 45 °C, 237 nm at 50 °C, and 235 nm at 55 °C. From 40 to 55 °C, the hydrodynamic size decreased by 27 nm. This observation is similar to the thermo-induced transition of PTEGMMA brushes on silica particles, which began at a lower temperature and continued over a broader temperature range than that of free polymer in solution.28

After the t-butyl group of PtBA was cleaved by the use of CF₃COOH, the particle size at 25 °C increased from 262 to 284 nm, which is due to the swelling of PAA core by water. Similarly, the hydrodynamic diameter of PTEGMMA brush-grafted PAA particles decreased with the increase of temperature. The onset temperature for the transition was slightly lower than that of PTEGMMA brushes on crosslinked PtBA particles; the hydrodynamic size of the particles at 40 °C (269 nm) was appreciably smaller than those
Figure 3.6. Average hydrodynamic diameters of (■) PTEGMMA brush-grafted PtBA particles and (●) Pd nanoparticle-embedded PTEGMMA brush-grafted PAA particles as a function of temperature. The concentrations of hairy particles in water were 0.01 mg/mL. At each temperature, at least eight measurements were made to give an average hydrodynamic diameter.
at 25 – 35 °C (281 – 284 nm). The hairy particles continued to shrink with the increase of temperature; the average hydrodynamic size of the particles at 55 °C was 35 nm smaller than that at 25 °C.

After the loading and reduction of Pd^{2+} ions, the average hydrodynamic size of hairy particles at 25 °C was 299 nm, which was 15 nm larger than that of PTEGMMA brush-grafted PAA particles. This size increase is likely due to the electrostatic repulsion from the surface changes of Pd nanoparticles and possible unreduced Pd^{2+} ions within the core and the brush layer. With the increase of temperature, the hydrodynamic size of hairy particles decreased from 297 nm (30 °C), to 280 nm (35 °C), to 270 nm (40 °C), to ~265 nm (45 and 50 °C), and 257 nm at 55 °C; the particles shrank by 42 nm through the studied temperature range. The width of the transition zone (~ 10 °C) was similar to that of PTEGMMA brush-grafted PtBA particles, but the onset temperature was nearly 5 and 10 °C lower than those of PTEGMA brush-grafted PAA particles and PTEGMMA brush-grafted PtBA particles. We speculate that this lower onset transition temperature might be related to the small amount of Pd nanoparticles in the brush layer (Figure 3.5). The Pd nanoparticles may act as coordination site, resulting in a higher local segment concentration and thus a lower onset temperature.

### 3.3.6 Hydrogenation in Biphasic System

In previous chapter, it was shown that PTEGMMA brush-grafted silica particles cannot be transported from water to toluene or other hydrocarbon solvents upon heating at 60 °C, providing us with an opportunity to develop water-dispersible supported catalysts for catalysis of aqueous/organic biphasic reactions. The aqueous dispersion of Pd nanoparticle-loaded hairy particles was used directly for hydrogenation of styrene in a
water/octane biphasic system. It should be noted that the aqueous dispersion of Pd nanoparticle-loaded hairy particles was very stable. No any precipitate was observed in days. Under a stationary state, only a very trace amount of black precipitate was observed after two months and was easily dispersed by gentle shaking. The particle dispersion was bubbled with $H_2$ for 1 h and then $N_2$ for 30 min prior to the reaction. For each hydrogenation reaction, an equal volume of a solution of styrene in octane (0.166 g of styrene in 4.0 mL of octane) was placed on top of aqueous dispersion of hairy particles (4.0 mL). The reactions were carried out at specific temperatures under 1 atm $H_2$ by vigorously stirring the liquids. The amounts of styrene and the product, ethylbenzene, in the octane layer were monitored by GC-MS.

The water-dispersible hairy particle-supported Pd nanoparticles were found to efficiently catalyze the biphasic hydrogenation of styrene. At 25 °C, the hydrogenation reaction reached a conversion of 98 % in 111 min and was complete in 125 min. The octane layer was separated from the aqueous dispersion of hairy particles. The aqueous layer was then bubbled with $N_2$ for 30 min to remove the volatile organic compounds. A fresh solution of styrene (0.166 g) in octane (4.0 mL) was added and the hydrogenation was carried out under the same condition as in the first cycle. The catalyst was reused consecutively for additional three times and the results are summarized in Table 3.1. In the first three cycles, the reactions were complete in 125 min, the yields in the fourth and fifth cycles decreased slightly to 94 and 83 % after the same period of time. The hydrogenation in the fifth cycle was eventually complete after the reaction time was extended to 275 min. The observed decrease in the reaction yields might be due to the
Table 3.1 The Yields of Hydrogenation of Styrene in a Water/Octane Biphasic System Using PTEGMMA Hairy Particle-Supported Pd Nanoparticles as Catalyst at 25 °C in Five Consecutive Cycles.

<table>
<thead>
<tr>
<th>Cycle  a</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
<th>5th</th>
</tr>
</thead>
<tbody>
<tr>
<td>111 min (%)  b</td>
<td>98</td>
<td>98</td>
<td>99</td>
<td>89</td>
<td>81</td>
</tr>
<tr>
<td>125 min (%)  b</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>94</td>
<td>83c</td>
</tr>
</tbody>
</table>

a The same aqueous dispersion of Pd nanoparticle-embedded hairy particle was used consecutively five times for catalyzing hydrogenation of styrene in a water/octane biphasic system. b The reaction yields were obtained from GC-MS using the integral values of the peaks of styrene and the product ethylbenzene. c The reaction was complete after 275 min (yield: > 99 %).
reduced surface area of Pd nanoparticles because of possible aggregation of small Pd nanoparticles into larger ones in the hairy particles.

3.3.7 Effect of Thermo-Induced Phase Transition of PTEGMMA Brushes on the Biphasic Hydrogenation of Styrene

Since the PTEGMMA brush-grafted particles cannot be transported to the octane layer, the reaction took place in the aqueous phase; styrene molecules diffused into the aqueous phase and reacted with H₂ on the surface of Pd nanoparticles inside the hairy particles. To look into whether and how the temperature-induced collapse of PTEGMMA brushes affect the rate of hydrogenation of styrene, we carried out a series of reactions under same conditions except at different temperatures. The reactions were monitored by GC-MS analysis of styrene and the product, ethylbenzene, in the octane layer. Samples (< 0.1 mL) from the octane layer were taken at various time intervals, diluted with methylene chloride, and analyzed by GC-MS. Figure 3.7 shows the kinetics plots of hydrogenation of styrene at 20, 25, 34.5, and 42 °C as examples. When the conversion was lower than 40 %, the concentration of styrene decreased linearly with time. The initial reaction rate was independent of styrene concentration; the hydrogenation was zero order in the concentration of styrene. With the increase of conversion, the reaction appeared to slow down for all temperatures. Note that a zero-order reaction kinetics was reported by Pellegatta et al. in biphasic hydrogenation of benzene by using rhodium particles as catalyst. Since the pressure of H₂ was a constant (1 atm), this zero-order reaction implied that the initial reaction rate was not affected by the mass transfer speed.
Figure 3.7. Kinetics of hydrogenation of styrene in a water/octane biphasic system using thermosensitive hairy particle-supported Pd nanoparticles as catalyst at 20 °C (▲), 25 °C (●), 34.5 °C (▼) and 42 °C (■).
of styrene from the octane layer to aqueous phase. The rate-determining step appeared to be the hydrogenation reaction on the surface of Pd nanoparticles. With the reaction continuing, the concentration of styrene in octane decreased, causing the mass transfer speed to decrease. At a certain point, the diffusion rate of styrene from the octane layer to the aqueous phase became comparable to and eventually slower than the rate of hydrogenation of styrene on the surface of Pd nanoparticles. Consequently, the reaction rate became dependent on the mass transfer speed.

From the kinetics plots, we determined the initial reaction rate constants for the studied temperature range. The results from linear regression fitting of the data points below 40 % conversion are summarized in Table 3.2. Except 39 °C (R = 0.990), the R values for other temperatures were ≥ 0.998. The effect of temperature on the reaction rate constant is usually expressed by Arrhenius equation, that is, lnk changes with the inverse temperature in a linear fashion. Figure 3.8 shows the plot of lnk versus 1/T for the hydrogenation of styrene in a water/octane biphasic system using thermosensitive hairy particle-supported Pd nanoparticles as catalyst. In the range of 30 to 36 °C, the temperature effect on the reaction rate constant did not follow Arrhenius equation; the initial reaction rate constants at 33, 34.5 and 36 °C were lower than that at 30 °C. We believe that this non-Arrhenius dependence of rate constant on temperature was due to the collapse of PTEGMMA brushes in this temperature range. The results from DLS studies indicated that the Pd nanoparticle-loaded PTEGMMA brush-grafted particles began to shrink when the temperature was above 30 °C and continued over a broad temperature range. The collapsed PTEGMMA brush layer likely presented a higher steric barrier for styrene molecules to diffuse from bulk aqueous dispersion to the surface of Pd
Table 3.2. Initial Reaction Rate Constants of Hydrogenation of Styrene in a Water/Octane Biphasic System Using Thermosensitive Hairy Particle-Supported Pd Nanoparticles as Catalyst at Different Temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>20</th>
<th>25</th>
<th>25</th>
<th>30</th>
<th>33</th>
<th>34.5</th>
<th>36</th>
<th>39</th>
<th>42</th>
</tr>
</thead>
<tbody>
<tr>
<td>R^a</td>
<td>0.999</td>
<td>0.999</td>
<td>0.998</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
<td>0.990</td>
<td>0.999</td>
</tr>
</tbody>
</table>

^a Initial reaction rate constants and R values were obtained from linear regression fitting of the data points below 40 % conversion.

Figure 3.8. lnk versus 1/T for the hydrogenation of styrene in a water/octane biphasic system using thermosensitive hairy particle-supported Pd nanoparticles as catalyst. k is the initial reaction rate constant at a specific temperature, obtained by linear regression fitting of the data points below 40 % conversions.
nanoparticles, causing the reaction to slow down. Thus, unlike at temperatures below 30°C where the rate-determining step was the hydrogenation reaction on the surface of Pd nanoparticles, the diffusion rate of styrene through the collapsed polymer brush layer became comparable to or perhaps slower than the hydrogenation rate of styrene. With further increasing temperature, the diffusion rate increased and the surface hydrogenation reaction became the rate determining step again. Using Arrhenius equation, the activation energies of the hydrogenation reaction below 30 °C and ≥ 36 °C were calculated and they were 30.6 and 29.4 kJ/mol, respectively. The results show that the reaction rate of hydrogenation of a hydrophobic alkene in a water/octane biphasic system can be modulated by the thermo-induced phase transition of the brush layer of the hairy particles.

3.4 Conclusions

We developed a recyclable Pd(0) catalyst using thermosensitive PTEGMMA brush-grafted polymeric particles as carrier. PTEGMMA brushes were grown from initiator-functionalized core-shell crosslinked PrBA particles by surface-initiated ATRP. The t-butyl group of PrBA was removed, producing a hydrophilic PAA core. Pd²⁺ ions were then introduced through ion exchange and reduced with ethanol at 70 °C to produce Pd nanoparticles. From TGA analysis, Pd content in the thermosensitive hairy particles was 9.5 wt %. DLS studies showed that the Pd nanoparticle-embedded thermosensitive hairy particles began to shrink above 30 °C and continued over a broad temperature range. The hairy particle-supported Pd nanoparticles were an efficient catalyst for aqueous biphasic hydrogenation of styrene. The catalyst was reused five times with no changes in the yields in the first three cycles and slight decreases in the conversions in the fourth and
fifth cycles after the same period of time. Kinetics studies showed that the reaction did not follow Arrhenius equation in the temperature range of 30 to 36 °C, which is believed to result from the collapse of PTEGMMA brushes. The collapsed PTEGMMA presented a higher steric barrier and slowed down the hydrogenation reaction.

References


Chapter 4. Environmentally Responsive "Hairy" Particles: Mixed Homopolymer Brushes on Silica Particles Synthesized by Living Radical Polymerization Techniques
4.1 Introduction

Hybrid particles composed of an inorganic or metal particle core and an organic polymer shell possess intriguing properties associated with the particles and the desired properties of polymers, including processability and compatibility to the environment.\textsuperscript{1-3} When densely tethered to the surface of particles by one end via a covalent bond, polymer chains are forced to stretch away from the grafting sites and assume an extended conformation due to the excluded volume interaction,\textsuperscript{1-7} resulting in “hairy” particles (polymer brushes on the particles). Generally, there are two approaches to chemically attach polymer chains to a surface: (1) the “grafting to” method, where the end-functionalized polymers react with an appropriate surface;\textsuperscript{8} (2) the “grafting from” method, where polymer chains are grown from initiator-terminated self-assembled monolayers (SAMs).\textsuperscript{1-5} Using the grafting from approach, Prucker and Rühe described in their seminal papers the growth of polystyrene (PS) from high-surface-area silica gels that were surface-functionalized with an azo monolayer.\textsuperscript{9,10} Controlled “living” radical polymerizations are advantageous over conventional free radical polymerizations as they can provide control on polymer architecture, molecular weight, and molecular weight distribution.\textsuperscript{11,12} A variety of living polymerization techniques, most notably, atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMRP), have been used in recent years by a number of research groups to synthesize polymer brushes from flat substrates,\textsuperscript{13-27} carbon nanotubes,\textsuperscript{28-30} and particles including silica and gold particles,\textsuperscript{31-42} quantum dots,\textsuperscript{43,44} and magnetic particles.\textsuperscript{45,46} Using Langmuir-Blodgett technique, Ohno et al. demonstrated that the distance between the gold particles can be well controlled by the chain length of the grafted polymer,
providing an excellent example on the potential applications of hairy particles in nanotechnology and advanced materials.\textsuperscript{40}

In this work, the synthesis, characterization, and properties of environmentally responsive hairy particles, mixed homopolymer brushes on silica particles were discussed (Scheme 4.1). Mixed brushes composed of two different homopolymer chains randomly or alternately immobilized on planar solid surfaces have been intensively studied in recent years because of their intriguing phase behavior and potential applications in “smart” materials.\textsuperscript{47-77} It has been theoretically predicted and experimentally demonstrated by several research groups that mixed homopolymer brushes undergo reorganization in response to external stimuli, exhibiting different surface wettability and surface morphology.\textsuperscript{47-77} By tuning parameters including grafting density, molecular weight, chemical composition, solvent, and temperature, a variety of surface structures and properties could be achieved by mixed brushes. Previously in our group, an effort has been initiated to synthesize well-defined mixed homopolymer brushes by controlled/living polymerization techniques and to explore their self-assembly behavior in selective solvents and under equilibrium melt conditions.\textsuperscript{68-72} ATRP and NMRP, which are two different controlled radical polymerization techniques and are performed under different conditions,\textsuperscript{11,12} have been used to grow two distinct homopolymers from either mixed initiator-terminated monolayers\textsuperscript{68,72} or asymmetric difunctional initiator-terminated SAMs (Y-SAMs)\textsuperscript{69-71} on silicon wafers. Y-SAMs were designed to ensure that the two initiators are well-mixed in the initiator monolayer. The effects of relative molecular weights and relative grafting densities of the two grafted polymers on the self-assembly have been studied.\textsuperscript{70-72} In this work, we applied our strategy to synthesize amphiphilic
Scheme 4.1. Synthesis of Mixed Poly(acrylic acid)/Polystyrene Brushes on Silica Particles.
mixed brushes on silica particles. It should be pointed out that no prior experimental work has been reported in the literature on mixed brushes on the surface of particles. One can envision that the success of the synthesis of well-defined mixed homopolymer brushes on particles would open an avenue to investigate their responsive properties, to explore the applications in nanotechnology and advanced materials, and to study how the two polymer chains phase separate in a confined geometry. Silica particles with an average diameter of 180 nm were prepared using the Stöber process\textsuperscript{78,79} and functionalized with a Y-SAM (the synthesis of Y-silane was shown in Scheme 4.2). Mixed poly(\textit{tert}-butyl acrylate) (PtBA)/PS brushes were synthesized by sequential surface-initiated ATRP of \textit{t}BA and NMRP of styrene. Removal of the \textit{tert}-butyl group of PtBA produced amphiphilic mixed poly(acrylic acid) (PAA)/PS brushes (Scheme 4.1). Infrared spectroscopy (IR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), \textsuperscript{1}H NMR, and gel permeation chromatography (GPC) were employed to characterize the particles and the polymers.

4.2 Experimental Part

4.2.1 Materials

Styrene (99\%, Aldrich) and \textit{tert}-butyl acrylate (\textit{t}-BA, 99\%, Aldrich) were distilled over CaH\textsubscript{2} under reduced pressure and stored in a refrigerator prior to use. CuBr (98\%, Aldrich) was purified according to the procedure described in the literature\textsuperscript{15} and stored in a desiccator. CuBr\textsubscript{2} (anhydrous, 99+\%, Acros) was used as received. \textit{N}, \textit{N}, \textit{N}', \textit{N}', \textit{N}''-pentamethyldiethylenetriamine was distilled and stored in a desiccator. Tetrahydrofuran (THF) was distilled from sodium and benzophenone and stored in a storage bottle. Tetraethoxysilane (98\%), ammonium hydroxide (25\% in water), iodotri-
**Scheme 4.2.** Synthesis of an Asymmetric Difunctional Initiator-Terminated Monochlorosilane, Y-Silane.
methylsilane (stabilized, 95~97%), 2,2,6,6-tetramethylpiperidinoxy (TEMPO) (98%), and 4-vinylbenzyl chloride (tech., 90 %) were purchased from Arcos and used as received. Chlorodimethylsilane (98%), 2-bromoisobutyryl bromide (98%), and allylmagnesium chloride (2.0 M solution in THF) were purchased from Aldrich and used as received. Platinum-divinyl tetramethyl-disiloxane complex in xylene (2.1~2.4% Pt concentration in xylene) was obtained from Gelest Inc. and used as received. The free initiator, 1-phenyl-1-(2’,2’,6’,6’-tetramethyl-1’-piperidinyloxy)-2-benzoyloxyethane (PTEMPO), was synthesized according to the literature. All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

4.2.2 Characterization

Gel permeation chromatography (GPC) was carried out at ambient temperature using PL-GPC 20 (an integrated GPC 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). The data were processed using Cirrus™ GPC/SEC software (Polymer Laboratories). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Standard monodisperse polystyrenes (Polymer Laboratories, USA) were used for calibration. The 1H and 13C NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer and the residual solvent proton signal as the internal standard. Mass spectroscopy was performed in the Mass Spectroscopy Center in the Chemistry Department at the University of Tennessee at Knoxville on a Micromass Quattro II tandem electrospray spectrometer run in the positive ion electrospray mode. Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C using TA Q-series Q50. Scanning electron microscopy
(SEM) images were acquired on a HITACHI S-4300SE/N electron microscope. SEM samples were prepared by adding a few drops of a dilute suspension on a clean silicon wafer and allowing the solvent to evaporate in air. IR spectra were recorded on a BOMEM MB-Series Fourier transform infrared instrument. The samples were prepared by adding several drops of a suspension of the particles on a NaCl plate and drying in vacuum oven at 35 °C for 30 min.

4.2.3 Synthesis of Silica Particles

Ammonium hydroxide (25% in water, 14.02 g) and tetraethoxysilane (TEOS) (7.08 g) were dissolved in ethanol (5 mL) separately and were added into a 500 mL flask containing 190 mL of ethanol. The concentrations of NH₃, TEOS, and water in the solution were 0.45 M, 0.15 M, 3.10 M, respectively. The mixture was stirred vigorously at room temperature for 4 h. The particles were isolated by centrifugation (Fisher Centrifuge Model 225 Benchtop Centrifuge, 5100 rpm), redispersed in ethanol, and centrifugated again. This washing process was repeated with ethanol one more time, water four times, and ethanol again. The particles were dried with a stream of air (1.99 g, 98%).

4.2.4 Synthesis of 1

Benzoyl peroxide (5.00 g, 20.6 mmol) and 4-vinylbenzyl chloride (47.3 g, 0.310 mol) were added into a 250 mL three-necked flask. The mixture was stirred under N₂ atmosphere in an ice bath, and 2,2,6,6-tetramethylpiperidinoxy (TEMPO, 9.07 g, 58.0 mmol) was added slowly. The flask was then placed in an oil bath with a preset temperature of 80 °C. After the reaction proceeded for 20 h, excess 4-vinylbenzyl chloride was removed under reduced pressure, and the crude product was purified by
column chromatography using a mixture of methylene chloride and hexanes with a volume ratio of 3:1 as eluent to give 1 (1.81 g, 10%). $^1$H NMR (CDCl$_3$) δ (ppm): 0.74, 1.04, 1.17, 1.33 (each br s, 12H, CH$_3$), 1.26-1.56 (m, 6H, -CH$_2$CH$_2$CH$_2$-), 4.49 (dd, 1H, -OCHH-), 4.56 (s, 2H, -CH$_2$Cl), 4.79 (dd, 1H, -COOCHH-), 5.03 (dd, 1H, -CH-), 7.35-7.71 (complex m, 7H, ArH), 7.87-7.91 (m, 2H, ArH). $^{13}$C NMR δ(ppm): 15.09, 0.37, 34.06, 40.35, 46.08, 60.11, 66.61, 83.55, 127.86, 128.29, 128.30, 129.52, 130.07, 132.86, 136.67, 140.96, 166.26. Mass spectrum: 430.1.

### 4.2.5 Synthesis of 2

A solution of compound 1 (1.10 g, 2.56 mmol) in dry THF (10 mL) was added into a 100 mL three-necked flask, followed by injection of 2.0 M allylmagnesium chloride in THF (12.0 mL, 24.0 mmol). The mixture was stirred at 60 °C for 2 h. Methanol (3.0 mL) was added into the flask to quench excess allylmagnesium chloride. After the solvents were removed by rotavapor, the residue was partitioned between water (30 mL) and methylene chloride (30 mL). The aqueous phase was extracted with methylene chloride (3 × 30 mL). The organic extracts were combined and dried over anhydrous sodium sulfate. After removal of the solvent, the crude product was purified by silica gel column chromatography using 4:1 hexanes/ethyl acetate to afford 2 (0.67 g, 79%). $^1$H NMR δ (ppm): 1.13, 1.20, 1.32, 1.49 (each s, 12H, CH$_3$), 1.24-1.61 (m, 6H, -CH$_2$CH$_2$CH$_2$-), 2.35 (q, 2H, -CH$_2$CH=CH$_2$), 2.68 (t, 2H, Ar-CH$_2$CH$_2$-), 3.68 (broad t, 1H, -OCHH-), 4.20 (dd, 1H, -OCHH-), 4.99 (m, 2H, -CH=CH$_2$), 5.26 (d, 1H, -CH-), 5.83 (m, 1H, -CH=CH$_2$), 5.88 (d, 1H, -OH), 7.13-7.27 (dd, 4H, ArH). $^{13}$C NMR δ (ppm): 17.11, 20.38, 20.69, 32.69, 34.56, 35.03, 35.34, 40.15, 40.36, 60.31, 61.65, 69.76, 83.36, 114.93, 126.71, 128.33, 136.32, 138.01, 141.55. Mass spectrum: 331.2.
4.2.6 Synthesis of 3

Methylene chloride (10 mL), compound 2 (0.77 g, 2.3 mmol), and triethylamine (0.86 g, 8.5 mmol) were added into a three-necked flask. The flask was then placed in an ice bath followed by addition of a solution of 2-bromo-2-methylpropionyl bromide (1.63 g, 7.1 mmol) in methylene chloride (10 mL) in a dropwise fashion. The reaction mixture was stirred at room temperature for 14 h, washed with an aqueous solution of ammonium chloride (4 × 20 mL), and dried over anhydrous sodium sulfate. After removal of methylene chloride using a rotavapor, the crude product was purified by column chromatography with 6:1 hexanes/ethyl acetate as eluent to afford 3 (0.97 g, 87%). \(^1\)H NMR \(\delta\) (ppm): 0.74, 1.04, 1.19, 1.33 (each s, 12H, \(\text{C}_\text{H}_3\)), 1.27-1.55 (m, 6H, -\(\text{CH}_2\text{CH}_2\text{CH}_2\text{H}_2\)), 1.77 (s, 6H, \(\text{CH}_3\)), 2.35 (q, 2H, -\(\text{CH}_2\text{CH}=\text{CH}_2\)), 2.69 (t, 2H, Ar-\(\text{CH}_2\text{CH}_2\)), 4.43 (dd, 1H, -OCHH-), 4.60 (dd, 1H, -OCHH-), 4.95 (t, 1H, -CH-), 4.97 (m, 2H, -CH=CH\(_2\)), 5.82 (m, 1H, -CH=CH\(_2\)), 7.11-7.26 (dd, 4H, Ar\(\text{H}\)). \(^{13}\)C NMR \(\delta\) (ppm): 17.11, 20.29, 30.71, 33.98, 35.07, 35.52, 40.33, 55.64, 60.05, 67.47, 83.26, 114.91, 127.60, 128.00, 137.58, 137.97, 141.17, 171.37. Mass spectrum: 479.2.

4.2.7 Synthesis of 2-{4-[4′-(Chlorodimethylsilyl)butyl]phenyl}-2-(2\(^\prime\),2\(^\prime\), 6\(^\prime\),6\(^\prime\)-tetramethyl-1-piperidinyloxy)ethyl 2-Bromo-2-methylpropionate (Y-Silane)

Compound 3 (0.15 g, 0.32 mmol) was added into a 25 mL two-necked flask and dried at room temperature in vacuum for 2 h. Chlorodimethylsilane (1.50 mL, 13.5 mmol) was injected into the flask under N\(_2\) atmosphere followed by addition of Pt complex in xylene (4 \(\mu\)L). \(^1\)H NMR microscopy was used to monitor the reaction. Once the reaction was complete, excess chlorodimethylsilane was removed by vacuum and the product was
used directly without further purification. $^1$H NMR $\delta$ (ppm): 0.36 (s, 6H, Si-CH$_3$), 0.71, 1.02, 1.17, 1.31 (each s, 12H, CH$_3$), 0.82 (t, 2H, Si-CH$_2$-), 1.35-1.47 (m, 8H, -CH$_2$CH$_2$CH$_2$- and Si-CH$_2$-CH$_2$-), 1.63 (Ar-CH$_2$-CH$_2$-CH$_2$-), 1.75 (s, 6H, Br-C-CH$_3$), 2.58 (t, 2H, Ar-CH$_2$-CH$_2$-), 4.40 (dd, 1H, -OCHH-), 4.57 (dd, 1H, -OCHH-), 4.92 (t, 1H, -CH-), 7.08-7.23 (dd, 4H, ArH). $^{13}$C NMR $\delta$ (ppm): 1.64, 17.11, 18.79, 20.29, 22.51, 30.72, 33.97, 34.59, 35.18, 40.34, 55.67, 60.04, 67.51, 83.28, 127.61, 127.93, 137.46, 141.78, 171.37.

4.2.8 Immobilization of Y-Initiator on Silica Particles

Silica particles (1.89 g) were dried at 110 °C in vacuum (30 millitorr) for 6-7 h, and were dispersed in dry THF (12 mL). A solution of Y-silane freshly synthesized from 0.25 g of compound 3 in THF (10 mL) was injected into the suspension via a syringe. The mixture was stirred at 70°C under N$_2$ atmosphere for 40 h. The particles were isolated by centrifugation, resuspended in THF, and centrifugated again. This washing process was repeated four times, followed by drying with a stream of air to yield dry particles (1.84 g).

4.2.9 Surface-Initiated ATRP of t-BA

The particles functionalized with Y-initiator (Y-initiator-particles, 1.21 g) were added into a three-necked flask containing CuBr (114.7 mg, 0.80 mmol) and CuBr$_2$ (5.5 mg, 24.6 μmol), and were dried at 35°C in vacuum (30 millitorr) overnight. Anisole (26.92 g) was then added into the flask and the particles were dispersed by ultrasonication, followed by injection of t-BA (52.92 g, 412.9 mmol), N, N, N', N'-pentamethyldiethylenetriamine (PMDETA) (135.4 mg, 0.78 mmol), and ethyl 2-bromoisobutyrate (EBiB) (145.5 mg, 0.746 mmol). The mixture was degassed by
freeze-pump-backfilling with N₂ four times, and then placed in an oil bath with a preset
temperature of 75 °C. After polymerization for 1805 min, the flask was removed from the
oil bath and opened to air. THF (80 mL) was added into the flask to dilute the mixture.
The particles were isolated by centrifugation, and the supernatant was passed through a
short column of aluminum oxide (neutral, activated). The particles were redispersed in
THF, allowed to stand overnight (the green precipitate was removed), and centrifuged
again. This washing process was repeated with THF one more time and chloroform three
times followed by drying the particles with a stream of air (PtBA-particle-3). The free
polymer (PtBA-3) formed in the solution was precipitated in methanol/water (1:1) and
dissolved in methylene chloride. The solution was dried over anhydrous sodium sulfate.
Removal of solvent produced a dry polymer which was then analyzed by ¹H NMR and
GPC. The Mₙ and Mₘ from GPC were 24,200 and 26,400, respectively. Two more
samples were taken at polymerization time t = 547 min (conversion: 14.1 %, the particles
were designated as PtBA-Particle-1 and the free polymer PtBA-1) and t = 1053 min
(conversion: 24.6 %, the particles designated as PtBA-Particle-2 and the free polymer
PtBA-2). The particles and free polymers were separated and purified by the procedure
described above.

4.2.10 Cleavage of the Grafted PtBA from Particles

PtBA particles (PtBA-particle-3, 55 mg) were dispersed in toluene (10 mL) in a
plastic bottle by ultrasonication followed by addition of hydrofluoric acid (HF, 48–51%
aq., 0.6 mL). After the mixture was stirred at room temperature for 4 h, a suspension of
Ca(OH)₂ in water was used to neutralize the mixture. The mixture was extracted with
toluene (2 × 10 mL) and the organic layer was separated. The organic extracts were
combined and dried with anhydrous sodium sulfate. After removal of toluene, the polymer was characterized by $^1$H NMR and GPC. GPC results: $M_n = 23,200$ and $M_w = 26,600$.

### 4.2.11 Dehalogenation of PtBA Particles

PtBA particles (PtBA-particle-3, 0.49 g) and CuBr (44.2 mg, 0.31 mmol) were added into a 100 mL three-necked and dried in vacuum at 35 °C for 3 h. Anisole (40 mL) was added into the flask and the particles were dispersed by ultrasonication, followed by addition of PMDETA (64.5 μL, 0.31 mmol) and EBiB (45 μL, 0.31 mmol). The mixture was degassed by freeze-pump-backfilling with N$_2$ four times, and then placed in an oil bath with a preset temperature of 75 °C. Tri(n-butyl)tin hydride (0.25 mL, 0.93 mmol) was injected via a microsyringe into the mixture over a period of 15 min. The reaction continued for 30 min. The particles were isolated by centrifugation, redispersed in hexanes, allowed to stand for ~2 h (the precipitate was removed), and centrifugated again. The washing process was repeated with hexanes one more time and chloroform three times followed by drying the particles with a stream of air (0.38 g of particles obtained).

### 4.2.12 NMRP of Styrene from Dehalogenated PtBA Particles

The dehalogenated PtBA particles (0.315 g) and the free initiator PTEMPO (95.8 mg, 0.251 mmol) were added into a 100 mL three-necked flask and dried in vacuum at 35 °C overnight. Anisole (17.4 g) was injected into the flask and the particles were dispersed by ultrasonication followed by addition of styrene (16.84 g, 161.7 mmol). The mixture was degassed by freeze-pump-backfilling with N$_2$ four times, and then placed in an oil bath with a preset temperature of 120 °C. After 950 min, the polymerization was stopped by cooling the mixture to room temperature and diluting it with CHCl$_3$. The particles were
isolated by centrifugation. The particles were redispersed in CHCl₃ and separated again. This washing process was repeated four times to ensure that the physically adsorbed polymers were removed. Drying with a stream of air yielded mixed PₜBA/PS particles (0.31 g). The polystyrene formed in the solution was precipitated in methanol and characterized by GPC. The Mₙ and Mₚ were 23,000 and = 25,300, respectively.

4.2.13 Cleavage of the Grafted Polymers from PₜBA/PS Particles

PₜBA/PS particles (0.126 g) were dispersed in toluene (10 mL) in a plastic bottle by ultrasonication followed by addition of hydrofluoric acid (HF, 48~51% aq., 0.7 mL). After the mixture was stirred at room temperature for 4 h, a suspension of Ca(OH)₂ in water was added to neutralize the mixture. The mixture was extracted with toluene (2 × 10 mL). The organic extracts were combined and dried with anhydrous sodium sulfate. After removal of solvent, the polymer mixture was characterized by ¹H NMR and GPC. The Mₙ and Mₚ of the polymer mixture were 37,500 and 43,200, respectively.

4.2.14 Hydrolysis of the Polymer Mixture Cleaved from PₜBA/PS Particles

A solution of sodium methoxide (50 mg, 1.3 mmol) in a mixed solvent of THF (10 mL) and methanol (0.75 mL) was added into the flask containing the polymer mixture cleaved from PₜBA/PS particles. The reaction mixture was stirred at 70 °C for 7 days. After removal of solvents, the residue was extracted with cyclohexane and the polymer in cyclohexane extracts was characterized by ¹H NMR and GPC. GPC results: Mₙ = 23,800 and Mₚ = 26,400.
4.2.15 Hydrolysis of PrBA by Use of Iodotrimethylsilane

A solution of PrBA (1.10 g, $M_n = 19,100$, $PDI = 1.14$) in CH$_2$Cl$_2$ (5 mL) was added into a two-necked flask followed by injection of iodotrimethylsilane (1.6 mL, 11 mmol) at room temperature under N$_2$ atmosphere. After the solution was stirred at room temperature for 6 h, the solvent and excess iodotrimethylsilane were removed under reduced pressure. A mixture of CH$_2$Cl$_2$ and CH$_3$OH (v/v, 20/1, 42 mL) was added into the flask. The precipitate was filtered, redissolved in CH$_3$OH, and precipitated again in CH$_2$Cl$_2$. This procedure was repeated one more time. A powder (0.20 g) was obtained.

4.2.16 Synthesis of Mixed PAA/PS Particles from PrBA/PS Particles

PrBA/PS particles (36 mg) were dispersed in CH$_2$Cl$_2$ (2 mL) in a 25 mL two-necked flask followed by addition of iodotrimethylsilane (0.2 mL). The mixture was stirred at room temperature for 6 h. The solvent and excess iodotrimethylsilane were removed under reduced pressure. The residue was dispersed in CH$_2$Cl$_2$/MeOH (v/v, 20/1) (21 mL). The particles were isolated by centrifugation, redispersed in CH$_2$Cl$_2$, and centrifugated again. This washing procedure was repeated with CH$_2$Cl$_2$, CH$_3$OH, and CH$_2$Cl$_2$/MeOH (v/v, 1/1). After drying with a stream of air, 25 mg of PAA/PS particles were obtained.

4.2.17 Tyndall Scattering Experiments

PS particles (synthesized from Y-initiator-particle, the $M_n$ and $M_w$ of free PS were 18,700 and 21,300, respectively), PAA particles (synthesized from PrBA-particle-2), and mixed PAA/PS particles, ~ 1.0 mg of each, were ultrasonicated in CHCl$_3$ or CH$_3$OH (2.0 mL) for 30 min. The Tyndall scattering experiment was performed with a laser beam. Pictures were taken with Sony DSC-V1 digital camera.
4.3 Results and Discussion

4.3.1 Synthesis of Y-Initiator-Functionalized Silica Particles

Spherical silica particles were prepared using the Stöber process, which involves the hydrolysis and condensation of tetraethoxysilane in an ammonia/ethanol solution.\textsuperscript{78,79} This process is well-known to produce silica particles with a relatively uniform size distribution, and the size of the particles can be conveniently controlled by the initial concentrations of the reactants. In this study, silica particles with an average diameter of 180 nm, determined from scanning electron microscopy (SEM) images (Figure 4.1a), were used to prepare environmentally responsive organic-inorganic hybrid particles by growing mixed homopolymer brushes from the surface. A Y-initiator-terminated monolayer was deposited on the surface of the particles through the reaction between the surface silanol groups and the Si-Cl of an initiator-terminated organosilane. Although denser SAMs can be obtained by use of organotrichlorosilanes, the reaction process is complex, and cross-linked polymeric species formed in the solution might precipitate on the surface.\textsuperscript{80} To avoid this issue, an asymmetric difunctional initiator-terminated monochlorosilane, Y-silane, was designed. Y-silane was prepared by a four-step procedure as outlined in Scheme 4.2. 4-Vinylbenzyl chloride reacted with the free radicals generated from benzoyl peroxide (BPO) at 80 °C in the presence of 2,2,6,6-tetramethylpiperidinoxy (TEMPO), producing 1. The reaction between allylmagnesium chloride and 1 afforded compound 2, which was then esterified with 2-bromo-2-methylpropionyl bromide to incorporate the moiety of an ATRP initiator. Y-silane was then obtained by hydrosilylation of the precursor 3 with dimethylchlorosilane using platinum divinyl tetramethyldisiloxane complex as catalyst. The $^1$H
Figure 4.1. Scanning electron microscopy images of (a) bare silica particles, (b) Y-initiator particles, (c) poly(tert-butyl acrylate) particles, (d) dehalogenated poly(tert-butyl acrylate) particles, (e) poly(tert-butyl acrylate)/polystyrene particles, and (f) poly(acrylic acid)/polystyrene particles. Scale bars: 200 nm.
NMR spectrum of Y-silane was showed in Figure 4.2. Detailed synthetic procedures and characterization data can be found in experimental section.

Bare silica particles were dried in vacuum (~30 mTorr) at 110 °C for 6-7 h, and were dispersed in dry tetrahydrofuran (THF) by ultrasonication. A solution of freshly synthesized Y-silane in dry THF was injected via a syringe to the flask containing THF-dispersed particles. The surface immobilization reaction was carried out under N\textsubscript{2} atmosphere at 70 °C for 40 h. The particles were then isolated by centrifugation and were redispersed in dry THF. This washing process was repeated four times, followed by drying with a stream of air. The IR spectrum (Figure 4.3b) of Y-initiator-functionalized particles (initiator particles) shows absorbance bands at 2983 and 2899 cm\textsuperscript{-1} that were characteristic of the alkyl C-H stretching vibration modes and were not present in the IR spectrum of bare particles (Figure 4.3a).\textsuperscript{81} From SEM images (Figure 4.1b), the average diameter of initiator particles was 181 nm, essentially the same as that of bare particles (180 nm). Thermogravimetric analysis (TGA), which was performed in air at a heating rate of 20 °C/min, indicated that the weight retention at 800 °C was 90.5% for bare particles and 86.9% for initiator particles (Figure 4.4). The weight loss of bare particles might be due to the continued condensation reaction and associated water loss.\textsuperscript{38} If the mass percent of the residue at 800 °C is used as the reference, the weight increase of initiator particles relative to that of bare particles would be 4.6%. Calculations show that the density of Y-initiator on the particle surface is ~0.33 nm\textsuperscript{2}/initiator. This result is consistent with the literature report.\textsuperscript{31,32}
Figure 4.2. $^1$H NMR spectrum of Y-silane.
Figure 4.3. IR spectra of (a) bare particles, (b) Y-initiator particles, (c) poly(tert-butyl acrylate) particles, (d) poly(tert-butyl acrylate)/PS particles, and (e) poly(acrylic acid)/PS particles.
Figure 4.4. Thermogravimetric analysis (TGA) of (a) bare particles, (b) Y-initiator particles, (c) PrBA-particle-1 obtained at the monomer conversion of 14.1%, (d) PrBA-particle-2 obtained at the monomer conversion of 24.6%, (e) PrBA-particle-3 obtained after the polymerization was stopped at the monomer conversion of 38.0%, (f) PAA/PS particles, and (g) PrBA/PS particles. TGA was performed in air at a heating rate of 20 °C/min.
4.3.2 Synthesis of PtBA Brushes from Y-Initiator Particles

Mixed PtBA/PS brushes were grown from Y-initiator particles by sequential ATRP of tBA at 75 °C and NMRP of styrene at 120 °C. We chose to synthesize mixed PtBA/PS brushes because PtBA can be easily converted to hydrophilic PAA,\textsuperscript{82,83} producing amphiphilic particles. Considering that the activation of an ATRP initiator by a metal complex is a bimolecular process and the free radicals in NMRP are generated by thermal decomposition, a unimolecular process, ATRP of tBA was conducted first. A unimolecular activation mechanism is preferred for the synthesis of the second type of polymer chains from the surface because of the possible steric hindrance presented by the existing polymer chains. Surface-initiated ATRP of tBA was carried out at 75 °C using CuBr/CuBr\textsubscript{2} and \textit{N},\textit{N},\textit{N}',\textit{N}'',\textit{N}'''-pentamethyldiethylenetriamine (PMDETA) as the catalytic system.\textsuperscript{84} We confirmed that the NMRP initiator was stable under typical ATRP conditions. A “free” ATRP initiator, ethyl 2-bromoisobutyrate (EB\textsubscript{i}B), was added into the reaction mixture to control the polymerization.\textsuperscript{13,14} The ratios of \([M]_o: [\text{free EBiB}]_o: [\text{CuBr}]_o: [\text{CuBr}_2]_o: [\text{PMDETA}]_o\) were 553:1:1.07: 0.033:1.05. CuBr\textsubscript{2} (3.1 mol % relative to CuBr) was added to ensure an efficient exchange between the dormant and active species. According to the EPR results from the Matyjaszewski group, about 3% Cu(II) species was formed spontaneously due to the persistent radical effect in ATRP of methyl acrylate at the molar ratio \([M]_o: [\text{RBr}]_o: [\text{Cu(I)}]_o = 200:1:1\) at 90 °C.\textsuperscript{85}

The polymerization was monitored by \textsuperscript{1}H NMR spectroscopy using the peaks located at 6.87-6.95 ppm, which are from the solvent anisole, as internal standard. The monomer conversion was determined by use of the integral value of the peak located at 6.28 ppm (1H from tBA) at time \(t\) and the value of the same peak at time \(t = 0\). The polymerization
was stopped when the conversion reached 38.0% at $t = 1805$ min. THF was added to dilute the mixture, and the particles were isolated by centrifugation. PtBA formed in the solution from the free initiator was collected and analyzed by $^1$H NMR spectroscopy and GPC relative to PS standards. The particles were repeatedly dispersed in THF and chloroform, isolated by centrifugation to remove physically adsorbed polymers, and characterized by FT-IR, $^1$H NMR spectroscopy, SEM, and TGA.

$^1$H NMR analysis showed that the methylene peak of the free initiator EBiB completely shifted from 4.21 to 4.09 ppm (Figure 4.5) after the polymerization was started, suggesting a quantitative initiator efficiency. To confirm that the ATRP of tBA under the described conditions was “living” throughout the course of the polymerization, $\ln([M]_0/[M])$ versus reaction time was plotted and is shown in Figure 4.6. A linear relationship indicated that the polymerization was a first-order reaction with respect to the monomer concentration, and the number of the growing chains was a constant throughout the course of the polymerization. Thus, the presence of silica particles has no negative effect on the polymerization.

### 4.3.3 Characterization of Free Polymers Formed in the Solution from the Free Initiator

To further study the ATRP of tBA under the described conditions, two samples were taken at $t = 547$ min (conversion = 14.1%, the particles were designated as PrBA-particle-1 and the free polymer PrBA-1) and 1053 min (conversion = 24.6%, the particles designated as PrBA-particle-2 and the free polymer PrBA-2) during the polymerization. The particles and free polymers were separated by centrifugation and
Figure 4.5. $^1$H NMR spectra of the polymerization mixture at $t = 0$ (a) and 30 min (b).

Figure 4.6. Relationship between $\ln([M]_0/[M])$ versus time for the ATRP of $t$BA at 75 °C. The ratios of $[M]_0$:[free EB][[CuBr]_0][CuBr_2]_0:[PMDETA]_0$ were 553:1:1.07:0.033:1.05.
purified. Figure 4.7 shows the GPC curves of PtBA-1, PtBA-2, and PtBA-3 (the polymer obtained after the polymerization was stopped at the conversion of 38.0%, and the corresponding particles designated as PtBA-particle-3). The GPC peak shifted from low molecular weight to high molecular weight with the increase of monomer conversion. The number-average molecular weights ($M_n$) of PtBA-1, PtBA-2, and PtBA-3 were 10,900, 17,600, 24,200, respectively, and the polydispersity decreased progressively from 1.16 (PtBA-1) to 1.13 (PtBA-2) to 1.09 (PtBA-3). To obtain the absolute molecular weights of the free polymers, $^1$H NMR analysis was performed (Figure 4.8, 4.9 and 4.10). The peaks located at 4.09 ppm can be clearly seen and are attributed to the methylene group of the residual initiator moiety. Using these peaks and the peak at 2.20 ppm, which is from the -CH- of PtBA, the values of $M_n$ of the free polymers were obtained and are summarized in Table 4.1. The molecular weights based on the conversions were also calculated using both of the ratios of monomer to free initiator and total initiator (free initiator + surface-immobilized initiator). The values of $M_n$ obtained from $^1$H NMR spectroscopy analysis were close to those calculated from the monomer conversion, especially to those calculated using the ratio of the monomer to the total initiator. Thus, both kinetics study and molecular weight analysis suggested that the polymerization was a living process, producing polymers with controlled molecular weights and relatively low molecular weight distributions.

4.3.4 Characterization of PtBA Brush-Grafted Particles

PtBA brush-grafted particles (PtBA particles) were found to be easily dispersed in organic solvents, such as THF and CHCl$_3$. It is interesting to observe that the PtBA particles exhibited a color of slight purple in the presence of THF after deposition in the
Figure 4.7. GPC curves of PrBA-1, PrBA-2, and PrBA-3.

Figure 4.8. $^1$H NMR spectrum of free PrBA-1 taken at the reaction time $t = 547$ min.
Figure 4.9. $^1$H NMR spectrum of free PtBA-2 taken from the mixture at reaction time $t = 1053$ minutes.

Figure 4.10. $^1$H NMR spectrum of free PtBA-3 (corresponding to PtBA-particle-3) obtained at the reaction time $t = 1805$ minutes.
Table 4.1. Number-Average Molecular Weights of $PrBA-1$, $PrBA-2$, and $PrBA-3$

Obtained from the Conversion, $^1$H NMR, and GPC Analysis.

<table>
<thead>
<tr>
<th></th>
<th>free polymer</th>
<th>conv. (%)</th>
<th>$M_e^a$</th>
<th>$M_i^b$</th>
<th>DP and $M_n$ from NMR</th>
<th>$M_n$</th>
<th>$M_M/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PrBA-1$</td>
<td>14.1</td>
<td>8800</td>
<td>10000</td>
<td>64 (8200)</td>
<td>10900</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>$PrBA-2$</td>
<td>24.6</td>
<td>15500</td>
<td>17400</td>
<td>121 (15500)</td>
<td>17600</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>$PrBA-3$</td>
<td>38.0</td>
<td>24000</td>
<td>26900</td>
<td>182 (23300)</td>
<td>24200</td>
<td>1.09</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Based on total initiator. $^b$ Based on free initiator. $^c$ DP = degree of polymerization.
bottom of the tubes by centrifugation. The spectrum of Figure 4.3c shows the characteristic vibration absorption of the carbonyl group of PrBA at 1729 cm\(^{-1}\) and the absorption peaks of alkyl C-H at 2977 and 2934 cm\(^{-1}\), confirming that the PrBA chains were successfully grown from the surface-immobilized Y-initiator. The presence of the grafted PrBA chains on the particle surface is also supported by \(^1\)H NMR analysis of PrBA-particle-3 dispersed in CDCl\(_3\) (Figure 4.11a). The peaks were broadened because the motion of the polymer chains was restricted by tethering one chain end to the solid surface.

TGA of PrBA-particle-1, PrBA-particle-2, and PrBA-particle-3 shows that the amount of the grafted PrBA increases with the increase of polymer chain length (Figure 4.4c-e). The weight retention at 800 °C decreased from 79.5% (PrBA-particle-1) to 75.0% (PrBA-particle-2) to 70.0% (PrBA-particle-3). Using the mass of the residual silica at 800 °C as reference, a quantitative analysis of TGA data indicates that the amount of the grafted PrBA increases linearly with the degree of polymerization (DP) calculated on the basis of the monomer conversion (Figure 4.12), implying that the number of growing chains on the silica surface is a constant. This result suggests that the surface-initiated polymerization was a living/controlled process. Since the amount of the surface-immobilized ATRP initiator is only 11.3 mol % of the total initiator, a living polymerization in the solution provides a good control on the surface-initiated polymerization.\(^{13,14}\) SEM image analysis shows that the size of the particles increases noticeably after the polymerization (Figure 4.1c is an SEM image of PrBA-particle-3). While the average size of Y-initiator particles was 181 nm (Figure 4.1b), the average
Figure 4.11. $^1$H NMR spectra of (a) PtBA-particle-3 and (b) mixed PtBA/PS particles dispersed in CDCl$_3$. 
Figure 4.12. The mass percent of the grafted PrBA relative to the mass of the residual silica at 800 °C corrected from Y-initiator particles versus the degree of polymerization of free polymers calculated on the basis of the monomer conversion. (■) Degree of polymerization calculated by use of the ratio of monomer to total initiator; (●) degree of polymerization obtained by use of the ratio of monomer to the free initiator. Relative mass increase) \[\frac{(1 - W_{pp})}{W_{pp}} - \frac{(1 - W_{ip})}{W_{ip}}\] × 100, where \(W_{pp}\) and \(W_{ip}\) represent the percent weight retention at 800 °C of PrBA particles and Y-initiator particles, respectively.
diameter of PtBA-particle-3 from SEM analysis was 198 nm, which is reasonably close to the calculated diameter, 206 nm, by use of TGA data.

The calculation of the diameter of PtBA particles from TGA data was shown below. We assume that \( m_{bp} \) (800 °C) = \( m_{ip} \) (800 °C) = \( m_{pp} \) (800 °C), where \( m_{bp} \), \( m_{ip} \), and \( m_{pp} \) represent the masses of a single bare particle, a single initiator particle, and a single PtBA particle, respectively, at 800 °C in TGA analysis.

\[
m_{bp} \text{ (800 °C)} = m_{bp} \text{ (r.t.)} \times W_{bp} = V_{bp} \times d_{bp} \times W_{bp}
\]

where \( m_{bp} \) (r.t.) is the mass of a single bare particle at room temperature, \( V_{bp} \) is the volume of a single bare particle, \( d_{bp} \) is the density of silica particles (assumed to be identical to bulk silica, 2.07g/cm\(^3\)),\(^{36}\) and \( W_{bp} \) is the percent weight retention of bare particles at 800 °C. The average diameter of bare particles from SEM study is 180 nm and the weight retention from TGA is 90.5 %. Thus, \( V_{bp} = 3.05 \times 10^{-21} \text{ m}^3 \) and \( m_{bp} \) (800 °C) = 5.71 \times 10^{-15} \text{ g}. By use of the mass of the residue at 800 °C as reference, the mass increase of PtBA-particle-3 relative to initiator particles is:

\[
[(1 – W_{pp})/W_{pp} – (1 – W_{ip})/W_{ip}] \times 100 = 28.2\%
\]

where \( W_{pp} \) and \( W_{ip} \) represent the percent weight retention of PtBA particles and initiator particles at 800 °C, respectively. The mass of PtBA (\( m_{PtBA} \)) on a single PtBA particle is \( m_{PtBA} = m_{bp} \times 28.2\% = 1.61 \times 10^{-15} \text{ g} \). The volume of PtBA on a single particle is \( V_{PtBA} = m_{PtBA}/d_{PtBA} = 1.52 \times 10^{-21} \text{ m}^3 \), where \( d_{PtBA} \) is the density of PtBA.\(^{86}\) Thus, the total volume of a single PtBA particle is \( V = V_{PtBA} + V_{bp} = 1.52 \times 10^{-21} \text{ m}^3 + 3.05 \times 10^{-21} \text{ m}^3 = 4.57 \times 10^{-21} \text{ m}^3 \). Therefore, the calculated diameter is 206 nm, which is reasonably close to that obtained from SEM analysis.
4.3.5 The Molecular Weight and Grafting Density of PtBA Brushes on Silica Particles

To determine the molecular weight and the molecular weight distribution of the grafted polymer, PtBA-particle-3 was destroyed with hydrofluoric acid (HF). The cleaved polymer was collected and characterized by $^1$H NMR and GPC. $^1$H NMR analysis shows that HF has no effect on the ester bond of PtBA as the $^1$H NMR spectrum of the PtBA cleaved from the particles was identical to that of free PtBA (Figure 4.13). Figure 4.14a and b shows the GPC curves of the cleaved and free polymers. The molecular weights of the grafted polymer were 23,200 ($M_{n,GPC}$) and 26,600 ($M_{w,GPC}$), essentially the same as those of free polymer ($M_{n,GPC} = 24,200$ and $M_{w,GPC} = 26,400$). However, the molecular weight distribution of the grafted PtBA was slightly broader (PDI = 1.15) than that of free polymer (PDI = 1.09). This result is consistent with those reported in the literature. From the degree of polymerization of PtBA-3 obtained by $^1$H NMR analysis, the average diameter of bare particles measured from the SEM image, and the TGA data, the average cross-sectional area per chain, $A$, was estimated along with assumptions that the particles are spherical and the density of silica particles is identical to that of bulk SiO$_2$ (2.07 g/cm$^3$). Calculations show that the grafting density was $\sim$2.5 nm$^2$ per PtBA chain, indicating that the polymer chains were highly stretched away from the surface and were in the brush regime (the thickness of the PtBA was 8.5 nm). This value is comparable to the typical grafting density of poly(methyl methacrylate) (PMMA) ($\sim$1.8 nm$^2$/chain) on silicon wafers reported in a previous work of our group, where an asymmetric difunctional initiator-terminated trichlorosilane was used to make initiator-terminated monolayers. As reported in the literature, in a control experiment
Figure 4.13. $^1$H NMR spectrum of cleaved PrBA.

Figure 4.14. GPC curves of the free (—) and cleaved polymers (・・・): (a) the PrBA cleaved from PrBA-particle-3; (b) free PrBA-3; (c) the polymer mixture cleaved from mixed PrBA/PS particles; (d) cleaved PS; and (e) free PS.
for the synthesis of mixed PMMA/PS brushes on silicon wafers, a piece of silicon wafer functionalized with a SAM of 11′-trichlorosilylundecyl 2-bromo-2-methylpropionate (ATRP SAM) was exposed to a typical NMRP condition. A ~2.0 nm PS film was observed grown on the surface. Presumably, the C-Br bond in the ATRP initiator was weak and acted as a chain transfer agent in NMRP. To eliminate the possibility of bromine capped PtBA chains and unreacted ATRP initiator in the monolayer acting as chain transfer agents in NMRP, we used tri(n-butyl)tin hydride to remove the bromine atoms.37,87,88 PtBA particles were dispersed in anisole, followed by addition of CuBr, PMDETA, and free initiator EBiB. After degassing, the flask containing the mixture was placed in a 75 °C oil bath, and excess tri(n-butyl)tin hydride was injected over a period of 15 min. The reaction continued for an additional 30 min. The particles were isolated by centrifugation, washed extensively with hexane and chloroform, and dried in vacuum at 35 °C overnight. Figure 4.1d shows the SEM image of dehalogenated PtBA particles cast from a dilute THF solution. The average diameter of the particles is 200 nm, close to that of PtBA particle-3 (198 nm) shown in Figure 4.1c. It is interesting to observe that the particles formed a hexagonal pattern upon evaporation of the solvent, similar to the observations reported in the literature.31,32,34

4.3.6 NMRP of Styrene from Dehalogenated PtBA Particles

Mixed PtBA/PS brushes were obtained after growing PS chains from the dehalogenated PtBA-particle-3 using NMRP. Surface-initiated polymerization of styrene was conducted at 120 °C in the presence of a free initiator, 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-2-benzoyloxyethane (PTEMPO). To reduce the viscosity of the polymerization mixture and to mitigate the possible problems associated with a
high viscosity, a large quantity of anisole (1:1 to monomer, w/w) was added as solvent and a molar ratio of monomer to the free initiator of 644 was used. The polymerization was monitored by $^1$H NMR spectroscopy using the peak located at 3.85 ppm, which is from the methyl group of anisole, as internal standard. The monomer conversion was determined by use of the integral value of the peaks located at 5.82 ppm (1H from the double bond of styrene) at time $t$ and the value of the same peaks at $t = 0$. After the polymerization reached a desired conversion at which the calculated DP of PS is comparable to that of PrBA, the polymerization was stopped by cooling the mixture to room temperature and diluting it with CHCl$_3$. The particles were isolated by centrifugation and repeatedly washed with CHCl$_3$ to remove the physically absorbed polymers. The free polymer produced in the solution was collected and analyzed by GPC against PS standards. The $M_n$ and $M_w$ of the free PS were 23,000 and 25,300, respectively, which were slightly higher than the molecular weights calculated from the conversion using the molar ratio of monomer to free initiator ($M_n = 22,100$). Figure 4.15 shows the kinetic plot. Except in the beginning of the polymerization, a linear relationship between $\ln([M]_o/[M])$ and reaction time was observed, suggesting that the polymerization was controlled. It is unclear why the polymerization in the beginning was slightly slower than anticipated. We could not offer any explanation for this but have repeatedly observed this phenomenon in the NMRP of styrene from particles. When deposited in the bottom of the tubes after centrifugation from THF or CHCl$_3$ suspension, the particles exhibited a color of slight red, in contrast to slight purple of PrBA particles. The particles were dried in vacuum followed by characterizations with IR, $^1$H NMR, TGA and SEM.
**Figure 4.15.** Relationship between \( \ln([M]_0/[M]) \) versus time for the NMRP of styrene at 120 °C. \([M]_0: \text{[Free initiator PTEMPO]} = 644:1.\)
The IR spectrum of the obtained particles shown in Figure 4.3d indicates that the new absorptions appear at 3027, 3065, and 3083 cm\(^{-1}\), which are characteristic for the aromatic C-H, demonstrating that the polystyrene chains were successfully grown from the surface. Figure 4.11b shows the \(^1\)H NMR spectrum of mixed PrBA/PS particles dispersed in CDCl\(_3\). Besides the characteristic peaks of PrBA at 1.42 and 2.20 ppm, two broad peaks appear in the range of 6.2-7.2 ppm, which are attributed to the aromatic protons of polystyrene. The average diameter of mixed PrBA/PS particles determined from Figure 4.1e is 219 nm, 19 nm greater than that of the dehalogenated PrBA particles. The calculated diameter of PrBA/PS particles based on the TGA data is 224 nm. From TGA analysis (Figure 4.4g), the weight retention at 800 °C decreased from 70.0 % for PrBA-particle-3 to 59.7 %. If the molecular weight of the free PS obtained from GPC analysis is used along with the TGA results (the \(M_n\) of the grafted PS is essentially identical to that of the free PS, see below), the average cross-sectional area per PS chain is 2.7 nm\(^2\), which is similar to that of PrBA (2.5 nm\(^2\) per PrBA chain). Considering both PrBA and PS chains, the average cross sectional area is 1.3 nm\(^2\) per polymer chain, close to that of mixed PMMA/PS brushes on silicon wafers (~1.0 nm\(^2\)/chain)\(^{37}\).

4.3.7 The Molecular Weight and Molecular Weight Distribution of the Grafted PS

To determine the molecular weight and polydispersity of the grafted PS, the silica in mixed PrBA/PS particles was etched by HF. The grafted polymers were collected and characterized by \(^1\)H NMR spectroscopy and GPC. By use of the integral values of the peaks from 6.20 to 7.20 ppm (the aromatic hydrogen atoms of PS) and the peak located at 2.20 ppm (-CH- from PrBA) (Figure 4.16), calculations show that the ratio of the number
of the total repeating units of PS to that of PtBA is 1.28:1. Using the molecular weight of
PS determined from GPC analysis and the $M_n$ of PtBA obtained from $^1$H NMR analysis,
the molar ratio of PS to PtBA, which is equal to the ratio of the grafting densities of the
two polymers (number of polymer chains per unit surface area) on the surface of silica
particles, is 1.06:1, which is slightly different from the value obtained from TGA analysis
(0.93:1). The discrepancy might come from the limitations of TGA and $^1$H NMR analysis.
From GPC analysis shown in Figure 4.14c, the $M_n$ and $M_w$ of the polymer mixture
cleaved from PtBA/PS particles were 37,500 and 43,200, respectively. These values are
much higher than those of either free PtBA or PS, but lower than those of the sum of two
free homopolymers ($M_n = 47,200$ and $M_w = 51,700$), suggesting that a considerable
portion of the mixture is the diblock copolymer composed of PtBA and PS initiated from
one Y-initiator molecule.

To obtain the molecular weight and the polydispersity of the grafted PS, the polymer
mixture cleaved from PtBA/PS particles was hydrolyzed in a solution of NaOCH$_3$ in
THF/CH$_3$OH (13:1, v/v) as the Y-initiator contains a hydrolyzable ester bond. The
reaction was run for 7 days followed by removal of the solvents in vacuum. Cyclohexane
was used to extract PS from the residual solid.$^{88}$ $^1$H NMR spectroscopy indicates that a
pure PS was obtained from the cyclohexane extract (Figure 4.17). GPC analysis (Figure
4.14d) shows that the $M_n$ and $M_w$ of the grafted PS were 23,800 and 26,400, respectively,
essentially the same as those of free polymer ($M_n = 23,000$ and $M_w = 25,300$) (Figure
4.14e). This has confirmed the assumption in previous publications from our group that
the molecular weights and polydispersities of the grafted and free polymers are
identical.$^{68-72}$
Figure 4.16. $^1$H NMR spectrum of PrBA/PS cleaved from the silica particles.

Figure 4.17. $^1$H NMR spectrum of PS obtained from cyclohexane extract.
4.3.8 Preparation of Amphiphilic Mixed PAA/PS Particles from Mixed PrBA/PS Particles and Their Responsive Properties in Selective Solvents

Amphiphilic mixed PAA/PS brush-grafted particles were prepared from mixed PrBA/PS particles by removing the tert-butyl group of PrBA with iodotrimethylsilane.\(^{51}\) A control experiment using a free PrBA showed that the reaction was complete within 6 h as the peak located at 1.42 ppm in \(^1\)H NMR spectrum, which is attributed to the three methyl groups of PrBA, disappeared, and the ratio of the integral values of the peak at 2.27 ppm (-CH-) and the peaks at 1.50-1.80 (-CH\(_2\)) is 1:2 (Figure 4.18). The reaction for the particles was run at room temperature for 6 h. The IR spectrum shows that a strong absorption appears at 1716 cm\(^{-1}\), while the carbonyl peaks of PrBA particles and mixed PrBA/PS particles are at 1729 cm\(^{-1}\). The absorption at 2977 cm\(^{-1}\) was no longer present in the spectrum, indicating that the tert-butyl was successfully cleaved. The average diameter of mixed PAA/PS particles measured from the SEM image in Figure 4.1f was 219 nm. From TGA data (Figure 4.4f), the weight retention at 800 °C changed from 59.7% (for mixed PrBA/PS particles) to 66.6%. Note that there is a difference of 1.6% between the two TGA curves at 200 °C. The diameters of PrBA/PS particles and PAA/PS particles were calculated by the same method as for PrBA particles and the results are summarized in Table 4.2.

While CHCl\(_3\) is a selective solvent for PS, methanol is a selective solvent for PAA. To study the dispersability of mixed PAA/PS particles, ~1.0 mg of PAA/PS particles was ultrasonicated in 2 mL of CHCl\(_3\) and in 2 mL of CH\(_3\)OH, respectively. For comparison, PS particles (synthesized from Y-initiator particles, the \(M_n\) and PDI of the free PS were 18,700 and 1.14, respectively) and PAA particles (prepared from PrBA-particle-2) were
Table 4.2. The Calculated and Observed Diameters of PtBA, PtBA/PS, and PAA/PS Particles.

<table>
<thead>
<tr>
<th>Particles</th>
<th>TGA data (percent weight at 800°C)</th>
<th>Calculated diameter (nm)</th>
<th>Diameter from SEM analysis (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare particles</td>
<td>90.5 %</td>
<td>NA</td>
<td>180</td>
</tr>
<tr>
<td>Initiator particles</td>
<td>86.9 %</td>
<td>NA</td>
<td>181</td>
</tr>
<tr>
<td>PtBA-particle-3</td>
<td>70.0 %</td>
<td>206</td>
<td>198</td>
</tr>
<tr>
<td>Dehalogenated PrBA</td>
<td>NA</td>
<td>206</td>
<td>200</td>
</tr>
<tr>
<td>PtBA/PS particles</td>
<td>59.7 %</td>
<td>224</td>
<td>219</td>
</tr>
<tr>
<td>PAA/PS particles</td>
<td>65.0 %*</td>
<td>214</td>
<td>219</td>
</tr>
</tbody>
</table>

* The difference of 1.6 % between the weight retentions of PAA/PS and PtBA/PS particles at 200 °C was taken into account.

**Figure 4.18.** $^1$H NMR spectra of (a) free poly($t$-butyl acrylate) in CDCl$_3$ and (b) poly(acrylic acid) in D$_2$O obtained from hydrolysis of poly($t$-butyl acrylate) with iodotrimethylsilane.
also ultrasonicated in these two solvents. While PS particles were easily dispersed in \( \text{CHCl}_3 \) but not in methanol, PAA particles were dispersed in \( \text{CH}_3\text{OH} \) but not in \( \text{CHCl}_3 \). Mixed PAA/PS particles were found to be dispersed in both \( \text{CHCl}_3 \) and \( \text{CH}_3\text{OH} \), forming stable dispersions. Figure 4.19 shows a simple Tyndall scattering experiment. A strong light scattering was observed in the dispersions of PS particles in \( \text{CHCl}_3 \), PAA particles in \( \text{CH}_3\text{OH} \), and mixed PAA/PS particles in both \( \text{CHCl}_3 \) and \( \text{CH}_3\text{OH} \).

To further study the chain reorganization of mixed PAA/PS brushes on the particles in selective solvents, we performed \( ^1\text{H} \) NMR analysis. Figure 4.20 shows the \( ^1\text{H} \) NMR spectra of mixed PAA/PS particles in \( \text{CDCl}_3 \), \( \text{N,N-dimethylformamide-d}_7 \) (DMF-\( \text{d}_7 \)), and \( \text{CD}_3\text{OD} \). DMF-\( \text{d}_7 \) is a good solvent for both PAA and PS. A drop of DMF-\( \text{d}_7 \) was added into the particles prior to \( \text{CDCl}_3 \) and \( \text{CD}_3\text{OD} \) to facilitate the chain reorganization and to increase the concentration of the dispersed particles. For the particles in DMF-\( \text{d}_7 \), the peaks in the range of 6.0-7.4 ppm, which are characteristic for PS, and the peak located at 2.45 ppm, which is attributed to the -CH- of PAA, were observed. While the peak at 2.45 ppm disappeared in \( \text{CDCl}_3 \) suspension, indicating that the PAA chains collapsed and PS chains were mobile, the aromatic hydrogen peaks were not present in the \( \text{CD}_3\text{OD} \) suspension, but the peak at 2.45 ppm remained visible, suggesting that the PS chains collapsed (a comparison of \( ^1\text{H} \) NMR spectra of mixed PAA/PS particles suspended in \( \text{CD}_3\text{OD} \) and a free polymer of PAA in DMF-\( \text{d}_7 \) can be found in Figure 4.21). These results were consistent with the Tyndall scattering experiments shown in Figure 4.19. Both studies have demonstrated that the mixed PAA/PS brushes can undergo reorganization in different selective solvents, imparting these hairy particles with a capability to respond to environmental changes.
Figure 4.19. Tyndall light scattering experiment shows the stable suspensions of PAA particles in CH$_3$OH but not in CHCl$_3$, PS particles in CHCl$_3$ but not in CH$_3$OH, mixed PAA/PS particles in both CHCl$_3$ and CH$_3$OH.
Figure 4.20. $^1$H NMR spectra of PAA/PS particles dispersed in (a) CDCl$_3$, (b) DMF-$d_7$, and (c) CD$_3$OD. A drop of DMF-$d_7$ was added into the particles prior to CDCl$_3$ and CD$_3$OD to increase the concentration of the dispersed particles.

Figure 4.21. $^1$H NMR spectra of (a) PAA free polymer dissolved in DMD-$d_7$ and (b) PAA/PS particles dispersed in DMD-$d_7$. 
4.4 Conclusions

By sequential ATRP of tBA and NMRP of styrene from Y-initiator-modified silica particles, we successfully prepared mixed PrBA/PS brushes on silica particles. Kinetics studies showed that the polymerizations were controlled. By cleaving the grafted polymers off the particles, we found that the molecular weights and polydispersities of both PrBA and PS were essentially identical to those of free polymers formed in the solutions from the free initiators. Amphiphilic mixed PAA/PS particles were prepared from mixed PrBA/PS particles by removing the tert-butyl group of PrBA with iodontrimethylsilane. The obtained particles were found to form stable dispersions in CHCl₃, a selective solvent for PS, and in methanol, a selective solvent for PAA, which were demonstrated by a Tyndall scattering experiment and ¹H NMR spectroscopy study. These well-defined organic-inorganic hybrid particles are an ideal system for the study of the phase behavior of the two polymers in a confined geometry. We are currently using differential scanning calorimetry, transmission electron microscopy, and other characterization techniques to study these hairy particles. Moreover, these environmentally responsive hairy particles might find applications in the controlled release of substances and as building blocks in the fabrication of nanostructured materials and responsive materials.⁸⁹,⁹⁰

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**Vita**

Dejin Li was born in Chongqing, China. He attended University of Science and Technology of China in Anhui between 1997 and 2002, where he received B.S. degrees majoring in Chemistry. In August 2003, he enrolled as a graduate student at the Chemistry Department of the University of Tennessee, Knoxville. He joined Dr. Bin Zhao's group to begin research in the field of polymer brush-grafted particles. Dejin Li received a Doctor of Philosophy Degree in Chemistry from the University of Tennessee in May 2008.