

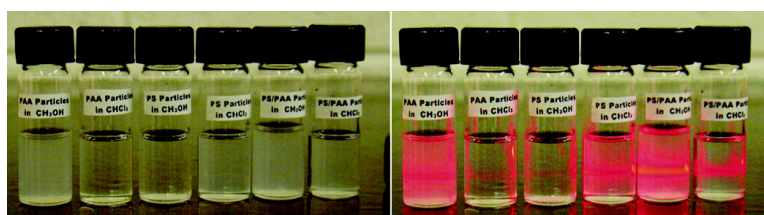
Article

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## Environmentally Responsive “Hairy” Nanoparticles: Mixed Homopolymer Brushes on Silica Nanoparticles Synthesized by Living Radical Polymerization Techniques

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**Abstract:** This article reports on the preparation of environmentally responsive “hairy” nanoparticles by growth of mixed poly(*tert*-butyl acrylate) (P*t*BA)/polystyrene (PS) brushes from silica particles using living radical polymerization techniques and subsequent hydrolysis of P*t*BA to produce amphiphilic mixed poly-(acrylic acid) (PAA)/PS brushes. Silica particles were synthesized by the Stöber process and were functionalized with an asymmetric difunctional initiator-terminated monolayer. Surface-initiated atom transfer radical polymerization of *t*BA was carried out in the presence of a free initiator. Kinetics study showed that the polymerization was well controlled. By cleaving P*t*BA off the particles, the molecular weights of the grafted and free polymers were found to be essentially identical. Mixed P*t*BA/PS brushes were obtained by the nitroxide-mediated radical polymerization of styrene from P*t*BA particles. The  $M_n$  of the grafted PS was found to be the same as that of the free PS formed in the solution from the free initiator. Amphiphilic mixed PAA/PS brush-coated nanoparticles were synthesized from mixed P*t*BA/PS particles by hydrolysis of P*t*BA with iodotrimethylsilane. Tyndall scattering experiments and  $^1\text{H}$  NMR study showed that the mixed PAA/PS particles can be dispersed and form a stable suspension in  $\text{CHCl}_3$ , a selective solvent for PS, and also in  $\text{CH}_3\text{OH}$ , a selective solvent for PAA, demonstrating the capability of these hairy nanoparticles to undergo chain reorganization in response to environmental changes.

### Introduction

Hybrid nanoparticles composed of an inorganic or metal particle core and an organic polymer shell possess intriguing properties associated with the nanoparticles and the desired properties of polymers, including processability and compatibility to the environment.<sup>1–3</sup> 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,<sup>1–5</sup> 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;<sup>6</sup> (2) the “grafting from” method, where polymer chains are grown from initiator-terminated self-assembled monolayers (SAMs).<sup>1–4</sup> Using the grafting from approach, Prucker and Rühle described in their seminal papers the growth of polystyrene (PS) from high-surface-area silica

gels that were surface-functionalized with an azo monolayer.<sup>7,8</sup> 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.<sup>9,10</sup> 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,<sup>11</sup>

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carbon nanotubes,<sup>12</sup> and nanoparticles including silica and gold nanoparticles,<sup>13</sup> quantum dots,<sup>14</sup> and magnetic nanoparticles.<sup>15</sup> Using Langmuir–Blodgett technique, Ohno et al. demonstrated that the distance between the gold nanoparticles 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.<sup>13j</sup>

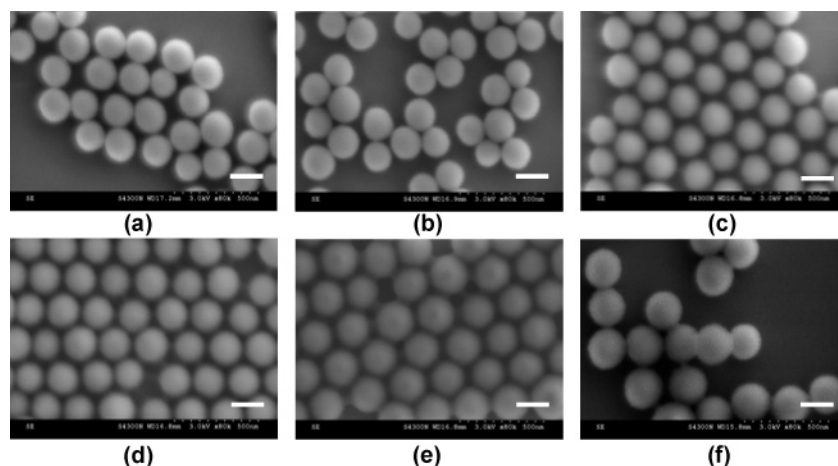
In this article, we report on the synthesis, characterization, and properties of environmentally responsive hairy particles, mixed homopolymer brushes on silica nanoparticles. Mixed brushes composed of two different homopolymer chains randomly or alternately immobilized on planar solid surfaces have been intensively studied in recent years because of their intriguing phase behavior and potential applications in "smart" materials.<sup>16–45</sup> It has been theoretically predicted and experi-

mentally demonstrated by several research groups that mixed homopolymer brushes undergo reorganization in response to external stimuli, exhibiting different surface wettability and surface morphology.<sup>16–45</sup> 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. We have initiated an effort 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.<sup>36–40</sup> ATRP and NMRP, which are two different controlled radical polymerization techniques and are performed under different conditions,<sup>9,10</sup> have been used to grow two distinct homopolymers from either mixed initiator-terminated monolayers<sup>36,40</sup> or asymmetric difunctional initiator-terminated SAMs (Y-SAMs)<sup>37–39</sup> 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.<sup>38–40</sup> In this work, we applied our strategy to synthesize amphiphilic mixed brushes on silica nanoparticles. It should be pointed out that no prior experimental work has been reported in the literature on mixed brushes on the surface of nanoparticles. One can envision that the success of the synthesis of well-defined mixed homopolymer brushes on nanoparticles 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<sup>46,47</sup> and functionalized with a Y-SAM. Mixed poly(*tert*-butyl acrylate) (PtBA)/PS brushes were synthesized by sequential surface-initiated ATRP of *t*BA and NMRP of styrene (Scheme 1). Removal of the *tert*-butyl group of PtBA produced amphiphilic mixed poly(acrylic acid) (PAA)/PS brushes. Infrared spectroscopy (IR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), <sup>1</sup>H NMR, and gel permeation chromatography (GPC) were employed to characterize the nanoparticles and the polymers.

## Results and Discussion

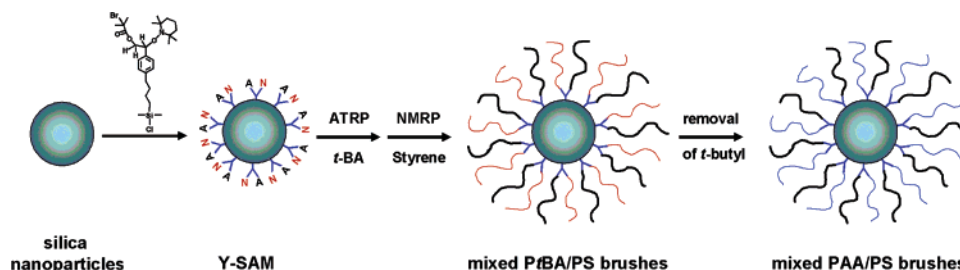
**Synthesis of Y-Initiator-Functionalized Silica Nanoparticles.** Spherical silica nanoparticles were prepared using the Stöber process, which involves the hydrolysis and condensation of tetraethoxysilane in an ammonia/ethanol solution.<sup>46,47</sup> This process is well-known to produce silica nanoparticles 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 1a), were used to prepare environmentally responsive organic–inorganic hybrid nanopar-

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**Figure 1.** Scanning electron microscopy images of (a) bare silica nanoparticles, (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.

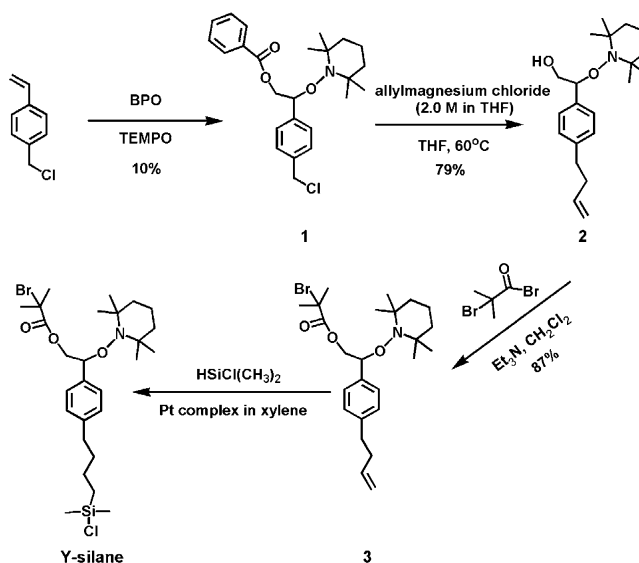
**Scheme 1.** Synthesis of Amphiphilic Mixed Poly(acrylic acid)/Polystyrene Brushes on Silica Nanoparticles



ticles 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.<sup>48</sup> To avoid this issue, an asymmetric difunctional initiator-terminated monochlorosilane, Y-silane (Scheme 2), was designed. Y-silane was prepared by a four-step procedure as outlined in Scheme 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-tetramethylpiperidinoxyl (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. Detailed synthetic procedures and characterization data can be found in the Supporting Information.

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 nanoparticles. The surface immobilization reaction was carried out under N<sub>2</sub> 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

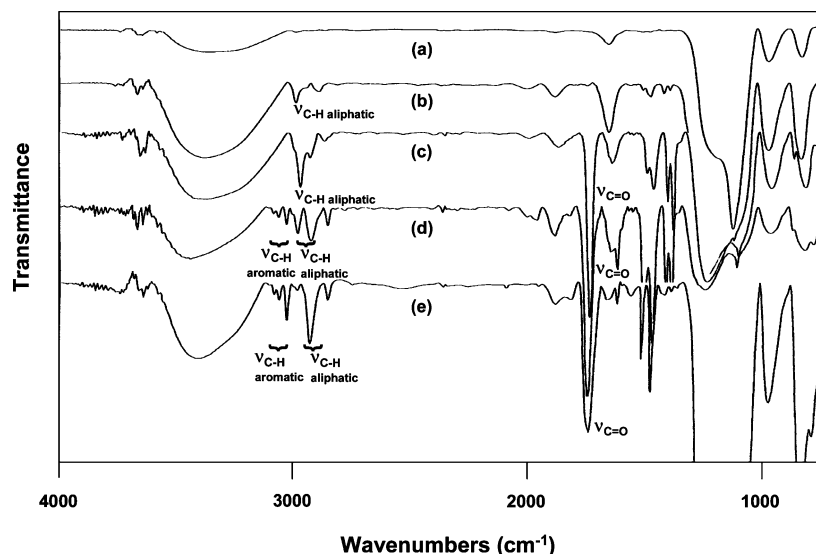
**Scheme 2.** Synthesis of an Asymmetric Difunctional Initiator-Terminated Monochlorosilane, Y-Silane



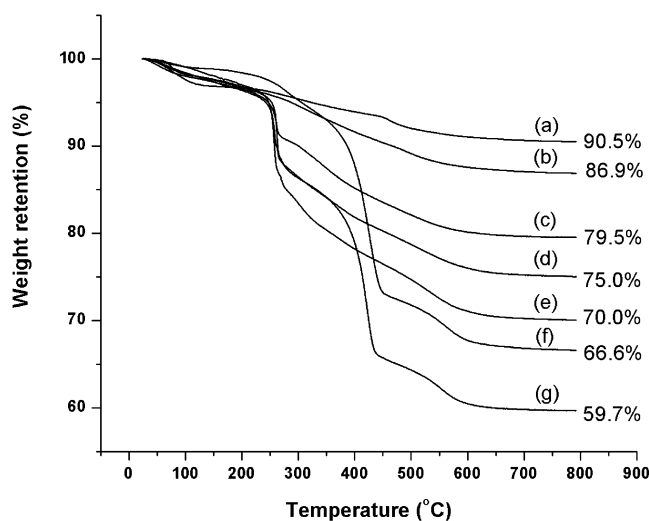
spectrum (Figure 2b) of Y-initiator-functionalized particles (initiator particles) shows absorbance bands at 2983 and 2899 cm<sup>-1</sup> that were characteristic of the alkyl C–H stretching vibration modes and were not present in the IR spectrum of bare particles (Figure 2a).<sup>49</sup> From SEM images (Figure 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

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**Figure 2.** 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 3.** 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.

90.5% for bare particles and 86.9% for initiator particles (Figure 3). The weight loss of bare particles might be due to the continued condensation reaction and associated water loss.<sup>13h</sup> 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  $\sim 0.33 \text{ nm}^2/\text{initiator}$ . This result is consistent with the literature report.<sup>13a,b</sup>

**Synthesis of PtBA Brushes from Y-Initiator Nanoparticles.** Mixed PtBA/PS brushes were grown from Y-initiator particles by sequential ATRP of *t*BA 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,<sup>50,51</sup> 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 *t*BA 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 *t*BA was carried out at 75 °C using CuBr/CuBr<sub>2</sub> and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) as the catalytic system.<sup>52</sup> We confirmed that the NMRP initiator was stable under typical ATRP conditions. A "free" ATRP initiator, ethyl 2-bromoisobutyrate (EBiB), was added into the reaction mixture to control the polymerization.<sup>11a,b</sup> The ratios of  $[\text{M}]_0$ : $[\text{free EBiB}]_0$ : $[\text{CuBr}]_0$ : $[\text{CuBr}_2]_0$ : $[\text{PMDETA}]_0$  were 553:1:1.07:0.033:1.05. CuBr<sub>2</sub> (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  $[\text{M}]_0$ : $[\text{RBr}]_0$ : $[\text{Cu(I)}]_0 = 200:1:1$  at 90 °C.<sup>53</sup>

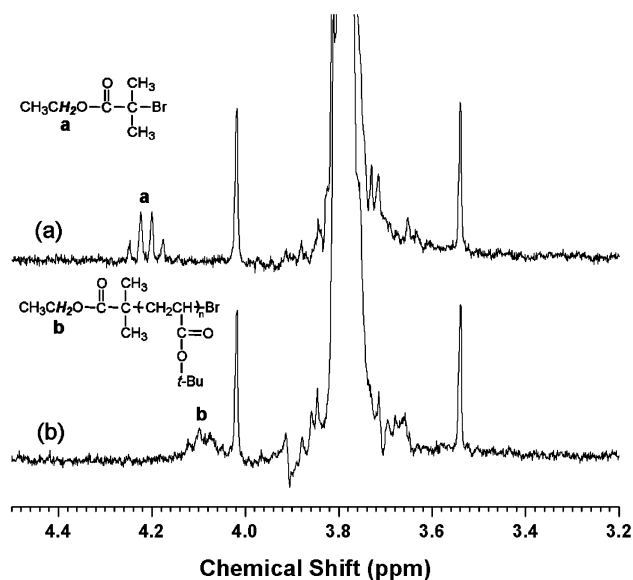
The polymerization was monitored by <sup>1</sup>H NMR spectroscopy using the peaks located at 6.87–6.95 ppm, which are from the solvent anisole, as internal standard. The monomer conversion was determined by use of the integral value of the peak located at 6.28 ppm (1H from *t*BA) at time *t* and the 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 nanoparticles were isolated by centrifugation. PtBA formed in the solution from the free initiator was collected and analyzed by <sup>1</sup>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 FTIR, <sup>1</sup>H NMR, SEM, and TGA.

<sup>1</sup>H NMR analysis showed that the methylene peak of the free initiator EBiB completely shifted from 4.21 to 4.09 ppm (Figure 4) after the polymerization was started, suggesting a quantitative

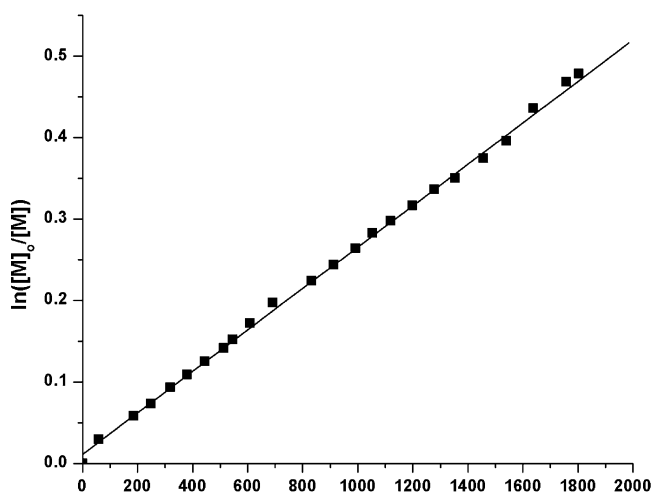
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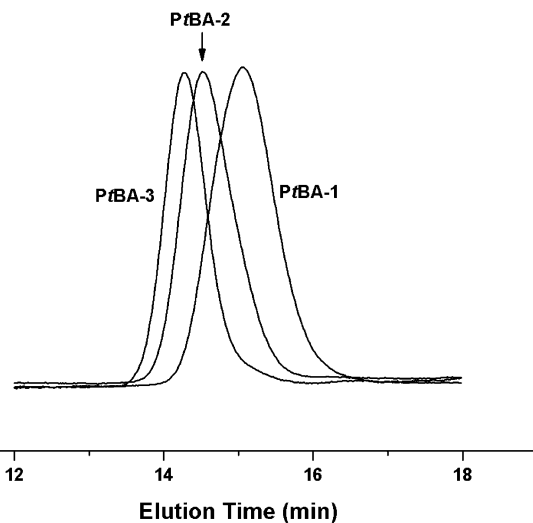
**Figure 4.**  $^1\text{H}$  NMR spectra of the polymerization mixture at  $t = 0$  (a) and 30 min (b).



**Figure 5.** Relationship between  $\ln([M]_0/[M])$  versus time for the ATRP of *t*BA at 75 °C. The ratios of  $[M]_0$ :[free EBiB] $_0$ :[CuBr] $_0$ :[CuBr] $_2$  $_0$ :[PMDETA] $_0$  were 553:1:1.07:0.033:1.05.

initiator efficiency. To confirm that the ATRP of *t*BA 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 5. 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 nanoparticles has no negative effect on the polymerization.

**Characterization of Free Polymers Formed in the Solution from the Free Initiator.** To further study the ATRP of *t*BA under the described conditions, two samples were taken at  $t = 547$  min (conversion = 14.1%, the particles were designated as PtBA-particle-1 and the free polymer PtBA-1) and 1053 min (conversion = 24.6%, the particles designated as PtBA-particle-2 and the free polymer PtBA-2) during the polymerization. The particles and free polymers were separated by centrifugation and purified. Figure 6 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



**Figure 6.** GPC curves of PtBA-1, PtBA-2, and PtBA-3.

**Table 1.** Number-Average Molecular Weights of PtBA-1, PtBA-2, and PtBA-3 Obtained from the Conversion,  $^1\text{H}$  NMR, and GPC Analysis

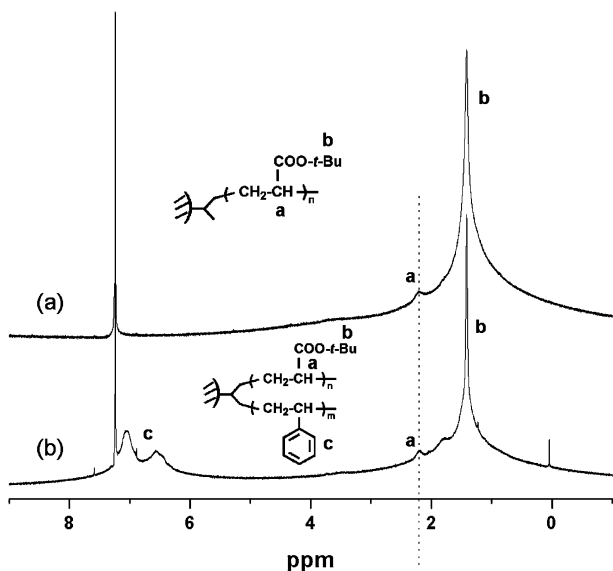
free polymer	conv. (%)	$M_n^a$	$M_n^b$	DP <sup>c</sup> and $M_n$ from NMR	$M_n$ GPC	$M_w/M_n$ GPC
PtBA-1	14.1	8800	10000	64 (8200)	10900	1.16
PtBA-2	24.6	15500	17400	121 (15500)	17600	1.13
PtBA-3	38.0	24000	26900	182 (23300)	24200	1.09

<sup>a</sup> Based on total initiator. <sup>b</sup> Based on free initiator. <sup>c</sup> DP = degree of polymerization.

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,  $^1\text{H}$  NMR analysis was performed.<sup>54</sup> 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  $-\text{CH}-$  of PtBA, the values of  $M_n$  of the free polymers were obtained and are summarized in Table 1. The molecular weights based on the conversion 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  $^1\text{H}$  NMR 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.

**Characterization of PtBA Brush-Coated Nanoparticles.** PtBA brush-coated nanoparticles (PtBA particles) were found to be easily dispersed in organic solvents, such as THF and  $\text{CHCl}_3$ . It is interesting to observe that the PtBA particles exhibited a color of slight purple in the presence of THF after deposition in the bottom of the tubes by centrifugation. The spectrum of Figure 2c shows the characteristic vibration

(54) The  $^1\text{H}$  NMR spectrum of PtBA-1 is included in the Supporting Information.

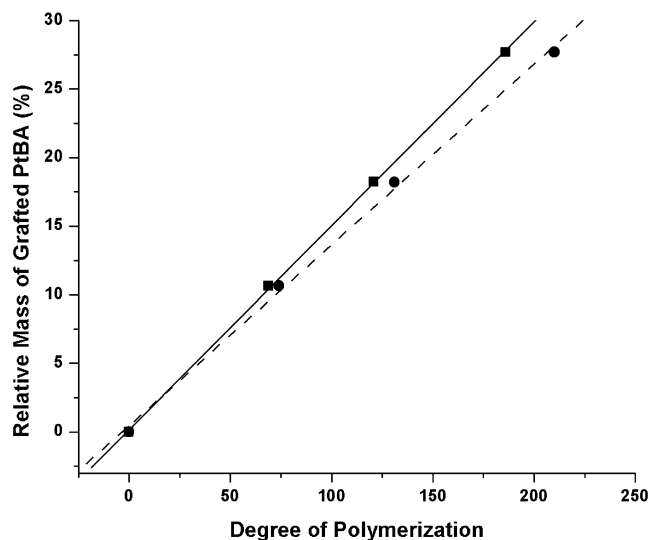


**Figure 7.**  $^1\text{H}$  NMR spectra of (a) PtBA-particle-3 and (b) mixed PtBA/PS particles dispersed in  $\text{CDCl}_3$ .

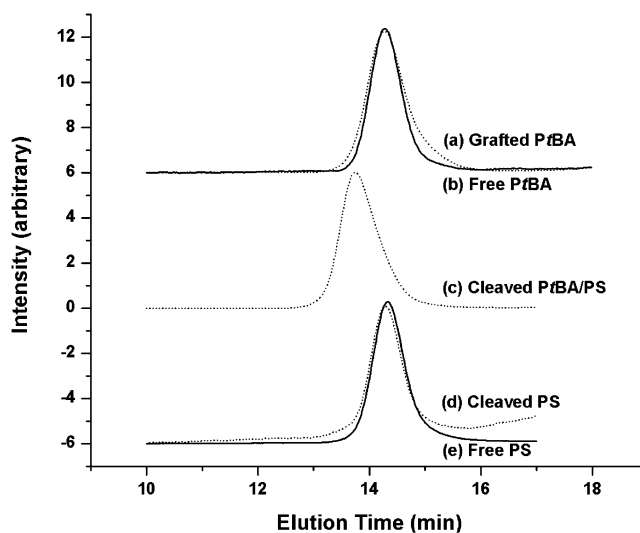
absorption of the carbonyl group of PtBA at  $1729\text{ cm}^{-1}$  and the absorption peaks of alkyl C–H at  $2977$  and  $2934\text{ cm}^{-1}$ , confirming that the PtBA chains were successfully grown from the surface-immobilized Y-initiator. The presence of the grafted PtBA chains on the particle surface is also supported by  $^1\text{H}$  NMR analysis of PtBA-particle-3 dispersed in  $\text{CDCl}_3$  (Figure 7a). The peaks were broadened because the motion of the polymer chains was restricted by tethering one chain end to the solid surface.

TGA of PtBA-particle-1, PtBA-particle-2, and PtBA-particle-3 shows that the amount of the grafted PtBA increases with the increase of polymer chain length (Figure 3c–e). The weight retention at  $800\text{ }^\circ\text{C}$  decreased from 79.5% (PtBA-particle-1) to 75.0% (PtBA-particle-2) to 70.0% (PtBA-particle-3). Using the mass of the residual silica at  $800\text{ }^\circ\text{C}$  as reference, a quantitative analysis of TGA data indicates that the amount of the grafted PtBA increases linearly with the degree of polymerization (DP) calculated on the basis of the monomer conversion (Figure 8), 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.<sup>11a,b</sup> SEM image analysis shows that the size of the particles increases noticeably after the polymerization (Figure 1c is an SEM image of PtBA-particle-3). While the average size of Y-initiator particles was 181 nm (Figure 1b), the average 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.<sup>55</sup>

**The Molecular Weight and Grafting Density of PtBA Brushes on Silica Nanoparticles.** To determine the molecular weight and the molecular weight distribution of the grafted polymer, PtBA-particle-3 was destroyed with hydrofluoric acid (HF).<sup>13a,b,h</sup> The cleaved polymer was collected and characterized by  $^1\text{H}$  NMR and GPC.  $^1\text{H}$  NMR analysis shows that HF has no effect on the ester bond of PtBA as the  $^1\text{H}$  NMR spectrum of



**Figure 8.** The mass percent of the grafted PtBA relative to the mass of the residual silica at  $800\text{ }^\circ\text{C}$  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 =  $[(1 - W_{pp})/W_{pp} - (1 - W_{ip})/W_{ip}] \times 100$ , where  $W_{pp}$  and  $W_{ip}$  represent the percent weight retention at  $800\text{ }^\circ\text{C}$  of PtBA particles and Y-initiator particles, respectively.



**Figure 9.** GPC curves of the free (—) and cleaved polymers (···): (a) the PtBA cleaved from PtBA-particle-3; (b) free PtBA-3; (c) the polymer mixture cleaved from mixed PtBA/PS particles; (d) cleaved PS; and (e) free PS.

the PtBA cleaved from the particles was identical to that of free PtBA.<sup>56</sup> Figure 9a and b shows the GPC curves of the cleaved and free polymers. The molecular weights of the grafted polymer were 23 200 ( $M_n$ ) and 26 600 ( $M_w$ ), essentially the same as those of free polymer ( $M_n = 24\ 200$  and  $M_w = 26\ 400$ ). 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.<sup>11b,13i</sup>

(55) Calculation of the diameters of PtBA particles, PtBA/PS particles, and PAA/PS particles from TGA data can be found in the Supporting Information.

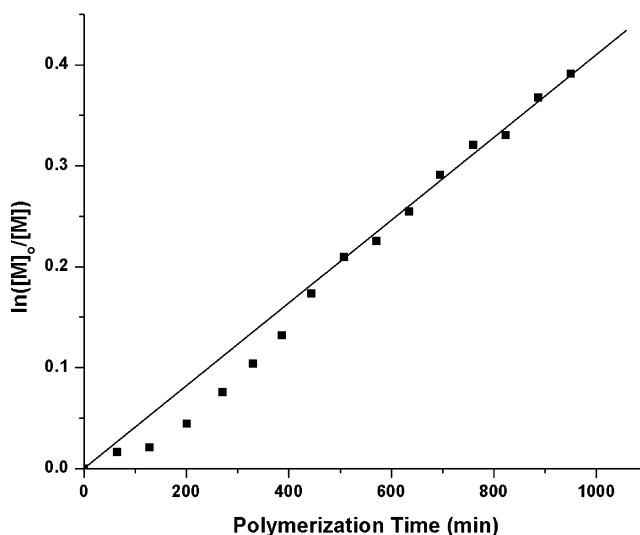
(56) The  $^1\text{H}$  NMR spectra can be found in the Supporting Information.

From the degree of polymerization of *Pt*BA-3 obtained by  $^1\text{H}$  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 nanoparticles is identical to that of bulk  $\text{SiO}_2$  ( $2.07 \text{ g/cm}^3$ ).<sup>13f</sup> Calculations show that the grafting density was  $\sim 2.5 \text{ nm}^2$  per *Pt*BA chain, indicating that the polymer chains were highly stretched away from the surface and were in the brush regime (the thickness of the *Pt*BA was 8.5 nm). This value is comparable to the typical grafting density of poly(methyl methacrylate) (PMMA) ( $\sim 1.8 \text{ nm}^2/\text{chain}$ ) on silicon wafers reported in a previous publication, where an asymmetric difunctional initiator-terminated trichlorosilane was used to make initiator-terminated monolayers.<sup>37</sup>

As reported in a previous publication,<sup>37</sup> in a control experiment 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. We observed a  $\sim 2.0 \text{ nm}$  PS film 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 *Pt*BA 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.<sup>37,57,58</sup> *Pt*BA 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  $75^\circ\text{C}$  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  $35^\circ\text{C}$  overnight. Figure 1d shows the SEM image of dehalogenated *Pt*BA particles cast from a dilute THF solution. The average diameter of the particles is 200 nm, close to that of *Pt*BA-particle-3 (198 nm) shown in Figure 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.<sup>13a,b,d</sup>

#### NMRP of Styrene from Dehalogenated *Pt*BA Particles.

Mixed *Pt*BA/PS brushes were obtained after growing PS chains from the dehalogenated *Pt*BA-particle-3 using NMRP. Surface-initiated polymerization of styrene was conducted at  $120^\circ\text{C}$  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  $^1\text{H}$  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



**Figure 10.** Relationship between  $\ln([M]_0/[M])$  versus time for the NMRP of styrene at  $120^\circ\text{C}$ .  $[M]_0:[\text{Free initiator PTEMPO}] = 644:1$ .

calculated DP of PS is comparable to that of *Pt*BA, the polymerization was stopped by cooling the mixture to room temperature and diluting it with  $\text{CHCl}_3$ . The particles were isolated by centrifugation and repeatedly washed with  $\text{CHCl}_3$  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 10 shows the kinetic plot. Except in the beginning of the polymerization, a linear relationship between  $\ln([M]_0/[M])$  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 nanoparticles. When deposited in the bottom of the tubes after centrifugation from THF or  $\text{CHCl}_3$  suspension, the particles exhibited a color of slight red, in contrast to slight purple of *Pt*BA particles. The particles were dried in vacuum followed by characterizations with IR,  $^1\text{H}$  NMR, TGA and SEM.

The IR spectrum of the obtained particles shown in Figure 2d indicates that the new absorptions appear at 3027, 3065, and  $3083 \text{ cm}^{-1}$ , which are characteristic for the aromatic C-H, demonstrating that the polystyrene chains were successfully grown from the surface. Figure 7b shows the  $^1\text{H}$  NMR spectrum of mixed *Pt*BA/PS particles dispersed in  $\text{CDCl}_3$ . Besides the characteristic peaks of *Pt*BA 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 *Pt*BA/PS particles determined from Figure 1e is 219 nm, 19 nm greater than that of the dehalogenated *Pt*BA particles. The calculated diameter of *Pt*BA/PS particles based on the TGA data is 224 nm.<sup>55</sup> From TGA analysis (Figure 3g), the weight retention at  $800^\circ\text{C}$  decreased from 70.0% for *Pt*BA-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  $2.7 \text{ nm}^2$ ,

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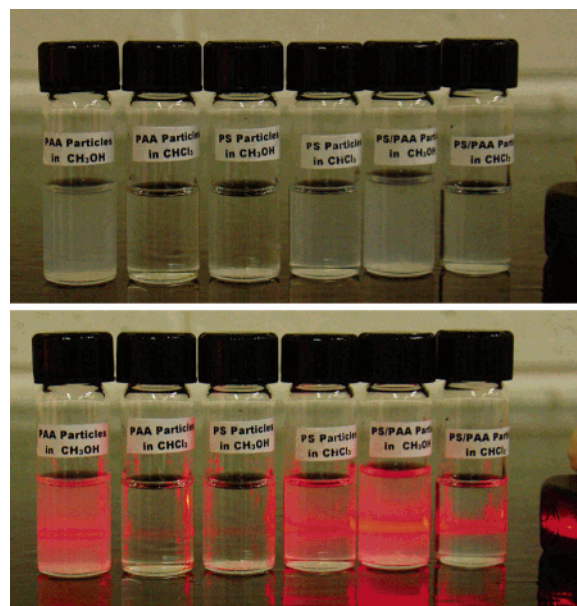


which is similar to that of *PtBA* (2.5 nm<sup>2</sup> per *PtBA* chain). Considering both *PtBA* and PS chains, the average cross-sectional area is 1.3 nm<sup>2</sup> per polymer chain, close to that of mixed PMMA/PS brushes on silicon wafers (~1.0 nm<sup>2</sup>/chain).<sup>37</sup>

**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 *PtBA*/PS nanoparticles was etched by HF. The grafted polymers were collected and characterized by <sup>1</sup>H NMR and GPC. By use of the integral values of the peaks from 6.2 to 7.20 ppm (the aromatic hydrogen atoms of PS) and the peak located at 2.20 ppm (–CH– from *PtBA*),<sup>56</sup> 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<sub>n</sub>* of *PtBA* obtained from <sup>1</sup>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 nanoparticles, 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 <sup>1</sup>H NMR analysis. From GPC analysis shown in Figure 9c, the *M<sub>n</sub>* and *M<sub>w</sub>* 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<sub>n</sub>* = 47 200 and *M<sub>w</sub>* = 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<sub>3</sub> in THF/CH<sub>3</sub>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.<sup>58</sup> <sup>1</sup>H NMR indicates that a pure PS was obtained from the cyclohexane extract.<sup>56</sup> GPC analysis (Figure 9d) shows that the *M<sub>n</sub>* and *M<sub>w</sub>* of the grafted PS were 23 800 and 26 300, respectively, essentially the same as those of free polymer (*M<sub>n</sub>* = 23 000 and *M<sub>w</sub>* = 25 300) (Figure 9e). This has confirmed the assumption in our previous publications that the molecular weights and polydispersities of the grafted and free polymers are identical.<sup>36–40</sup>

**Preparation of Amphiphilic Mixed PAA/PS Particles from Mixed *PtBA*/PS Particles and Their Responsive Properties in Selective Solvents.** Amphiphilic mixed PAA/PS brush-coated nanoparticles were prepared from mixed *PtBA*/PS particles by removing the *tert*-butyl group of *PtBA* with iodotrimethylsilane.<sup>51</sup> A control experiment using a free *PtBA* showed that the reaction was complete within 6 h as the peak located at 1.42 ppm in <sup>1</sup>H NMR spectrum, which is attributed to the three methyl groups of *PtBA*, 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<sub>2</sub>) is 1:2.<sup>56</sup> 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<sup>–1</sup>, while the carbonyl peaks of *PtBA* particles and mixed *PtBA*/PS particles are at 1729 cm<sup>–1</sup>. The absorption at 2977 cm<sup>–1</sup> 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

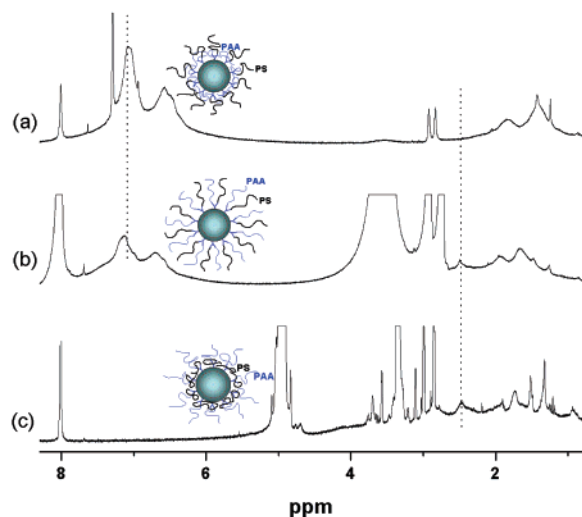


**Figure 11.** Tyndall light scattering experiment shows the stable suspensions of PAA particles in CH<sub>3</sub>OH but not in CHCl<sub>3</sub>, PS particles in CHCl<sub>3</sub> but not in CH<sub>3</sub>OH, mixed PAA/PS particles in both CHCl<sub>3</sub> and CH<sub>3</sub>OH.

the SEM image in Figure 1f was 219 nm. From TGA data (Figure 3f), the weight retention at 800 °C changed from 59.7% (for mixed *PtBA*/PS particles) to 66.6%. Note that there is a difference of 1.6% between the two TGA curves at 200 °C.

While CHCl<sub>3</sub> 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 nanoparticles was ultrasonicated in 2 mL of CHCl<sub>3</sub> and in 2 mL of CH<sub>3</sub>OH, respectively. For comparison, PS particles (synthesized from Y-initiator particles, the *M<sub>n</sub>* and polydispersity of the free PS were 18 700 and 1.14, respectively) and PAA particles (prepared from *PtBA*-particle-2) were also ultrasonicated in these two solvents. While PS particles were easily dispersed in CHCl<sub>3</sub> but not in methanol, PAA particles were dispersed in CH<sub>3</sub>OH but not in CHCl<sub>3</sub>. Mixed PAA/PS particles were found to be dispersed in both CHCl<sub>3</sub> and CH<sub>3</sub>OH, forming stable suspensions. Figure 11 shows a simple Tyndall scattering experiment. A strong light scattering was observed in the suspensions of PS particles in CHCl<sub>3</sub>, PAA particles in CH<sub>3</sub>OH, and mixed PAA/PS particles in both CHCl<sub>3</sub> and CH<sub>3</sub>OH.

To further study the chain reorganization of mixed PAA/PS brushes on the particles in selective solvents, we performed <sup>1</sup>H NMR analysis. Figure 12 shows the <sup>1</sup>H NMR spectra of mixed PAA/PS particles in CDCl<sub>3</sub>, *N,N*-dimethylformamide-*d*<sub>7</sub> (DMF-*d*<sub>7</sub>), and CD<sub>3</sub>OD. DMF-*d*<sub>7</sub> is a good solvent for both PAA and PS. A drop of DMF-*d*<sub>7</sub> was added into the particles prior to CDCl<sub>3</sub> and CD<sub>3</sub>OD to facilitate the chain reorganization and to increase the concentration of the dispersed nanoparticles. For the particles in DMF-*d*<sub>7</sub>, 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 CDCl<sub>3</sub> suspension, indicating that the PAA chains collapsed and PS chains were mobile, the aromatic hydrogen peaks were not present in the CD<sub>3</sub>OD suspension, but the peak at 2.45 ppm remained visible, suggesting that the PS chains collapsed (a comparison of <sup>1</sup>H NMR spectra of mixed PAA/PS particles suspended in CD<sub>3</sub>-



**Figure 12.**  $^1\text{H}$  NMR spectra of PAA/PS particles dispersed in (a)  $\text{CDCl}_3$ , (b)  $\text{DMF-}d_7$ , and (c)  $\text{CD}_3\text{OD}$ . A drop of  $\text{DMF-}d_7$  was added into the particles prior to  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  to increase the concentration of the dispersed nanoparticles.

OD and a free polymer of PAA in  $\text{DMF-}d_7$  can be found in the Supporting Information<sup>56</sup>). These results were consistent with the Tyndall scattering experiments shown in Figure 11. Both studies have demonstrated that the mixed PAA/PS brushes can undergo reorganization in different selective solvents, imparting these hairy nanoparticles with a capability to respond to environmental changes.

## Conclusions

By sequential ATRP of *t*BA and NMRP of styrene from Y-initiator-modified silica nanoparticles, we successfully prepared mixed *Pt*BA/PS brushes on silica particles. Kinetics studies showed that the polymerizations were controlled. By cleaving the grafted polymers off the nanoparticles, we found that the molecular weights and polydispersities of both *Pt*BA 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 *Pt*BA/PS particles by removing the *tert*-butyl group of *Pt*BA with iodotrimethylsilane. The obtained particles were found to form stable suspensions in  $\text{CHCl}_3$ , a selective solvent for PS, and in methanol, a selective solvent for PAA, which were demonstrated

by a Tyndall scattering experiment and  $^1\text{H}$  NMR study. These well-defined organic–inorganic hybrid nanoparticles 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 nanoparticles. Moreover, these environmentally responsive hairy nanoparticles might find applications in the controlled release of substances and as building blocks in the fabrication of nanostructured materials and responsive materials.<sup>59</sup>

**Acknowledgment.** B.Z. thanks the University of Tennessee at Knoxville (start-up funds), American Chemical Society Petroleum Research Fund (PRF# 40084-G7), and Ralph E. Powe Junior Faculty Enhancement Award for supporting this research.

**Supporting Information Available:** Experimental section including materials, characterization, synthesis of silica nanoparticles, synthesis of Y-silane, immobilization of Y-initiator on silica nanoparticles, surface-initiated ATRP of *t*BA, cleavage of the grafted *Pt*BA from the nanoparticles, dehalogenation of *Pt*BA particles, NMRP of styrene from dehalogenated *Pt*BA particles, cleavage of the grafted polymers from *Pt*BA/PS particles, hydrolysis of the polymer mixture cleaved from *Pt*BA/PS particles, hydrolysis of *Pt*BA by use of iodotrimethylsilane, synthesis of PAA/PS particles from *Pt*BA/PS particles, Tyndall scattering experiments, calculation of the diameters of *Pt*BA particles, *Pt*BA/PS particles, and PAA/PS particles from TGA data;  $^1\text{H}$  NMR spectrum of Y-silane;  $^1\text{H}$  NMR spectrum of free *Pt*BA-1 taken at polymerization time  $t = 547$  min;  $^1\text{H}$  NMR spectrum of poly(*tert*-butyl acrylate) cleaved from *Pt*BA-particle-3;  $^1\text{H}$  NMR spectrum of the polymer mixture cleaved from *Pt*BA/PS particles;  $^1\text{H}$  NMR spectrum of polystyrene obtained from the cyclohexane extract;  $^1\text{H}$  NMR spectra of (a) free poly(*tert*-butyl acrylate) in  $\text{CDCl}_3$  and (b) poly(acrylic acid) in  $\text{D}_2\text{O}$  obtained from hydrolysis of poly(*tert*-butyl acrylate) with iodotrimethylsilane;  $^1\text{H}$  NMR spectra of (a) PAA free polymer dissolved in  $\text{DMF-}d_7$  and (b) PAA/PS particles suspended in  $\text{CD}_3\text{OD}$ ; complete refs 11b,c. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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