Synthesis and Characterization of Organic/Inorganic Hybrid Nanoparticles: Kinetics of Surface-Initiated Atom Transfer Radical Polymerization and Morphology of Hybrid Nanoparticle Ultrathin Films

Jeffrey Pyun, Shijun Jia, Tomasz Kowalewski,* Gary D. Patterson, and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, Center for Macromolecular Engineering, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received February 13, 2003; Revised Manuscript Received May 9, 2003

ABSTRACT: The synthesis of hybrid nanoparticles was conducted by the atom transfer radical polymerization (ATRP) of styrene and (meth)acrylates from colloidal surfaces. Colloidal initiators were prepared by the functionalization of silica colloids with 2-bromoisobutyrate groups. ATRP from colloidal surfaces was then performed to attach well-defined homopolymers and block copolymers to an inorganic core. Kinetics of the ATRP of styrene (Sty), *n*-butyl acrylate (BA), and methyl methacrylate (MMA) under identical reaction conditions were investigated. Hybrid nanoparticles containing block copolymers of pSty-b-pBA ($M_n = 22\ 300$; $M_w/M_n = 1.20$), pMMA-b-pBA ($M_n = 29\ 400$; $M_w/M_n = 1.28$), and pBA-b-pMMA ($M_n = 17\ 300$; $M_w/M_n = 1.28$) were prepared, and hydrolysis of silica cores by hydrofluoric acid treatment enabled characterization of cleaved copolymers using size exclusion chromatography and ¹H NMR. Ultrathin films of hybrid nanoparticles were examined using transmission electron microscopy and atomic force microscopy.

Introduction

The synthesis of nanocomposite materials from (co)polymers and colloids has been widely investigated. The preparation of copolymers possessing incompatible segments yields materials ordered on the nanoscale via microphase separation in the solid state¹ or self-assembly in solution.² Colloids of uniform size and precise morphology have been synthesized from a variety of emulsion, precipitation, and "sol-gel" approaches.³⁻⁵ The combination of these two materials enables the preparation of a hybrid material composed of a welldefined colloidal platform and copolymers capable of organization into distinct domains.^{6,7}

The preparation of organic/inorganic hybrid materials^{8,9} composed of organic (co)polymers and inorganic colloids has been recently pursued as a route to combine the advantageous properties of both classes of macromolecules into one material. In these methodologies, the use of living or controlled polymerization¹⁰ techniques has been critical to incorporate organic (co)polymers of precise molar mass, composition, and functionality to the inorganic substrate. Recently, controlled/living radical polymerization, namely, atom transfer radical polymerization (ATRP),11-19 was conducted from colloidal surfaces to prepare hybrid nanoparticles composed of an inorganic colloidal core and chain end immobilized organic (co)polymers.²⁰ The functionalization of various colloids, including silica (SiO₂),^{21–27} gold,^{28–30} silver,³¹ germanium,³² PbS,³³ carbon black,³⁴ iron oxides,³⁵ metal oxide systems,^{36–38} and other surfaces,^{39,40} was achieved, allowing for subsequent application as initiators for the ATRP of styrene and (meth)acrylate monomers.

Previously, our group reported the preparation of hybrid nanoparticles with block copolymers covalently attached to a polysilsesquioxane $(SiO_{1.5})^{41}$ core. This methodology was a versatile route to prepare multilayered core-shell colloids by the sequential surface-initiated ATRP of styrenes and acrylates. Control of both

the degree of polymerization (DP) of each tethered segment as well as of the functionality of the selected monomers enabled precise engineering of both colloidal surfaces and of the properties of the resulting hybrid nanoparticle. Ultrathin films of the hybrid nanoparticles containing block copolymers tethered to SiO_{1.5} colloids were also reported to yield phase-separated microstructures when cast onto mica.⁴¹ Of particular interest was the effect of composition, blocking sequence, and DP_n of each tethered polymeric segment on the organization of hybrid nanoparticle (sub)monolayers deposited onto surfaces.

Herein, we report the synthesis and characterization of hybrid nanoparticles composed of a silica colloidal core and of an outer shell of tethered homopolymer/block copolymers. In contrast to our previous reports, commercially available silica nanoparticles were employed as colloidal initiators, which greatly facilitated scaleup synthesis. Kinetics of surface-initiated ATRP of styrene and (meth)acrylate monomers was investigated under identical reaction conditions and compared with ATRP using monomeric initiators. Various core-shell colloids containing tethered AB diblock copolymers were synthesized using different combinations of styrene and (meth)acrylates in ATRP reactions from surfaces.

Experimental Section

Materials. *n*-Butyl acrylate (99%, Acros), styrene (99%, Aldrich), and methyl methacrylate (99%, Acros) were stirred over calcium hydride (coarse granules, 95%, Aldrich) overnight and distilled before use. 1-(Chlorodimethylsilyl)propyl 2-bromoisobutyrate was prepared using previously reported procedures.⁴² Copper(I) bromide (99.999%, Aldrich) and 4,4'-(di-5-nonyl)-2,2'-bipyridine (dNbpy) were purified and prepared according to previously reported procedures.⁴³ Copper(II) bromide (99.999%, Aldrich), Aliquat 336 (Aldrich), toluene (Fisher), hydrofluoric acid (50 vol % HF, Acros), and colloidal silica (30 wt % silica in methyl isobutyl ketone dispersion, effective diameter = 20 nm, MIBK-ST, Nissan) were used as received.

Characterization. Size exclusion chromatography (SEC) was performed in tetrahydrofuran at 35 °C using a Waters 510 pump set to a flow rate of 1 mL/min, three Styragel columns (Polymer Standards Service, pore sizes 10⁵, 10³, and 10² Å), and a Waters 2410 refractive index detector. Calculations of molar mass were determined using the PSS software using a calibration based on linear polystyrene and poly-(methyl methacrylate) standards (from PSS). ¹H NMR analysis was done on a 300 MHz Bruker spectrometer using the Tecmag software. Elemental analysis was conducted by Midwest Microlab (Indianapolis, IN). Tapping-mode atomic force microscopy (AFM) analysis was carried out using the Nanoscope-III Multimode system (Digital Instruments, Santa Barbara, CA). The images were acquired in air with standard silicon TESP probes (nominal spring constant and resonance frequency respectively 50 N/m and 300 kHz). In the case of deformable hybrid nanoparticle monolayers, rigid colloidal silica cores were well contrasted from the deformable polymer matrix with the increase of the effective tapping force, adjusted by decreasing the set-point ratio A/A_0 , where A_0 and A denote respectively the unperturbed cantilever amplitude and "tapping" amplitude.3 Samples for AFM were prepared by spincoating hybrid particle solutions (1 mg/mL chloroform solution, rotational speed 4000 rpm) onto freshly cleaved mica. Transmission electron microscopy was conducted using a Hitachi H-7100 electron microscope. TEM samples of nanoparticles and hybrid nanoparticles were prepared by casting one drop of a dilute colloid solution onto a carbon-coated copper grid. The light scattering setup consisted of a Spectra Physics model 2020 argon ion laser operated at 514.5 nm. Scattered light was measured at 90° with a Brookhaven Instruments model BI-240 goniometer. Intensity measurements and correlation function calculations were carried out with a Brookhaven Instruments model BI-9000 correlator. Particle sizes were determined using the method of cumulants.

Synthesis of 2-Bromoisobutyrate Functional Silica **Colloids.** The silica dispersion (52 g of 30 wt % SiO₂ in methyl isobutyl ketone (MIBK)) was added to a 100 mL three-neck flask with magnetic stir bar and fitted with a reflux condenser and gas inlet adapter. 1-(Chlorodimethylsilyl)propyl 2-bromoisobutyrate (6.0 mL, 27 mmol) was then added via syringe, and the orange, slightly opaque dispersion became cloudy. The reaction mixture was gently refluxed for a period of 24 h and cooled to room temperature. Hexamethyldisilazane (HMDZ) (6.0 mL, 28 mmol) was then added to the dispersion, stirred for 3 h at room temperature, and then slightly heated for 6-8h. A white solid precipitated from the dispersion after reflux of HMDZ. The precipitate was removed by centrifugation, and the clear orange dispersion was then added dropwise into methanol/H₂O (4:1 vol) to precipitate colloids. After recovery by filtration, particles were redissolved in 50 mL of tetrahydrofuran (THF) and precipitated into hexane (500 mL). Particles were allowed to settle in the hexane mixture for a few hours, and approximately 400 mL of the top clear hexane fraction was decanted. Fresh hexane (400 mL) was added to the remaining cloudy colloid mixture, and the mixture was stirred for 30 min. Particles were again allowed to settle for a few hours, and the hexane layer was decanted. These washing cycles were repeated 12 times. Particles were then recovered by centrifugation, and the wet gel was dried under vacuum (1-5 mm Hg) overnight. A slightly yellow granular powder was collected (12 g, 76% yield relative to original SiO₂ mass).

ATRP of Sty from 2-Bromoisobutyrate Functional Colloids. Silica colloidal initiators (500.0 mg, 0.13 mmol), Cu-(I)Br (12.0 mg, 0.13 mmol), Cu(II)Br₂ (2.0 mg, 0.01 mmol), and dNbpy (121 mg, 0.29 mmol) were added to a 25 mL Schlenk flask containing a magnetic stir bar. The flask was fitted with a rubber septum and evacuated (1-5 mm Hg) for a period of 5 h. The flask was then backfilled with nitrogen, and the flask was evacuated again for 5 min, followed by additional backfilling with nitrogen. This evacuation/backfilling cycle was repeated, and then Sty (6.9 g, 67 mmol) (bubbled for 1 h with nitrogen before use) was added to the flask was replaced with a greased glass stopper under high nitrogen purge, and the

reaction mixture was homogenized by agitation on a vortex mixer for 5–10 min. Reaction flasks were then placed in a 90 °C oil bath. Samples were taken periodically via syringe for kinetic analysis of the polymerization. After 20.2 h, a monomer conversion of 14% was reached, as determined from gravimetric analysis. Samples were diluted with tetrahydrofuran, filtered through neutral alumina, concentrated in vacuo to a volume of approximately 10 mL, and precipitated into 500 mL of methanol, yielding a white solid (M_n SEC cleaved pSty = 9200; $M_w/M_n = 1.21$).

ATRP of BA from 2-Bromoisobutvrate Functional Colloids. Silica colloidal initiators (500.0 mg, 0.13 mmol), Cu-(I)Br (12.0 mg, 0.130 mmol), Cu(II)Br₂ (2.0 mg, 0.010 mmol), and dNbpy (121.0 mg, 0.29 mmol) were added to a 25 mL Schlenk flask containing a magnetic stir bar. The flask was fitted with a rubber septum, and the flask was evacuated (1-5)mmHg) for a period of 5 h. The flask was then backfilled with nitrogen, and the flask was evacuated again for 5 min, followed by additional backfilling with nitrogen. This evacuation/ backfilling cycle was repeated, and then BA (8.6 g, 67 mmol) (bubbled for 1 h with nitrogen before use) was added to the flask via syringe. The rubber septum fitted on the Schlenk flask was replaced with a greased glass stopper under high nitrogen purge, and the reaction mixture was homogenized by agitation on a vortex mixer for 5-10 min. The reaction flasks were then placed in a 90 °C oil bath. Samples were taken periodically via syringe for kinetic analysis of the polymerization. After 52.6 h, a monomer conversion of 10% was reached, as determined from gravimetric analysis. Samples were diluted with tetrahydrofuran, filtered through neutral alumina, concentrated in vacuo to a volume of approximately 10 mL, and precipitated into solution of methanol (400 mL) and deionized water (50 mL), yielding a clear viscous oil

 $(M_{n \text{ SEC cleaved } pBA} = 6800; M_w/M_n = 1.26).$ ATRP of MMA from 2-Bromoisobutyrate Functional Colloids. Silica colloidal initiators (500.0 mg, 0.13 mmol) were added to a 25 mL Schlenk flask containing a magnetic stir bar. The flask was then fitted with a rubber septum and evacuated (1-5 mmHg) for 1 h, followed by the addition of MMA (6.5 g, 65 mmol) (bubbled for 1 h with nitrogen before use). To a separate 4 mL vial containing a magnetic stir bar were added Cu(II)Br₂ (2.0 mg, 0.013 mmol), dNbpy (10.0 mg, 0.026 mmol), and (1.0 mL, 9.3 mmol) of MMA. The vial was fitted with a snap-top lid, and the solids were allowed to dissolve. The maroon solution was then transferred to the 25 mL Schlenk flask via syringe, and the entire mixture was subjected to two freeze-pump-thaw cycles. While in the frozen state, the rubber septum was removed and Cu(I)Br (12.0 mg, 0.13 mmol) and dNbpy (110.0 mg, 0.27 mmol) were added. The flask was then subjected to two additional freeze-pumpthaw cycles and was then placed in a 90 °C oil bath. Samples were taken periodically via syringe for kinetic analysis of the polymerization. After 10 min, a monomer conversion of 13% was reached, as determined from gravimetric analysis. Samples were then diluted with tetrahydrofuran, passed through neutral alumina, concentrated in vacuo to a volume of approximately 10 mL, and precipitated in 500 mL of methanol, yielding a white solid ($M_{\rm n \ SEC \ cleaved \ pMMA} = 14\ 900; M_{\rm w}/M_{\rm n} =$ 1.34)

Synthesis of Hybrid Nanoparticles Possessing Block Copolymers. Hybrid nanoparticles possessing grafted homopolymers of pS, pBA, and pMMA were prepared using the same general procedure as described previously, except with a higher ratio of monomer to initiating sites $(DP_n = \Delta[M]/[I]_0 = 1000)$.

SiO₂-g-(pSty-b-pBA). SiO₂-g-pSty hybrid nanoparticles (500.0 mg, 0.029 mmol) were added to a 25 mL Schlenk flask containing a magnetic stir bar. The flask was then fitted with a rubber septum and evacuated (1–5 mmHg) for 1 h, followed by the addition of BA (3.7 g, 29 mmol) (bubbled for 1 h with nitrogen before use) under a nitrogen atmosphere. After dissolution of the solids, two freeze–pump–thaw cycles were performed. Cu(I)Br (4.0 mg, 0.029 mmol), Cu(II)Br₂ (0.6 mg, 0.003 mmol), and dNbpy (26.0 mg, 0.063 mmol) was added to the Schlenk while the reaction mixture was in the frozen state.

Two additional freeze–pump–thaw cycles were performed, and the reaction vessel was then placed in a 90 °C oil bath. Samples were taken periodically via syringe for kinetic analysis of the polymerization. After 21.7 h, a monomer conversion of 3% was reached, as determined from gravimetric analysis. Samples were then diluted with tetrahydrofuran, passes through neutral alumina, concentrated in vacuo to a volume of approximately 5 mL, and precipitated in 300 mL of methanol, yielding a white rubbery solid ($M_{n \text{ SEC cleaved pSty–b-pBA} = 22 300; M_w/M_n = 1.20$).

SiO2-g-(pMMA-b-pBA). SiO2-g-pMMA hybrid nanoparticles (500.0 mg, 0.036 mmol) were added to a 25 mL Schlenk flask containing a magnetic stir bar. The flask was then fitted with a rubber septum and evacuated (1-5 mmHg) for 1 h, followed by the addition of BA (4.6 g, 36 mmol) (bubbled for 1 h with nitrogen before use) under a nitrogen atmosphere. After dissolution of the solids, two freeze-pump-thaw cycles were performed. Cu(I)Br (10.3 mg, 0.072 mmol), Cu(II)Br₂ (1.6 mg, 0.007 mmol), and dNbpy (64.0 mg, 0.158 mmol) were added to the Schlenk while the reaction mixture was in the frozen state. Two additional freeze-pump-thaw cycles were performed, and the reaction vessel was then placed in a 90 °C oil bath. Samples were taken periodically via syringe for kinetic analysis of the polymerization. After 14.3 h, a monomer conversion of 16% was reached, as determined from gravimetric analysis. Samples were then diluted with tetrahydrofuran, passed through neutral alumina, concentrated in vacuo to a volume of approximately 10 mL, and precipitated in a solution of methanol (250 mL) and deionized water (50 mL), yielding a white rubbery solid ($M_{n \text{ SEC cleaved } pMMA-b-pBA} = 29400; M_w/M_n$ = 1.28).

SiO₂-g-(pBA-b-pMMA). SiO₂-g-pBA hybrid nanoparticles (500.0 mg, 0.038 mmol) were added to a 25 mL Schlenk flask containing a magnetic stir bar. The flask was then fitted with a rubber septum and evacuated (1-5 mmHg) for 1 h, followed by the addition of MMA (3.8 g, 38 mmol) (bubbled for 1 h with nitrogen before use) under a nitrogen atmosphere. After dissolution of the solids, two freeze-pump-thaw cycles were performed. Cu(I)Cl (3.7 mg, 0.038 mmol), Cu(II)Cl₂ (0.5 mg, 0.003 mmol), and dNbpy (34.0 mg, 0.084 mmol) were added to the Schlenk while the reaction mixture was in the frozen state. Two additional freeze-pump-thaw cycles were performed, and the reaction vessel was then placed in a 90 °C oil bath. Samples were taken periodically via syringe for kinetic analysis of the polymerization. After 45 min, a monomer conversion of 3.5% was reached, as determined from gravimetric analysis. Samples were then diluted with tetrahydrofuran, passed through neutral alumina, concentrated in vacuo to a volume of approximately 5 mL, and precipitated in a solution of methanol (250 mL) and deionized water (50 mL), yielding a white rubbery solid $(M_{n \text{ SEC cleaved } pBA-b-pMMA})$ = 17 300; $M_{\rm w}/M_{\rm n} = 1.28$).

General Procedure for Cleavage of (Co)polymers from Particles. SiO₂-*g*-pS hybrid nanoparticles (100.0 mg) were dissolved in 1 mL of toluene, along with Aliquat 336 (phase transfer catalyst, 10.0 mg, 0.024). A 49% HF(aq) solution (1 mL) was added to the particle solution, and the reaction was allowed to stir at room temperature overnight. PS was recovered by precipitation into methanol and vacuum filtration through fine grain glass frit, yielding a white powder (50 mg). Similar procedures were followed for the cleavage of pMMA, pBA, and block copolymers. Recovery of cleaved pBA was performed after stirring in the toluene/HF mixture by evaporation of volatiles in air.

Calculation of the Number of Initiation Sites and Tethered Chains per Nanoparticle. The number of possible initiation sites for silica nanoparticle was determined from elemental analysis, which yielded the total moles of Br per gram of nanoparticle. The average molar mass of nanoparticles was determined by first measuring the average hydrodynamic radius (R_h) of bare silica nanoparticles using dynamic light scattering. Assuming a spherical geometry for silica colloids ($V = \frac{4}{3\pi T^3}$) and a density $\rho_{silica} = 2.07 \text{ g/cm}^{3,44}$ the average molar mass of nanoparticle was calculated. The total number

Scheme 1. Synthetic Methodology To Prepare Hybrid Nanoparticles^a



^{*a*} ATRP of styrene, *n*-butyl acrylate, or methyl methacrylate was conducted from silica colloidal initiators (X = 2-bromoisobutyrate groups) yielding hybrid nanoparticles possessing tethered homopolymers. Chain extension of these hybrid nanoparticles resulted tethering of AB diblock copolymers in formation of core-shell colloids with outer and inner shells of different copolymer segments.

of sites per particle was determined using the following relation:

no, of sitos por papoparticlo — <u>m</u> a	oles of Br			
$\frac{100}{g}$ of n	nanoparticle ^			
av MW _{nanoparticle}	moles of Br			
1 mol of nanoparticle	moles of nanoparticle			

The number of tethered chains was determined from gravimetric analysis, where the mass of incorporated polymer relative to silica was first measured, followed by SEC of cleaved polymer chains to determine M_n . The number of tethered chains was then calculated as follows:

where

moles of grafted polymer =
$$\frac{\text{mass of grafted polymer (gravimetry)}}{M_{\text{n,SEC}} \text{ cleaved chains}}$$

and

moles of nanoparticle =
$$\frac{\text{mass of silica colloid}}{\text{av } MW_{\text{nanoparticle}}}$$

Results and Discussion

The methodology used to prepare hybrid nanoparticles is presented in Scheme 1. In the first stage of the reaction, silica colloids possessing silanol groups on the surface were functionalized with ATRP initiating groups. These colloids were isolated and then redispersed in an ATRP reaction mixture to polymerize styrene (Sty), *n*-butyl acrylate (BA), or methyl methacrylate (MMA) from the nanoparticle surface. From this approach, hybrid nanoparticles possessing a shell of tethered organic homopolymers and a core of silica were prepared. In these hybrid nanoparticles, sufficient retention of active end groups enabled the synthesis of tethered AB diblock copolymers by chain extension reactions with a different monomer.

Synthesis of Silica Colloidal Initiators for ATRP. The colloidal initiator was prepared by the silylation of silica nanoparticles using both a functional chlorosilane (1-(chlorodimethylsilyl)propyl 2-bromoisobutyrate) and hexamethyldisilazane. Colloids were preformed and dispersed into methyl isobutyl ketone before use, allowing direct addition of functional silanes to the colloidal dispersion. Dynamic light scattering (DLS) measurements of dilute solutions of the silica colloids revealed an average effective diameter ($D_{\text{eff}} = 2R_{\text{h}}$) of 20 nm. The

Table 1. Conditions for the ATRP of Sty, BA, and MMA from 2-Bromoisobutyrate Functional Nanoparticles

experiment	colloidal initiator	monomer	conditions ^a	reaction time (min)	conv ^c (%)	M _{n SEC}	$M_{\rm w}/M_{\rm n}$
1	2-bromoisobutyrate	BA	500:1:1:0.1:2.2, 90 °C	3156	10	6 800	1.26
2	functional silica 2-bromoisobutyrate functional silica ^b	Sty	500:1:1:0.1:2.2, 90 °C	1211	14	9 200	1.21
3	2-bromoisobutyrate	MMA	500:1:1:0.1:2.2, 90 °C	10	13	14 900	1.34
4	2-bromoisobutyrate	sty	1000:1:1:0.1:2.2, 90 °C	1872	13	18 200	1.21
5	2-bromoisobutyrate	MMA	1000:1:1:0.1:2.2, 90 °C	17	9	17 600	1.41
6	2-bromoisobutyrate functional silica	BA	1000:1:1:0.1:2.2, 90 °C	3690	7	12 000	1.28
7	2-bromoisobutyrate functional silica	MMA	2000:1:1:0.1:2.2, 90 °C	37	11	30 100	1.23
8 9 10d	SiO ₂ - <i>g</i> -pSty ₁₇₅ SiO ₂ - <i>g</i> -pMMA ₁₇₅	BA BA	1000:1:1:0.1:2.2, 90 °C 1000:1:1:0.1:2.2, 90 °C	1305 860	3 16 2 5	22 300 29 400	1.20 1.28
10 ⁻ 11 ^d	SiO ₂ - <i>g</i> -(pBA ₉₄ - <i>b</i> -pMMA ₆₂)	MMA	3450:1:3:0.3:6.6, 90 °C	45 232	3.5 4	14 200	3.10

^{*a*} Conditions correspond to molar ratios of monomer, 2-bromoisobutyrate groups on silica colloids, Cu(I)Br, Cu(II)Br₂, and dNbpy. All reactions were performed in bulk monomer. ^{*b*} 2-Bromoisobutyrate silica colloids contained 0.27 mmol of Br/1 g of nanoparticle. ^{*c*} Conversion values determined using gravimetric analysis. ^{*d*} Cu(I)Cl was used instead of Cu(I)Br.

average molar mass of silica colloids ($M_{\rm w} = 5.2 \times 10^6$ g/mol) was calculated using particle size data from DLS along with assumptions that colloids were spheres ($V = 4/_3 \pi r^3$), and the density was comparable to bulk SiO₂ ($\rho_{\rm SiO_2} = 2.07$ g/cm³). Elemental analysis of the functionalized silica colloid confirmed the incorporation of bromine (2.48 wt %, 0.135 mmol of Br/1 g of SiO₂), and calculations indicated that approximately 1400 initiation sites per colloidal particle were present (see Experimental Section for calculation).

Homopolymerization Kinetics. In the first step toward preparing hybrid nanoparticles, the homopolymerization kinetics of Sty, MMA, and BA ATRP from silica colloidal initiators was investigated (Table 1). Polymerizations were performed using identical stoichiometric ratios and concentrations of monomer, catalyst, and colloidal initiator. In this comparative kinetic study, reactions were carried out in bulk monomer (7-9 M) using a high molar ratio of monomer to initiator sites per nanoparticle, where the average concentration of bromine containing groups was approximately 2×10^{-2} M. Colloidal initiators were diluted to approximately 5-8 wt % relative to the selected monomer in the reaction mixture. The catalytic system employed in these reactions consisted of copper(I) bromide/4,4'-di(5-nonyl)-2,2'-bipyridine (Cu(I)Br/dNbpy) and copper(II) bromide/4,4'di(5-nonyl)-2,2'-bipyridine (Cu(II)Br₂/dNbpy) complexes at concentrations approximately 2×10^{-2} and 2×10^{-3} M, respectively. Overall, the initial molar ratios of monomer $([M]_0)$, initiating sites ([I]₀), Cu(I)Br, Cu(II)Br₂, and dNbpy were the following: 500:1:1:0.1:2.2. Surface-initiated ATRP reactions were all performed at 90 °C. Polymerizations were stopped at monomer conversions under 15%, as higher conversions resulted in interparticle coupling or gelation.

Figure 1a shows the ATRP kinetics of Sty, BA, and MMA from colloidal surfaces presented as semilogarithmic plots of monomer consumption with time. The rate of BA ATRP from 2-bromoisobutyrate functional silica colloids (1, Table 1) was slowest of the three monomers, as a conversion of 9% required a reaction time of 3150 min (52 h, 30 min). In the case of Sty polymerization (2, Table 1) a monomer conversion of 14% was reached in 1210 min (20 h, 10 min). Compari-



Figure 1. (a) Semilogarithmic plots of monomer conversion vs time for the ATRP of BA (filled circles), Sty (filled squares), and MMA (filled triangles), using 2-bromoisobutyrate colloidal initiators at stoichiometric ratios of 500:1:1:0.1:2.2 for [M]:[I]: [Cu(II)]:[dNbpy] at 90 °C. Conditions are listed in Table 1, entries **1**, **2**, **3**, respectively. (b) Semilogarithmic plots of monomer conversion vs time for the ATRP of BA (open circles), Sty (open squares), and MMA (open triangles), using ethyl 2-bromoisobutyrate at stoichiometric ratios of 500:1:1:0.1:2.2 for [M]:[I]:[Cu(II)]:[Cu(II)]:[dNbpy] at 90 °C.

son of the apparent rate constants (k_{app} , i.e., slopes from semilogarithmic plots) for Sty and BA surface-initiated ATRP showed that the rate of Sty polymerization was 4 times faster. The rate of MMA ATRP from colloidal initiators (**3**, Table 1) was the fastest as gelation due to

interparticle radical coupling reactions occurred within 15 min. The observation of gelation in ATRP from multifunctional initiators has also been reported in the synthesis of (hyper)branched⁴⁵ and star⁴⁶ copolymers. Values of k_{app} for the ATRP of MMA indicated that the rate of polymerization was 430 times greater than obtained in the surface initiated BA ATRP reactions. We anticipated that the rate of MMA ATRP from colloids would be faster than those of Sty and BA.⁴⁷ However, the faster rates for Sty ATRP vs BA at 90 °C from colloidal surfaces were unexpected, since in the previous kinetic investigations using small molecule initiators acrylates homopolymerized faster than styrene under comparable conditions.^{43,48} In the surfaceinitiated ATRP of MMA, Sty, and BA, 10 mol % Cu(II)Br₂ (relative to Cu(I)Br) was added at the very beginning of the reaction to ensure efficient exchange reactions between dormant and active species. We anticipate on the basis of previous EPR measurements^{49,50} that 10 mol % of Cu(II)Br₂ is much more than what is generated spontaneously in the ATRP of acrylates and styrene due to the persistent radical effect.⁵¹ The EPR results indicated that at the molar ratios [M]₀: $[RBr]_0:[Cu(I)]_0 = 100:1:1 \text{ at } \sim 100 \text{ °C about } 6\% \text{ of } Cu(II)$ species was formed for styrene and about 2% for acrylates. Because of much higher dilution in the current system (500:1:1), the concentration of spontaneously formed Cu(II) should be much smaller. Thus, the addition of the same large excess of Cu(II) (10%) should suppress the rate of ATRP of acrylate stronger than that of styrene. To corroborate this hypothesis, the rates of polymerization for Sty, BA, and MMA using conventional ATRP initiators were pursued.

A fundamental question pertaining to colloidal initiator systems is whether the kinetic behavior of ATRP reactions is comparable to untethered, small moleculeinitiated ATRP. A key difference in colloidal systems is the presence of initiating groups at high local concentrations due to immobilization on nanoparticle surfaces. This is in direct contrast to small molecule initiators, which are homogeneously distributed throughout the reaction media, along with the monomer and catalyst. Thus, the ATRP of Sty, BA, and MMA was performed using ethyl 2-bromoisobutyrate as the initiator, employing identical concentrations of reagents as for the colloidal initiator systems.

Figure 1b shows the first-order plots of monomer consumption with time for the ATRP of Sty, BA, and MMA using ethyl 2-bromoisobutyrate as the initiator. The polymerization rates followed the same trends as for ATRP reactions from colloidal initiators, as the rate of monomer consumption scaled as follows: $R_{\rm p\ MMA} \gg R_{\rm p\ Sty} > R_{\rm p\ BA}$. The rates of ATRP reactions initiated with ethyl 2-bromoisobutyrate were also faster than the corresponding polymerizations from colloidal initiators.

The kinetic data from ATRP of three monomers using monomeric initiator in the presence of a large excess of Cu(II) allows comparison of ATRP equilibrium constants for the three monomers, using available free radical propagation rate constants, k_p . The slopes of semilogarithmic plots, the apparent propagation rate coefficients, k_p^{app} , are products of k_p and concentration of radicals [P*]. Since the equilibrium constant, K_{eq} , equals

$$K_{\rm eq} = ([P^*][Cu(II)])/([RBr][Cu(I)])$$
 (1)

values were calculated, assuming a near constant ratio of two copper species (eq 2).

Table 2. Summary of Rate and Equilibrium Constants Determined from the Homopolymerization of Sty, BA, and MMA in the ATRP from Ethyl 2-Bromoisobutyrate^a

monomer	$k_{ m p}{}^{ m app}$, s $^{-1}$	$k_{\rm p},{ m M}^{-1}~{ m s}^{-1}$	$K_{ m eq}$	$k_{\rm i}$, ${ m M}^{-1}~{ m s}^{-1}$
MMA Sty BA	$2 imes 10^{-4} \ 2 imes 10^{-6} \ 5 imes 10^{-7}$	1615 895 56780	$7 imes 10^{-7}\ 4 imes 10^{-8}\ 4 imes 10^{-10}$	$3.7 imes 10^3\ 5.5 imes 10^3\ 1.2 imes 10^3$

^{*a*} K_{eq} values obtained from ATRP using ethyl 2-bromoisobutyrate initiator, Cu(I)Br/Cu(II)Br₂/dNbpy catalyst at 90 °C, assuming constant ratio [Cu(I)]:[Cu(II)] = 10, [RBr]₀ = 0.013-0.018 M. Initiation rate constants at 21 °C (k_i) for isobutyrate radical addition to respective monomers (ref 56). Rate constant of propagation (k_p) (ref 57).

$$K_{\rm eq} = (k_{\rm p}^{\rm app}/k_{\rm p})[{\rm Cu(II)}]/([{\rm RBr}][{\rm Cu(I)}])$$
(2)

Table 2 presents pertinent rate constants and equilibrium constants for the three monomers are presented. The ATRP K_{eq} values at 90 °C of MMA and Sty (K_{eq} MMA = 7 × 10⁻⁷, K_{eq} Sty = 4 × 10⁻⁸) were higher with the smallest for BA (K_{eq} BA = 4 × 10⁻¹⁰). This agrees with the better radical stabilization effect of phenyl substituents relative to carboalkoxy group and also the higher stability of tertiary radicals over secondary.

In direct comparisons of ATRP from colloids and small molecule initiators, the polymerization rates were generally slower from 2-bromoisobutyrate functional nanoparticles. Using eqs 1 and 2, K_{eq} values for the ATRP of MMA, Sty, and BA were also calculated from 2-bromoisobutyrate functional colloidal initiators, with the assumption of a constant ratio of Cu(I) to Cu(II) species. Although ATRP rates for MMA were fast for both types of initiators, Sty and BA polymerization were noticeably slower from colloidal surfaces. Because of the slower rates of polymerization, calculated values of K_{eq} from 2-bromoisobutyrate functional silica nanoparticles were lower than those from the ethyl 2-bromoisobutyrate initiator ($K_{eq-SiO_2 MMA} = 7 \times 10^{-7}$, $K_{eq-SiO_2 Sty} = 1 \times 10^{-8}$, $K_{eq-SiO_2 BA} = 7 \times 10^{-11}$). It is unlikely that the K_{eq} from colloidal vs monomeric initiator would be drastically different; thus, discrepancies in calculated K_{eq} values arise from a variation in the ratio of Cu(I) and Cu(II) complexes in ATRP from 2-bromoisobutyrate functional nanoparticles. While it is known from EPR measurements that less than 10 mol % Cu(II) is typically formed in conventional ATRP systems with monomeric initiator,49,50 the amount of Cu(II) formed in ATRP from colloidal initiators may be higher.

Discrepancies observed in the ATRP kinetics from colloids may be explained by differences in the rates of termination of surface-immobilized radicals vs carboncentered radicals formed in solution. If termination events occur faster for surface tethered radicals, then a higher Cu(II) concentration relative to small molecule initiator systems may be generated. These intramolecular termination events can be qualitatively measured using SEC as the formation of dead polymer chains will also be accompanied by an increase in polydispersity $(M_{\rm w}/M_{\rm n})$, particularly in chain extension experiments (i.e., block copolymerization) from SiO₂-g-pSty, SiO₂-g-BA, and SiO₂-g-pMMA colloidal initiators. Because of the large difference in $K_{eq BA}$ and $K_{eq SiO_2 BA}$, BA systems should generate the highest amount of dead chains relative to Sty and MMA ATRP reactions. This point will be discussed in later sections.

Plots of $M_{n \text{ SEC}}$ of (cleaved) pSty vs conversion were constructed comparing the evolution of molar mass for polymers grown from colloidal surfaces and from mon-



Figure 2. Plots of M_n and M_w/M_n vs conversion for the ATRP of Sty from 2-bromoisobutyrate colloidal initiators (filled squares, M_n ; filled circles, M_w/M_n) and ethyl 2-bromoisobutyrate (open squares, M_n ; open circles, M_w/M_n) using stoichiometric ratios of 500:1:1:0.1:2.2 for [M]:[I]:[Cu(I)]:[Cu(II)]: [dNbpy] at 90 °C.



Figure 3. Plots of M_n and M_w/M_n vs conversion for the ATRP of BA from 2-bromoisobutyrate colloidal initiators (filled squares, M_n ; filled circles, M_w/M_n) and ethyl 2-bromoisobutyrate (open squares, M_n ; open circles, M_w/M_n) using stoichiometric ratios of 500:1:1:0.1:2.2 for [M]:[I]:[Cu(I)]:[Cu(II)]: [dNbpy] at 90 °C. An expanded plot showing early conversion points of M_n vs conversion is shown in the upper right.

omeric initiators. Hybrid nanoparticles were treated with hydrofluoric acid to hydrolyze the silica core and cleave tethered polymers for SEC analysis. As shown in Figure 2, the relationship between $M_{\rm n}$ SEC and conversion is linear for both polymerizations initiated from small molecules and colloids. For the ATRP of Sty using ethyl 2-bromoisobutyrate as the initiator, the initiation efficiency (~99%) was very high, where the initiation efficiency is defined as the ratio of $M_{\rm n}$ theoretical ($[M]_0/[I]_0 \times \text{conversion} \times FW_{\rm monomer}$) and $M_{\rm n}$ SEC. PSty of low polydispersity was also obtained ($M_{\rm w}/M_{\rm n} < 1.18$). Polymerizations of Sty from 2-bromoisobutyrate-functional colloids (**2**, Table 1) resulted in a lower initiation efficiency (~70%), yielding polymers with polydispersity in the range of $M_{\rm w}/M_{\rm n} = 1.2-1.3$.

The polymerization of BA from both silica colloids and ethyl 2-bromoisobutyrate was also assessed from plots of $M_{n SEC}$ vs conversion (Figure 3). A progressive increase of molar mass with conversion was observed in both plots, although deviation from linearity occurred in the early stages of BA ATRP from colloidal initiators. Contrary to Sty ATRP using a monomeric initiator, the ATRP of BA using ethyl 2-bromoisobutyrate proceeded with a lower initiation efficiency (~80%). Polymers had low polydispersity as determined from SEC ($M_w/M_n <$ 1.18). The ATRP of BA from 2-bromoisobutyrate colloids exhibited features of a slow initiation process, as the initiation efficiency gradually increased from 50% to 80% with increasing conversion. Initiation efficiency values eventually became comparable to those obtained



Figure 4. Plot of M_n vs conversion for the ATRP of MMA from 2-bromoisobutyrate colloidal initiators (filled squares, M_n ; filled circles, M_w/M_n) and ethyl 2-bromoisobutyrate (open squares, M_n ; open circles, M_w/M_n) using stoichiometric ratios of 500:1: 1:0.1:2.2 for [M]:[I]:[Cu(I)]:[Cu(II)]:[dNbpy] at 90 °C.

from the monomeric initiator system. Polydispersity of cleaved pBA ranged from $M_w/M_n = 1.3-1.5$.

Similar features of a slow initiation process were also obtained for the ATRP of MMA from 2-bromoisobutyrate functional colloids (Figure 4). For polymerizations using ethyl 2-bromoisobutyrate as the initiator, the plot of $M_{\rm n \ SEC}$ vs conversion was linear, with a high initiation efficiency (~90%). The polydispersity of pMMA formed from ethyl 2-bromoisobutyrate initiators was below M_w/ $M_{\rm n}$ < 1.2. However, for the ATRP of MMA from colloids (3, Table 1), the initiation efficiencies (20%) were low from the initial stages of the reaction, as a molar mass of cleaved pMMA was approximately 5000 g/mol higher than theoretical predictions. As the reaction proceeded, the molar mass of cleaved pMMA approached theoretical values, indicating that the initiation efficiency also increased with reaction time. Typically, in ATRP processes with efficient initiation, comparable initiation efficiencies are maintained throughout the polymerization, indicative that a constant number of chains are formed and grown with increasing conversion. In the case of MMA ATRP from colloids, a gradual increase in the initiation efficiency revealed that new chains were continuously formed with longer reaction times. Despite the large difference in $M_{\rm n \ theoretical}$ vs $M_{\rm n \ SEC}$ values, cleaved pMMA had low polydispersity $(M_w/M_n = 1.2 -$ 1.3). The lower efficiency of initiation from colloidal surfaces may be explained by steric congestion of 2-bromoisobutyrate groups. Similar behavior has been reported by Patten et al., ³² using 2-bromoisobutyratefunctional silica colloids (particle size = 75 nm) for the ATRP of MMA. Additionally, Miller et al.⁵² observed incomplete initiation in the ATRP of deuterated MMA using 12-arm dendritic initiators. In that report, incomplete initiation was observed for star polymers of low degree of polymerization (DP). However, quantitative consumption of initiator groups occurred at higher DP and conversion. The particular differences between kinetic behavior of MMA in comparison to Sty and BA are related to the ATRP equilibrium constants for polymerization and initiating species as well as to the rates of the addition of isobutyrate radicals to each monomer (cf. Table 2).

The kinetics of the ATRP of MMA using 2-bromoisobutyrate-functional colloids was further investigated with varying ratios of monomer to initiator, keeping equimolar stoichiometry of initiators sites and catalyst. Because of the very fast polymerization rates in the MMA polymerization from colloids (**3**, Table 1), ATRP conditions using a 2-fold (**6**, Table 1) and 4-fold



Figure 5. Semilogarithmic plots of monomer conversion vs time for the ATRP of MMA using 2-bromoisobutyrate colloidal initiators using conditions of [M]:[I]:[Cu(I)]:[Cu(II)]:[dNbpy]: filled triangles (500:1:1:0.1:2.2, 90 °C), filled diamonds (1000: 1:1:0.1:2.2, 90 °C), inverted triangle (2000:1:1:0.1:2.2, 90 °C). Conditions listed in Table 1, entries **3**, **5**, and **7**, respectively.

dilution (**7**, Table 1) of initiator sites and catalyst were also investigated. Thus, in these reactions, the molar ratios of monomer to initiator sites were as follows: 500:1 (**3**, Table 1), 1000:1 (**6**, Table 1), 2000:1 (**7**, Table 1).

As shown in Figure 5, the rates of the polymerization for MMA from 2-bromoisobutyrate colloidal initiators decreased with higher dilution of initiator and catalyst. Polymerizations were very fast for experiments 3 and 6 (Table 1) as gelation occurred within 20 min. The ATRP of MMA from colloidal initiators was extended to 40 min before the formation of gels using conditions of higher dilution (7, Table 1 and Figure 5). From the slope and intercept of lines in first-order plots of monomer consumption with time (Figure 5, Table 2), a small induction period was present for all three polymerization conditions. Comparison of the k_{app} for reactions 6 and 7 relative to 3 (Table 1) revealed that the rates of polymerization decreased by a factor of 2 and 4, respectively. Predictions of the polymerization rates based on the rate expression of homogeneous bulk ATRP reactions (eq 3) implied that 2- and 4-fold dilution of initiator concentration would reduce the rate by the same factor, since the ratio [Cu(I)]/[Cu(II)] was constant (~ 10) . This also indicates that the amount of spontaneously formed Cu(II) was relatively small in comparison with that initially added.

$$R_{\rm p} = k_{\rm p} K_{\rm eq}[{\rm M}][{\rm I}] \times [{\rm Cu}({\rm I})]/[{\rm Cu}({\rm II})]$$
(3)

The plots of $M_{n SEC}$ of cleaved pMMA vs conversion (Figure 6) were linear for all three conditions (**3**, **6**, **7**; Table 1) employed in the ATRP from 2-bromoisobutyrate functional colloids. The $M_{n SEC}$ of cleaved pMMA was found to progressively increased as a functional of dilution and higher target DP_n. Polydispersities of cleaved pMMA chains were all below $M_w/M_n < 1.4$. Furthermore, features of a slow initiation process were seen in all of the conditions used in the surface-initiated ATRP of MMA. For all conditions (**3**, **6**, **7**; Table 1) for MMA polymerization, $M_n SEC$ of cleaved polymers formed at very low conversion were significantly higher than predicted. However, as for the other systems, the initiation efficiencies gradually increased with reaction time.

Similar kinetic behavior of slow initiation was reported in the ATRP of Sty and MMA from larger silica



Figure 6. Plots of M_n (a) and M_w/M_n (b) vs conversion for the ATRP of MMA from 2-bromoisobutyrate colloidal initiators using conditions of $[M]:[I]:[Cu(I]):[Cu(II]):[dNbpy]: 500:1:1:0.1: 2.2, 90 °C (filled triangles, <math>M_n$; open triangles, M_w/M_n); 1000: 1:1:0.1:2.2, 90 °C (filled diamonds, M_n ; open diamonds, M_w/M_n); 2000:1:1:0.1:2.2, 90 °C (filled inverted triangles, M_n ; open inverted triangles, M_w/M_n). Conditions listed in Table 1, entries **3**, **5**, and **7**, respectively.

colloids.²² For both the ATRP of Sty from 2-bromopropionate functional colloids and for the MMA ATRP from 2-bromoisobutyrate nanoparticles, initiation efficiencies were low from very low monomer conversion and increased with reaction time. This result was unexpected as methyl 2-bromopropionate and ethyl 2-bromoisobutyrate are relatively efficient initiators for the ATRP of Sty and MMA, respectively. Thus, the crowded steric environment on colloidal initiator surfaces may hinder quantitative atom transfer of halogens from alkyl halides to copper complexes, but over time these sites may be accessible for initiation.

It is also important to note that while gelation due to interparticle radical coupling occurred in the ATRP of MMA from 2-bromoisobutyrate colloidal initiators at higher conversion, SEC did not reveal bimodal distributions in cleaved pMMA from nanoparticle gels. In general, pMMA cleaved from gelatinous polymerization mixtures prepared for a variety of ATRP conditions were completely soluble after HF hydrolysis of the core and molar mass distributions were monomodal and fairly narrow ($M_w/M_n < 1.4$). While coupling reactions could yield bimodal distributions in cleaved polymers, SEC revealed monomodal distributions indicating that only a few tethered chains were needed to induce gelation in ATRP reaction mixtures. Both the high number of tethered chains per particle (\sim 1000) and the viscosity of the polymerization mixture contribute to the rapid onset of gelation despite the absence of measurable amounts of coupled chains from SEC.

Synthesis of Core–Shell Colloids. The synthesis of hybrid nanoparticles containing tethered block copolymers was performed by sequential ATRP reactions from 2-bromoisobutyrate-functional silica colloids. A

previous study that prepared polystyrene-block-poly-(benzyl acrylate) block copolymers tethered to a SiO1.5 colloidal core was conducted.⁴¹ In the current report, a more thorough investigation into the synthesis of hybrid nanoparticles tethered with AB diblock copolymers was explored, focusing on the variation of copolymer composition, blocking sequence, and DP (Scheme 1). Using this approach, core-shell colloids composed of a hard inorganic core and a shell of copolymers containing both rubbery and glassy segments were prepared. Rubbery segments were incorporated into colloidal materials by the ATRP of BA, while the ATRP of either Sty or MMA resulted in the attachment of glassy segments to nanoparticle surfaces. Additionally, chain extension experiments from SiO₂-g-pSty, SiO₂-g-pBA, and SiO₂-g-pMMA qualitatively revealed the amount of dead and active chains present in ATRP reactions from colloids.

In the first block copolymer system, hybrid nanoparticles of silica-graft-(polystyrene-block-poly(n-butyl acrylate) (SiO₂-g-(pSty-b-pBA)) were prepared by the chain extension of SiO₂-g-pSty with BA. In the first step of the synthesis, SiO₂-g-pSty hybrid nanoparticles were prepared by the ATRP of Sty from colloidal initiators, with a slightly higher ratio of monomer to initiator sites $([M]_0/[I]_0 = 1000; 4$, Table 1). Under these conditions, a monomer conversion of 13% was reached in 15 h. SEC of cleaved pSty measured molar mass and DP (M_n = 18 200; $M_w/M_n = 1.21$; DP_{n pS} = 175). From gravimetric analysis of incorporated pSty, the number of tethered chains per nanoparticle (N_t) was calculated to be approximately $N_{\rm t} = 1000$ (see Experimental Section for calculation). Chain extension with BA used similar reaction conditions as those in the synthesis of the SiO₂g-pSty colloid (8, Table 1). Because of the higher molar mass of the SiO₂-g-pSty colloid relative to the bare silica colloidal initiator, a higher weight percentage of hybrid nanoparticle solid (10 wt %, relative to monomer) was required in the chain extension reaction with BA. Using these conditions, the incorporation of BA units to the SiO₂-g-pSty colloid was successful, requiring 18 h to obtain a monomer conversion of 7% before the reaction was quenched. ¹H NMR analysis of SiO₂-g-(pSty-b-pBA) hybrid nanoparticles confirmed the presence of both pSty and pBA protons. Integration of pBA methylene protons $\delta = 4.0$ ppm and pSty aromatic protons at $\delta =$ 6.8–7.2 ppm enabled determination of molar compositions of the tethered segments (80 mol % pSty, 20 mol % pBA). Since the DP_n of the starting tethered pSty was predetermined, the DPn of pBA segments was calculated in conjunction with ¹H NMR composition data (SiO₂-g-(pSty₁₇₅-b-pBA₄₂)). SEC of the cleaved copolymers confirmed an increase in molar mass relative to the starting pSty segment ($M_{n \text{ SEC pSty}-b-pBA} = 22 300, M_w/M_n = 1.20$; Figure 7). The comparable polydispersities of cleaved (co)polymers before and after chain extension indicate that a significant number of active tethered chains were maintained. DLS in dilute tetrahydrofuran (THF) hybrid nanoparticle solutions showed an increase in effective diameter for SiO₂-g-pSty₁₇₅ ($D_{eff} = 55$ nm) and SiO_2 -g-(pSty₁₇₅-b-pBA₄₂) ($D_{eff} = 60$ nm) relative to bare colloidal silica ($D_{\rm eff} = 20$ nm).

Similar hybrid nanoparticles possessing a glassy inner block and a rubbery outer segment were obtained by the synthesis of SiO₂-*g*-(pMMA-*b*-pBA) colloids. In the preparation of the SiO₂-*g*-pMMA precursor, higher ratios of monomer to initiator ($[M]_0/[I]_0 = 1000$; **6**, Table



Figure 7. SEC of cleaved (co)polymers from SiO₂-*g*-pSty₁₇₅ and SiO₂-*g*-(pSty₁₇₅-*b*-pBA₄₂) hybrid nanoparticles: cleaved pS (dotted line, $M_n = 18\ 200$; $M_w/M_n = 1.21$) and cleaved pS-*b*-pBA ($M_n = 22\ 300$; $M_w/M_n = 1.20$).



Figure 8. SEC of cleaved (co)polymers from SiO₂-*g*-pMMA₁₇₅ and SiO₂-*g*-(pMMA₁₇₅-*b*-pBA₇₉) hybrid nanoparticles: cleaved pMMA (dotted line, $M_n = 17600$; $M_w/M_n = 1.41$) and cleaved pMMA-*b*-pBA ($M_n = 29400$; $M_w/M_n = 1.28$).

1) were also employed in the ATRP of MMA from silica colloids. In the reaction mixture, SiO₂-g-pMMA colloids were present in 11 wt % relative to monomer for the chain extension with BA. Polymerizations were fast as a monomer conversion of 10% was achieved in 17 min before the reaction was guenched. From SEC of the cleaved pMMA, molar mass and DP_n were determined $(M_{\rm n \ SEC \ pMMA} = 17 \ 600; M_{\rm w}/M_{\rm n} = 1.41; DP_{\rm n \ pMMA} = 175).$ From gravimetric analysis, calculation of the number of tethered pMMA chains per particles was $N_{\rm t} = 600$. The lower number of chains per particle relative to $N_{\rm t pS}$ calculated for SiO₂-g-pSty was attributed to slow initiation processes, as discussed previously. In the chain extension of SiO₂-g-pMMA with BA (9, Table 1), a conversion of 16% was obtained in 860 min (14 h, 20 min). ¹H NMR analysis of the product recovered after the chain extension reaction confirmed the presence of both pMMA and pBA protons. Composition of the tethered copolymers (72 mol % pMMA, 27 mol % pBA) determined from ¹H NMR spectroscopy was performed by integration of pBA methylene protons $\delta = 4.0$ ppm and pMMA methyl protons at $\delta = 3.6$ ppm. The DP_n of the tethered block copolymer was also calculated on the basis of predetermined DPn of the pMMA segment with composition data from ¹H NMR (SiO₂-g-pMMA₁₇₅-bpBA₇₉). SEC of the cleaved copolymer also confirmed in an increase in apparent molar mass relative to the first pMMA segment ($M_{n pMMA-b-pBA} = 29 400; M_w/M_n$ = 1.28, Figure 8). The polydispersities of cleaved (co)polymers before and after chain extension were comparable to the SiO₂-g-pSty-b-pBA case, showing that while some tethered chains may undergo intramolecular termination, a sufficient number of active chains were retained. DLS in dilute tetrahydrofuran (THF) hybrid nanoparticle solutions confirmed an increase in effective



Figure 9. SEC of cleaved (co)polymers from SiO₂-*g*-pBA₉₄ and SiO₂-*g*-(pBA₉₄-*b*-pMMA₄₁) hybrid nanoparticles: cleaved pBA (dotted line, $M_n = 12\ 000$; $M_w/M_n = 1.28$) and cleaved pBA-*b*-pMMA ($M_n = 15\ 000$; $M_w/M_n = 1.46$).

diameter for SiO₂-g-pMMA₁₇₅ ($D_{eff} = 60$ nm) and SiO₂-g-(pMMA₁₇₅-b-pBA₇₉) ($D_{eff} = 80$ nm).

Alternatively, hybrid nanoparticles possessing a rubbery inner block and glassy outer blocks were prepared by changing the sequence of connectivity of pBA and pMMA bound to the silica colloid. SiO₂-g-pBA colloids were prepared by the ATRP from a 2-bromoisobutyratefunctional colloid (6, Table 1). BA polymerizations required long reaction times (61 h, 30 min), reaching a monomer conversion of 7%. SEC of the cleaved pBA chains were performed to measure molar mass and DP $(M_{\rm n \ SEC \ pBA} = 12 \ 000; M_{\rm w}/M_{\rm n} = 1.28; DP_{\rm n \ pBA} = 94)$. The number of tethered pBA chains per colloid calculated from gravimetric analysis was comparable to those from SiO₂-g-pS systems ($N_{t pBA} = 1000$). Block copolymers of pBA-b-pMMA grafted to silica colloids were prepared by chain extension of SiO₂-g-pBA with MMA. In these reactions, the halogen-exchange technique was required, where a bromine-terminated SiO₂-g-pBA colloid was reacted with a Cu(I)Cl complex in the presence of MMA.⁵³ As for the linear copolymer systems, chain extension was observed using SEC analysis of the cleaved product ($M_{n \text{ SEC pBA}-b-pMMA} = 15\ 000; M_w/M_n =$ 1.46, Figure 9). ¹H NMR analysis of the product after chain extension confirmed the incorporation of pMMA (40 mol %) by extension from the inner pBA segment (60 mol %). The low molar mass mass tail (Figure 9) in SEC and the higher polydispersity obtained after chain extension from SiO₂-g-pBA was attributed to the presence of dead chains formed in the initial ATRP of BA from the bare silica nanoparticle. The detection of dead chains in SEC was consistent with kinetic observations in the ATRP of BA from silica colloidal initiators where slower rates and formation of excess Cu(II) pointed to intramolecular termination of surface-immobilized radicals. The average DP_n of the cleaved copolymers was determined using ¹H NMR(SiO₂-g-(pBA₉₄-b-pMMA₆₂)). DLS of hybrid nanoparticles in dilute tetrahydrofuran (THF) solutions confirmed an increase in effective diameter for SiO₂-g-pBA₉₄ ($D_{eff} = 42$ nm) and SiO₂-g- $(pBA_{94}-b-pMMA_{62})(D_{eff} = 60 \text{ nm}).$

Morphology of Ultrathin Films. The morphology of 2-bromoisobutyrate-functional silica colloids and hybrid nanoparticles possessing tethered homopolymers of pSty, pBA, and pMMA was investigated using TEM (Figure 10). Samples were prepared by drop-casting dilute solutions of SiO₂ and hybrid nanoparticles onto carbon-coated copper grids, followed by evaporation of the solvent in air. Images of SiO₂ colloidal initiators (Figure 10a) indicated that nanoparticles assembled into two-dimensional aggregates of discrete particles, indi-



Figure 10. TEM images of hybrid nanoparticle cast onto carbon-coated copper grids: (a) 2-bromoisobutyrate functional silica colloidal initiators; (b) SiO_2 -*g*-pSty₁₇₅ hybrid nanoparticles (Figure 7, SEC; **4**, Table 1); (c) SiO_2 -*g*-pBA₉₄ hybrid nanoparticles (Figure 9, SEC; **6**, Table 1); (d) SiO_2 -*g*-pMMA₁₇₅ (Figure 8, SEC; **5**, Table 1). Black bar = 200 nm.

cating efficient silylation of surface silanol groups on nanoparticle surfaces had occurred. The particle size of SiO₂ colloidal initiators was polydisperse, although the majority of nanoparticles possessed $D_{\rm eff} \leq 20$ nm. TEM of hybrid nanoparticles for pSty, pBA, and pMMA systems confirmed the assembly of ultrathin films consisting of a matrix of tethered homopolymer and dispersed silica cores arising from entanglements of neighboring polymer chains.^{21,41} The distance between the particles was governed by the radius of gyration of tethered chains filling space between silica cores. The majority of silica colloids imaged in ultrathin films of SiO₂-g-pSty₁₇₅ (Figure 10b), SiO₂-g-pBA₉₄ (Figure 10c), and SiO₂-g-pMMA₁₇₅ (Figure 10d) hybrid nanoparticles possessed $D_{\rm eff} \leq 20$ nm, consistent with sizes observed for bare silica colloid samples.

Hybrid nanoparticles tethered with block copolymers were cast as ultrathin films onto carbon-coated copper grids and imaged using TEM. In general, features of these ultrathin films were almost identical to those of their parent homopolymer containing hybrid nanoparticles. In all cases, silica cores ($D_{\rm eff} \sim 20$ nm) were well dispersed in a continuous phase of the tethered copolymers. As shown in SEC of cleaved block copolymers from hybrid nanoparticles (Table 1 and Figures 7-9), the dimensions of the outer block segments incorporated to SiO₂-g-pSty, SiO₂-g-pBA, and SiO₂-g-pMMA hybrid nanoparticles were relatively short. Thus, visualization of subtle differences in interparticle spacing was difficult. Furthermore, the observation of distinct copolymer domains using TEM was not possible without selective staining of one of the tethered copolymer segments. Thus, tapping-mode AFM^{41,54,55} was chosen to image the effects of grafting block copolymers to silica cores on the morphology of ultrathin films, as the presence of both rubbery and rigid domains was anticipated to impart sufficient compliance-based contrast.

AFM images of SiO₂-*g*-(pSty₁₇₅-*b*-pBA₄₂) (**8**, Table 1) ultrathin films revealed a morphology of rigid particles dispersed in a rubbery matrix. We anticipated that each



Figure 11. Tapping mode AFM of an ultrathin film from SiO₂*g*-(pS₁₇₅-*b*-pBA₄₂) hybrid nanoparticles. SEC of cleaved pSty*b*-pBA from Figure 7, conditions for synthesis, **8**, Table 1. Large spherical features correspond to SiO₂-*g*-pS domains, embedded in the matrix formed by the outer segments of tethered pBA.

component of the hybrid nanoparticle would be visualized, as for previously prepared SiO_{1.5}-g-(pSty-b-pBzA) materials.⁴¹ From the composition of the tethered pSty₁₇₅-*b*-pBA₄₂ segments and blocking sequence, dispersion of rigid domains in a thin rubbery matrix was expected due to low content of pBA in the material. Hybrid nanoparticles were spin-coated onto freshly cleaved mica depositing submonolayer aggregates of colloids onto the flat surface. Ultrathin films of these hybrid nanoparticles were deformable due to the presence of a rubbery outer shell of pBA segments, as rigid domains were clearly discernible with increasing the effective tapping force. AFM images of submonolayers composed of SiO₂-g-(pSty₁₇₅-b-pBA₄₂) colloids (Figure 11) revealed the presence of spherical particles slightly spaced in a continuous matrix. Spherical features visualized in AFM images of these submonolayers were significantly larger than silica cores imaged in TEM of SiO₂-g-(pSty₁₇₅-*b*-pBA₄₂) ultrathin films, indicating that they corresponded to silica cores surrounded by the glassy pSty shell. The variation of size of spherical features seen in Figure 11 presumably reflects the polydispersity of silica colloidal initiators as previously shown by TEM (see Figure 10a).

AFM images of ultrathin films SiO_2 -*g*-(pMMA₁₇₅-*b*-pBA₇₉) (**9**, Table 1) prepared under similar conditions as SiO_2 -*g*-(pSty₁₇₅-*b*-pBA₄₂) also revealed a morphology consistent with rigid particles dispersed in a rubbery matrix (Figure 12). The rubbery character of the matrix was apparent when the tip–sample force was increased from "light tapping" (Figure 12a) to hard tapping conditions (Figure 12b). As with the previous sample, the spherical features in AFM images of SiO_2 -*g*-(pMMA₁₇₅-*b*-pBA₇₉) were larger than silica cores observed in TEM, indicating that they corresponded to silica cores surrounded by glassy pMMA shells. However, the interparticle spacings were considerably larger than for the SiO_2 -*g*-(pSty₁₇₅-*b*-pBA₄₂) system, presumably due to the higher DP of pBA in the outer shell.

Of particular interest in AFM analysis was the SiO₂g-(pBA_{94} -b- $pMMA_{62}$) system (**10**, Table 1) with the soft phase (pBA) sandwiched between the silica core and glassy shell (pMMA). However, the AFM images of ultrathin films of these particles prepared by spincoating on mica did not reveal the expected presence of more compliant zones separating the silica cores from the glassy matrix. This was attributed to the low DP of the outer pMMA segment, preventing it from segregat-



Figure 12. Tapping mode AFM images of an ultrathin film from SiO₂-*g*-(pMMA₁₇₅-*b*-pBA₇₉) hybrid nanoparticles acquired under light tapping (a) and hard tapping (b) conditions. SEC of cleaved pMMA-*b*-pBA from Figure 8, conditions for synthesis, 9, Table 1. Large spherical features correspond to SiO₂-*g*-pMMA domains, while matrix is outer segment of tethered pBA. Under hard tapping conditions, the soft pBA matrix became compressed, revealing subsurface SiO₂-*g*-pMMA domains.



Figure 13. Tapping mode AFM images of an ultrathin film from SiO_2 -*g*-(pBA₉₄-*b*-pMMA₃₅₂) hybrid nanoparticles acquired under light tapping (a) and hard tapping (b) conditions. Under hard tapping conditions, the soft pBA shells sandwiched between rigid cores and rigid pMMA matrix appeared as characteristic depressed halos.

ing into a continuous rigid matrix upon casting onto mica. To test this hypothesis, SiO₂-*g*-(pBA₉₄-*b*-pMMA₆₂) hybrid nanoparticles were further chain extended with MMA (**11**, Table 1) to increase the DP of the pMMA outer shell. SEC of the cleaved pBA-*b*-pMMA copolymer indicated that while low molar mass impurities increased the overall polydispersity of the pBA-*b*-pMMA block copolymer ($M_{n \text{ SEC pBA}-b-pMMA} = 14\ 200;\ M_w/M_n =$ 3.10), the major product formed a high molar mass peak

from incorporation of pMMA ($M_{n \text{ main peak pBA-b-pMMA}} =$ 39 100; $M_w/M_n = 1.29$). ¹H NMR analysis also confirmed an increase from 40 to 80 mol % in the molar composition of pMMA after the chain extension reaction. The final DP of each segment determined from ¹H NMR analysis was SiO₂-g-(pBA₉₄-b-pMMA₃₅₂).

Following the extension of pMMA segment, the AFM images of ultrathin films of SiO₂-g-(pBA₉₄-b-pMMA₃₅₂) (11, Table 1) acquired under light tapping (Figure 13a) and hard tapping conditions (Figure 13b) revealed the expected presence of more compliant (and thus depressed in height images) zones of pBA, separating the rigid cores from the rigid, glassy pMMA matrix.

Conclusion

Hybrid nanoparticles consisting of silica cores tethered with homopolymers and copolymers were prepared by the ATRP of styrene and (meth)acrylate monomers from silica colloidal initiators. Comparative kinetics studies of Sty, BA, and MMA polymerizations from surfaces in conjunction with control experiments conducted with the corresponding small molecule initiator, ethyl 2-bromoisobutyrate, revealed the complex nature of surface-initiated polymerization. However, despite the complexity of kinetics, ATRP is suitable for the preparation of hybrid nanoparticles with tethered (co)polymers of well-defined composition and degree of polymerization. TEM and AFM studies showed the impact of graft composition on the nanoscale morphology of ultrathin films of these hybrid nanoparticles.

Acknowledgment. The NSF (for K.M., DMR 00-90409; for T.K., DMR-9871874; for G.D.P., DMR-9988451) and the Controlled Radical Polymerization Consortium and Legacy Fellowship at CMU (for J.P.) are gratefully acknowledged for financial support.

References and Notes

- (1) Bates, F. S.; Fredrickson, G. H. Annu. Rev. Phys. Chem. 1990, 41, 32.
- Lee, M.; Cho, B. K.; Zin, W. C. Chem. Rev. 2001, 101, 3869. (2)
- (3) Matjievic, E. Chem. Mater. 1993, 5, 412.
- (4) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. Adv. Mater. 2000, 12, 693. (5) Caruso, F. Adv. Mater. 2001, 13, 11.
- Ulrich, R.; Du Chesne, A.; Templin, M.; Wiesner, U. Adv. (6) Mater. 1999, 11, 141.
- (7)MacLachlan, M. J.; Manners, I.; Ozin, G. A. Adv. Mater. 2000, 12. 675.
- (8) Novak, B. M. Adv. Mater. 1993, 5, 422.
- (9) Wen, J.; Wilkes, G. L. Chem. Mater. 1996, 8, 1667.
 (10) Webster, O. W. Science 1991, 251, 887.
- (11) Wang, J.-S.; Matyjaszewski, K. J. Am. Chem. Soc. 1995, 117, 5614
- (12) Matyjaszewski, K.; Xia, J. Chem. Rev. 2001, 101, 2921.
- Kamigaito, M.; Ando, T.; Sawamoto, M. Chem. Rev. 2001, 101, (13)3689.
- (14) Wang, J.-S.; Matyjaszewski, K. Macromolecules 1995, 28, 7901.
- (15) Patten, T. E.; Matyjaszewski, K. Adv. Mater. 1998, 10, 901.
- Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. Science **1996**, 272, 866. (16)
- (17) Patten, T. E.; Matyjaszewski, K. Acc. Chem. Res. 1999, 32, 895
- (18) Matyjaszewski, K. Chem.-Eur. J. 1999, 5, 3095.
- Coessens, V.; Pintauer, T.; Matyjaszewski, K. Prog. Polym. (19)Sci. 2001, 26, 337.
- (20) Pyun, J.; Matyjaszewski, K. Chem. Mater. 2001, 13, 3436.

- (21) von Werne, T.; Patten, T. E. J. Am. Chem. Soc. 1999, 121, 7409
- (22) von Werne, T.; Patten, T. E. J. Am. Chem. Soc. 2001, 123, 7497.
- (23) Farmer, S. C.; Patten, T. E. Chem. Mater. 2001, 13, 3920.
- (24) Carrot, G.; Diamanti, S.; Manuszak, M.; Charleux, B.; Vairon, J. P. J. Polym. Sci., Part A: Polym. Chem. 2001, 39, 4294.
- (25) Savin, D. A.; Pyun, J.; Patterson, G. D.; Kowalewski, T.; Matyjaszewski, K. J. Polym. Sci., Part B: Polym. Phys. 2002, 40, 2667.
- (26) Mori, H.; Seng, D. C.; Zhang, M.; Mueller, A. H. E. Langmuir 2002, 18, 3682
- (27) Chen, X.; Randall, D. P.; Perruchot, C.; Watts, J. F.; Patten, T. E.; von Werne, T.; Armes, S. P. J. Colloid Interface Sci. 2003, 257, 56.
- (28) Nuss, S.; Bottcher, H.; Wurm, H.; Hallensleben, M. L. Angew. Chem., Int. Ed. 2001, 40, 4016.
- (29) Mandal, T. K.; Fleming, M. S.; Walt, D. R. Nano Lett. 2002,
- (30) Ohno, K.; Koh, K.-m.; Tsujii, Y.; Fukuda, T. Macromolecules **2002**, *35*, 8989.
- (31)Zhu, M.-Q.; Wei, L.-H.; Zhang, W.-C.; Du, F.-S.; Li, Z.-C.; Li, F.-M. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 2002, 43, 68.
- (32) Tanke, R.; Kauzlarich, S. M.; Patten, T. E.; Pettigrew, K. A.; Murphy, D. L.; Thompson, M. E.; Lee, H. W. H. Chem. Mater., in press.
- (33) Wang, J.-Y.; Chen, W.; Liu, A.-H.; Lu, G.; Zhang, G.; Zhang, J.-H.; Yang, B. J. Am. Chem. Soc. 2002, 124, 13358.
- (34)Tsubokawa, N.; Yoshikawa, S. Rec. Res. Dev. Polym. Sci. 1998, 2, 211.
- (35) Vestal, C. R.; Zhang, Z. J. J. Am. Chem. Soc. 2002, 124, 14312
- (36) Kickelbick, G.; Holzinger, D.; Brick, C.; Trimmel, G.; Moons, E. Chem. Mater. 2002, 14, 4382.
- (37) Gu, B.; Sen, A. Macromolecules 2002, 35, 8913.
- (38) Costa, R. O. R.; Vasconcelos, W. L.; Tamaki, R.; Laine, R. M. Macromolecules 2001, 34, 5398.
- (39) Zhao, B.; Brittian, W. J. Prog. Polym. Sci. 2000, 25, 677.
- (40) Qiu, J.; Charleux, B.; Matyjaszewski, K. Prog. Polym. Sci. 2001, 26, 2083.
- (41) Pyun, J.; Matyjaszewski, K.; Kowalewski, T.; Savin, D.; Patterson, G.; Kickelbick, G.; Huesing, N. J. Am. Chem. Soc. 2001. 123. 9445.
- (42) Miller, P. J.; Matyjaszewski, K. Macromolecules 1999, 32, 8760.
- (43) Matyjaszewski, K.; Patten, T. E.; Xia, J. J. Am. Chem. Soc. 1997, 119, 674.
- (44)Weast, R. C., Ed.; Handbook of Chemistry and Physics, 53rd ed.; The Chemical Rubber Co.: Cleveland, 1972.
- (45) Matyjaszewski, K.; Pyun, J.; Gaynor, S. G. Macromol. Rapid Commun. 1998, 19, 665.
- (46) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. Macromolecules 2000, 33, 7261
- Wang, J.-L.; Grimaud, T.; Matyjaszewski, K. Macromolecules (47)1997, 30, 6507.
- (48) Davis, K. A.; Paik, H.-j.; Matyjaszewski, K. Macromolecules 1999, 32, 1767.
- (49)Kajiwara, A.; Matyjaszewski, K. Macromol. Rapid Commun. **1998**, *19*, 319.
- Kajiwara, A.; Matyjaszewski, K. Polym. J. 1999, 31, 70. (50)
- (51) Fischer, H. J. Polym. Sci., Part A: Polym. Chem. 1999, 37, 1885.
- (52) Heise, A.; Diamanti, S.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. Macromolecules 2001, 34, 3798.
- (53)Shipp, D. A.; Wang, J.-L.; Matyjaszewski, K. Macromolecules 1998, *31*, 8005.
- Leclere, P.; Moineau, G.; Minet, M.; Dubois, P.; Jerome, R.; (54)Bredas, J. L.; Lazzaroni, R. Langmuir 1999, 15, 3915.
- Yu, M. F.; Kowalewski, T.; Ruoff, R. S. Phys. Rev. Lett. 2000, (55)85. 1456.
- (56)Fischer, H. In Free Radicals in Biology and Environment; Minisci, F., Ed.; Kluwer Acad. Publ.: Dordrecht, 1997.
- (57) Beuermann, S.; Buback, M. Prog. Polym. Sci. 2002, 27, 191.

MA034188T