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Synthesis of Mixed Poly(ε-caprolactone)/Polystyrene Brushes from Y-Initiator-Functionalized Silica Particles by Surface-Initiated Ring-Opening Polymerization and Nitroxide-Mediated Radical Polymerization

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Abstract

This article reports on the synthesis of mixed homopolymer brushes grafted on silica particles composed of poly(ε-caprolactone) (PCL), a chemically and biologically degradable polymer, and polystyrene (PS), a vinyl polymer, by sequential surface-initiated ring-opening polymerization (ROP) of ε-caprolactone (εCL) at 75 °C and nitroxide-mediated radical polymerization (NMRP) of styrene at 120 °C. The silica particles were functionalized with an asymmetric difunctional initiator (Y-initiator) bearing a hydroxyl group, an initiator for ROP, and an alkoxyamine moiety, an initiator for NMRP. We found that for ROP, PCL with $M_{n,SEC}$ values of ~ 25 kDa and narrow polydispersity indexes (≤ 1.20) relative to PS standards can be reproducibly synthesized at 75 °C using tin(II) 2-ethylhexanoate as catalyst after the Y-initiator-functionalized silica particles and the catalyst were thoroughly dried. Both surface-initiated ROP and NMRP polymerizations were carried out in the presence of a free initiator. The polymer brushes were cleaved from silica particles using hydrofluoric acid, and the SEC analysis showed that the molecular weights of the grafted polymers were close to those of the free polymers formed from the free initiators. The overall grafting density of mixed PCL/PS brushes can be tuned from 1.24 to 0.40 chains/nm^2 by

varying the mass ratio of Y-initiator-terminated triethoxysilane to bare silica particles in the

initiator immobilization step, though the grafting density of PS was always higher than that of

PCL.

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Introduction

Binary mixed brushes, composed of two chemically distinct homopolymers randomly or alternately grafted by one end on a solid substrate, are an intriguing class of surface-responsive materials.[1-5] These multicomponent brushes can undergo spontaneous self-reorganization in response to environmental changes, exhibiting different nanostructures and properties under different conditions. The intriguing self-assembly behavior of binary mixed brushes has attracted considerable interest in both theoretical and experimental studies in the past years.[1-5] Marko and Witten were the first to study symmetric mixed homopolymer brushes and predicted that they phase separate laterally in melt and the feature size of the formed "ripple" nanopattern is on the order of the polymer chain root-mean-square end-to-end distance.[1] Their seminal work stimulated tremendous research activities on mixed brushes.[1-14] The effects of various molecular parameters on the self-assembly behavior of mixed brushes were elucidated by theoretical and computer simulation studies, and a rich variety of nanostructures was predicted.[1-8]

In general, binary mixed homopolymer brushes can be made by using three methods: (i) "grafting from", where two different polymers are grown from the surface by surface-initiated polymerization,[9-11] (ii) "grafting to", where two preformed, end-functionalized polymers are grafted onto a solid substrate via the reaction with surface functional groups,[12,13] and (iii) combination of "grafting to" and "grafting from", where one polymer is grafted onto the substrate while another polymer is grown from the surface.[14] Sidorenko et al. reported the synthesis of first binary mixed brushes of polystyrene (PS)/poly(2-vinylpyridine) (PVP) by a "grafting from" method.[9a] An azo free radical initiator was immobilized on silicon wafers, followed by a two-step conventional free radical polymerization process to grow two polymers; the second polymer was grown from the residual surface azo initiator that did not decompose in

the synthesis of the first polymer.[9a] The obtained mixed brushes exhibited switching properties in response to environmental changes. We previously reported the synthesis of well-defined binary mixed brushes by sequential atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMRP) from asymmetric difunctional initiator (Y-initiator)-functionalized silica substrates.[10] The use of Y-initiators ensures that the two types of initiators are well mixed, in fact alternately distributed, on the silica surface and thus it is possible to make well-mixed binary polymer brushes. The molecular weights and molecular weight distributions of two tethered polymers can be well controlled, allowing the study of microphase separation of mixed brushes by transmission electron microscopy and differential scanning calorimetry.[10f-l]

The "grafting to" method is straightforward and allows the use of polymers with controlled molecular weights, well-defined end groups, and predetermined architectures for the preparation of binary mixed brushes.[12,13] For example, Minko et al. reported the synthesis of mixed PS/PVP brushes by sequentially grafting carboxyl-terminated PS and PVP onto silica wafers that were functionalized with 3-glycidoxypropyltrimethoxysilane.[12a,b] Julthongpiput et al. prepared Y-shaped brushes by grafting diblock copolymers to silicon wafers via the reaction between the carboxylic acid group at the junction point of the two blocks and the silica surface.[13a] ABC triblock copolymers with a reactive, short central B block were also employed to make mixed brushes by reacting the B block with the surface of a solid substrate, either flat or curved.[13b-e] Although "grafting to" is simple, the thickness of the obtained brushes tends to be low because of the steric hindrance presented by the grafted polymer to the incoming polymer chains.

Duan et al. reported a method for the synthesis of binary mixed brushes grafted on gold nanoparticles by combining "grafting to" and "grafting from" techniques.[14] A thiol-terminated poly(ethylene glycol) (PEG) with a molecular weight of 5 kDa and a dithiol-terminated ATRP

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initiator were co-assembled onto gold nanoparticles via the formation of Au-S bonds, followed by surface-initiated ATRP to grow the second polymer from gold nanoparticles, yielding well-defined binary mixed brushes.[14]

The experimental studies of mixed brushes thus far mainly focus on the brush systems composed of two vinyl polymers; there are only a few examples of mixed brushes containing nonvinyl polymers or chemically or biologically degradable polymers in the literature.[9h,14] Recent experimental studies have shown that mixed brushes can phase separate into a variety of morphologies ranging from isolated, nearly spherical nanodomains in the matrix of another polymer, to short cylindrical nanodomains, to bicontinuous wormlike nanopatterns, and two-layered structures.[10h,i] If one polymer is etchable under mild conditions, many interesting porous nanostructures can be fabricated from such multicomponent hairy particles, and the obtained nanomaterials may find applications, e.g., in separation or catalysis. Therefore, we embarked on an effort to synthesize mixed brushes on silica particles composed of one degradable polymer and one vinyl polymer.

In the present work, we synthesized mixed poly(ϵ-caprolactone) (PCL)/PS brushes from silica particles that were functionalized with an asymmetric difunctional initiator (Y-initiator) bearing a hydroxyl group, an initiator for ring-opening polymerization (ROP),[15] and an NMRP initiator by combining metal-catalyzed ROP of ϵ-caprolactone (ϵCL) and NMRP of styrene (Scheme 1). The triethoxysilane-terminated Y-initiator was immobilized onto the surface of bare silica particle via an ammonia-catalyzed hydrolysis and condensation process.[10i-k,16] The surface-initiated ROP of ϵCL was carried out at 75 °C in the presence of a free initiator with tin(II) 2-ethylhexanoate (Sn(Oct)$_2$) as catalyst, followed by the NMRP of styrene at 120 °C. We also showed that the overall grafting density of mixed PCL/PS brushes can be tuned by changing the

mass ratio of the triethoxysilane-terminated Y-initiator to bare silica particles in the initiator immobilization step. The method described in this article can be extended to the synthesis of mixed brushes containing other degradable polymers, which could open up new opportunities for applications of mixed brush-grafted particles. Note that the preparation of block copolymers by combining ROP and NMRP from difunctional initiators in solution has been previously demonstrated.[17]

Scheme 1. Synthesis of Mixed Poly(ε-caprolactone) (PCL)/Polystyrene (PS) Brushes on Silica Particles Functionalized with a Y-initiator Bearing a Hydroxyl Group and a TEMPO Moiety by Combining Sn(Oct)₂-Catalyzed Ring-Opening Polymerization (ROP) of ε-Caprolactone (εCL) and Nitroxide-Mediated Radical Polymerization (NMRP) of Styrene.
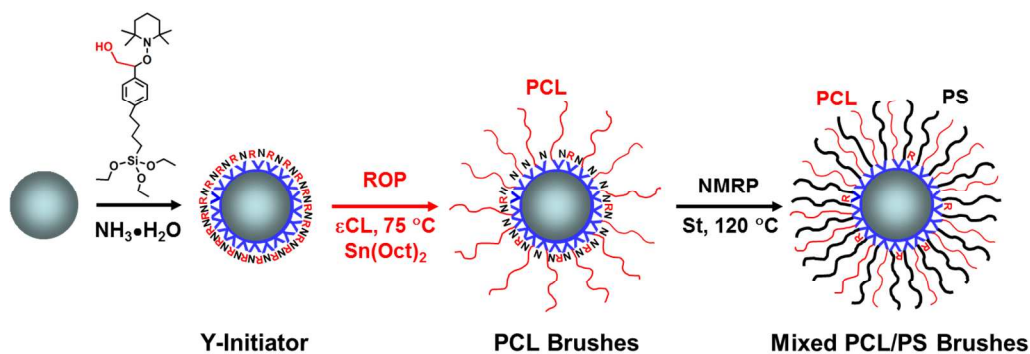
Experimental

Materials

Tetraethyl orthosilicate (or tetraethoxysilane, TEOS, 98%), ammonium hydroxide (25% in water), triethoxysilane (HSi(OC₂H₅)₃, 95%), and 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 98%) were purchased from Acros Organics and used as received. The platinum−divinyltetramethyldisiloxane complex in xylene (2.1−2.4% Pt concentration in xylene) was obtained from Gelest, Inc. 2-[4-(But-3-enyl)phenyl]-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethanol (Y-silane precursor) was prepared according to a procedure described in

a previous publication.[10d] Styrene (99%, Aldrich) and ε-Caprolactone (εCL, 99%, Acros Organics) were dried with CaH_2 and distilled under reduced pressure. The purified monomers were stored in a refrigerator prior to use. Tin(II) 2-ethylhexanoate (Sn(Oct)$_2$, ~ 95%) was obtained from Sigma-Aldrich. ω-Undecylenyl alcohol (98%) was purchased from Aldrich and used as the free initiator for ROP in the synthesis of PCL brushes on silica particles. 1-Phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (STEMPO), an initiator for NMRP, was prepared by following a procedure from the literature.[10k,18] Toluene and tetrahydrofuran (THF) were dried by refluxing over sodium and benzophenone under nitrogen atmosphere until the color changed to purple, and then distilled and used immediately. Ethanol (200 proof) was obtained from Decon Laboratories, Inc. All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

Instrumentation

Size exclusion chromatography (SEC) was carried out at ambient temperature using PL-GPC 20 (an integrated SEC system from Polymer Laboratories, Inc.) with a differential refractive index detector, one PLgel 5 μm guard column (50 × 7.5 mm), and two PLgel 5 μm mixed-C columns (each 300 × 7.5 mm, linear range of molecular weight from 200 to 2000000 according to Polymer Laboratories, Inc.). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Polystyrene standards (Polymer Laboratories, Inc.) were employed for calibration. The data were processed using Cirrus GPC/SEC software (Polymer Laboratories, Inc.). PCL free polymers, formed from the free initiator in the synthesis of PCL brushes, were also analyzed at 40 °C by PL-GPC 120 equipped with a Precision Detector PD2040 (a two angle static light scattering detector, 15° and 90°), Viscotek 220 differential viscometer, and a Polymer Laboratories differential refractometer. The system consists of four Polymer Laboratories PLgel columns (300

× 7.5, 10 μm particles with pore sizes of 500, 10^3, 10^5, and 10^6 Å, respectively). The calibration range is 600 to 7500000 Da using either PS or PMMA standards. A dn/dc value of 0.075 mL/g for PCL, which was from a literature paper,[19] was employed in the measurements of PCL absolute molecular weights by PL-GPC 120 with a two-angle light scattering detector. ^{1}H NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer with tetramethylsilane (TMS) as the internal standard in ^{1}H NMR spectra. Thermogravimetric analysis (TGA) was performed at a heating rate of 20 °C/min from room temperature to 800 °C using either TA Q-series Q50 in air or a SII Nanotechnology TG/DTA 320 in pure oxygen. The hairy particle samples were dried at 55 °C in vacuum for at least 6 h prior to TGA analysis. Mass spectrometric analysis was performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer equipped with an ESI ion source and an integrated syringe pump (AB Sciex, Foster City, CA, USA).

Transmission electron microscopy (TEM) was employed to study PCL brush-grafted and mixed PCL/PS brush-grafted silica particles. Chloroform, a good solvent for PCL and PS, was used to prepare hairy particle dispersions. For each sample, 1 − 2 mg of particles was dispersed in 1 mL of chloroform in a small vial by ultrasonication. The particle dispersion was drop cast onto a carbon-coated, copper TEM grid using a glass pipette and was allowed to dry at ambient condition. The samples were solvent annealed with $CHCl_3$ vapor in a closed container at room temperature for > 3 h. Transmission electron microscopy (TEM) images were acquired using a Zeiss Libra 200 MC transmission electron microscope equipped with a Gatan UltraScan US1000XP CCD camera.

Synthesis

Synthesis of 2-[4-(1-Triethoxysilylbutyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethanol (Y-silane)

2-[4-(But-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethanol (Y-silane precursor, 0.465 g, 1.404 mmol) was added into a 25 mL two-necked flask and dried under vacuum at room temperature for 1 h. Triethoxysilane ($HSi(OC_2H_5)_3$, 2.50 mL, 13.5 mmol) was injected into the flask via a syringe under N_2 atmosphere, followed by addition of the platinum-divinyltetramethyldisiloxane complex in xylene (80 μL). The mixture was stirred at 45 °C under nitrogen and the hydrosilylation reaction was monitored by ^{1}H NMR spectroscopy analysis. Once the reaction was complete, excess triethoxysilane was removed under high vacuum at 45 °C, and the product was further purified by silica gel column chromatography using methylene chloride as eluent (yield: 64.3%). ^{1}H NMR δ (ppm, $CDCl_3$, tetramethylsilane (TMS) as internal standard): 0.59 (t, 2H, SiCH_2CH$_2$-), 1.08, 1.18, 1.27, 1.43 (each s, 12H, -C(CH_3)$_2$), 1.14 (t, 9H, -OCH$_2$CH_3), 1.30-1.66 (m, 10H, -C(CH$_3$)$_2$CH_2CH_2CH_2C(CH$_3$)$_2$- and -SiCH$_2$CH_2CH_2CH$_2$-), 2.53 (t, 2H, -ArCH_2CH$_2$-), 3.62 (dd, 1H, HOCHH-), 3.73 (q, 6H, -SiOCH_2CH$_3$), 4.15 (dd, 1H, HOCHH-), 5.20 (dd, 1H, HOCH$_2$CHO-), 5.83 (br, 1H, -OH), 7.13 (dd, 4H, ArH). ^{13}C NMR δ (ppm, TMS as internal standard): 9.23, 16.13, 17.29, 21.44, 28.69, 33.71, 34.23, 39.18, 39.39, 57.30, 68.73, 82.42, 125.65, 127.34, 135.04, 141.41. Mass spectrum: $[M + H]^+$ at *m/z* 496.343.

Synthesis of Bare Silica Particles

Ammonium hydroxide (25% in water, 14.181 g) and tetraethoxysilane (TEOS, 7.101 g) were each mixed with ethanol (5 mL) to form homogeneous solutions. The two solutions were added into a 500 mL flask that contained 190 mL of ethanol under stirring. The concentrations of NH_3, TEOS, and water in the solution were 0.45, 0.15, and 3.10 M, respectively. After the mixture was stirred vigorously at room temperature for 12 h, the silica particles were isolated by

centrifugation (Eppendorf 5804 centrifuge, 6000 rpm), redispersed in ethanol, and centrifugated again. This washing process was repeated with ethanol one more time, water three times, and ethanol again. Particles were then dried with a stream of air flow (1.936 g).

Synthesis of Y-Initiator-Functionalized Silica Particles

The triethoxysilane-terminated Y-initiator (Y-silane, Scheme 1) was immobilized onto the surface of silica particles via an ammonia-catalyzed hydrolysis/condensation process.[10i-k,16] Seven batches of Y-initiator-functionalized silica particles (YI-Particles) were prepared using different mass ratios of Y-silane to bare silica particles. The following is the procedure for the preparation of YI-P-3 (Table 1) using a Y-silane-to-silica particle mass ratio of 87.5%. Other initiator particles were made using the same procedure except different mass ratios of Y-silane to bare silica particles.

Bare silica particles (149.2 mg) were dispersed in ethanol (10 mL) in a flask by ultrasonication to form a homogeneous, stable dispersion. A solution of ammonium hydroxide (25% in water, 1.10 g) in ethanol (5.0 mL) was added dropwise into the particle dispersion. The mixture was stirred at 40 °C for 2 h, followed by the addition of a solution of Y-silane in ethanol with a concentration of 3.21 wt % (4.065 g). After the immobilization reaction proceeded at 40 °C for 19 h, the Y-initiator-functionalized silica particles were isolated by centrifugation and re-dispersed in THF. This washing process was repeated for a total of five times. The obtained initiator particles, YI-P-3, were then dried with a stream of air flow (127.9 mg) and used for the preparation of mixed PCL/PS brush-grafted silica particles.

Synthesis of PCL Brushes from Y-Initiator-Functionalized Silica Particles by Surface-Initiated Ring Opening Polymerization of ε-Caprolactone (εCL)

The synthesis of PCL brushes from YI-P-3 by surface-initiated ROP of εCL is described in the following. Similar procedures were used to grow PCL brushes from other initiator particles.

Y-initiator functionalized silica particles (YI-P-3, 116.9 mg) and dry toluene (2.0 mL) were added into a 25 mL two-necked flask. The mixture was ultrasonicated in an ultrasonic water bath to form a dispersion. The toluene was then distilled under vacuum to remove the trace amount of water in the flask. The azeotropic distillation with dry toluene was repeated one more time, and the initiator particles were further dried at 55 °C in vacuum for 8 h. The catalyst for ROP, tin(II) 2-ethylhexanoate (Sn(Oct)$_2$, 343.3 mg, 0.847 mmol), was weighed into a 50 mL two-necked flask and dried first at room temperature via azeotropic distillation with dry toluene and then at 100 °C in vacuum for 8 h. The flasks were removed from the oil bath and allowed to cool to room temperature. Freshly dried THF (4.0 mL) was injected via a dry syringe into the flask that contained the initiator particles under the N$_2$ atmosphere. The mixture was ultrasonicated to form a homogeneous stable dispersion, which was then transferred into the catalyst flask using a syringe. The mixture was stirred at 40 °C under N$_2$ for 30 min. After the flask was cooled to room temperature, ω-undecylenyl alcohol (54.7 mg, 0.321 mmol) and ε-caprolactone (16.575 g, 145.2 mmol) were injected using syringes while stirring. The polymerization mixture was degassed by three freeze−pump−thaw cycles, and then the flask was placed in an oil bath with a preset temperature of 75 °C to start the polymerization. SEC was employed to monitor the reaction. After 13 h, the flask was removed from the oil bath and opened to air. THF (20 mL) was added into the flask to dilute the mixture and a small amount of acetic acid was added to quench the polymerization. The particles were separated by centrifugation and redispersed in THF. This washing process was repeated with THF for a total of five times, followed by drying the particles with a stream of air flow. The $M_{n,SEC}$ and polydispersity index (PDI) of the free PCL

formed from the free initiator in the polymerization were 24.3 kDa and 1.20, respectively, measured by SEC analysis using PS standards for calibration.

Synthesis of Mixed PCL/PS Brushes from PCL Brush-Grafted Silica Particles by Surface-Initiated Nitroxide-Mediated Radical Polymerization

The PCL brush-grafted silica particles (made from YI-P-3, PCL $M_{n,SEC}$ = 24.3 kDa, 0.0695 g) were dispersed in anisole (8.019 g) in a 25 mL two-necked flask using an ultrasonic water bath. The particle dispersion was then transferred into a 50 mL two-necked flask that contained 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (STEMPO, 46.6 mg, 0.178 mmol) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 1.0 mg, 0.0064 mmol), followed by the addition of styrene (10.165 g, 97.6 mmol). After the mixture was degassed by three freeze-pump-thaw cycles, the polymerization was started by placing the flask in a 120 °C oil bath and monitored by SEC. Three samples were taken from the reaction mixture during the polymerization when the molecular weight of the free polystyrene reached the desired values. The polymerization was stopped after 19.5 h. The mixed PCL/PS brush-grafted particles were isolated by centrifugation, redispersed in THF, and centrifugated again. This washing process was repeated four times to remove the physically adsorbed free polymer. The hairy particle samples were then dried with a stream of air flow.

Cleavage of PCL Brushes from Silica Particles

PCL brush-grafted silica particles made from YI-P-3 (18.1 mg, PCL $M_{n,SEC}$ = 24.3 kDa and PDI = 1.20) were dispersed in toluene (2.5 mL) in a Teflon centrifuge tube by ultrasonication, followed by the addition of tetraoctylammonium bromide (21.3 mg), hydrofluoric acid (HF, 48 ~ 51 % aqueous solution, 0.3 mL), and water (1.5 mL). After the mixture was stirred at room temperature for 2.5 h, ammonium hydroxide (25% in water) was added to neutralize the

hydrofluoric acid (until the mixture was neutral, tested by pH paper). The mixture was extracted with toluene twice (10 mL × 2), and the organic layer was separated. The organic extracts were combined and washed with water twice. After the solvent was removed using a rotary evaporator, the polymer was dried under high vacuum and characterized by SEC. The values of $M_{n,SEC}$ and PDI were 18.8 kDa and 1.39, respectively.

Molecular Weight and Molecular Weight Distribution of Grafted Polystyrene in Mixed PCL/PS Brush-Grafted Silica Particles (MB-3-4)

To determine the molecular weight and molecular weight distribution of the grafted polystyrene in the mixed brushes synthesized by surface-initiated NMRP from PCL brush-grafted silica particles, we cleaved the mixed PCL/PS brushes off the silica particles (MB-3-4) using HF, hydrolyzed the obtained polymer mixture, and then extracted polystyrene using cyclohexane. The detailed procedure is presented in the following.

Mixed PCL/PS brush-grafted silica particles (MB-3-4, $M_{n,PCL}$ = 24.3 kDa, $M_{n,PS}$ = 24.6 kDa, 20.4 mg) were dispersed in toluene (5 mL) in a Teflon centrifuge tube by ultrasonication, followed by addition of tetraoctylammonium bromide (24.6 mg) and hydrofluoric acid (HF, 48~51% aqueous solution, 1.0 mL). After the mixture was stirred at room temperature overnight, ammonium hydroxide (25% in water) was used to neutralize the mixture. The mixture was extracted with toluene (10 mL × 2) and the organic layer was separated. The organic extracts were combined, washed with water twice, and dried under high vacuum. A 30 wt % solution of sodium methoxide in methanol (52.3 mg) was added into the flask that contained the polymer mixture cleaved from MB-3-4 along with THF (2 mL) and methanol (0.15 mL). The reaction mixture was stirred at 70 °C for 6 days. After the removal of solvents, the residue was extracted

with cyclohexane and the obtained polymer was characterized by ^{1}H NMR spectroscopy and

SEC. SEC results (relative to polystyrene standards): $M_{n,SEC}$ = 25.9 kDa and $M_{w,SEC}$ = 31.9 kDa.

Results and Discussion

Synthesis of Y-Initiator-Functionalized Silica Particles

The triethoxysilane-terminated Y-initiator (Y-silane) bearing a hydroxyl group, an initiator

for ROP of cyclic esters,[15] and an NMRP initiator was synthesized by platinum-catalyzed

hydrosilylation   reaction   of   2-[4-(but-3-enyl)phenyl]-2-(2′,2′,6′,6′-tetramethyl-1′-

piperidinyloxy)ethanol (Y-silane precursor) with $HSi(OC_2H_5)_3$ (Scheme 2). The combination of

two different initiators into one molecule ensures that they are alternately distributed in the

initiator layer on the surface of silica particles, allowing the preparation of well-mixed PCL/PS

brushes. The obtained Y-silane, 2-[4-(1-triethoxysilylbutyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-

piperidinyloxy)ethanol, was purified by silica gel column chromatography using methylene

chloride as eluent, and the molecular structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy

and mass spectrometry analysis. Figure 1 shows the ^{1}H NMR spectrum of Y-silane with the

characteristic peaks assigned and labelled.

Scheme 2. Synthesis of Y-Silane by Platinum-Catalyzed Hydrosilylation of Y-Silane Precursor with Triethoxysilane ($HSi(OC_2H_5)_3$).
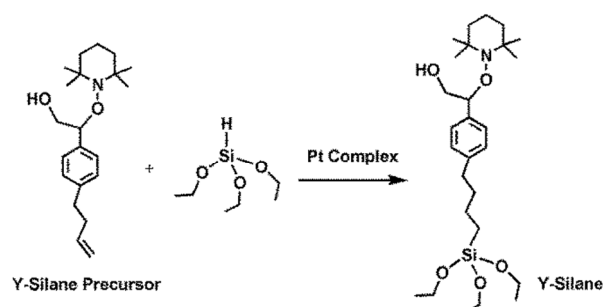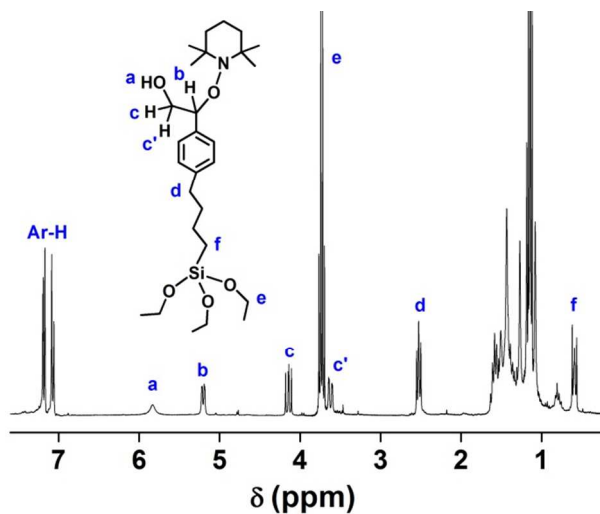
Figure 1. ^{1}H NMR spectra of 2-[4-(1-triethoxysilylbutyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethanol (Y-Silane). CDCl$_3$ was used as solvent.

The bare silica particles used in the present work were made by the Stöber process.[20] The average diameter of the bare silica particles was 157 nm, measured from transmission electron microscopy (TEM) micrographs (a typical TEM image is shown in Figure 2a). The Y-initiator was immobilized onto the surface of silica particles via an ammonia-catalyzed hydrolysis and condensation process in ethanol, similar to those reported in the literature for other triethoxysilane-terminated initiators.[10i-k,16] As shown in a previous work, the initiator density and hence the grafting density of polymer brushes can be systematically tuned by varying the mass ratio of the triethoxysilane-terminated initiator to bare silica particles in the initiator immobilization process.[10k] Using this method, we made seven batches of Y-initiator-functionalized silica particles (YI-Particles) with the mass ratio of Y-silane to silica particles ranging from 153.4% (the obtained initiator-functionalized particles denoted as YI-P-1), to 127.4% (YI-P-2), to 87.5% (YI-P-3), to 64.3% (YI-P-4), to 29.0% (YI-P-5), to 18.7% (YI-P-6), and 14.4% (YI-P-7). After the immobilization reactions proceeded at 40 °C for 19 h, the Y-initiator-functionalized silica particles were isolated by centrifugation and repeatedly washed
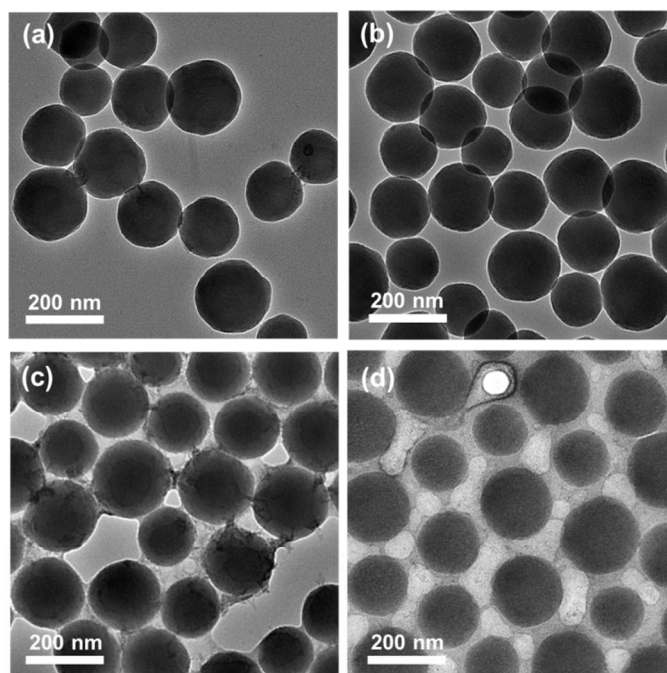
Figure 2. Transmission electron microscopy micrographs of (a) bare silica particles, (b) Y-initiator-functionalized silica particles prepared by using the mass ratio of Y-silane to bare silica particles of 87.5% in the initiator immobilization step (YI-P-3), (c) PCL brush-grafted silica particles made from YI-P-3 with PCL $M_{n,SEC}$ of 24.3 kDa, and (d) Mixed PCL/PS brush-grafted silica particles prepared from YI-P-3 with PCL $M_{n,SEC}$ of 24.3 kDa and PS $M_{n,SEC}$ of 24.6 kDa.

with THF. The YI-Particles were then characterized by thermogravimetric analysis (TGA).

Figure 3a and b shows the TGA curves of bare silica particles and YI-P-3 with the weight

retentions at 800 °C of 90.7%, and 88.5%, respectively, which are similar to our previous

observations for similarly sized bare silica particles and corresponding silica particles

functionalized with a Y-initiator containing ATRP and NMRP initiators.[10k] A typical TEM

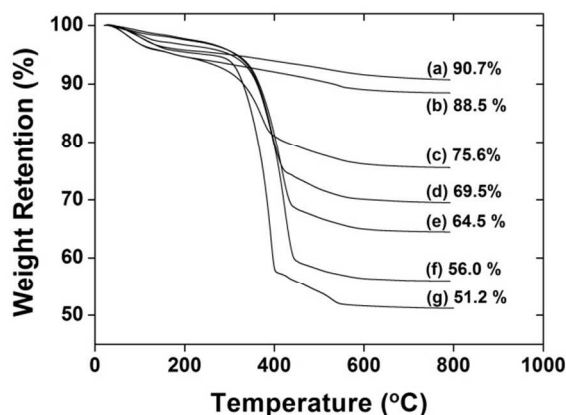micrograph of YI-P-3 is shown in Figure 2b.

Figure 3. Thermogravimetric analysis (TGA) of (a) bare silica particles, (b) Y-initiator-functionalized silica particles (YI-P-3), (c) PCL brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.3 kDa synthesized from YI-P-3, (d) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.3 kDa and PS $M_{n,SEC}$ of 7.1 kDa, (e) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.3 kDa and PS $M_{n,SEC}$ of 11.4 kDa, (f) mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.3 kDa and PS $M_{n,SEC}$ of 17.3 kDa, and (g) mixed PCL/PS brush-grafted particles with PCL $M_{n,SEC}$ of 24.3 kDa and PS $M_{n,SEC}$ of 24.6 kDa. TGA was performed in air (curves a-f) or in pure oxygen (curve g) at a heating rate of 20 ^{o}C/min from room temperature to 800 °C.

Synthesis of PCL Brushes from Y-Initiator-Functionalized Silica Particles

Ring-opening polymerization of εCL catalyzed by Sn(Oct)$_2$ is usually carried out at relatively high temperatures, typically around 120 °C.[15] This condition cannot be applied to the synthesis of PCL brushes from Y-initiator-functionalized silica particles because of the thermally induced decomposition of the NMRP initiator. Therefore, we focused on the growth of PCL brushes by ROP of εCL at 75 °C, at which the TEMPO moiety has been proven to be stable.[10a-d] Our initial attempt in the synthesis of PCL brushes from Y-initiator particles in dry THF at 75 °C using Sn(Oct)$_2$ as catalyst and ω-undecylenyl alcohol as the free initiator produced relatively low molecular weights even after prolonged polymerization time and broad molecular weight distributions. The reproducibility was also poor. Recognizing that the moisture in the reaction system could affect the ROP, we azeotropically distilled freshly dried toluene twice from YI-

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particles to remove water and further dried the particles under high vacuum at 55 °C for 8 h. The catalyst for ROP of εCL, tin(II) 2-ethylhexanoate, was also dried by azeotropic distillation with toluene and then under high vacuum at 100 °C for 8 h. Moreover, we increased the amount of the catalyst with respect to the free initiator from a molar ratio of ~ 1 : 1 to ~ 2.5 : 1.[21] We found that this condition reproducibly yielded PCL polymers with $M_{n,SEC}$ of ~ 25 kDa (relative to polystyrene standards) and polydispersity indexes of ≤ 1.20.

Using this condition, we carried out a surface-initiated ROP of εCL to grow PCL brushes from YI-P-3 in THF at 75 °C in the presence of a free initiator, ω-undecylenyl alcohol. The molar ratios of εCL : ω-undecylenyl alcohol : Sn(Oct)$_2$ = 452 : 1.0 : 2.6. After the polymerization proceeded for 13 h, the viscosity of the reaction mixture was high and the stir bar stopped moving. The flask was removed from the oil bath and the mixture was diluted with THF, and the particles were isolated by centrifugation, re-dispersed in THF, and centrifugated again. This washing process was repeated for a total of five times to remove the physically adsorbed PCL. The $M_{n,SEC}$ and PDI of the free PCL formed from ω-undecylenyl alcohol was 24.3 kDa and 1.20 (Figure 4a), relative to polystyrene standards. The narrow PDI indicated that the polymerization was controlled. The actual molecular weight $M_{n,abs}$ of the free PCL determined by SEC using a multi-angle light scattering detector was 16.0 kDa, using a dn/dc value of 0.0750 for PCL in THF.[19] Thermogravimetric analysis showed that the weight retention of the obtained PCL brush-grafted silica particles at 800 °C was 75.6 %, much lower than that of YI-P-3. From the TEM micrograph (Figure 2c), the PCL brushes can be clearly seen. By using the size of silica particles (157 nm), TGA data, and the $M_{n,abs}$ of PCL, and assuming that the density of silica particles was identical to that of bulk SiO$_2$ (2.07 g/cm^3)[10k] and the molecular weights of the

grafted PCL and the free PCL are the same, the grafting density of PCL (σ_{PCL}) was calculated to
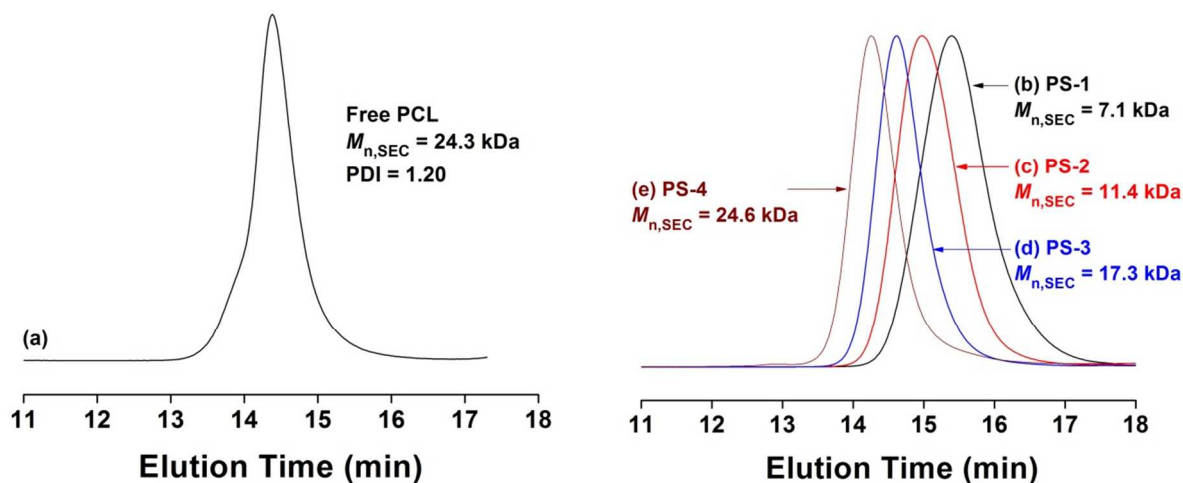
be 0.40 chains/nm^2.[22]

Figure 4. Size exclusion chromatography analysis of (a) the free PCL, formed from the free initiator in the synthesis of PCL brush-grafted silica particles from YI-P-3, and the free polystyrene formed from the free initiator STEMPO in the synthesis of mixed PCL/PS brush-grafted silica particles from PCL brush-grafted silica particles by NMRP of styrene at 5.0 h (b), 8.3 h (c), 13.0 h (d), and 19.5 h (e).

Synthesis of Mixed PCL/PS Brushes from PCL Brush-Grafted Silica Particles by

Surface-Initiated NMRP

The PCL brush-grafted silica particles made from YI-P-3 with PCL $M_{n,SEC}$ of 24.3 kDa were

then used for the synthesis of mixed PCL/PS brushes by surface-initiated NMRP of styrene. The

polymerization was carried out in anisole at 120 °C with addition of a free initiator, 1-phenyl-1-

(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane (STEMPO), and a small amount of free radical

TEMPO (3.6 mol% with respect to STEMPO), and was monitored by SEC. Three samples were

taken at 5.0 h, 8.3 h, and 13.0 h before the reaction was stopped at 19.5 h. The hairy particles

were separated by centrifuge and repeatedly washed; the free PS polymers were analyzed by

SEC.

Figure 4b-e shows the GPC traces of four free PS polymers, respectively. With the increase of the polymerization time from 5.0 to 8.3, to 13.0, and 19.5 h, the peak gradually shifted to the high molecular weight side. The $M_{n,SEC}$ of PS increased from 7.1 kDa (PS-1; the corresponding mixed PCL/PS brush-grafted particle sample designated as MB-3-1), to 11.4 kDa (PS-2; the particles designated as MB-3-2), to 17.3 kDa (PS-3; the particles designated as MB-3-3), and 24.6 kDa (PS-4; the particles designated as MB-3-4). The PDI decreased from 1.32 (PS-1) to 1.23 (PS-2) to 1.18 (PS-3 and PS-4), indicating that the polymerization was controlled. The mixed PCL/PS brush-grafted silica particles were characterized by TGA. As can be seen from Figure 3d-g, the weight retention of mixed PCL/PS brush-grafted silica particles at 800 ^{o}C decreased with the increase of PS $M_{n,SEC}$, from 69.5% for MB-3-1, to 64.5% for MB-3-2, to 56.0% for MB-3-3, and 51.2% for MB-3-4. A further analysis showed that the amount of the grafted polymers increased nearly linearly with the PS molecular weight (Figure 5), suggesting that the surface-initiated NMRP is also controlled. Figure 2d shows a typical TEM micrograph of MB-3-4. Clearly, the interstitial space among silica particles was filled with the grafted polymers; compared with the corresponding PCL brush-grafted particles (Figure 2c), the interparticle distance became larger, consistent with the increased polymer content in the hairy particles.

By using the bare silica particle size, TGA data, and the molecular weights of free PS, and assuming that the density of silica particles was identical to that of bulk SiO_2 (2.07 g/cm^3) and the values of M_n of the grafted PS and the free PS are the same, the grafting densities of PS in four mixed brush samples were calculated.[22] They were 0.71, 0.74, 0.90, and 0.83 chains/nm^2 for MB-3-1, MB-3-2, MB-3-3, and MB-3-4, respectively. The grafting density increased slightly with the polymerization time, similar to our previous observation in the study of the effect of the
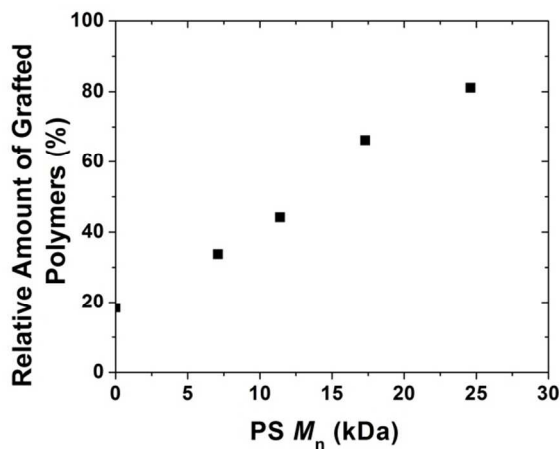
Figure 5. The amount of the grafted polymers relative to the residual silica at 800 °C versus the PS molecular weight determined by SEC. The relative amount of the grafted polymers was calculated using the equation $[(1 - W_{HP})/W_{HP} - (1 - W_{YI-P-3})/W_{YI-P-3}] \times 100$, where W_{HP} and W_{YI-P-3} represent the percent weight retention at 800 °C of hairy particles and Y-initiator particles (YI-P-3), respectively, corrected for the weight retention difference at 100 °C, which was presumably from the adsorbed water or other volatiles.

chain length disparity on microphase separation of mixed homopolymer brushes grafted on silica particles.[10h,i] This is likely because that not all alkoxyamine moieties on the surface of silica particles successfully initiated the polymerization at the same time, leading to a lower initiator efficiency at the beginning of the polymerization. We previously observed in the kinetics study of the TEMPO-mediated NMRP of styrene that the initial polymerization was slower than expected.[10d] Note that the grafting densities of PS in these mixed brush samples are significantly higher than that of PCL (0.40 chains/nm^2). This is likely because the initiating radicals in NMRP are generated by thermal decomposition of the TEMPO moiety, which is a unimolecular process,[23] while the initiation in ROP involves the formation of Sn-alkoxide on the surface and the insertion of monomer molecules.[15] Consequently, the surface-initiated ROP is more sensitive than NMRP to the steric hindrance presented by the confined geometry on the surface of silica particles and the inherent heterogeneity of the particle surface and the initiator layer.

Tuning Overall Grafting Density of Mixed PCL/PS Brushes - Effect of Different Mass Ratios of Y-Silane to Bare Silica Particles Used in the Initiator Immobilization Step

We previously reported that the overall grafting density of mixed homopolymer brushes synthesized by sequential ATRP and NMRP can be tuned by changing the mass ratio of the initiator to bare silica particles in the initiator immobilization process.[10k] In the present work, we prepared a series of Y-initiator-functionalized silica particles from the same batch of bare silica particles using different mass ratios of Y-silane to bare particles: 153.4% (YI-P-1), 127.4% (YI-P-2), 87.5% (YI-P-3), 64.3% (YI-P-4), 29.0% (YI-P-5), 18.7% (YI-P-6), and 14.4% (YI-P-7). Using the same procedure for the synthesis of mixed PCL/PS brushes from YI-P-3, we carried out surface-initiated ROP of ε-CL and NMRP of styrene sequentially from other initiator-functionalized silica particles. The values of $M_{n,SEC}$ of PCL and PS (relative to polystyrene standards) were targeted at ~ 25 kDa. The obtained PCL brush- and mixed PCL/PS brush-grafted silica particles were characterized by TGA, and the absolute molecular weights of free PCL were measured by SEC with a multiangle light scattering detector. The data are summarized in Table 1. Using the same assumptions that we made in the calculation of grafting densities of polymer brushes prepared from YI-P-3, we estimated the grafting densities of PCL (σ_{PCL}) and PS (σ_{PS}) in each mixed brush particle sample (Table 1) as well as the overall grafting density ($\sigma_{overall} = \sigma_{PCL} + \sigma_{PS}$). For comparison, the data for MB-3-4 are also included in Table 1.

As can be seen from Table 1, there is a general trend that the overall grafting density decreased with the decrease of the mass ratio of Y-silane to bare silica particles in the initiator immobilization step, from above 1.0 chains/nm^2 in MB-1, -2, and -3 to 0.40 chains/nm^2 for MB-7, though the $\sigma_{overall}$ of MB-1 (1.06 chains/nm^2) was slightly lower than those of MB-2 (1.24 chains/nm^2) and MB-3 (1.23 chains/nm^2). The individual grafting densities of PCL and PS also

Table 1. Characterization Data for Mixed PCL/PS Brush-Grafted Silica Particles Synthesized by Sequential Surface-Initiated ROP and NMRP from Y-Initiator-Functionalized Particles Prepared by Using Different Mass Ratios of Y-Silane to Bare Silica Particles in the Initiator-Immobilization Step

Sample No	Initiator Particles	Mass Ratio of Y-Silane to Bare Particles [a]	PCL $M_{n,SEC}$ and PDI [b]	PCL $M_{n,abs}$ [c]	PS $M_{n,SEC}$ and PDI [b]	σ_{PCL}, σ_{PS} (chains/nm^2)[d]	$\sigma_{overall}$ (chains/nm^2)
MB-1	YI-P-1	153.4%	25.8 kDa, 1.14	17.0 kDa	24.5 kDa, 1.16	0.37, 0.69	1.06
MB-2	YI-P-2	127.4%	25.4 kDa, 1.14	16.7 kDa	25.2 kDa, 1.17	0.38, 0.86	1.24
MB-3-4	YI-P-3	87.5%	24.3 kDa, 1.20	16.0 kDa	24.6 kDa, 1.18	0.40, 0.83	1.23
MB-4	YI-P-4	64.3%	24.0 kDa, 1.20	16.0 kDa	24.0 kDa, 1.15	0.25, 0.53	0.78
MB-5	YI-P-5	29.0%	25.6 kDa, 1.17	16.8 kDa	24.3 kDa, 1.16	0.14, 0.53	0.67
MB-6	YI-P-6	18.7%	27.1 kDa, 1.19	18.7 kDa	24.2 kDa, 1.16	0.19, 0.45	0.64
MB-7	YI-P-7	14.4%	24.2 kDa, 1.14	16.1 kDa	23.8 kDa, 1.14	0.15, 0.25	0.40

[a] The mass ratio of the triethoxysilane-terminated Y-initiator (Y-silane) to the bare silica particles in the initiator immobilization step. [b] Molecular weight ($M_{n,SEC}$) and polydispersity index (PDI) were determined by using SEC relative to polystyrene standards. [c] PCL absolute molecular weight ($M_{n,abs}$) determined by SEC with a multi-angle light scattering detector. [d] The grafting densities were calculated using the size of bare silica particles (157 nm), TGA data, and the molecular weights of free polymers ($M_{n,abs}$ for PCL and $M_{n,SEC}$ for PS), and assuming that the density of silica particles was identical to that of bulk SiO_2 (2.07 g/cm^3) and the molecular weights of the grafted PCL and the free PCL are the same.

exhibited a similar trend, but there were some irregularities, particularly σ_{PCL}, which is likely because ROP is more sensitive to the polymerization conditions and the possible impurities in the reaction systems. Similar to MB-3-4, the PCL grafting density was noticeably smaller than that of the corresponding PS; in most cases, σ_{PCL} was only about half of σ_{PS} or even smaller. Overall, Table 1 showed that the overall grafting density can be tuned by changing the mass ratio of Y-silane to bare silica particles.

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Molecular Weight and Molecular Weight Distribution of the Grafted PCL on Silica Particles

Many researchers have reported that the molecular weights and molecular weight distributions of polymer brushes grafted on (nano)particles synthesized by surface-initiated "living"/controlled (radical) polymerization were essentially the same as those of the free polymers formed from the free initiators.[10d,16,24] To measure the molecular weight and molecular weight distribution of the grafted PCL, we cleaved the PCL brushes from silica particles (made from YI-P-3) using hydrofluoric acid (HF) to etch the silica core in an aqueous/toluene biphasic system in the presence of a phase transfer catalyst, tetraoctylammonium bromide. The reaction was allowed to proceed at room temperature for 2.5 h, and then the mixture was neutralized with 25% ammonium hydroxide in water. The cleaved polymer was collected and characterized by SEC (Figure 6). The peak of the cleaved PCL overlapped to a great extent with that of the free PCL, but it was broader. The $M_{n,SEC}$ and PDI (relative to polystyrene standards) were 18.8 kDa and 1.39, respectively, in contrast to those of the free PCL ($M_{n,SEC} = 24.3$ kDa and PDI = 1.20). It is unclear why the molecular weight distribution of the grafted PCL is slightly broader. We suspect that it might be caused by the metal-catalyzed transesterification reaction within the polymer brush layer because of the high concentration of the ester bonds. The undesired transesterification reaction among the free growing PCL chains in the bulk solution appeared to be suppressed as indicated by the narrower PDI. Because we did not do the cleavage experiments for other PCL brush-grafted silica particles, to be consistent, we still used the molecular weights of free polymers in the calculation of PCL grafting densities as shown in Table 1.
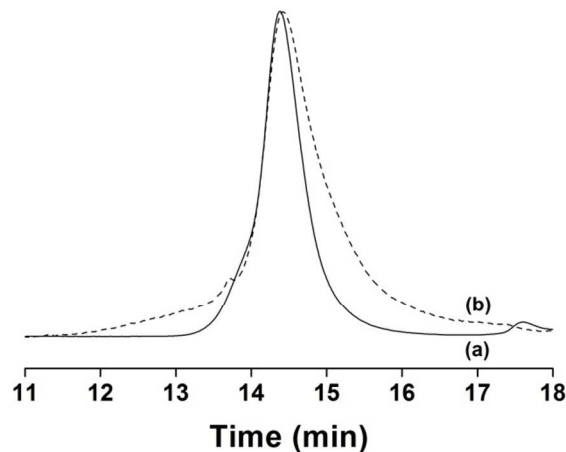
Figure 6. Size exclusion chromatography traces of (a) the free PCL ($M_{n,SEC}$ of 24.3 kDa and PDI of 1.20) formed from the free initiator in the synthesis of PCL brushes from YI-P-3 (solid line) and (b) the grafted PCL cleaved from the corresponding PCL brush-grafted silica particles.

Molecular Weight and Molecular Weight Distribution of the Grafted Polystyrene Cleaved from the Mixed PCL/PS Brush-Grafted Silica Particles

We also compared the molecular weight and molecular weight distribution of the grafted PS in the mixed PCL/PS brushes with those of the free PS formed from the free initiator. The mixed PCL/PS brush-grafted silica particles with PCL $M_{n,SEC}$ of 24.3 kDa and PS M_n of 24.6 kDa (MB-3-4) were etched with HF in a aqueous/toluene biphasic system. The collected polymer mixture was treated under a basic condition in a mixed solvent of THF and methanol to hydrolyze the PCL. The volatiles were removed and the PS was extracted from the solid residue with cyclohexane. Figure 7 shows the SEC traces of the cleaved PS and the corresponding free PS; the $M_{n,SEC}$ of the cleaved PS was 25.9 kDa, reasonably close to that of the free polymer ($M_{n,SEC}$ = 24.6 kDa). This confirmed that the surface-initiated NMRP was controlled. However, the two curves did not superimpose each other entirely, though the two samples were run on the same SEC system back to back; there was a small shift, reflected by the slightly higher $M_{n,SEC}$ of the cleaved PS. ^{1}H NMR spectroscopy analysis indicated the absence of ester bonds of PCL.
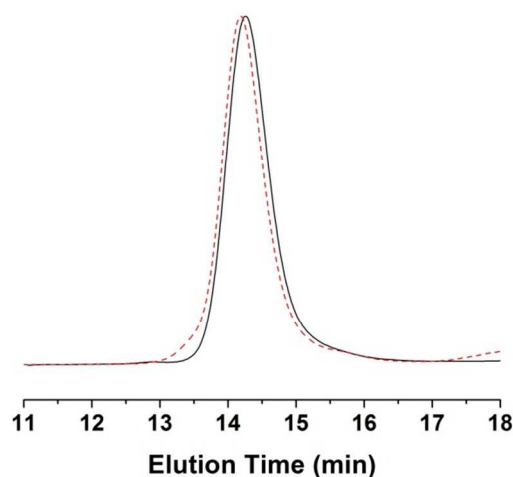
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Figure 7. Size exclusion chromatography traces of the free PS ($M_{n,SEC}$ = 24.6 kDa, solid line) and the PS cleaved from MB-3-4 ($M_{n,SEC}$ = 25.9 kDa, dashed line).

Conclusions

Mixed PCL/PS brushes were grown from silica particles functionalized with a Y-initiator bearing a hydroxyl group and a TEMPO moiety by sequential ROP of εCL at 75 °C using Sn(Oct)$_2$ as catalyst and NMRP of styrene at 120 °C. Both surface-initiated polymerizations were carried out in the presence of a free initiator. By carefully drying Y-initiator-functionalized silica particles and catalyst Sn(Oct)$_2$, PCL with $M_{n,SEC}$ values of ~ 25 kDa and narrow polydispersities (PDI ≤ 1.20) can be reproducibly synthesized by ROP. The grafting density of PCL was found to be lower than that of PS, likely because of the different initiation mechanisms of ROP and NMRP. The overall grafting density of mixed PCL/PS brushes can be tuned from 1.24 chains/nm^2 to 0.40 chains/nm^2 by changing the mass ratio of the triethoxysilane-terminated Y-initiator to bare silica particles in the initiator immobilization step. Cleavage experiments showed that the molecular weights of the grafted polymers were close to those of the free

polymers formed from the free initiators. The method reported can be extended to the synthesis of mixed brushes containing other chemically or biologically degradable polymers.

Acknowledgements

Electronic Supplementary Information Available: TGA data of other Y initiator-functionalized silica particles and corresponding hairy particles.

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22.　The difference between weight retentions of Y-initiator-functionalized silica particles and polymer brush-grafted silica particles at 100 °C is presumably caused by the water or other volatiles. This difference was taken into consideration in the calculation of grafting densities of polymer brushes by vertically shifting the curves to the same position – the higher weight retention at 100 °C as described in the following paper: Horton, J. M.; Bao, C. H.; Bai, Z. F.; Lodge, T. P.; Zhao, B. *Langmuir* **2011**, *27*, 13324-13334.

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Graphical Abstract

Synthesis of Mixed Poly(ε-caprolactone)/Polystyrene Brushes from Y-Initiator-Functionalized Silica Particles by Surface-Initiated Ring-Opening Polymerization and Nitroxide-Mediated Radical Polymerization

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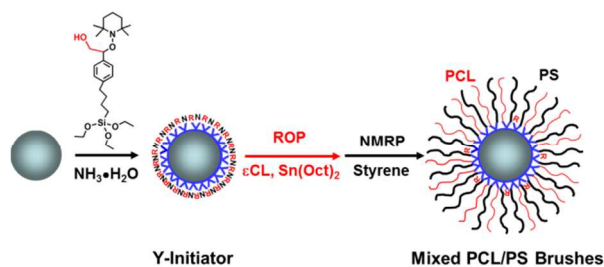
This article reports the synthesis of mixed poly(ε-caprolactone)/polystyrene brushes by sequential surface-initiated ring-opening polymerization (ROP) of ε-caprolactone (εCL) and nitroxide-mediated radical polymerization (NMRP) of styrene from Y-initiator-functionalized silica particles.