Synthesis and Characterization of Silicon-Containing Block Copolymers from Nitroxide-Mediated Living Free Radical Polymerization

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ABSTRACT: High etch resistance to oxygen plasma for silicon-containing polymers, and the high thermal and mechanical robustness of the etching product, silicon oxide, make it attractive to design novel siliconcontaining block copolymers for direct patterning of nanostructures on a desired substrate. Here, we report the synthesis of a series of block copolymers from silicon-containing styrenic monomers and styrene (St) or 4-acetoxystyrene (AcOSt) using living free radical polymerization via a α -hydride nitroxide-mediated unimer (α -H unimer). Controlled polymerization with narrow polydispersity (PDI < 1.25) and high yield (up to 80%) were achieved by optimizing polymerization time and temperature, addition of solvents, use of rate accelerants, monomer addition sequence, and solvent polarity. Block copolymer morphologies before and after O₂ plasma were studied using small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). When silicon-containing block formed the major phase and silicon concentration was greater than 12 wt %, the morphology and domain size were maintained after O₂ plasma.

Introduction

The spontaneous self-assembly of block copolymers into nanometer domains is simple, fast, and low cost compared to conventional lithography. The accessibility to a wide range of periodic structures with feature size less than 30 nm makes block copolymers especially attractive as templates for nanopatterning.^{1–5} However, steps such as selective ozonolysis or staining with heavy metals of a particular block^{1,2} to increase etch selectivity between blocks is necessary for pattern transfer of the nanostructures from the block copolymers. In addition, an intermediate layer, such as SiN, is always required for successful pattern transfer to a substrate of interest. In general, the use of organic block copolymers limited at high temperatures because of low thermal/mechanical stabilities. Thus, direct pattering of III-V semiconductors on block copolymer templates is nearly impossible due to the high crystal growth temperatures (>600 °C).

In comparison to other block copolymers, siliconcontaining block copolymers may be suitable as a template for direct patterning of nanostructures without a complicated multiple-step process. When exposed to oxygen plasma, the silicon-containing polymers are oxidized to silicon oxide, whose high thermal and mechanical stability has made it a long-time dielectric insulator in microchip fabrication. The high etch resistance to oxygen plasma compared to organic polymers makes silicon-containing polymers favorable as bilayer resists to pattern high aspect ratio structures^{6–9} as well as to create nanoporous ceramic thin films with a

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variety of morphologies.^{10,11} The use of silicon-containing thin film as a template may provide an alternative approach to broaden the application of block copolymers for nanopatterning. Block copolymers of polystyrene and hydrosiloxane-modified poly(diene) have been demonstrated as bilayer photoresists that provide high sensitivity and etch selectivity.^{7,12,13} Thus, the possibility of combining photolithographic groups and silicon-containing groups in block copolymers offers a new route to pattern hierarchical nanostructures.

The recent advances in controlled living free radical polymerization (LFRP),¹⁴ including nitroxide-mediated radical polymerization (NMRP),^{15–17} atom transfer radical polymerization (ATRP),^{18,19} and reversible additionfragmentation chain transfer (RAFT),20-23 make it possible to design and synthesize a variety of block copolymers with novel functionalities. Here we report (i) the synthesis of narrow dispersed silicon-containing homopolymers from three kinds of silicon-containing styrenic monomers, including 4-(pentamethyldisilyl)styrene (Si₂St), 4-(bis(trimethylsilyl)methyl)styrene (Si₂-CSt), and 4-(pentamethyldisiloxymethyl)styrene (OSi₂-St), each containing two silicon atoms to enhance the etch selectivity, and (ii) the synthesis of block copolymers from silicon-containing styrenic monomers with styrene and photosensitive acetoxystyene by sequential monomer addition using an α -hydride nitroxide unimer. Since many silicon-containing monomers are known to be temperature sensitive, we kept the reaction at 100 °C to obtain narrow dispersed silicon-containing homopolymers or block copolymers. To increase the polymerization conversion and shorten the reaction time, we introduced acetic anhydride as a rate accelerating agent. The solvent polarity and monomer addition sequence were found critical in controlling the copolymerization. The synthesized block copolymers showed cylindrical and lamellae structures as revealed by small-

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Table 1. Homopolymerization Conditions of Silicon-Containing Monomers

			GPC^c				
entry	$monomer^a$	feed ratio ^{b} ([M] ₀ /[I] ₀)	time (h)	temp (°C)	yield (%)	$\overline{M_{ m n} imes 10^{-3}}$	PDI
1	${ m Si}_2{ m St}$	50	16	130	86	gel^{f}	NA ^f
2	Si_2St	50	16	100	47	5.6	1.13
3	${ m Si}_2{ m St}$	60	60	100	74	8.7	1.15
4^d	${ m Si}_2{ m St}$	60	64	100	76	9.7	1.14
5	Si_2CSt	60	64	100	44	5.6	1.09
6	Si_2CSt	60	128	100	61	7.8	1.07
7	OSi_2St	60	34	128	78	11.9	1.15^{g}
8	OSi_2St	60	64	100	57	7.5	1.08
9	OSi_2St	60	128	100	77	10.4	1.08
10^e	OSi_2St	60	64	100	81	12.1	1.07

^{*a*} Abbreviations of monomers: Si₂St, 4-(pentamethyldisilyl)styrene; Si₂CSt, 4-(bis(trimethylsilyl)methyl)styrene; OSi₂St, 4-(pentamethyldisiloxymethyl)styrene; ^{*b*} Feed ratio for the homopolymerization; $[M]_0/[I]_0 = [monomer]_0/[initiator]_0 (mol/mol)$. ^{*c*} The number- and weight-average molecular weights (M_n and M_w) and polydispersity (PDI = M_w/M_n) were determined by GPC from refractive index (RI) detector in a flow rate of 1.0 mL/min in THF at 40 °C. Narrow dispersed polystyrenes were used as standards for universal calibration. ^{*d*} Dichlorobenzene (DCB) was added as a solvent (10 wt % of monomer). Otherwise, polymerization was carried out in bulk. ^{*e*} Acetic anhydride (AA) was added (1.5 equiv to initiator) to accelerate the reaction. ^{*f*} GPC was not measured due to gel formation. ^{*g*} GPC trace indicated a shoulder at higher molecular weight region.

angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). When silicon-containing block formed the major phase and silicon concentration was greater than 18 wt %, the morphology and domain size were maintained after exposure to O_2 plasma for more than 10 min.

Experimental Section

Chemicals. Unless noted, all chemicals were purchased from Aldrich, Inc. and used as received. Anhydrous tetrahydrofuran (THF, 99.9%), 1,2-dichlorobenzene (DCB, 99%), and N,N-dimethylformamide (DMF, 99.8%) were used in experiments. N-(1'-Methylbenzyloxy)-2',2',6',6'-tetramethylpiperidine (TEMPO unimer) was purchased from Binrad Industries, Inc., and vacuum-dried before use.

2,2,5-Trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (α -H Unimer). An α -hydride nitroxide-mediated unimolecular initiator (denoted as α -H unimer) was synthesized following the literature²⁴ with minor modification. The coupling reaction between 2,2,5-trimethyl-3-(1-phenylethoxy)-4phenyl-3-azahexane-3-nitroxide (α -H radical) and styrene in the presence of the Jacobsen's catalyst [N,N'-bis(3,5-di-*tert*butylsalicylidene)-1,2-cyclohexanediaminemanganese(III) chloride] was carried out under oxygen bubbling.²⁵

4-(Pentamethyl disilyl)styrene (Si₂St). Si₂St was synthesized according to the literature.²⁶ The purification was carried out by column chromatography (eluent: hexane) and vacuum distillation (bp 51–52 °C at 2.5×10^{-4} Torr). The overall yield was 51.8%.

4-(Bis(trimethylsilyl)methyl)styrene (Si₂CSt). Bis(trimethylsilyl)chloromethane (24.9 g, 128 mmol) was added to activated magnesium tunings (9.72 g, 400 mmol) in THF (25.0 mL) with good agitation under reflux conditions in a nitrogen atmosphere. After the completion of addition, the reaction mixture was refluxed for 2 h and transferred via cannula into an additional funnel attached to a second round-bottom flask. The Grignard reagent was added dropwise over 20 min into the solution of p-bromostyrene (21.0 g, 115 mmol) and tetrakis-(triphenylphosphine)palladium²⁷ (0.786 g, 0.680 mmol) as a catalyst in THF (100 mL). After the addition, the reaction mixture was refluxed for 12 h and decomposed with water. The product was extracted with ether, dried with magnesium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (eluent: hexane) and vacuum distillation (bp 64–65 °C at 3.6 \times 10⁻⁴ Torr). The overall yield was 20.0 g (66.3%). IR (NaCl, ν , cm⁻¹): 2954 (C– H, vinyl), 1627 (C=C, vinyl), 1604 (C=C, Ar), 1249 (Si-CH₃). ¹H NMR (δ, ppm): 7.23 (d, 2H, Ar-H), 6.87 (d, 2H, Ar-H), 6.65 (dd, 1H, $CH_2 = CH - Ar$), 5.64 (d, 1H, $CH_2 = CH$), 5.11 (d, 1H, CH₂=CH), 1.50 (s, 1H, ArCHSi₂), 0.01 (s, 18H, Si(CH₃)₃). $^{13}\mathrm{C}$ NMR ($\delta,$ ppm): 143.15, 136.86, 132.80, 128.79, 125.99, 111.57, 29.66, 0.11.

4-(Pentamethyldisiloxymethyl)styrene (OSi₂St). The Grignard reagent was prepared in the way similar to that of Si₂CSt, using magnesium turnings (21.9 g, 900 mmol) in THF (40 mL) and chloromethylpentadisiloxane (39.3 g, 200 mmol). It was then added dropwise to the solution of *p*-bromostyrene (30.2 g, 165 mmol) and tetrakis(triphenylphosphine)palladium (1.04 g, 0.900 mmol) in THF (120 mL) over 30 min, followed by additional reflux for 12 h and decomposition by water. The product was extracted with ether, dried with magnesium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (eluent: hexane) and vacuum distillation (bp 52–54 °C at 3.1 \times 10 $^{-4}$ Torr). The overall yield was 18.1 g (41.5%). IR (NaCl, v, cm⁻¹): 2958 (C-H, vinyl), 1627 (C=C, vinyl), 1608 (C=C, Ar), 1253 (Si-CH₃), 1060 (Si–O). ¹H NMR (δ , ppm): 7.27 (d, 2H, Ar–H), 6.99 (d, 2H, Ar-H), 6.67 (dd, 1H, CH2=CH-Ar), 5.67 (d, 1H, CH2= CH), 5.14 (d, 1H, CH₂=CH), 2.11 (s, 2H, ArCH₂Si), 0.05 (s, 6H, CH₂Si(CH₃)₂O), 0.04 (s, 9H, OSi(CH₃)₃). ¹³C NMR (δ , ppm): 139.44, 136.88, 133.59, 128.42, 126.03, 111.92, 28.52, 1.84, -0.06.

Synthesis of Silicon-Containing Macroinitiators. Preparation of Poly(4-(pentamethyldisilyl)styrene) (Poly(Si₂St), Entry 4 in Table 1). As an example, a mixture of α -H unimer (0.048 g, 0.15 mmol), Si₂St (2.11 g, 9.0 mmol), and DCB (0.16 mL, 10 wt % of the total feed) was first degassed by three freeze/thaw cycles and placed in a preheated oil bath set at 100 °C with stirring. After 64 h, the mixture in the reaction flask became solidified and could no longer be stirred. Further reaction did not seem to increase the molecular weight substantially. Thus, the reaction was quenched with an ice bath at 64 h. The mixture was dissolved in dichloromethane and reprecipitated into methanol. The resulting precipitate was filtered off and dried under vacuum at room temperature, resulting in desired macroinitiator, poly(Si₂St), as white solid 1.62 g (yield of 76.4%); $M_n = 9700$ and PDI = 1.14.

Preparation of Poly(4-(bis(trimethylsilyl)methyl)styrene) (Poly(Si₂CSt), Entry 6 in Table 1). The procedure was similar to that of poly(Si₂St) with yield of 60.9%, M_n = 7800, and PDI = 1.07. ¹H NMR (δ, ppm): 6.53-6.26 (br, m, 4H), 1.79 (br, s, 1H), 1.31 (br, s, 3H), -0.01 (br, s, 18H). ¹³C NMR (δ, ppm): 139.10, 127.89, 126.98, 39.82, 28.62, 0.30.

Preparation of Poly(4-(pentamethyl disiloxymethyl)styrene) (Poly(OSi₂St), Entry 9 in Table 1). The procedure was similar to that of poly(Si₂St) with yield of 76.8%, $M_n =$ 10 400, and PDI = 1.08. ¹H NMR (δ, ppm): 6.71–6.27 (br, m, 4H), 2.01 (br, s, 2H), 1.79 (br, s, 1H), 1.34 (br, s, 2H), 0.03 (br, s, 15H). ¹³C NMR (δ, ppm): 135.81, 127.64, 125.58, 40.42, 28.01, 1.94, -0.05.

Synthesis of Silicon-Containing Block Copolymers. Preparation of Poly{styrene-b-[4-(pentamethyldisilyl)styrene]} (Poly(St-b-Si₂St), Entry 11 in Table 4). Polystyrene (PSt) macroinitiator was synthesized in the way similar to that of poly(Si₂St). 0.340 g of PSt (0.097 mmol; $M_n = 3500$, PDI = 1.17) was first dissolved in DMF (0.52 g, 20 wt % of total reactants) and Si₂St (2.27 g, 9.71 mmol; ca. 3 equiv to PSt) was added as second monomer with stirring under nitrogen until a clear solution was formed. The mixture was degassed by three freeze/thaw cycles before immersing into preheated oil bath at 100 °C. After stirring for 64 h, the reaction was quenched by an ice bath to stop the polymerization. The mixture was dissolved in dichloromethane and reprecipated into methanol. The precipitate was filtered off and dried under the vacuum at room temperature to yield 1.89 g (72.6%) of block copolymer, $M_n = 18700$ and PDI = 1.07.

Polymer Characterizations. The infrared (IR) measurements were made using a Horiba FT-210 spectrophotometer. Chemical compositions of the block copolymers and their degree of polymerization (DP_n) were calculated from ¹H NMR (360 MHz) and ¹³C NMR (90 MHz) spectra using a Bruker AM-360 MHz NMR spectrometer. Deuterated chloroform (CDCl₃) was used as a solvent at room temperature. The number- and weight-average molecular weights $(M_n \text{ and } M_w)$ and polydispersity (PDI = M_w/M_n) were determined by gel permeation chromatography (GPC) using a Viscotek TDA-300 with three columns (Waters Styragel HR-3 (×2) and Viscotek GMH-H (×1), molecular weight range of 30-500K and >50 M, respectively, RI detector) at a flow rate of 1.0 mL/min in THF at 40 °C. Narrow dispersed polystyrenes were used as standards for universal calibration. The glass-transition temperatures $(T_{\sigma}s)$ were studied by a Perkin-Elmer DSC-7 at a heating rate of 10 °C/min under nitrogen and calibrated by indium. The midpoint of the change in heat capacity during the second heat was reported as $T_{\rm g}$ in our experiments. Monomer density was estimated by measuring average weight in 1 mL at 25 °C.

Small-Angle X-ray Scattering (SAXS). A 2D SAXS experiment was performed at synchrotron X-ray beamline $\times 3A2$ in the National Synchrotron Light Source, Brookhaven National Laboratory. The wavelength of the X-ray beam was 0.154 nm. The beam center was calibrated using silver behenate with the primary reflection peak at 1.076 nm⁻¹. Typical data acquisition time was 1 min. 2D images were obtained using Fuji imaging plates equipped with a Fuji BAS-2500 scanner. One-dimensional (1D) SAXS curves were obtained by integration of the corresponding 2D SAXS patterns.

Transmission Electron Microscopy (TEM). TEM experiments were performed on a Philips EM300 at an accelerating voltage of 80 kV. Thin sections with a thickness of \sim 75 nm were obtained with a diamond knife at room temperature on a Leica Ultracut UCT microtome. The thin sections, floating on a water boat, were then collected onto 400 mesh TEM grids and dried at room temperature for 3 days. Brightfield TEM images were directly obtained without staining since silicon-containing polymers provided enough electron density contrast with respect to hydrocarbon chains. The TEM grids with thin sections were treated with O₂ plasma for various amount of time for different samples.

Results and Discussion

The ability to transfer block copolymer morphologies to the underlying substrate makes it attractive to pattern nanometer-sized features beyond the capability of conventional lithography. However, the poor etch selectivity between blocks and low thermal/mechanical stability at high temperatures has limited the use of organic block copolymers for direct pattern transfer nanostructures into semiconductors. Silicon-containing polymers have been used in lithography due to their high etching resistance under oxygen plasma compared to organic moieties (C, H, O, N, etc.). To take advantage of the high etch resistance and high thermal/mechanical stability of silicon oxide, we synthesized a series of block copolymers from silicon-containing styrenic monomers and styrene (St) or 4-acetoxystyrene (AcOSt) using nitroxide-mediated living free radical polymerization.

Synthesis of Silicon-Containing Styrenic Monomers. Large etch selectivity in organic materials can





be achieved when 10 wt % or more of silicon is introduced.²⁶ Thus, three kinds of silicon-containing styrenic monomers with each containing two silicon atoms were selected and synthesized (Scheme 1). Si_2St was synthesized following the literature procedure. Both Si₂CSt and OSi₂St were prepared by a cross-coupling reaction in the presence of palladium catalyst²⁷ with p-bromostyrene and the corresponding Grignard reagents, which were prepared from silicon-containing methyl chlorides. Although syntheses of Si₂CSt has been studied previously,²⁸ the cross-coupling reaction we report here is more straightforward, and it eliminates possible side reaction, which only has one trimethylsilyl group substituted on a benzene ring, resulting in 4-(trimethylsilylmethyl)styrene. The silicon contents of Si_2St , Si_2CSt , and OSi_2St are 24.0, 21.4, and 21.2 wt %, respectively (Table 3). The structures of synthesized monomers were characterized by ¹H NMR spectroscopy. As shown in Figures 1a and 2a, characteristic peaks assigned to the CH=CH bond (5.1–6.7 ppm), CH_2 (1.50 ppm), and $C((CH_3)_2Si)_2$ (~0 ppm) in Si₂CSt and the CH=CH bond (5.1-6.7 ppm), CH₂ (2.11 ppm), and $(CH_3)_2Si-O-Si$ $(CH_3)_2$ (~0 ppm) for OSi_2St , respectively, indicating formation of the desired monomers.

Homopolymerization of Silicon-Containing Styrenic Monomers. Controlling polymerization is crucial to achieve well-defined morphologies with sharp phase boundary between blocks. We first investigated homopolymerization conditions for Si₂St, Si₂CSt, and OSi₂St to obtain narrow dispersed silicon-containing macroinitiator (see Scheme 2 and Table 1). To create nanostructures with feature size less than 20 nm for future nanopatterning of quantum dots, we kept the feed ratio of monomer to initiator (mol/mol) no greater than 60 so that the final molecular weight was in a range of $10\ 000-20\ 000$.

Si₂St was polymerized at a relatively mild temperature (100 °C) because this monomer is not stable at normal polymerization condition for styrene (\sim 130 °C). The Si–Si bond has a lower bond energy (80.5 kcal/mol) than that of Si-C bond (89.4 kcal/mol).²⁹ Gelation was observed after Si₂St was polymerized at 130 °C for 16 h (Table 1, entry 1). When the polymerization temperature was lowered to 100 °C, a narrow dispersed poly- (Si_2St) was obtained (Table 1, entries 2 and 3). Addition of a small amount of solvent, such as dichlorobenzene (DCB, 10 wt % of a monomer), led to higher molecular weight of poly(Si₂St) while maintaining a narrow molecular weight distribution (Table 1, entry 4). This may be attributed to improved solubility of the propagating radical in DCB. Narrow dispersed poly(Si₂CSt)s were obtained at 100 °C (Table 1, entries 5, 6). Despite polymerization of Si₂CSt for a long time (128 h) at 100 °C, a narrow dispersed poly(Si₂CSt) (PDI of 1.07) was obtained. A similar temperature dependence was observed in the polymerization of OSi₂St (Table 1, entries 7-9). It has been suggested that Si-O bonds can be



Figure 1. ¹H NMR spectra of (a) Si_2CSt and (b) $poly(Si_2CSt)$ (polymerized in bulk at 100 °C for 128 h using α -H unimer; entry 6 in Table 1). (*) Impurities from solvents: acetone, 2.17 ppm; H₂O, 1.56 ppm.

Scheme 2. Syntheses of Macroinitiators and Block Copolymers by NMRP at 100 °C



cleaved off by organolithium through nucleophilic attack in anionic polymerization.³⁰ As expected, living free radical polymerization is more tolerant to the functional groups in the monomers, and no gel formation was observed in the polymerization of OSi₂St at 100 °C.

To better understand the reactivity of monomer under living free radical conditions, the homopolymerization of para-substituted Sts, including Si₂St, Si₂CSt, Si₂OSt, and AcOSt, was studied, and their reactivities were compared to that of St. The reactivity of each monomer depends on a number of parameters such as polarity, inductive effect, and steric effects of the para-substituents. All polymerizations were carried out at 100 °C for 64 h, and the degree of polymerization (DP_n) was estimated by comparing the peak areas of alkyl protons in α -H unimer (0.7–1.1 ppm) and aromatic protons (6.0–6.8 ppm) in the repeating units in the ¹H NMR spectrum (Figures 1b and 2b). The results shown in Table 2 indicate the following reactivity order: AcOSt

Table 2. Degree of Polymerization (DP_n) Calculated from 1 H NMR Data^a

$monomer^b$	$M_{ m n}{}^c imes 10^{-3}$	$\mathrm{DP_n}^d$	$T_{\mathrm{g}}^{\ e}(^{\mathrm{o}}\mathrm{C})$
\mathbf{St}	3.5	32	99
AcOSt	5.0	36	122
Si_2St^f	9.7	37	100
OSi_2St	7.5	23	0.5
${ m Si_2CSt}$	5.6	21	122

^{*a*} All polymerizations were carried out at 100°C for 64 h with $[M]_0/[I]_0 = 60$. ^{*b*} Abbreviations of monomers: St, styrene; AcOSt, 4-acetoxystyrene; Si₂St, 4-(pentamethyldisilyl)styrene; Si₂CSt, 4-(bis(trimethylsilyl)methyl)styrene; OSi₂St, 4-(pentamethyldisiloxymethyl)styrene. ^{*c*} Estimated from GPC. ^{*d*} Calculated from alkyl protons of α -H unimer and aromatic protons of each repeating unit in a¹H NMR. ^{*e*} Determined by DSC (10 °C/min under nitrogen). ^{*f*} Dichlorobenzene (DCB) was added as a solvent (10 wt % of monomers) in the reaction. Without solvent, a shoulder was observed at the higher molecular weight region with DP_n of 32.



Figure 2. ¹H NMR spectra of (a) OSi_2St and (b) $poly(OSi_2St)$ (polymerized in bulk at 100 °C for 128 h using α -H unimer; entry 9 in Table 1). (*) Impurities from H₂O: 1.56 ppm.

 \geq Si₂St > St > OSi₂St, Si₂CSt, which is consistent with the studies done both in conventional and living free radical polymerization of para-substituted styrenes³¹⁻³³ using 2,2'-azobis(isobutyronitrile) (AIBN) or benzoyl peroxide (BPO) as a radical initiator. These studies suggest that electron-withdrawing groups can stabilize the propagating radicals. Namely, silicon atom directly attached to the aromatic group (α -position) acts as an electron-withdrawing group, while silicon atom attached though methylene (β -position) acts an electron-donating group compared to styrene for radical polymerization. When silicon atom is directly attached to the aromatic group (α -position; e.g., Si₂St), it acts as an electronwithdrawing group due to the interaction of the $d_{\pi}-p_{\pi}$ orbital; when the silicon atom is attached through methylene (β -position; e.g., Si₂CSt, OSi₂St) linkage, it acts as an electron-donating group due to $\sigma - \pi$ hyperconjugation of $CH_2^{\delta-}$ -Si^{$\delta+$}.³² Therefore, the propagating

Table 3. Density and Silicon Content of Each Monomer

monomer ^a	FW (g/mol)	density ^b , d (g/mL)	Si content (wt %)
St	104.15	0.903	0
AcOSt	162.19	1.061	0
$\rm Si_2St$	234.48	0.870	24.0
OSi_2St	262.51	0.899	21.2
Si_2CSt	262.54	0.894	21.4

 a Abbreviations of monomers: St, styrene; AcOSt, 4-acetoxy-styrene; Si₂St, 4-(pentamethyldisilyl)styrene; Si₂CSt, 4-(bis(trimethylsilyl)methyl)styrene; OSi₂St, 4-(pentamethyldisiloxymethyl)styrene. b Estimated by measuring average mass of each monomer in 1 mL at 25 °C.

site on a polymer chain bearing electron-withdrawing groups, such as Si_2St , can stabilize radicals more strongly than that bearing electron-donating groups, such as OSi_2St and Si_2CSt , resulting in a higher degree of polymerization under similar conditions. In our studies 10 wt % of DCB was added as solvent in Si_2St polymerization to obtain narrow dispersed polymers. Hence, it is possible that the actual reactivity of Si_2St is higher than that of AcOSt.

Although polymerization at a low temperature (100 °C) produces narrow dispersed polymers, longer reaction time is typically required to achieve higher yields of silicon-containing homopolymers. To resolve this, a rate accelerating agent, acetic anhydride (AA),³⁴ was employed. Rate acceleration was clearly observed in the polymerization of Si₂OSt, which was the least compared to other monomers (Table 2). The polymerization of OSi₂St in the presence of AA (1.5 equiv to unimer) at 100 °C for 64 h proceeded smoothly, resulting in narrow dispersed macroinitiators with the highest yield and number-average molecular weight in its category (Table 1, entry 10).

The polymers were characterized by¹H NMR and GPC. For example, in the ¹H NMR spectrum of poly(Si₂-CSt), resonances at 0 ppm (18 H) and 6.0–6.8 ppm (4 H) corresponding to trimethylsilyl and aromatic protons, respectively, were always observed while vinyl protons in Si₂CSt disappeared completely as the polymerization proceeds (Figure 1b). As shown in Figure 3, all GPC chromatographs showed symmetrical unimodal peaks,



Figure 3. GPC profiles of (a) poly(OSi_2St)^a, (b) poly(Si_2St)^b, (c) poly(OSi_2St), and (d) poly(Si_2CSt). All polymerization was conducted in bulk at 100 °C for 64 h. a: Acetic anhydride (1.5 equiv to α -H unimer) was added into the reaction. b: *N*,*N*-Dimethylformamide (DMF) (10 wt %) was added into the reaction.

which clearly supports the formation of well-defined homopolymers.

Synthesis of Silicon-Containing Block Copolymers. Block copolymerization was carried out in a similar way as the synthesis of homopolymers described above (Scheme 2) and precipitated in methanol. The molar ratio between blocks was calculated from the integrated intensities of aromatic and trimethylsilyl protons in ¹H NMR spectrum. It was then converted to volume ratio using measured monomer density (see Table 3). The polymerization conditions and the resulting block copolymer characteristics are summarized in Table 4.

Since the macroinitiators were not soluble in the second monomers at 100 °C, a small amount of solvent (20 wt % of the total feed of macroinitiator and second monomer), such as DCB or DMF, was added to dissolve both the macroinitiators and second monomers. All block copolymerization proceeded smoothly, giving the

Table 4. Synthesis Conditions of Silicon-Containing Block Copolymers from Various Macroinitiators and Their Block Copolymer Characteristics

								block copolymer					
				block copolymerization						block first/s	ratio: econd		
entry	first block^a	$M_{ m n} imes 10^{-3}$	second block ^a	[M ₂]/[MI], ^b (w/w)	time (h)	temp (°C)	$\mathrm{solvent}^c$	yield (%)	${M_{ m n}}^d imes 10^{-3}$	PDI^d	$\operatorname{mol}_{\%^e}$	vol % ^f	Si content (wt %)
11	PSt	3.5	PSi_2St	3	64	100	DMF (20)	72.6	18.7	1.07	30/70	15/85	20.2
12	PSt	7.6	PSi_2St	1	20	100	DCB (30)	26.3	10.8	1.10	81/19	65/35	8.3
13	PSt	7.0	PSi_2CSt	1	40	130	N/A	78.1	16.4	1.15	61/39	38/62	13.2
14	PSt	5.5	$POSi_2St$	2	40	100	DCB (20)	17.4	7.7	1.10	87/13	73/27	5.8
15	PSt	5.5	$POSi_2St$	2	80	100	DCB (20)	20.6	8.1	1.11	86/14	70/30	6.3
16	$POSi_2St$	7.5	\mathbf{PSt}	2	40	100	DCB (20)	43.2	11.1	1.07	51/49	73/27	15.4
17	$POSi_2St$	7.5	\mathbf{PSt}	3	41	128	DCB (28)	77.4	12.7	1.20	25/75	46/54	9.8
18	$POSi_2St$	7.5	PAcOSt	2	40	100	DCB (20)	28.6	13.1	1.07	45/55	61/39	12.2
19	PAcOSt-α	5.0	PSi_2St	3	64	100	DMF (20)	58.7	21.3	1.08	31/69	21/79	18.2
20	PAcOSt-a	5.0	PSi_2CSt	1	94	100	DMF (20)	31.5	10.2	1.10	25/75	46/54	10.6
21	PAcOSt-T	4.1	PSi_2CSt	4	64	130	DMF (20)	14.3	9.0	1.24	62/38	33/67	13.6

^{*a*} Abbreviations of polymers: PSt, polystyrene; PAcOSt, poly(4-acetoxystyrene; PSi₂St, poly(4-(pentamethyldisilyl)styrene); PSi₂CSt, 4-(bis(trimethylsilyl)methyl)styrene; POSi₂St, poly(4-(pentamethyldisiloxymethyl)styrene); PAcOSt- α (entries 19, 20), 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane-3-nitroxide (α -H radical) terminated macroinitiator of PAcOSt; PAcOSt-T (entry 21), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) terminated macroinitiator of PAcOSt. ^{*b*} Feed ratio for the block copolymerization; [M₂]/[MI] = [second monomer]/[macroinitiator] (w/w). ^{*c*} Amount of solvent is indicated as wt % of total reactants. ^{*d*} The number- and weight-average molecular weights (M_n and M_w) and polydispersity (PDI = M_w/M_n) were determined by GPC from refractive index (RI) detector in a flow rate of 1.0 mL/min in THF at 40 °C. Narrow dispersed poly(St)s were used as standards for universal calibration. ^{*e*} Calculated from ¹H NMR (e.g., see Figure 5 for poly(AcOSt-*b*Si₂CSt), entry 20). ^{*f*} Calculated from molar ratio and monomer density from Table 3.

Table 5. Characteristics of Silicon-Containing Block Copolymers

entry in Table 4	block copolymers	$M_{ m n}$	PDI	vol ratio	Si (wt %)	$morphology^a$	d(100) (nm) before O_2 plasma ^b	$d(100)~({ m nm}) \ { m after}~{ m O}_2 \ { m plasma}^c$
12	$P(St-b-Si_2St)$	$10\ 840$	1.10	65/35	8.3	disordered		
16	$P(OSi_2St-b-St)$	$11\ 110$	1.07	73/27	15.4	disordered		
17	$P(OSi_2St-b-St)$	$12\ 720$	1.20	46/54	9.8	lamellae	14.1	
18	$P(OSi_2St-b-AcOSt)$	$13\ 070$	1.14	61/39	12.2	cylinder	16.7	10.6
19	$P(AcOSt-b-Si_2St)$	21270	1.08	21/79	18.2	cylinder	19.3	18.0
20	$P(AcOSt\text{-}b\text{-}Si_2CSt)$	10 190	1.10	46/54	10.6	lamellae	13.8	d

^a Confirmed from both SAXS and TEM. ^b Measured from SAXS. ^c Measured from TEM and normalized based on the SAXS data before exposed to oxygen plasma for 10 min. ^d The lamellae delaminated after oxygen plasma treatments.

desired block copolymers with narrow PDIs at 100 °C. Block copolymerization of polystyrene macroinitiator with Si₂CSt under normal conditions (130 °C) without solvent yielded a narrow PDI. Unlike monomers with Si–Si bond, lower polymerization temperature was not necessary for Si₂CSt as Si–C bond is more robust (Table 4, entry 13).

Further, the effect of sequence of monomer addition on the synthesis of block copolymers was studied. The poly(OSi₂St) macroinitiator was more effective in initiating St polymerization (Table 4, entry 16) than the reverse addition sequence (Table 4, entries 13), resulting in shorter reaction time at 100 °C in DCB and higher yield. These results can be explained by the higher reactivity of second monomer (St > OSi₂St as discussed earlier) and higher solubility of the propagating chain in DCB. The synthesis of poly(OSi₂St-*b*-AcOSt) block copolymer follows a similar trend since AcOSt is more reactive than OSi₂St (Table 4, entry 18).

Previously, silicon-containing block copolymers have been synthesized as photoresists for higher sensitivity and etch resistance.^{7,12} By combining bottom-up (selfassembly) and top-down (lithography) approaches in photosensitive silicon-containing block copolymers, complex hierarchical hybrid structures can be created. Here we investigate the block copolymerization of 4-acetoxystyrene (AcOSt) with silicon-containing monomers. Poly-(AcOSt) has been studied as chemically amplified photoresist, which can be hydrolyzed to poly(hydroxystyrene) in the presence of acid and dissolved away by aqueous base solution to generate patterns when exposed to UV light. Narrow dispersed poly(AcOSt) has been synthesized using TEMPO unimer by Barclay et al.,³⁵ and the PDI was found to be important in controlling the dissolution rate of poly(4-hydroxystyrene). In this study we used both nitroxide unimers, α -H unimer, and TEMPO-unimer to evaluate the effect of initiator reactivity on block copolymerization. Two types of poly-(AcOSt) macroinitiators (Table 4, entries 19-21) were synthesized: poly(AcOSt)- α from α -H unimer and poly-(AcOSt)-T from TEMPO unimer. Both the macroinitiators show similar GPC profiles with M_n (PDI) as 5000 (1.13) and 4100 (1.16), respectively. Since both AcOSt and Si₂CSt are relatively stable, polymerization of the second block could be conducted at 130 °C using poly-(AcOSt)-T as the macroinitiator. GPC traces suggest that the efficiency of propagation of the second block depends on the nature of the capping group on the macroinitiator (see Figure 4). Poly(AcOSt-b-Si₂CSt)-a shows narrow distribution in GPC even with smaller feed of second monomer (i.e., $poly(AcOSt-\alpha)/Si_2CSt =$ 1/1 vs poly(AcOSt-T)/Si₂CSt = 1/4), while poly(AcOStb-Si₂CSt)-T has a shoulder in a larger retention volume region, which can be assigned to unreacted poly(AcOSt-T). This behavior can be explained by the lower reactiv-



Figure 4. GPC traces of poly(AcOSt-*b*-Si₂CSt) from different initiators using (a) poly(AcOSt-T) macroinitiator, (b) TEMPOunimer as initiator (see entry 21 in Table 4), (c) poly(AcOSt- α) macroinitiator, and (d) α -H unimer as initiator (see entry 20 in Table 4).



Figure 5. ¹H NMR spectrum of poly(AcOSt-*b*-Si₂CSt) corresponding to entry 20 in Table 4. Block ratio of poly(AcOSt) and poly(Si₂CSt) was estimated from the integrations of a (assigned to acetyl groups) and b (assigned to trimethylsilyl groups). (*) Impurities from solvent and H_2O .

ity of the terminal TEMPO-radicals compared to that of the α -H radicals to initiate Si₂CSt monomers, which is consistent to the results reported by Hawker et al.,¹⁵ and the nitroxide structure plays an important role in the control of polymerization. The ¹H NMR spectrum of poly(AcOSt-*b*-Si₂CSt)- α showed five broad signals at 0, 1.3, 1.7, 2.2, and 6.0–6.8 ppm for the trimethylsilyl, methylene, methyne, acetyl, and aromatic protons, respectively (Figure 5). These GPC traces and ¹H NMR spectra confirmed the synthesis of the desired block copolymers.

Morphology Characterization of the Silicon-Containing Block Copolymers. To understand the



Figure 6. Small-angle X-ray scattering (SAXS) results of silicon-containing block copolymers. The entry numbers are the same as those in Table 4.



Figure 7. Transmission electron micrograph (TEM) images of $PAcOSt-PSi_2CSt$ (46/54 v/v, entry 20 in Tables 4 and 5) before and after O_2 plasma for 5 min.

structures of these newly synthesized block copolymers and their response to oxygen plasma, we have used TEM and small-angle X-ray scattering (SAXS) to characterize their morphologies before and after oxygen plasma (see Table 5). Since silicon has larger mass than carbon, silicon-containing block provides enough electron density contrast with respect to the non-silicon-



Figure 8. Transmission electron micrograph (TEM) images of PAcOSt–PSi₂St (21/79 v/v, entry 19 in Tables 4 and 5) before and after O₂ plasma for 10 min.

containing block such that we are able to obtain the bright-field TEM images without staining. SAXS profiles seen in Figure 6 suggest that these block copolymers form disordered (sample 12 and 16), cylinder (sample 18 and 19), and lamellae (sample 17 and 20) structures depending on their volume ratios between two blocks and their molecular weight, which agrees well with TEM results. The microtomed thin films (~ 75 nm) on TEM grids were subject to O_2 plasma for 1.5, 5, and 10 min for samples 18, 20, and 19, respectively. The film with lamellar structures fell apart after O₂ plasma (see Figure 7) due to the loss of more than half of the mass. In contrast, when silicon-containing block is the major phase (sample 18 and 19), the film morphologies are preserved after exposure to O_2 for more than 10 min (see Figure 8).

The domain size before and after O_2 plasma is found highly dependent on the silicon content in the block copolymers. For example, the *d* spacing of sample 19 (18.2 wt % Si) almost did not change, from 19.38 to 18.0 nm, while that of sample 18 (12.2 wt % Si) decreased from 16.7 to 10.6 nm, based on TEM observations. Our results are consistent with the previous study, which suggests that large etch resistance to O_2 plasma can be achieved when polymers have greater than 10 wt % of silicon.²⁶

Conclusion

Well-defined, narrow dispersed silicon-containing block copolymers were synthesized from the corresponding silicon-containing monomers and St or AcOSt using

unimolecular nitroxide-mediated living free radical polymerization. The monomer addition sequence, use of polar solvents (DMF vs DCB), and highly reactive α -hydride unimer as an initiator are the key to the success of copolymerization. Polymerization conditions, including time and temperature of polymerization, monomer reactivity, and addition of rate accelerating agent, were also investigated in detail to control the polymerization and achieve high conversion. The polymerization temperature was chosen at 100 °C to minimize thermal decomposition of the synthesized monomers at the normal polymerization temperature for styrene (\sim 130 °C). Both TEM and SAXS data showed that these polymers formed cylindrical, lamellae, or disordered structures depending on the volume ratio between the blocks and their molecular weights. When silicon-containing block was the major phase, the block copolymer films were more robust to oxygen plasma and maintained the morphologies. When silicon content in cylindrical block copolymers was greater than 12 wt %, domain size changed very little.

Successful synthesis of the novel silicon-containing block copolymers could enable potential applications as (1) direct nanopatterning of III–V semiconductors at high temperatures (>600 °C), (2) formation of nanoporous ceramic films by selectively removing the nonsilicon blocks, and (3) fabrication of hierarchical hybrid nanostructures using photosensitive silicon-containing block copolymers.

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