Macromolecules

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Anionic Synthesis of Mono- and Heterotelechelic Polystyrenes via Thiol−Ene "Click" Chemistry and Hydrosilylation

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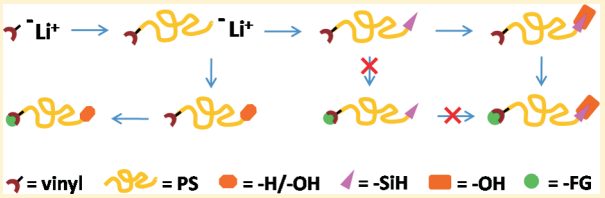
Supporting Information

ABSTRACT: A series of precisely defined, mono- and heterotelechelic polystyrenes have been facilely synthesized by combining living anionic polymerization with other efficient chemical transformations, such as thiol−ene "click" chemistry and hydrosilylation reactions, leading to a versatile and general functionalization methodology for chain-end-functionalized anionic polymers. Specifically, α-vinyl-ended poly(styryl)lithiums, which were prepared using 4-pentenyllithium as an initiator under high-vacuum conditions, were reacted with different end-capping reagents using living functionalization methods to afford various chain-end functionalities quantitatively, namely, α-vinylpolystyrene, α-vinyl-ω-hydroxylpolystyrene, and α-vinyl-ω-hydrosilylpolystyrene. Subsequent functionalizations using photoinitiated thiol−ene "click" chemistry and hydrosilylation reactions allow facile and efficient installation of diverse functionalities onto the α- and ω-chain ends of these polymers, respectively, including amine groups, carboxylic acid groups, hydroxyl groups, and perfluorinated alkyl chains. It was found that the heterofunctionalization should be carried out in the sequence of hydrosilylation and then thiol−ene reaction to achieve precisely defined products, probably due to the side products associated with the reaction between silyl hydrides and radical intermediates. The polymers have been thoroughly characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, SEC, and MALDI-TOF mass spectrometry to establish their chemical structures and chain-end functionalities, which indicates precisely defined mono- and heterotelechelic polystyrenes with 100% functionalities. These polymers serve as important model compounds in the study of their bulk properties as well as self-assembling behaviors.



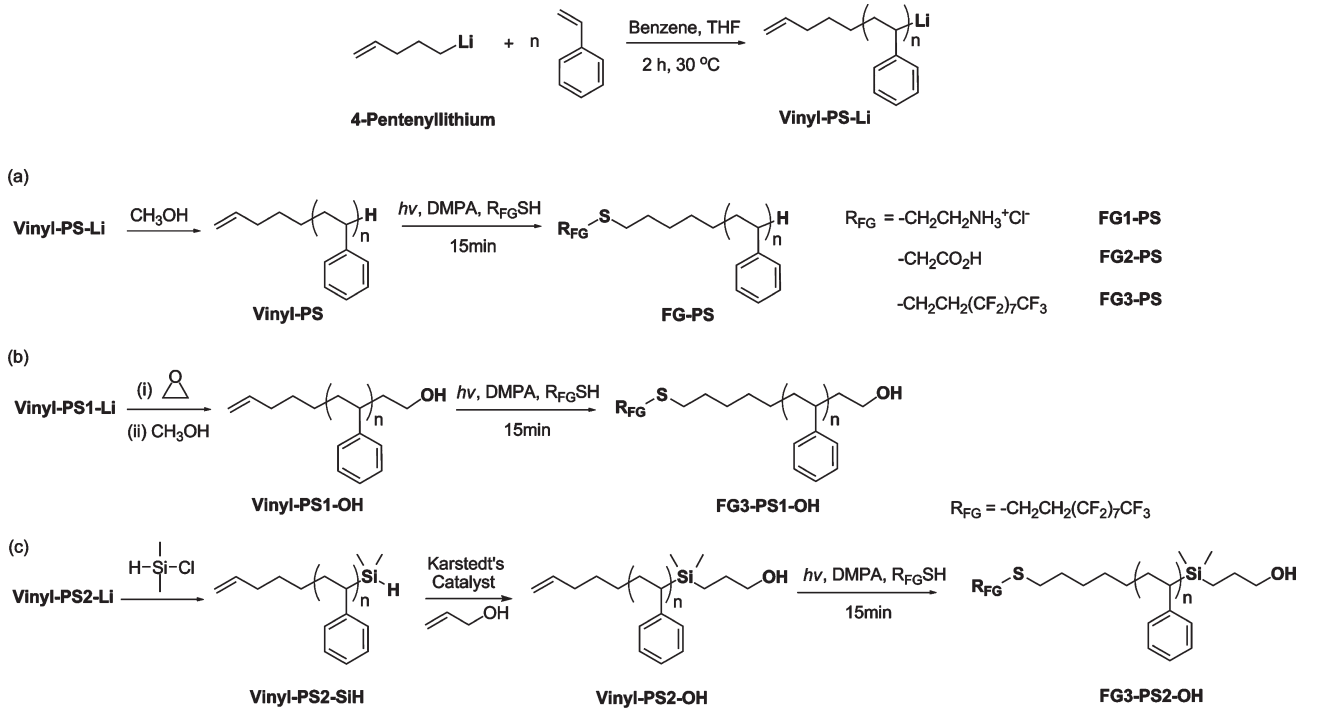
INTRODUCTION

In recent years, there has been increasing interest in well-defined telechelic (chain-end-functionalized) polymers with one or more types of tailored end groups offering strong abilities to interact or couple with other molecular units[1−5] or nano-objects.[2,3,6,7] This attractive class of materials has given rise to basic understanding useful for developing new functional materials with novel properties and industrial applications, such as the synthesis of functional block copolymers,[8] fluorescently or magnetic labeled polymeric chains,[9,10] surface-modified particles,[11,12] branched macromolecular architectures,[13] etc. Although many synthetic methods have been employed for this purpose, a facile, general methodology to access well-defined, asymmetric telechelic polymers with precise control over the major molecular parameters affecting polymer properties remains a challenge. It is highly desirable to develop general functionalization methodologies (GFM) using appropriate, modular, and efficient chemical transformations for facile synthesis of both mono- and heterotelechelic polymers.

Living anionic polymerization, particularly alkyllithium-initiated polymerization, provides one of the best methods to control the major variables affecting polymer properties including molecular weight, polydispersity, copolymer composition, and molecular architecture. It also offers versatile routes for the synthesis of chain-end-functionalized polymers,[14−16] including the utilization of functionalized initiators or termination with functionalized terminating agents. The former usually involves protection of the functional group in the initiator, such as 3-(*tert*-butyldimethylsiloxyl)-1-propyllithium,[17] and deprotection after polymerization.[18] The latter mainly includes quenching with functionalized diphenylethylene derivative[19] or functionalized chlorosilanes.[20,21] Despite the high efficiency in many of the living functionalization methods, the difficulty in preparing and handling functional terminating agents and the requisite protection/deprotection prevents the scaling-up and practical application of these methods. To address this, Quirk et al. have proposed a general functionalization scheme based on anionic polymerization and hydrosilylation. A series of chain-end, hydrosilyl-functionalized polystyrenes have been synthesized by quenching the living poly(styryl)lithiums with chlorodimethysilane.[22−24]

Received: February 16, 2011
Revised: April 5, 2011
Published: April 14, 2011

Scheme 1. General Functionalization Methodology for the Synthesis of Mono- and Heterotelechelic Polymers Using Combinations of Living Anionic Polymerization, Chain-End Functionalization, Thiol−ene Chemistry, and Hydrosilylation



The resulting ω-hydrosilyl-functionalized polystyrenes are stable in air and can be reacted with readily available, substituted alkenes to yield well-defined telechelic polystyrenes with amine,[22] perfluoroalkyl,[25] and cyano functionalities.[23,24] The versatility of living anionic polymerization also allows simultaneous introduction of different functional groups onto the polymeric skeletons by functionalized initiators and termination agents. Therefore, it was of great interest to extend this GFM further to stepwise or even orthogonal modifications for the facile synthesis of asymmetric telechelic polymers.

The expanding toolbox of "click" chemistry is the perfect choice for a GFM. By definition, "click" chemistry refers to a class of highly efficient, selective, and modular reactions that requires minimum work-up and purification.[26,27] Because of the reduced chain-end reactivity in polymers and the difficulty associated with purification, the concept of "click" chemistry is very important in the functionalization of polymers.[26,28] Several types of "click" chemistry have been well established in the field, namely, the Cu(0)-catalyzed azide−alkyne [3 + 2] cycloaddition reaction,[29] thiol−ene reaction,[30] and Diels−Alder reactions.[31] In particular, thiol−ene chemistry, which denotes the photo/thermal- initiated radical addition of thiols across double bonds, has emerged as an attractive "click" process since it is highly efficient, rapid, regiospecific (anti-Markovnikov addition), and insensitive to the presence of water and oxygen.[32−47] The introduction of the thiol−ene "click" process to the design and synthesis of novel functional polymers has led to significant developments in fields ranging from nanotechnology to drug discovery.[32,33,45,48,49] It is thus promising to incorporate these "click" chemistry reactions into the GFM of anionic polymerization.

Considering the ready availability of precisely defined, vinyl-functionalized polystyrenes synthesized using 4-pentenyllithium as the initiator, the proof-of-concept synthesis will be preparation of the monochain-end-functionalized polymers using thiol−ene chemistry as a valid GFM, as outlined in Scheme 1a.[50] In addition, it is also possible to combine it with the living functionalization methods of anionic polymerization (Scheme 1b) as well as other GFM, such as hydrosilylation (Scheme 1c), to prepare α, ω-heterofunctional polymers. Specifically, 4-pentenyllithium was first employed as a functional initiator for the preparation of α-vinyl-functionalized poly(styryl)lithium (vinyl-PS-Li),[50] which can be subject to further functionalization. For example, when quenched with methanol, the resulting α-vinyl PS (vinyl-PS) can react with diverse, commercially available, functional thiols to obtain the desired α-functionalized PS (FG-PS) (Scheme 1a); the quantitative monoend-capping of vinyl-PS-Li with ethylene oxide[51] followed by quenching with methanol gives α-vinyl-ω-hydroxylpolystyrene (vinyl-PS1-OH) (Scheme 1b); when terminated with chlorodimethylsilane, it gives heterofunctionalized PS (vinyl-PS2-SiH) which can undergo sequential functionalization using hydrosilylation and thiol−ene chemistry (Scheme 1c). In this work, we report the design, synthesis, and characterization of these precisely defined, model functional polystyrenes and demonstrate that thiol−ene chemistry is an efficient and viable "click" process for the development of a GFM using anionic polymerization. The polymers have been thoroughly characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, SEC, and MALDI-TOF mass spectrometry to establish their chemical structures and chain-end functionality. The results clearly indicate the cleanness of the reaction, the precisely defined structure, and the high degree of functionalization (∼100%). The polymers thus synthesized serve as important model compounds in the study of their bulk properties as well as self-assembling behaviors.

EXPERIMENTAL SECTION

Chemicals and Solvents. Benzene (Certified ACS, EM Science), tetrahydrofuran (THF, Certified ACS, EM Science), ethylene oxide (99.5+%, Aldrich), and styrene (99%, Aldrich) were purified as previously reported.[52,53] Benzene and THF were distilled as needed

from poly(styryl)lithium into the polymerization reactors. Chlorodimethylsilane (98%, Aldrich) was purified by stirring over calcium hydride with periodic degassing for 12 h followed by distillation onto a second batch of calcium hydride and finally distillation and collection of the middle fraction into calibrated, flame-sealed ampules. Karstedt's catalyst, 1,3-divinyltetramethyldisiloxane−platinum (Gelest, 1.2−1.4 wt % Pt in xylene), was used as received. Methanol (Fisher Scientific, reagent grade) was degassed on the vacuum line before distillation into ampules and flame-sealed. Toluene (Certified ACS), chloroform (Certified ACS), and hexanes (Certified ACS) were used after distillation. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%, Acros Organics), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (97%, Aldrich), mercaptoacetic acid (97%, Acros Organics), 2-aminoethanethiol hydrochloride (98%, Acros Organics), allyl alcohol (99%, Acros), and 5-bromo-1-pentene (95.0+%, Fluka) were used as received. Silica gel (VWR, 230−400 mesh) was activated by heating to 140 °C for 12 h. 4-Pentenyllithium was prepared according to the literature procedure[50] and used after double titration with allyl bromide.[54]

Polymerizations. Vinyl-PS-Li was prepared under high-vacuum conditions in sealed, all-glass reactors using 4-pentenyllithium as the initiator in THF/benzene mixed solvent (v/v = 1/10) at 30 °C (10−15 vol % monomer). After 2 h and prior to functionalization, an aliquot of vinyl-PS-Li was transferred to an empty ampule, flame-sealed, and quenched with degassed methanol to obtain a base sample. Vinyl-PS-Li was then reacted with different end-capping reagents to give several polystyrene precursors, namely, vinyl-PS, vinyl-PS1-OH, and vinyl-PS2-SiH.

Vinyl-PS. Vinyl-PS-Li (15.8 g, 6.3 mmol, $M_n = 2.4 \times 10^3$ g/mol, $M_w/M_n = 1.06$) was terminated with anhydrous, degassed methanol at room temperature and precipitated into cold methanol. The white solids were collected after filtration and dried thoroughly on the high-vacuum line for 2 days (vinyl-PS, 15.1 g, 95%).

Vinyl-PS1-OH. Vinyl-PS1-Li (20.8 g, 8.5 mmol, $M_n = 2.5 \times 10^3$ g/mol, $M_w/M_n = 1.03$) was reacted with ethylene oxide (1.5 mL in 27 mL of benzene, 1.3 g, 0.03 mol) for about 1 h. The orange color disappeared several minutes after the addition of ethylene oxide. The mixture was quenched with degassed, anhydrous methanol at room temperature. The product was removed from the reactor and precipitated into cold methanol; the resulting polymer was collected after filtration and several washings with methanol. The samples were dried on the high-vacuum line for 2 days to afford a white solid (vinyl-PS1-OH, 18.4 g, 88%).

Vinyl-PS2-SiH. This compound was prepared analogously to the reported procedure for chain-end, hydrosilyl-functionalized polystyrene reported by Quirk et al.[23] Vinyl-PS2-Li (19.7 g, 1.8 mmol, $M_n = 1.1 \times 10^4$ g/mol, $M_w/M_n = 1.02$) was terminated with chlorodimethylsilane (1.00 g, 1.18 mL, 0.0107 mol) in benzene at room temperature followed by precipitation into cold methanol and filtration. The samples were thoroughly dried on the high-vacuum line for 2 days to afford a white solid (vinyl-PS2-SiH, 16.8 g, 85%).

General Procedure for the Preparation of α-Functionalized Polystyrenes (FG-PS) Using Thiol−Ene Chemistry. In a vial, vinyl-functionalized PS (1.0 equiv of vinyl), functional thiol (1.1 equiv), and DMPA (0.05 equiv) were mixed and dissolved in minimal amount of solvent ($CHCl_3$ or THF) followed by irradiation without stirring for 15 min under a UV 365 nm lamp at room temperature (25 °C). Functionalized polymers were purified by repeated precipitation.

FG1-PS. Vinyl-PS ($M_n = 2.4 \times 10^3$ g/mol, 200 mg, 83 μmol), 2-aminoethanethiol hydrochloride (10.5 mg, 93 μmol), and DMPA (1.1 mg, 4.3 μmol) were dissolved in 3 mL of THF/methanol mixed solvent (v/v = 7/3). After irradiation for 15 min, the solution was precipitated into cold methanol twice. The sample was dried in a vacuum oven overnight to afford a white powder (FG1-PS, 179 mg; yield 83%).

FG2-PS. Vinyl-PS ($M_n = 2.4 \times 10^3$ g/mol, 200 mg, 83 μmol), mercaptoacetic acid (8.5 mg, 92 μmol), and DMPA (1.1 mg, 4.3 μmol) were dissolved in 2 mL of THF. After irradiation for 15 min, the mixture was directly precipitated into aqueous NaOH solution (40 mL, pH = 10). The solid was collected, dissolved again in THF, and precipitated into aqueous HCl solution (40 mL, pH = 1). After precipitation again in distilled water (40 mL), the sample was collected by filtration and dried in a vacuum oven overnight to give a white powder (FG2-PS, 173 mg; yield 83%).

FG3-PS. Vinyl-PS ($M_n = 2.4 \times 10^3$ g/mol, 200 mg, 83 μmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (44.1 mg, 92 μmol), and DMPA (1.1 mg, 4.3 μmol) were dissolved in 2 mL of THF, followed by irradiation for 15 min. The solution was precipitated into cold hexanes/methanol mixed solvent (v/v = 1/30) three times. The sample was dried in a vacuum oven overnight to give a white powder (FG3-PS, 178 mg; yield 74%).

Preparation of Heterotelechelic Polystyrenes. *FG3-PS1-OH.* Vinyl-PS1-OH ($M_n = 2.5 \times 10^3$ g/mol, 300 mg, 0.12 mmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (63.5 mg, 0.13 mmol), and DMPA (1.6 mg, 6.3 μmol) were dissolved in 3 mL of THF, followed by irradiation without stirring for 15 min. The solution was then precipitated into cold hexanes/methanol mixed solvent (v/v = 1/30) three times. The sample was dried in a vacuum oven overnight to give white powder (FG3-PS1-OH, 277 mg; yield 77%).

Vinyl-PS2-OH. Vinyl-PS2-SiH ($M_n = 1.1 \times 10^4$ g/mol, 200 mg, 18 μmol) was reacted with 11 mg of allyl alcohol (190 μmol, 10 equiv) in distilled dry toluene (4 mL) in the presence a single drop of fresh Karstedt's catalyst, 1,3-divinyltetramethyldisiloxane-platinum, at room temperature. The reaction was monitored by FT-IR. After 14 h, there was no detectable Si−H absorbance (2110 cm^{-1}). After further stirring for 2 days, only one spot was observed on the TLC plate. The polymer was then isolated by silica gel column chromatography using toluene as eluent. About 3% unreacted vinyl-PS2-SiH (~6 mg) eluted first from the column. The next fractions were combined, concentrated, and precipitated into cold methanol. The sample was dried in a vacuum oven overnight to give white powder (vinyl-PS2-OH, 187 mg; yield 94%).

FG3-PS2-OH. Vinyl-PS2-OH ($M_n = 1.1 \times 10^4$ g/mol, 100 mg, 0.0091 mmol), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol (6 mg, 0.013 mmol), and DMPA (0.2 mg, 0.00078 mmol) were dissolved in 3 mL of THF, followed by irradiation for 15 min. The solution was then precipitated into cold hexanes/methanol mixed solvent (v/v = 1/30) three times. The sample was dried in a vacuum oven overnight to offer white powder (FG3-PS2-OH, 75.1 mg; yield 72%).

Characterization. Size exclusion chromatographic analyses (SEC) for the synthesized polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10^3/10^4 Å), mixed bed (10^3, 10^4, 10^6 Å)], and a triple detector system. The three detectors included a differential refractometer (Waters 410), a differential viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF was used as eluent with a flow rate of 1.0 mL/min at room temperature.

All ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired in $CDCl_3$ (Aldrich, 99.8% D) using a Varian Mercury 300 NMR spectrometer. The ^{1}H NMR spectra were referenced to the residual proton impurities in the $CDCl_3$ at δ 7.27 ppm. The ^{13}C NMR spectra were referenced to $^{13}CDCl_3$ at δ 77.00 ppm.

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting polymer films on KBr plates from polymer solutions with subsequent drying at 40−50 °C. The data were processed using Win-IR software.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (335 nm). All spectra were measured in positive reflection or linear mode. The instrument was calibrated prior to each

measurement with external PMMA or PS standard at the molecular weight under consideration. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, >99%) served as matrix and was prepared in $CHCl_3$ at concentration of 20 mg/mL. Silver trifluoroacetate served as cationizing agent and was prepared in MeOH/$CHCl_3$ (v/v = 1/3) at concentrations of 5 mg/mL. All the thiol−ene functionalized anionic polystyrenes were dissolved in CH_3Cl for future MALDI-TOF mass evaluations. The matrix and AgTFA were mixed with the ratio of 10/1 (v/v). The sample preparation involved depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample (sandwich method).[55] After evaporation of the solvent, the plate was inserted into the MALDI source. The attenuation of the Nd:YAG laser was adjusted to minimize unwanted polymer fragmentation and to maximize the sensitivity.

Thin-layer chromatographic analyses (TLC) of the functionalized polymers were carried out on by spotting and developing polymer samples on flexible silica gel plates (Selecto Scientific, Silica Gel 60, F-254 with fluorescent indicator) using toluene or its mixture with other polar solvents as eluents.

RESULTS AND DISCUSSION

Anionic Synthesis of Vinyl-Functionalized Polymers. Vinyl-functionalized polymers can be synthesized by a variety of methods, such as cationic,[56] anionic,[50,57] and radical polymerization.[46,58−62] The ring-opening polymerization of functionalized lactones is naturally a straightforward way to prepare vinyl-functionalized polymers, considering its compatibility with double bonds.[61,62] Reported methods using ATRP,[46,59] RAFT chain transfer methods,[58,60] and other radical polymerization methods[63] were based on the reactivity differentiation between vinyl groups and other methacrylates/styrenic monomers. For anionically prepared polymers, it was found that 4-pentenyllithium was an effective functional initiator for polymerization of styrene in benzene in the presence of a promoter (5 equiv of THF), giving well-defined, α-vinyl-functionalized polystyrene with a low polydispersity index. THF was used to increase the rate of initiation relative to propagation, which was necessary to maintain a low polydispersity index. An additional advantage in using a vinyl-functionalized initiator in anionic polymerization is that the ω-chain-ends remain reactive and can be subjected to various chain-end modification methods, block copolymerization, and linking reactions to give polystyrenes of complex architectures with precise control on the location of chain-end vinyl functional groups (star, branched, midchain functionalized, etc.) with high yields, which will be elaborated further in the following sections. The subsequent functionalization could bring diverse functionalities to these precisely controlled locations in polymers where the vinyl groups originally reside.

The polymerization initiated by 4-pentenyllithium in the presence of THF was allowed to proceed for 2 h before it was quenched to avoid the possible decomposition of living poly(styryl)lithium chain end. The conversion was quantitative because of the enhanced rate of polymerization. The vinyl-functionalized polystyrenes were thoroughly characterized by SEC, FTIR, NMR, and MALDI-TOF mass spectrometry to confirm their structures and purity. When quenched with methanol, an α-vinyl-functionalized polystyrene (vinyl-PS) was prepared. The ^{1}H NMR spectrum clearly showed characteristic alkene proton peaks at δ 5.7 and 4.9 ppm, with an integration ratio of 1.0:2.0 as

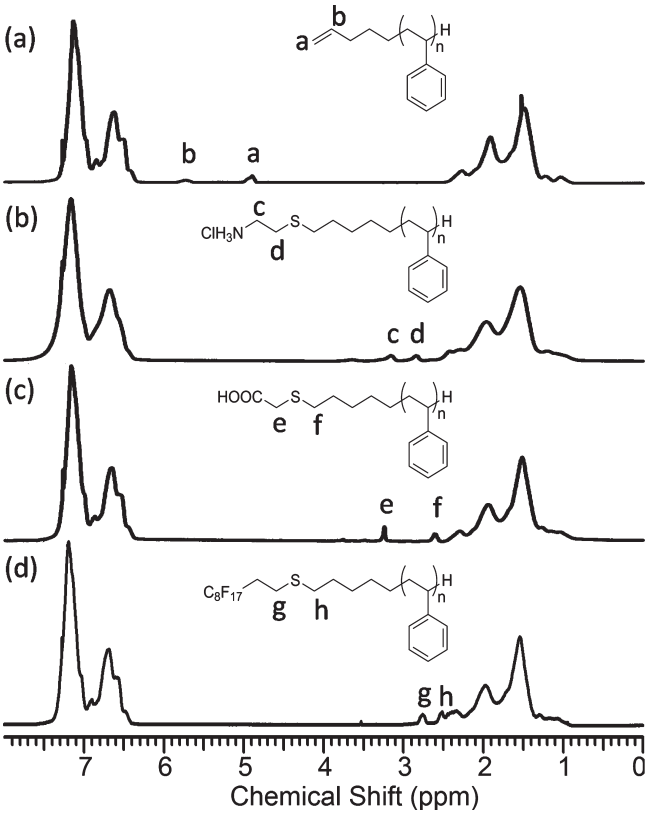


Figure 1. ^{1}H NMR spectra of (a) vinyl-PS, (b) FG1-PS, (c) FG2-PS, and (d) FG3-PS. The polystyrene molecular weights were around 2.5K.

expected (Figure 1a). The vinyl carbons could also be observed at δ 114.1 and 138.9 ppm in the ^{13}C NMR, which was readily distinguished from the aromatic sp^2 carbons of polystyrene (Figure S1). A typical SEC trace is shown in Figure 2a. A symmetric curve can be seen with low polydispersity (PDI = 1.06). The number-average molecular weight obtained from SEC ($M_{n,SEC}$ = 2.4 kg/mol) agrees well with that calculated from the integration raito between the vinyl chain end and aromatic unit ($M_{n,NMR}$ = 2.6 kg/mol). The MALDI-TOF mass spectrum (Figure 3) further confirmed the uniformity and precisely defined structure of the sample with only one narrow distribution of molecular weights corresponding to the proposed structure. A representative monoisotopic mass peak at m/z 2466.5 corresponds to the 22-mer of $[\text{vinyl-PS}\cdot\text{Ag}]^+$, or $C_5H_{10}(C_8H_8)_{22}Ag$, with calculated monoisotopic mass = 2466.4 Da. This was then used as the model compound to demonstrate the concept and the effectiveness of thiol−ene "click" process.

Mono-Functionalization of Vinyl-PS Using Thiol−Ene "Click" Chemistry. To evaluate the versatility and efficiency of thiol−ene "click" process as a new general functionalization method for anionically prepared polymers, three distinct thiols with various functionalities were studied, namely, 2-aminoethanethiol hydrochloride (which is a quaternary ammonium salt), mercaptoacetic acid with carboxylic acid groups, and a thiol with a long perfluorinated alkyl chain, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol. In all of these cases, the functionalization simply involved mixing these commercially available thiols with vinyl-PS and the photoinitiator, DMPA, in a common solvent and irradiating for 15 min. The purification was readily achieved by repeated precipitation to give PS with different α-chain-end

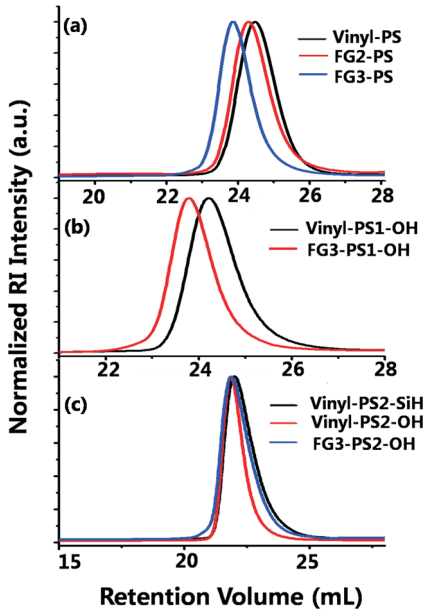


Figure 2. SEC overlays of series of telechilic polystyrenes: (a) monotelechelic polystyrenes (vinyl-PS, FG2-PS, and FG3-PS); (b) heterotelechelic polystyrene by living chain-end functionalization (vinyl-PS1-OH and FG3-PS1-OH); and (c) heterotelechelic polystyrenes by hydrosilylation and thiol−ene chemistry (vinyl-PS2-SiH, vinyl-PS2-OH, and FG3-PS2-OH).

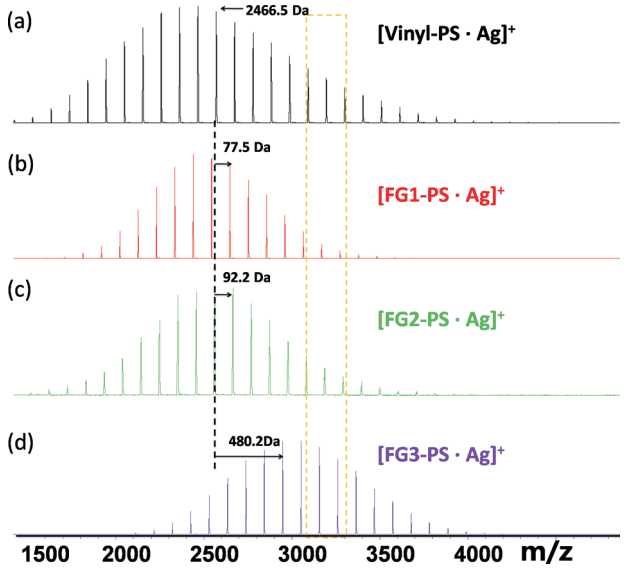


Figure 3. MALDI-TOF mass spectra of (a) vinyl-PS, (b) FG1-PS, (c) FG2-PS, and (d) FG3-PS.

functionalities (FG-PS). All of the major impurities, including excess thiol, the initiator residue, and disulfide byproduct, were easily removed by repeated precipitation, and no chromatography was required. The ease in experimental setup and the ready availability of thiols makes the method a general, modular, and efficient one for the functionalization of anionically prepared polymers.

The ^{1}H NMR spectra of the FG-PS series are shown in Figure 1. Compared to that of vinyl-PS, the peaks assignable to alkene protons (a and b) completely disappeared, which indicates complete reaction within a few minutes. This is in good agreement with the disappearance of the vinyl sp^{2} carbon signals at δ 114.1 and 138.9 ppm in ^{13}C NMR spectra (Figure S1). There are also characteristic resonance peaks emerging in the ^{1}H NMR spectra that are attributed to the formation of thiol ether bonds. For FG1-PS with quaternary ammonium salt functionality, the two methylene protons from the α-chain end can be clearly seen at δ 3.2 ppm for $-NCH_2-$ (c) and δ 2.9 ppm for $-NCH_2CH_2S-$ (d), respectively (Figure 1b). The other thiol ether methylene proton signals are superimposed with polystyrene backbone protons and could not be distinguished clearly. For FG2-PS with carboxylic acid group functionality, the methylene protons (e) between the carbonyl group and to sulfur can be observed at δ 3.3 ppm while the other methylene protons near sulfur (f) show the characteristic peaks at δ 2.5 ppm with the integration ratio being around 2.0: 2.0 as expected (Figure 1c).[36] For FG3-PS, the two methylene protons on each side of the thiol ether linkage could be observed at δ 2.8 and 2.5 ppm for protons (g) and (h), respectively (Figure 1d). The chemical shifts of the methylene protons near CF_2 ($-CH_2CF_2-$) could not be clearly identified and assigned since it overlaps with the peaks from polystyrene backbone protons in the ^{1}H NMR spectra. The successful attachment of new functional groups to the polymer was also supported by the ^{13}C NMR where characteristic peaks for each functional group can be easily identified (Figure S1). The most striking evidence is provided by the MALDI-TOF mass spectra shown in Figure 3. From the overview of the spectra, all of the samples show only one single, narrow distribution of molecular weights. Apparent shifts of m/z 77.5, 92.2, and 480.2 in comparison to vinyl-PS were clearly visible for FG1-PS, FG2-PS, and FG3-PS, respectively, corresponding well to the molecular weight of cysteamine (only cysteamine, instead of its hydrochloride salt, was observed in MALDI-TOF mass spectrum), mercaptoacetic acid, and 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol, respectively. Thus, the corresponding functionalized 22-mers were observed at m/z = 2558.6 for $[FG1\text{-}PS\cdot Ag]^+$, m/z = 2543.9 for $[FG2\text{-}PS\cdot Ag]^+$, and m/z = 2946.7 for $[FG3\text{-}PS\cdot Ag]^+$, respectively. This is consistent with the size exclusion chromatography (SEC) characterizations. In the SEC overlay of FG-PS series (Figure 2a), symmetric, narrow dispersed peaks were observed at different, lower retention volumes as compared to vinyl-PS in the order of FG3-PS < FG2-PS < vinyl-PS (FG3-PS: M_n = 2.8 kg/mol, PDI = 1.04; FG2-PS: M_n = 2.5 kg/mol, PDI = 1.08; vinyl-PS: M_n = 2.4 kg/mol, PDI = 1.06), matching the incorporation of thiols of different sizes onto the base polymer chain end. Probably due to the presence of quaternary ammonium functional groups that strongly interact with each other and with the column during the elution process, we were unable to obtain a good SEC trace with flat baselines,[64,65] and it is thus not shown for comparison. The zoom-in views of the MALDI-TOF mass spectra in selected ranges are shown in Figure S2, which provide the details of monoisotopic mass patterns for vinyl-PS, FG1-PS, FG2-PS, and FG3-PS. Table 1 summarizes the molecular weight characterizations for each polymer reported in this paper for ready comparison. The facts that the experimentally observed m/z values agree well with the calculated molar masses and no unfunctional polymer residue (vinyl-PS) was observed indicate the rapid and complete transformation as well as the high consistency and accuracy of the resulting chemical structures. Although some results (e.g., yields, polydispersities) may be affected, in part, by the repeated precipitation that removed some of the lower molecular weight polymers, it is less likely that any

Table 1. Summary of Molecular Weight Characterizations for the Polymers

sample	molecular formula	M (calcd)[a] (Da)	m/z[b] (obsd)	$M_{n,SEC}$ (g/mol)	PDI
vinyl-PS	$C_{181}H_{186}Ag^+$	2466.4	2466.5	2.4K	1.06
FG1-PS	$C_{183}H_{194}NSAg^+$	2544.4	2543.9	2.5K	1.08
FG2-PS	$C_{183}H_{192}O_2SAg^+$	2558.4	2558.6		
FG3-PS	$C_{191}H_{191}F_{17}SAg^+$	2946.4	2946.7	2.8K	1.04
vinyl-PS1-OH	$C_{183}H_{190}OAg^+$	2510.4	2510.1	2.5K	1.04
FG3-PS1-OH	$C_{193}H_{195}OF_{17}SAg^+$	2990.4	2990.3	2.8K	1.04
vinyl-PS2-SiH	$C_{847}H_{856}SiAg^+$	11171.8		11K	1.02
vinyl-PS2-OH	$C_{850}H_{862}OSiAg^+$	11229.9	11229.7	11K	1.01
FG3-PS2-OH	$C_{860}H_{867}OSiF_{17}SAg^+$	11710.1	11710.0	12K	1.02

[a] Calculated monoisotopic molecular weight of vinyl-PS, FG1-PS, FG2-PS, FG3-PS, vinyl-PS1-OH, FG3-PS1-OH, and average moeluclar weight of vinyl-PS2-SiH, vinyl-PS2-OH, FG3-PS2-OH. [b] Experimentally observed m/z are based on 22-mers of vinyl-PS, FG1-PS, FG2-PS, FG3-PS, vinyl-PS1-OH, FG3-PS1-OH, and 105-mers of vinyl-PS2-SiH, vinyl-PS2-OH, FG3-PS2-OH with a silver ion ($M \cdot Ag^+$).

polymeric impurities can be selectively removed in this way. In addition, the characterization of the crude products right after reaction using ^{1}H NMR confirmed the quantitative transformation of the alkene groups. Therefore, it could be concluded that the polymers possessing 100% functionality and precisely defined structures were readily synthesized by using thiol−ene "click" chemistry as a GFM coupled with alkyllithium-initiated anionic polymerization.

Heterotelechelic Functionalization by Living Anionic Chain-End Modification. In addition to α-functionalized polystyrenes, the combination of anionic polymerization with thiol−ene "click" process presents a facile and versatile method for the preparation of more complex polymeric architectures, such as the α,ω-heterofunctionalized telechelic polystyrenes, enabled by living anionic chain-end functionalization. The living chain-end functionalization of anionic polymers has been studied thoroughly and shown to generate many functional groups in high efficiency, including the hydroxyl groups, thiol groups, silyl hydrides, etc. The end-capping of poly(styryl)lithium by ethylene oxide is known to proceed quantitatively, and only monoaddition is possible in hydrocarbon solvents, resulting in a well-defined, ω-hydroxyl-functionalized polystyrene.[51] The creation of a hydroxyl group at the ω-position also provides numerous possibilities for further functionalization, such as esterification, and growth of a second block by ring-opening polymerization, etc. This simple functionalization scheme was chosen as a proof-of-concept. Indeed, the reaction between vinyl-PS1-Li with ethylene oxide was rapid, and the orange color of vinyl-PS-Li disappeared completely within minutes. Vinyl-PS1-OH was obtained after quenching with methanol. In the ^{1}H NMR spectrum (Figure 4a), there were peaks at δ 5.7 and 4.9 ppm with integration ratio of 1:2 attributable to the vinyl group a as well as new resonance at δ 3.3 ppm that is characteristic for the methylene protons adjacent to hydroxyl group at the ω-chain end.[51] The carbon adjacent to the hydroxyl group is also evident in ^{13}C NMR spectrum at δ 61.8 ppm (Figure S3). In the MALDI-TOF mass spectrum (Figure 5), a single narrow distribution can be clearly seen with the m/z value of 22-mer (2510.1) of vinyl-PS1-OH, in excellent agreement with the calculated monoisotopic molecular mass (2510.4 Da, see also Table 1), which indicates that the vinyl group in the initiator does not interfere with the end-capping reaction and it still proceeds as a quantitative, monoaddition with a precisely defined hydroxyl group at the ω-chain end.

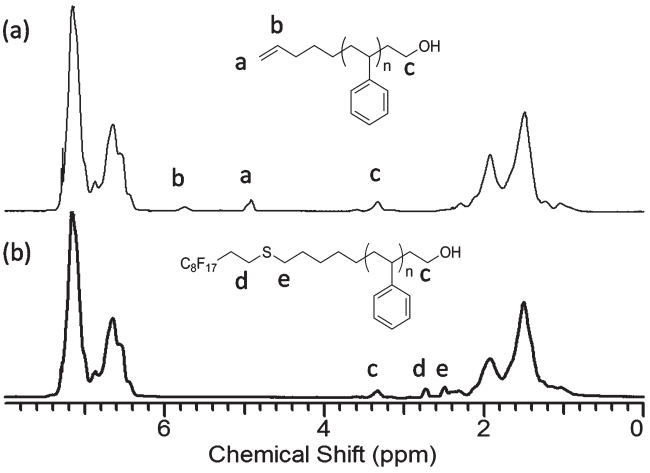


Figure 4. ^{1}H NMR spectra of (a) vinyl-PS1-OH and (b) FG3-PS1-OH.

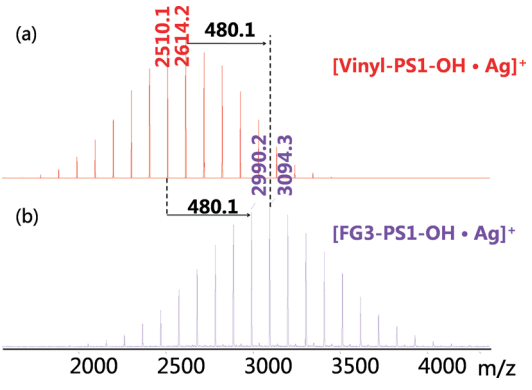


Figure 5. MALDI-TOF mass spectra of (a) vinyl-PS1-OH and (b) FG3-PS1-OH.

Meanwhile, the α-chain-end vinyl group remains reactive and can be converted into various functionalities by thiol−ene chemistry, as shown before. In this work, a perfluorinated thiol was employed as the model reaction because of the possibility to introduce novel self-assembling behavior from the resulting amphiphile. Following the general procedure, pure FG3-PS1-OH was obtained (Scheme 1b). Successful synthesis was confirmed by NMR, SEC, and MALDI-TOF mass spectrometry. As

expected and similar to that of FG3-PS, the disappearance of the resonances at δ 5.7 and 4.9 ppm and the appearance of the new resonances at δ 2.5 and 2.7 ppm in the ^{1}H NMR spectra of FG3-PS1-OH suggest the efficient functionalization and incorporation of the perfluorinated alkyl chains via a thiol−ether linkage. The formation of a thiol−ether linkage is also supported by the new characteristic peak at δ 22.3 ppm in the ^{13}C NMR spectrum (Figure S3). On the other hand, the resonance peak at δ 3.3 ppm in the ^{1}H NMR spectrum, assignable to the methylene protons of $-CH_2OH$ at the ω-end, remains unchanged, indicating that the presence of a hydroxyl group does not interfere with the thiol−ene reaction and no protection/deprotection protocol is necessary. The comparison of the MALDI-TOF mass spectra of vinyl-PS1-OH and FG3-PS1-OH is shown in Figure 5, highlighting a single narrow distribution of peaks for each polymer and an increase of m/z = 480.1 for peaks corresponding to FG3-PS1-OH relative to vinyl-PS1-OH with the same repeating units. Their observed representative monoisotopic masses both agree well with that of the calculated ones (Figure 5 and Table 1), confirming their high purity and precisely defined structure. Similarly, the SEC curve in Figure 2b shows a decrease in retention volume and thus an increase in molecular weight for FG3-PS1-OH relative to vinyl-PS1-OH. The low polydispersity index is maintained (vinyl-PS1-OH: M_n = 2.5 kg/mol, PDI = 1.04; FG3-PS1-OH: M_n = 2.8 kg/mol, PDI = 1.04). The combination of this evidence proves that the presence of a vinyl group in the polymer is compatible with the living chain-end modifications such as end-capping with ethylene oxide and that subsequent thiol−ene "click" chemistry can install a second functionality to the initiating chain end without protection of the hydroxyl group. Therefore, this methodology provides a convenient and versatile general methology for the preparation of α,ω-heterofunctionalized telechelic polymers.

Heterofunctionalization Based on the Combination of Different General Functionalization Methods. Recently, we proposed a general functionalization methodology for anionically prepared polymers in an effort to circumvent the stringent conditions involved in the living chain-end functionalization, to increase the efficiency by eliminating protection/deprotection schemes, and to expand the scope of functional groups that can be incorporated into a single common precursor polymer.[22,23] Hydrosilylation reaction was found to be a typical, versatile general functionalization method because of the following features: (1) the hydrosilyl-functionalized polystyrenes can be synthesized readily in large quantities, and they are stable at room temperature in the presence of oxygen over long time periods; (2) their transformation into various functional groups, catalyzed by Karstedts' catalyst, was very effective and highly tolerant to the presence of functional groups.[22−24,66] The most desirable features about general functionalization methods can be described as robust, efficient, and orthogonal. It will be extremely beneficial to accelerate the construction of novel functional polymers and discovery of new materials if different GFMs can be combined without mutual interference. Strictly speaking, thiol−ene chemistry and hydrosilylation reactions are not orthogonal since both involve olefinic reactants. However, it might be possible to perform sequential functionalization by controlling the stoichiometry of the reactants and the choice of alkene reactivity by effecting hydrosilylation functionalization first. Therefore, a heterofunctional telechelic polystyrene precursor, vinyl-PS2-SiH, was synthesized by end-capping the living vinyl-PS-Li with chlorodimethylsilane to test this idea. To evaluate the efficiency

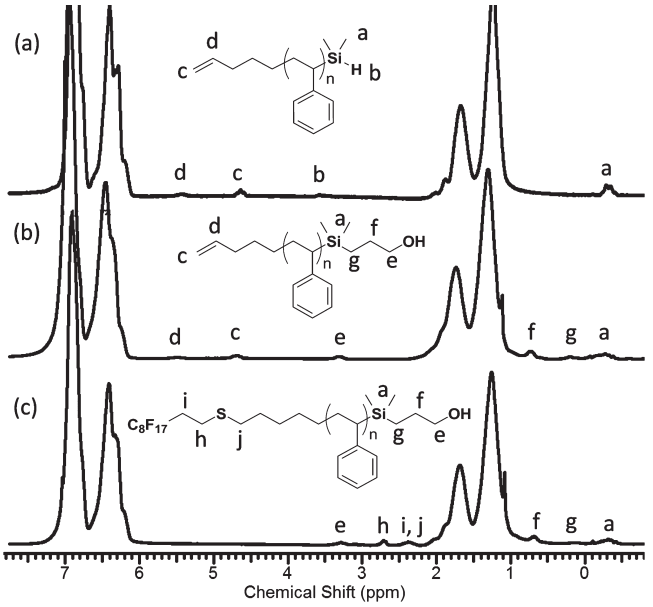


Figure 6. ^{1}H NMR spectra of (a) vinyl-PS2-SiH, (b) vinyl-PS2-OH, and (c) FG3-PS2-OH.

in functionalization of both thiol−ene chemistry and hydrosilylation reactions, a higher molecular weight polymer was adopted (11K of vinyl-PS2-SiH vs 2K of vinyl-PS and vinyl-PS1-OH). In the ^{1}H NMR spectrum (Figure 6), the peak at around δ 3.7 ppm is the characteristic resonance for the proton on silicon.[22] In addition, the integration ratio between the peaks at δ 0.1 ppm - (attributed to two methyl groups loaded to the silicon atom) and the vinyl group peaks at δ 4.9 ppm and at 5.7 ppm is about 6:2:1, confirming the desired structure. Also, there appears a clear absorbance peak at 2110 cm^{-1} in FTIR spectra (Figure S4),[22] which provides direct evidence for the Si−H bond formation. In the SEC trace of vinyl-PS2-SiH (Figure 2c), a single symmetric peak could also be observed (M_n = 11 kg/mol, PDI = 1.02).

To prove the versatility of this α,ω-heterofunctionalization method, we aimed at the same polymer as described in the previous section, FG3-PS1-OH. Hydrosilylation with allyl alcohol and thiol−ene reaction with 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol are the necessary two steps to achieve this. The key is the sequence of the reactions. At first glance, the most straightforward one would be doing the thiol−ene reaction first followed by hydrosilylation. In the absence of the Karstedts' catalyst, the hydrosilylation should not interfere with thiol−ene reaction. However, the hydrosilylation reaction can also proceed by a free radical chain mechanism in which a radical abstracts the proton from Si−H bonds.[67−69] Indeed, when the thiol−ene reaction was implemented first, significant deactivation of Si−H bonds was observed, leading to unseparable side products and high molecular weight impurities in the subsequent hydrosilylation reaction (data not shown).

Fortunately, the side reactions in the hydrosilylation step (e.g., cyclization and condensation) can be suppressed by the addition of a large excess of allyl alcohol (10 equiv). In fact, no cyclized products or polycondensation products could be observed at all after hydrosilylation, evidenced by MALDI-TOF mass spectra and SEC chromatogram of the products. In the ^{1}H NMR spectrum shown in Figure 6, the characteristic resonance peak for the proton of Si−H at δ 3.7 ppm is absent in the

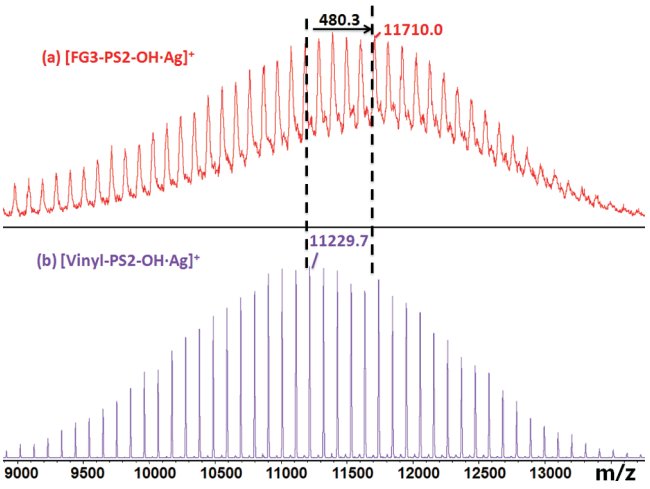


Figure 7. MALDI-TOF mass spectra of (a) vinyl-PS2-OH and (b) FG3-PS2-OH.

hydrosilylation product (vinyl-PS2-OH). The peaks at δ 3.4, 0.8, and 0.3 ppm can be assigned to the newly formed methylene protons at $-CH_2OH$, $-CH_2CH_2OH$, and $-SiCH_2-$, respectively, suggesting that only anti-Markovnikov addition occurred in hydrosilylation. The retention of the resonances at δ 4.9 and 5.7 ppm demonstrates the integrity of vinyl groups at the α-chain end after hydrosilylation. The ^{13}C NMR spectrum of vinyl-PS2-OH further confirmed the successful installation of hydroxyl functionality. The characteristic carbons can be clearly observed, e.g., CH_2OH at 65.8 ppm and $-SiCH_2CH_2CH_2OH$ at 28.8 ppm. In addition, there is no detectable Si−H absorbance at 2110 cm^{-1} in FTIR spectra as shown in Figure S4, indicating again the successful and efficient chain-end functionalization by hydrosilylation.[22,66] The SEC trace of vinyl-PS2-OH (Figure 2c) shows a monomodal, symmetric peak with a narrow molecular weight distribution (M_n = 11 kg/mol, PDI = 1.01). There was very little change in retention volume compared to vinyl-PS2-SiH (M_n = 11 kg/mol, PDI = 1.02), as expected from the simple modification of a single chain end. The characterization of such high molecular weight polymer by MALDI-TOF mass spectrometry is not easy. However, using the linear mode, we were able to obtain an informative spectrum (Figure 7). Only one distribution of peaks is present without any other distributions corresponding to cyclization or condensation side products. The representative peak at m/z = 11229.7 agrees well with the calculated highest mass peak for the 105-mer of $[\text{vinyl-PS2-OH}\cdot\text{Ag}]^+$, $C_{10}H_{22}OSi(C_8H_8)_{105}Ag$, 11 229.9 Da. The very minor distribution, or the shoulder peaks, may be due to the breaking down of functional groups and loss of an allyl alcohol unit from the polymer (about m/z = 58 between each shoulder and related main peak), which is common when employing strong laser energy for ionization of high molecular weight PS samples using the linear mode. In TLC, only one spot was observed at R_f = 0.4 when eluted with toluene. On the basis of these observations, we are assured that a single, precisely defined product was obtained from the hydrosilylation of vinyl-PS2-SiH with allyl alcohol to give vinyl-PS2-OH in the presence of Kartedt's catalyst in quantitative yield.

The subsequent thiol−ene "click" functionalization of vinyl-PS2-OH turned out to be fully compatible and efficient. Even for a molecular weight of 11 kg/mol, it still proceeded in a "click" fashion. The ^1H NMR peaks at δ 5.7 and 4.9 ppm, corresponding to the vinyl group, completely disappeared after 15 min of reaction, and the new protons at the thiol−ether linkages can be clearly observed at around δ 2.8 and 2.5 ppm (Figure 6), as discussed before. All of the resonances related to the ω-chain-end functionality (a, g, e, f) remain intact. Despite the even higher molecular weight than vinyl-PS2-OH with the incorporation of a perfluorinated alkyl chain, the ionization ability of FG3-PS2-OH is still comparably good and sufficient to give an informative MALDI-TOF mass spectrum (Figure 7). There is mainly only one distribution of peaks matching those of the calculated (Table 1). The m/z peaks shifts of $[\text{FG3-PS2-OH}\cdot\text{Ag}]^+$ relative to $[\text{vinyl-PS2-OH}\cdot\text{Ag}]^+$ corresponded to the addition of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-decanethiol unit. The SEC overlay of FG3-PS2-OH with vinyl-PS2-OH (Figure 2c) now showed a single symmetric peak at slightly lower retention volume, owing to the increase in molecular weight (M_n = 12 kg/mol, PDI = 1.02). Therefore, a precisely defined, α,ω-heterofunctionalized telechelic polystyrene was achieved by sequential modification of vinyl-PS2-SiH precursor by hydrosilylation reaction and thiol−ene "click" chemistry. The thiol−ene reactions were found to be compatible with hydrosilylation in this reaction sequence of α-vinyl-ω-silyl hydride polymers. Although the polymer thus synthesized is basically the same as that described in the previous section, this approach possesses advantages in wider scope and better safety considerations since the use of toxic, gaseous ethylene oxide is avoided in the latter case.

CONCLUSIONS

In summary, a series of precisely defined chain-end mono- and heterofunctionalized polystyrenes have been successfully prepared by using the general functionalization methodologies based on anionic polymerization, thiol−ene "click" chemistry, and hydrosilylation reactions. The vinyl group was found to be compatible with anionic polymerization conditions, allowing the preparation of telechelic polystyrenes with various architecture and precise locations of vinyl functionality. The thiol−ene reaction was demonstrated to be a highly efficient and convenient way to introduce different functionalities, such as quaternary ammonium salts, carboxylic acid groups, and perfluorinated alkyl chains, into anionic polymers in a modular way. Precisely defined, α,ω-heterofunctionalized telechelic polymers were facilely synthesized by a combination of thiol−ene chemistry with living anionic chain-end modification or other general functionalization methods such as hydrosilylation reaction. Because of the complications from the side reaction of hydrosilyls with the radical intermediates involved in thiol−ene reaction, the sequence for heterofunctionalization should be carried out in the order of (1) hydrosilylation and (2) thiol−ene chemistry. Moreover, the precursor polymers can be synthesized in large quantity and high purity and are stable over long-term storage, which presents a significant advantage over other functionalization methods. In general, these functionalization methodologies are very versatile, tolerant to a large number of functional groups, require no protection, and may be extended to other anionically polymerizable monomers such as substituted styrenes, vinylaromatics, and vinylpyridines. As a GFM, it has equally important implications in other polymerization systems where the "click" functionalities can be installed. The ability to routinely prepare precisely defined telechelic polymers with modular functionalities, controlled molecular weights, and low polydispersity represents the key feature of the GFM using "click" reactions in

polymer chemistry. We are further developing other functionalization methodologies in combination with anionic polymerization to allow synthesis of more complex architectures, such as in-chain-functionalized or star polymers not readily accessible from other polymerization mechanisms, and possibly orthogonal functionalization to allow more efficient, one-pot functionalization or in-situ modification for various applications. The model telechelic polymers reported in this paper are also interesting intermediates or targets for the study of the self-assembling behavior of fluoro-containing amphiphiles and may serve as building blocks for more complex polymer architectures.

■ ASSOCIATED CONTENT

Supporting Information. Additional information on the synthesis and characterization of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

This work was supported by the National Science Foundation (DMR-0906898, DMR-0821313, CHE-1012636).

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