Anionic Synthesis of Chain-End and In-Chain, Cyano-Functionalized Polystyrenes by Hydrosilylation of Allyl Cyanide with Silyl Hydride-Functionalized Polystyrenes

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ABSTRACT: ω-Cyano-functionalized polystyrene has been prepared in 87% isolated yield using the general functionalization methodology based on anionic polymerization, silyl hydride functionalization, and hydrosilylation with allyl cyanide. First, an ω-silyl hydride-functionalized polystyrene was prepared quantitatively from poly(styryl)lithium by reaction with dimethylchlorosilane in hydrocarbon solution. Then the silyl hydride-functionalized polystyrene was added to allyl cyanide using Karstedt's Pt(0) hydrosilylation catalyst. This general functionalization methodology was also used to develop a new synthesis of in-chain functionalized polymers. First, an in-chain, silyl hydride-functionalized polystyrene was prepared quantitatively from the reaction of excess poly(styryl)lithium with dichloromethylsilane in hydrocarbon solution. The excess poly(styryl)lithium was reacted with ethylene oxide to form an easily separable, hydroxyl-functionalized polystyrene. Then the purified, in-chain silyl hydride-functionalized polystyrene was added to allyl cyanide using Karstedt's Pt(0) hydrosilylation catalyst. The resulting in-chain, cyano-substituted polystyrene was isolated in 58% yield. The silyl hydride- and cyano-functionalized polystyrenes were characterized by SEC, FTIR, ^{1}H and ^{13}C NMR, and MALDI-TOF mass spectrometry.

Introduction

One of the unique features of living polymerizations, in general, and alkyllithium-initiated polymerizations, in particular, is the ability to prepare chain-end functionalized polymers.[1] After complete monomer consumption, the resulting polymeric organolithiums can react with electrophiles to form ω-chain-end functionalized polymers.[2−4] Although many such reactions have been investigated, most of these functionalization reactions are not quantitative and each must be optimized.[5] Thus, it has been of interest to develop general anionic functionalization methods (GFM). GFM encompass reactions that efficiently introduce a variety of functional groups using the same chemistry for all groups.[2]

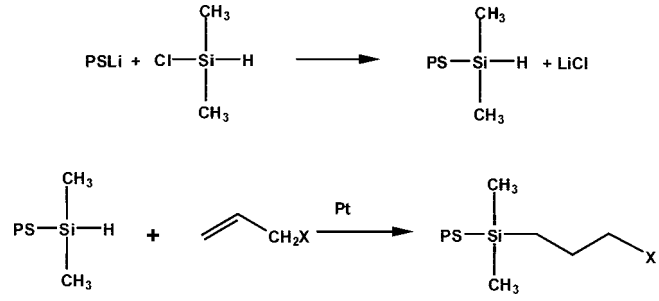
We have recently reported a new general functionalization method based on the combination of living anionic polymerization and hydrosilylation chemistry, as illustrated in Scheme 1.[6] First, living poly(styryl)lithium is terminated with chlorodimethylsilane to prepare chain-end, silyl hydride-functionalized polystyrene. The resulting ω-silyl hydride-functionalized polymer can then react with a variety of readily available substituted alkenes to obtain the desired chain-end functionalized polymer. With this new methodology the living anionic chain end is terminated prior to exposure to the functionalizing agent, eliminating the need for protecting groups in most cases. This methodology has been successfully applied to the synthesis of amine-,[6,7] epoxy-,[8] and perfluoroalkyl-functionalized polymers.[9−11] On the basis of this general functionalization method, it was desired also to investigate its applicability to the synthesis of well-defined, in-chain functionalized polymers, as shown in Scheme 2.

In order to further demonstrate the versatility of this GFM, the incorporation of the cyano functionality was chosen as the target for these studies. The incorporation of cyano functionality can impart polar properties to a material without altering the bulk properties. The large dipole moment of the cyano group has been utilized for the attachment of antibodies[12] and metals.[13] Also, the cyano functionality can easily be transformed to acid, ester, amide, and amine functionalities.[14−16] The cyano group can be transformed into tetrazoles by cycloaddition reactions with azides[17−19] (click chemistry[20]).

Chain-end, cyano-functionalized polystyrene has been produced using ATRP.[21] 2-Bromopropionitrile and *p*-cyanobenzyl bromide were used as ATRP initiators to produce polystyrenes with M_n = 5500 and 5100 Da and with M_w/M_n = 1.10 and 1.09, respectively. Although narrow molecular weight distributions were achieved with high efficiency of functionalization, monomer conversions were limited to less than 50%.

Synthesis of cyano-functionalized products from anionically synthesized materials in hydrocarbon solvent at room temperature or above has not yet been reported. DeSimone et al.[22] proposed that termination of a polymeric organolithium com-

Scheme 1. General Functionalization Methodology for Chain-End Functionalization, Using Chlorosilane Functionalization Followed by Hydrosilylation



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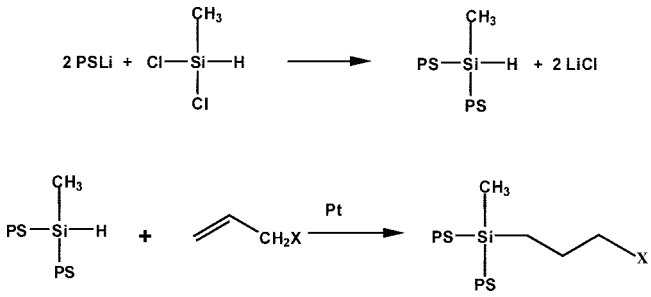
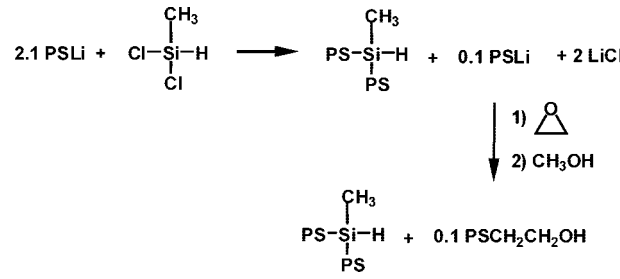
Scheme 2. General Functionalization Method for Synthesis of In-Chain Functionalized Polymers



Scheme 3. Synthesis of In-Chain, Silyl Hydride-Functionalized Polystyrene



pound with a cyano-functionalized chlorosilane could be used to prepare the corresponding cyano-functionalized polymer, but no evidence for this reaction was presented. The acidity of the proton alpha to the cyano functionality (example: Ph−CH_2−CN, pK_a = 21.9)[23] creates a unique challenge for the controlled synthesis of a cyano-functionalized material. One would expect uncontrolled termination of poly(styryl)lithium (PSLi) (estimated pK_a = 43 for the conjugate acid of PSLi based on toluene)[23] in the presence of an aliphatic cyano functionality.

Nakahama et al.[24] investigated the anionic polymerization of 2-, 3-, and 4-cyanostyrenes at −78 °C in THF. Although the polymerizations of 2- and 3-cyanostyrenes were not controlled, anionic polymerization of 4-cyanostyrene with a variety of anionic initiators proceeded to form the corresponding polymers quantitatively with controlled molecular weights and narrow molecular weight distributions. Polymerization at higher temperatures resulted in loss of control and poor conversion even after long reaction times.

Herein we report the application of the general functionalization methodology involving anionic polymerization, silyl chloride linking, and hydrosilylation with allyl cyanide for the synthesis of both well-defined chain-end and in-chain, cyano-functionalized polystyrenes.

Experimental Section

Chemicals and Solvent. Benzene (Certified ACS, EM Science) and styrene (99%, Aldrich) were purified as previously described.[25] Benzene was distilled as needed from poly(styryl-)lithium directly into the polymerization reactor. *sec*-Butyllithium (Chemetall Foote Corp.; 12 wt % in cyclohexane) was used as received after double titration with allyl bromide.[26] Chlorodimethylsilane (98%, Aldrich) and dichloromethylsilane (98%, Aldrich) were 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. Allyl cyanide (98%, Aldrich) was purified by stirring over calcium hydride with periodic degassing for 12 h followed by distillation into an ampule equipped with a Rotoflo stopcock. 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. Silica gel (VWR, 230−400 mesh) was activated by heating to 140 °C for 12 h.

Polymerizations. Poly(styryl)lithiums were prepared under high-vacuum conditions in sealed, all-glass reactors using *sec*-butyllithium as the initiator in benzene (10−15 vol % monomer) at 30 °C.[27] After 12 h and prior to functionalization, an aliquot of poly(styryl)lithium was transferred to an empty ampule, flame-sealed, and quenched with degassed methanol to obtain a base sample.

Synthesis of Chain-End, Silyl Hydride-Functionalized Polystyrene. Chain-end, silyl hydride-functionalized polystyrene was prepared as previously reported by Quirk et al.[6] Poly(styryl)-lithium (10.19 g, 0.00463 mol, M_n = 2200 Da) was terminated with chlorodimethylsilane (1.00 g, 1.18 mL, 0.0107 mol) in benzene at room temperature followed by precipitation into methanol and drying.

Chain-End Functionalization with Allyl Cyanide. Silyl hydride, chain-end functionalized polystyrene (1.00 g, 0.45 mmol, M_n = 2200 Da), dry benzene (10 mL), allyl cyanide (0.0610 g, 0.91 mmol), and Karstedt's catalyst (0.10 mL) were added into a 25 mL, round-bottomed flask in the drybox. The flask was fitted with a reflux condenser and septum, then removed from the drybox, and placed under positive argon pressure at room temperature for a period of 2 weeks. Silica gel was added, stirred overnight, and the mixture was separated via column chromatography using 3/1(v/v) mixture of toluene/cyclohexane; the nonfunctional polystyrene was eluted, and then the desired product was eluted using toluene. The product was extracted with water (3 × 10 mL), concentrated under reduced pressure, and freeze-dried from a benzene solution (0.87 g, 87%).

Preparation of Silyl Hydride, In-Chain Functionalized Polystyrene. Functionalization of poly(styryl)lithium (16.4 g, 0.0137 mol, M_n = 1200 Da) was effected directly in the polymerization reactor by smashing the break-seal for the ampule containing the dichloromethylsilane (0.70 mL, 0.0067 mol, solution in 4.0 mL of benzene) at room temperature. Since a slight excess poly(styryl)lithium was used, the characteristic orange color of the poly(styryl)lithium remained. After 1 day, the resulting polymer was reacted with ethylene oxide (0.5 mL, 0.441 g, 0.01 mol, solution in 9.5 mL of benzene) to functionalize the unreacted poly(styryl-)lithium with a polar end group (Scheme 3). After 1 h the colorless mixture was quenched with methanol. The product was removed from the reactor and precipitated into methanol; the resulting polymer was filtered and dried in a vacuum oven overnight. The silyl hydride, in-chain functionalized polymer was separated from the hydroxyl-functionalized polymer by silica gel column chromatography using a 3/1 (v/v) mixture of toluene/cyclohexane as eluent. The silyl hydride-functionalized polymer eluted first from the mixture; these fractions were combined, concentrated under reduced pressure, and then freeze-dried from a benzene solution (14.8 g, 96%).

In-Chain Functionalization with Allyl Cyanide. Silyl hydride, in-chain functionalized polystyrene (0.5154 g, 0.23 mmol, M_n = 2200 Da), dry toluene (10 mL), allyl cyanide (0.0365 g, 0.54 mmol), and 0.10 mL of Karstedt's catalyst were added into a 25 mL, round-bottomed flask in the drybox. The flask was fitted with a reflux condenser and a septum, removed from the drybox, and allowed to stir in an oil bath (90 °C) under pressure from a balloon filled with a 1/1 mixture of oxygen and argon for a period of 14 days. Incomplete reaction was observed by thin layer chromatography after a period of 5 days, and additional catalyst (0.10 mL) and allyl cyanide (0.0355 g, 0.53 mmol) were added. After no further progress was observed, activated silica was added and stirred for 12 h. Then the nonpolar product was separated via column chromatography using 3/1 (v/v) mixture of toluene/cyclohexane. The desired product was eluted using 3/1 (v/v) mixture of toluene/ethyl acetate, extracted with water (3 × 10 mL), concentrated under reduced pressure, and freeze-dried using benzene (yield: 0.30 g, 58%).

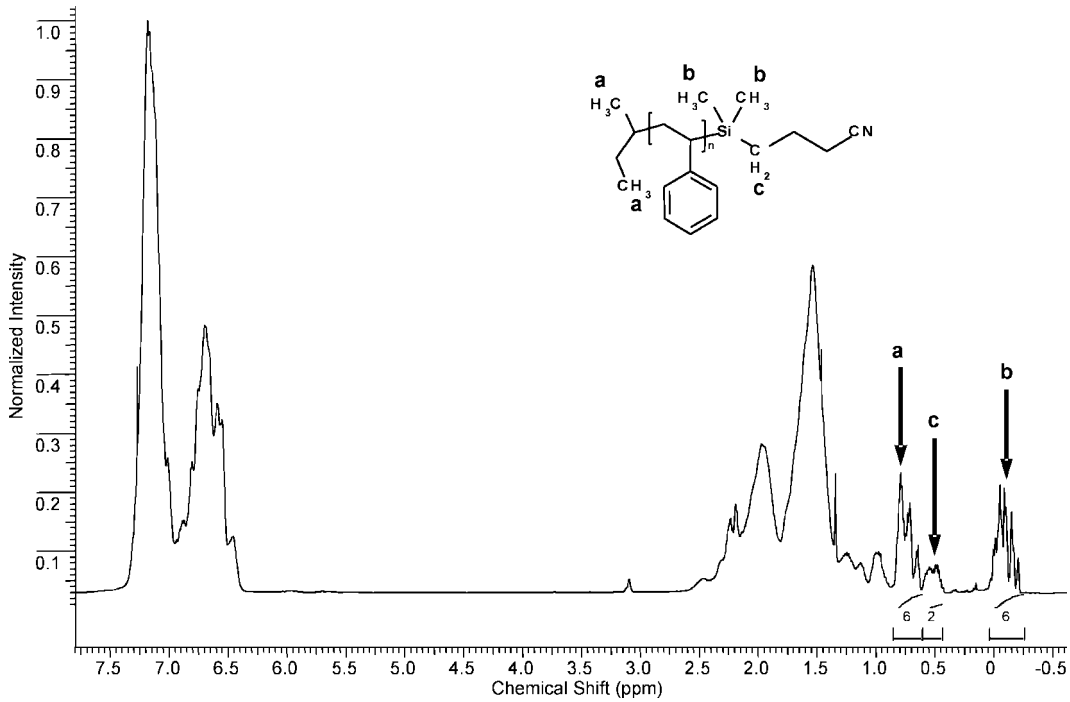


Figure 1. ^{1}H NMR spectrum ($CDCl_3$) of chain-end, cyano-functionalized polystyrene.

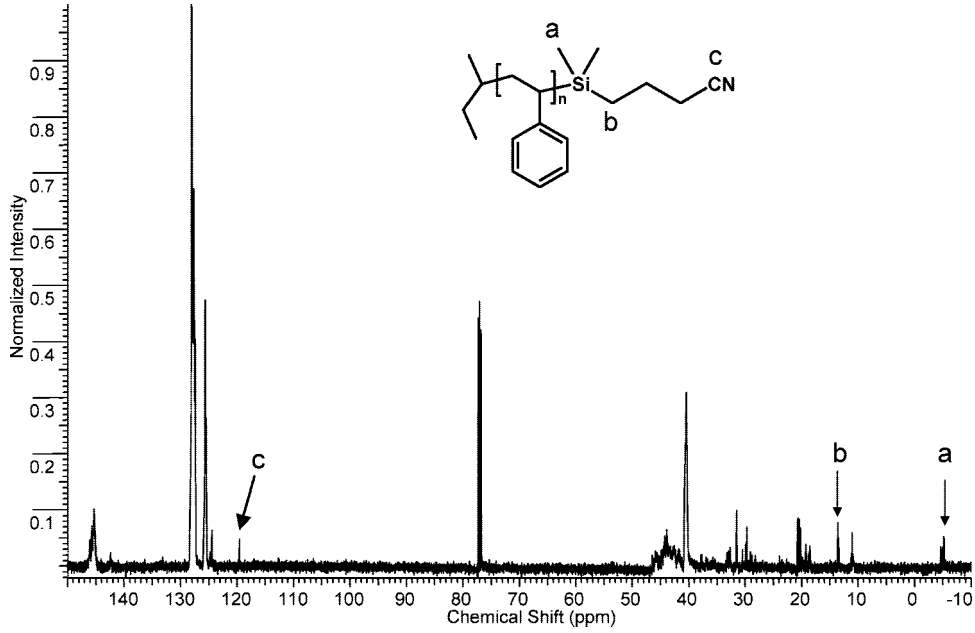


Figure 2. ^{13}C NMR spectrum ($CDCl_3$) of chain-end, cyano-functionalized polystyrene.

Polystyrene Pyrolysis. Chain-end, cyano-functionalized polystyrene (3.5 g, $M_n = 2200$ Da) was placed in a ceramic boat and then transferred to a muffle furnace and maintained at a temperature of 600 °C for a period of 25 min. The residual platinum was dried in an oven at 110 °C for 18 h and then weighed on an analytical balance (residual weight, 0.0036 g). The procedure was repeated for the crude reaction mixture (residual weight, 0.0221 g). The difference in residual platinum was weighed on an analytical balance.

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, $\lambda = 670$ nm). THF was used as eluent with a flow rate of 1.0 mL/min at 30 °C. The sample preparation ($M_n = 1000-8000$ Da) was performed with concentrations ranging from 0.5 to 13.0 mg/mL in THF. Prior to injection, the samples were filtered through a Teflon filter with a 0.45 μm pore size.

All ^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$ (Aldrich, 99.8% D) as solvent using a Varian Mercury 300 or Varian 500 NMR spectrometer. The ^{1}H NMR spectra were referenced to the residual proton impurities in the $CDCl_3$ at δ 7.26 ppm. ^{13}C NMR spectra were referenced to $^{13}CDCl_3$ at δ 77.36 ppm. NMR samples were prepared in 5 mm NMR tubes with ~40 mg of polymer in 1.0 mL of $CDCl_3$.

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting polymer films

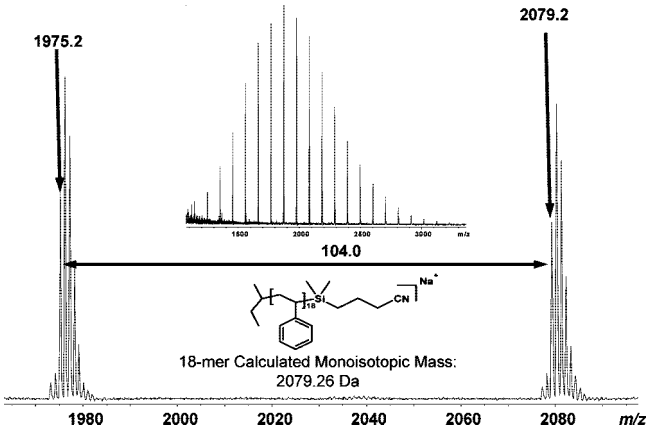


Figure 3. MALDI-TOF mass spectrum of chain-end, cyano-functionalized polystyrene.

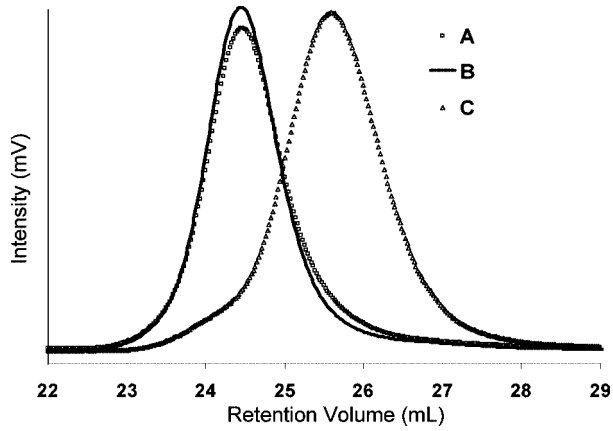


Figure 4. SEC chromatograms of (A) crude product (B) purified product and (C) base sample for the reaction of excess poly(styryl)lithium (M_n = 1.2 × 10^3 g/mol) with dichloromethylsilane, followed by ethylene oxide.

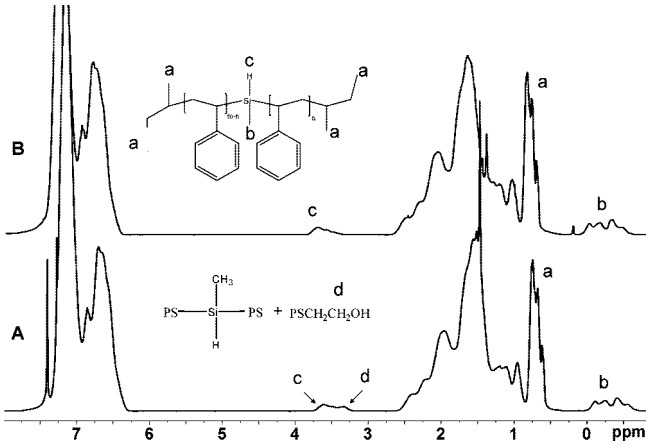


Figure 5. ^{1}H NMR spectrum ($CDCl_3$) of (A) crude product and (B) purified product from the reaction of excess poly(styryl)lithium (M_n = 1.2 × 10^3 g/mol) with dichloromethylsilane, followed by ethylene oxide.

on KBr plates from polymer solutions with subsequent drying at 40−50 °C to remove solvent. The data were processed using Win-IR software.

Thin-layer chromatographic analyses (TLC) were performed by spotting and developing functionalized polymer samples on flexible silica gel plates (Selecto Scientific, Silica Gel 60, F-254 with

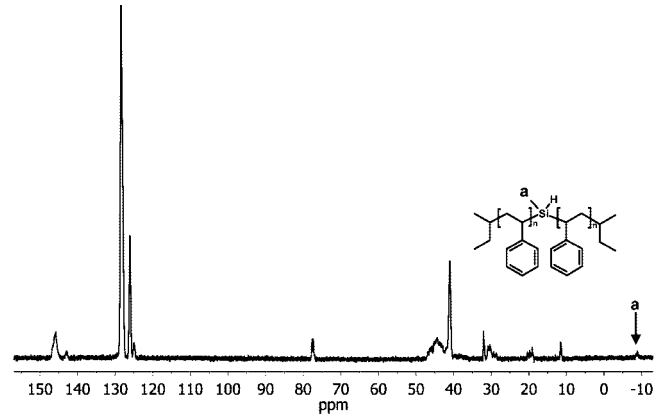


Figure 6. ^{13}C NMR spectrum ($CDCl_3$) of the purified product from the reaction of excess poly(styryl)lithium (M_n = 1.2 × 10^3 g/mol) with dichloromethylsilane.

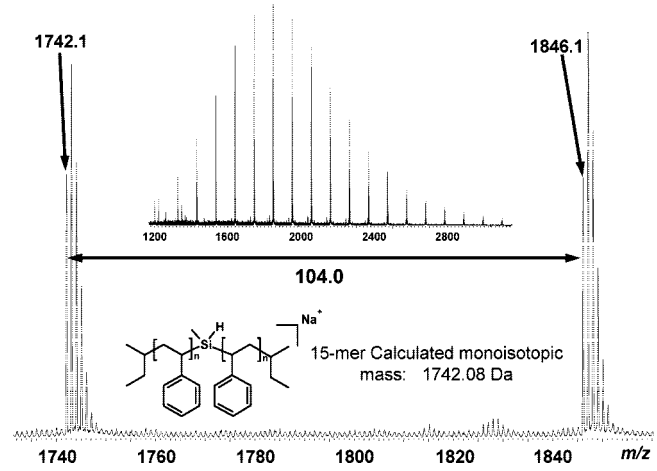


Figure 7. MALDI-TOF mass spectrum of in-chain, silyl hydride-functionalized polystyrene.

fluorescent indicator) using a mixture of toluene and cyclohexane as eluent.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed ion extraction source, and a two-stage gridless reflector. Solutions of dithranol (20 mg/mL) (Alfa Aesar, 1,8,9-anthracenetriol, 97+%), polymer sample (10 mg/mL), silver trifluoroacetate (10 mg/mL) (Aldrich, 98%), or sodium iodide (10 mg/mL) (MCD, 99%) were prepared in THF (Aldrich, 99.9%). These solutions were mixed in the ratio of matrix: cationizing salt:polymer (10:1:2), and 0.5 μL of the mixture was applied to the MALDI sample target and allowed to dry. In order to minimize polymer fragmentation, the intensity of the nitrogen laser pulses was frequently attenuated and adjusted to obtain the optimal signal intensity. Mass spectra were measured in the linear and reflecton modes, and the mass scale was calibrated externally using the peaks of a polystyrene standard at the molecular weight under consideration.

Results and Discussion

Synthesis of Chain-End, Silyl Hydride-Functionalized Polystyrene. In order to investigate the versatility of the previously reported[6] general functionalization method using anionic polymerization, silyl chloride linking, and hydrosilylation chemistry (see Scheme 1), the synthesis of cyano-functionalized polymers was investigated. The first step in this methodology involves preparation of a silyl hydride-

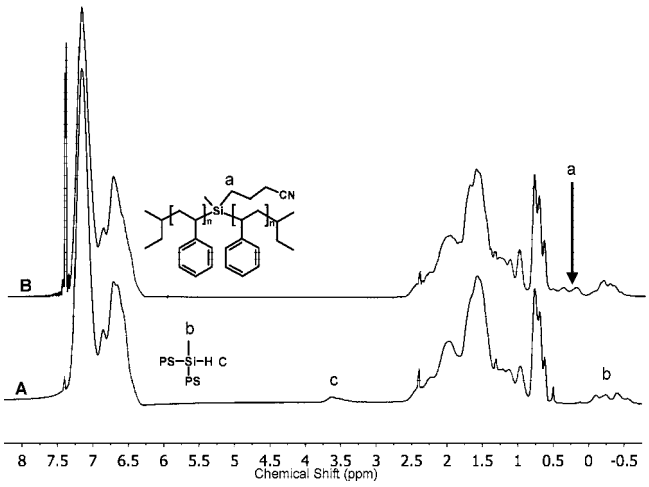


Figure 8. ^{1}H NMR spectrum ($CDCl_3$) of (A) in-chain, silyl hydride-functionalized polystyrene and (B) purified in-chain, cyano-functionalized polystyrene.

functionalized polymer. Chain-end silyl hydride-functionalized polystyrene was prepared as previously reported.[6] The SEC chromatogram showed a narrow, monomodal curve with $M_n = 2200$ Da and $M_w/M_n = 1.05$. For MALDI-TOF analysis of the silyl hydride-functionalized polymers, sodium iodide was used as the cationizing agent to prevent oxidation of the Si−H group to Si−OH as observed previously when silver trifluororacetate was used as the cationizing agent.[6] The MALDI-TOF mass spectrum showed only one distribution with a representative monoisotopic mass peak at m/z 2012.4 corresponding to the 18-mer, silyl hydride-functionalized polystyrene, $C_4H_9-(C_8H_8)_{18}-SiH(CH_3)_2 \cdot Na^+$; calculated monoisotopic mass = 2012.22 Da. The ^{1}H NMR spectrum showed the characteristic peaks for the −SiH proton at δ 3.5−3.8 ppm and the characteristic resonance peaks for the methyl protons on the carbon bonded to silicon at δ −0.1 to −0.4 ppm.[6]

Synthesis of Chain-End, Cyano-Functionalized Polystyrene. The chain-end, silyl hydride-functionalized polystyrene ($M_n = 2200$ Da) was reacted with allyl cyanide in the presence of Karstedt's catalyst (1,3-divinyltetramethyldisiloxane−platinum) at room temperature in benzene solution. The reaction was monitored by thin layer chromatography using toluene as eluent. The silyl hydride-functionalized polystyrene moved to the top of the TLC plate, while the cyanide chain-end functionalized polymer remained near the bottom of the plate. After 2 weeks when only one spot was detected, silica gel was added and stirred for 12 h to aid in catalyst separation.[28] The functionalized polymer was purified by column chromatography using a mixture of toluene and cyclohexane as eluent for the nonfunctional polymer and toluene as eluent for the cyano-functionalized polymer. The cyano, chain-end functionalized polymer was isolated in 87% yield.

The ^{1}H NMR spectrum of the purified product (Figure 1) shows that the characteristic peaks for the −SiH proton at δ 3.5−3.8 ppm have disappeared. The characteristic peaks for the methylene protons in the carbon bonded to silicon are observed at δ 0−0.3 ppm.[8] The integration ratios of the initiator methyl proton resonances from the *sec*-butyl initiator fragment/methylene protons bonded to the carbon adjacent to silicon/methyl protons bonded to carbon adjacent to silicon were 6/2/6, as expected for the cyano chain-end functionalized polystyrene. The ^{13}C NMR spectrum of the purified product (Figure 2) shows the characteristic resonance peak for the carbon in the cyano functional group at δ 119.5 ppm.[29] The characteristic resonance peak for the methyl carbons bonded to silicon is observed at δ −0.9 ppm. The FTIR spectrum shows the disappearance of the characteristic resonance at 2110 cm^{-1} for the −SiH group stretching band[9,29] and a new resonance at 2247 cm^{-1} that corresponds to the nitrile stretching band.[24,29] These results are consistent with the formation of chain-end, cyano-functionalized polystyrene.

The MALDI-TOF mass spectrum of the purified product (Figure 3) shows one distribution. A representative monoisotopic mass peak at $m/z = 2079.3$ corresponds to the 18-mer, in-chain, cyano-functionalized polystyrene $C_4H_9-(C_8H_8)_{18}-$

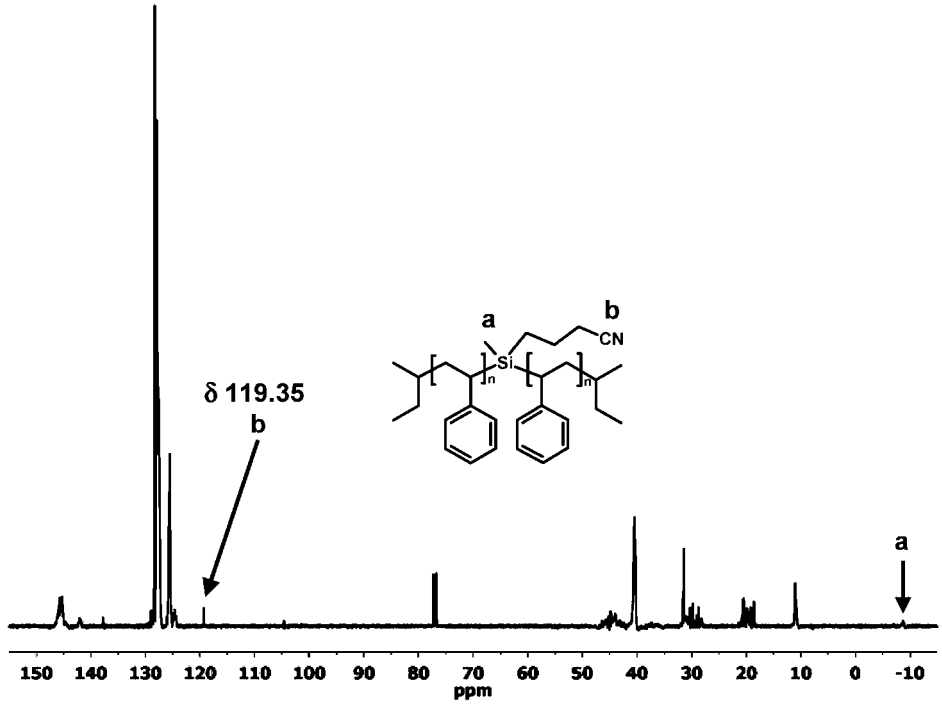


Figure 9. ^{13}C NMR spectrum ($CDCl_3$) of purified in-chain, cyano-functionalized polystyrene.

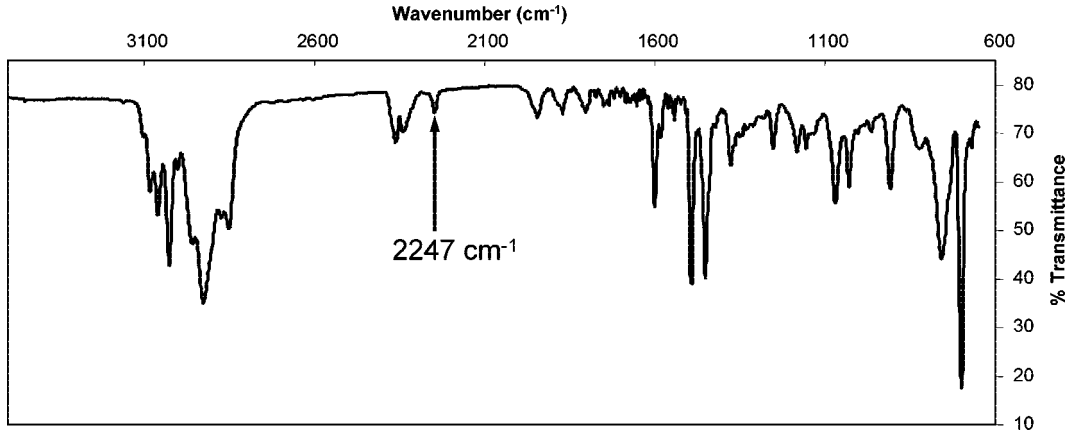


Figure 10. FTIR spectrum of the purified in-chain, cyano-functionalized polystyrene.

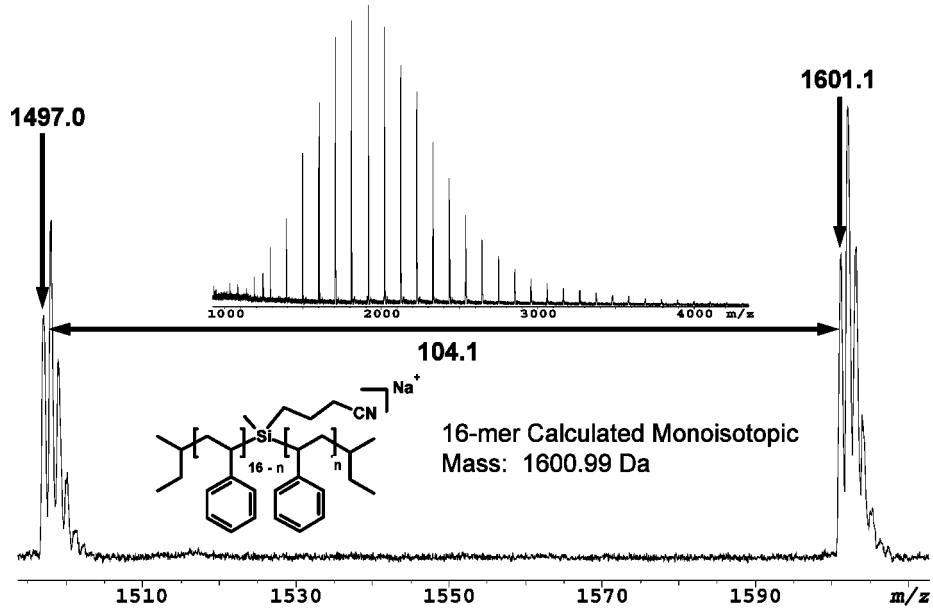


Figure 11. MALDI-TOF mass spectrum of in-chain, cyano-functionalized polystyrene.

$Si(CH_3)_2(CH_2CH_2CH_2CN)\cdot Na^+$; calculated monoisotopic mass = 2079.26 Da. It is worth noting that there are no peaks corresponding to the 18-mer silyl hydride-functionalized polystyrene, $C_4H_9-(C_8H_8)_{18}-SiH(CH_3)_2\cdot Na^+$; calculated monoisotopic mass = 2012.22 Da.

Synthesis of In-Chain, Silyl Hydride-Functionalized Polystyrene. The living functionalization reactions of polymeric organolithium compounds with substituted 1,1-diphenylethylenes is one of the few general functionalization reactions that can be used to prepare in-chain functionalized polymers since this is a living functionalization reaction and the product is a substituted, polymeric 1,1-diphenylalkyllithium that can be used to initiate polymerization of a second monomer.[30] This method suffers from the limitation of most anionic functionalization reactions that protecting groups must be used for many functional groups of interest, e.g., 1° and 2° amine, hydroxyl, carboxyl, and thiol. Therefore, it was of interest to investigate the utility of the GFM method based on the hydrosilylation of silyl hydride-functionalized polystyrenes for the preparation of in-chain functionalized polymers, as illustrated in Scheme 3.

In order to prepare pure, silyl hydride, in-chain functionalized polymers, an excess of poly(styryl)lithium ($M_n = 1.2 \times 10^3$ g/mol, $M_w/M_n = 1.1$) was reacted with dichloromethylsilane, as shown in Scheme 3. After the linking reaction, the excess poly(styryl)lithium was functionalized with ethylene oxide, a very efficient hydroxyl-functionalizing agent.[31,32] Then, after methanol termination, the hydroxyl-functionalized polystyrene could be easily removed from the desired in-chain functionalized product by simple silica gel column chromatography rather than by fractionation, as is common for silyl chloride linking reactions.[33] The SEC chromatogram (Figure 4) of the crude reaction products shows a slightly broadened peak corresponding to the desired coupled product plus some low molecular weight hydroxyl-functionalized polymer. After silica gel column chromatography, the chromatogram of the purified product (Figure 4) shows a narrower, monomodal curve; the molecular weight of the product $M_n = 2.2 \times 10^3$ g/mol is roughly double the molecular weight of the precursor ($M_n = 1.2 \times 10^3$ g/mol) and the narrow molecular weight distribution is narrow ($M_w/M_n = 1.06$), as expected.

The ^{1}H NMR spectra for the crude and the purified products are shown in Figure 5. The characteristic resonance for the −SiH proton is observed at δ 3.2−3.8 ppm. It overlaps with the resonance peak for the methylene hydrogens bonded to the carbon adjacent to the hydroxyl group in the ethylene oxide repeat unit at δ 3.2 ppm.[31,32] After purification by column chromatography, this resonance peak corresponding to the hydroxyl-functionalized polystyrene is not observed. The methyl

protons bonded to the carbon adjacent to silicon have characteristic resonance peaks observed at δ −0.6 to 0 ppm.[6] The ^{13}C NMR of the purified product (Figure 6) shows the characteristic resonance peaks for the methyl carbon attached to the silicon at δ −0.9 ppm.[6]

The MALDI-TOF mass spectrum (Figure 7) of the purified product shows one distribution. A representative monoisotopic mass peak at m/z = 1742.1 corresponds to the 15-mer, in-chain, silyl hydride-functionalized polystyrene $C_4H_9-(C_8H_8)_n-SiH(CH_3)-(C_8H_8)_{15-n}-C_4H_9\cdot Na^+$; calculated monoisotopic mass = 1742.08 Da. This result is consistent with quantitative in-chain, silyl hydride functionalization of poly(styryl)lithium using dichloromethylsilane.

Synthesis of In-Chain, Cyano-Functionalized Polystyrene. The in-chain, silyl hydride-functionalized polymer ($M_n = 2.2 \times 10^3$ Da) was reacted with allyl cyanide in the presence of Karstedt's catalyst. After 2 weeks, no change in the yield of product was observed by TLC analysis; therefore, silica gel was added and stirred for 12 h to aid in catalyst separation. The functionalized polymer was purified by column chromatography using 3:1 toluene:cyclohexane as eluent for the nonfunctional polymer and 3:1 toluene:ethyl acetate as eluent for the cyano-functionalized polymer. The cyano, in-chain functionalized polymer was isolated in 58% yield. The lower yield obtained compared to the chain-end, cyano-functionalized polymer (87%) is probably due to steric crowding around the −Si−H group from the two styryl units and one methyl group bonded to this silicon. It is known that inefficient linking reactions can occur when excess poly(styryl)lithium is reacted with silicon tetrachloride.[33] Steric effects have also been shown to be important in hydrosilylation reactions.[34]

The ^{1}H NMR spectrum of the purified product (Figure 8) shows the disappearance of the characteristic peak for the −SiH proton at δ 3.2−3.8 ppm.[6] The characteristic peaks for the methylene protons on the carbon bonded to silicon are observed at δ 0−0.3 ppm.[8] The ^{13}C NMR spectrum of the purified product (Figure 9) shows the characteristic resonance peak for the carbon in the cyano-functional group at δ 119.4 ppm, almost identical to the analogous cyano chain-end functionalized polymer (δ 119.5 ppm). The characteristic resonance peak for the methyl carbon bonded to silicon is observed at δ −0.9 ppm. The FTIR spectrum (Figure 10) shows the disappearance of the characteristic absorption peak for the −SiH at 2110 cm^{-1} and a new absorption peak at 2247 cm^{-1} that corresponds to the nitrile stretching band.[24,29] These results are consistent with the formation of the expected in-chain, cyano-functionalized polystyrene (see Scheme 3).

The MALDI-TOF mass spectrum of the purified product (Figure 11) showed one distribution. A representative monoisotopic mass peak at m/z = 1601.1 corresponds to the 13-mer, in-chain, cyano-functionalized polystyrene $C_4H_9-(C_8H_8)_n-Si(CH_3)(CH_2CH_2CH_2CN)-(C_8H_8)_{13-n}-C_4H_9\cdot Na^+$; calculated monoisotopic mass = 1600.99 Da. It is worth noting that there are no peaks corresponding to the 14-mer silyl hydride-functionalized polystyrene $C_4H-(C_8H_8)_n-SiH(CH_3)-(C_8H_8)_{14-n}-C_4H_9\cdot Na^+$; calculated monoisotopic mass = 1638.02 Da.

Catalyst Removal. Upon heating, untreated samples of both in-chain and chain-end, cyano-functionalized polymers exhibited color. This is likely due to interaction between residual platinum catalyst and the functionalized product. Catalyst removal was effected by stirring the reaction mixture with activated silica gel followed by column chromatography.[28] The purified product was then extracted with water and freeze-dried using benzene. To test the effectiveness of this method, the sample was pyrolized 600 °C for 25 min, and the residuals were analyzed. It was found that 84% of the platinum catalyst was removed.

Conclusions

The recently developed general functionalization methodology utilizing living alkylyllithium-initiated anionic polymerization in hydrocarbon solution, functionalization with dimethylchlorosilane, and hydrosilylation of allyl cyanide using Karstedt's catalyst has been shown to provide an efficient, facile method for the synthesis of ω-cyano chain-end functionalized polymers. We are unaware of a previously reported anionic method for preparation of these cyano-functionalized polymers. This general functionalization methodology has been found to also be applicable for the synthesis of in-chain functionalized polymers. The reaction of dichloromethylsilane with excess poly(styryl)lithium produces the requisite in-chain, silyl hydride-functionalized polystyrene in quantitative yield. Reaction of this in-chain, silyl hydride-functionalized polystyrene with allyl cyanide in the presence of Karstedt's catalyst produced the corresponding in-chain, cyano-functionalzed polystyrene. However, the yield was only 58%. We are currently investigating methods to improve the yield for this in-chain functionalization chemistry.

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