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Anionic Syntheses of Chain-End and In-Chain Functionalized Polymers by Silyl Hydride Functionalization and Hydrosilylation Chemistry

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Summary: A new general anionic functionalization methodology is described based on (a) the quantitative silyl hydride functionalization of well-defined polymeric organolithium compounds with either dimethylchlorosilane (ω-chain end functionalization) or dichloromethylsilane (in-chain functionalization) and (b) reaction of the silyl hydride-functionalized polymer with a functionalized alkene using Karstedt's *Pt(0)* hydrosilylation catalyst.

Keywords: anionic polymerization; functionalization of polymers; hydrosilylation; living polymerization; MALDI MS; polyisoprene; polystyrene

Introduction

Synthesis of Chain-End Functionalized Polymers

One of the unique features of liviing 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 organolithium can react with electrophiles to form ω-chain-end functionalized polymers.[2-6] Although many such reactions have been investigated, there are few carefully investigated, quantitative functionalization reactions and each must be optimized.[6] 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 functional groups.[2]

We have recently described a new general functionalization method based on the combination of living anionic polymerization and hydrosilylation chemistry as illustrated in Scheme 1.[7] 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-,[7,8] epoxy-,[9] trialkoxysilyl,[10] perfluoroalkyl,[11] and cyano-functionalized polymers.[12]

Synthesis of In-Chain, Functionalized Polymers

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

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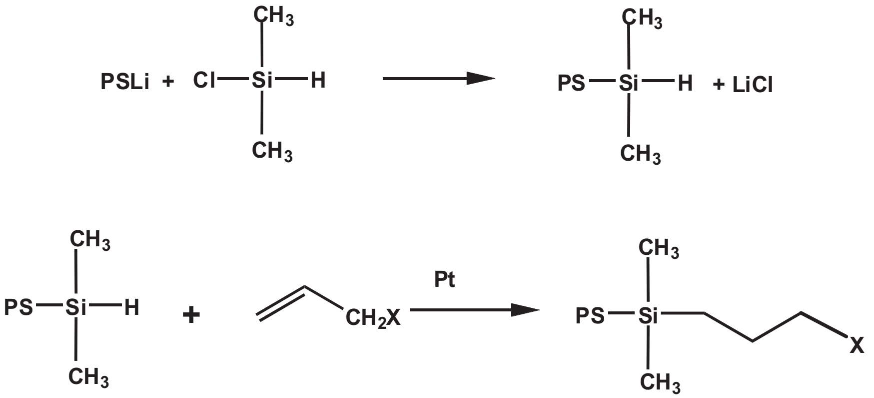


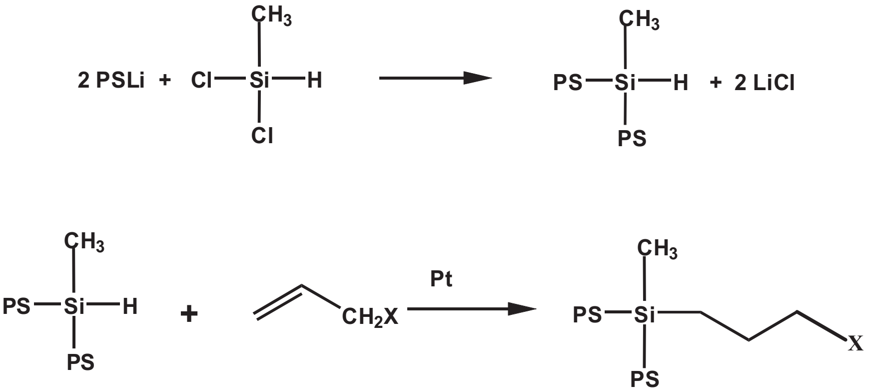
Scheme 1.
General functionalization methodology for chain-end functionalization, using chlorosilane functionalization followed by hydrosilylation.

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.[13] 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., primary and secondary amine, hydroxyl, carboxyl and thiol.[5,14,15] 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 2.[12]

Experimental Part

Chemicals and Solvent

Benzene (Certified ACS, EM Science) and styrene (99%, Aldrich) were purified as previously described.[16] 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.[17] 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



Scheme 2.
General functionalization method for synthesis of in-chain, functionalized polymers.

second batch of calcium hydride, and finally distillation and collection of the middle fraction into calibrated, flame-sealed ampoules. 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 ampoules and flame-sealed.

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.[18] After 12 h and prior to functionalization, an aliquot of poly(styryl)lithium was transferred to an empty ampoule, flame-sealed and quenched with degassed methanol to obtain a base sample.

Synthesis of Chain-End, Functionalized Polystyrene

Chain-end, silyl hydride-functionalized polystyrene was first prepared as previously reported by Quirk et al.[7] Poly(styryl)lithium (10.19 g, 0.00463 mol, $M_n = 2{,}200$ 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. Silyl-hydride, chain-end functionalized polystyrene (1.00 g, 0.45 mmol, $M_n =$ 2,200 Da), dry benzene (10 mL), a substituted allyl derivative (0.91 mmol), and Karstedt's catalyst (0.10 mL) were added into a 25 mL, round-bottomed flask in the dry box. 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 periods ranging from days to weeks. Silica gel was added, stirred overnight, and the mixture was separated via column chromatography using 3/1 (vol/vol) mixture of toluene/cyclohexane; the non-functional polystyrene was eluted, 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.

Synthesis of In-Chain Functionalized Polystyrene

Functionalization of poly(styryl)lithium (16.4 g, 0.0137 mol, $M_n = 1{,}200$ Da) was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing the dichloromethylsilane (0.70 mL, 0.0067 mol, solution in 4.0 mL benzene) at room temperature. Since a slight excess poly(styryl)lithium was used, the characteristic orange color of the poly(styryl)lithium remained. After one 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. 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 (vol/vol) 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%). Silyl-hydride, in-chain functionalized polystyrene (0.5154 g, 0.23 mmol, $M_n = 2200$ Da), dry toluene (10 mL), functionalized allyl derivative (0.54 mmol), and 0.10 mL of Karstedt's catalyst were added into a 25 mL, round-bottomed flask in the dry box. The flask was fitted with a reflux condenser and a septum, removed from the dry box, 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 periods ranging from days to weeks. These reactions were monitored by TLC, FTIR and ^{1}H NMR spectroscopy. Standard work-up procedures followed as described above.

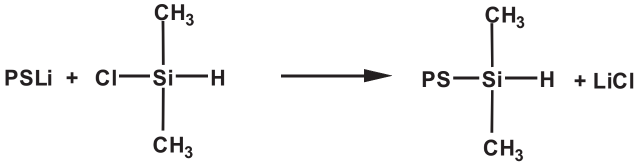
MALDI-TOF Mass Spectrometric Characterization

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).[19] 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. The intensity of the nitrogen laser pulses was adjusted to obtain optimal signal intensity and minimal polymer fragmentation. 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 Polymers

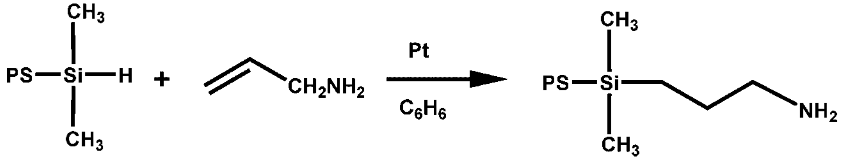
For the general chain-end functionalization method outlined in Scheme 1, the first step is the formation of a silyl hydride functionalized polymer by reaction of poly(styryl)lithium (or other polymeric organolithium) with dimethylchlorosilane, a reactive, readily available reagent. A typical reaction of poly(styryl)lithium ($M_n = 2.2 \times 10^3$ g/mol, $M_w/M_n = 1.02$) with 2.3 mol equiv of chlorodimethylsilane was effected in benzene at room temperature as shown in Equation 1. Precipitate formation was observed immediately after smashing the breakseal containing chlorodimethylsilane; a color change from red to colorless occurred within a few minutes, indicating a very fast reaction rate. The silyl hydride end-functionalized polystyrene was generally isolated in essentially quantitative yield. These silyl hydride-functionalized polymers exhibited characteristic ^{1}H and ^{13}C NMR spectra, and FTIR spectra, and were unambiguously characterized from their monoisotopic masses by MALDI-TOF mass spectral analyses.[7,19] It is noteworthy, however, that the normal cationizing agent used for MALDI-TOF mass spectral analysis, silver trifluoroacetate, could not be used because this reagent effected the oxidation of the Si-H functionality to Si-OH; sodium and potassium cationizing agents were required.[7]



$$\mathrm{PSLi} + \mathrm{Cl{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{{-}H} \longrightarrow \mathrm{PS{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{{-}H} + \mathrm{LiCl}$$

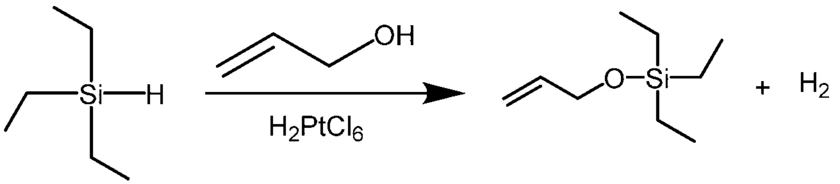
(1)

One of the primary advantages of the GFM described herein, in contrast to most direct, post-polymerization, anionic functionalization reactions with electrophilic reagents, is that protecting groups are not required for most functional groups in the hydrosilylation functionalization step. One of the most dramatic demonstrations of this advantage is the primary amine functionalization using allyl amine (3.1 equivalents) at room temperature as shown below in Equation 2.[7] Although this reaction is relatively slow, requiring 72 hours, the corresponding amine-functionalized polymer was isolated in 98% yield.



(2)

Another example of the value of this general functionalization method and the use of Karstedt's catalyst concerns the preparation of hydroxyl chain-end functionalization. According to existing literature, the hydroxyl group is one of the few functional groups that must be protected during hydrosilylation reactions. Thus, it was reported that direct hydrosilylation cannot be used directly for hydroxyl functionalization using hexachloroplatinic acid (Speier's catalyst).[20] Instead, these alkenes react rapidly with silyl hydride groups in the presence of this catalyst for form Si–O–C bonds by dehydrogenative coupling (see Equation 3); this results in formation of siloxy alkenes instead of the hydroxyl product by Si–C bond formation across the double bond.



(3)

In order to explore these reactions, the tetrabutylammonium analog of Spier's catalyst, Lukevics' catalyst,[21] was first investigated. Thus, allyl alcohol (3.2 molar equivalents) was reacted with silyl hydride-functionalized polystyrene ($M_n = 1.8 \times 10^3$ g/mol, $M_w/M_n = 1.03$) in the presence of a catalytic amount of tetrabutylammonium hexachloroplatinate(IV) catalyst in benzene. The SEC of the products is shown

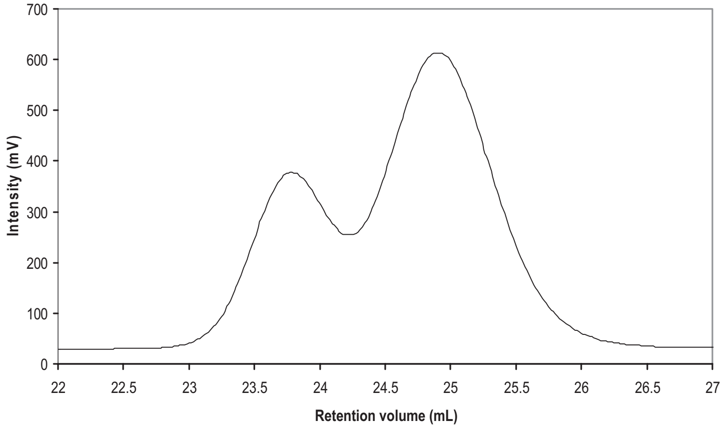
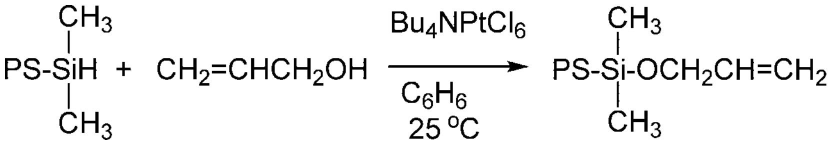


Figure 1.

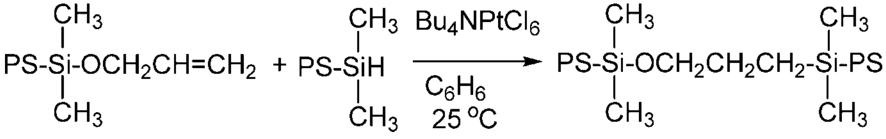
SEC chromatogram for the products from the hydrosilylation of allyl alcohol with silyl hydride-functionalized polystyrene using Bu_4NPtCl_6 as catalyst.

in Figure 1. The formation of a significant amount of dimer is an indication of the complexity of this reaction in contrast to all of our previous functionalizations using Karstedt's catalyst for the hyrosilylations. After thorough characterization of the reaction products (TLC, NMR, FTIR, MALDI-TOF mass spectrometric analysis),[22] it was determined that the main product from this reaction resulted from dehydrogenative coupling of allyl alcohol with the silyl-hydride-functionalized polystyrene (Equation 4). The dimeric product resulted from hydrosilylation of this product with silyl-hydride- functionalized polystyrene (Equation 5). It is interesting to note that MALDI-TOF mass spectrometric analysis provided no evidence for the formation of the expected hydrosilylation product, the ω-hydroxypropyl-functionalized polystyrene. These results are consistent with previous results of hydrosilylations with allyl alcohol using Speier's catalyst in that the C=C bond of the alcohol is not hydrosilated.[20] However, when this hydroxyl functionalization reaction was effected in benzene solution using Karstedt's catalyst, the hydroxyl-functionalized polystyrene was isolated in quantitative yield after 12 hour at room temperature (Equation 6). The ^{1}H NMR spectrum of the product (Figure 2) indicated that only the desired hydroxylated polystyrene was formed. There were no peaks observed in the δ 5–6.5 ppm region for the allylic protons of the siloxy alkene (see Equation 4) or at δ 3.8 ppm for unreacted silyl hydride-functionalized polystyrene. The observance of a peak in the regions of δ 3.4–3.6 ppm corresponding to the methylene protons adjacent to oxygen indicates the successful synthesis of the desired product. The 6: 6: 2 integration of the six methyl protons of the initiator to the 6 methyl protons adjacent to the silicon to the 2 methylene protons adjacent to the hydroxyl group is consistent with quantitative functionalization.

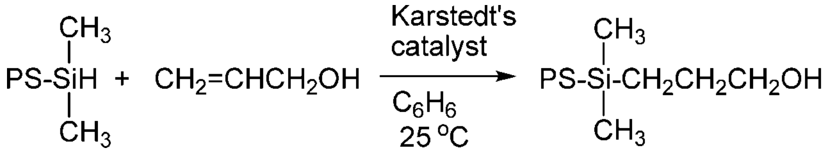
These results further document the utility, uniqueness and specificity of the use of Karstedt's catalyst for the functionalization of polymeric silyl hydrides with substituted alkenes. This procedure also provides an alternative to the use of epoxides for anionic synthesis of well-defined, ω-hydroxyl-functionalized polymers.[23,24]



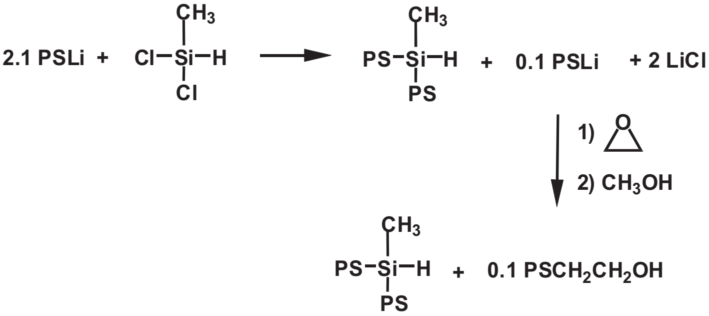
$$\mathrm{PS\text{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{H} + \mathrm{CH_2{=}CHCH_2OH} \xrightarrow[\mathrm{C_6H_6},\ 25\,^{\circ}\mathrm{C}]{\mathrm{Bu_4NPtCl_6}} \mathrm{PS\text{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{\text{-}OCH_2CH{=}CH_2} \qquad (4)$$



$$\mathrm{PS\text{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{\text{-}OCH_2CH{=}CH_2} + \mathrm{PS\text{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{H} \xrightarrow[\mathrm{C_6H_6},\ 25\,^{\circ}\mathrm{C}]{\mathrm{Bu_4NPtCl_6}} \mathrm{PS\text{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{\text{-}OCH_2CH_2CH_2\text{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{\text{-}PS} \qquad (5)$$



$$\mathrm{PS\text{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{H} + \mathrm{CH_2{=}CHCH_2OH} \xrightarrow[\mathrm{C_6H_6},\ 25\,^{\circ}\mathrm{C}]{\text{Karstedt's catalyst}} \mathrm{PS\text{-}}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{\text{-}CH_2CH_2CH_2OH} \qquad (6)$$



Scheme 3.
Synthesis of in-chain, silyl hydride-functionalized polystyrene.

Synthesis of In-Chain, Functionalized Polymers

As described in the Introduction, there are few reliable methods, other than the use of substituted 1,1-diphenylethylene chemistry,[13] to prepare well-defined, in-chain functionalized polymers. 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 2.

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.[23,24] 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.[25] After purification, the SEC chromatogram of the coupled product exhibited a narrow ($M_w/M_n = 1.06$), monomodal curve and the molecular weight of the product ($M_n = 2.2 \times 10^3$ g/mol) was roughly double the molecular weight of the precursor ($M_n = 1.2 \times 10^3$ g/mol).

The ^{1}H NMR spectra for the purified in-chain, silyl hydride-functionalized polystyrene exhibited the characteristic resonance for the $-$SiH proton at δ 3.2–3.8 ppm. The MALDI-TOF mass spectrum (Figure 3) 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.

The incorporation of the cyano functionality was chosen as a target functionality for illustrating the versatility of this GFM method for the synthesis of in-chain functional polymers.[12] Synthesis of cyano-functionalized products from anionically synthesized materials in hydrocarbon solvent at room temperature or above has not yet been reported.

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 two weeks, no change in the yield of product was observed by TLC analysis. The cyano, in-chain functionalized polymer was isolated in 58% yield after column chromatography. The lower yield obtained compared to the analogous preparation of 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

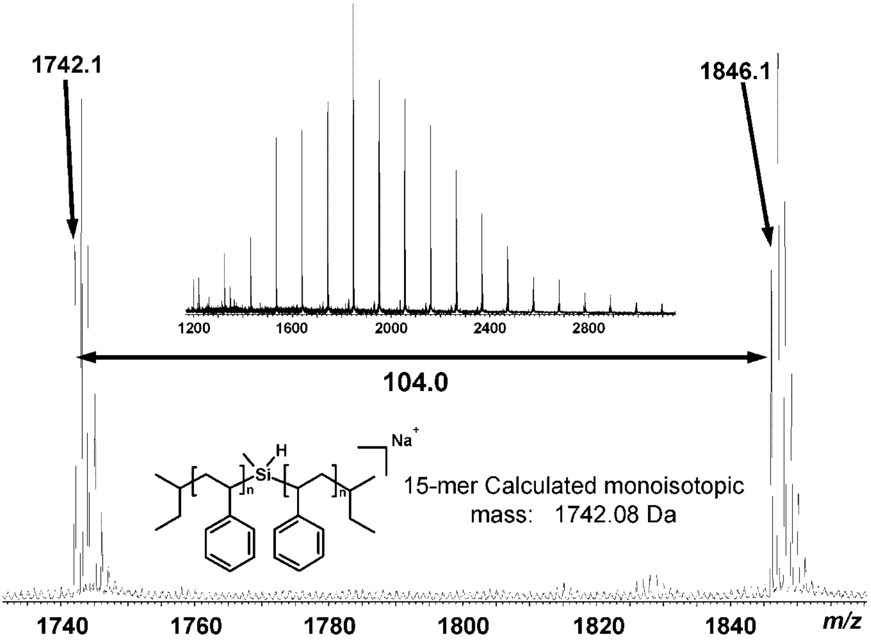


Figure 3.
MALDI-TOF mass spectrum of in-chain, silyl hydride-functionalized polystyrene ($M_n = 2{,}200$ g/mol).

silicon. It is known that inefficient linking reactions can occur when excess poly(styryl)lithium is reacted with silicon tetrachloride.[25] Steric effects have also been shown to be important in hydrosilylation reactions.[26] The structure of this in-chain, cyano-functionalized polystyrene was characterized by FTIR, ^{1}H and ^{13}C NMR and

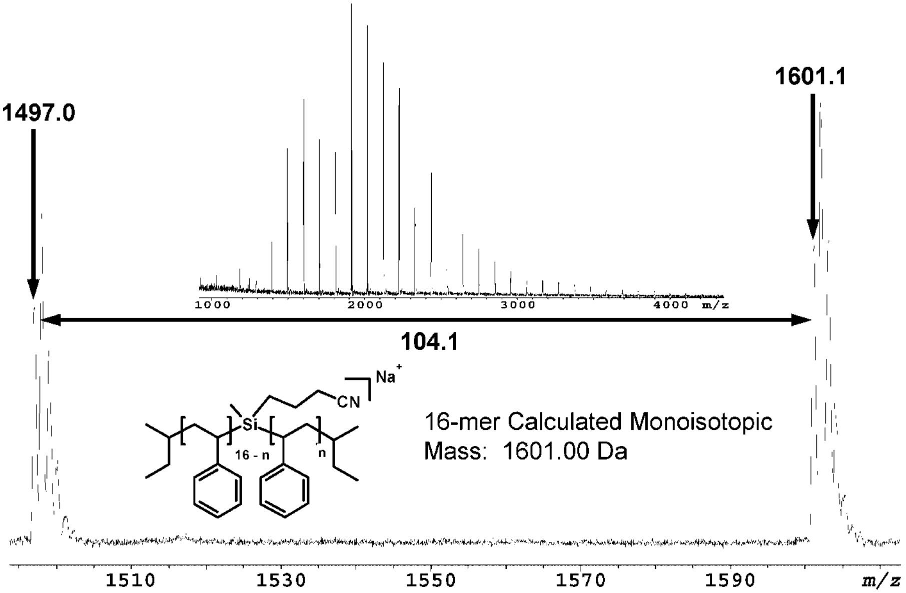


Figure 4.
MALDI-TOF mass spectrum of the in-chain, cyano-functionalized polystyrene.

MALDI-TOF mass spectrometry. The MALDI-TOF mass spectrum of the purified product (Figure 4) 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 = 1601.00 Da.

Conclusions

The recently developed general functionalization methodology utilizing living alkyllithium-initiated anionic polymerization in hydrocarbon solution, functionalization with dimethylchlorosilane and hydrosilylation of functional allyl derivatives using Karstedt's catalyst has been shown to provide an efficient, facile method for the synthesis of chain-end functional polymers. Analogously, this method has been extended to the synthesis of in-chain functionalized polymers by using dichloromethylsilane as the anionic silyl hydride functionalizing and linking agent. The advantages of this method are (a) the method is versatile and can be used to prepare a wide range of functional polymers; (b) the silyl hydride functionalized polymer can be isolated by normal precipitation methods and transferred in air; (c) in contrast to anionic post-polymerization electrophilic functionalization reactions, the use of protecting groups is not required generally for most functional groups during the hydrosilylation step; (d) only catalytic amounts (ppm) of Karstedt's catalyst are required; (e) a wide range of substituted allyl derivates are readily available.

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[1] O. S. Webster, *Science* **1991**, *251*, 887.

[2] H. L. Hsieh, R. P. Quirk, *Anionic Polymerization: Principles and Practical Applications*, Marcel Dekker, New York **1996**.

[3] R. P. Quirk, D. L. Gomochak, *Rubber Chem. Technol.* **2003**, *76*, 812.

[4] R. P. Quirk, D. L. Pickel, in *Living and Controlled Polymerization. Synthesis, Characterization and Properties of Respective Polymers and Copolymers*, J. Jagur-Grodzinski, Ed., Nova Science Publishers, Hauppage, New York **2006**, p. 235–255.

[5] A. Hirao, M. Hayashi, *Acta Polym.* **1999**, *50*, 219.

[6] R. P. Quirk, in *Comprehensive Polymer Science*, First Supplement S. L. Aggarwal, S. Russo, Eds., Pergamon, Oxford **1992**, p. 83.

[7] R. P. Quirk, H. Kim, M. J. Polce, C. Wesdemiotis, *Macromolecules* **2005**, *38*, 7895.

[8] K. Loos, A. H. Müller, *Biomacromolecules* **2002**, *3*, 368.

[9] R. B. Jayaraman, J. V. Facinelli, J. S. Riffle, S. E. George, *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 1543.

[10] R. P. Quirk, M. Ocampo, R. L. King, M. J. Polce, C. Wesdemiotis, *Rubber Chem. Technol.* **2008**, *81*, 77.

[11] R. P. Quirk, H. Kim, S. R. Chowdhury, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2005**, *46*(2), 583.

[12] R. P. Quirk, J. Janoski, S. R. Chowdhury, C. Wesdemiotis, D. E. Dabney, *Macromolecules* **2009**, *42*, 494.

[13] R. P. Quirk, T. Yoo, Y. Lee, J. Kim, B. Lee, *Adv. Polym. Sci.* **2000**, *153*, 67.

[14] A. Hirao, S. Nakahama, *Acta Polym.* **1998**, *49*, 133.

[15] T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd ed. Wiley-Interscience, New York **1999**.

[16] R. P. Quirk, W.-C. Chen, *Makromol. Chem.* **1982**, *183*, 2071.

[17] H. Gilman, F. K. Cartledge, *J. Organomet. Chem.* **1964**, *2*, 447.

[18] M. Morton, L. J. Fetters, *Rubber Chem. Technol.* **1975**, *48*, 3.

[19] M. A. Arnould, M. J. Polce, R. P. Quirk, C. Wesdemiotis, *Internat. J. Mass Spectrometry* **2004**, *238*, 245.

[20] B. Marciniec, *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford **1992**.

[21] I. G. Iovel, Y. Sh. Goldberg, M. V. Shymanska, E. Lukevics, *Organometallics* **1987**, *6*, 1410.
[22] Unpublished work of Michael Olechnowicz, Ph.D. Thesis, University of Akron, **2008**.
[23] R. P. Quirk, R. T. Mathers, C. Wesdemiotis, M. Arnould, *Macromolecules* **2002**, *35*, 2912.
[24] R. P. Quirk, J.-J. Ma, *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2031.
[25] M. Morton, T. E. Helminiak, S. O. Gadkary, F. Bueche, *J. Polym. Sci.* **1962**, *57*, 471.
[26] J. Stein, L. N. Lewis, K. A. Smith, L. X. Lettko, *Inorg. Organomet. Polym.* **1991**, *1*, 325.