Anionic Synthesis of Primary Amine Functionalized Polystyrenes via Hydrosilation of Allylamines with Silyl Hydride Functionalized Polystyrenes

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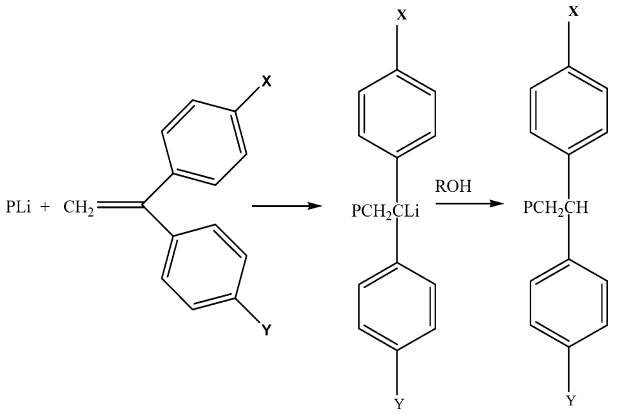
ABSTRACT: A general anionic ω-chain-end functionalization methodology is described and illustrated by the synthesis of ω-primary amine functionalized polystyrenes. First, the quantitative ω-silyl hydride functionalization of well-defined poly(styryl)lithium (M_n = 2200 and 14 100 g/mol) was effected with dimethylchlorosilane in hydrocarbon solution at room temperature. In the second step, involving amination by hydrosilation, the silyl hydride functionalized polystyrene was added quantitatively to 3-[*N*,*N*-bis-(trimethylsilylamino]-1-propene, a protected amine, using Karstedt's Pt(0) hydrosilation catalyst in benzene. One of the principal advantages of this method is the fact that it is not necessary to use protecting groups for many functional groups, as illustrated by the quantitative primary amine functionalization of ω-silyl hydride functionalized poly(styryl)lithium with allylamine using the Karstedt's hydrosilation catalyst. The silyl hydride and amine functionalized polystyrenes were characterized by SEC, FTIR, ^{1}H and ^{13}C NMR, MALDI-TOF mass spectrometry, and end-group titration.

Introduction

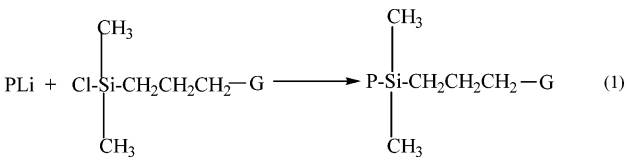
One of the unique features of living polymerizations is the ability to prepare chain-end-functionalized polymers by termination of the living ends with appropriate reagents.[1] Alkyllithium initiated anionic polymerization has proven to be a useful methodology for the synthesis of chain-end-functionalized polymers with low degrees of compositional heterogeneity.[2−5] Under appropriate conditions, alkyllithium initiated polymerizations of styrenes, dienes, and (meth)acrylates are living and form stable anionic chain ends when all of the monomer has been consumed. These anionic chain ends can react with various electrophiles to form a diverse array of chain-end-functionalized polymers. Despite the potential of this methodology, there are relatively few well-characterized, efficient chain-end functionalization reactions.[5] One problem is that the introduction of each different functional group generally requires a different electrophilic terminating agent. Thus, optimized reaction conditions must be found for each new functionalization reaction. As an alternative to these specific functionalization reactions, researchers have sought *general functionalization reactions* that proceed efficiently to introduce a wide variety of functional groups using one type of mechanistic chemistry and substrate.[2]

One general, efficient chain-end functionalization methodology is the reaction of polymeric organolithium compounds with substituted 1,1-diphenylethylene compounds and their analogues (Scheme 1; X, Y represent different functional groups or their protected derivatives).[6] This reaction is a quantitative, stoichiometric addition reaction that can be monitored by UV−visible spectroscopy, and a wide variety of substituted 1,1-diarylethylenes, readily prepared from the corresponding ketones, has been investigated. Unlike most electrophilic functionalization reactions that terminate the carbanionic chain end, this method has the advantage that it is a living functionalization reaction, i.e., the product is a polymeric organolithium compound that can initiate polymerization of other monomers or undergo further reactions.[6]

Scheme 1



The reaction of polymeric organolithium compounds with substituted silyl halides is another general functionalization reaction that is not complicated by competing side reactions (eq 1 where G is a functional group or protected functional group).[7,8] This chemistry has been used to prepare primary amine-, hydroxyl-, and perfluoroalkyl-terminated polymers.[7,8]



(1)

One of the principle limitations of both of these general termination methodologies is the requirement

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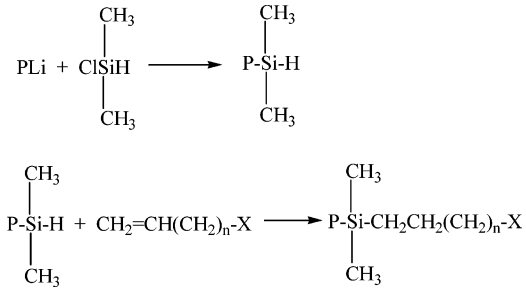
Scheme 2



that many reactive groups, e.g., primary and secondary amine, hydroxyl, carboxyl, and thio, must be converted to stable derivatives using suitable protecting groups.[4,9−11] The synthesis of these protected functional group derivatives is often a multistep process, and the protecting groups must be removed after the functionalization reaction.

Herein a general functionalization methodology is described that involves first the quantitative termination of living polymeric organolithium compounds with dimethylchlorosilane to form the corresponding ω-silyl hydride functionalized polymer. The resulting silyl hydride functionalized polymer can then react with a variety of readily available substituted alkenes to form the corresponding chain-end-substituted polymers via efficient, regioselective transition metal catalyzed hydrosilation reactions (Scheme 2).[12−15] Riffle and coworkers[16] first described this methodology to prepare an epoxide-functionalized polymer by reacting poly(butadienyl)lithium (prepared in THF/cyclohexane) with chlorodimethylsilane, hydrogenating the double bonds, and then effecting hydrosilation with allyl glycidyl ether. Recently, Loos and Müller[17] prepared maltoheptaose-*block*-polystyrene by the hydrosilation reaction of a silyl hydride functionalized polystyrene (prepared in THF at −78 °C) with trieicosaacetyl-*N*-allylmaltoheptaonamide.

One of the unrealized advantages of this methodology is that the hydrosilation reaction is relatively insensitive to anionically reactive functional groups such as carboxyl, phenol, and nitro, as well as primary and secondary amine groups, i.e., no protecting groups are required.[14] The utility of this methodology is illustrated herein by its application to the facile synthesis of ω-primary amine functionalized polystyrene for which few other simple, efficient anionic functionalization procedures are available.[7,8,18−27]

Experimental Section

Chemicals and Solvents. Styrene (99% Aldrich) and benzene (EM Science, ACS grade) were purified as described previously.[28] *sec*-Butyllithium (FMC, Lithium Division; 12 wt % in cyclohexane) was used as received after double titration with allyl bromide.[29] Chlorodimethylsilane (98% Aldrich) was stirred over CaH_2, vacuum transferred onto and stored over activated 3 Å molecular sieves, followed by distillation into calibrated, flame-sealed ampules. Potassium *N,N*-bis(trimethylsilyl)amide (95%, Aldrich) was used after evacuation and drying under high vacuum. Allyl bromide (97%, Aldrich) was purified by drying over $CaCl_2$ followed by distillation. Karstedt's catalyst, 1,3-divinyltetramethyldisiloxane−platinum, (Gelest, 2.1−2.4% Pt conc in xylene) and hexamethyldisilazane (99%, Aldrich, HMDS) were used as received. Allylamine (99%, Aldrich) was dried over activated 3 Å molecular sieves. Argon and nitrogen gases were passed through columns filled with mixtures of alumina and deoxygenation catalyst (De-Ox, Alfa Aesar) activated by heating at 250 °C under vacuum.

Synthesis of 3-[*N,N*-bis(trimethylsilyl)amino]-1-propene.[30] A solution of allyl bromide (8.9 g, 45 mmol) in 5 mL of hexamethyldisilazane (HMDS) was slowly added via cannula to a suspension of potassium *N,N*-bis(trimethylsilyl)amide (5.1 g, 42 mmol) in 50 mL of HMDS under a dry argon atmosphere at 0 °C and stirred for 1 h, followed by stirring at room temperature overnight. The resulting slurry was filtered through Celite 545 in the drybox to remove the precipitated salts. The silyl-protected allylamine was isolated by fractional vacuum distillation, yielding 5.2 g (26 mmol, 62% yield) of a colorless, clear liquid (bp 85 °C at 35 mbar; lit.[7] bp 82 °C at 30 mbar). **^{1}H NMR**: δ 0.106 (**s**, 18H, $Si(CH_3)_3$), 3.461 (d, 2H, CH_2N), 5.061 ppm (dd, 2H, CH_2=), 5.791 (m, 1H, =CH). **^{13}C NMR**: δ 2.152 ($Si(\boldsymbol{C}H_3)_3$), 47.504 ($\boldsymbol{C}H_2N$), 113.500 ($\boldsymbol{C}H_2$=), 141.459 ppm (=$\boldsymbol{C}$H).

Synthesis of 1-(Chlorodimethylsilyl)-3-[*N,N*-bis(trimethylsilyl)amino]propane.[30] Two drops of Karstedt's catalyst, 1,3-divinyltetramethyldisiloxane−platinum complex, was added to a mixture of 3-[*N,N*-bis(trimethylsilyl)amino]-1-propene (4.3 g, 21 mmol) and chlorodimethylsilane (4.1 g, 43 mmol) under a dry argon atmosphere at room temperature. Immediately after injection of a drop of Karstedt's catalyst, an exotherm was observed with a color change to light yellow. While stirring the solution overnight, a continuous color change was observed from light yellow through deep yellow to light brown. 1-(Chlorodimethylsilyl)-3-[*N,N*-bis(trimethylsilyl)amino]propane was isolated in 81% yield (4.9 g, 17 mmol) by fractional vacuum distillation as a colorless, clear liquid (bp 115 °C at 1 mbar; lit.[30] bp 104 °C at 1 mbar). **^{1}H NMR**: δ 0.106 (s, 18H, $Si(CH_3)_3$), 0.422 (s, 6H, $ClSiCH_3$), 0.705 (m, 2H, $ClSiCH_2$), 1.437 (m, 2H, CH_2), and 2.766 ppm (m, 2H, NCH_2). **^{13}C NMR**: δ 1.826 ($ClSi(\boldsymbol{C}H_3)_3$), 2.305 ($NSi(\boldsymbol{C}H_3)_3$), 16.571 ($\boldsymbol{C}H_2$), and 28.779 ppm ($ClSi(\boldsymbol{C}H_3)_2$), 48.827 ($N\boldsymbol{C}H_2$).

Polymerizations. All polymerizations were effected in benzene at room temperature using *sec*-butyllithium as initiator in all-glass sealed reactors with breakseals and standard high-vacuum techniques.[31] The concentration of styrene to benzene (mL/mL) was 10 vol %. 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.

Functionalizations of Poly(styryl)lithium. Functionalization of poly(styryl)lithium (22.6 g, 9.8 mmol, $M_n = 2.2 \times 10^3$ g/mol, $M_w/M_n = 1.04$) was effected directly in the polymerization reactor by smashing the breakseal for the ampule containing chlorodimethylsilane (2.5 mL, 22.5 mmol) in benzene at room temperature; loss of the red color and salt precipitation were observed almost immediately. After 11 h, the resulting solution was precipitated into an 8-fold excess of anhyd methanol and stirred for 1 h. After filtration and washing, the white solid polystyrene derivative was dried in a vacuum oven, followed by further intensive drying on the high-vacuum line for 48 h. The final silane end-functionalized polystyrene was isolated in 98% yield.

Functionalizations of poly(styryl)lithium with benzene solutions of 1-(chlorodimethylsilyl)-3-[*N,N*-bis(trimethylsilyl)-amino]propane (3 mol equiv) were effected by breaking the respective ampule connected directly to the reactor containing poly(styryl)lithium. After 12−24 h, the functionalized polymers were isolated by precipitation into excess anhyd methanol, filtered, and dried.

Functionalization by Hydrosilation. Silane-functionalized polystyrene (3.0 g, 1.3 mmol, $M_n = 2200$ g/mol), allylamine (0.3 mL, 0.23 g, 4.0 mmol), and dry benzene (12 mL) were added into a two-necked round-bottomed flask (25 mL) equipped with a stopcock and septum in the drybox. The flask was then removed from the drybox and was connected to a Schlenk line. To the mixture was added 2 drops of Karstedt's catalyst with vigorous stirring under an argon atmosphere at room temperature. The resulting solution was stirred for 72 h and subsequently precipitated into a 7-fold excess of anhyd methanol followed by filtration and freeze-drying in benzene. Pure functional polymer was obtained in 98% yield (3.0 g, 1.3 mmol).

Protected amine functionalized polystyrene was also synthesized in good yield (3.1 g, 95%) by the same procedure

except for the use of 3-[*N*,*N*-bis(trimethylsilyl)amino]-1-propene (0.8 g, 4.0 mmol) as functionalizing agent.

Characterization. Size-exclusion chromatographic analyses (SEC) for the base polymers and functionalized polymers were performed using a Waters 150-C Plus instrument equipped with a Viscotek model 301 triple detector system with THF as eluent at a flow rate of 1.0 mL/min at 30 °C, where the detector system consisted of a differential refractometer (Waters 410), a differential viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ nm). Regular SEC calibrations were conducted with polystyrene standards (Polymer Laboratories). Static light scattering measurements were performed using a Brookhaven laser light scattering system composed of computer-controlled BI-200SM goniometer, Melles Griot 35 mW He−Ne laser (632.8 nm), and EMI-9863 photomutiplier. Five sample solutions with different concentrations of 0.903, 1.718, 3.403, 4.968, and 6.681 mg/mL in THF were individually put into 27 mm diameter cylindrical scattering cells that were placed in the center of a thermostated bath filled with decahydronaphthalene for refractive index matching. Absolute molecular weight was determined from Zimm plots from light scattering measurements at nine different scattering angles (30, 50, 60, 70, 80, 90, 105, 120, and 130°), respectively. All ^{1}H (300 MHz), ^{13}C (75 MHz), and DEPT ($\theta = 135°$) NMR spectra were acquired in $CDCl_3$ (Aldrich, 99.8% D) using Varian Mercury 300 or Gemini 300 MHz NMR spectrometers. Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting polymer films on KBr plates from THF solutions with subsequent drying at 40−50 °C for 5 min.

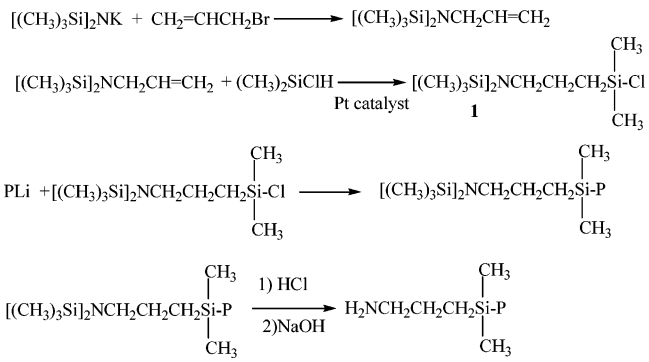
Matrix-assisted laser desorption−ionization time-of-flight mass spectra (MALDI-TOF) were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337-nm nitrogen laser (3-nm pulse width), a single-stage pulsed ion extraction source, and a two-stage gridless reflector. Solutions of dithranol (20 mg/mL) (Fluka, 1,8,9-anthracenetriol, 99%), polymer sample (10 mg/mL), and silver or sodium trifluoroacetate (10 mg/mL) (Aldrich, 98%) 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. To minimize undesirable polymer fragmentation and to achieve optimal intensity, the intensity of the nitrogen laser pulses was frequently attenuated and adjusted. Mass spectra were measured in the linear and reflection modes, and the mass scale was calibrated externally using the peaks of a polystyrene standard at the molecular weight under consideration.

Thin-layer chromatographic analyses (TLC) were carried out on the functionalized polymers by spotting and developing polymer samples on flexible silica gel plates (Selecto Scientific, Silica Gel 60, F-254 with fluorescent indicator), using toluene as eluent. Separation of functionalized polymers from the unfunctionalized polymers was effected by quantitative column chromatography using silica gel (EM Science, Silica Gel 60) with particle size of 0.040−0.063 mm (230−400 mesh). Toluene or toluene/hexane (50:50, v/v) was employed to separate unfunctionalized or protected functionalized polymers, and then THF/toluene (75:25, v/v) was used to elute the remaining functionalized polymers from the column. The amine group functionality for the ω-aminopolystyrene ($M_n = 2300$) prepared by hydrosilation with allylamine was determined by perchloric acid titration in glacial acetic acid/chloroform (1:1, v/v) using methyl violet as an indicator.[32]

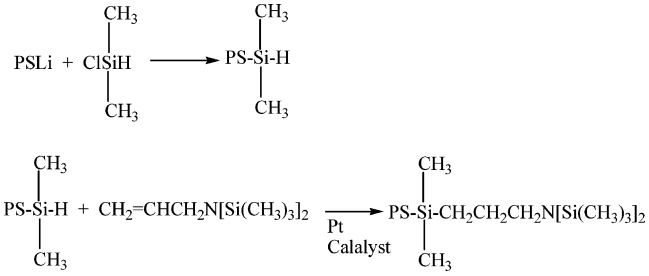
Results and Discussion

In the search for a general anionic methodology for the synthesis of primary amine functionalized polymers, the procedure of DeSimone and co-workers[7,8] utilizing the termination of polymeric organolithium compounds with a chlorosilane functionalized with a bis(trimethylsilyl)amino group was examined. Scheme 3 illustrates this method, including an improved synthesis of the silylamine-functionalized silyl chloride recently reported by Schlaad and co-workers.[30] It was found that the chlorosilane derivative, **1**, did not store well in a sealed flask in the drybox and that the desired amine-functionalized polymer was obtained in only 64% yield; it was contaminated with trimethylsilyl-functionalized polymer and nonfunctional polymer. One of the main advantages of this method is the fact that the reaction of polymeric organolithium compounds with silyl chlorides is a relatively facile reaction that proceeds without significant side reactions. As shown in Scheme 3, this reaction does require the use of protecting groups, and these protecting groups must be removed to recover the desired functional end group.

Scheme 3



Scheme 4



Upon careful examination of the DeSimone functionalization methodology[7,8] outlined in Scheme 3, it can be seen that the two key reactions are chlorosilane functionalization of polymeric organolithium compounds and hydrosilation for functionalization. This recognition, in turn, suggested that one could slightly modify these steps and develop a general functionalization methodology as illustrated in Scheme 4 for primary amine group functionalization. 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. The second step, hydrosilation, is a reaction that proceeds readily and efficiently with a variety of substituted alkenes to form the product from anti-Markovnikov addition of the silyl hydride to the alkene using typical platinum-based catalysts. To evaluate the usefulness of this methodology, the primary amine chain-end functionalization of poly(styryl)lithium was investigated.

Preparation of Silyl Hydride Functionalized Polystyrene. The 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 (eq 2). Precipitate formation was observed

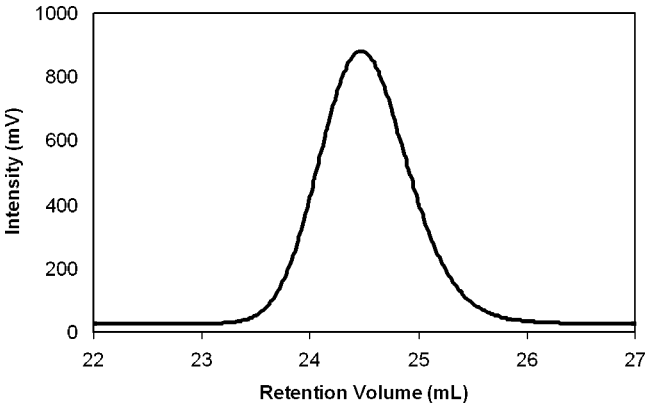
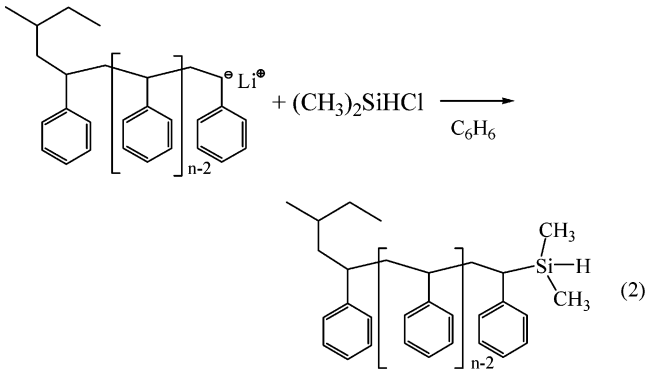


Figure 1. SEC chromatogram for the silyl hydride functionalized polystyrene (M_n = 2200 g/mol).

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 isolated in 98% yield.



(2)

The SEC chromatogram (Figure 1) for the silane-functionalized polystyrene ($M_n = 2.2 \times 10^3$ g/mol; $M_w/M_n = 1.04$) showed a narrow monomodal curve. The ^{1}H NMR spectrum of this polymer displayed characteristic resonances for the silane proton at δ 3.8 ppm,[16] and for the silicon-bonded methyl groups attached, δ −0.1 ppm (Figure 2). From the integration ratio of the six methyl protons of the dimethylsilane unit to the other six methyl protons from the *sec*-butyl end group, the silane functionality of this polymer was readily calculated (100%). The ^{13}C NMR spectrum also showed distinct resonances for the silicon-bonded methyl carbons at δ −5.5 ppm (Figure 3). It is also noteworthy that no resonance was observed at δ 33.6 ppm, which would correspond to the terminal benzyl group in unfunctionalized polystyrene.[33] FTIR spectroscopic analysis was found to be a useful tool for confirmation of the incorporation of silyl hydride functionality. A strong absorption band corresponding to an Si−H streching vibration mode was observed at 2111 cm^{-1}, along with CH_3 deformation and CH_3 rocking absorptions of CH_3-Si at 1249 and 882 cm^{-1}, respectively (Figure 4).[34,35]

It has been shown that MALDI-TOF mass spectrometry is a powerful tool for the analysis of anionically prepared chain-end-functionalized polymers.[36−40] The MALDI-TOF mass spectrum of the silyl hydride functionalized polystyrene using silver trifluoroacetate as cationizing agent is shown in Figure 5. Although it is a momonodal distribution as expected, the peaks do not correspond to the expected structure. For example, as shown in the expanded region between *m/z* 2000 and 2200, the peak at *m/z* 2008.04 corresponds to C_4H_9-$(C_8H_8)_{18}$-$Si(CH_3)_2OH{\cdot}Ag^+$; the calculated monoisotopic mass is 57.07(C_4H_9) + 17 × 104.06[$(C_8H_8)_{17}$] + 75.027-[$Si(CH_3)_2OH$] + 106.90(Ag^+) = 2008.02 Da. The unexpected formation of the silanol chain end can be explained by the oxidation of the silyl hydride functionality by a silver ion in the presence of dithranol.[41] When sodium was used as the cationizing agent, the mass spectrum of the silyl hydride functionalized polystyrene was observed (Figure 6). The expanded trace of the mass spectrum exhibited two different series of peaks. The main series corresponds to the silyl hydride functionalized polymers as shown in the expanded region between *m/z* 2000 and 2200. The peak at *m/z* = 2012.15 corresponds to C_4H_9-$(C_8H_8)_{18}$-$SiH(CH_3)_2{\cdot}Na^+$; the cal-

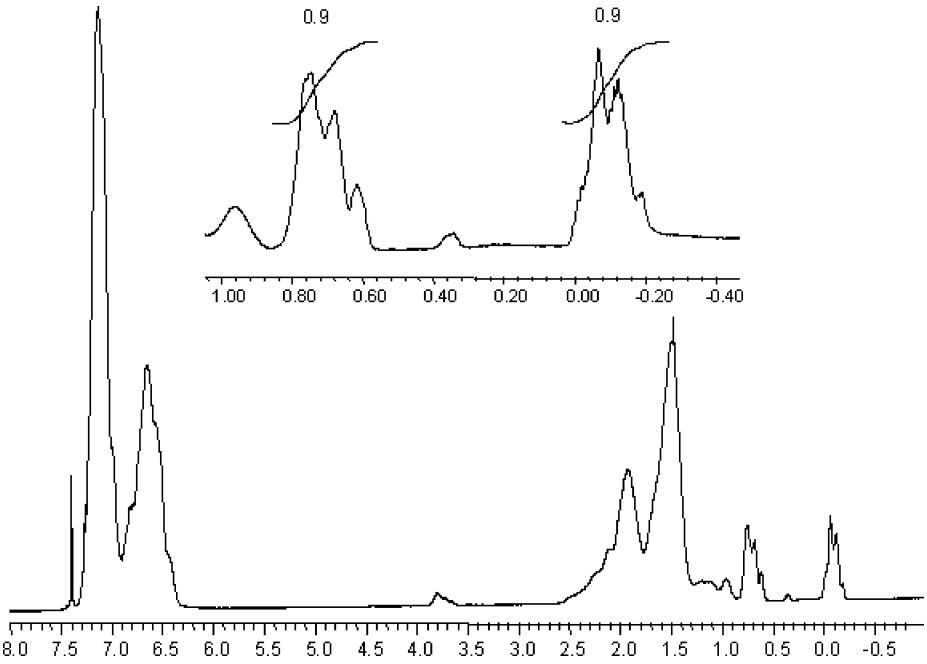


Figure 2. ^{1}H NMR spectrum ($CDCl_3$) for the silyl hydride functionalized polystyrene.

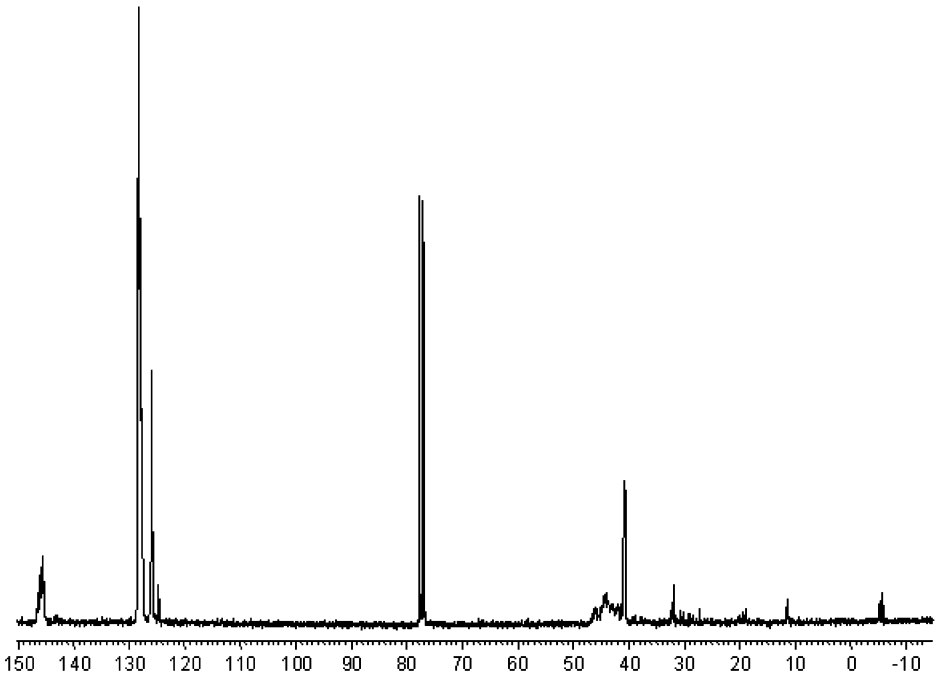


Figure 3. ^{13}C NMR spectrum ($CDCl_3$) for the silyl hydride functionalized polystyrene.

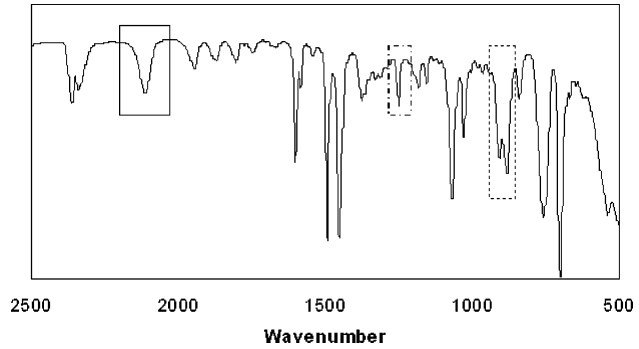
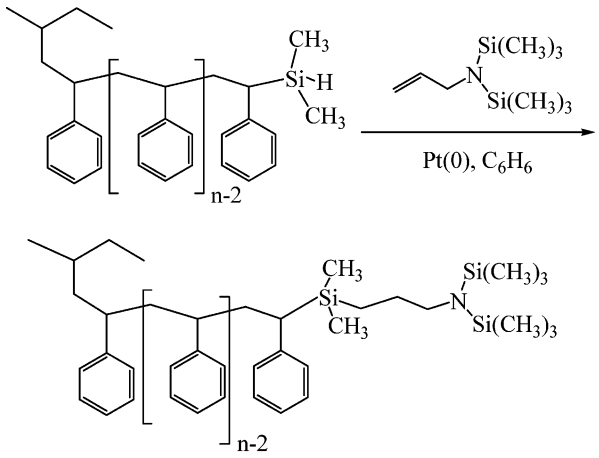


Figure 4. FTIR spectrum for the silyl hydride functionalized polystyrene.

culated monoisotopic mass is $57.07(C_4H_9) + 18 \times 104.06[(C_8H_8)_{18}] + 59.03[Si(CH_3)_2H] + 22.99(Na^+) = 2012.17$ Da. The minor series, which appears 40 Da above the main distribution, has not been identified; it is probably formed during the analysis, although the degradation mechanism is not obvious.[42−44] In summary, the reaction of poly(styryl)lithium with dimethylchlorosilane in hydrocarbon solution at room temperature results in the quantitative formation of the corresponding ω-silyl hydride functionalized polystyrene, on the basis of NMR, FTIR, and MALDI-TOF MS analyses.

Preparation of ω-*N*,*N*-bis(trimethylsilyl)aminopolystyrene Protected Amine-Functionalized Polystyrene by Hydrosilation of Silane-Functionalized Polystyrene. The second step in development of the proposed general functionalization procedure involves the reaction of silyl hydride functionalized polystyrene with substituted alkenes (see Scheme 2). For synthesis of the primary amine functionalized polystyrene, the hydrosilation reaction of silyl hydride functionalized polystyrene with 3-[*N*,*N*-bis(trimethylsilyl)amino]-1-propene was investigated (eq 3). This protected amine was the precursor for the silyl chloride used in the previous amine functionalization studies of DeSimone and co-workers[7,8] and Schlaad and co-workers[30] (see Scheme 3).



(3)

Hydrosilation can be catalyzed by a variety of transition metal complexes, including those of Pt, Rh, Ru, Ir, Os, and Pd.[14] Among these complexes, Pt catalysts exhibit the highest activity.[45,46] Spier's original soluble Pt(IV) catalyst, H_2PtCl_6 in 2-propanol, and Karstedt's Pt (0) catalyst, $Pt_2[CH_2{=}CSi(CH_3)_2OSi(CH_3)_2CH{=}CH_2]_3$, are two of the most commonly used catalysts for hydrosilation.[14] However, Karstedt's catalyst was chosen because it is soluble in hydrocarbon solvents; thus, hydrosilation reactions were easily monitored by simple ^1H NMR spectroscopy in C_6D_6. It was also considered that use of the Karstedt's catalyst would minimize undesirable hydrolysis of Si−H with adventitious water or alcohol impurities, which are more likely in polar media. Karstedt's catalyst is also an extremely efficient hydrosilation catalyst, i.e., concentrations of less than 1 ppm are sufficient to complete the reaction.[47]

For the hydrosilation reaction, the silane functionalized polystyrene (M_n = 2200 g/mol) was stirred overnight with 3.0 mol equiv of 3-[*N*,*N*-bis(trimethylsilyl)-amino]-1-propene and one drop of Karstedt's catalyst

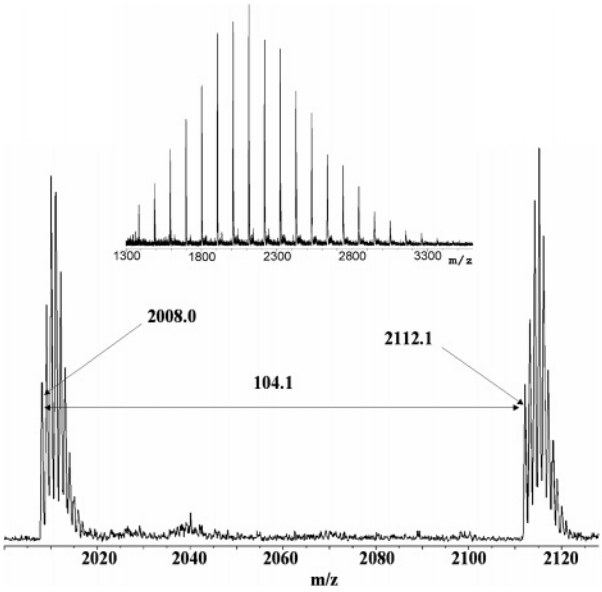


Figure 5. MALDI-TOF mass spectrum for the silyl hydride functionalized polystyrene with silver trifluoroacetate as cationizing agent.

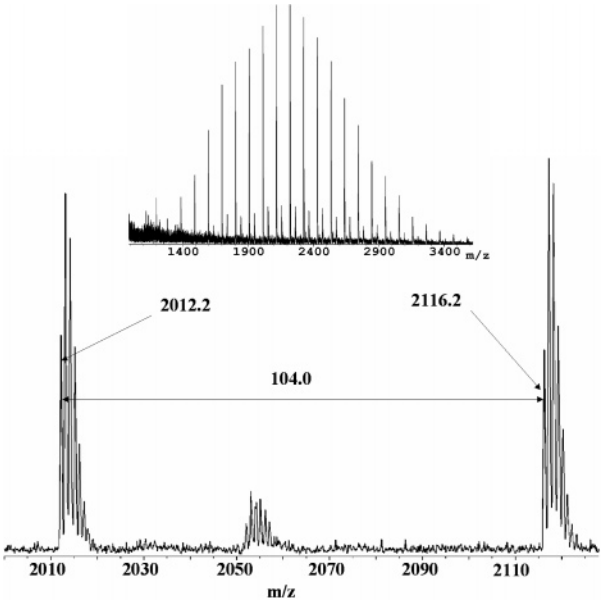


Figure 6. MALDI-TOF mass spectrum for silyl hydride functionalized polystyrene with sodium trifluoroacetate as a cationizing agent.

in dry benzene under a dry argon atmosphere. Within 10 min after injection of the platinum catalyst, a light-yellow color appeared, indicating formation of the active colloidal species;[48] the color gradually turned to brown during the course of hydrosilation. The ω-*N*,*N*-trimethylsilylamino functionalized polystyrene was isolated in good yield (3.1 g, 95%) after standard workup. The polymer exhibited a monomodal SEC chromatogram (Figure 7) as expected ($M_n = 3.0 \times 10^3$ g/mol, $M_w/M_n = 1.06$).

The ^{1}H NMR spectrum for the protected amine-functionalized polystyrene (Figure 8) exhibited distinct resonances from the 18 methyl protons of trimethylsilyl protecting groups at ca. δ 0.05 ppm and from the 6 methyl protons connected to the silicon from dimethylchlorosilane functionalization near δ −0.2 ppm with a relative integration ratio of 2.5:1 which is lower than the expected value of 3:1. This discrepancy was attributed to partial deprotection of the *N*,*N*-bistrimethylsilyl protecting groups when the polymer was recovered from solution by precipitation into methanol. Two new, discrete methylene resonances appeared at δ 2.6 and 0.2 ppm, corresponding to CH_2N and CH_2Si groups, respectively. The absence of a peak corresponding to the silyl hydride at δ 3.8 ppm is consistent with efficient functionalization of the chain end. In the ^{13}C NMR spectrum for the protected amine-functionalized polystyrene (Figure 9), two different sets of resonances corresponding to methyl carbons attached to silicon atoms were observed at δ −4.7 ppm (CH$_3$Si−C) and 2.3 ppm (CH$_3$Si−N), as well as resonances for two characteristic methylene carbons corresponding to CH$_2$Si and CH$_2$N at δ 11.3 and 49.4 ppm, respectively.

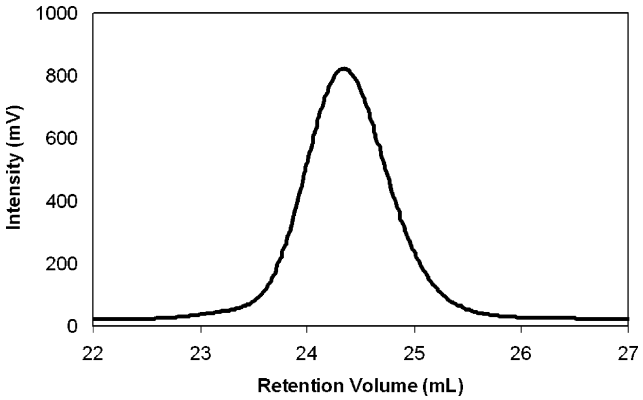


Figure 7. SEC chromatogram for the protected amine-functionalized polystyrene ($M_n = 3000$ g/mol).

The FTIR spectrum (Figure 10) for the protected amine-functionalized polystyrene exhibited a high-intensity absorption for the $(CH_3)_2$Si deformation band (symmetric bending mode) at 1249 cm^{-1} along with a new weak absorption at 1413 cm^{-1} coming from asymmetric methyl bending modes due to the introduction of six $(CH_3)_3$Si groups into the polymer molecule.[34,35] The absence of the unique Si−H stretching band (2111 cm^{-1}) is consistent with efficient chain-end functionalization.

The nature of the end groups from this protected amine functionalization was provided by MALDI-TOF MS. Unexpected results were obtained using the silver trifluoroacetate/dithranol system, the most commonly used cationizing agent/matrix system for polystyrenes. The MALDI-TOF mass spectrum (Figure 11) for the protected amine-functionalized polystyrene exhibited two overlapping series of peaks. For the lower *m/z* series, the peaks are assigned to the deprotected protonated amine-functionalized polymers, C_4H_9-$(C_8H_8)_n$-$SiC_5H_{12}NH_3^+$. As shown in the expanded spectrum, the peak at *m/z* 2047.1 has the exact mass for the polystyrene 18-mer with butyl and protonated amine end groups, C_4H_9-$(C_8H_8)_{18}$-$SiC_5H_{12}NH_3^+$; the calculated monoisotopic mass is {57.07(C_4H_9) + 18 × 104.06-[$(C_8H_8)_{18}$] + 117.10[$SiC_5H_{12}NH_3$]} = 2047.25 Da. The peak at *m/z* 2151.2 corresponds to the 19-mer in this series. For the higher *m/z* series, the peaks are assigned to the deprotected silver-complexed amine-functionalized polymers, C_4H_9-$(C_8H_8)_n$-$SiC_5H_{12}NH_2Ag^+$. As shown in the expanded spectrum, the peak at *m/z* 2049.0 has the exact mass for the polystyrene 17-mer with one butyl and a silver-complexed amine end group, C_4H_9-$(C_8H_8)_{17}$-$SiC_5H_{12}NH_2{\cdot}Ag^+$; the calculated monoisotopic mass is {57.07(C_4H_9) + 17 × 104.06[$(C_8H_8)_{17}$] +

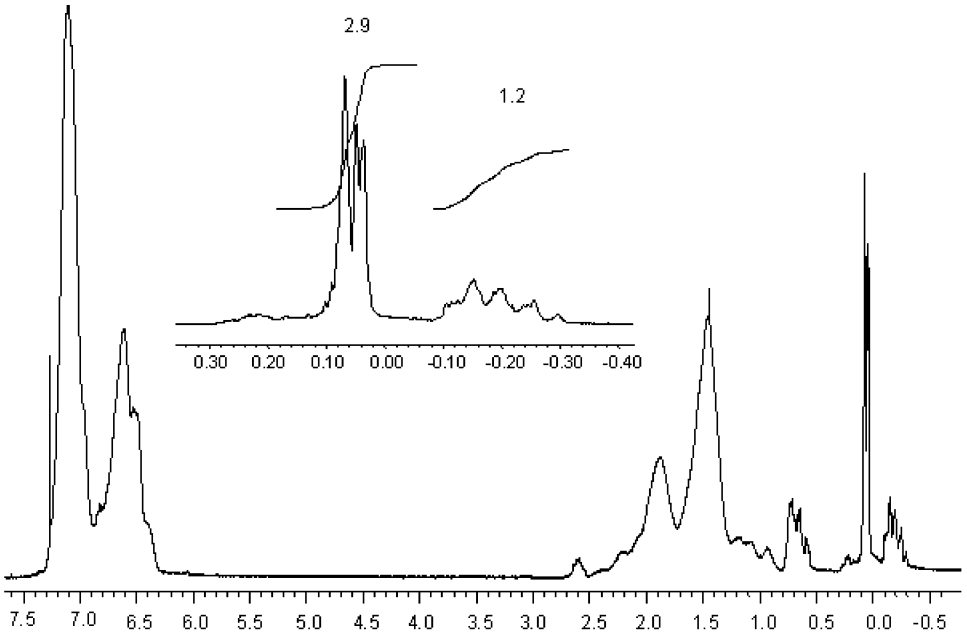


Figure 8. ^{1}H NMR spectrum ($CDCl_3$) for protected amine-functionalized polystyrene.

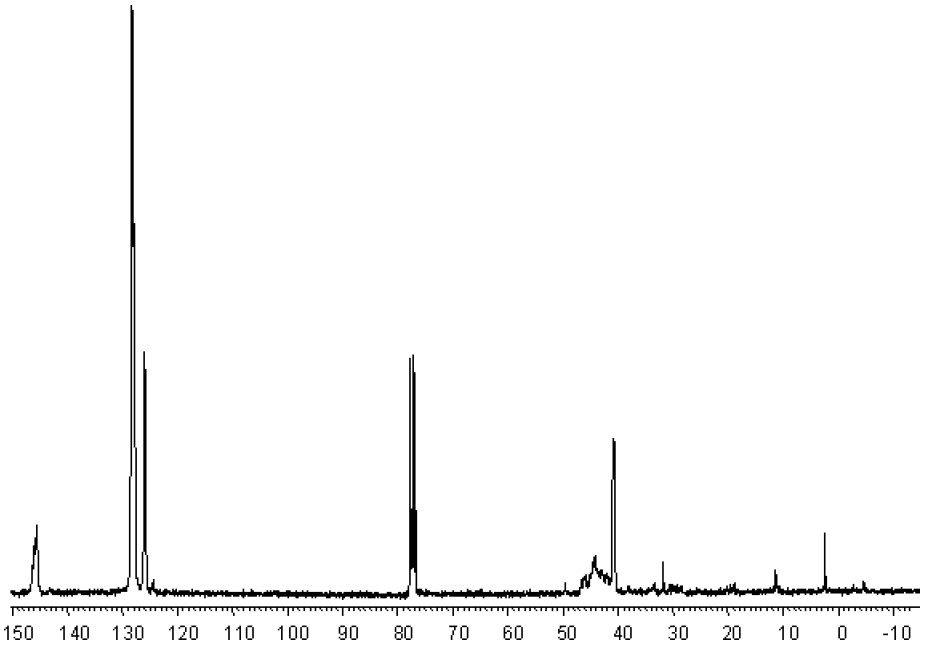
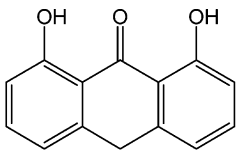


Figure 9. ^{13}C NMR spectrum ($CDCl_3$) for protected amine-functionalized polystyrene.

116.09[$SiC_5H_{12}NH_2$] + 106.905(Ag^+)} = 2049.09 Da. The smaller series of peaks is assigned to the unsaturated chain end, C_4H_9-$(C_8H_8)_n$-CH═CH(C_6H_5)·Ag^+ arising from elimination of chain-end functionality during the analysis. Some unfunctionalized PS chains, C_4H_9-$(C_8H_8)_n$-H·Ag^+, may also be present in this distribution.



(4)

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It was surprising to find no MS evidence for the protected amine functional polymer. This unusual phenomenon may arise from cleavage of the Si−N bonds by the slightly acidic phenolic hydroxy groups of dithranol (**2**) in the presence of Ag^+, generating the NH_2 functional group. Amine-terminated PS chains can ionize by Ag^+ addition as well as by protonation because of the high intrinsic basicity of the amine group. As a result, overlapping isotope clusters are observed in Figure 11 for the same oligomers. This finding suggested that it might be possible to obtain the MALDI-TOF MS spectrum of the protected amine-functionalized polystyrene in the absence of Ag^+ ion simply by using the protons of dithranol as cationizing agents. When MALDI-TOF MS analysis was carried out using dithranol as cationizing agent as well as matrix, it was possible to record the mass spectrum of the amine-functionalized polymer with the protecting groups intact (see Figure 12). In the expanded portion of the spectrum between *m/z* 2000 and 2200, the peak at *m/z* 2087.3 corresponds

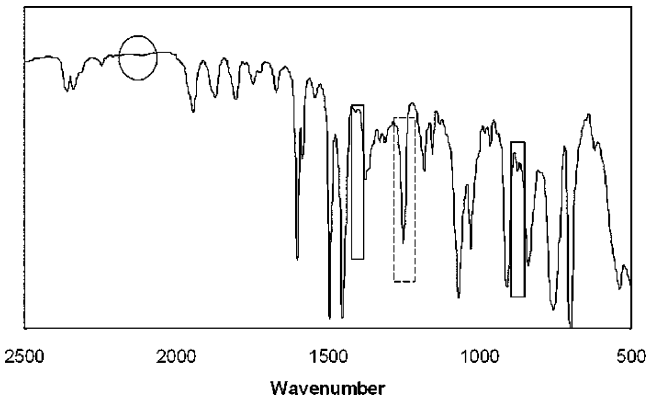


Figure 10. FTIR spectrum for protected amine-functionalized polystyrene.

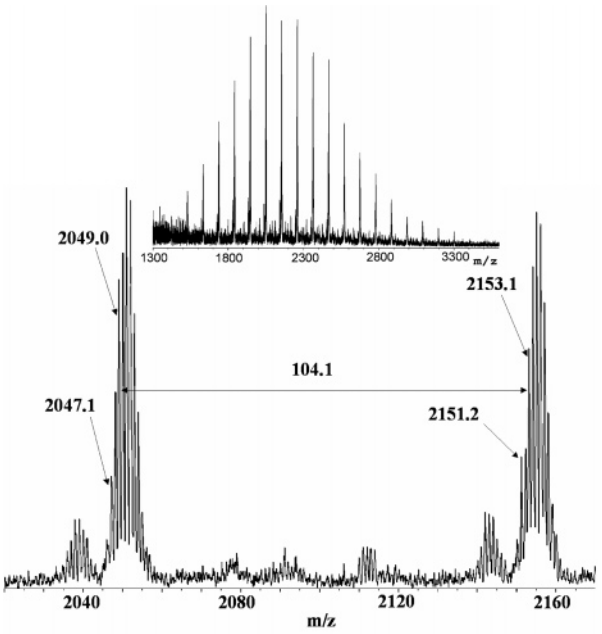


Figure 11. MALDI-TOF MS spectrum for protected amine-functionalized polystyrene with silver trifluoroacetate as cationizing agent.

to the functionalized 17-mer, C_4H_9-$(C_8H_8)_{17}$-$SiC_5H_{12}N$-$(SiC_3H_9)_2$·H^+; the calculated monoisotopic mass is {57.07-(C_4H_9) + 1769.02[$(C_8H_8)_{17}$] + 100.071[SiC_5H_{12}] + 161.11-[$N(SiC_3H_9)_2$·H]} = 2087.27 Da. Deprotected protonated amine functionalized polystyrene was also observed as the second major species implying that partial hydrolysis still occurred even in the absence of Ag^+ ion. Two additional series of peaks were detected, which were not observed with Ag^+ ion. One series of peaks corresponds to the dehydrogenated, half-deprotected amine-functionalized 17-mer with only one trimethylsilyl group {e.g. *m/z* 2191.41 − 74.06 [$Si(CH_3)_3$−H] = 2117.35}. The other minor series could not be identified.

On the basis of the NMR, FTIR, and mass spectral analyses of the hydrosilation product, it is concluded that the hydrosilation reaction of 3-[*N*,*N*-bis(trimethylsilyl)amino]-1-propene with silyl hydride functionalized polystyrene can be performed successfully and efficiently without any detectable side reaction using Karstedt's catalyst in benzene solution at room temperature.

Preparation of ω-Aminopolystyrene by Hydrosilation of Silyl Hydride Functionalized Polystyrene with Allylamine. The general functionalization procedure outline in Scheme 2 has a powerful advantage over most direct anionic functionalization reactions that involve reaction of electrophiles with polymeric organolithium compounds. These reactions must utilize protecting groups that are stable to the anionic chain end. However, the platinum-catalyzed hydrosilation reaction does not require the use of protecting groups for many functional groups of interest. Platinum catalysts can tolerate a wide variety of functional groups including nitro, cyano, amine, sulfonate, phenol, ester, ether, thioether, isocyanate, phenylthio, epoxide, and perfluoroalkyl, i.e., these groups do not interfere with the hydrosilation reaction.[14,47] Functional groups that do react directly with silyl hydride groups and platinum catalysts include hydroxyl, thiol, ketone, aldehydes, and acids.

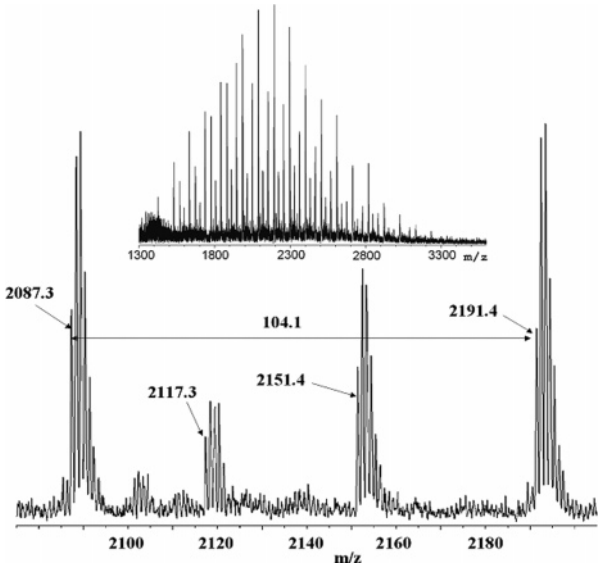
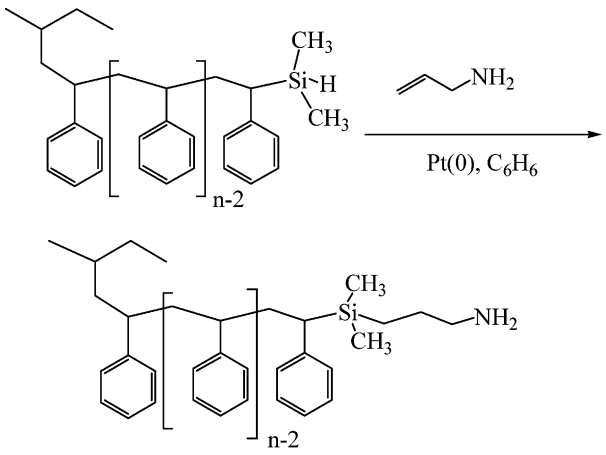


Figure 12. MALDI-TOF mass spectrum for protected amine-functionalized polystyrene obtained without using silver trifluoroacetate as cationizing agent.

To demonstrate the versatility and simplicity of the silyl hydride based functionalization procedure, the hydrosilations of ω-silyl hydride functionalized polystyrenes (M_n = 2200 and 14 400 g/mol, M_w/M_n = 1.04 and 1.01, respectively) with allylamine were investigated (eq 5).



(5)

The silane functional polystyrene (M_w = 2300 g/mol) was reacted with 3.1 mol equiv of allylamine and Karstedt's catalyst. Contrary to the corresponding reaction with the silyl-protected amine, the characteristic

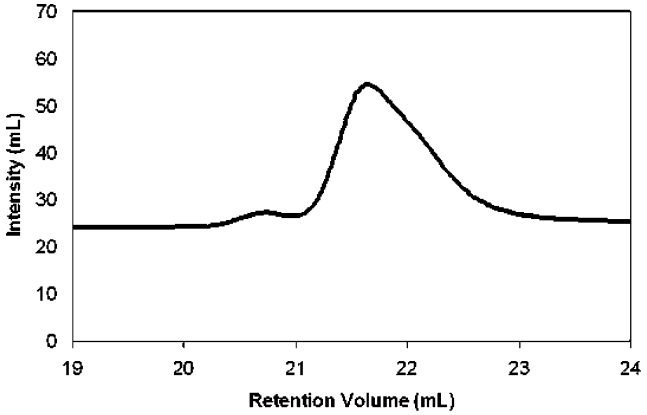


Figure 13. SEC chromatogram for the unprotected ω-aminopolystyrene (M_n (base) = 14 100 g/mol).

light-yellow color appeared very slowly over several hours, indicating a relatively long induction period; in addition, further color changes to brown appeared much slower than for the corresponding protected amine. The reduced reaction rate has been ascribed to the ligand coordination of the amine group to the active platinum center, thus competing with the vinyl groups.[48,49] Amine derivatives are currently used industrially as retarders to control hydrosilation reactions.[50−52]

A total of 72 h was required to complete this hydrosilation reaction, compared with less than 12 h for the analogous reaction with the protected amine. The ω-aminopropyl functionalized polystyrene was isolated in high yield (98%) after standard workup. TLC analysis of the resulting polymer exhibited only one spot at the bottom of silica gel plate, consistent with a high yield of amine-functionalized polymer (≥98%).[25] The high yield of amine functionalization (96%) was also confirmed by end-group titration of the amine groups with perchloric acid in glacial acetic acid.[32]

The SEC chromatograms for both amine-functionalized polystyrenes [M_n (base) = 2200 and 14 100 g/mol] exhibited very broad, unsymmetrical curves with very low intensity [see Figure 13 for the polymer with M_n (base) = 14 100 g/mol]. Previous investigations of amine-functionalized polystyrenes reported a similar phenomenon, and it was proposed that it results from physical adsorption of the primary amine onto the column packing during the elution process.[7,21] Consequently, light scattering analysis was used to determine the molecular weight for the amine-functionalized polystyrene with M_n (base) = 14 100 g/mol. The data were collected for the polymer solutions in THF in five different concentrations at nine different scattering angles (see Figure 14). The weight-average molecular weight determined from the Zimm plot (M_w = 15 300 g/mol) was in good agreement with the value expected on the basis of the unfunctionalized base polymer sample (14 300 g/mol).

The ^{1}H NMR spectrum for the lower molecular weight ω-amine functionalized polystyrene (Figure 15) exhibited characteristic resonances for the $-CH_2NH_2$ protons at δ 2.6 ppm and the $-Si(CH_3)_2CH_2$ protons at δ 0.4 ppm, along with the $Si(CH_3)_2$ protons near δ −0.1 ppm. The functionality (>95%) was determined from the integration ratio of the two $-CH_2NH_2$ protons compared to six $Si(CH_3)_2$ protons. No resonances corresponding to vinyl or silyl hydride residues were detected. The amine functional polystyrene proved to be rather stable in $CDCl_3$ in air at room temperature; no detectable oxidation or decomposition products were observed by ^{1}H NMR spectroscopy over a 2 week period. A DEPT-135 ^{13}C NMR spectrum (Figure 16) distinctly exhibited three negative signals at δ 10.9 ($-SiCH_2$-CH_2-CH_2N-), 28.3 ($SiCH_2$-CH_2-CH_2N) and 45.8 ppm $SiCH_2$-CH_2-CH_2N), respectively, arising from the three different CH_2 units between the silyl group and the amine group at the terminal chain end of the functional polystyrene (see eq 5). Characteristic positive signals for the $(CH_3)_2$-Si group were observed at δ −4.7 ppm. It is noteworthy that no negative signal at 33.6 ppm corresponding to

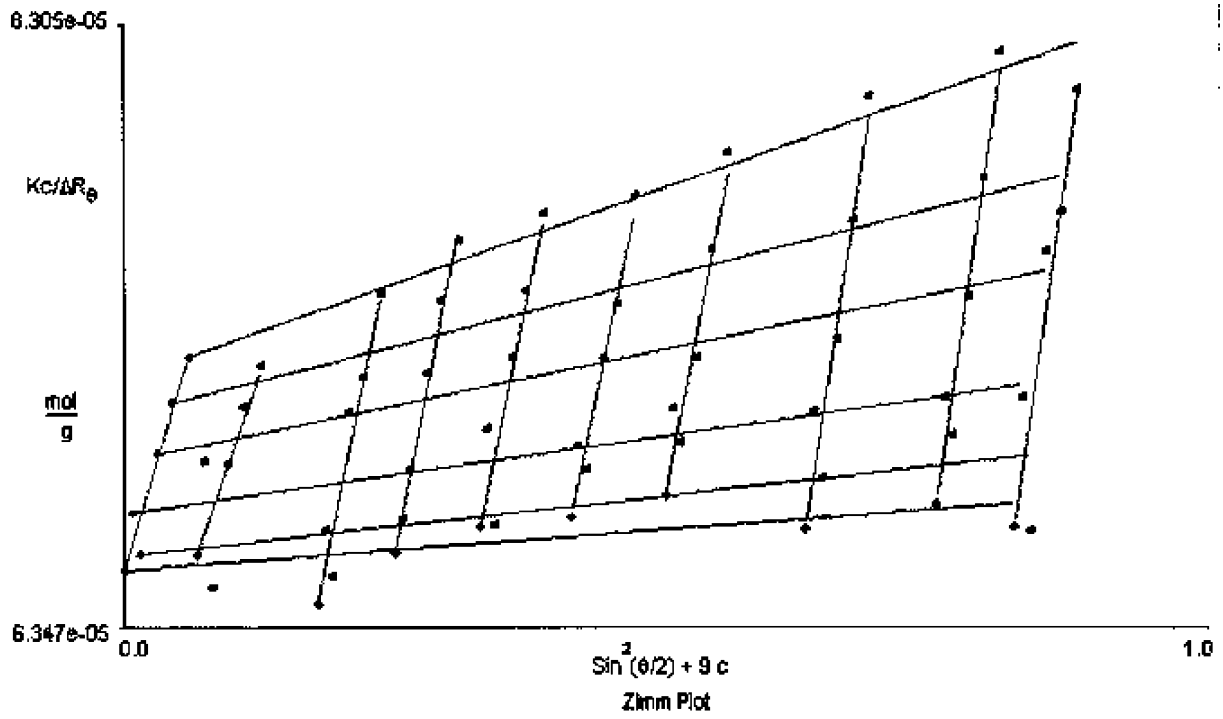


Figure 14. Zimm plot for the unprotected ω-aminopolystyrene [M_n (base) = 14 100 g/mol].

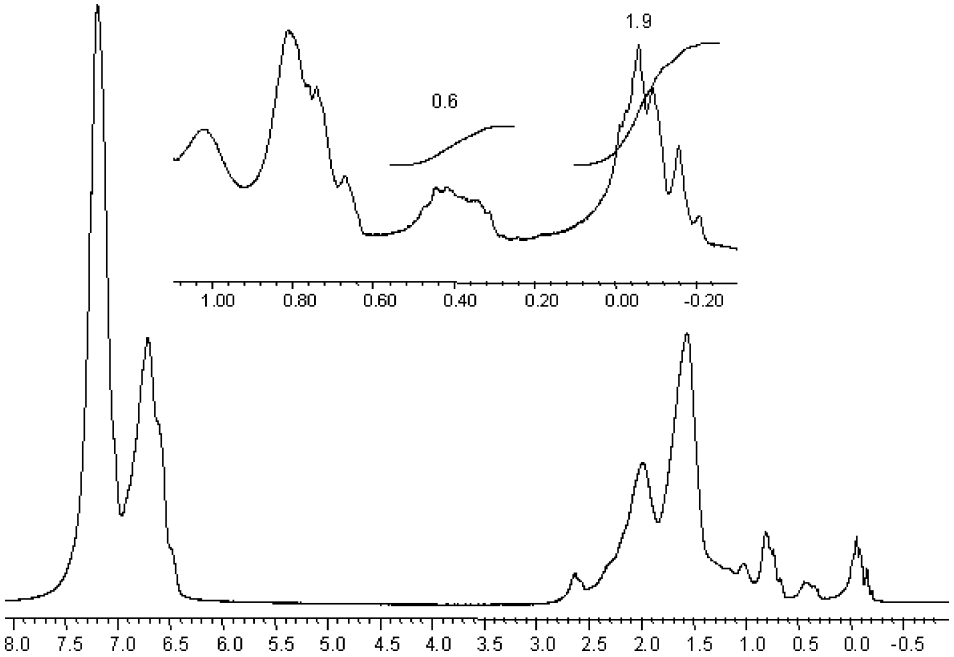


Figure 15. ^{1}H NMR spectrum ($CDCl_3$) for the unprotected ω-aminopolystyrene [M_n (base) = 2200 g/mol].

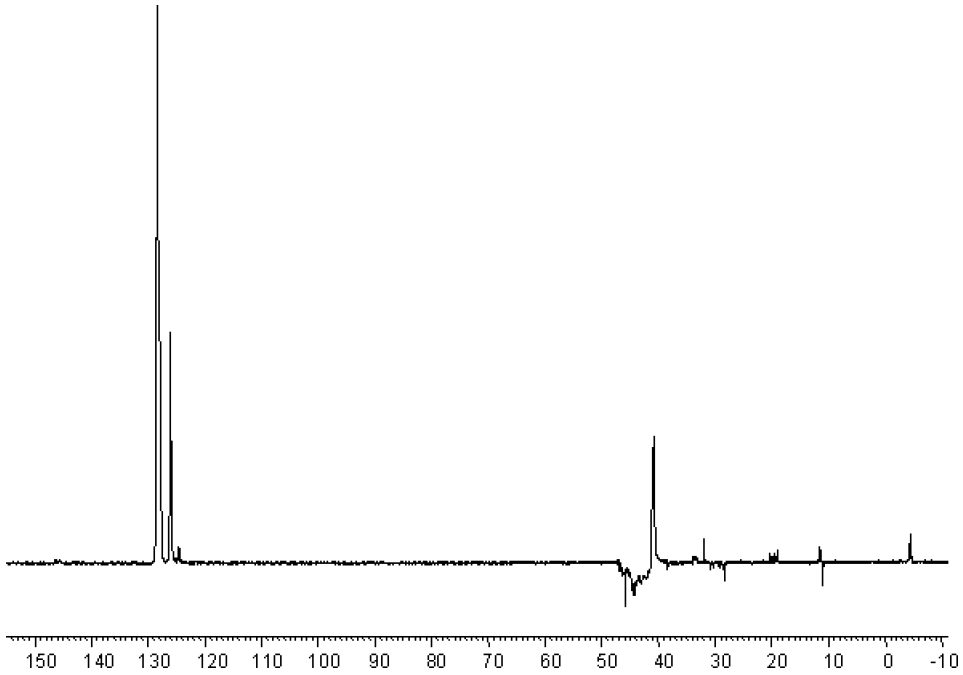


Figure 16. DEPT-135 spectrum ($CDCl_3$) for the unprotected ω-aminopolystyrene (M_n (base) = 2200 g/mol).

the terminal benzylic carbon of unfunctionalized polystyrene was detected.[33]

FTIR spectroscopic analysis provided further supporting evidence for the incorporation of amine functionality at the terminal polystyrene chain end. Characteristic absorption bands for symmetric and asymmetric N−H stretching modes were observed at 3380 and 3320 cm^{-1}, respectively (Figure 17). In contrast to the bis(trimethylsilyl)-protected amine-functionalized polystyrene, only a relatively low intensity CH_3 deformation absorption band at 1249 cm^{-1} is observed. The completion of hydrosilation reaction was evidenced by the lack of the characteristic Si−H stretching band (2111 cm^{-1}).

MALDI-TOF MS analysis of the ω-primary amine functionalized polystyrene was performed using the

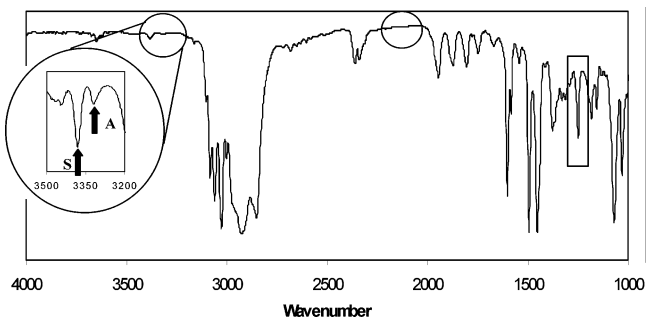


Figure 17. FTIR spectrum for the unprotected ω-aminopolystyrene (M_n (base) = 2200 g/mol).

silver trifluoroacetate/dithranol system (Figure 18). The resulting MS spectrum presented two series of peaks where the main series comprised two overlapping

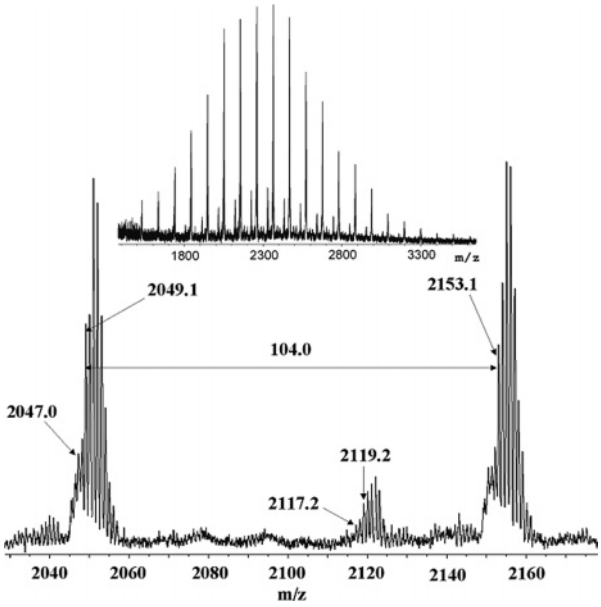


Figure 18. MALDI-TOF mass spectrum for the unprotected ω-aminopolystyrene (M_n (base) = 2200 g/mol) using silver trifluoroacetate as a cationizing agent.

isotope clusters originating from C_4H_9-$(C_8H_8)_{17}$-SiC_5H_{12}-NH_2·Ag^+ and C_4H_9-$(C_8H_8)_{17}$-$SiC_5H_{12}NH_2$·H^+, as observed also for the bistrimethylsilyl-protected amine-functionalized polystyrene. Contrary to the protected amine case, however, the peaks for the protonated (H^+) species were less abundant and, hence, not well resolved. As shown in the expanded spectrum for *m/z* between 2000 and 2200, the main series of peaks corresponds to the silver-cationated amine-functionalized polystyrene, C_4H_9-$(C_8H_8)_n$-$SiC_5H_{12}NH_2$·Ag^+. Thus, the peak at *m/z* 2049.08 has the exact mass for the polystyrene 17-mer with one butyl and a silver-complexed amine end group, C_4H_9-$(C_8H_8)_{17}$-$SiC_5H_{12}NH_2$·Ag^+; the calculated monoisotopic mass is {57.07(C_4H_9) + 17 × 104.06[$(C_8H_8)_{17}$] + 116.09[$SiC_5H_{12}NH_2$] + 106.905(Ag^+)} = 2049.09 Da. Similarly, the peak at *m/z* 2047.0 corresponds to C_4H_9-$(C_8H_8)_{18}$-$SiC_5H_{12}NH_3^+$. The other minor series is observed at 70 Da above the main series and also appears to be composed of overlapping Ag^+- and H^+-cationized oligomers; this series could not be identified. Nevertheless, the predominant products observed are the desired primary amine-functionalized PS oligomers.

Because of the appearance of these other series of peaks observed for the ω-amine functionalized polystyrene using silver as cationizing agent, a complementary MALDI-TOF MS experiment was conducted where the amine functional polystyrene was analyzed without Ag^+, i.e., using H^+ as a cationizing agent. Interestingly, in the resulting MS spectrum (Figure 19), the distribution C_4H_9-$(C_8H_8)_n$-$SiC_5H_{12}NH_3^+$ (18-mer at *m/z* 2047.00) is less abundant than that corresponding to the byproduct observed at 70 Da higher (e.g., at *m/z* 2116.98). The origin of the latter product is currently under investigation.

On the basis of the NMR, FTIR, and mass spectral analyses, it is concluded that the hydrosilation reaction of unprotected amine, allylamine, with silyl hydride functionalized polystyrene, can be performed successfully and efficiently using Karstedt's catalyst in benzene solution at room temperature.

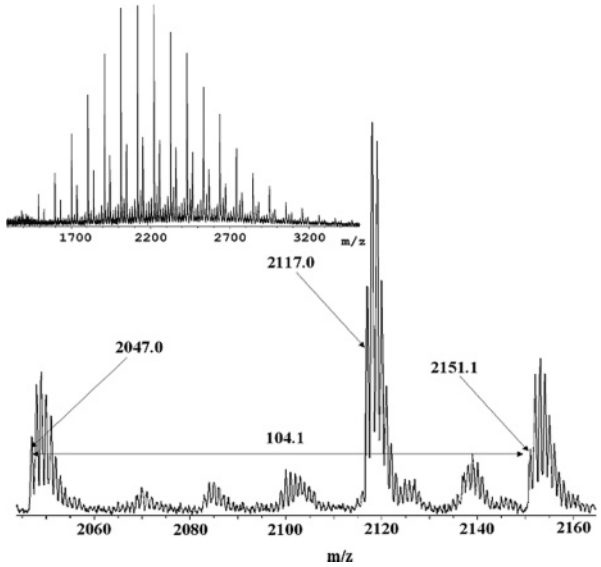


Figure 19. MALDI-TOF mass spectrum for the unprotected ω-aminopolystyrene (M_n (base) = 2200 g/mol) obtained without using silver trifluoroacetate as a cationizing agent.

Conclusions

A general two-step anionic functionalization method has been described. The first step involves the quantitative silyl hydride functionalization of well-defined polymeric organolithium compounds with dimethylchlorosilane in hydrocarbon solution at room temperature. In the second hydrosilation step, the silyl hydride functionalized polymer is added to a functionalized alkene using a platinum catalyst. The utility of this procedure has been illustrated by effecting the primary amine functionalization of poly(styryl)lithium (M_n = 2200 and 14 100 g/mol) using first the protected amine, 3-[*N*,*N*-bis(trimethylsilyl)amino]-1-propene, and also with the unprotected analogue, allylamine. All results from the analyses of the resulting amine-functionalized polymers are consistent with functionalization in high yield. The versatility of this methodology arises from the fact that the silyl hydride functionalized polymer can be reacted with a wide variety of readily available substituted alkenes, and the hydrosilation reaction is tolerant to a variety of functional groups of interest,[14,47] thus eliminating the need for protection of the functional groups (normally required for anionic functionalizations by electrophilic termination reactions) and subsequent deprotection. Work is in progress to delineate the scope and limitations of this functionalization methodology.

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