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General Functionalization Method for Synthesis of α-Functionalized Polymers by Combination of Anionic Polymerization and Hydrosilation Chemistry

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Summary: A new general functionalization method (GFM) of synthesizing α-functionalized polymers has been developed. α-Vinyl-functionalized polystyrene was obtained by anionic polymerization of styrene using 4-pentenyllithium as an initiator. Chloromethyldimethylsilane-functionalized polystyrene was successfully synthesized from vinyl-functionalized polystyrene by hydrosilation using Karstedt's catalyst. Nucleophilic substitution of this polymer was carried out in presence of pyrrolidine to obtain α-pyrrolidine-functionalized polystyrene. α-Triethoxysilylpolystyrene was obtained by hydrosilation of a-4-pentenylpolystyrene with triethoxysilane using Karstedt's catalyst.

Keywords: anionic polymerization; functionalized initiator; functionalization

Introduction

One of the unique features of living polymerizations, and alkyllithium-initiated polymerizations in particular, is the ability to prepare chain-end functionalized polymers.[1,2] After complete monomer consumption, the resulting polymeric organolithiums can react with electrophiles to form ω-chain-end functionalized polymers. Although many such reactions have been investigated, most of these *specific functionalization reactions* are not quantitative and each must be optimized. 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. GFM of importance include the reactions of polymeric organolithium compounds with (a) substituted chlorosilanes,[3] (b) substituted 1,1-diphenylethylenes,[4–6] (c) substituted alkyl chlorides,[7–9] (d) substituted epoxides,[10–12] and more recently (e) chlorodimethylsilane to form the corresponding ω-silyl hydride-functionalized polymers followed by platinum-catalyzed hydrosilation with substituted alkenes.[13–17]

For functionalizations at the initiating chain end, no GFM have been developed and α-functionalizations have generally required the use of functionalized alkyllithium initiators with all of their attendant limitations;[2,18] however, it is noteworthy that functionalized initiators with protected alcohol groups (e.g. trialkylsiloxy-functionalized organolithium compounds) have found widespread applications.[19–22] Herein a new GFM is described that is based on a combination of the use of an unsaturated, hydrocarbon-soluble, alkyllithium initiator with hydrosilation chemistry.

Experimental Part

Materials. Styrene (99%, Sigma-Aldrich) and benzene (99% ACS grade, EMD) were purified as described previously.[23] Lithium

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metal (98%, stabilized with Na, FMC), Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex, 2.1–2.4 wt% Pt in xylene, Gelest), chloromethyldimethylsilane (95%, Gelest) and pyrrolidine (99%, Aldrich) were used as received. Diethyl ether (ACS grade, EMD) and heptanes (99%, EMD) were stirred over calcium hydride overnight and distilled under vacuum. 4-Bromopentene (Aldrich, 97%) was fractionally distilled in vacuo into an all-glass ampoule prior to use; the middle fraction was collected.

Synthesis of 4-Pentenyllithium[24]

To a 250-mL Morton (creased), glass reactor equipped with a diethyl ether ampoule (20 mL), 5-bromopentene ampoule (6.4 mL, 8.05g, 0.0540 mol), Roto-flo® stopcock, and stir bar in the dry box was added lithium metal (FMC, 3.749g, 0.5402 mol). The reactor was removed from the dry box and placed under high vacuum. Heptane (50 mL) was distilled into the reactor and the reactor was separated from the vacuum line. Then, the 5-bromopentene ampoule was broken and the reaction was allowed to stir at room temperature for a period of 3 days. The reactor and diethyl ether ampoule was cooled to 0 °C and the contents of the ampoule were added. The reaction was stirred for a period of 24 h at 0 °C. Then, the reactor was again placed on the vacuum line and the solvent and volatile components were removed via high vacuum. The reactor was then placed in the dry box and the 4-pentenyllithium was taken up in heptane (50 mL) and filtered using a coarse glass frit. The product was characterized by double titration to yield 0.74 M 4-pentenyllithium (70%).

Synthesis of α-4-Pentenylpolystyrene

4-Pentenyllithium (4.2 mL, 0.00319 mol) was added to an all-glass reactor equipped with a styrene ampoule (5.4 mL, 4.91 g, 0.047 mol), a tetrahydrofuran ampoule (1.09 mL, 0.9698 g, 0.0135 mol), and a methanol ampoule (~2 mL). The reactor was placed under high vacuum and then benzene (60 mL) was distilled in. Then the reactor was flame-sealed from the line and the THF ampoule was broken followed by the styrene ampoule. The reaction was placed in a water bath at 30 °C. After a period of 6 h the methanol ampoule was broken. The reaction solution was precipitated into MeOH to yield the desired product ($M_n = 1{,}600$; PDI = 1.06). Calculated $M_n = 1{,}600$ g/mol.

Functionalization of α-4-Pentenylpolystyrene Using Chloromethyldimethylsilane

α-4-Pentenylpolystyrene (0.35 g, 0.012 mmol), chloromethyldimethylsilane (40 mg, 0.036 mmol), Karstedt's catalyst (2 drops), and toluene (2 mL) were mixed in a 20-mL glass vial. After stirring the mixture at room temperature for 48 h, the solution was precipitated into methanol and dried under vacuum for 24 h to obtain α-chloromethyldimethylsilane-functionalized polystyrene (0.31 g, 88%).

Functionalization of α-Chloromethyldimethylsilane-Functionalized Polystyrene with Pyrrolidine (PS-N)

α-Chloromethyldimethylsilane-functionalized polystyrene (0.13 g, 0.05 mmol), pyrrolidine (0.2 g, 28 mmol), and toluene (5 mL) were added to a round-bottomed flask. After attaching a reflux condenser, argon was bubbled into the flask at room temperature for 30 min. The reaction mixture was then stirred at 80 °C for 48 h. Pyrrolidine-functionalized polystyrene (0.10 g, 84%) was obtained after precipitating the solution into methanol and drying under vacuum for 24 h.

Functionalization of α-4-Pentenylpolystyrene Using Triethoxysilane

α-4-Pentenylpolystyrene (0.0982 g), dry benzene (1 mL), triethoxysilane (0.0253g) and Karstedt's catalyst (2 drops) were added to a 5-mL, round-bottomed flask in the dry box. The reaction was stirred at room temperature for a period of 12 h to quantitatively yield the desired α-triethoxysilyl-functionalized polystyrene.

Gel Permeation Chromatography (GPC) and NMR Spectroscopy

A Waters 150-C Plus instrument attached with three HR-styragel columns [100 Å, mixed bed (50/500/1000/10000 Å), mixed bed (1000, 10000, 1000000 Å)] and a triple detector system was used for GPC analysis of polymers. A differential refractometer (Waters 410), differential viscometer (Viscotek 100) and laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ nm) were the three detectors used for GPC analysis. The flow rate of solution was 1.0 mL/ min with THF as a solvent at 35 °C. The sample concentrations were varied between 25 mg/mL to 1 mg/mL in THF depending on the molecular weights (800,000 g/mol to 2,000 g/mol). The samples were filtered using Teflon® filter with 0.45 μm pore size before injection. NMR spectra were recorded using Varian 500 NMR spectrometers. For measuring ^{1}H NMR of polymers, ~ 40 mg of polymer was dissolved in deuterated solvent (chloroform). For ^{13}C NMR, ~ 150 mg of polymer was dissolved in 1.0 mL of deuterated solvent (chloroform).

MALDI-TOF Mass Spectrometry

A Bruker-Ultraflex-III-TOF/TOF (Bruker Dlatonics, Billerica, MA) mass spectrometer was used for matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry analysis. This instrument was equipped with a pulsed Nd:XAG laser (355 nm, 100 Hz repetition rate), a single stage ion extraction source and a two-stage, gridless reflector. THF solutions of dithranol (20 mg/mL) (Alfa Aesar, 1,8,9-anthracenetriol, 97%), or *t*-2-[3-(4-*t*-butylphenyl)2-methyl-2-propenylidene]macronitrile (DCTB) (Fluka, 99%), sodium trifluoroacetate (99%, Fluka) or silver trifluoroacetate (98%, Aldrich) and polymer (10 mg/ mL) were prepared for MALDI-TOF MS analysis. The above solutions were mixed in a ratio of matrix:cationizing salt:polymer (10:1:2), and 0.5 μL of this solution was deposited onto the MALDI sample target and was allowed to dry. The intensity of the nitrogen laser was attenuated to obtain optimum signal strength. Positive reflectron modes were used for recording mass spectra and calibration of the mass scale was done externally by using polystyrene standard molecular weights.

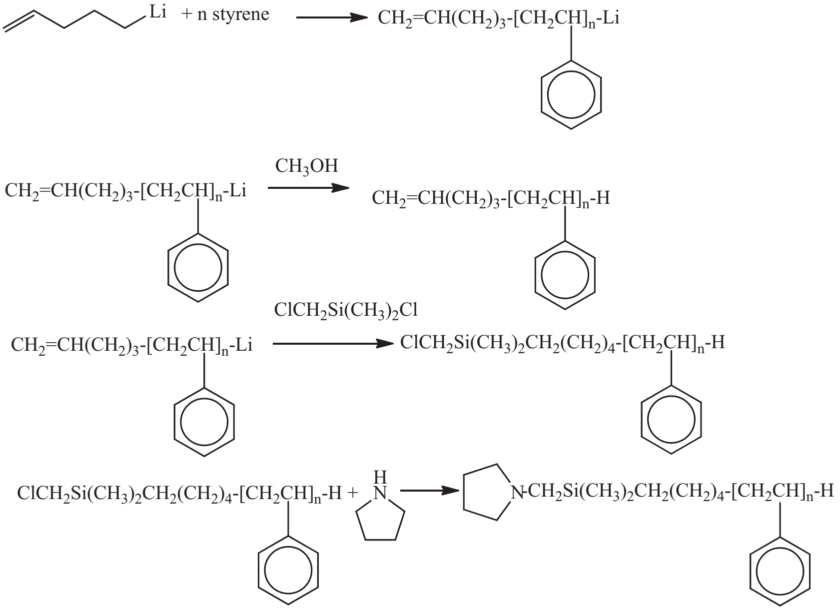
Electrospray Ionization Mass Spectrometry (ESI)

Electrospray ionization (ESI) mass spectra were acquired with a SYNAPT HDMS™ Q/ToF mass spectrometer (Waters, Beverly, MA) equipped with a Z-spray electrospray source. The instrument was operated at a voltage of 3.5 kV, sample cone voltage of 35 V and extraction cone voltage of 3.5 V. The desolvation gas flow was 800 L/h (N_2) and the source temperature was 90 °C. The sample flow rate was set at 10 μL/min. The concentration of the electrosprayed samples was 0.2 mg/mL in THF/MeOH, 1:1, v:v.

Results and Discussion

Anionic Synthesis of α-Pentenylpolystyrenes

The anionic polymerization of styrene using 4-pentenyllithium as initiator has been investigated for use as the first step in the development of a new general functionalization method as outlined in Scheme 1. In order for this initiator to be useful in this regard, it is essential that it provide α-pentenyl-functionalized polystyrenes with controlled molecular weights and narrow molecular weight distributions. Using α-4-pentenylithium with 4 equivalents of THF to promote the rate of initiation relative to propagation,[1] it was possible to prepare narrow molecular weight distribution, α-4-pentenylpolystyrenes with controlled molecular weights [e.g., $M_n(\text{calc}) = 1500$ g/mol; $M_n(\text{obs}) = 1600$ g/mol; $M_w/M_n = 1.06$]. This procedure has been used to effect the synthesis of



Scheme 1.

α-pentenylpolystyrenes with controlled M_n and narrow polydispersity ($M_w/M_n = 1.02–1.10$) in the molecular weight range of 2,500 to 37,000 g/mol.[25] The ^1H NMR spectrum of the vinyl-functionalized polystyrene (PS-V; $M_n = 1,600$) exhibited the expected terminal vinyl peaks δ 4.90 and 5.73 ppm.[24]

The MALDI-TOF mass spectrum clearly shows a clean and successful synthesis of the desired product. Without fractional distillation of the 5-bromopentene prior to the synthesis, however, more than one product distribution was observed in the mass spectrum. When high purity reagents were used, one distribution was observed. The MALDI-TOF mass spectrum (Figure 1) shows the desired distribution with a representative monoisotopic peak at *m/z* = 1446.06 corresponding to the 13-mer, α-4-pentenylpolystyrene, C_5H_9-$(C_8H_8)_{13}$-$H \cdot Na^+$; calculated monoisotopic mass = 1445.94 Da. The calculated and observed masses are in excellent agreement, further documenting the successful synthesis of pure α-4-Pentenylpolystyrene.

Functionalization of α-4-Pentenylpoly-Styrene Using Chloromethyl-Dimethylsilane

Hydrosilation chemistry was used to functionalize α-pentenylpolystyrene using chloromethyldimethylsilane as shown in Scheme 1. The reaction of α-4-pentenylpolystyrene ($M_n = 2,500$ g/mol) with 3 equivalents of chloromethyldimethylsilane was effected in toluene in the presence of a few drops of Karstedt's catalyst solution at room temperature. After 48 hours the polymeric product was isolated by precipitation into methanol. The SEC chromatogram was monomodal with $M_n = 2,600$ g/mol and $M_w/M_n = 1.02$. The ^1H NMR spectrum of the product exhibited new peaks at δ 0.09 and 2.77 ppm corresponding to the $-Si(C\underline{\mathbf{H}}_3)_2$ protons and the $-C\underline{\mathbf{H}}_2Cl$ protons, respectively. No signals corresponding to the vinyl protons (δ 4.90 and 5.73 ppm) were observed.

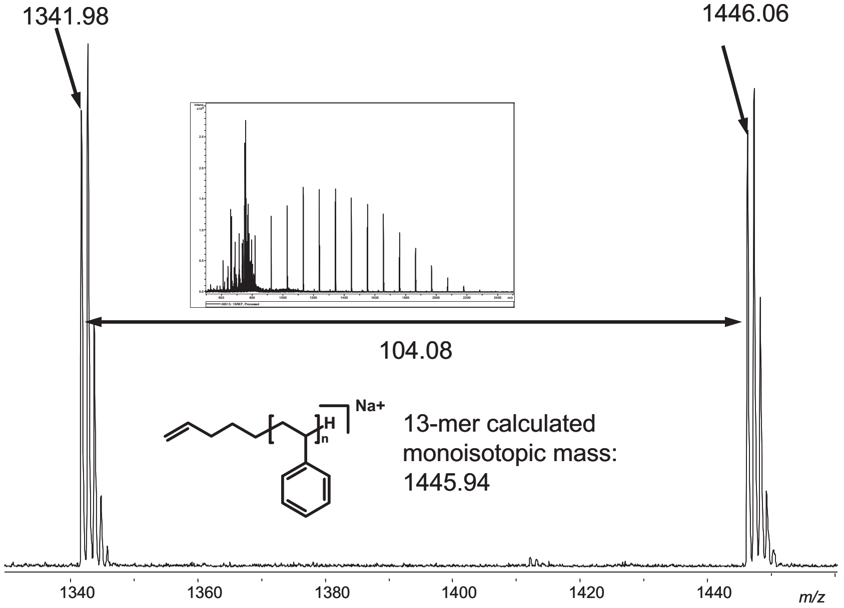


Figure 1.
MALDI-TOF mass spectrum of α-4-pentenylpolystyrene.

Functionalization of α-Chloromethyldimethylsilane-Functionalized Polystyrene with Pyrrolidine

As an example of the utility of chloromethylsilyl-substituted styrenes for synthesis of various alpha-functionalized polymers by reaction with nucleophiles, this polymer was reacted with excess pyrrolidine in toluene under reflux for 48 hours (See Scheme 1). The resulting α-pyrrolidine-functionalized polystyrene was isolated in 84% yield. The SEC chromatogram was monomodal with $M_n = 2{,}700$ g/mol and $M_w/M_n = 1.03$. The ^{1}H NMR spectrum of this product exhibited a new peak at δ 2.57 ppm corresponding to the $–C\underline{H}_2$-N- group and the disappearance of the peak corresponding to the $–C\underline{H}_2Cl$ group (δ 2.77 ppm). The ^{13}C NMR spectrum of this product exhibited a new peak at δ 58.11 ppm corresponding to the $–\underline{C}H_2$-N- groups.

The ESI mass spectrum of the α-pyrrolidine-functionalized polystyrene showed two distributions (one major, one minor). A representative monoisotopic mass peak of the major distribution at *m/z* 1879.7 corresponds to protonated pyrrolidine-functionalized polystyrene with 16 repeating styrene units, $[(CH_2)_4NH^+](C_3H_8Si)(C_5H_{10})(C_8H_8)_{16}$-H; calculated monoisotpic mass $= 71.0734 + 72.0395 + 70.07825 + 104.0626 \times 16 + 1.007825 = 1879.2$ Daltons. Similarly, a peak observed at *m/z* 1983.8 corresponds to pyrrolidine-functionalized polystyrene with 17 styrene repeating units, $[(CH_2)_4NH^+](C_3H_8Si)(C_5H_{10})(C_8H_8)_{17}$-H; calculated monoisotpic mass $= 71.0734 + 72.0395 + 70.07825 + 104.0626 \times 17 + 1.007825 = 1983.3$ Daltons. A representative peak corresponding to minor distribution [*m/z* 1967.7] could not be assigned to a particular structure. Based on the ratio of intensities of the peaks at *m/z* 1967.7 and 1879.2, the percentage of the unknown product was calculated to be 7.5%.

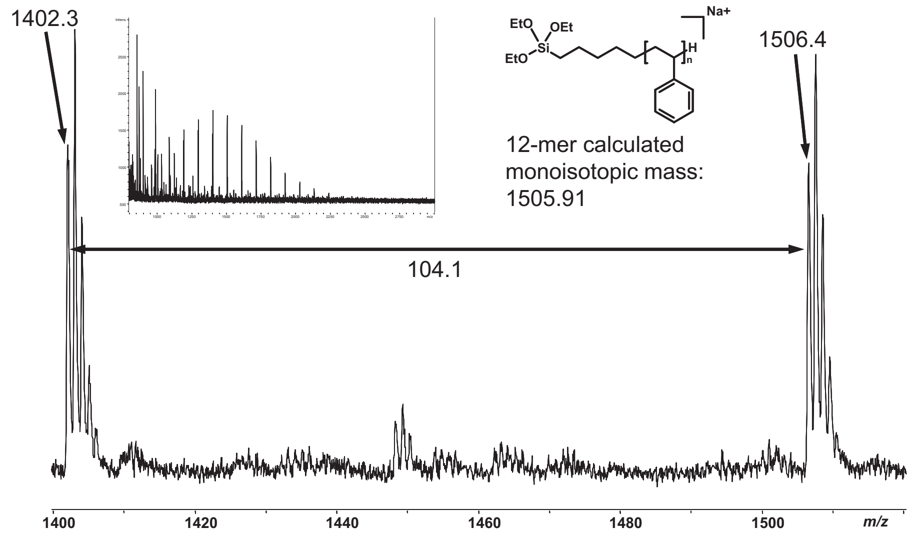
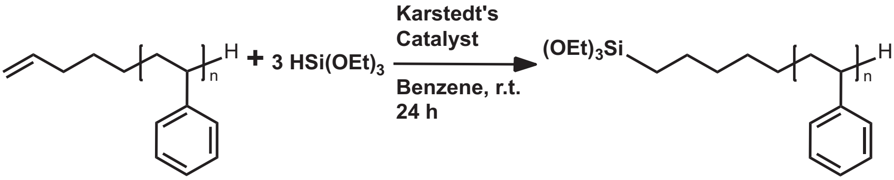


Figure 2.
MALDI-TOF mass spectrum of triethoxysilane-functionalized polystyrene.

Synthesis of α-Triethoxysilylpolystyrene

The generality of these procedures was also illustrated by the synthesis of α-triethoxysilyl-functionalized polystyrene by hydrosilation of α-4-pentenylpolystyrene with triethoxysilane using Karstedt's catalyst as shown in eqn. (1).



(1)

This reaction was performed in the dry box at room temperature over a period of 12 hours, and proceeded to completion with no detectable side reactions. ^{1}H NMR spectroscopy revealed the absence of vinyl protons at δ 4.9 and 5.7 ppm. In addition, the methylene protons adjacent to oxygen were apparent at δ 3.9 ppm.[26] The MALDI-TOF mass spectrum (Figure 3) showed the desired distribution with a representative monoisotopic mass peak at $m/z = 1506.4$ corresonding to the 12-mer, triethoxysilane-functionalized polystyrene, $(CH_3CH_2O)_3Si\text{-}C_5H_{10}\text{-}(C_8H_8)_{12}\text{-}H \cdot Na^+$; calculated monoisotopic mass = 1505.91 Da. The peak corresponding to the 13-mer sodiated starting material was not observed at $m/z = 1445.94$. There was a small peak present at $m/z = 1448$ corresponding to the 13-mer hydrogenated starting material. This peak can arise from either an impurity of bromopentane in the initial material, or a side reaction of hydrogenation during hydrosilation, a commonly observed side reaction for hydrosilation reactions.[27–30]

This facile, efficient synthesis trialkoxylsilyl-functionalized polymers stands in sharp contrast to the general difficulties of generating these polymers by normal chain-end functionalization reactions of polymeric organolithium compounds because of the reactivity of the trialkoxysilyl groups with the organolithium chain ends.[31,32]

α,ω-Functionalization

The living α-pentenylpoly(styryl)lithium can also react with terminal functionalizing agents, e.g. ethylene sulfide[33] or chlorodimethylsilane,[13–17] to form α-4-pentenyl-ω-functionalized polymer chain ends. α,ω-Telechelic and α,ω-heterotelechelic polymers can then be formed using the chemistry outlined herein.

Conclusion

A new general functionalization methodology for alpha (initiating) chain-end functionalization has been developed based on the combination of an unsaturated alkyllithium initiator, 4-pentenyllithium, hydrosilation with chloromethyldimethylsilane, and nucleophilic displacement of the resulting primary alkyl chloride. The intermediate α-4-pentenyl-functionalized polymer can also react with a functionalized silane, e.g.triethoxysilane,to form the corresponding α-functionalized polymer. Since alkyllithium initiator can also be used to initiate anionic polymerizations of 1,3-dienes, vinylpyridines and alkyl methacrylates,[1] the methodology described herein should also be adaptable to these polymerizations.

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