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Termination of Living Anionic Polymerizations Using Chlorosilane Derivatives: A General Synthetic Methodology for the Synthesis of End-Functionalized Polymers

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Abstract: The transformation of living polymer chain ends is the most widely used technique to synthesize end-functionalized polymeric materials. Herein we report the development of a new synthetic methodology which is able to give very high degrees of functionalization to living anionic polymer chains. This methodology is based on termination reactions with chlorosilane derivatives containing protected functional groups and is described with particular emphasis on the introduction of primary aliphatic amines and primary aliphatic alcohols. The extent of functionalization was verified by using conventional techniques such as gel permeation chromatography (GPC), end group titration, multinuclear magnetic resonance spectroscopy, and TLC, but was also examined by using time-of-flight secondary ion mass spectrometry (TOF-SIMS). The usefulness of these materials for construction of supramolecular assemblies is illustrated by the coupling of the polymeric amine to [Ru(bpy)$_2$(4-CH$_3$-4′-CO$_2$Hbpy)](PF$_6$)$_2$ (bpy = 2,2′-bipyridine).

Introduction

Living polymerization techniques provide one means by which chain length, chain composition, and end groups can be controlled.[1−3] Due to the unique structure of the propagating chain end, the transformation of the living chain end into a specific functional group has provided a simple and controlled way to synthesize end-functionalized polymers, polymers which contain a reactive end group on one or both chain ends. Such polymers have been used in the synthesis of block copolymers,[4] in chain extension reactions with multifunctional polymers,[5] and as reactive groups for use as molecular scaffolding[6] to create new materials with precise control over composition and molecular and supramolecular structure.

End-functionalized polymers are generally prepared using two different techniques. One approach utilizes functionalized initiators which can initiate the polymerization of specific monomers.[7,8] These often encounter serious solubility problems and are limited in the types of monomers that can be polymerized in a living manner. The most widely used approach involves transformation of a living anionic chain end into a specific functional group. These generally involve the addition of certain electrophiles to functionally terminate living polymerizations but can often involve a highly sophisticated procedure to achieve high degrees of functionalization. Quirk et al. have quantified the various termination reactions in terms of their specific side reactions and have optimized the reaction conditions for a variety of systems to obtain the highest degree of functionalization.[9]

A unified, general methodology for the introduction of a wide range of functional groups to the termini of different types of polymers[10,11] with high degrees of functionality has not previously been developed for functional termination reactions. Shown here is a general scheme which outlines a new approach for the synthesis of functionalized polymers. This new synthetic methodology utilizes chlorosilane derivatives which contain protected functional groups to terminate living polymeric anions. The protecting groups are chosen from those which were utilized by Nakahama to protect functionalized monomers for anionic living polymerizations.[12] This methodology should be applicable to the entire range of polymeric nucleophiles from polysiloxanolates to polystyrenics and may also be applicable

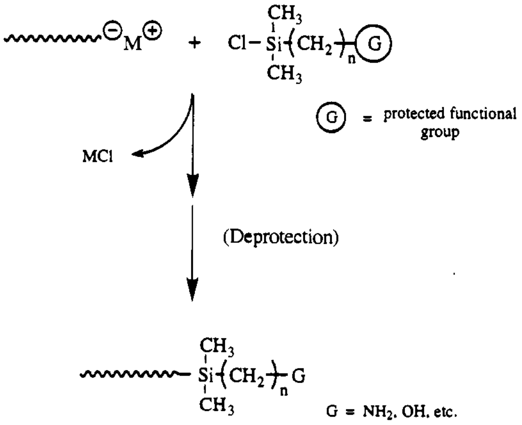

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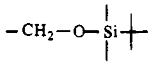
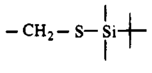
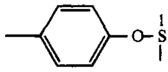
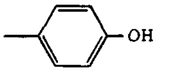
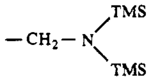
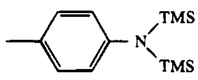
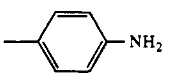
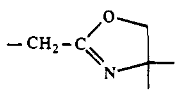
Table 1. Possible Functional Groups

Protected Functional Group	Functional Group
	$-CH_2-OH$
	$-CH_2-SH$
	
	$-CH_2-NH_2$
	
	$-CH_2-CO_2H$
$-CH_2-C\equiv N$	$-CH_2-CO_2H$ $-CH_2-NH_2$

to enolates derived from the polymerization of *tert*-butyl acrylates.[13] The versatility of this methodology should provide a general means for introducing a wide range of functional groups, including those listed in Table 1, to the terminus of different polymer systems.

Experimental Section

Reagents. *N,N*-Bis(trimethylsilyl)lithium amide (1.00 M in hexane), chloromethyl methyl ether, allylmagnesium bromide (1.0 M in ethyl ether), allyl alcohol, (benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate (BOP), 1-hydroxybenzotriazole hydrate (HOBT), 4-(dimethylamino)pyridine (DMAP), 4-methylmorpholine (NMM), pentamethyldiethylene triamine and chloroplatinic acid were all used as received (Aldrich). Bis(phenylethenyl)benzene was graciously supplied by DOW and used as received. Chlorodimethylsilane (Huls) was distilled prior to use. *tert*-Butyldimethylsilyl chloride was used as received. *sec*-Butyllithium and dibutylmagnesium were graciously supplied by Lithco Corporation and used as received. The concentration of the *sec*-butyllithium solution was determined by using the Gillman double titration procedure.[14] Cyclohexane (Phillips Petroleum) was stirred over concentrated sulfuric acid for ca. two weeks, decanted, and distilled under argon from sodium metal. Tetrahydrofuran (THF) (Fisher, Certified Grade) was distilled under argon from the violet sodium/benzophenone ketyl. Styrene and isoprene (Fisher, Certified Grade) were vacuum distilled from dibutylmagnesium following three freeze—thaw cycles.

N,N-Bis(trimethylsilyl)methoxymethylamine (1). To a 300-mL, two-neck round bottom flask fitted with an addition funnel and purged with argon was added 135 mL of a 1.0 M solution (0.135 moles) of *N,N*-bis(trimethylsilyl)lithium amide in hexane. The solution was cooled to 0 °C which resulted in the formation of a yellow precipitate. Dry tetrahydrofuran was added slowly to create a homogeneous 23% v/v THF/hexane solution. (Close attention must be paid to the composition of this mixture because too much THF will solubilize the lithium chloride salt, a byproduct of the reaction with chloromethyl methyl ether, and severely decrease the yield of desired reaction.) Chloromethyl methyl ether was added dropwise from the addition funnel, and after a short time, lithium chloride salt precipitated from the reaction mixture. After stirring for 8 h, the salt was filtered, solvent was removed on a rotary evaporator, and the product was purified by vacuum distillation to give 22 g of a clear liquid (80% yield). ^{1}H NMR ($CDCl_3$): δ 4.26 (s, 2H, CH_2), 3.15 (s, 3H, CH_3), 0.11 (s, 18H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 80.8, 53.4, 1.8. ^{29}Si NMR ($CDCl_3$) δ 7.72.

N,N-Bis(trimethylsilyl)-1-butenylamine (2). To a 200-mL, three-neck round bottom flask fitted with a rubber septum, an addition funnel, and a mechanical stirrer was added 80 mL of a 1.0 M allylmagnesium bromide solution (0.08 mol) in ether. The flask was cooled to 0 °C, and a 0.8 M solution of **1** (0.08 mol) in ether was added dropwise from the addition funnel. A gray salt precipitated even before addition of **1** was complete. After 12 h, the salt was filtered away, ether was removed on the rotary evaporator, and the product was purified by vacuum distillation to give 9.5 g of a clear liquid (55% yield). ^{1}H NMR ($CDCl_3$): δ 5.6–5.8 (m, 1H, CH=), 4.9–5.1 (m, 2H, CH_2=), 2.7–2.9 (m, 2H, CH_2), 2.0–2.1 (m, 2H, CH_2N), 0.08 (s, 18H, 2 × $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 136.2, 115.4, 45.1, 39.9, 2.1. ^{29}Si NMR ($CDCl_3$) δ 5.60.

Allyl (*tert*-butyldimethyl)silyl ether (3). Allyl alcohol (0.147 moles, 8.54 g) was placed in a 300-mL round bottom flask with 1.8 g (0.0147 mol) of DMAP and 70 mL of CH_2Cl_2. *tert*-Butyldimethylsilyl chloride (26.5 g, 0.176 mol) was dissolved in 30 mL of CH_2Cl_2 and added dropwise to the alcohol solution via an addition funnel. After 12 h, the reaction mixture was washed three times with a saturated aqueous $NaHCO_3$ solution. Removal of solvent and vacuum distillation gave the corresponding allyl silyl ether as a clear, colorless liquid in 86% yield. ^{1}H NMR ($CDCl_3$): δ 5.80–6.00 (m, 1H, CH=), 5.00–5.31 (m, 2H, CH_2=), 4.1–4.2 (m, 2H, CH_2O), 0.9 (s, 9H, $C(CH_3)_3$), 0.09 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 17.92, 18.29, 25.82, 63.94, 113.71, 137.33. ^{29}Si NMR ($CDCl_3$): δ 18.8.

Hydrosilylation Reactions. To a two-neck, 50-mL round bottom flask fitted with a reflux condenser and a septum were added the olefin, 2 equiv of chlorodimethylsilane, and a catalytic amount of chloroplatinic acid. The mixture was slowly heated to 60 °C under an inert argon atmosphere until an exotherm was observed. The heat was removed, and the reaction was stirred at room temperature for 2 h. The resulting chlorosilanes were purified by vacuum distillation and stored under an argon atmosphere. Characterization of the resulting chlorosilanes is as follows.

(N,N-Bis(trimethylsilyl)amino)butylchlorodimethylsilane (4): 83% yield; ^{1}H NMR ($CDCl_3$) δ 2.75 (t, 2H, CH_2N), 1.25–2.5 (m, 4H, 2 × CH_2), 0.80 (t, 2H, CH_2Si), 0.40 (s, 6H, $ClSi(CH_3)_2$), 0.08 [s, 18H, $N\{Si(CH_3)_3\}_2$]; ^{13}C NMR ($CDCl_3$) δ 45.2, 38.7, 20.6, 18.9, 2.1, 1.7; ^{29}Si NMR ($CDCl_3$) δ 31.9, 5.5.

***tert*-Butyldimethylsilyl 3-(chlorodimethylsilyl)propyl ether (5).** 55% yield; ^{1}H NMR ($CDCl_3$) δ 3.57 (t, 2H, CH_2O), 1.49–1.69 (m, 2H, CH_2), 0.71–0.87 (m, 2H, CH_2Si), 0.87 (s, 6H, $ClSi(CH_3)_2$), 0.39 (s, 6H, $Si(CH_3)_2$), 0.03 (s, 9H, $SiC(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 65.22, 26.35, 25.97, 18.35, 14.89, 1.61, −5.26; ^{29}Si NMR ($CDCl_3$) δ 32.3, 18.8.

Polymerization of Hydrocarbon Monomers. Synthesis of Monofunctional Materials. Purified styrene (or isoprene) monomer (10 g, 0.1058 mol) was added to 100 mL of dry cyclohexane in a 200-mL, round bottom flask which had been previously capped with a septum, flame dried, and purged with argon. A typical polymerization (for a target $\langle Mn \rangle$ = 1 kg/mol) was initiated with 6.29 mL (0.0100 mol) of a 1.59 M solution of *sec*-butyllithium which generated a dark orange solution (polyisoprenyl lithium is not colored in cyclohexane). After 3 h, 2% v/v of THF was added (the color of the solution became a dark ruby red) and the polymerizations were terminated as described below. After termination was complete, polystyrene was precipitated

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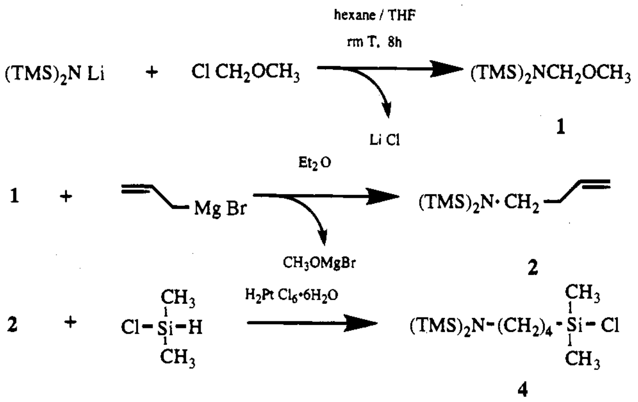
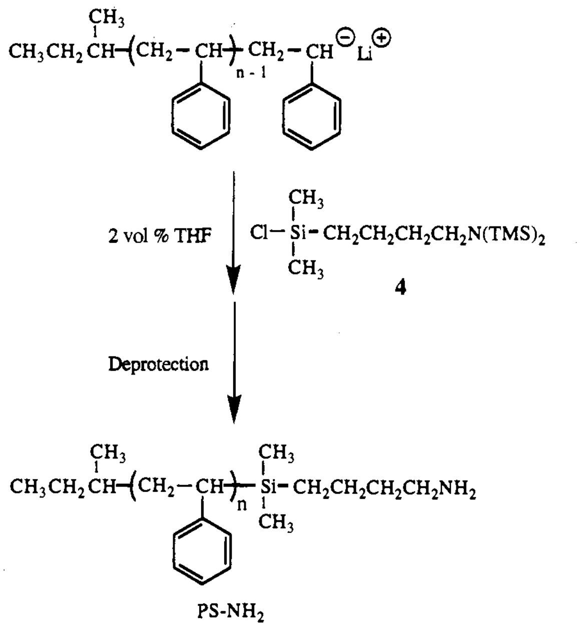
[13] Polymerization of acrylic monomers proceeds through an enolate propagating chain end, and termination with functionalized chlorosilanes would conceivably create a large fraction of unstable *o*-silylated products. However, Teyssie has recently shown that addition of LiCl to the termination reaction of chlorosilanes with living *tert*-butyl acrylate living chain ends provides primarily *c*-silylated products and would provide a means for stable, end-functionalization in these systems using our methodology (see: Teyssie, P.; Varshney, S. K.; Jerome, R.; Bayard, P.; Jacobs, G.; Fayt, R. *Macromolecules* **1992**, *25*, 5578).

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

Scheme 1. Synthesis of [*N*,*N*-Bis(trimethylsilyl)amino]butylchlorodimethylsilane



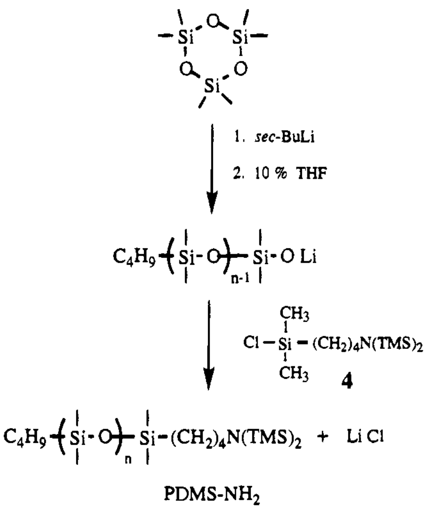
Scheme 2. Synthesis of Amine-functionalized Polystyrene



in a 5-fold excess of methanol, filtered, and dried in a vacuum oven. Polyisoprene was precipitated in a 5-fold excess of methanol and coagulated on the bottom of the precipitation flask. Excess solvent and methanol were decanted, and the polymer was redissolved in a small amount of CH_2Cl_2 with 0.5 mol % of antioxidant (Irganox 2010) to reduce oxidation of the unsaturated bonds in the backbone. The solvent was then removed by rotary evaporation, and the polymer was dried in the vacuum oven in the dark and without heat. Low molecular weight polymers (1–2 kg/mol) were isolated by rotary evaporation of the reaction solvent and washed several times with H_2O to remove the lithium salts.

Synthesis of α,ω-Difunctional Materials. Bis(phenylethenyl)benzene (1.55 g, 6.0 mmol) was placed in a 500-mL round bottom flask and fitted with a septum. Dry cyclohexane (184 mL) was added via cannula to make a 0.03 M solution. Pentamethyldiethylenetriamine (0.12 g, 0.72 mmoles) was added, and the solution was deaerated for several minutes with argon. *sec*-Butyllithium (1.50 M in cyclohexane) was added dropwise until a red color was formed. A stoichiometric amount of *sec*-butyllithium was then added, and the solution was stirred at 60 °C overnight. A small portion was removed and terminated with methanol. All solvent was removed, and the residue was examined by ^1H NMR. Loss of the resonance corresponding to the olefin was evidence that the reaction was complete. This initiator solution was then utilized to initiate the polymerization of styrene monomer. For low molecular weight materials (2–5 kg/mol), the monomer was added to this initiator solution due to the low initiator concentration. Forhigher molecular weight materials, the initiator was added to a solution of the monomer in cyclohexane. The monomer concentration was kept near 10% wt/vol in all cases.

Scheme 3. Synthesis of Amine-Functionalized Poly(dimethyl siloxane)



Scheme 4. Synthesis of α,ω-Diamine-Functionalized Polystyrene

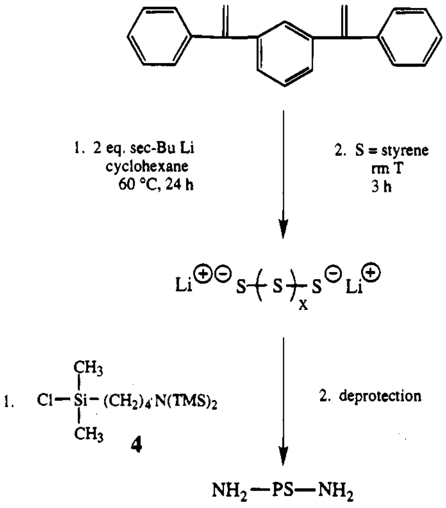


Table 2. End-Group Characterization[a]

polymer	Mn(GPC) × 10^{-3} g/mol	Mn(titration) × 10^{-3} g/mol	*f*	MWD
PS−NH₂	2.1	2.2	0.94	1.04
PS−NH₂	10.7	10.3	1.04	1.04
PS−NH₂	19.7	21.3	0.92	1.04
PDMS−NH₂	5.0	5.3	0.94	1.06
PDMS−NH₂	9.6	10.2	0.94	1.03
PDMS−NH₂	17.4	19.5	0.89	1.02
PI−NH₂	5.9	6.8	0.87	1.09
P(S-*b*-I)−NH₂	31.1	32.4	0.96	1.02
H₂N−PS−NH₂	6.0	3.4	1.76	1.18
H₂N−PS−NH₂	11.5	6.3	1.83	1.18

[a] *f* = Mn(GPC)/Mn(titration); PS = polystyrene; PI = polyisoprene; PDMS = poly(dimethyl siloxane).

Synthesis of Poly(styrene-*b*-isoprene). To synthesize a 50/50 w/w block copolymer of styrene and isoprene, purified isoprene monomer (10 g, 0.147 mol) was added to the colored polystyryl anion via syringe. The bright anion color diappeared immediately upon addition of the isoprene monomer. After 3 h the polymerization was terminated as described below. Polystyrene homopolymer (a contaminant in the synthesis of the block copolymer) was removed by precipitation into acetone. The polymer was redissolved in CH_2Cl_2, and 0.5 mol % antioxidant was added. Solvent was removed by rotary evaporation.

Polymerization of Silicone Monomer. Purification of D_3. Hexamethylcyclotrisiloxane (D_3) (200 g) was stirred at 60 °C overnight with 5 g of calcium hydride under an argon atmosphere in a 1-L, two-neck, round bottom flask. This flask was then attached under an argon

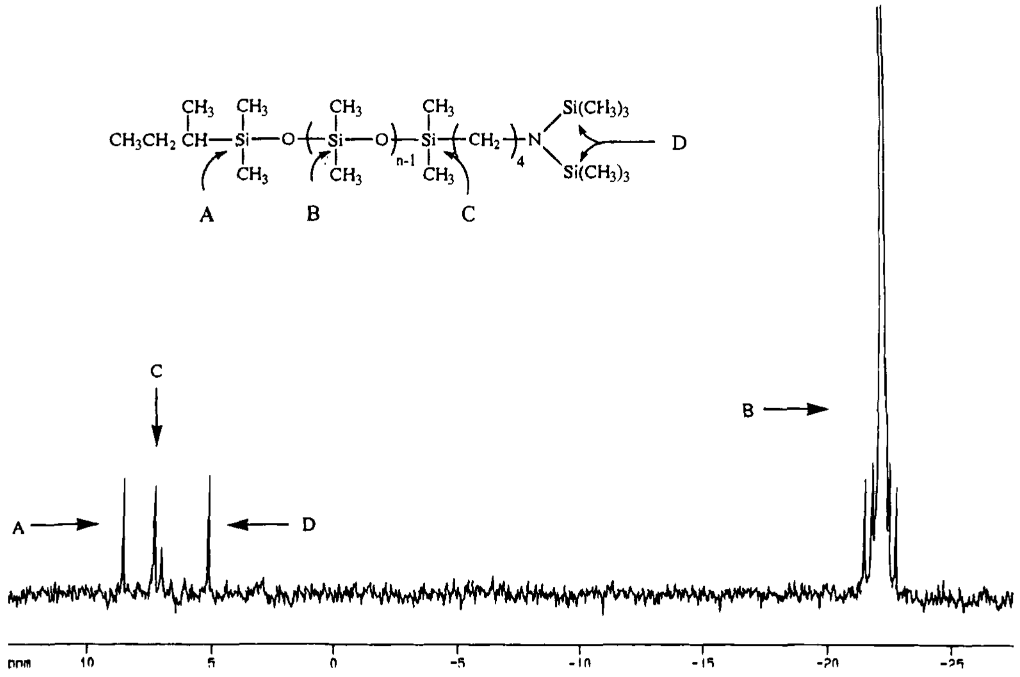


Figure 1. ^{29}Si NMR spectrum of PDMS$-$NH$_2$.

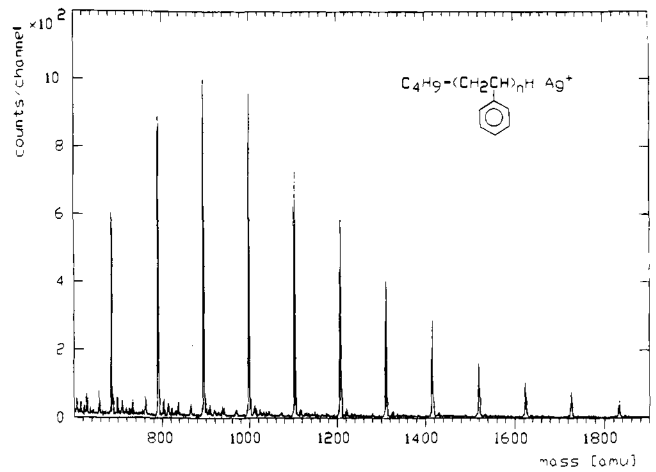


Figure 2. TOF-SIMS data of a polystyrene aliquot.

purge to a vacuum distillation apparatus which had been previously flame dried and purged with argon. The monomer was then sublimed under vacuum (to ~90% completion) into a tared round bottom flask containing a stir bar. The distillation/sublimation apparatus was then refilled with argon, and ~100 mL of dry cyclohexane was transferred to dissolve the purified monomer. This solution was then transferred via cannula to a previously dried 500-mL volumetric flask and was diluted to obtain a stock solution of a known concentration.

Polymerization of D$_3$. The D$_3$ monomer was transferred to a 36% wt/v solution in cyclohexane (27.8 mL, 10 g of D$_3$) via syringe into a dry 200-mL round bottom flask. The polymerization was initiated by addition of 1.18 mL of *sec*-butyllithium (1.7 M, 2.01 mmol) for a target number average molecular weight of 5 × 10^3 g/mol. After 2 h at room temperature, 10 vol % of dry tetrahydrofuran (3 mL) was added via syringe to allow propagation to occur. The reaction was allowed to proceed for 48 h and was terminated as described below. Poly(dimethyl siloxane) materials were precipitated into methanol and coagulated on the bottom of the precipitation flask. Excess solvent was decanted, and the polymer was then dried to constant weight under vacuum.

Amine and Hydroxyl-Terminated Materials. An aliquot was separated from each living polymer solution and terminated with deoxygenated methanol (or chlorodimethylsilane in the case of PDMS) for use in comparison to the functionally terminated materials. The functionalized chlorosilane was distilled prior to the termination of the living polymerization and a 2-fold excess of the chlorosilane was added directly to the polymer solution via syringe. (For the highest degrees of functionalization, ~5 mol % of *sec*-butyllithium was added directly to the chlorosilane after distillation to scavenge any impurities and to ensure that the chlorosilane was of very high purity.) In the termination of polystyryl systems, the color of the solution immediately became pale yellow, gradually faded to colorless, followed by precipitation of LiCl. Termination of the colorless anions, polyisoprenyl lithium and polysiloxanyl lithium, was accompanied by the precipitation of LiCl in less than 5 min after addition of the terminating reagent. The functional groups were deprotected by addition of methanol to the reaction solution prior to workup. Deprotection was verified by TLC and TOF-SIMS.

Ru(bpy)$_3$$^{2+}$-Derivatized Poly(styrene). Procedures for synthesis of [Ru(bpy)$_2$(4-CH$_3$-4′-CH$_2$Hbpy)](PF$_6$)$_2$ are described elsewhere.[15] Amine-functionalized polystyrene (0.50 g, 0.211 mmol) was dissolved in 0.5 mL of distilled dimethylformamide (DMF). [Ru(bpy)$_2$(4-CH$_3$-4′-CO$_2$Hbpy)](PF$_6$)$_2$ (0.19 g, 0.211 mmol), *N*-methylmorpholine (0.043 g, 0.422 mmol), BOP (0.186 g, 0.422 mol), and HOBt (0.043 g, 0.317 mmoles) were also dissolved in 0.5 mL of DMF. This latter solution was transferred into the polymer solution and stirred for 10 min. DMAP (0.026 g, 0.211 mmol) was added, and the solution was stirred overnight. The resulting polymer was precipitated into an aqueous 0.5 M NaHCO$_3$ solution, filtered, and washed with NaHCO$_3$ in water until the filtrate was colorless. The polymer was then redissolved in THF

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(15) Peek, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, G. J.; Meyer, T. J.; Erickson, B. W. *Int. J. Pept. Protein Res.* **1991**, *38*, 114.

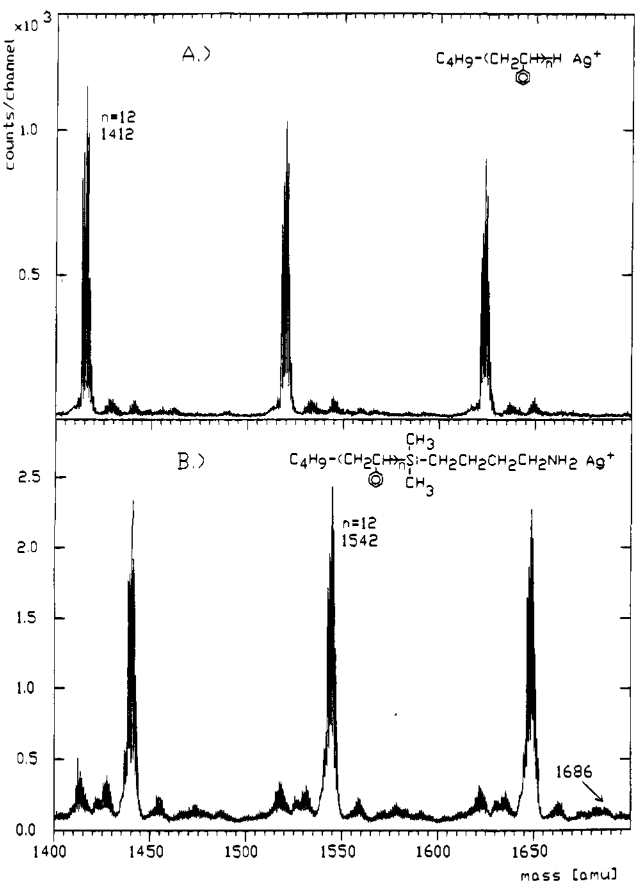
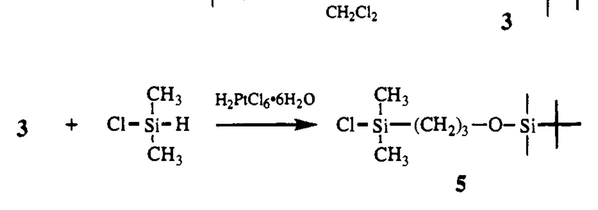


Figure 3. TOF-SIMS data of the amine-functionalized polystyrene. (A) Polystyrene aliquot; (B) amine-functionalized polystyrene.

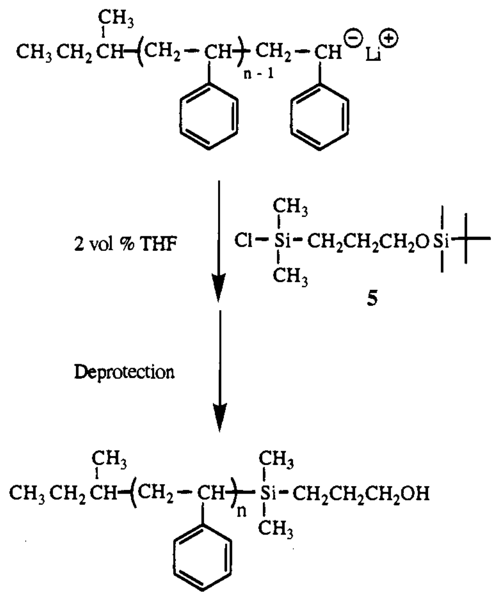
Scheme 5. Synthesis of *tert*-Butyldimethylsilyl 3-(Chlorodimethylsilyl)propyl Ether



and precipitated into an ice-cold solution of hexafluoroammonium phosphate. The precipitated polymer was stirred for 10 min, filtered, and washed with ice-cold water several times. This material was ruby red in color. The polymer was further purified by column chromatography using an alumina stationary phase and a 2:1 toluene/acetonitrile mobile phase, and the polymer was recovered by precipitation into a 10-fold excess of hexanes. This material was dried in the vacuum oven overnight in the dark.

Characterization. GPC: A Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100, 500, 10^3, 10^4, and 10^5 Å porosities in tetrahydrofuran was used with polystyrene standards (Showa Denko) for the determination of molar mass and molar mass distribution. Analysis of the Ru(bpy)$_3$ derivatized polystyrene material was performed on a Waters GPC equipped with a Waters 410 Differential Refractometer and a Waters 996 Photodiode Array Detector. This GPC used a methylene chloride mobile phase, contained three Ultrastyragel columns (linear, 10^3, and 500 Å), and was calibrated with Showa Denko polystyrene standards. **TOF-SIMS:** Time-of-flight secondary ion mass spectrometry (TOF-SIMS) spectra were acquired using the TOF-II reflectron instrument developed and located at the University of Muenster.[16] Typical instrumental conditions during TOF-II spectrum acquisition include a 1.2 pA primary Ar^+ current with a pulse width of 1 ns and a repetition rate of 150 μs. The primary ions beam struck a 0.25 mm^2 analysis area during a 200 s acquisition period. Thus analysis conditions were maintained within the static regime with primary ion doses at approximately 3×10^{11} ions/cm^2. A 10 keV post ionization was employed. Samples were prepared by depositing 1 mL of polymer solution in chloroform (1 mg/mL) on about 80 mm^2 of an etched silver substrate (monolayer preparation). **NMR:** ^{1}H and ^{13}C NMR of the chlorosilanes and polymers were performed on a Bruker AC200 spectrophotometer. ^{29}Si NMR was performed on a Bruker AMX 300 MHz spectrophotometer. **TLC:** TLC was performed on 250 μm silica gel TLC plates containing a fluorescent indicator. Amine- and hydroxy-terminated materials were analyzed using a toluene mobile phase. **Titration:** Nonaqueous titrations of amine end groups were performed in a chloroform/acetic acid mixture with 0.1 M $HClO_4$ and a methyl violet indicator.[17] Titrant solutions were standardized with potassium hydrogen phthalate (KHP).

Scheme 6. Synthesis of Hydroxyl-Functionalized Polystyrene



Results and Discussion

Chlorosilanes have been used previously to terminate living polymerizations for the synthesis of star polymers,[18] macromonomers,[19] and fluorinated block copolymers,[20] but have not been utilized as part of a general procedure for the introduction of functional groups, such as amino, hydroxyl, and carboxyl moieties. Chlorosilanes are more reactive in termination reactions than the analogous alkylhalide derivatives due to the highly polarized silicon–chloride bond and therefore provide a highly efficient methodology for the quantitative introduction of a wide range of functional groups. The use of chlorosilane derivatives eliminates the complexity generally associated with functional termination of living polymerizations and allows functionalization of a large range of polymer systems.

Amine-Terminated Materials. One of the most difficult functional groups to introduce using living polymerization methods is the primary aliphatic amine.[21,22] Our methodology replaces the often complex reactions used to introduce this

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(16) Niehuis, E.; Heller, T.; Feld, H.; Benninghoven, A. *J. Vac. Sci. Technol.* **1987**, *A5* (4), 1243.

(17) Fritz, J. S. *Acid-Base Titration in Nonaqueous Solvents*; Allyn and Bacon: Boston, 1973; Chapter 2.

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(19) Milkovich, R.; Chiang, M. U.S. Patent 3786116, 1974. Greber, G.; Balciunas, A. *Makromol. Chem.* **1963**, *69*, 193. Rempp, P.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*. DeSimone, J. M.; York, G. A.; McGrath, J. E.; Gozdz, A. S.; Bowden, M. J. *Macromolecules* **1992**, *25*, 4457.

(20) Hunt, M. O.; Belu, A. M.; Linton, R. W.; DeSimone, J. M. *Macromolecules* **1993**, *26*, 4854.

(21) Quirk, R. P.; Cheng, P. *Macromolecules* **1986**, *19* (5), 1291.

(22) Ueda, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939.

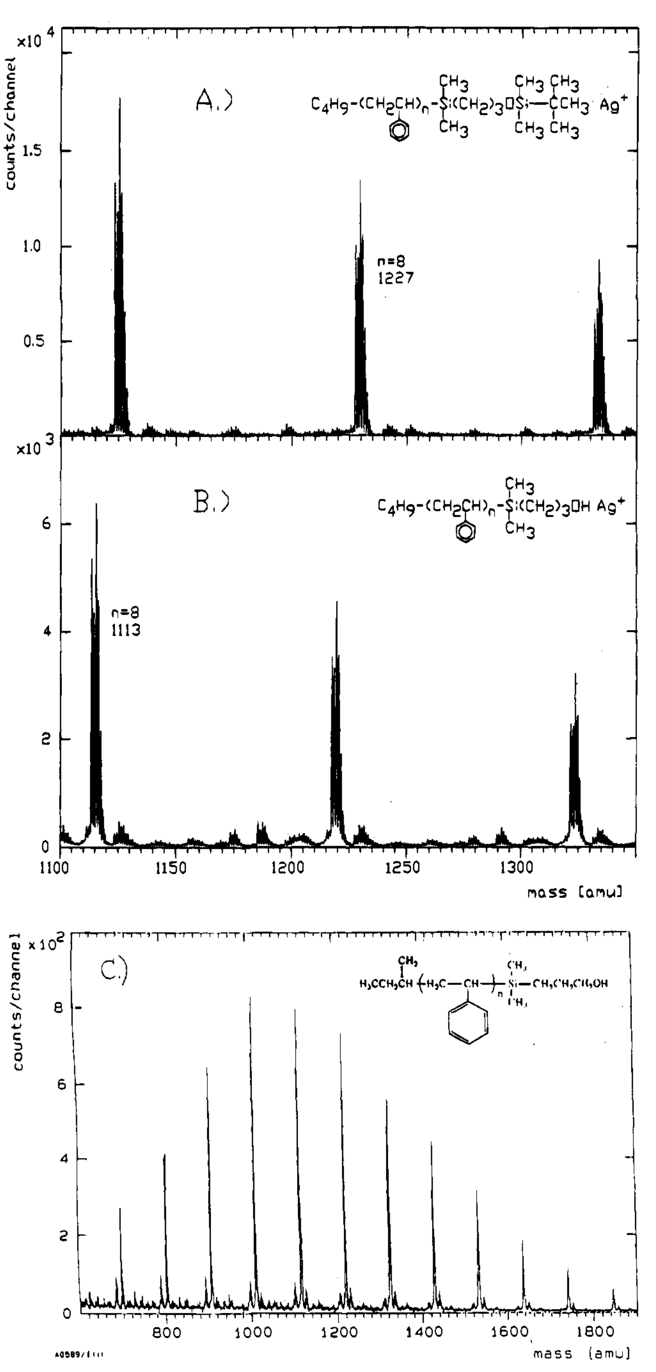
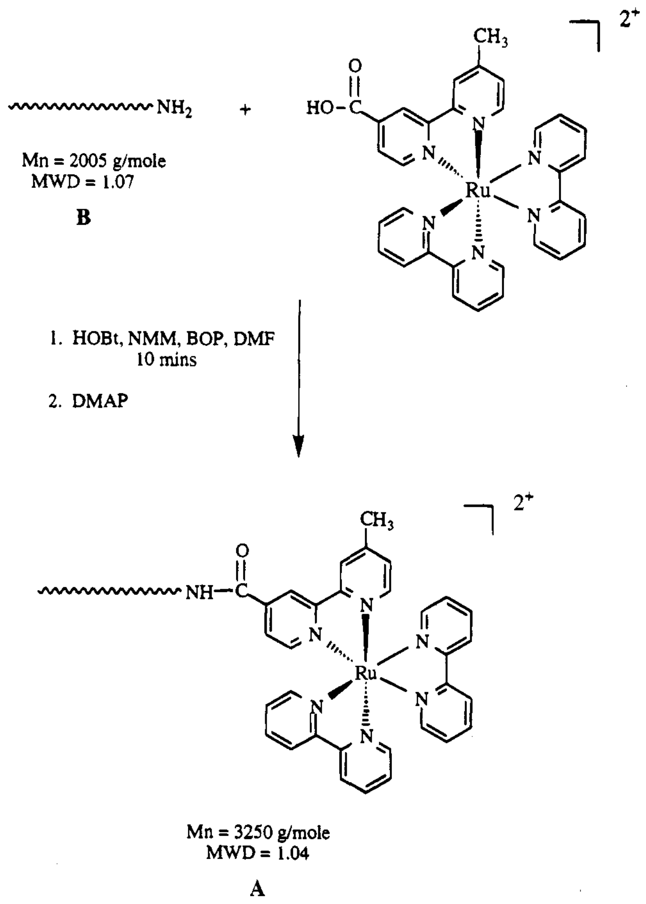


Figure 4. TOF-SIMS data of hydroxyl-functionalized polystyrene. (A) Protected hydroxyl-functionalized polystyrene; (B) deprotected hydroxyl-functionalized polystyrene; (C) full mass distribution.

moiety by addition of a protected amine chlorosilane derivative to the living chain end. The synthesis of this chlorosilane derivative began with formation of the protected amine α-olefin by addition of *N,N*-bis(trimethylsilyl)lithium amide to chloromethyl methyl ether followed by a Grignard reaction with allylmagnesium bromide.[23,24] This α-olefin was hydrosilylated with dimethylchlorosilane by using Speier's catalyst (Scheme 1) to give primarily the terminal addition product.[25] The use of *N,N*-bis(trimethylsilyl)lithium amide during this synthesis ensured that both protons on the amine are quantitatively protected. This was imperative since partially protected amines can be difficult to remove and are known to reduce the degree of functionalization in living polymerizations.[26]

Scheme 7. Synthesis of Ru(bpy)$_3$-Functionalized Polystyrene



Following rigorous purification procedures, various monomers were polymerized using standard living anionic polymerization techniques (inert atmosphere and syringe/cannula transfers). After all of the monomer was consumed, the protected amine chlorosilane was used to terminate the polymer chain end (Scheme 2). This procedure was used to efficiently terminate the anionic polymerization of styrene (Scheme 2) and hexamethylcyclotrisiloxane (Scheme 3), whose conjugate acids have pK_a values of 42 and 10, respectively. Termination was complete in less than 1 h as detected by the precipitation of LiCl (and loss of the color in the case of the polymerization of styrene). THF (2 vol %) was added to this reaction to increase the rate of termination by reducing the state of aggregation of the ion pairs.[27] After termination, the chain ends were deprotected by addition of methanol to the reaction mixture.[28]

Another advantage offered by living polymerizations is the ability to synthesize block copolymers by sequential addition of monomers to the living chain end. The polymerization of styrene monomer followed by addition of a calculated amount of isoprene created a living poly(styrene-*b*-isoprenyl)lithium which was terminated with the functionalized chlorosilane. This created a block copolymer with a primary aliphatic amine on the isoprene chain end [Poly(S-*b*-I)−NH$_2$]. The block copolymer has a number average molecular weight (Mn) of 31 Kg/

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(23) Morimoto, T.; Takahashi, T.; Sekiya, M. *J. Chem. Soc., Chem. Commun.* **1984**, 794.

(24) Hattori, I.; Hirao, A.; Yamaguchi, K.; Nakahama, S.; Yamaguchi, N. *Makromol. Chem.* **1983**, *184*, 1355.

(25) Hiyama, T.; Kusumoto, T. *Comp. Org. Syn.* **1991**, *8*, 763.

(26) Hattori, I.; Hirao, A.; Yamaguchi, K.; Nakahama, S.; Yamaguchi, N. *Makromol. Chem.* **1983**, *184*, 1355.

(27) Morton, M.; Fetters, L. J.; Pett, R. A.; Meier, J. F. *Macromolecules* **1970**, *3*, 327.

(28) We investigated several methods for deprotection of the amine end groups. Fluoride ion is known to remove silicon protecting groups, and a common source of fluoride ion is tetrabutylammonium fluoride (TBAF). After heating at reflux for several hours in THF and TBAF, however, TBAF also cleaved the α-silicon attached to the polymer chain end, on the basis of TLC analysis. A less rigorous deprotection method involves addition of methanol (1 vol %) to the polymerization solution prior to workup.

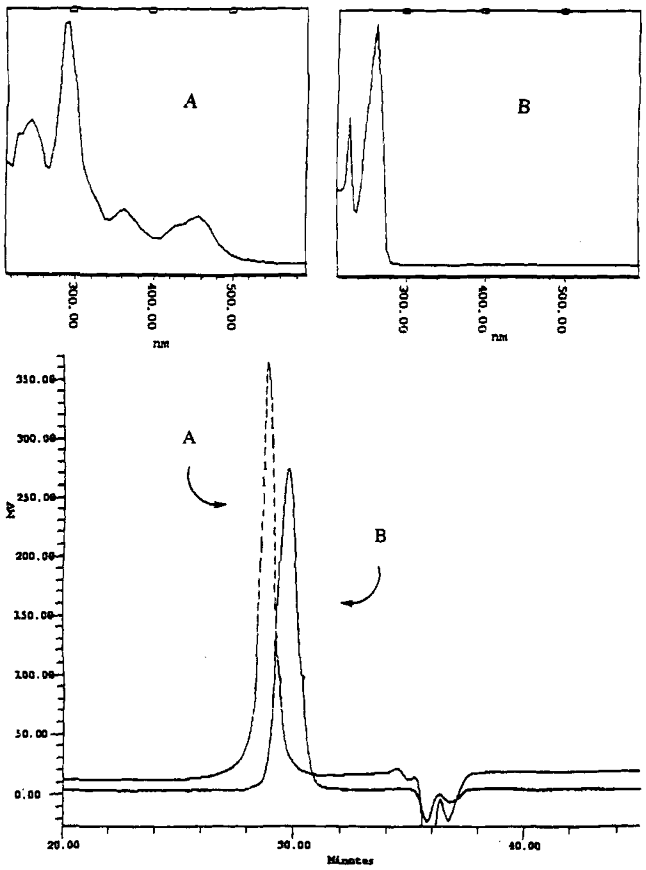

Figure 5. GPC overlay chromatograms and the corresponding UV spectra of (A) Ru(bpy)$_3$-functionalized polystyrene and (B) amine-functionalized parent material.

mol and a polydispersity of 1.02 as determined by GPC. By ^{1}H NMR, the block copolymer was composed of 36 mol % styrene and 64 mol % isoprene and a high 1,4 microstructure (91%) of the isoprene block was obtained by polymerization in a hydrocarbon solvent such as cyclohexane.

Difunctional materials were also readily synthesized using this methodology with a difunctional initiator followed by termination of the α,ω-difunctional anions with the functionalized chlorosilane derivative (Scheme 4). Most difunctional initiators require the use of very polar solvents to maintain solubility of the growing polymeric anions, but recently a new initiator based on a derivative of diphenylethylene (bis(phenylethenyl)benzene, DDPE) has been studied and shown to polymerize hydrocarbon monomers in a nonpolar solvent such as benzene.[29,30] The polymerization of diene monomers such as butadiene using this initiator has provided a means to synthesize α,ω-polydienes which possess a very high 1,4 microstructure.[31] Addition of 2 equiv of *sec*-butyllithium to DDPE in cyclohexane creates the initiator utilized to polymerize the styrene monomer. After 8 h at room temperature, the dianion was terminated by addition of the chlorosilane containing a protected primary amine.

The degree of functionalization was determined using various analytical techniques such as TLC, multinuclear magnetic resonance spectroscopy, titrimetric analysis, and TOF-SIMS. Qualitative analysis of these amine-terminated polymers by TLC revealed little unfunctionalized material. This technique has been reported to detect as little as 1−2% unfunctionalized impurities.[32] Nonaqueous titration of the amine-terminated polymer samples with perchloric acid allowed the calculation of the number average molecular weight through end group analysis. Comparison of these titrated molecular weights to those determined by GPC (Table 2) provided a measure of the degree of functionalization (f).[33] A range of polymer systems was functionalized with primary amines including polyisoprene (PI−NH$_2$), poly(dimethylsiloxane), and polystyrene, and in all cases, the termination reaction was very efficient (f > 0.90). α,ω-Difunctional polystyryl anions were also terminated with these chlorosilanes and also gave high degrees of functionalization (f > 1.75).

McGrath and co-workers have utilized ^{29}Si NMR to quantify the extent of functionalization in poly(dimethylsiloxane) macromonomers due to the sensitivity of the silicon atom to its environment.[34] Shown in Figure 1 is a ^{29}Si NMR spectrum of the 5 k, PDMS-NH$_2$ material described in Table 2. Peak A corresponds to resonances associated with the silicon atom attached to the α-chain end, and peak C corresponds to the silicon at the ω-chain end. A resonance which is attributed to the silicon protecting groups is also observed (peak D). A quantitative ^{29}Si NMR was not obtained, but this spectrum does provide a good understanding of the material synthesized with this termination reaction.

Unequivocal evidence for the success of the termination reactions was obtained using TOF-SIMS. The TOF-SIMS spectrum of an unfunctionalized polystyrene oligomer is shown in Figure 2. The most intense series of signals corresponds to the mass of an intact polystyrene oligomer of a specific degree of polymerization (n), which includes the mass of the *sec*-butyl initiator group on the α-chain end, the hydrogen terminal group on the ω-chain end, and a silver cation (polymer deposition as a monolayer film on a silver substrate aids in the ionization process via silver cationization of the sputtered oligomers). The distance between these signals is equal to the mass of a repeat unit (104 g/mol). From the intensities of the oligomer signals and the masses at which they arise, the molecular weight distribution was calculated to be 1.06, which is in agreement with that measured by GPC. A selected region of the TOF-SIMS spectrum of the amine-functionalized (deprotected) polystyrene is shown in Figure 3. Comparison of a specific degree of polymerization, n = 12, in the amine-terminated polymer (Figure 3B) with the same degree of polymerization in the proton-terminated polystyrene aliquot (Figure 3A) reveals a mass difference in 129 amu. This difference corresponds to the mass of the deprotected chlorosilane derivative. The absence of signals representing oligomers with the protected end group suggests successful deprotection of the amine. The high mass resolution of TOF-SIMS provides confirmation of molecular identities, including the presence of peaks containing heavy isotopes for each intact oligomer signal. The absence of significant amounts of unfunctionalized material in these spectra

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[29] Yamagishi, A.; Szwarc, M.; Tung, L.; Lo, G. Y.-S. *Macromolecules* **1978**, *11*, 607.

[30] Quirk, R. P.; Ma, J. J. *Polym. Int.* **1991**, *24* (4), 197.

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[32] Quirk, R. P.; Lynch, T. *Macromolecules* **1993**, *26*, 1206.

[33] Analysis of the amine-functionalized polymers by GPC is complicated by specific interactions of the primary amine end group with stationary phase. Because of these interactions, Mn values were obtained by adding the mass of a deprotected chlorosilane derivative to the Mn measured for the aliquot. This number is in good agreement with results from TOF-SIMS. For example:

$$\text{Mn(aliquot)} = 1420 \text{ g/mol}$$

$$\text{Mn(amine)} = \text{Mn(aliquot)} + 130 \text{ g/mol} = 1550 \text{ g/mol}$$

$$\text{Mn(TOF-SIMS)} = 1560 \text{ g/mol}$$

[34] Riffle, J. S.; Sinai-Zinde, G.; DeSimone, J. M.; Hellstern, A. M.; Chen, D. H.; Yilgor, I. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 93.

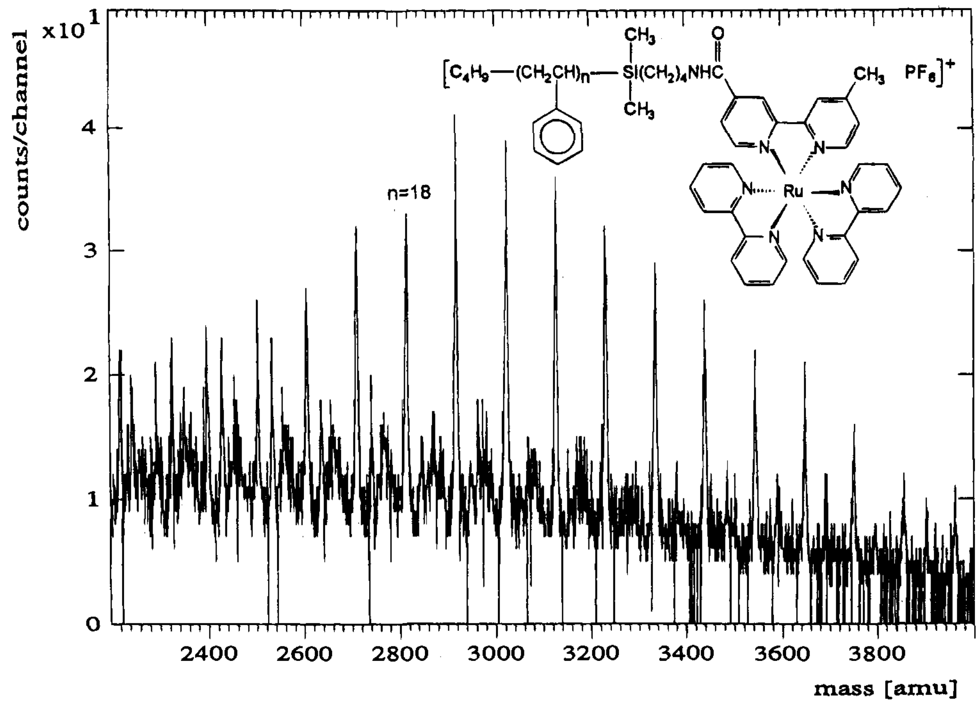

Figure 6. TOF-SIMS data of the Ru(bpy)$_3$-functionalized polystyrene.

indicates that these materials are highly functionalized with a primary aliphatic amine and that the deprotection methods are efficient. It should be noted that our previous work has shown that *different sputtering ionization efficiencies may be observed for the intact oligomers due to end group effect.*[35] Thus, simple ratioing of the corresponding peak intensities for the protected versus the deprotected versus proton-terminated oligomers of a given degree of polymerization (n) may not give a highly accurate measure of the extent of functionalization. Presently, we are evaluating the potential of TOF-SIMS to quantify percent functionalization by accounting for differences in the probability of sputtering, ionization and detection as a function of endgroup composition.[36]

Hydroxyl-Terminated Materials. The versatility of this functionalization methodology also allows access to a wide range of functional groups. This is shown by the introduction of primary aliphatic alcohols. Traditionally, the introduction of these functional groups involved addition of ethylene oxide to living polymeric anions whose conjugate acids of the propagating carbanions have pK_a values near 42.[37] The incorporation of these functional groups into silicone polymers or into certain hydrocarbon polymers (e.g., alkyl methacrylates) cannot be obtained by the addition of this electrophile. Termination of difunctional polymeric anions synthesized in hydrocarbon solvents represents a particularly difficult system for termination using these conventional procedures. Hydrocarbon solvents are necessary in the synthesis of diene polymers to achieve a high 1,4 microstructure (the structure responsible for the elasticity in natural rubber). With conventional procedures, addition of the terminating reagent (ethylene oxide) to the anionic chain end increases the state of aggregation of the chain ends and induces physical gel formation.[38] This increase in aggregation is caused by the transformation of carbanion chain ends into oxyanion chain ends in the form of lithium alkoxides. The use of chlorosilanes circumvents the problem of gel formation since the functional groups are protected and do not form oxyanion intermediates during the termination reaction. The functional groups are then deprotected to create α,ω-difunctional materials with high degrees of functionalization.

Hydroxyl-terminated polymers were synthesized in a manner similar to that of the amine. The hydroxyl-containing α-olefin is protected as the *tert*-butyldimethyl silyl ether and then hydrosilylated as before (Scheme 5). This chlorosilane is then used to functionally terminate polystyryl anions (Scheme 6) with high degrees of functionality as observed by TLC and by TOF-SIMS. TOF-SIMS characterization of these hydroxyl-functionalized materials is shown in Figure 4. A selected region of the spectrum of the protected form of the hydroxyl-functionalized polymer is shown in Figure 4A. A similar region of the same polymer after deprotection is shown in Figure 4B. At a specific degree of polymerization (n = 8), the peak in Figure 4B (MW = 1113 g/mol) shows a mass difference of 114 g/mol (the mass of the silyl protecting group) from the same degree of polymerization in Figure 4A (MW = 1227 g/mol). The absence of significant amounts of proton-terminated materials in these spectra indicates that these polymers possess a very high degree of functionalization.

Derivatization of Amine-Terminated Materials. To demonstrate potential applications of such materials, the amine-terminated polymers have been used in subsequent reactions as molecular scaffolding. Recent work by Meyer et al. involved introduction of a monocarboxylic acid derivative of the chromophore [Ru^{II}(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridine) onto amino acid assemblies.[39] As an extension to this work, the carboxylic acid derivative was coupled with an amine-terminated polystyrene material (Scheme 7). Attachment of this chromophore to the terminus of polystyrene adds film-forming properties to the

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[35] Belu, A. M.; Hunt, M. O., Jr.; DeSimone, J. M.; Linton, R. W. *Macromolecules* **1994**, *27*, 1905.

[36] The ionization efficiencies of the free amine-functionalized polymer and the protected amine-functionalized polymer must be compared to the unfunctionalized, proton-terminated polymer at equivalent degrees of functionalization to allow determination of the degree of functionalization directly from TOF-SIMS.

[37] Reed, S. F. *J. Polym. Sci.: Pt. A-1* **1971**, *9*, 2029.

[38] Hsieh, H. Personal communication, 1993.

[39] Mecklenburg, S. L.; Peak, B. M.; Schoonover, J. R.; McCafferty, D. G.; Wall, C. G.; Erickson, B. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 5479.

chromophore and also provides the opportunity for microphase separation between the metal complex and the polymer matrix. GPC analysis of the derivatized material (Mn = 3250 g/mol) and the parent, amine-functionalized material (Mn = 2000 g/mol) shows a shift in the number average molecular weight which corresponds to the molecular weight of the complex (Figure 5A and 5B respectively). Comparison of the UV spectrum (obtained at each elution volume from a photodiode array detector of the GPC) for both polymeric materials clearly shows the success of the attachment. Spectrum A of Figure 5 is the UV spectrum for the derivatized polystyrene sample [$Ru^{II}(bpy)_3$-containing sample], and spectrum B of Figure 5 is the UV spectrum for the underivatized material. UV absorptions characteristic of the $Ru(bpy)_3$ complex are clearly present in Figure 5A. The polydispersity of this material is 1.04.

The TOF-SIMS spectrum of the $Ru^{II}(bpy)_3{}^{2+}$-derivatized polystyrene is shown in Figure 6. The masses of the signals represent polystyrene oligomers with $Ru(bpy)_3$ end groups and only one PF_6^- counter ion (The complex was initially associated with 2 PF_6^- counter ions before derivatization). This spectrum demonstrates the capability of the TOF-SIMS technique to allow desorption, ionization, and analysis of these derivatized materials, and, in concert with GPC analysis, this provides unequivocal confirmation of the derivatization reaction.

Conclusions

Termination of living polymeric chain ends with functionalized chlorosilane derivatives has been utilized to introduce primary aliphatic amine and hydroxyl functional groups to various polymer chain ends. Structural characterization based on conventional techniques (TLC, titration, multinuclear magnetic resonance spectroscopy, etc.) and TOF-SIMS show that end-functionalized polymers with primary aliphatic amine and hydroxyl end groups have been synthesized in very high yields. These termination reactions take place in hydrocarbon solvents at room temperature and represent a significant advantage over other techniques for introduction of these functional groups. This technique should also be applicable as a general methodology by which other functional groups (aromatic analogs, thiols, etc.) can be introduced to various polymeric nucleophiles.

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