Anionic Synthesis of Primary Amine-Functionalized Polystyrenes Using 1-[4-[N,N-Bis(trimethylsilyl)amino]phenyl]-1-phenylethylene

Roderic P. Quirk*,† and Thomas Lynch

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325

Received June 29, 1992; Revised Manuscript Received November 19, 1992

ABSTRACT: ω-Aminopolystyrenes were synthesized in quantitative yields by reacting poly(styryl)lithium with 1-[4-[N,N-bis(trimethylsilyl)amino]phenyl]-1-phenylethylene (2) in benzene at room temperature. The primary amine-functionalized polymers were characterized by size-exclusion chromatography, vapor phase osmometry, thin layer and column chromatography, infrared and ultraviolet-visible spectroscopy, end-group titration, elemental analysis, and both ^1H and ^{13}C NMR. 1-[4-[N,N-Bis(trimethylsilyl)amino]phenyl]-1-phenylethylene (2) was synthesized in two steps in 50% yield starting from 4-aminobenzophenone.

Introduction

Alkyllithium-initiated anionic polymerization of many substituted vinyl, diene, and heterocyclic monomers has been shown to proceed without termination or chain transfer, yielding polymers with predictable molecular weights and narrow molecular weight distributions.[1-5] The reactive carbanionic chain ends of these living polymer systems may undergo a variety of addition and substitution reactions, resulting in the incorporation of useful functionality at the chain end.[2,6] Numerous examples of the preparation of hydroxyl- and carboxyl-terminated polymers have been reported.[6-9] A variety of methods are also available for the preparation of polymers functionalized with tertiary amine end groups.[10-12] The primary amine-terminated polymers, however, have been particularly elusive due to the acidity of the amine protons.[13] Thus, chain-end amination reactions require indirect methods such as the use of protecting groups.

Primary amine-functionalized polystyrenes have been prepared by the reaction of poly(styryl)lithium with the product of the reaction of methoxyamine and methyllithium at low temperatures.[14-16] Using a 2-fold excess of the methoxyamine/methyllithium reagent at −78 °C in a mixture of THF/benzene/hexane, poly(styryl)lithium ($M_n = 2 \times 10^3$) was aminated in 92% yield after methanol workup.[14] The telechelic diamine, α,ω-diaminopolystyrene, was prepared in 80% yield by amination of α,ω-dilithiopolystyrene ($M_n = 10 \times 10^3$) using similar procedures.[15]

Most recent reports describing the preparation of primary amine-functionalized polymers include the use of the trimethylsilyl moiety in place of the active amine protons. Schulz and Halasa[17] first demonstrated the utility of the trimethylsilyl protecting group in the preparation of amine-functionalized polybutadiene and polyisoprene using *p*-lithio-*N,N*-bis(trimethylsilyl)aniline as the initiator. Although the use of this hydrocarbon-insoluble initiator produced polymers with low 1,4 microstructure and broad molecular weight distributions, consistently high incorporation of the amine functionality was obtained. Nakahama and co-workers[18,19] attempted to improve upon these results by adding *N*-benzylidene(trimethylsilyl)-amine to living polymers prepared in hydrocarbon solvents using *sec*-butyllithium as the initiator. This approach provided functionalized polymers with narrow molecular weight distributions and high 1,4 microstructure. A careful reexamination of this system, however, showed that because of complicating side reactions only 69% of the desired functional polymer was obtained.[20] More recently, Nakahama and co-workers[21] have described the use of α-halo-ω-aminoalkanes utilizing 1,1,4,4-tetramethyl-1,4-disilabutane as the protecting group. It was reported that yields of >94% were readily obtained for the functionalization reactions of poly(styryl)lithium, poly(isoprenyl)-lithium, and α,ω-dipotassiopolyisoprene at −78 °C in the presence of tetrahydrofuran with the α-bromo- and α-chloro-ω-silyl-protected aminopropanes and the α-bromo-ω-silyl-protected aminoethane to produce the corresponding monofunctional and telechelic amine-functionalized polymers. Dickenstein and Lillya[22,23] have reported that a useful protected primary amine initiator can be generated by the reaction of *sec*-butyllithium with *p*-[bis-(trimethylsilyl)amino]styrene in benzene or cyclohexane solution at 25 °C by careful control of the stoichiometry of the reaction. The authors reported that no oligomerization occurred under these conditions, resulting in an initiator containing a single amine functionality. The authors described the preparation of poly(dimethylsiloxane) using this hydrocarbon-soluble initiator with >95% incorporation of the desired amine functionality. Thus, it appears that the use of silyl-protected amine derivatives has resulted in a number of successful approaches for introducing the primary amine functionality into polymers prepared via anionic polymerization. In this paper, however, we would like to report an alternative method for introducing the primary amine functionality into polymers which offers some advantages over those cited above.

It has been shown that the addition of substituted 1,1-diphenylethylenes to either poly(styryl)lithium or poly-(dienyl)lithium proceeds via a simple, quantitative addition reaction which results in the incorporation of a single functional group at the chain end.[6,10,24,25] The utility of this chemistry as a means of preparing end-functionalized polymers has been demonstrated for both the *tert*-butyldimethylsilyl ether and dimethylamine functionalities.[10,24] In both cases monofunctional polymers with quantitative incorporation of the respective functional groups were obtained following termination with methanol.

Telechelic polymers have also been prepared by exploiting the living nature of the addition of alkyllithium compounds to substituted 1,1-diphenylethylenes. For example, the initiator resulting from the addition of *sec*-

† Visiting Professor, 1991, Institut Charles Sadron, CNRS, Strasbourg, France.

0024-9297/93/2226-1206$04.00/0

butyllithium to 1-[4-(dimethylamino)phenyl]-1-phenylethylene was used to initiate the polymerization of styrene. Treating the resulting monofunctional living polymer with a second equivalent of 1-[4-(dimethylamino)phenyl]-1-phenylethylene yielded the telechelic polystyrene with an amine group functionality of 2.1.[10]

Herein, the general nature of this functionalization reaction is extended to the preparation of primary amine-functionalized polymers using 1-[4-[*N*,*N*-bis(trimethylsilyl)amino]phenyl]-1-phenylethylene in a hydrocarbon solvent at room temperature.

Experimental Section

Materials. CH_3Li (1.4 M) in diethyl ether (Aldrich) and 3.1 M phenylmagnesium bromide (Aldrich) were used as received. Styrene, benzene, and THF were purified as described previously.[26] 4-Aminobenzophenone, 98% (Aldrich), was dried under vacuum before use. Methyltriphenylphosphonium iodide (Lancaster Synthesis Ltd.) was washed with benzene and dried under vacuum at 100 °C for 24 h. Trimethylchlorosilane (Aldrich) was treated with a small quantity of water and then distilled from CaH_2 under argon. Solutions of *sec*-butyllithium [FMC Corp., Lithium Division; 1.4 M (12 wt %)] in cyclohexane were analyzed using the double titration method with 1,2-dibromoethane.[27] Tetramethylammonium hydroxide (Aldrich; 20 wt % in methanol) was used as received. Silica gel 60 (EM Science; 230–400 mesh) was used for column chromatography after activation by heating at 150 °C under vacuum for 2 h.

1-(4-Aminophenyl)-1-phenylethylene (1). Dry THF (100 mL) was vacuum distilled into a 250-mL, three-neck, round-bottomed flask containing 15.1 g (37 mmol) of methyltriphenylphosphonium iodide. After applying a static positive pressure of Ar(g), 26.4 mL (37 mmol) of 1.4 M CH_3Li in diethyl ether was added dropwise via a syringe. The resulting phosphoryl ylide was then added dropwise via a cannula to 6.1 g (31 mmol) of 4-aminobenzophenone in 50 mL of dry THF at 0 °C. The reaction was heated under reflux using an Ar(g) atmosphere for 24 h and then quenched with a few drops of methanol. Triphenylphosphine oxide was removed by filtration followed by column chromatography using toluene as the eluent. Triphenylphosphine, which is an impurity in commercial methyltriphenylphosphonium iodide, was also removed during chromatography. Vacuum sublimation of the product at 75 °C yielded 5.0 g (83%) of a white crystalline solid. Mp: 80–81 °C. IR (KBr): 3466, 3373 cm^{-1} (m, N–H stretch). ^1H NMR ($CDCl_3$): δ 7.32 (5 H, m, Ar–H), 7.18, 7.12, 6.68, 6.61 (4 H, AA'XX', Ar–H), 5.28, 5.38 (2 H, s, C=CH_2), 3.7 (2 H, br s, N–H). Anal. Calcd for $C_{14}H_{13}N$: C, 86.12; H, 6.71; N, 7.17. Found: C, 86.38; H, 6.71; N, 6.88.

1-[4-[*N*,*N*-Bis(trimethylsilyl)amino]phenyl]-1-phenylethylene (2). To 0.92 g (4.72 mmol) of 1 in 20 mL of dry THF under Ar(g) in a three-neck, round-bottomed flask fitted with rubber septa was added 8.4 mL (11.79 mmol) of a 1.4 M solution of CH_3Li in THF. After 1 h, 1.5 mL (11.79 mmol) of trimethylsilyl chloride was added dropwise via a syringe. The resulting slurry was filtered, and the volatiles were removed using a rotary evaporator. The product was vacuum distilled twice from 0.07 mL (0.05 equiv) of 3.1 M phenylmagnesium bromide in diethyl ether. The product distilled as a clear, colorless liquid at 130 °C under high vacuum. GLPC of the product showed only one peak. The yield was 0.98 g (61%). IR (KBr): 1218, 1255 cm^{-1} (Si–CH_3). ^1H NMR ($CDCl_3$): δ 7.32 (5 H, m, Ar–H), 7.18, 7.15, 6.85, 6.80 (4 H, AA'XX', Ar–H), 5.42, 5.35 (2 H, s; C=CH_2), 0.08 (18 H, s, $Si(CH_3)_3$). Anal. Calcd for $C_{20}H_{29}NSi_2$: C, 70.73; H, 8.61; N, 4.12; Si, 16.54. Found: C, 70.94; H, 8.53; N, 4.12; Si, 16.41.

Polymerizations. Polymerizations were carried out in benzene at room temperature using *sec*-butyllithium as initiator in all-glass, sealed reactors using break-seals and standard high-vacuum techniques.[28] The concentration of styrene to benzene (mL/mL) was 10–12 vol %. The molar concentration of organolithium chain ends was (3–4) × 10^{-2} M. After 12 h and prior to functionalization, an aliquot of poly(styryl)lithium (8% of the total volume) was removed from the reaction and terminated with degassed methanol.

Functionalized Polystyrene 4. In a drybox, a 0.2 M excess of 2 (based on the amount of *sec*-butyllithium used) and 1 mol % of *sec*-BuLi (based on moles of 2) were added to an ampule fitted with a break-seal and a Rotoflo stopcock (Fisher Scientific). The ampule was then attached to a high-vaccum line, and a 10-fold excess (v/v) of benzene was distilled into the ampule. The ampule was cooled to −78 °C and heat sealed under vacuum at a point between the ampule and the stopcock. The resulting red color of this solution served as an indication of the absence of reactive impurities. Termination reactions with 2 (0.3 M excess) were affected by smashing the break-seal of the ampule containing this terminating agent. The extent of the functionalization reaction was monitored by UV–vis spectroscopy at 416 nm. After 12 h the reaction was terminated with degassed methanol. The functionalized polymer was isolated in quantitative yield by precipitating the product into excess methanol and drying under vacuum at room temperature.

Functionalized Polystyrene (5). Hydrolysis of 4 was effected by dissolving the polymer in 100 mL of freshly distilled THF containing 1% concentrated HCl (v/v) and stirring at 25 °C for 1 h under Ar(g). After neutralization with 20 wt % $Me_4N^+OH^-$ in MeOH, the polymer was precipitated into excess MeOH. The polymer was then dried under vacuum at room temperature. Yield: 89–95%. IR: 3466, 3373 cm^{-1} (N–H stretch). End-group titration: 102 ± 4% NH_2 groups/chain (based on VPO M_n). Elemental analysis (based on VPO M_n = 3270): $C_4H_9[CH_2CH(C_6H_5)]_{29}CH_2CH(C_6H_5)C_6H_4NH_2$. Anal. Calcd for $C_{250}H_{255}N$: C, 91.73; H, 7.85; N, 0.43. Found: C, 92.26; H, 7.85; N, 0.42.

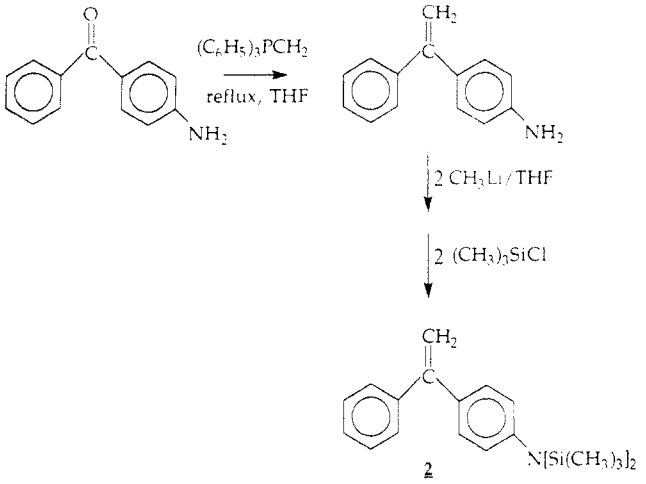
Characterization. The purity of 1 and 2 was analyzed by GLPC using a 550P GOW/MAC gas chromatograph. The column specifications were as follows: 4 ft × $^1/_8$ in., 5% OV-101 on CHROM-P-AW-DMCS, 80–100 mesh. The operating conditions were as follows: He(g) flow rate of 17 mL/min, chart speed of 2 cm/min, and injector, detector, and column temperatures of 320, 310, and 300 °C, respectively.

Number-average molecular weights were determined using vapor pressure osmometry (VPO) and size-exclusion chromatography. VPO measurements were made using a Knauer Type 11.00 osmometer in toluene (Fisher Scientific, certified ACS) which was distilled from freshly crushed CaH_2. Size-exclusion chromatographic analyses of polymers were performed at a flow rate of 1.0 mL min^{-1} in tetrahydrofuran at 30 °C using a Waters HPLC component system (RI or UV detector) equipped with six ultra-μ-styragel columns (two 500, two 10^3, 10^4, and 10^5 Å) after calibration with standard polystyrene samples obtained from Polymer Laboratories.

IR, UV–vis, and ^1H NMR were recorded on Beckman FT2100, HP 8452A diode array, and Varian Gemini-200 spectrometers, respectively.

Silica gel plates (Whatman Diamond Series) with a fluorescent indicator (λ = 254 nm) were used for thin-layer chromatographic (TLC) analyses. TLC plates used for analyzing silylamine compounds were treated first by capillary action with a 2% solution of triethylamine in ethyl acetate. The plates were allowed to air dry before use. The limit of detection of unfunctionalized polymer (i.e., homopolystyrene) by TLC was assessed by preparing solutions of accurately known amounts of unfunctionalized and functionalized polymer in THF. Both polymer and solvent were weighed on an analytical balance. The contribution of polymer to the total volume was taken into account using the density for polystyrene (1.04 g/mL). The solution of functionalized polymer consisted of 0.100 g of functionalized polymer in 0.6 g of THF, resulting in a concentration of 0.13 g/mL. Two solutions of unfunctionalized polymer were prepared. The first solution consisted of 0.0092 g of polymer in 2.982 g of THF. The second solution consisted of 0.004 g of polymer in 3.009 g of THF. The concentrations of these two solutions were 0.0028 and 0.0012 g/mL. Equal volumes of each solution were spotted on a TLC plate. The spot intensities resulting from the application of the unfunctional polymer solutions to the plate correspond to the presence of 2 and 1 wt % of unfunctionalized polymer in the functionalized polymer solution, respectively, if it is present. The plate was eluted with toluene to the midpoint of the plate in order to reduce the degree of spot broadening. The plate was then analyzed with a UV lamp (λ = 254 nm).

Scheme I



The amount of unfunctional polymer was determined by column chromatography using flash chromatography techniques.[29] For example, 5.6 g of functional polymer was chromatographed on 6 in. of activated silica gel in a 2-in.-diameter column. Distilled benzene and cyclohexane were used as the eluents. The column was prepared in cyclohexane. Mixtures of eluent consisting of benzene and cyclohexane were added in 500-mL increments, increasing by 20 vol % in benzene each time. The flow rate was 1 in./2 min under an Ar(g) pressure of 5 psi. A small amount (0.03 g; 0.5 wt %) of unfunctionalized polymer was isolated as a front running band. A total of 5.51 g (98.5%) of the pure functionalized polymer, **5**, was isolated from the column.

The molar concentration of the amine functional groups per gram of polymer was determined by duplicate titration of 0.5-g samples of polymer in 40 mL of a 1/1 (v/v) mixture of chloroform and glacial acetic acid using 0.1 N perchloric acid in glacial acetic acid as the titrant and methyl violet as the indicator.[30] The perchloric acid standard solution was free of acetic anhydride. Polymer samples analyzed by titration were heated to 140 °C under high vacuum for 2 h to ensure the removal of residual solvent and absorbed carbon dioxide.[31,32]

Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

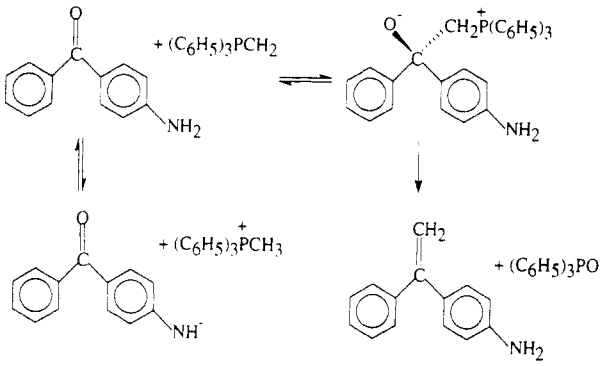
Results and Discussion

Synthesis. The preparation of 1-[4-[*N*,*N*-bis(trimethylsilyl)amino]phenyl]-1-phenylethylene (**2**) involved a two-step synthesis starting with 4-aminobenzophenone (Scheme I). Surprisingly, the Wittig reaction (1st step) gave an 83% yield of the purified 1-(4-aminophenyl)-1-phenylethylene. One might expect that the acidic amine protons would decompose the ylide, resulting in a poor yield. However, the pK_a's of 4-aminobenzophenone and the methyltriphenylphosphonium cation in DMSO have been reported to be 25.3 and 22.5, respectively.[33,34] Therefore, it seems reasonable that a mechanism involving a reversible nondeleterious proton transfer between 4-aminobenzophenone and the methyltriphenylphosphonium ylide coupled with an irreversible decomposition of the betaine would account for the high yields observed in this reaction (Scheme II).

As has been reported, disilylation of the amine (2nd step, Scheme I) can be accomplished in one step using trimethylsilyl chloride (TMSCl) and 2 equiv of a metal alkyl.[35] In this case the use of methyllithium gave a 61% yield after vacuum distillation from phenylmagnesium bromide. The ^{1}H NMR spectrum of **2** is shown in Figure 1. This spectrum shows no evidence of any amine protons remaining after silylation and distillation.

Terminal Functionalization Reactions. One of the advantages of using substituted 1,1-diphenylethylene

Scheme II



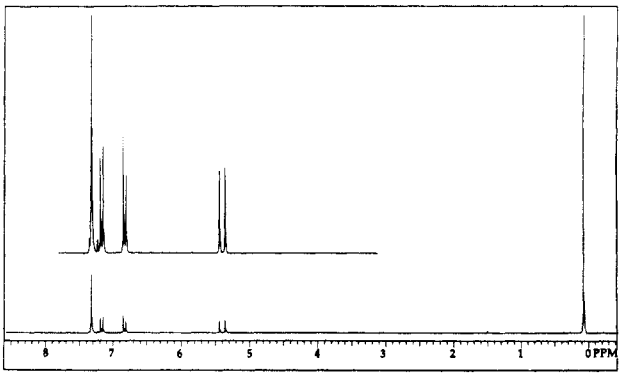
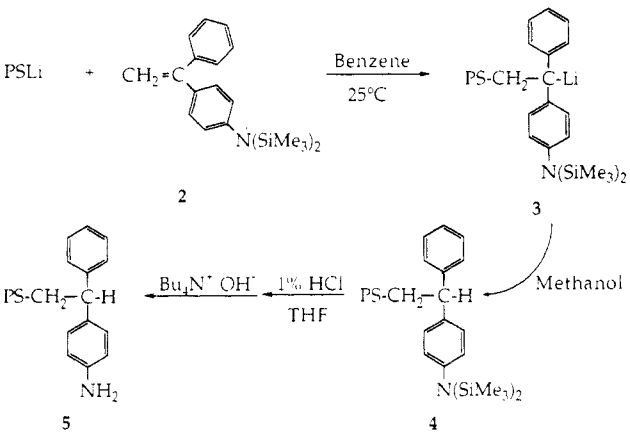


Figure 1. ^{1}H NMR ($CDCl_3$) of 1-[4-[*N*,*N*-bis(trimethylsilyl)-amino]phenyl]-1-phenylethylene (**2**).

Scheme III



chemistry as a general functionalization technique is that the progress of the reaction can be conveniently monitored by UV–vis spectroscopy. Thus, the addition of poly(styryl)lithium (λ_{max} = 334 nm[36]) to **2** (Scheme III) to form the corresponding bis(trimethylsilyl)amine-substituted diphenylalkyllithium adduct, **3** (λ_{max} = 416 nm), could be monitored using a UV–vis cell attached to the polymerization reactor. A plot of the ratio of the intensities for the peaks corresponding to the poly(styryl)lithium chain end and the 1,1-diphenylalkyllithium chain end versus time is shown in Figure 2. It is apparent from these results that the addition reaction of poly(styryl)lithium [(3–4) × 10^{-2} M] to **2** is complete within 6 h at 25 °C, using a 0.3 M excess of **2**. This result is similar to the rate of addition of unsubstituted 1,1-diphenylethylene (1 equiv) to poly(styryl)lithium (1×10^{-2} M) in benzene which also appears to be complete in 6 h.[37] The reactivity of **2** is surprising because it has been reported that the addition of 1-[4-(dimethylamino)phenyl]-1-phenylethylene (1.15 equiv) to poly(styryl)lithium (2×10^{-2} M) required more than 48 h to go to completion.[10,38] While the reactivity of 1-[4-

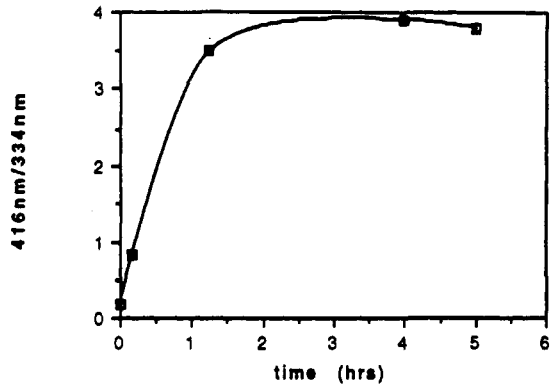


Figure 2. Ratio of absorptions of the diphenylalkyllithium chain end (416 nm) and the poly(styryl)lithium chain end (334 nm) versus time for the crossover reaction of poly(styryl)lithium with **2** (Scheme III).

Table I
Basicities of *N*-Alkylanilines and *N,N*-Dialkylanilines[42]

derivative	pK_a in water	derivative	pK_a in water
N-methyl	4.85	*N*-*tert*-butyl	7.00
N-isopropyl	5.77	*N,N*-diisopropyl	7.37

(dimethylamino)phenyl]-1-phenylethylene toward addition to poly(styryl)lithium is consistent with the Hammett ρ value of +1.8 reported for this reaction,[39] the reactivity of **2** appears to be significantly altered by the presence of the trimethylsilyl groups.

One explanation for the difference in reactivity between these two amine-substituted 1,1-diphenylethylenes invokes the involvement of back-bonding of the unshared pair of electrons on nitrogen into the empty d-orbitals of silicon. This interaction would reduce the usual electron-donating character of an amine attached to a phenyl ring. Such p_π–d_π bonding between silicon and nitrogen has been used to rationalize the reduced basicity of silylamines relative to their corresponding *N*-alkylamines as well as to rationalize the coplanarity about nitrogen for a number of di- and trisilylamines.[40] More specifically, quantum mechanical treatments of both *N,N*-dimethylaniline and *N,N*-bis(trimethylsilyl)aniline have been reported[41] and the results of these theoretical treatments show that the d_π–p_π bond between silicon and nitrogen reduces the C–N p_π–p_π bond order from 0.346 in $PhNMe_2$ to 0.275 in $(Me_3Si)_2NPh$. However, it was assumed by these authors that $(Me_3Si)_2NPh$ assumed a coplanar conformation about nitrogen in this calculation.

It is also possible that steric inhibition to resonance can account for the increase in reactivity of **2** relative to 1-[4-(*N,N*-dimethylamino)phenyl]-1-phenylethylene. For example, it has been observed that the basicity of both *N*-alkylanilines and *N,N*-dialkylanilines increases as one increases the steric bulkiness of the alkyl groups (see Table I).[42] The increases in basicity are reportedly too large to be accounted for by inductive effects. It was reasoned that steric inhibition to resonance played an important role in determining the basicity of these N-substituted anilines. In a similar fashion, the bulky trimethylsilyl groups in **2** could force the nitrogen's unshared pair of electrons to rotate toward the plane of the aromatic ring, resulting in a decrease in the interaction between the nitrogen's unshared pair of electrons and the π system of the aromatic ring. In fact, steric inhibition to resonance has been cited to rationalize the UV spectroscopic results obtained for a number of disilylated anilines.[17,43] Table II shows that replacing the amine protons with trimethylsilyl groups results in a hypsochromic shift for both

Table II
UV Absorption Maxima and Molar Absorptivities for Aniline Derivatives

	E-band		B-band	
compd	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
$PhNH_2$[a]	234	9130	288	1860
$PhN(SiMe_3)_2$[a]	234	3250	265	445
p-$BrPhNH_2$[b]	240	15300	296	1760
p-$BrPhN(SiMe_3)_2$[b]	222	9400	280	664

[a] Reference 43. [b] Reference 17.

the E and B-bands as well as a dramatic decrease in the corresponding molar absorptivities. Thus it can be rationalized that this apparent decrease in resonance due to the bulkiness of the *N*-trimethylsilyl substituents would also significantly reduce the effect that this aromatic amine substituent would have in destabilizing the diphenylmethyl carbanion which forms upon addition of poly(styryl)-lithium to **2**.

^{13}C NMR gives additional supporting evidence for the reduced electron-donating character of the disilylated aromatic amine substituent. Phenyl carbons *ortho* to an electron-donating substituent usually show an upfield shift relative to carbon in an unsubstituted benzene ring which absorbs at 128.5 ppm.[44] This is illustrated by the ^{13}C NMR spectra of 1-[4-(*N,N*-dimethylamino)phenyl]-1-phenylethylene and 4-aminodiphenylethylene (Figure 3). The observed resonances for the carbons ortho to the amine substituent in these compounds appear at 112.0 and 115.2 ppm, respectively. In the case of 1-[4-[*N,N*-bis(trimethylsilyl)amino]phenyl]-1-phenylethylene, however, the resonance for these ortho carbons has shifted to 128.8 ppm. This chemical shift is consistent with that reported for the same carbon in *N,N*-bis(trimethylsilyl)aniline (130.1 ppm).[45] Thus, it appears that the trimethylsilyl protecting groups have effectively neutralized the normal electron-donating effects of the amine substituent. These results are consistent with the increased reactivity of **2** toward addition to poly(styryl)lithium relative to the corresponding addition reaction with 1-[4-(dimethylamino)phenyl]-1-phenylethylene.

It has been shown that the resonance substituent constants (σ°_R) can be determined from ^{13}C NMR chemical shifts of monosubstituted benzenes.[45] A value of σ°_R = –0.24 was calculated for the bis(trimethylsilyl)amine substituent using ^{13}C NMR data.[45] This is a much smaller value than the value of σ°_R = –0.62 calculated for the dimethylamino substituent.[45] Thus, the σ substituent constants are also consistent with the observed differences in reactivity between 1-[4-(dimethylamino)phenyl]-1-phenylethylene and **2**.

A typical SEC curve for the hydrolyzed product **5** is shown in Figure 4. The molecular weights for amine-functionalized polymers from five different polymerizations with M_n ranging from 2×10^3 to 4×10^3 are shown in Table III along with the measured degree of functionality from titration. All of the polymers had molecular weight distributions (M_w/M_n) less than 1.05. The various molecular weights determined by the different methods appear to be in agreement with each other within the experimental error of the methods used. The degree of functionality measured by end-group titration is consistent with a single amine functionality per chain end.

Thin layer chromatography of the functionalized polymer containing the disilylated amine end group, **4**, and the corresponding polymer following hydrolysis, **5**, are shown in Figure 5. The TLC for the disilylamine polymer shows two spots corresponding to the functionalized

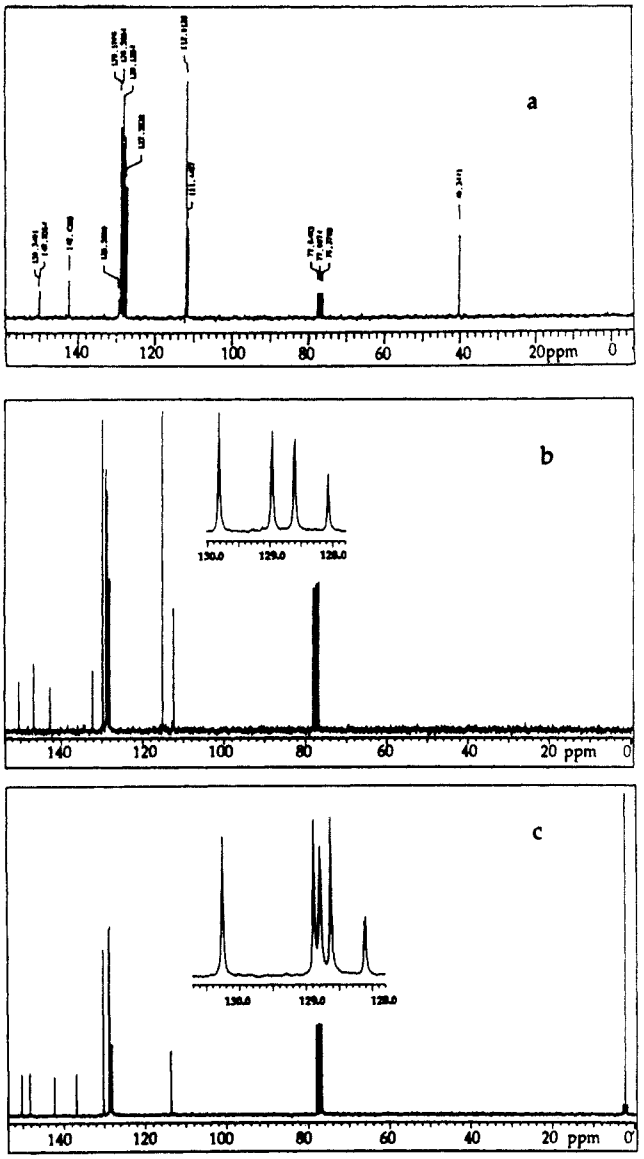


Figure 3. ^{13}C NMR spectra of 1-[4-(dimethylamino)phenyl]-1-phenylethylene (a), 1-(4-aminophenyl)-1-phenylethylene (b), and 1-[4-[*N*,*N*-bis(trimethylsilyl)amino]phenyl]-1-phenylethylene (c).

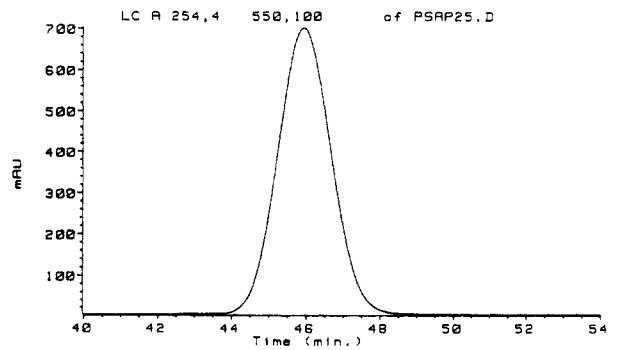


Figure 4. Size-exclusion chromatogram of hydrolyzed polymer **5**. $M_n = 3.3 \times 10^3$ (VPO); $M_w/M_n = 1.04$.

polymer (vide infra) and unreacted **2**. After hydrolysis of the silyl protecting group and reprecipitation into methanol, the TLC shows only the amine-functionalized product. The limits of the ability of TLC to detect unfunctionalized polymer were examined (see the *Experimental* Section). It was found that as little as 2 wt % of unfunctionalized polymer could be detected with confidence. The functionalized polymer showed no unfunctional polymer by TLC using these conditions.

Table III
Characterization Data for ω-Aminopolystyrenes 5

	M_n[a]				
reaction	calc	GPC	titration	VPO	amine functionality, %[b]
1	2.2	1.9	2.2	2.2	100
2	2.7	2.5	2.7	2.8	104
3	2.7	2.6	3.0	3.0	100
4	3.7	3.3	3.4	3.3	97
5	4.0	3.9	4.0	4.3	107

[a] All values given in $\times 10^{-3}$. [b] Titration M_n compared with VPO M_n.

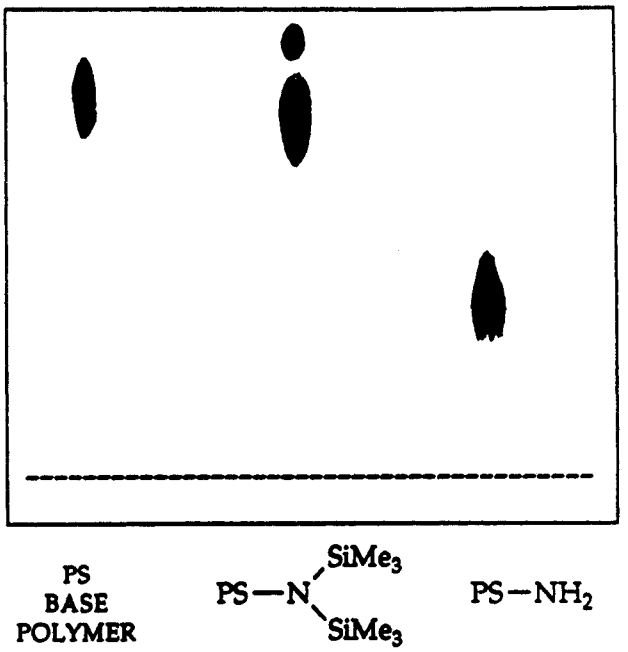


Figure 5. Thin layer chromatography of the base polymer taken as an aliquot prior to the functionalization reaction (Scheme III), the product of the functionalization reaction, **4**, and the hydrolyzed product, **5**, for reaction 4 in Table III.

Two different samples of accurately weighed functionalized polymer, **5**, were chromatographed on silica gel using flash chromatography conditions with benzene as the eluent. In both cases the amount of unfunctional polymer which was isolated from the column was 0.5 wt %. The amount of pure, functionalized polymer, **5**, which was isolated corresponded to 98.5% of the sample; the remainder was a collection of unresolved fractions containing the functionalized polymer and a base-line spot. These results are consistent with the observations made by TLC.

Spectroscopic results are also consistent with the incorporation of the amine functionality at the polymer chain end. The infrared spectrum of the disilylamine polymer, **4**, shows the characteristics absorption bands for the Si–CH_3 stretching mode (1218 and 1255 cm^{-1}; Figure 6).[17] These absorption bands are not present in the hydrolyzed functionalized polymer, **5**, but have been replaced by the characteristic absorption bands of the N–H stretching mode (3373 and 3466 cm^{-1}). The ^1H NMR spectrum of the disilylated amine polymer, **4**, shows a resonance at 0.08 ppm corresponding to the trimethylsilyl protons (Figure 7). This reasonance appears as a multiplet due to the diastereomeric nature of the chain end.[10] In addition, a resonance at 3.45 ppm is observed. This resonance has been previously assigned to the terminal

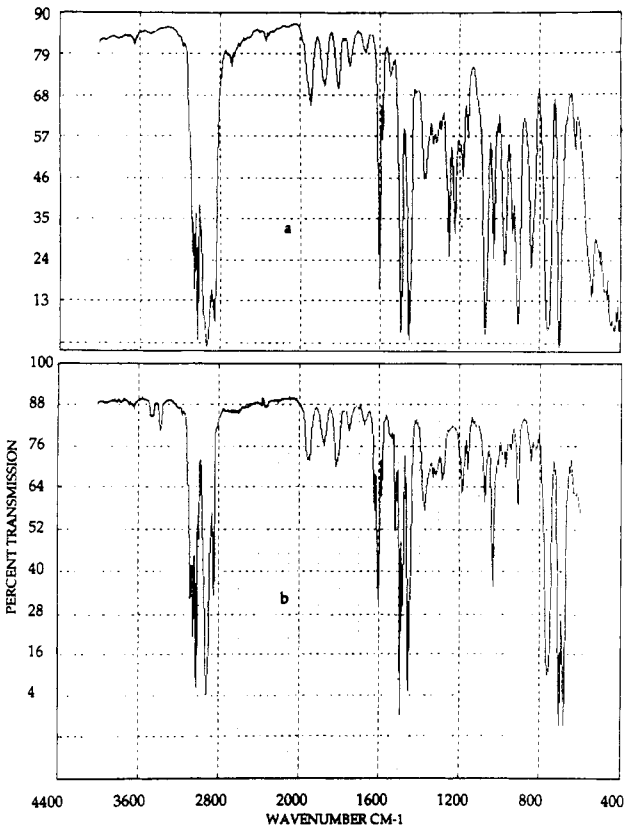


Figure 6. Infrared spectrum (KBr) of the functionalized polymer **4** (a) and the corresponding hydrolyzed product **5** (b) for reaction 4 in Table III.

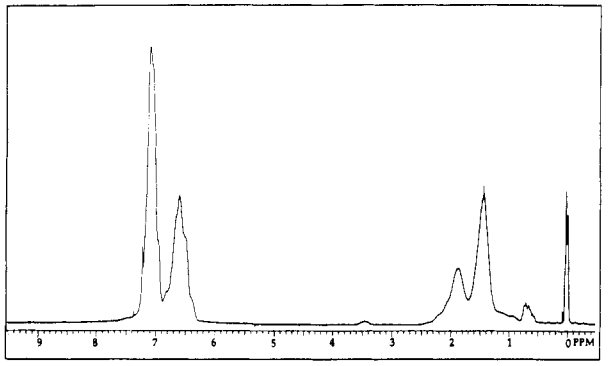


Figure 7. ^{1}H NMR ($CDCl_3$) of the functionalized polymer **4** for reaction 3 in Table III.

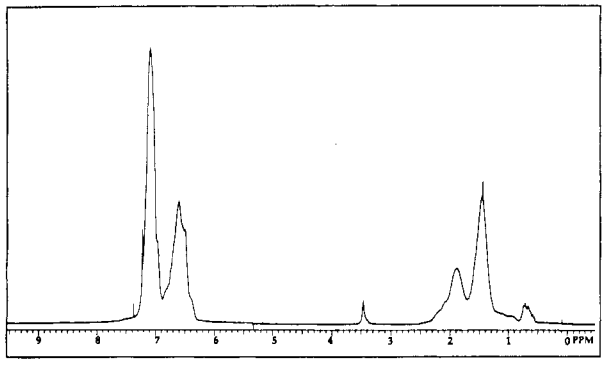


Figure 8. ^{1}H NMR ($CDCl_3$) of ω-aminopolystyrene **5** for reaction 3 in Table III.

diphenylmethine proton.[10] The ^{1}H NMR spectrum of the hydrolyzed functional polymer, **5**, shows that the multiplet at 0.08 ppm has been replaced by a resonance at 3.47 ppm corresponding to the N–H protons (Figure 8). The ^{13}C NMR spectrum of the hydrolyzed polymer, **5**, shows no

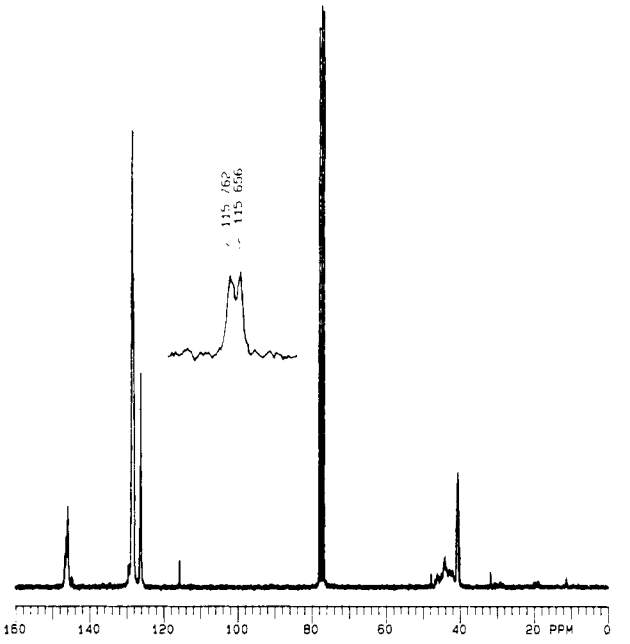


Figure 9. ^{13}C NMR ($CDCl_3$) of ω-aminopolystyrene **5** for reaction 4 in Table III.

resonance at 33.71 ppm for the terminal benzylic carbon as observed for unfunctionalized polystyrene (Figure 9).[7] Instead, a resonance is observed at 48.0 ppm which has been assigned to the terminal diphenylmethyl methine carbon. An absorption at 47.36 ppm was previously observed for the analogous dimethylamino-substituted polystyrene obtained by the functionalization of poly(styryl)lithium with 1-[4-(dimethylamino)phenyl]-1-phenylethylene.[10] In addition, this spectrum shows resonances at 115.66 and 115.76 ppm corresponding to the phenyl carbons ortho to the amine substituent. The presence of two peaks in this region is expected due to the diastereomeric nature of the chain end.[10,46]

Conclusion. The addition reaction of poly(styryl)lithium with 1-[4-[*N*,*N*-bis(trimethylsilyl)amino]phenyl]-1-phenylethylene provides a general method for incorporation of the primary amine functionality after removal of the silyl protecting groups. The reaction is complete after several hours in benzene at room temperature. All of the characterization results presented in this paper are consistent with essentially a quantitative yield of the amine-functionalized polymer. This methodology would be applicable to the preparation of polymers functionalized at the initiating end as well as within the polymer chain.

Acknowledgment. The authors are grateful to The Dow Chemical Co. for a Cooperative Research Grant in support of this work. We also want to thank FMC (Lithium Division) for providing samples of *sec*-butyllithium.

References and Notes

(1) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983.
(2) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.
(3) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1.
(4) Bywater, S. *Prog. Polym. Sci.* **1975**, *4*, 27.
(5) Bywater, S. Anionic Polymerization. In *Encyclopedia of Polymer Science and Engineering*; Krowschwitz, J., Ed.; Wiley-Interscience: New York, 1985; Vol. 2, p 1.
(6) Quirk, R. P.; Yin, J.; Guo, S.-H.; Gu, X.-W.; Summers, G.; Kim, J.; Zhu, L.-F.; Ma, J.-J.; Takizawa, T.; Lynch, T. *Rubber Chem. Technol.* **1991**, *64*, 648.
(7) Quirk, R. P.; Ma, J.-J. *J. Polym. Sci., Part A* **1988**, *26*, 2031.
(8) Quirk, R. P.; Yin, J.; Fetters, L. F. *Macromolecules* **1989**, *22*, 85.

(9) Quirk, R. P.; Yin, J.; Fetters, L. F.; Kastrup, R. V. *Macromolecules* **1992**, *25*, 2262.
(10) Quirk, R. P.; Zhu, L. *Br. Polym. J.* **1990**, *23*, 47.
(11) Charlier, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1986**, *19*, 1831.
(12) Stewart, M. J.; Shepherd, N.; Service, D. M. *Br. Polym. J.* **1990**, *22*, 319.
(13) Higginson, W. C. E.; Wooding, N. S. *J. Chem. Soc.* **1952**, 760.
(14) Quirk, R. P.; Cheng, P. L. *Macromolecules* **1986**, *19*, 1291.
(15) Quirk, R. P.; Chen, W.-C.; Cheng, P.-L. *Reactive Oligomers*; Harris, F. W., Spinelli, H. J., Eds.; ACS Symposium Series 282; American Chemical Society: Washington, DC, 1985; Chapter 12, p 139.
(16) Beak, P.; Kokko, B. J. *J. Org. Chem.* **1982**, *47*, 2822.
(17) Schulz, D. N.; Halasa, A. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2401.
(18) Hirao, A.; Hattori, I.; Sasagawa, T.; Yamaguchi, K.; Nakahama, S.; Yamazaki, N. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 59.
(19) Hattori, I.; Hirao, A.; Yamaguchi, K.; Nakahama, S.; Yamazaki, N. *Makromol. Chem.* **1983**, *184*, 1355.
(20) Quirk, R. P.; Summers, G. *Br. Polym. J.* **1990**, *22*, 249.
(21) Ueda, K.; Jirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939.
(22) Dickenstein, W. H.; Lillya, C. P. *Macromolecules* **1989**, *22*, 3882.
(23) Dickenstein, W. H.; Lillya, C. P. *Macromolecules* **1989**, *22*, 3886.
(24) Quirk, R. P.; Zhu, L. *Makromol. Chem.* **1989**, *190*, 487.
(25) Quirk, R. P.; Takizawa, T.; Lizarraga, G.; Zhu, L.-F. *J. Appl. Polym. Sci., Symp. Ser.* **1992**, *50*, 23.
(26) Quirk, R. P.; Chen, W.-C. *Makromol. Chem.* **1982**, *183*, 2071.
(27) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.
(28) Morton, M.; Fetters, L. *Rubber Chem. Technol.* **1975**, *48*, 359.
(29) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(30) Fritz, J. S.; Schenk, G. H. *Quantitative Analytical Chemistry*, 3rd ed.; Allyn and Bacon, Inc.: Boston, 1974.
(31) Hoffman, J. J.; Leir, C. M. *Polym. Int.* **1991**, *24*, 131.
(32) Diaf, A.; Beckman, E. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 956.
(33) Bordwell, F. G.; Algrim, D. J. *J. Am. Chem. Soc.* **1988**, *410*, 2964.
(34) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.
(35) Pratt, J. R.; Massey, W. C.; Pinkerton, F. H.; Thames, S. F. *J. Org. Chem.* **1975**, *40*, 1090.
(36) Bywater, S.; Johnson, A. F.; Worsfold, C. J. *Can. J. Chem.* **1964**, *42*, 1255.
(37) Lee, B. Ph.D. Dissertation, The University of Akron, Akron, OH, 1991.
(38) Zhu, L. Ph.D. Dissertation, The University of Akron, Akron, OH, 1991.
(39) Busson, R.; Van Beylen, M. *Macromolecules* **1977**, *10*, 1320.
(40) Kwart, H.; King, K. *d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur*; Springer-Verlag: Berlin, Heidelberg, and New York, 1977; p 16.
(41) Nagy, J. *J. Organomet. Chem.* **1972**, *38*, 261.
(42) Smith, J. W. Basicity and complex formation. In *The Chemistry of the Amino Group*; Patai, S., Ed.; John Wiley and Sons: New York, 1968; p 161.
(43) Pitt, C. G.; Fowler, M. S. *J. Am. Chem. Soc.* **1967**, *89* (25), 6793.
(44) Silverstein, R. G.; Bassler, G.; Morrill, M. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons, Inc.: New York, 1981.
(45) Glukhikh, V. I.; Voronkov, M. G. *Dokl. Akad. Nauk. SSSR* **1979**, *248* (1), 142.
(46) Bheda, M. C.; Gibson, H. W. *Macromolecules* **1991**, *24*, 2703.