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Amine-Terminal Polystyrenes: A New Strategy for Synthesis and New Methods for Determination of Functionality

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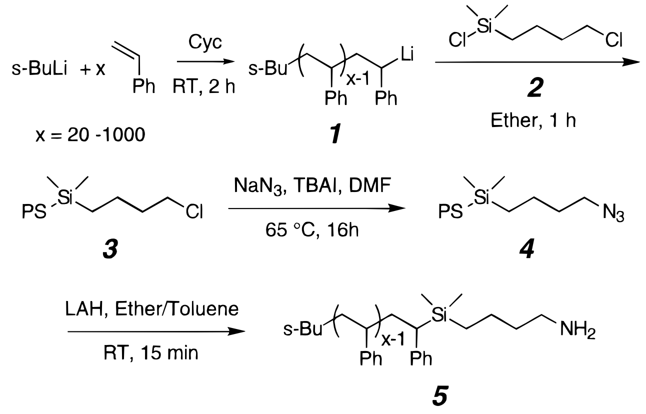
ABSTRACT: Polymers bearing a single alkyl chloride at the chain end were synthesized using anionic polymerization techniques. Specifically, living polystyrene (PS) anions were treated with commercially available (4-chlorobutyl)dimethylchlorosilane and found to react chemoselectively at the electrophilic silicon atom.[1] The pendant alkyl chloride on these PS chains was subsequently transformed into alkyl azide and aliphatic amine functionalities. The gel permeation chromatograms for the synthesized polymers were found to have relatively narrow molecular weight distributions ($M_w/M_n < 1.09$) after the end-capping reaction. Nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) studies were used to quantify the degree of functionalization.

Polymers bearing reactive functional groups represent an intriguing class of materials having potential application in several areas including surface modification, lubrication, catalysis, drug delivery, and compatibilization of polymer blends.[2] We are interested in blending and have found that *in situ* block copolymer formation via a chemical reaction (reactive blending) can be an effective means to compatibilize polymer blends.[2,3] On an industrial level, randomly functionalized copolymers are often used as blend compatibilizers (e.g. Nylon 6, and EP-*g*-maleic anhydride).[4] In these systems a complex mixture of graft copolymer compatibilizers necessarily results, making it difficult to investigate important fundamental aspects related to polymer blending. For this reason we are initially studying the reactivity of immiscible *monofunctional* polymers that form simple A−B diblocks during melt blending.

It is desirable to make block copolymers rapidly during blending; therefore, fast coupling reactions are attractive. Of the reactive pairs we have investigated, the primary aliphatic amine/cyclic anhydride system has the most promising reaction kinetics.[5] We have observed extremely fast melt-coupling reactions (homogenous and heterogeneous) and remarkable reactive self-assembly phenomena with this reactive pair.[6] These exciting initial results led us to develop new, straightforward methods for synthesizing polymers bearing a single, terminal, reactive functional group.[7] Specifically, we have designed synthetic methods that utilize readily available materials as trapping agents for living polymer anions and that are amenable to large-scale. We have also used a simplified procedure for purifying all monomers and solvents used in our anionic polymer synthesis. Passing the neat materials [styrene and cyclohexane here; and methacrylates, isoprene, $(Me_2SiO)_3$ in cyclohexane, diphenylethylene, toluene, THF, and heptane in other instances] through basic alumina after pretreatment with a reactive drying reagent (e.g., LAH, Et_3Al, or CaH_2) provides starting materials of sufficiently high purity for many anionic polymerizations. In contrast to the more commonly used multiple bulb-to-bulb distillations using break-seal and/or high vacuum apparatus for purification and transfer of monomers and solvents, these modifications permit efficient and convenient (e.g., less time-consuming) preparations.

Scheme 1



We now report a new method for synthesizing polystyrenes (PS) having a single aliphatic amine at the chain end (Scheme 1). It consists of trapping living Li−PS (**1**) with 4-(chlorobutyl)dimethylchlorosilane (**2**), substitution of the alkyl chloride in **3** by azide to give **4**, and reduction of the azide to the primary amine **5**. Amino-terminal polymers ranging in molecular mass from 2 to 100 kg/mol were synthesized in 5−50 g batches using these techniques. Several methods for the synthesis of amine-terminal PS, encompassing both aliphatic amine- and aniline-terminal PS, have been previously reported.[8] Aliphatic amines were of particular interest to us since their reaction with cyclic anhydride is orders of magnitude faster than the analogous anilines.[5] Specifically, Quirk et al.[8c] have described a functionalization method that utilizes a mixture of methoxylamine/MeLi[9] to endcap PS−Li, providing the corresponding benzylic amine-terminal PS ($f \leq 0.92$). Nakahama and Hirao[8d] endcapped PS−Li with 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane (a bis-silyl protected 3-bromo-1-pro-

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pylamine) to give highly functionalized aliphatic amine-terminal PS chains ($f > 0.95$). This same group had previously synthesized PS having benzylic amine chain ends by endcapping PS−Li with the *N*-trimethylsilyl imine of benzaldehyde.[8b] DeSimone et al.[8f] have also successfully incorporated aliphatic amine on the chain end of PS. Their method involves reaction of PS−Li with (*N*,*N*-bis(trimethylsilyl)amino)butyldimethylchlorosilane. Again they were able to obtain highly amine-functionalized PS ($f = 0.92-1.04$).

There are several advantages to the strategy we have developed. Some of the trapping reagents utilized in the previous methods are tedious to prepare and purify and/or are hydrolytically unstable.[8a,b,d−f] Scale-up could be problematic for these functionalization agents. Our method utilizes a commercially available, reactive trapping reagent [4-(chlorobutyl)dimethylchlorosilane (**2**)]. The alkyl chlorides **3** and azides **4** are versatile intermediates that can be used as precursors for the incorporation of other types of functionality. Our method is potentially applicable to the synthesis of amino-terminal polyolefins via reduction of the corresponding polydienes. Specifically, we have been unsuccessful in efficiently hydrogenating all alkenes in polydienes already bearing an aliphatic amino group on its chain end, whereas alkyl chlorides (cf. **3**) are compatible with the exhaustive hydrogenation of polydienes.[10] It has also been our experience that polymers bearing reactive aliphatic amine functionality are prone to undergo degradative reactions with oxygen and carbon dioxide when stored over periods of months. To avoid such complications we have found it convenient to store precursors to amine-terminal PS (i.e. alkyl chlorides **3** and azides **4**).

Polymer Synthesis and Characterization. Monofunctional polymers were synthesized using anionic polymerization techniques (cf. Scheme 1). Styrene (20−1000 equiv) was treated with *sec*-butyllithium in cyclohexane for 2 h at room temperature to give the living polystyryllithium adduct **1**. The reaction of adduct **1** with an excess (2 equiv) of commercially available (4-chlorobutyl)dimethylchlorosilane (**2**) took place exclusively at the more reactive chlorosilane to give the alkyl chloride functional polymers **3a**−**g**, which varied in molecular weight from 2 to 100 kg/mol.[11] Each PS−alkyl chloride **3** was treated with sodium azide and tetrabutylammonium iodide ((TBAI) to generate the corresponding alkyl iodide *in situ*) to efficiently give an azide-functional PS **4**. Each azide was subsequently reduced with lithium aluminum hydride (LAH) to give an amine-functional PS **5**. The 100 kg/mol sample **5g** appears to be one of the largest amine-terminal polystyrenes ever reported.[8b] The α,*ω*-diamine-terminal PS {$[H_2N(CH_2)_4SiMe_2PS-]_2$, **8**} was also synthesized in an analogous fashion, by trapping α,*ω*-polystyryldipotassium[12] with **2** to give the dichloride-terminal PS **6** $[Cl(CH_2)_4SiMe_2PS-]_2$. Displacement with azide ion gave **7** $[N_3(CH_2)_4SiMe_2PS-]_2$, and subsequent reduction provided **8**.

The molecular weights of the alkyl chloride-terminal polymers were very close to those targeted (GPC). All exhibited narrow molecular weight distributions as well (Table 1 PDI's: 1.04−1.09). GPC analysis was also performed on several of the azide- and amine-terminal polymers to verify that the molecular weight characteristics remained constant through the subsequent chemical transformations.[13]

Table 1. Molecular Weight Data for Chloride-Terminal Polystyrenes 3a−g and 6 and Functionality Data for Amine-Terminal Polystyrenes 5a−g and 8

PS−Cl	M_n (kg/mol) calcd	M_n (kg/mol) obsd	PDI	PS−NH_2	functionality (f)[a] method A[b]	method B[c]	method C[d]
3a	2.1	2.2	1.07	**5a**	0.98		0.99
3b	7.0	8.1	1.05	**5b**	0.90		
3c	10	11.5	1.04	**5c**	0.93		
3d	15.0	15.5	1.05	**5d**	0.90		0.89
3e	21	23.0	1.04	**5e**	0.93	0.98	0.98
3f	50	56.0	1.06	**5f**		0.87	
3g	98	101	1.09	**5g**		0.97	
6	21	21.4	1.06	**8**	0.97[c]	0.92[e]	

[a] f is defined as the fraction of chains having a terminal amine group. [b] ^1H NMR analysis of end groups. [c] ^1H NMR analysis of resulting PS−PEG block copolymer after derivatization with PEG−NPC (**9**). [d] GPC analysis after derivatization with monoanhydride functionalized PS of similar molecular weight. [e] In the case of the α,*ω*-diaminopolystyrene **8**, f is defined as the fraction of chain ends bearing a terminal amine group.

Polymers were also characterized by ^1H NMR spectroscopy. The protons corresponding to the newly incorporated (4-chlorobutyl)dimethylsilyl moiety in **3** are clearly visible in all of the polymers synthesized, even in the case of the 101 kg/mol **3g**. The methylene protons of the chloromethylene (CH_2Cl, $\delta = 3.45$ ppm), silylated methylene (CH_2Si $\delta = 0.35$ ppm), and dimethylsilyl ($SiMe_2$ $\delta = -0.2$ ppm) groups are readily distinguished. The sequence of transformations of **3** to **4** to **5** could be monitored by NMR spectroscopic changes of the terminal CH_2X protons. Spectra for the 23.0 kg/mol samples **3e**/**4e**/**5e** are shown in Figure 1. The pendant alkyl chloride was cleanly converted into azide and amine functionalities, respectively. The methylene protons alpha to the chloride (CH_2Cl) were shifted upfield from δ 3.45 ppm to δ 3.15 ppm upon conversion to azide (CH_2N_3). This resonance is again shielded to δ 2.60 ppm upon reduction of the terminal azide **4e** to amine **5e** (CH_2NH_2).

Functionality Determination. The functionality of the amine-terminal polymers was examined three ways. Method A uses direct integration of initiator vs end-group resonances in the ^1H NMR spectra, method B involves ^1H NMR integration of a $PS-NHCO_2-PEG$ block copolymer, and method C relies upon GPC data of a coupling reaction with a similar MW anhydride-terminal PS.

Method A. The integrated ratio of the *sec*-butyllithium initiator methyl protons (H_b, overlapping broad resonances, 6H, $\sim\delta = 0.7$ ppm) to various resonances associated with the silicon-containing terminating reagent (H_a, CH_2NH_2; H_c, CH_2Si; H_d, Me_2Si) was compared to the theoretical 6 to 2:2:6, respectively. For the case of **5e** (Figure 1) the observed ratio was 0.84 to 0.26:0.25:0.79 corresponding to $f = 0.93-0.89$. Simple ^1H NMR integral analysis was a reliable method ($\sim\pm5\%$) for determining the % functionality (f) of polystyrenes having a molecular mass below 20 kg/mol (Table 1, **5a**−**e**, **8**). Above this molecular weight, accurate peak integration was more difficult to achieve, but qualitative characterization of end-functionality was still viable.

Method B. Amine-terminal polymers were derivatized with a ≥2-fold molar excess of the commercial 4.25 kg/mol 4-nitrophenylcarbonate-functional PEG (PEG−NPC) (**9**) as shown in Scheme 2 for the 56 kg/mol PS **5f**. After derivatization for 8 h in THF at 65 °C, the excess **9** was easily separated from the high MW

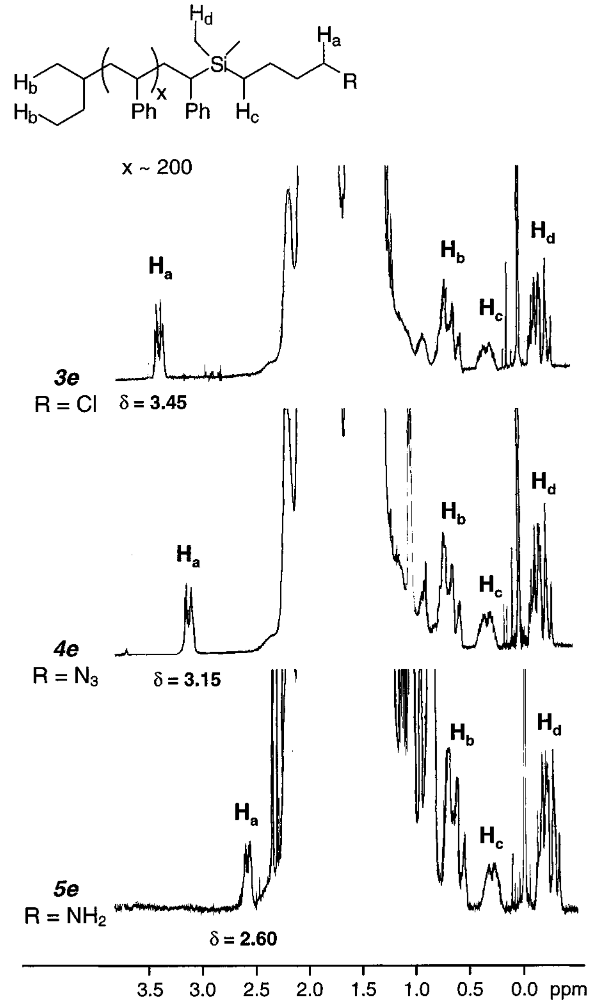
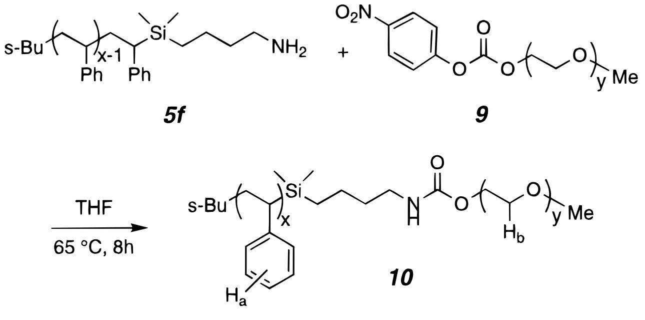


Figure 1. ^{1}H NMR spectra showing quantitative conversion of polystyrene mono-functionalized with an alkyl chloride (**3e**) to alkyl azide (**4e**) and amine (**5e**). Polymer molecular mass = 23 kg/mol.

Scheme 2



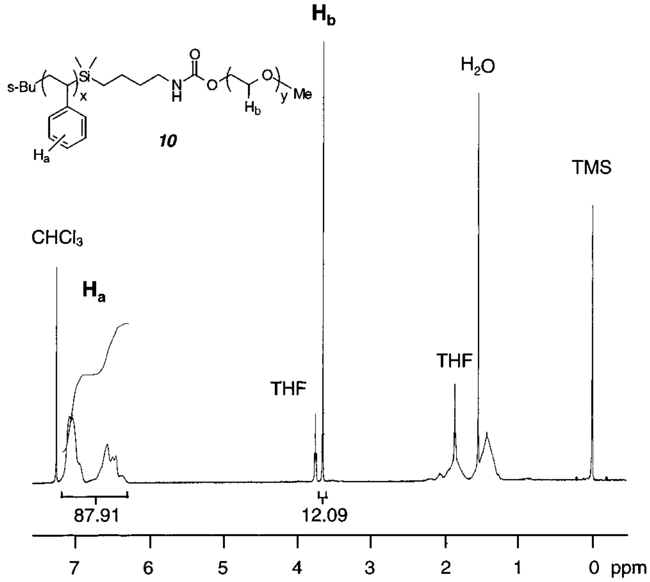
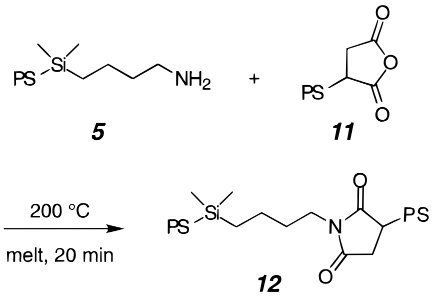


Figure 2. ^{1}H NMR spectrum of PS–PEG block copolymer **10**, made by derivatization of **5f** (56.0 kg/mol) with nitrophenyl carbonate-functional PEG **9** (4.25 kg/mol).

Scheme 3



polymer fraction [GPC (~2 mg injection through a train of two 300 × 7.8 mm, Phenogel columns (5 mm/1000 Å and 5 mm/500 Å), THF elution)]. The latter contained both the PS–PEG copolymer **10** and any unfunctional polymer molecules present in the original sample of PS **5f**. The functionality of the high-MW derivatized polymer sample was determined using ^{1}H NMR spectroscopy. Specifically, by comparing the integral ratio of the PS aromatic protons H_a (δ 6.3–7.2 ppm) to the PEG backbone protons H_b δ 3.62 ppm) in the newly formed PS–PEG block copolymer, the % functionality could be calculated. The ^{1}H NMR spectrum of **10** is shown in Figure 2. The theoretical integral ratio H_a/H_b for the resulting PS–PEG (56–4.25 kg/mol) diblock is 6.28/1.00. The observed integral ratio was 7.27/1.00, indicating the presence of some unfunctional PS (13%) in **5f**. The functionalities listed in Table 1 for **5e–g** and **6** were determined using this method. This procedure was not applicable for determining the extent of functional group incorporation for polystyrene sample having a molecular weight less than ~20 kg/mol because the PEG–NPC derivatizing agent was not completely resolved from the unfunctional PS/PS–PEG block copolymer in the GPC purification step.[14]

Method C. Coupling reactions following by GPC analysis were developed to verify the extent of functional group incorporation in polymers **5a**, **5d**, and **5e**. Specifically, these amino-functional polystyrenes were melt mixed with a 2-fold molar excess of anhydride-functional PS[15] **11** of similar molecular weight at 200 °C for 20 min (Scheme 3).[16] GPC analysis of the resulting mixture was employed to quantify the formation of PS–PS block copolymer **12**. It was assumed that the extent of block copolymer formation was directly proportional to the extent of functional group incorporation in the amino–PS samples.

Each of the above derivatization methods indicated that chain ends of these polymers were highly functional (f = 0.87–0.99).[17] In all cases, there was relatively good agreement between each of these techniques (~±5% for each technique).

Summary. A new method for the synthesis of amine-terminal polymers has been achieved. Chloride-terminal polystyrenes (2–100 kg/mol) were synthesized by trapping their corresponding anions with (4-chlorobutyl)dimethylchlorosilane. This method owes its success to the fact that polystyryl anion chemoselectively reacts at the more electrophilic silicon center of the trapping agent. Furthermore, the resulting alkyl chloride at the chain end was very efficiently transformed into an aliphatic amine functionality. The functionality of these polymers was determined using ^{1}H NMR spectroscopy and gel permeation chromatography techniques. Notably, we have developed reliable techniques for determining the extent of functional group incorporation in polymers with high molecular weights by derivatizing them with 4-nitrophenylcarbonate end-functional PEG (followed by preparatory GPC and ^{1}H NMR analysis). Using this technique (as well as other GPC coupling experiments), the *polymers synthesized were determined to have a high extent of chain-end amine incorporation* ($f = 0.87-0.99$). Currently, we are using these materials for model polymer blending studies and for investigating the phenomenon of reactive self assembly.[6]

Experimental Section

Materials. Styrene and cyclohexane were pretreated with lithium aluminum hydride, passed through basic alumina (Brockmann I), and stored over activated 4 Å molecular sieves under an argon atmosphere. THF (unstabilized) was purified by passage through a stainless steel column containing activated alumina.[18] Diethyl ether (unstabilized) was distilled from sodium-benzophenone ketyl. *sec*-Butyllithium was stored at −20 °C and was titrated using menthol and 2,2′-bipyridyl. Nitrophenylcarbonate-functional polyethylene glycol (4.25 kg/mol, $f = 0.99$/chain) was stored under an atmosphere of argon at −20 °C and used as received (Shearwater).

Polymer Synthesis. All polymers were synthesized under an inert atmosphere of argon. The reactor, magnetic stirbars, and syringes were stored in an oven (110 °C) and removed just prior to use. Each syringe was purged three times with argon before use. The reactor was evacuated and filled with argon five times. The inside of the reactor was rinsed with *sec*-BuLi (1.4 M, 2.0 mL) to scavenge any unwanted impurities. After rinsing, the *sec*-BuLi was diluted with dry cyclohexane (100 mL) and removed from the reactor by cannula.

Synthesis of Alkyl Chloride-Terminal Polystyrenes 3a−g. The synthesis of **3e** is given as an example. Cyclohexane (200 mL) was cannulated into a 1 L reactor. Styrene (20.0 g, 0.192 mol) was charged into the reactor via syringe, and the resulting solution was magnetically stirred with an ~3 cm stirbar so as to maintain a vortex column in the liquid. *sec*-BuLi (0.70 mL, 1.4 M in hexanes, 0.98 mmol) was then injected at once into the reactor via syringe through a septum and a characteristic orange color gradually intensified over 2 min. The polymerization was allowed to continue at room temperature for 2 h. Diethyl ether (20 mL) was cannulated into the reactor, and (4-chlorobutyl)dimethylchlorosilane (**2**, 0.53 g, 2.86 mmol) was then added to the polystyryl anion via a gastight syringe. The solution was stirred at room temperature until the characteristic orange color completely vanished (~1 h). The polymer was precipitated by pouring the reactor contents into 800 mL of methanol. The resulting polymer was filtered and dried under vacuum for 24 h to yield 19.8 g (98%) of **3e**.

Synthesis of Azide-Terminal Polystyrenes 4a−g. The synthesis of **4e** is given as an example. Chloride-terminated polystyrene **3e** (10.0 g, 0.592 mmol) was placed in a 50 mL culture tube fitted with Teflon lined cap and stirbar. Dimethylformamide (20 mL), sodium azide (0.65 g, 5.0 mmol), and tetrabutylammonium iodide (0.100 g, 0.27 mmol) were added to the flask. The slurry was purged with argon and the tube was capped. The reaction mixture was magnetically stirred at 65 °C for 16 h and allowed to cool to 25 °C. The resulting solution was poured into 150 mL of methanol to precipitate the polymer. The resulting polymer was filtered and dried under vacuum at room temperature for 24 h to yield 9.50 g (95%) of **4e**.

Synthesis of Amine-Terminal Polystyrene 5a−h. The synthesis of **5e** is given as an example. Azide-terminated polystyrene **4e** (5.0 g, 0.246 mmol) was placed in a 250 mL Erlenmeyer flask. Ether (100 mL) and toluene (50 mL) were added to the flask. Lithium aluminum hydride (0.5 g, 13.2 mmol) was carefully added to the polymer solution in portions over 15 min with vigorous magnetic stirring. After 15 min, 0.5 mL of water, 0.5 mL of 15% NaOH, and 1.5 mL of water were slowly added sequentially. The resulting slurry was filtered, and the filtrate was poured into 400 mL of methanol to precipitate the polymer. The resulting polymer was filtered and dried under vacuum at room temperature for 24 h to yield 4.25 g (85%) of **5e**.

Synthesis of α,ω-Alkyl Chloride-Terminal Polystyrene 6. THF (500 mL) was cannulated into a 1 L reactor and the solution was cooled to −78 °C with an ether/CO_2 bath. In a separate 50 mL round bottom flask under argon, potassium naphthalenide was prepared by adding a cube of freshly cut potassium (70.0 mg, 1.8 mmol) to anhydrous THF (15 mL) containing naphthalene (0.115 g, 0.90 mmol). This mixture was stirred at room temperature for 1 h to produce a 0.058 M solution. The resulting deep green solution was cannulated into the main reactor. Styrene (9.1 g, 0.0875 mol) was then added slowly and dropwise over 15 min with vigorous magnetic stirring so as to maintain a vortex column in the liquid. The green initiator solution quickly changed to dark brownish red and then to cherry red soon after styrene addition was begun. The polymerization was allowed to stir at −78 °C for 30 min after styrene addition was complete. (4-Chlorobutyl)dimethylchlorosilane (**2**, 0.5 g, 2.70 mmol) was added at −78 °C through a septum to the solution of α,ω-polystyryl dianion via a gastight syringe. The characteristic cherry red solution became colorless instantly. The polymer was precipitated by pouring the cold reactor contents into 800 mL of methanol. The resulting polymer was filtered and dried under vacuum for 24 h to yield 8.75 g (95%) of **6**. α,ω-Alkyl chloride-terminal PS **6** was subsequently converted to the corresponding diazide **7** and diamine **8** using the experimental procedures described for the corresponding transformations used to convert monofunctional PS **3** into **5** via **4**.

Derivatization of 5e−g and 8 with PEG−NPC (9) to Prepare PS−PEO Diblocks 10. *Method B (Table 1).* Derivatization of **5f** is given as an example. Amine-functional polystyrene **5f** (25 mg, 0.50 μmol) and PEG-NPC (**9**) (20 mg, 4.7 μmol) were placed in a 10 mL culture tube equipped with a magnetic stirbar. Dry THF (2 mL) was added, and the solution was purged with argon for 5 min. The tube was sealed with a Teflon-lined screw cap and placed in a oil bath. The solution was magnetically stirred for 8 h at 65 °C. The solution was cooled to room temperature, and a 0.1 mL aliquot (≈2.2 mg total sample) was removed for GPC analysis. The high (~60 kg/mol) and low (4.25 kg/mol) molecular weight fractions (i.e., **10** and unreacted **9**) from the crude reaction mixture were collected in separate round-bottomed flasks as each eluted from the column. Each solution (THF) was concentrated under vacuum and analyzed by ^{1}H NMR spectroscopy ($CDCl_3$).

Derivatization of 5a, 5d, and 5e with PS−Anhydrides 11 to Prepare PS−PS 12. *Method C (Table 1).* Derivatization of **5e** is given as an example. Amine-functional polystyrene **5e** (25 mg, 1.0 μmol) and anhydride functional PS (**11**, 25 kg/mol) (50 mg, 2.0 μmol) were placed in a glass parallel plate mixer apparatus [This mixer composed of a simple glass cup (inside diameter = 7 mm) and glass rod affixed to an electric drill motor. The top of the mixing chamber also contains an inlet for an inert gas.] The mixing chamber was immersed in an oil bath at 200 °C and the mixer was engaged (~280 rpm). Mixing was allowed to continue for 20 min under a nitrogen atmosphere. The mixing chamber was removed from the bath and cooled to room temperature. The resulting PS−PS coupled polymer **12** was dissolved with THF (2 mL) and diluted for GPC analysis (to ~1 mg/mL).

Compound Characterization Tools. Polymer molecular weights were estimated using a Waters 150-C A1C-BC GPC equipped with three Phenogel columns (5 mm/1000 Å and two 5 mm/500 Å) and UV (256 nm) and RI detectors. THF was used as the eluent. Ten standard polystyrenes were used for the calibration. Semipreparative GPC separations were carried out using a Perkin-Elmer Series 2 liquid chromatograph equipped with two Phenogel columns (5 mm/1000 Å and 5 mm/500 Å) and UV and RI detectors. ^{1}H NMR spectra were recorded on a Varian 500 MHz spectrometer.

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(11) No bimodal character to the GPC's was observed for polymer **3** synthesized in cyclohexane. However, when **1** was treated with less than 1 equiv of trapping agent **2**, the formation of 2:1 adducts arising from subsequent displacement of the alkyl chloride was observed in the GPC.

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(13) For example, samples **6**, **7**, and **8** had number average molecular weights of 21.4, 21.6, and 21.9, respectively. The polydispersities of **6**, **7**, and **8** were also constant for these samples (1.04). It should also be noted that the amine-terminal polystyrenes were acetylated with acetic anhydride (pyridine, room temperature, 2 h) before GPC analysis (THF eluent). Poor chromatographic behavior was observed for the underivatized amines. Such behavior has been previously reported in the literature.[5c]

(14) Alternatively, ∼2 kg/mol PEG−NPC is commercially available upon request (Shearwater). This reagent should be useful for determining the extent of amine incorporation in lower molecular weight polystyrenes (to ∼5 K).

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(16) Both the homogenous and heterogeneous cross-coupling reaction between polymers bearing aliphatic amines and cyclic anhydrides is extremely fast in the melt. Reaction is essentially complete after very short mixing times (∼5 min at 200 °C). These reactions can also be performed in solution (∼1 mM in THF), but reaction times are considerably longer (24 h at RT).

(17) Each of the amino-functionalized PS polymers could be obtained in chromatographically pure form (i.e. $f = 1.0$) by simple column chromatography on silica gel by gradient elution with cyclohexane/ether (10:1, then 1:1 respectively) as the solvent (even in the case of 101 kg/mol of **5g**). We have found this solvent gradient to be useful for purifying a variety of monofunctional polystyrenes.

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