Macromolecules **2004,** *37,* 6385−6394

A New Methodology for the Synthesis of Star Polymers Utilizing the Reaction of Living Polymers with Alkoxysilyl-Functionalized Polymers

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Received February 6, 2004; Revised Manuscript Received June 7, 2004

ABSTRACT: A novel method for linking polymeric organolithium compounds to form heteroarm (miktoarm) star-branched polymers has been demonstrated. After functionalization of a polymeric organolithium compound with excess multifunctional chlorosilane linking agent, the resulting polymeric chlorosilyl groups were converted to methoxysilyl groups with anhydrous methanol followed by precipitation into methanol. This procedure removed excess, nonvolatile, linking agent required to prevent linking reactions. Polystyrene-*b*-oligo(butadienyl)lithium (PS-*b*-oligoBD) was functionalized with excess 1,2-bis(dichloromethylsilyl)ethane in benzene with added triethylamine to minimize linking reactions during conversion of chlorosilyl to methoxysilyl groups. Quantitative conversion and complete removal of excess linking agent were demonstrated by SEC, ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR analyses. MALDI−TOF mass spectral analysis of the methoxysilyl-functionalized PS-*b*-oligoBD was consistent with the proposed structure and indicated the absence of side reaction products. A 4-arm, star-branched polystyrene prepared by treating methoxysilyl-functionalized PS-*b*-oligoBD with excess PS-*b*-oligoBDLi was essentially indistinguishable from an analogous polymer prepared using only 1,2-bis(dichloromethylsilyl)ethane. While the method has been demonstrated for synthesis of a 4-arm star, its use will have greatest benefit for the synthesis of higher order, multibranched, miktoarm star materials.

Introduction

Well-defined, star-branched polymers with narrow molecular weight distributions play an important role as model materials in the study of the effects of molecular architecture on single chain properties[1−3] as well as thermodynamic properties,[4,5] viscoelastic behavior,[6,7] and dynamic properties[8] of polymer blends. Anionic polymerization has proven to be one of the most powerful methods[9] for the creation of such polymers and thus has been the subject of intense interest over the past few decades.[10−16]

In recent years the synthesis of well-defined polymers with complex architectures involving internal branch points has gone beyond the synthesis of regular star polymers using anionic polymerization. Polymers having complex architectures have been synthesized using monosilane-type linking agents and benzyl bromide moieties as junction points. Archer and Varshney,[17] for example, used anionic polymerization to synthesize π-shaped, branched polybutadienes with six end groups using tetrachlorosilane as the junction point. In their method, a precursor polymer with two living end groups was synthesized by anionic polymerization using a dilithium initiator. This precursor was end-capped using excess tetrachlorosilane, and then the excess linking agent was removed by simply drying or by freeze-drying under a high vacuum utilizing the low boiling point of the chlorosilane linking agent. The α,ω-difunctionalized polymer functionalized with the linking agent was then joined with excess of living anionic arm polymer. This procedure for making a heteroarm star,[18] an H-shaped,[19] or a π-shaped branched polymer[17] using monosilane-type linking agents always requires the use of excess linking agent to completely end-cap the polymer without formation of higher molecular weight adducts. Therefore, the procedure is relatively simple if the excess linking agent is volatile and can be eliminated by simple distillation or freeze-drying. However, there is a limitation to this method because chlorosilane linking agents with more than one silicon, which are used for creating higher functionality junction points, usually have such high boiling points that they cannot be removed by distillation or freeze-drying. Therefore, the linking agents in these methods have been restricted to monosilane-type linking agents having low boiling points, and the number of end groups of the branched polymers has therefore been limited to six.

Methods using chloromethyl- or bromomethylbenzene moieties were developed by Hirao et al.[20−22] Living polymers were reacted with 1,1-bis(3-methoxymethylphenyl)ethylene in tetrahydrofuran (THF) at −78 °C, and then the methoxyphenyl end groups of the polymers were transformed into chloromethyl or bromomethyl moieties by a reaction with BCl_3 in CH_2Cl_2 or with trimethylsilyl chloride and LiBr in $CHCl_3/CH_3CN$. This step had to be repeated until the number of functional end groups reached the desired number of branches. Finally, the functionalized polymers with halomethyl end groups were reacted with living polymers, making a branched polymer. This method can create polymers with a high number of end groups as well as heteroarm star polymers. However, the major drawback of this method is that the complex synthetic procedure has to be repeated to get the desired number of branch points. Also, the use of halogen compounds for making the branch points can be accompanied by side reactions such as lithium−halogen exchange.[23] Finally, the requisite use of THF at −78 °C limits its general applicability.

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10.1021/ma049733k CCC: $27.50

Another procedure used to make star-branched polymers utilized the hydrosilylation reaction. A polybutadiene oligomer with a high portion of 1,2-butadiene units was prepared in the presence of 1,2-bispiperdinoethane at 4 °C,[24] and then the pendant double bonds of the poly(1,2-butadiene) units were hydrosilated using $HSi(CH_3)_2Cl$ or $HSi(CH_3)_2Cl_2$ in the presence of a platinum catalyst. The subsequent addition of poly(styryl)lithium chains led to the formation of star[25] or highly branched polymers.[26] This method provides the ability to prepare complicated polymer architectures. However, using a poly(1,2-butadiene) oligomeric block having a distribution of molecular weights as a linking agent will not allow for the preparation of polymers with well-defined arm functionality compared to those that can be made using a truly monodisperse silane-type linking agent.[23]

In this work, a new method for making well-defined, highly branched heteroarm polymers is presented. This method expands the scope of the traditional functionalization of polymeric organolithiums with excess chlorosilane linking agents. We have investigated the use of conversion of the resulting chlorosilyl groups to methoxysilyl groups followed by precipitation into methanol as a method to purify the reactive, silyl-functionalized polymers and to remove excess linking agent. The utility of the method has been demonstrated by the synthesis of a model, 4-armed, star-branched polystyrene using 1,2-bis(dichloromethylsilyl)ethane as the functionalizing agent.

Experimental Section

Materials. Benzene (Fisher, >99%) was purified sequentially by stirring with CaH_2 and sodium metal followed by distillation into a reservoir containing 1,1-diphenylhexyllithium as an indicator. The reservoir was attached to a vacuum line. The desired amount of purified benzene was transferred by distillation into the reactor for each reaction. Styrene (Aldrich, >99%) was stirred over CaH_2 for 1 day and then distilled into a flask containing neat dibutylmagnesium (FMC, Lithium Division). After stirring for several hours, the purified styrene was distilled into a calibrated ampule and heat-sealed with a flame. Triethylamine (TEA) (Aldrich, 99.5%) was purified by stirring over freshly crushed CaH_2 and vacuum transferred onto neat *n*-butyllithium (Aldrich, 1.6 M in hexanes) on the vacuum line. Triethylamine was stirred for 4 h and then distilled into an ampule followed by heat sealing with a flame. Butadiene (Air Products, 99%) was treated with sodium metal, vacuum transferred onto neat *n*-butyllithium, and then distilled into a calibrated ampule which was heat-sealed with a flame. Solutions of *sec*-butyllithium (Chemetall Foote Corp., 12.16 wt % in cyclohexane) were analyzed by the double-titration method with 1,2-dibromoethane.[27]

1,2-Bis(dichloromethylsilyl)ethane (DMSE) (Aldrich, 98%) was purified by distillation at 120 °C on the vacuum line. The first third of the distillate was discarded; the next third was collected, diluted with purified benzene in a drybox, ampulized, and heat-sealed on the vacuum line. Methanol (Fisher, 99.8%) was dried by stirring with freshly crushed CaH_2 and, after degassing, was distilled into a storage reservoir with molecular sieves. The anhydrous methanol was checked for the absence of water (δ 0.38 ppm in C_6D_6) with ^1H NMR spectroscopy.

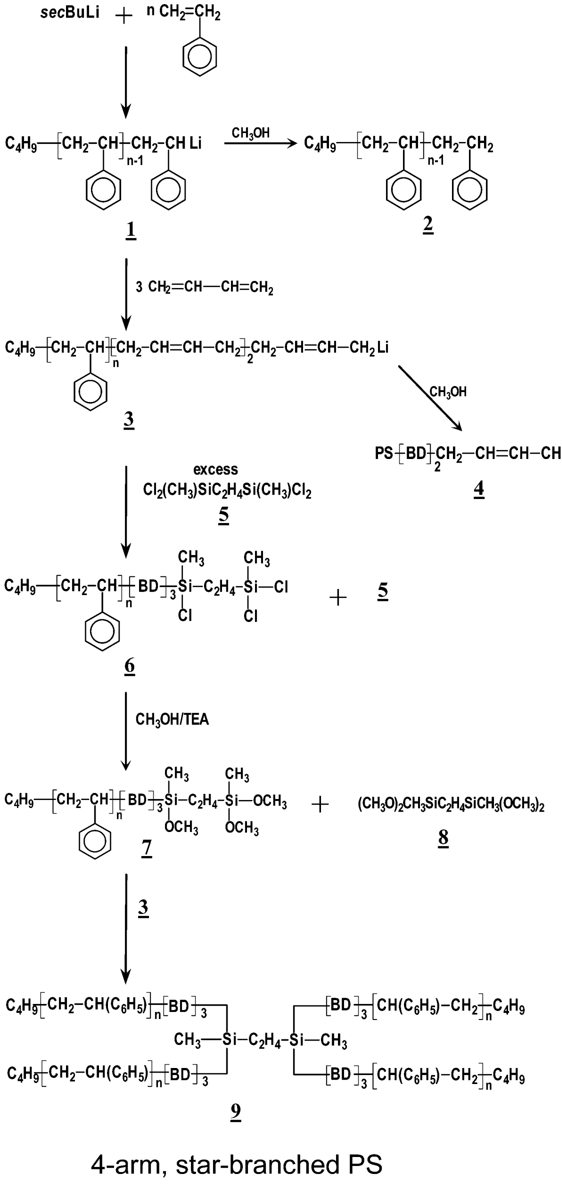
Polymerization. The syntheses were carried out using standard high-vacuum techniques in sealed glass reactors with break-seals.[28] For the 4-armed star-branched polymer, a living arm of poly(styryl)lithium was made first. The reactor, outfitted with a styrene monomer ampule and a UV cell to probe the crossover reaction, was dried for 1 day under high vacuum. The *sec*-butyllithium solution, 3.43 mL (0.005 mol, 1.43 M), was injected through a sidearm into the reactor under a N_2 purge using a gastight syringe. After heat-sealing the sidearm, benzene (250 mL) was distilled into the reactor and the reactor was flame-sealed off of the vacuum line. The reaction was started by breaking the break-seal on the styrene (19.6 g, 0.189 mol) ampule and then stirred overnight at room temperature. An aliquot was taken from the reactor and was quenched with degassed methanol for characterization. The poly(styryl)lithium thus prepared was then converted to butadienyllithium ends. Three equivalents of purified butadiene (1.17 mL, 0.015 mol) for each equivalent of poly(styryl)lithium was distilled into a dried ampule, which was attached to the reactor via a break-seal. This monomer was then added to the solution containing poly(styryl)lithium. The crossover reaction was monitored using UV−vis spectroscopy. After allowing the crossover reaction to proceed overnight, one-fourth of the solution was transferred into ampule "A" (65 mL, 1.3×10^{-3} mol) and three-fourths of the solution (200 mL, 4.0×10^{-3} mol) was transferred into a large ampule "B". Both were sealed off with a flame. These ampules were stored in a freezer until needed.

Functionalization. Ampule A of polystyrene-*b*-oligo(butadienyl)lithium (PS-*b*-BDLi) (65 mL, 1.3×10^{-3} mol) was attached to a reactor that had a methanol (10 mL, 0.25 mol) ampule (4-fold excess relative to [SiCl]), a DMSE linking agent (3.20 g, 0.0125 mol) ampule (9-fold excess relative to [PS-*b*-BDLi]), a reservoir connected by a glass filter, and a TEA (55.6 mL, 0.4 mol) ampule (7-fold excess relative to [SiCl]) or with no TEA ampule. The end-capping functionalization reaction by the linking agent was carried out by breaking the seal of the A ampule to let the polystyrene-*b*-oligo(butadienyl)lithium solution flow into the solution that contained excess 1,2-bis(dichloromethylsilyl)ethane. After 8 h, an aliquot was removed from the reactor to check the result using SEC analysis. The functionalization was carried out twice, once without adding TEA and then a second time with TEA in the solution having excess chlorosilane linking agent. Then the previously prepared anhydrous methanol was slowly added into the solution by ampule. After stirring for 1 day, the solution with the TEA was separated into two phases. The upper phase was transferred into the reservoir through a coarse fritted-glass filter. The lower phase was discarded. The collected solution was precipitated two times into anhydrous methanol in a drybox, and then the precipitated polymer was dried under high vacuum. In the absence of TEA, the one-phase solution was precipitated into anhydrous methanol. The dried polymer was dissolved in purified benzene and then was freeze-dried to remove the remaining methanol. After drying, a small amount of the dried polymer was taken for characterization.

Linking Reaction. The dried methoxysilyl-functionalized PS-*b*-oligoBD (M_n = 4000 g/mol, 1.1×10^{-3} mol) was dissolved in purified benzene and transferred to a dried ampule in a drybox followed by heat-sealing on the vacuum line. Then the ampule was attached to the reactor with ampule B attached. After drying the reactor for 1 day, the linking reaction was started by adding polystyrene with 1-(dimethoxymethylsilyl)-2-methoxysilylethane chain ends into the excess polystyrene-*b*-oligo(butadienyl)lithium (200 mL, 4.0×10^{-3} mol). Samples of the reaction mixture were taken several times during the reaction. After 1 week, the solution was quenched with degassed methanol to terminate the excess polystyrene-*b*-oligo(butadienyl)lithium. The 4-arm, star-branched polystyrene was separated from the excess arm polymer by fractionation using toluene and methanol.

Characterization. Size exclusion chromatographic (SEC) analyses of the unfunctionalized polystyrene, butadiene-functionalized polystyrene, and methoxysilyl-functionalized polystyrene were carried out with a Viscotek model 301 triple detector system equipped with a differential refractometer (Waters 140R), a differential viscometer (Viscotek DM 400), and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). The eluting solvent was THF at a flow rate of 1 mL/min at 30 °C. The UV−vis absorption spectra of the polymeric organolithiums were obtained using a Hewlett-Packard 8452A diode array spectrophotometer with a 1 mm UV cell attached to the reactor. The ^1H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded on a Varian 300

Scheme 1. Anionic Synthesis of 4-Arm, Star-Branched Polystyrene Using 1,2-Bis(dichloromethysilyl)Ethane as Functionalizing Agent for Polystyrene-*b*-oligo(butadienyl)lithium followed by methanolysis and linking with Polystyrene-*b*-oligo(butadienyl)lithium.



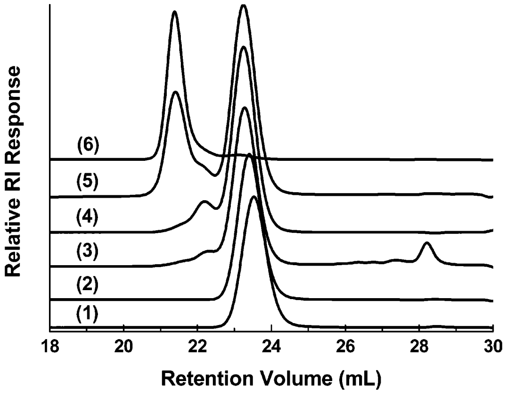


Figure 1. SEC chromatograms at each reaction step without TEA: curve 1, linear polystyrene as an arm polymer; curve 2, polystyrene-*b*-oligobutadiene (PS-*b*-oligoBD) after crossover reaction with 3 equiv of butadiene; curve 3, end-capped PS-*b*-oligoBD with excess 1,2 bis(dichloromethylsilyl)ethane; curve 4, methoxysilyl-functionalized PS-*b*-oligoBD after functionalization and precipitation into anhydrous methanol without TEA; curve 5, after 1 week linking reaction between methoxysilyl-functionalized PS-*b*-oligoBD and excess PS-*b*-oligoBDLi; curve 6, after fractionation.

MHz spectrometer using $CDCl_3$ as the solvent at room temperature. The ^{29}Si NMR (79.4 MHz) spectra were acquired with a Varian Inova 400 MHz spectrometer using a 10 mm diameter NMR tube. Polymer films for the FT-IR measurements were cast onto KBr plates directly from $CDCl_3$ solutions and were dried by heating on a hot plate at 40−50 °C for 5 min. FT-IR spectra were obtained using an ATI Mattson FT-IR instrument at room temperature. The scan resolution was 4 cm^{-1}, and the data represent an average of 64 measurements. The mass spectra were obtained on a Bruker Daltonics Reflex III MALDI−TOF mass spectrometer. Individual solutions of dithranol (20 mg/mL) as the matrix, silver trifluoroacetate (10 mg/mL) as the metal salt, and the polymer (10 mg/mL) were made in THF. These solutions were mixed in matrix/metal salt/polymer ratios of 10:1:2, and a small aliquot (0.5 μL) of the final mixture was applied to the sample holder. All ions observed were Ag^+ adducts of PS and PS-*b*-oligoBD oligomers. The reflectron resolution was sufficient to obtain resolved isotopic patterns. For this reason, the mass-to-charge ratios (*m*/*z*) quoted are monoisotopic; i.e., they refer to the PS·Ag^+ or PS-*b*-oligoBD·Ag^+ oligomer containing the lowest-mass isotopes (^{12}C, ^{1}H, ^{16}O, ^{28}Si, ^{107}Ag). Since singly charged ions were formed upon MALDI, the *m*/*z* value of an ion and the mass of this ion in daltons have identical numerical values. To determine the intrinsic viscosity of the 4-arm star polymer, toluene solutions of four concentrations were made, and then the flow time for each concentration was determined as the average for five trials measured using a Cannon-Ubbelohde viscometer at 30 °C. The intrinsic viscosity was determined by simultaneously extrapolating to zero concentration using the Huggins and Kraemer equations[29] and averaging the values of the intercepts. Glass transition temperatures were measured using a TA Instruments DSC 2910 differential scanning calorimeter. Samples weighing 15−30 mg were run under a stream of N_2 with equal heating and cooling rates of 10 °C/min. Data were recorded only for the second heating cycle. The value of T_g was taken as the temperature at which half of the specific heat change had been accomplished during the glass transition.

Results and Discussion

Precursor Preparation for the Functionalization. Poly(styryl)lithium (**1**) was synthesized by the *sec*-butyllithium-initiated polymerization of styrene in benzene as shown in Scheme 1. An aliquot was removed from the reactor and terminated with methanol (**2**) for SEC analysis (M_n = 3800 g/mol; M_w/M_n = 1.02; see curve 1 in Figures 1 and 2). Poly(styryl)lithium was end-capped with 3 equiv of butadiene to convert the chain ends to less-hindered butadienyllithium chain ends (**3**).

The crossover reaction was investigated using UV−vis spectroscopy. In the UV−vis absorbance spectra (see Figure 3), the PSLi peak at 335 nm disappeared and a new peak at 295 nm, corresponding to PBDLi, was observed after adding the butadiene. Correspondingly, the solution changed from dark red (PSLi) to light yellow (PBDLi). This meant that the poly(styryl)lithium was completely end-capped by the butadiene. It is well-known, from kinetic studies of copolymerization,[30] that the crossover reaction of poly(styryl)lithium chain ends with butadiene is the fastest reaction among the four styrene/butadiene copolymerization reactions. An aliquot of this end-capped polymer was terminated with methanol (**4**) and was analyzed by SEC (see curve 2 in Figures 1, 2; M_n = 4000 g/mol; M_w/M_n = 1.02). One-fourth of the polystyrene-*b*-oligo(butadienyl)lithium (PS-

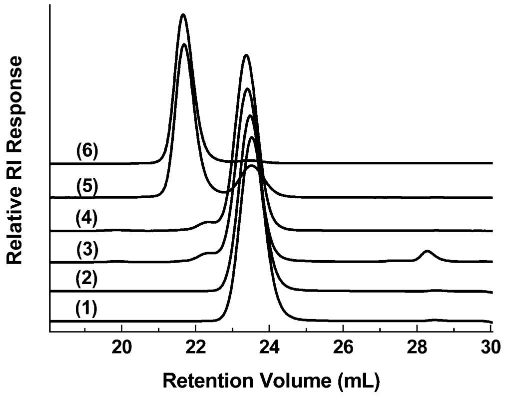


Figure 2. SEC chromatograms at each reaction step with TEA: curve 1, linear polystyrene as an arm polymer; curve 2, polystyrene-*b*-oligobutadiene after crossover reaction with 3 equiv of butadiene; curve 3, end-capped PS-*b*-oligoBD with excess 1,2-bis(dichloromethylsilyl)ethane; curve 4, methoxysilyl-functionalized PS-*b*-oligoBD after functionalization and precipitation into anhydrous methanol with TEA; curve 5, after 1 week linking reaction between methoxysilyl-functionalized PS-*b*-oligoBD and excess PS-*b*-oligoBDLi; curve 6, after fractionation.

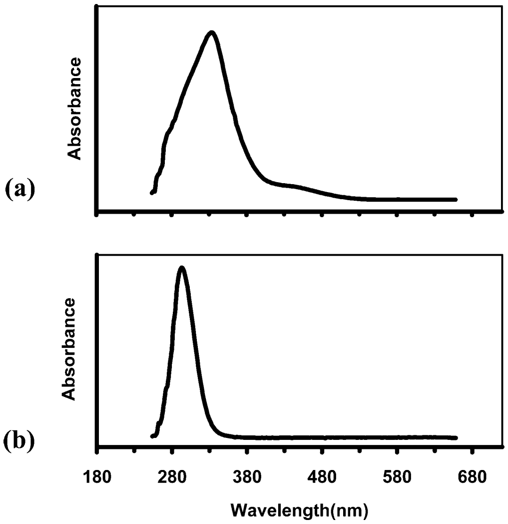
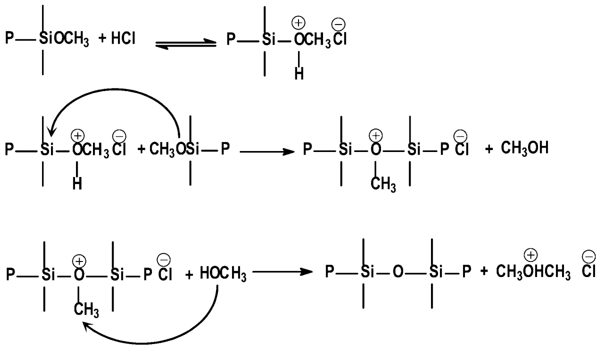


Figure 3. UV–vis absorption spectra of the reaction mixture for the crossover from poly(styryl)lithium to polystyrene-*b*-oligo(butadienyl)lithium in benzene: (a) before the crossover reaction; (b) after the crossover reaction.

b-oligoBDLi) was transferred into ampule A and used to form the polymeric linking agent, and the remaining PS-*b*-oligoBDLi was transferred into ampule B and used for the final linking reaction. The living polymer in ampule A was added into the purified benzene solution of the excess 1,2-bis(dichloromethylsilyl)ethane, **5** ([Cl]/[Li] > 100)]. As the living arm polymer flowed into the solution, the arm's light yellow color disappeared. An aliquot was taken from the reactor for SEC analysis. The aliquot was dried two times by freeze-drying under high vacuum; then the remaining polymer was dissolved in purified THF. The SEC chromatograms (see curve 3 in Figures 1 and 2) showed a small bump at 22.3 mL retention volume, next to the main peak at 23.3 mL that corresponds to the functionalized arm polymer, **6**, and another small bump at a retention volume of 28.4 mL after end-capping with linking agent, **5**. The small bump at 22.3 mL retention volume corresponds to a small amount of coupling product with twice the M_n of the arm polymer (M_n = 10 800 g/mol). The coupled polymer comprised less than 6 wt % of the total polymer based on comparison of areas of the various peaks in the SEC chromatogram. The small peak at the retention volume of 28.4 mL was assigned to the excess linking agent by comparison with the retention volume determined by injection of a solution of only 1,2-bis(dichloromethylsilyl)ethane on the SEC column. The SEC analysis thus showed that most of the excess linking agent was not removed, even though the solution was subjected to two cycles of freeze-drying. Usually, a silane-type linking agent with two or more silicon atoms, such as 1,2-bis(dichloromethylsilyl)ethane or 1,6-bis(trichlorosilyl)hexane, has a boiling point above 200 °C; therefore, the linking agent cannot be removed simply by freeze-drying or by mild heating under high vacuum. It is clear that the presence of excess linking agent is not acceptable because this would result in a complex mixture of products from the subsequent linking reaction with a polymeric organolithium compound.

Scheme 2. Possible Side Reaction



Functionalization. To remove the excess linking agent, all of the chlorosilane groups were first converted into methoxysilyl groups by treatment with anhydrous methanol in both the presence and absence of added TEA. This was attempted first without TEA. Five equivalents of anhydrous methanol (relative to chlorosilane group concentration) was added to the solution containing the excess 1,2-bis(dichloromethylsilyl)ethane (**5**) and the trichlorosilyl end-capped polymer (**6**). This amount of methanol was insufficient to precipitate the end-capped polymers. After stirring overnight, the solution was transferred into a drybox and poured into a large amount of anhydrous methanol to precipitate the trimethoxysilyl end-capped polymer (**7**). The precipitation procedure was repeated two times to remove the transformed excess linking agent, **8**. The excess transformed linking agent with four methoxy groups (**8**) dissolved readily in methanol, while the polymer end-capped with moieties having three methoxysilyl groups (**7**) was insoluble in methanol. Curves 3 and 4 in Figure 1 correspond to the SEC chromatograms of the end-capped polymers before and after adding the methanol in the absence of TEA, respectively. After functionalization and precipitation, the peak for the excess transformed linking agent at a retention volume of 28.4 mL disappeared, but the content of the coupled polymer increased from 3.5 to 20 wt %. During the functionalization, the substitution reaction of methoxy for chloride produced hydrochloric acid as a byproduct, as shown in Scheme 2. The acid can readily catalyze the condensation of methoxysilyl groups as shown in Scheme 2. Higher order degrees of linking are also evident in chromatogram 4 in Figure 1. After the methoxy-functionalized polymer was added to the excess PS-*b*-BDLi

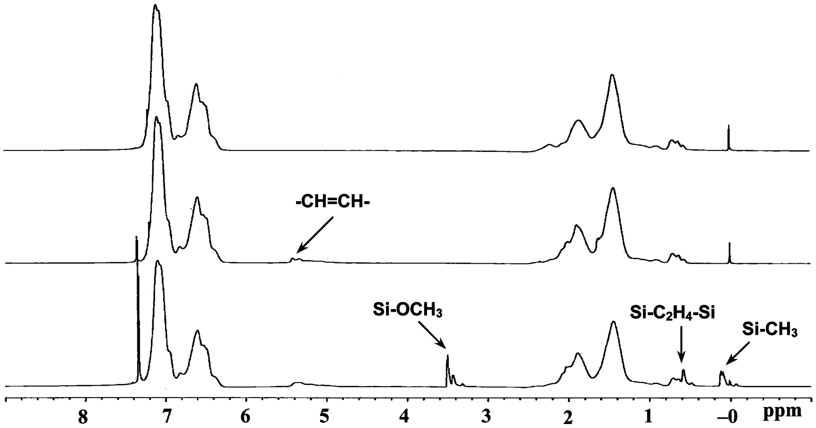


Figure 4. ^{1}H NMR spectra ($CDCl_3$) of the unfunctionalized polystyrene, **2** (top), butadiene end-capped polystyrene, **4** (middle), and methoxysilyl-functionalized polystyrene-*b*-oligoBD, **7** (bottom).

(1.2 equiv relative to [$SiOCH_3$]) solution to produce a 4-arm star polymer, the extent of the linking reaction was tracked by SEC analysis. The linking reaction progressed no further after 1 week (see chromatogram 5 in Figure 1), and therefore it was terminated by addition of methanol. After the linking reaction, the chromatogram showed two peaks corresponding to the 4-arm star polymer and the excess arm polymer. However, there still was a bump between the peaks for the star polymer and the arm polymer, presumably due to the presence of coupled polymer produced during functionalization.

To remove the HCl formed during the functionalization reaction, a small amount of purified triethylamine ([TEA]/[MeOH] = 8) was mixed with the solution containing the excess chlorosilane linking agent (**5**) and the chlorosilane end-capped polymer (**6**). Then methanol (4-fold excess relative to [SiCl]) was added to convert each chloride into a methoxy. The methanol was added very slowly, and the solution became viscous and milky due to the production of an ammonium salt by the reaction between HCl and TEA. The solution separated into two phases after stirring for 1 day. The lower phase contained the majority of the triethylammonium salt, and the upper phase contained the majority of the polymer (**7**) and excess transformed linking agent (**8**). The upper phase was filtered through a coarse fritted-glass filter into an ampule to remove the remaining salt. The filtered solution with methoxysilyl-functionalized polymer and excess transformed linking agent was precipitated into a large amount of anhydrous methanol in a drybox to collect the methoxysilyl-functionalized polymer. Then it was dried two times by freeze-drying under high vacuum. The dried polymer was added to excess PS-*b*-oligoBDLi to make a 4-arm star polymer. Figure 2 shows the SEC chromatograms for each step of the process effected in the presence of TEA. Specifically, chromatogram 4 in Figure 2 shows no increase in the amount of coupled polymer upon methanol transformation and no peak corresponding to the transformed linking agent after the end-capping reaction with the linking agent and the methoxy functionalization. Chromatogram 5 in Figure 2 shows only two peaks, where the first peak corresponds to the 4-arm star polymer (**9**) and the second peak corresponds to the excess arm polymer after the linking reaction. This indicates that the addition of TEA prevented the coupling reactions observed during the methanol transformation in the absence of TEA. The methoxy-functionalized polymer synthesized in the presence of TEA was characterized before the final linking reaction by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, FT-IR, and MALDI−TOF MS to track the residue of the linking agent and to measure the functionality of the polymer.

Characterization of the Unfunctionalized and Functionalized Polymers. ^{1}H NMR. The ^{1}H NMR spectra of the unfunctionalized and functionalized polymers are shown in Figure 4. The spectrum of the unfunctionalized polystyrene (**2**) initiated by *sec*-BuLi (top in Figure 4) shows peaks typical of PS. The peaks in the δ 0.4−2.6 ppm region are assigned to the aliphatic part of the polystyrene and the *sec*-butyl initiator group. The peaks at δ 6.4−7.4 ppm are assigned to the aromatic ring hydrogens of polystyrene. The ratio of the area of the aromatic hydrogen peaks of PS (δ 6.4−7.4 ppm) to the area of the methyl peaks in the *sec*-Bu group (δ 0.55−0.8 ppm) was 39, which corresponds to M_n = 3.8 × 10^3 g/mol. This result is in good agreement with molecular weight determined by SEC ($M_n = 3.8 \times 10^3$ g/mol). After the crossover reaction with butadiene, the ^{1}H NMR spectrum (see Figure 4, middle spectrum) showed new peaks in the region δ 4.8−5.6 ppm assignable to the protons on the double bonds of the BD units. This 4.8−5.6 ppm region included peaks for the protons from −**CH**=**CH**− units in the oligomeric butadiene chain having *cis*-1,4- and *trans*-1,4-microstructure as well as peaks for protons from vinyl groups (C**H**$_2$=C**H**−) in the units with 1,2-microstructure. The vinylidene protons from the CH_2= groups in the 1,2-microstructure are assigned to resonance in the δ 4.8−5.01 ppm region, and the protons from the −CH= groups in the units with *cis*-1,4-, *trans*-1,4-, and 1,2-microstructure are assigned to the δ 5.03−5.6 ppm region.[31] In the spectrum (middle in Figure 4), the peak assignable to the CH_2= protons in the 1.2-microstuctural unit was not separated clearly from the peak of the −CH= protons in the *cis*-1,4-, *trans*-1,4-, and 1,2-microstructural units due to the styrene unit next to butadiene. Allowing for the overlap of the peaks, the best estimate of the amount of 1,2-microstructure that can be made is 2−5 mol %. Thus, the number of BD units added to the arms was estimated from the ratio of the area for peaks corresponding to the −CH=CH− and CH_2=CH− of BD (2H; δ 4.8−5.6 ppm) to the area for the methyl part of *sec*-Bu (6H; δ 0.45−0.8 ppm); the observed area ratio was 0.75. This calculation yields an estimate of 2.2 butadiene units per molecule. The discrepancy between the number of BD units expected from the amount of monomer

Table 1. Expected and Observed ^{1}H Chemical Shifts According to the Structural Groups on Silicon

structural group	Si−OCH$_3$	Si−CH$_3$	Si−CH$_2$CH$_2$−Si
expected	3.3−3.8[a]	−0.8−1.2[a]	0.58−1.5[a]
observed	3.40−3.55	0.08−0.15	0.6

[a] Reference 33.

added (3.0) and the number calculated from NMR (2.2) probably reflects the uncertainty in the amount of the distilled BD.

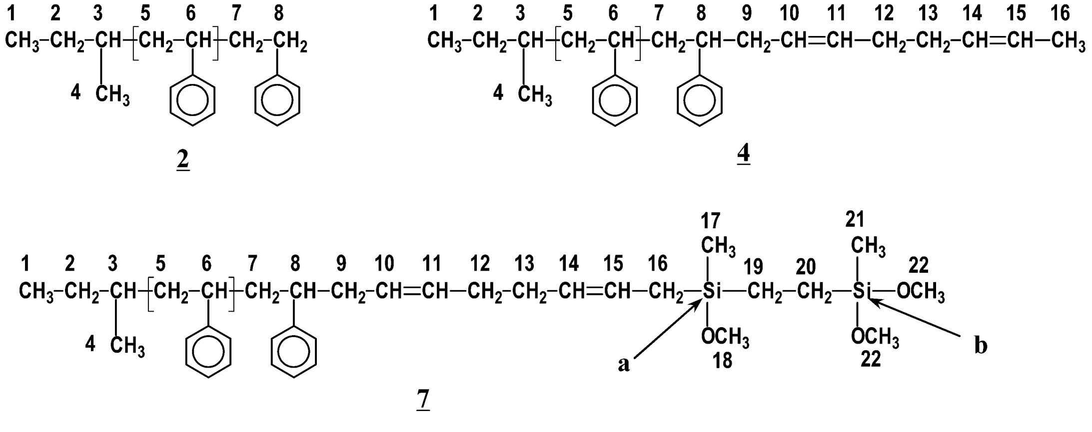
The polymer with the BD units end-capped with a 1,2-bis(dichloromethylsilyl)ethane (**6**) was transformed into the corresponding methoxysilyl-functionalized polymer by reaction with purified methanol and then was precipitated into a large amount of methanol to remove the excess linking agent. The ^{1}H NMR spectrum (bottom spectrum in Figure 4) of the methoxysilyl-functionalized polymer (**7**) showed several new peaks, assigned as shown in the figure. The observed shifts agree well with those expected from literature precedent[32,33] for the various moieties in the end-capping unit, as shown in Table 1. The Si−OCH$_3$ moieties were separated into two peaks, reflecting the two methoxysilyl positions of the end group. The calculated ratio between the areas for the two different positions of the methoxysilyl moieties also coincided with the theoretical proton ratio (2/1) for those two positions. In general, Si−OCH$_3$ moieties can be easily hydrolyzed in the presence of a protic solvent such as water. If this had occurred in our case, a peak corresponding to a hydrolyzed Si−OH group would have been found in the 4−7 ppm region.[33] However, no evidence for Si−OH groups due to hydrolysis was found in the ^{1}H NMR spectrum of the methoxysilyl-functionalized polymer (**7**). The ethylene part of the end groups was reflected by a prominent single peak at δ 0.6 ppm in the ^{1}H NMR spectrum even though the peak overlapped with the broad peaks of the *sec*-Bu moieties. New peaks in the 0.08−0.15 ppm region corresponded to the CH$_3$−Si moieties in the functionalizing agent group. The peaks were slightly separated because of the different numbers of geminal methoxysilyl substituents. Next to each new peak in the ^{1}H NMR spectrum of the functionalized polymer were small peaks. Presumably, these peaks are due to the formation of coupled polymer during the end-capping reaction with the linking agent. The amount of coupled polymer was calculated from the ratio of the integration areas for peaks corresponding to the methoxysilyl part (−OCH$_3$) of the end-functionalized polymer (9H) at δ 3.4−3.8 ppm to the area for the methoxysilyl part of the coupled polymer (6H) at δ 0.5−0.95 ppm. The observed ratio was 22.0, and the calculated amount of coupled polymer was 6.7 mol %, which compared well with the amount of coupled polymer (6 wt %) estimated from SEC chromatograms. If each polymer chain with a *sec*-Bu residue was functionalized by one linking agent, the yield of the desired functionality could be determined by comparison of the area (A) of the Si−OCH$_3$ peaks (9H) (δ 3.4−3.8 ppm) to the area (B) of the peaks corresponding to methyl groups of the *sec*-Bu initiator residue (6H) in the 0.5−0.95 ppm region after correction for the contribution from the ethylene groups (SiCH$_2$CH$_2$Si) from the linking agent. With A measured to be 4.83 and B to be 5.38, the conversion ratio was calculated as follows:

$$\frac{\text{moles of SiOH}_3\text{ end group}}{\text{moles of }\textit{sec}\text{-Bu group}} = \frac{a}{b} = \frac{A/9}{[B - (4/9)A]/6} \quad (1)$$

The value of 0.997 calculated for the ratio a/b using eq 1 suggests that the functionalization went to completion. From the ^{1}H NMR spectrum of the methoxy-functionalized polymer it was concluded that every chloride of the end groups was changed into a methoxy moiety and that all residue from the excess linking agent was eliminated after the precipitation.

^{13}C NMR. The three polymers **2**, **4**, and **7** (Chart 1) were investigated by ^{13}C NMR to further verify the degree of methoxysilyl functionalization. Figure 5 shows three enlargements of the portions of the spectra corresponding to the aliphatic parts of the molecules. The three curves correspond to different stages in the synthesis. The peaks for the unfunctionalized polystyrene (**2**) (top spectrum in Figure 5) were assigned by comparison of observed chemical shifts with chemical shifts calculated using the empirical additivity equations developed by Grant and Paul.[34,35] For purposes of discussion, the carbons are numbered on each structure, and the assignments are indicated on the spectra using these numbers. The assignments are in good agreement with the chemical shifts of a typical polystyrene homopolymer (structure **2**).[36] The ^{13}C NMR spectrum (see middle spectrum, Figure 5) of the polystyrene end-capped with butadiene units (**4**) was similar to the spectrum of a styrene/butadiene block copolymer. The peak for the methine (C-8) in the styrene adjacent to the butadiene overlapped with the peaks of the repeating units (C-6) in the 41−47 ppm region. The peak for carbon 9 of the butadiene unit is found at δ 32.4−33.5 ppm. This chemical shift was in good agreement with that for one of the first carbons of butadiene when the

Chart 1



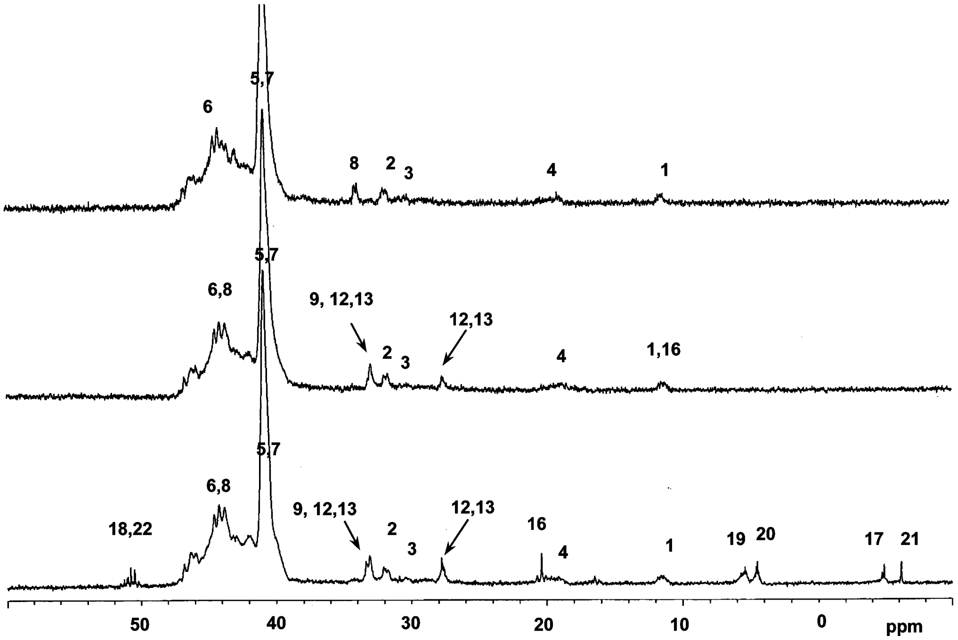


Figure 5. ^{13}C NMR spectra ($CDCl_3$) of the aliphatic parts of the unfunctionalized polystyrene, **2** (top), butadiene end-capped polystyrene, **4** (middle), and methoxysilyl-functionalized polystyrene-*b*-oligoBD, **7** (bottom).

Table 2. Expected and Observed ^{13}C Chemical Shifts According to the Substituents on Silicon

structural group	Si−OCH$_3$ (C_{18}, C_{22})	Si−CH$_3$ (C_{16}, C_{17}, C_{21})	Si−CH$_2$CH$_2$−Si (C_{19}, C_{20})
expected	49−50[a]	−15−20[a]	3−18[a]
observed	50−52	−4 to −6.2	4−6

[a] Reference 33.

preceding unit was styrene.[37−39] Peaks for C-12 and C-13 in the butadiene units were broad due to tacticity. If the C-12/C-13 pair of carbons were in a dyad of two *cis*-1,4-butadienes or one styrene and one *cis*-1,4-butadiene unit, the chemical shifts would be expected in the 27.3−27.5 ppm region based on published ^{13}C NMR studies of styrene/butadiene copolymers.[38,39] If C-12/C-13 were in a dyad of one *trans*-1,4-butadiene and one *cis*-1,4-butadiene, the signal would appear at δ 32.7−33.9 ppm, which would overlap with the chemical shift of C-9.[37−39] Both possibilities of chemical shifts for C-12/C-13 appear in the ^{13}C NMR spectrum of the functionalized polystyrene with an average of 2.25 units of butadiene because the butadiene was not uniformly distributed on the polystyrene chain ends. Some polymer chains may have had up to four units of butadiene at the end, which produced a cis/trans sequence. Evidence of *trans*-1,4-butadiene could also be found in the FT-IR spectrum at 965 cm^{-1}.[40] The chemical shift of C-16 was presumed to overlap with the chemical shift for C-1 (δ 18.1−21.0 ppm). Signals for the carbons in the allylic vinyl parts (−CH=) of the butadiene units (C-10, C-11, C-14, and C-15) could not be observed due to overlapping with signals for the carbons of the aromatic part of styrene unit (δ 124−130 ppm).

The ^{13}C NMR spectrum (bottom spectrum in Figure 5) of the methoxysilyl-functionalized polystyrene (structure **7**) showed several new peaks. Generally, silicon substituents on an aliphatic carbon result in a shielding effect so that the substituents on the silicon are found upfield in the ^{13}C NMR spectrum. The expected and observed ^{13}C chemical shifts are listed in Table 2 according to the substituent on silicon. For the Si−CH$_3$ carbons, C-21 in structure **7** resonated slightly farther upfield (δ −6.2 ppm) compared to the resonance of C-17 (δ −4.5 to −4.8 ppm) because of the shielding effect of the two methoxy substituents on silicon **b** vs one methoxy on silicon **a**. There was a small peak next to a large peak associated with C-17, presumably due to the presence of the coupled polymer or polymer tacticity. This coupling affected the chemical shift of carbon 16. Carbons (C-16, C-19, C-20) in Si−CH$_2$−X groups would generally be expected to resonate in the range 2−35 ppm, with the precise shift depending on the identity of X. When X is CH= from the BD unit, the carbon next to the silicon (C-16) resonated downfield (δ 20.2 ppm). The chemical shifts of C-19 and C-20 when X was CH$_2$− appeared farther upfield (δ 4−6 ppm) than that of C-16.[33] Peaks for C-19 and C-20 were separated due to the fact that the silicon atoms to which they are attached have different substituents. The peaks of most interest, those for the methoxy groups (C-18, C-22), appeared at about δ 50−52 ppm. The chemical shifts were split into multiple peaks, presumably due to different degrees of butadiene oligomerization and the tacticity at the chain end. The chemical shifts appeared slightly downfield from those for the normal methoxy groups on the silicon (δ 49−50 ppm) because of the other structural groups on the silicon.

^{29}Si NMR and FT-IR. ^{29}Si NMR is the most discriminating technique for characterizing the end groups for methoxysilyl-functionalized polymers (**7**). There were only two peaks in the ^{29}Si NMR spectrum of **7** that correspond to the two different chain-end silicons (Figure 6). The chemical shift (δ −1 ppm) of the silicon with two methoxy groups (Si-**b**, structure **7**) was similar to the chemical shift (δ −2.2 ppm) reported for $(CH_3)_2Si(OCH_3)_2$.[33] The chemical shift (δ 16.8 ppm) of Si-**a** with one methoxy group was in good agreement with that reported for $(CH_3)_3SiOCH_3$ (δ 16.0 ppm). The discrepancies between the observed shifts and the reported shifts were expected because of the different substituents on the silicons. The portion of the spectrum for Si-**a** had a small peak next to a large peak, presumably because of the tacticity. If the coupled polymer were produced by condensation of Si−OCH$_3$ groups, the peak

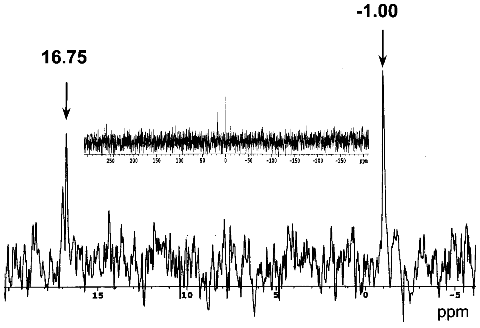


Figure 6. ^{29}Si NMR spectrum (79.4 MHz, $CDCl_3$) of the methoxysilyl-functionalized polystyrene-*b*-oligoBD (**7**); M_n = 4000 g/mol.

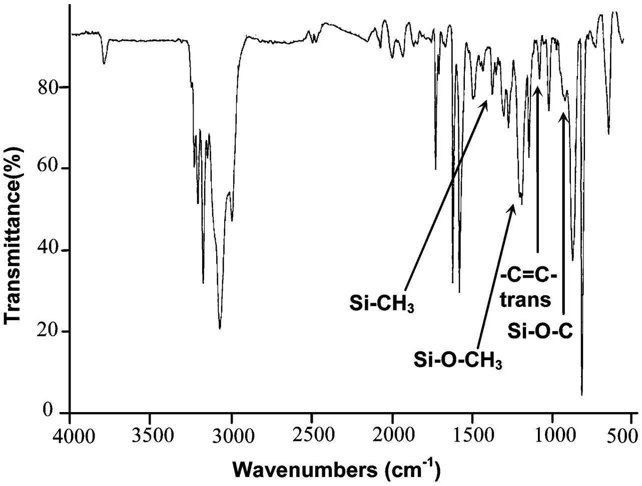


Figure 7. FT-IR spectrum of methoxysilyl-functionalized polystyrene-*b*-oligobutadiene (**7**).

associated with the Si−O−Si linkage should appear at around δ −55 to −75 ppm. However, no peak could be found in that region, so coupled polymer formed by the possible side reaction indeed appears to have been suppressed in the presence of TEA.

In the FT-IR spectrum of **7**, shown in Figure 7, an absorbance band was observed at 965 cm^{-1} for the polystyrene functionalized with butadiene due to the double bond of the *trans*-1,4-BD unit. The band due to *cis*-1,4-BD units[40,41] at 675−729 cm^{-1} could not be resolved because of overlap with the band (699 cm^{-1}) from the aromatic ring on polystyrene (±4 cm^{-1}). As expected, after the linking reaction new bands were seen for the methoxysilyl-functionalized polystyrene at 1254 cm^{-1}, reflecting the Si−CH_3 bond, at 1083 cm^{-1} due to the presence of Si−OCH_3, and at 808 cm^{-1} for Si−O−C.[42]

MALDI−TOF MS. Analysis by MALDI−TOF MS provided additional characterization of the functionalized polymer (**7**). In the mass spectrum of the unfunctionalized polystyrene (**2**), shown in Figure 8a, each major peak was assigned to a homopolystyrene with a different number of repeating units [e.g., *sec*-Bu-$(C_8H_8)_{34}$−H·Ag$^+$, calcd monoisotopic mass 3703.1 Da, *m*/*z* observed = 3703.4]. The small unresolved peaks found between those for the polymer oligomers were fragment ions produced from metastable oligomer ions (i.e., oligomer ions fragmenting after leaving the ion source) which were mass separated by the reflectron analyzer. These artifacts were not observed above noise level when the spectrum was collected in the linear detection mode where oligomer and metastable fragment peaks overlap.[43] After the crossover reaction, peaks appeared in the spectrum at 54.0 Da intervals, as shown in Figure 8b, confirming the incorporation of butadiene units. The broadening of the peaks was due to overlapping of the isotopic distributions of two oligomers with different numbers of styrene and BD repeat units but similar overall masses. For example, the mass for ionized oligomer with 33 units of styrene and one unit of BD

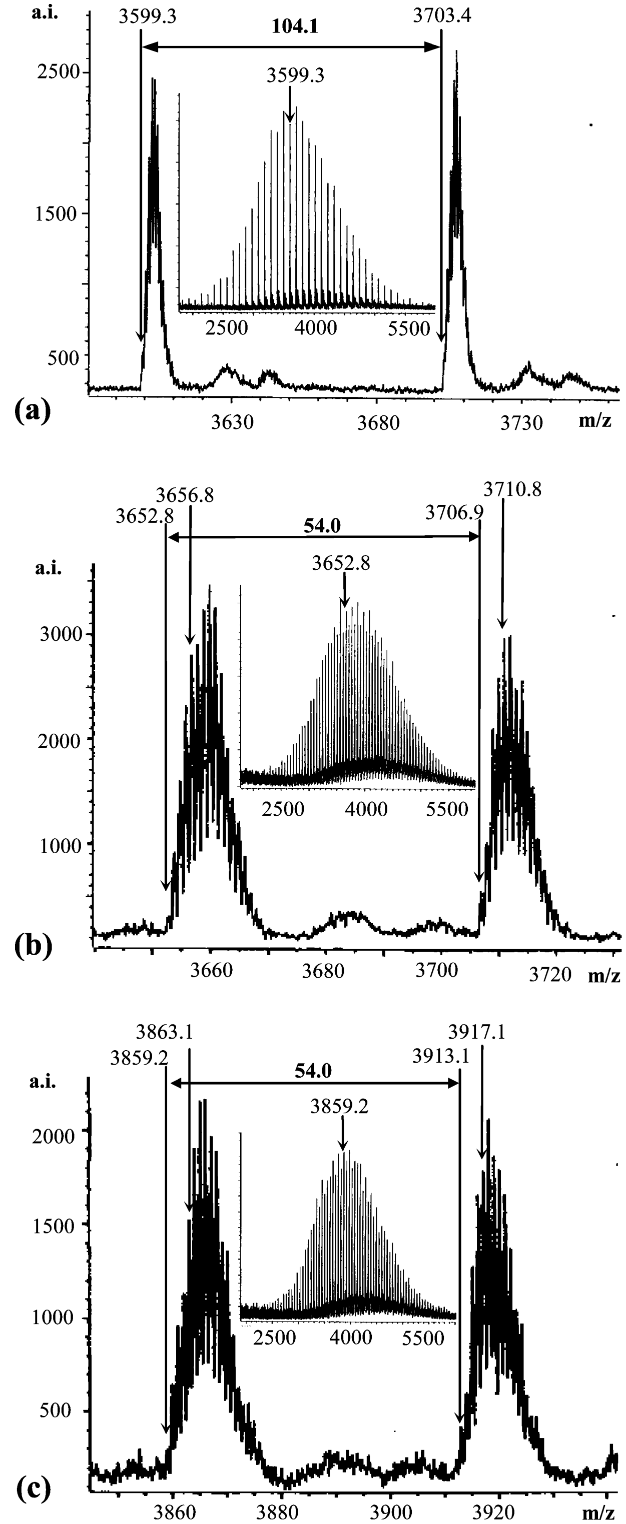


Figure 8. MALDI−TOF mass spectra for (a) the unfunctionalized polystyrene (**2**), (b) butadiene end-capped polystyrene (**4**), and (c) methoxysilyl-functionalized polystyrene-*b*-oligoBD (**7**).

Table 3. Characterization of Fractionated 4-Arm, Star-Branched Polystyrenes Prepared Using Two Methods

samples	method	$M_{n(arm)}{}^{a}$ (g/mol)	$M_{n(star)}{}^{a}$ (g/mol)	M_w/M_n	f^{b}	$[\eta]_{star}{}^{c}$ (dL/g)	$g'^{\,d}$	$T_g{}^{e}$ (°C)
4-arm	methoxysilyl groups	3900	15 500	1.02	3.97	0.089	0.78	78
4-arm	chlorosilyl groups	4100	16 300	1.02	3.98	0.090	0.76	77

[a] SEC measurement coupled with light scattering (±5%). [b] The degree of branching; $f = M_{n(star)}/M_{n(arm)}$. [c] Determined in toluene at 30 °C (±0.005). [d] Branching factor; $g' = [\eta]_{star}/[\eta]_{linear}$ (±0.04), $[\eta]_{linear} = 1.46 \times 10^{-4}M^{0.69}$ (ref 46). [e] Measured at a heating rate of 10 °C/min using DSC (±1 °C).

[i.e., *sec*-Bu-$(C_8H_8)_{33}-C_4H_7\cdot Ag^+$, calcd monoisotopic mass 3653.1 Da, *m*/*z* observed = 3652.8] was similar to that for the oligomer with 32 units of styrene and three units of BD [i.e., *sec*-Bu-$(C_8H_8)_{32}-C_{12}H_{19}\cdot Ag^+$, calcd monoisotopic mass 3657.1 Da, observed as part of *m*/*z* 3656.8 in the isotope cluster]. Counting of the peaks in the isotopic distribution observed in the spectrum and comparing it to the theoretical number of peaks of the two convoluted theoretical isotopic distributions verifies the overlapping of the two products. Similarly, the peaks centered around 3707 Da in Figure 8b are composed of overlapping peaks for oligomer molecules with 33 units of styrene and two units of BD [i.e., *sec*-Bu-$(C_8H_8)_{33}-C_8H_{13}\cdot Ag^+$, calcd monoisotopic mass 3707.1 Da, *m*/*z* observed = 3706.9] and oligomer molecules with 32 units of styrene and four units of BD [i.e., *sec*-Bu-$(C_8H_8)_{32}-C_{16}H_{25}\cdot Ag^+$, calcd monoisotopic mass 3711.2 Da, observed as part of the *m*/*z* 3710.8 in the isotope cluster]. Thus, it was concluded that the number of butadiene units attached to the poly(styryl)lithium ranged from one to four, with isotope patterns suggesting that 3BD > 1BD and 2BD > 4BD, which qualitatively agrees with the ^{1}H NMR results.

The MALDI−TOF mass spectrum after methoxysilyl functionalization is shown in Figure 8c. The peak position of a methoxysilyl-functionalized oligomer [e.g., *sec*-Bu$-(C_8H_8)_{33}-C_4H_6-C_7H_{19}Si_2O_3\cdot Ag^+$, calcd monoisotopic mass 3859.2 Da, observed as *m*/*z* 3859.2] increased by 206.4 *m*/*z* units relative to that of the corresponding butadiene-functionalized oligomer [e.g., *sec*-Bu$-(C_8H_8)_{33}-C_4H_7\cdot Ag^+$, calcd monoisotopic mass 3653.1 Da, *m*/*z* observed = 3652.8], which was consistent with the theoretical mass shift of 206.1 Da expected if a terminal hydrogen (1.0 Da) was replaced by the $C_7H_{19}Si_2O_3$ end group (207.1 Da). It should be noted that the masses of a methoxysilyl-functionalized oligomer and a butadiene-functionalized oligomer with two additional polystyrene units are similar [e.g., *sec*-Bu$-(C_8H_8)_{33}-C_4H_6-C_7H_{19}Si_2O_3\cdot Ag^+$, calcd monoisotopic mass 3859.2 Da, and *sec*-Bu$-(C_8H_8)_{35}-C_4H_6-H\cdot Ag^+$, calcd monoisotopic mass 3861.2 Da]. Because of the previously mentioned overlapping of isotopic clusters caused by the distribution in butadiene units and the fact that hydrogen-terminated and methoxysilyl-terminated oligomers differ by only two mass units, the linear MALDI−TOF detection mode and calculated average masses would be insufficient to unequivocally identify the products. Using the reflectron mode, sufficient isotopic resolution and signal intensity were obtained for identifying the peak containing the lowest-mass isotopes and thus positively identifying the correct polymer end group.

Peaks in the mass spectrum for the coupled polymer with high molecular weight (M_n = 10 800 g/mol by GPC) could not be resolved from the baseline noise because the amount of coupled polymer was small (6 wt %), and its ionization efficiency was poorer than that of the lower molecular weight arm polymer. Because of overlapping isotope distributions, it could not be determined from the mass spectra if there were small amounts of unreacted butadiene terminated polymer in the methoxysilyl-functionalized polymer sample. However, it is significant to note that no unfunctionalized polymer or other side reaction products were observed in the mass spectra shown in Figure 8b,c.

Linking Reaction and Characterization of 4-Arm Star PS. Typically the reaction of chlorosilane linking agents with poly(styryl)lithiums that have been crossed over to butadiene (PS-*b*-oligoBDLi) is completed in 2 days or less.[44] In contrast, the linking reaction of the methoxy-end-functionalized PS with PS-*b*-oligoBDLi required 1 week, even though the butadienyllithium chain ends have reduced steric hindrance compared to PSLi. The sluggishness of the linking reaction is due to the lower reactivity of the methoxy moieties as compared to the corresponding chlorides. Results of the characterization of the fractionated 4-arm star PS prepared using methoxysilyl end groups are compared in Table 3 with those for a fractionated 4-arm star PS prepared using 1,2-bis(dichloromethylsilyl)ethane and poly(styryl)lithium capped with 2 BD units (on average) by the traditional method.[44] The functionality of the 4-arm, star-branched polystyrene prepared using methoxysilyl groups almost reached 4.0 and also compared well with the functionality of the 4-arm, star-branched polymer prepared using chlorosilyl groups. Thus, the methoxysilyl groups give good linking efficiency with organolithiums. The values of the branching parameter *g*′ for characterizing the branching of a star polymer were determined for both polymers. The theoretical value of *g*′ for a regular, 4-armed, star-branched polymer in good solvent according to the model of Zimm and Kilb[45] is 0.79. The experimentally determined *g*′ values were similar for the two 4-arm, star-branched polystyrenes, 0.78 and 0.76, and these values agreed with the theoretical value within the experimental uncertainty (±0.04). Therefore, the 4-arm star PS synthesized by the new synthetic route exhibited properties very similar to those of the 4-arm star PS made using the conventional linking reaction.

Conclusions

A new method for linking reactions of polymeric organolithium compounds to form heteroarm (miktoarm) star-branched polymers has been demonstrated. This method involves the conversion of chlorosilyl groups to methoxysilyl groups by treatment with anhydrous methanol followed by precipitation into methanol. This procedure removes the requisite excess linking agent that is used to prevent dimeric and higher linking during the functionalization reaction. A procedure of this type is required when nonvolatile linking agents are used to obtain higher ultimate degrees of branching. Thus, polystyrene-*b*-oligo(butadienyl)lithium was functionalized with an excess of 1,2-bis(dichloromethylsilyl)ethane in benzene. In the absence of TEA, extensive linking reactions were observed during the conversion of chlorosilyl groups to methoxysilyl groups with methanol; in the presence of TEA, these reactions were minimized. The conversion of the chlorosilyl- to the methoxysilyl-functionalized polymer was determined to be quantitative by ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR. These analyses and SEC confirmed that the excess linking agent had been completely removed by the methanolysis and precipitation procedures. MALDI–TOF mass spectral analysis of the methoxysilyl-functionalized PS-*b*-oligoBD was consistent with the proposed structure and indicated the absence of other side reaction products. To demonstrate the effectiveness of these procedures, a 4-arm, star-branched polystyrene was prepared by treating the methoxysilyl-functionalized PS-*b*-oligoBD with excess PS-*b*-oligoBDLi. It was noted that this linking reaction was slower than an analogous model reaction performed using the normal procedures (freeze-drying to remove excess linking agent) with 1,2-bis(dichloromethylsilyl)ethane. The two routes produced 4-arm, star-branched polymers that were essentially indistinguishable. The greatest benefit of the new method will be found in its application to the synthesis of higher order, multibranched, miktoarm star polymers using the reaction of polymeric organolithium compounds.

Acknowledgment is made to the donors of The American Chemical Society Petroleum Research Fund for partial support of this research. Partial support from an Ohio Board of Regents challenge grant is also gratefully acknowledged. The authors are grateful to Chemetall Foote Corp. for samples of *sec*-butyllithium.

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MA049733K