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Synthesis and Characterization of Well-Defined, Regularly Branched Polystyrenes Utilizing Multifunctional Initiators

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ABSTRACT: A series of well-defined, long-branched polystyrenes (PS) of various architectures, but the same overall molecular weight, suited to the systematic study of branching effects, have been synthesized by anionic polymerization and characterized. Three end-branched, star-branched polystyrenes with 6, 9, and 13 end branches were synthesized with a trifunctional organolithium initiator; the synthesis of the 13-end molecule required a recently developed methoxysilyl functionalization and precipitation procedure to remove excess linking agent. In these architectures the number of branch points was fixed at four, while the number of chain ends varied. A 6-end, pom-pom (dumbbell-shaped) PS with two branch points was synthesized with a difunctional organolithium initiator. A regular 6-arm star polystyrene having one branch point was included to provide a comparison among three polymers, each having 6 ends, but having the number of branch points equal to 1, 2, or 4. The intrinsic viscosities and infinite dilution diffusion coefficients (and therefore the branching factors and hydrodynamic radii) decrease with increasing number of chain ends but do not vary monotonically with number of branch points. The values of T_g for the molecules reflect both the effects of tethering by junction points and increases in free volume due to the multiplication of chain ends as well as the presence of butadiene units used to facilitate linking.

Introduction

Over the past few decades, the physical properties of branched polymers have attracted considerable attention.[1−11] Branching in a polymer can result in solution,[12] surface,[13−16] and bulk properties[17−20] markedly different than those of its linear homologue. In these studies, the availability of well-defined branched polymers with controlled architectures and narrow molecular weight distributions is crucial to understand the branching effect.[9] One of the most powerful methods for the creation of such polymers has been anionic polymerization.[21]

In recent years the synthesis of the highly branched polymers with complex architectures having internal branch points has gone beyond the synthesis of regular star polymers using anionic polymerization. Specifically, highly branched polymers can be prepared by the "core-first" method using multifunctional initiators.[22−24] The general synthetic procedure for the core-first method is shown schematically in Scheme 1. First, a precursor polymer having multiple living end groups is created using the multifunctional initiator. Then the precursor can be reacted with an excess of a multifunctional electrophilic linking agent depending on the number of arms one desires to attach. The resulting precursor polymer end-capped with linking agent can be reacted with living arm polymer prepared using anionic polymerization. Furthermore, it is possible to prepare highly branched polymers using an end-linking reaction between a polymeric organolithium compound and a star precursor prepared with a multifunctional initiator and functionalized with an electrophilic linking agent.[22,25] The advantages of the multifunctional initiator approach are primarily a consequence of the fact that the star precursor retains the carbanionic living chain ends of the arms after the monomer is consumed. Unfortunately, attempts to prepare multifunctional initiators generally have resulted in the formation of insoluble, three-dimensionally associated species in hydrocarbon media[21,26−29] because of the tendency of chain ends to exist as associated species.

The core-first method has been used with a difunctional initiator to produce H-shaped,[25] pom-pom,[22] or dumbbell-shaped[30] polymers via anionic polymerization. Using sodium naphthalenide[25] as a difunctional initiator required the use of a polar medium such as tetrahydrofuran (THF) at low temperature (4 °C) to break the association of the initiator molecules, but these conditions led to a loss of microstructure control in the synthesis of polybutadienes. Another difunctional initiator has been prepared by the treatment of divinylbenzene with butyllithium. However, it was not effective for the synthesis of hyperbranched polymers using the core-first method.[26] Since the difunctional initiator could be contaminated by higher functionality initiator resulting from oligomerization of the divinylbenzene, the core precursor polymer created this way had a substantial polydispersity ($M_w/M_n = 1.2-4.1$). Recently, the reaction of high-purity *sec*-butyllithium with pure *m*-divinylbenzene at −79 °C in the presence of 10 mol % triethylamine was reported to result in an initiator with overall functionality of 1.98 and no traces of tri- and tetrafunctional impurities.[31] A similar reaction with pure *p*-divinylbenzene at 0 °C was reported to form a similar dilithium initiator with 96% difunctionality and 4% monofunctitionality.[32] Another simple, stable, reproducible difunctional initiator that is soluble in hydrocarbon media has been created using the titration of 1,3-bis(1-phenyethyl)benzene with butyllithium.[33−36] 1,1-Diphenylethylene and its analogues usually are classified as nonhomopolymerizable monomers.[37] Specifically, Quirk and Ma[35] produced a hydrocarbon-soluble difunctional initiator by the quantitative addition of 2 mol of *sec*-butyllithium (*s*-BuLi) to 1,3-bis(1-phenylethenyl)benzene and prepared polystyrene and polybutadiene

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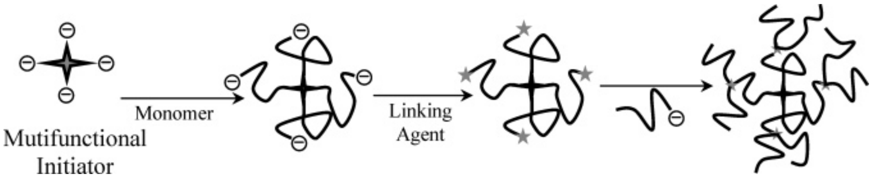
Scheme 1. General Synthetic Scheme Using the Core-First Method



having narrow, monomodal molecular weight distributions using the dilithium initiator in the presence of THF ([THF]/[Li] = 14−32) or lithium *sec*-butoxide ([LiOBu]/[difunctional initiator] = 1.1), respectively.

Quirk and Tsai[38] developed a novel hydrocarbon-soluble, trifunctional initiator by an extension of the quantitative addition chemistry of organolithium compounds to 1,1-diphenylethylene compounds.[37] The trifunctional initiator was prepared by the reaction of 3 mol of *sec*-butyllithium with 1,3,5-tris(1-phenylethenyl)benzene. Using this initiator, living 3-armed, star-branched polystyrene with a narrow, monomodal molecular weight distribution was prepared in the presence of THF ([THF]/[*sec*-BuLi] = 20), and its carbonation product exhibited a functionality close to 3. The g' value of the resulting 3-armed star polystyrene compared well to that of a 3-arm star-branched polymer made using 1,3,5-tris(1-phenylethenyl)benzene as a linking agent. Well-defined 3-arm star-branched polybutadiene could also be produced using the same initiator in the presence of lithium *sec*-butoxide ([*s*-BuLi]/[*s*-BuOLi] = 2).[37]

In the present work, a series of well-defined, highly branched polystyrenes of various architectures, but the same overall molecular weight, useful for the study of branching effects, have been synthesized by reactions between living arm polymers and appropriate chlorosilyl end-functionalized precursor polymers or methoxysilyl end-functionalized precursor polymers. The precursor polymers have been prepared using a difunctional or trifunctional initiator. In the end-branched polymers, the number of end branches was varied from 6 to 13 while the number of branching points was fixed at 4. Inclusion of other architectures in the series allows comparison among three polymers all having 6-end groups, but with the number of branch points varying from 1 to 4. Measurements of the intrinsic viscosities, hydrodynamics radii, and glass transition temperatures of these molecules of varying architecture revealed how each of these important properties varies with the details of the chain topology.

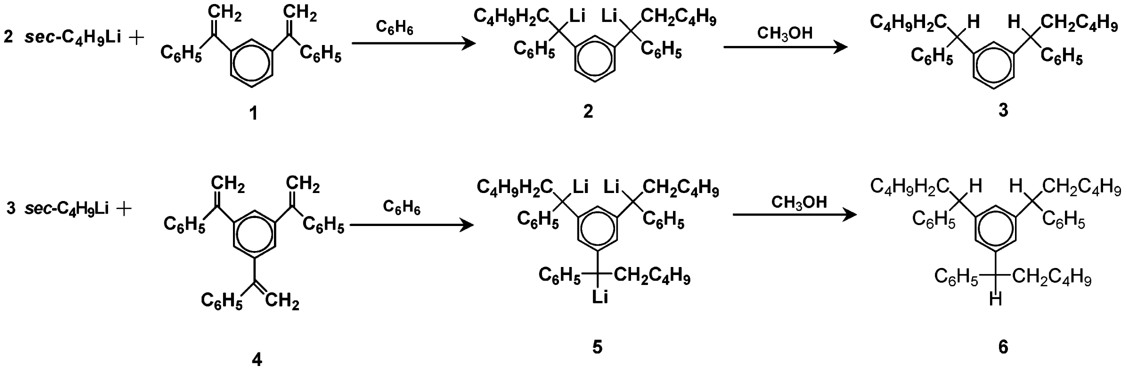
Experimental Section

Materials. Styrene (Aldrich, >99%), benzene (Fisher, >99%), and tetrahydrofuran (EMD Chemicals Inc., 99.8%) were purified as described previously.[39,40] The purification of the triethylamine (Aldrich, 99.5%) was carried out by stirring, degassing, and distilling from freshly crushed CaH_2 and then *n*-butyllithium. 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. Tetrachlorosilane (Aldrich, 99.998%) and methyltrichlorosilane (Aldrich, 99%) were purified by stirring and degassing over freshly crushed CaH_2 and then distilled. In each case the second one-third of the distillate was collected while both the first and third portions of the distillate were discarded. 1,2-Bis(trichlorosilyl)ethane (Aldrich, 98%) was purified by vacuum distillation at 120 °C. Methanol (Fisher, 99.8%) was dried by stirring with freshly crushed CaH_2 and, after degassing, was distilled into a storage reservoir with 4 Å molecular sieves. Solutions of *sec*-butyllithium (Chemetall Foote Corp., 12.16 wt % in cyclohexane) were used for initiation after double-titration analysis.[41] 1,3,5-Tris(benzoyl)benzene, mp 113−115 °C [lit.[38] mp 113−114 °C], was synthesized in 56% yield by a Friedel−Crafts reaction of 1,3,5-benzenetricarbonyl trichloride (Aldrich, 98%) with aluminum chloride in benzene followed by recrystallization in methanol. 1,3,5-Tris(1-phenylethenyl)benzene and 1,3-bis(1-phenylethenyl)benzene were synthesized from purified 1,3,5-tris(benzoyl)benzene and 1,3-bis(benzoyl)benzene, respectively, via the Wittig reagent[42] generated from methyltriphenylphosphonium iodide and methyllithium in THF using a procedure analogous to that reported by Schulz and Höcker.[43] Silica gel chromatography with toluene as the eluent was used to purify both crude products. Recrystallization in methanol produced pure samples of **1**: mp 46−48 °C [lit.[43] mp 46], 300 MHz ^1H NMR ($CDCl_3$): δ 7.36 (m, 14 H, arom C*H*), 5.47 ppm (m, 4 H, $=CH_2$). The same recrystallization method was also used to purify **4**: mp 90−91 °C [lit.[38] mp 90−91 °C], 300 MHz ^1H NMR ($CDCl_3$): δ 7.36 (m, 18 H, arom C*H*), 5.47 ppm (m, 6 H, $=CH_2$). Each white crystalline product (**1** and **4**) showed only one peak by HPLC analysis, and the carbonyl absorption at 1656 cm^{-1}, characteristic of the ketone precursor, was absent from the FTIR spectrum of each product.

Initiatior Preparations. The addition reactions of *sec*-butyllithium with **1** or **4** were performed in an argon atmosphere glovebox. The argon atmosphere was purified by continuous recirculation through towers of molecular sieves and manganous oxide as described by Brown et al.[44] To obtain precise stoichiometric control, *sec*-butyllithium was added stepwise to a benzene solution of **1** (ca. 5.0×10^{-3} mol, 3.29 mL) or **4** (ca. 1.6×10^{-2} mol, 11.49 mL) at room temperature. Following each addition, a sample was removed from the reaction mixture, quenched with degassed methanol, and analyzed by SEC using a UV detector to monitor the extent of the addition reaction.[38] The concentrations of the difunctional and trifunctional initiator solutions were 2.3×10^{-2} and 1.98×10^{-2} M, respectively; these solutions were distributed into calibrated ampules and sealed under high vacuum, using previously described procedures.[35,38]

Polymerizations. All polymerizations were carried out using standard high-vacuum techniques.[45] The precursor polystyrene for the 6-end pom-pom polystyrene was prepared by anionic polymerization of styrene (10.1 g, 9.7×10^{-2} mol) in benzene (160 mL) using dilithium initiator **2** (1.1×10^{-3} mol, 2.3×10^{-2} M in 46.6 mL of benzene) in the presence of THF (0.0438 mol, [THF]/[RLi] = 20). After 90 min of reaction in an ice−water bath (8 °C), the reaction solution with α,ω-poly(styryl)lithium was slowly added into another solution containing a large excess of tetrachlorosilane ([$SiCl_4$]/[Li] > 200) in order to convert the anionic living ends to trichlorosilyl end groups. The excess linking agent was removed from the desired star polymer precursor by freeze-drying a benzene solution of the products on a high-vacuum line.[46] The living 3-armed star polystyrene precursors for the targeted 6-, 9-, and 15-end branched polymers were prepared from the trilithium initiator using a similar procedure as described for the 6-end pom-pom polymer. Each polymerization was monitored by UV−vis spectroscopy via a UV cell attached to the reactor. Each precursor polymer was end-capped with a large excess of the appropriate linking agent: methyltrichlorosilane ([$SiCH_3Cl_3$]/[Li] > 200) for the 6-end branched, tetrachlorosilane ([$SiCl_4$]/[Li] > 200) for the 9-end branched, and 1,2-bis(trichlorosilyl)ethane [$Cl_3(CH_3)SiCH_2CH_2Si(CH_3)Cl_3$]/[Li] > 50) for the targeted 15-end branched polystyrene. The precursor polymer for the targeted 15-end branched polystyrene was treated with anhydrous methanol in the presence of TEA to

Scheme 2. Preparation of Difunctional Initiator (2) from 1,3-Bis(1-phenylethenyl)benzene (1) and Trifunctional Initiator (5) from 1,3,5-Tris(1-phenylethenyl)benzene (4) by the Titration with *sec*-Butyllithium and the Methanolysis of Its Initiators



convert the silyl chlorides into methoxy groups.[47] The precursor polystyrene was precipitated into anhydrous methanol in a drybox to separate the methoxysilyl functionalized precursor from the transformed excess linking agent according to a recently developed method.[47] The living arm polystyrenes for each branched polymer were synthesized by the *sec*-butyllithium-initiated polymerization of styrene in benzene, and the ends were then converted to butadienyllithiums using 2 equiv of purified butadiene for each equivalent of poly(styryl)lithium to reduce the steric hindrance during the linking reaction.[48,49] The crossover reaction was monitored using UV−vis spectroscopy.

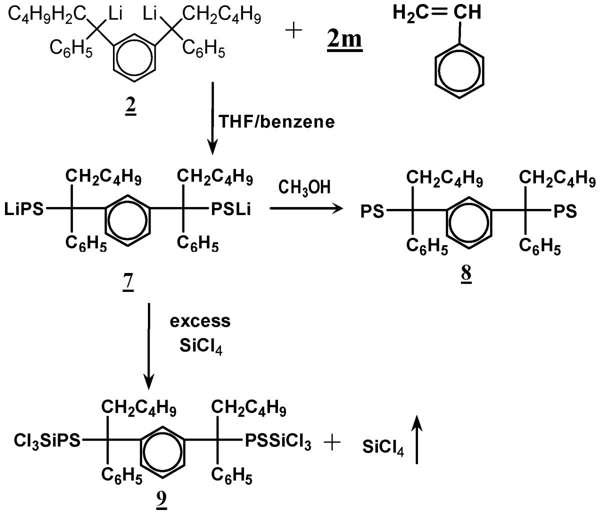
Linking Reactions. The linking reactions between the precursor polymers with chlorosilyl functionalized end groups and excess polystyrene-*b*-oligo(butadienyl)lithium (PS-*b*-oligoBDLi) ([PLi]/[SiCl] = 1.2−1.4) were carried out in benzene for 1 week at 40 °C in the presence of triethylamine ([Et_3N]/[PLi] = 20). For an end-branched star PS with a target of 15 ends, the linking reaction between the precursor polymer with methoxysilyl-functionalized end groups and excess PS-*b*-oligoBDLi ([PLi]/[$SiOCH_3$] = 1.3) was continued for 3 weeks. After 1 or 3 weeks, all end-branched polystyrenes were separated from excess arm polystyrene by fractionation using toluene as the good solvent and methanol as the poor solvent.[50] For comparison, linear and 6-arm star polystyrenes with overall molecular weights matching those of the newly produced branched polystyrenes were also prepared using conventional approaches.[48]

Characterization. Size-exclusion chromatographic (SEC) analyses of the titration products of initiators were performed at a flow rate 1.0 mL/min in THF at 30 °C using a Waters HPLC component system (RI and Hewlett-Packard 1040 diode array detector) equipped with ultra-microstyragel columns (50 and 100 Å). Absolute molecular weights of the precursor polystyrenes, the arm polystyrenes, and branched polystyrenes were determined by using a SEC−RI−viscometer−LS system. The system consisted of a gel permeation chromatograph (Waters 510), a differential refractometer (Waters 410), a differential viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ 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 ^{1}H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded on a Varian 300 MHz spectrometer using $CDCl_3$ as the solvent at room temperature. To determine the number of butadiene (BD) units on the arm polymers for each branched polymer before and after the butadiene end-capping, mass spectra were obtained on a Bruker Daltonics Reflex III matrix-assisted laser desorption ionization time-of-flight (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. To determine the intrinsic viscosities of each branched polystyrene, toluene solutions at 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 35 °C. The intrinsic viscosity was determined by simultaneously extrapolating to zero concentration using the Huggins and Kraemer equations and averaging the values of the intercepts.[51] The dynamic light scattering measurements were made using a Brookhaven Instruments Corp. package which includes a computer-controlled BI-200SM goniometer, BI-9000AT correlator, and an EMI-9863 photomultiplier tube for photon counting. A Melles Griot 35 mW He−Ne laser was used as light source (632.8 nm). A cylindrical glass scattering cell with diameter of 12 or 27 mm was placed in the center of a thermostated bath (±0.01 °C) with decahydronaphthalene used for refractive index matching. The measurements were carried out at a 90° scattering angle at 25 °C. The scattered light was evaluated by an autocorrelator with 80 channels and the correlation function determined using the Non-Negatively Constrained Least Squares (NNLS) algorithm. Solutions of nine different concentrations were prepared in toluene (99.5%, spectrophotometric grade, Aldrich) for each polymer. Before light scattering measurements, each solution was filtered with a poly(tetrafluoroethylene) 0.2 μm filter three times into a thoroughly clean, dust-free sample cell. Glass transition temperatures were measured using a Perkin-Elmer PYRIS Diamond differential scanning calorimeter. Samples weighing 4−6 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.[47]

Results and Discussion

Initiator Preparation and Stoichiometric Control. The preparation of the dilithium initiator (**2**) and trilithium initiator (**5**) by the gradual addition of 2 mol of *sec*-BuLi to 1,3-bis(1-phenylethenyl)benzene (**1**) or of 3 mol *sec*-BuLi to 1,3,5-tris(1-phenylethenyl)benzene (**4**), respectively, in benzene requires careful attention to stoichiometric control (see Scheme 2). The addition products from the reaction of *sec*-BuLi with **1** or **4** in benzene were monitored by SEC. After the addition of the stoichimetric amount (100 mol %), only one SEC peak was observed for each initiator (**2** and **5**). The structures of the dilithium adduct (**2**) and trilithium adduct (**5**) were confirmed by ^{1}H NMR analyses of the products isolated after methanol quenching of the solution of **2** or **5**.[35,38] If the precursors for the difunctional initiator and trifunctional initiator were stoichiometrically titrated by *sec*-Bu initiator, the values of the

Scheme 3. Anionic Synthesis of α,ω-Poly(styryl)lithium (7) Initiated by Difunctional Initiator (2) and End-Functionalization of α,ω-Poly(styryl)lithium (7) with Tetrachlorosilane



ratios of the integrals for the two methyl protons from the initiator at δ 0.7−0.95 ppm and the tertiary 1,1-diphenyalkyl CH protons at δ 3.9−4.05 ppm should be 6.[35,38] The calculated integral ratios from the ^{1}H NMR spectra of the methanolysis products (**3** and **6**) for the difunctional initiator and the trifunctional initiator were 5.9 ± 0.1 (85.5/14.5) and 6.0 ± 0.1 (85.7/14.3), respectively. Thus, the values of both ratios were equal to the target value to within experimental uncertainty.

Preparation of Precursor Polystyrenes from 2 and 5 and End-Capping with Linking Agents. Previous studies[35,38] using the dilithium initiator (**2**) and trilithium initiator (**5**) suggested that inefficient initiation resulted when the initiator molecules were strongly associated with one another. To promote efficient initiation, this strong association or cross-association of organolithium chain ends can be reduced by the addition of a Lewis base such as THF, since it is known that THF and other Lewis bases break up highly aggregated organolithiums either to aggregates of lower degree of aggregation or to unassociated species.[45,53,54] However, the amount of THF added should be minimized because proton transfer by the reaction between an organolithium compound and THF forms an ethylene molecule and a lithium enolate of acetaldehyde and results in the deactivation of a living end.[21,55] Therefore, an amount of THF corresponding to [THF]/[RLi] = 20 was added before the crossover reaction from either **2** or **5** to styrene. Previous studies have established that 14−32 equiv of THF are effective for eliminating the effects of chain end association on initiation rates for the multifunctional initiators.[35,38,54]

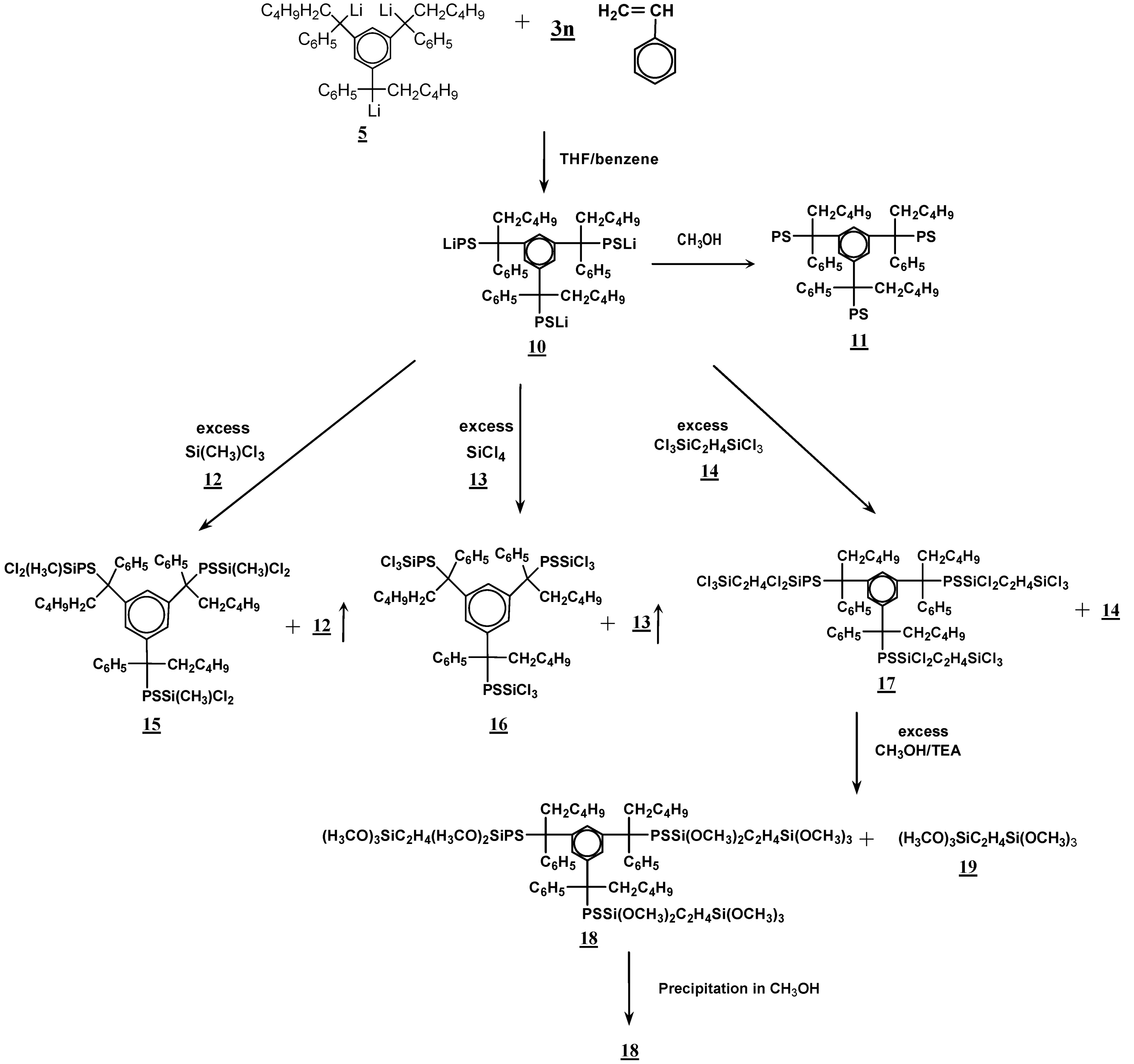
The crossover reactions from **2** and **5** with styrene to form poly(styryl)lithium active centers, presented in Schemes 3 and 4, were monitored by UV−vis spectroscopy as described previously.[35,38] When styrene monomer was added to a solution with initiator **2** or **5**, the decrease in the absorbance of the initiators, **2** and **5** at 480 nm,[35,38] and the appearance of the poly(styryl)lithium absorbance at 332 nm were monitored. The polymerization was completed after 90 min in an ice−water bath. For the bis[poly(styryl)lithium] precursor, **7** (see Scheme 3), of the 6-end pom-pom (dumbbell-shaped) polystyrene, the SEC chromatogram [curve (1) in Figure 1] of the product of the polymerization in the presence of THF and methanolysis, **8**, exhibited a monomodal peak. The SEC chromatogram [curve (1) in Figure 2] of the product, **11** (see Scheme 4), after the methanolysis of the tris[poly(styryl)lithium], **10**, for the 6-end, 9-end, and targeted 15-end branched polymers showed a small peak next to the big peak corresponding to 3-armed star-branched polystyrene. The retention volume corresponding to the maximum of the small peak agrees with the retention volume expected for the arm polystyrene. Thus, the small peak probably is due to the existence of a small amount of *sec*-BuLi in the initiator mixture, and the free "arm" resulting from the presence of this *sec*-BuLi accounted for about 5 wt % of the total product.

The molecular weights of the precursor polymers, **8** and **11**, prepared in the presence of THF, after methanolysis, are listed in Table 1. The observed number-average molecular weight of the precursor for the 6-end pom-pom polymer was in good agreement with the molecular weight calculated on the basis of the initiator stoichiometry. The molecular weight of the 3-arm star precursor was 15% larger than the calculated molecular weight due to the presence of excess *sec*-BuLi, estimated from the area of the small peak in the SEC chromatogram [see curve (1) in Figures 2 and 3] to be of the order of 5 wt %. The observed narrow molecular weight distributions show that the rate of initiation is competitive with or faster than the rate of propagation.[21] Thus, the initiators **2** and **5** are efficient and sufficiently reactive in the presence of THF to polymerize styrene to form the well-defined precursor polymers **7** and **10**.

After completion of the polymerization, the living precursor for each branched polymer was end-capped using an excess of the corresponding linking agent. To make the 6-end pom-pom polystyrene, a solution with α,ω-poly(styryl)lithium, **7**, prepared using difunctional initiator **2**, was slowly added in a drybox into a solution having a large excess of tetrachlorosilane ([$SiCl_4$]/[Li] > 200) in order to convert the anionic living ends to trichlorosilyl end groups (**9**). Curve (2) in Figure 1 presents the SEC chromatogram after freeze-drying of the end-capped precursor polystyrene for the 6-end pom-pom, **9**. The small bump at retention volume of 20.3 mL in curve (2) corresponds to a small amount of coupled product with more than twice the M_n of the precursor polymer (M_n = 36.0 kg/mol). The coupled polymer comprised less than 6 wt % of the total polymer based on comparison of the areas of the various peaks in the SEC chromatogram. The main peak at 21.4 mL corresponds to the functionalized precursor polymer, **9**, in Scheme 3.

To prepare the precursor polystyrenes (**15**−**17**) for each end-branched star polymer, the solution with tris[poly(styryl)lithium], **10**, was added slowly, after 90 min of polymerization, into three solutions, each containing a different linking agent (see Scheme 4): methyltrichlorosilane (**12**) for the 6-end branched polymer, tetrachlorosilane (**13**) for the 9-end branched polymer, and 1,2-bis(trichlorosilyl)ethane (**14**) for the targeted 15-end branched polymer. After these additions, the reaction mixtures no longer had the dark red color characteristic of **10,** but rather were colorless, which indicated that the anionic living ends had been converted to chlorosilyl end groups. It was known that the methyltrichlorosilane linking agent used to synthesize the functionalized 6-end branched polystyrene precursor and the tetrachlorosilane linking agent used to synthesize the func-

Scheme 4. Anionic Synthesis of Tris[poly(styryl)lithium] (10) Initiated by Trifunctional Initiator (5), the End-Functionalization of 10 with Three Different Linking Agents (12−14), and the Methoxyl-Functionalization of the ω,ω,ω-Chlorosilyl-Functionalized, 3-Arm Polystyrene (17)



tionalized 9-end branched polystyrene precursor can be easily removed by the freeze-drying method because of their low boiling points.[47] Curve (2) in Figure 2 is the SEC chromatogram of the precursor polystyrene (**15**) for the 6-end branched polystyrene after the chlorosilyl functionalization with methyltrichlorosilane and freeze-drying. The small peak at 20.6 mL retention volume before the big peak is due to the presence of coupled precursor polymer formed during functionalization. For the targeted 15-end branched polystyrene, excess 1,2-bis(trichlorosilyl)ethane (**14**) was used to end-functionalize the tris[poly(styryl)lithium] in order to attach five chlorosilyl groups at the end of each of the three arms of the 3-arm precursor polystyrene (**17**). Chlorosilane linking agents with more than one silicon such as 1,2-bis(trichlorosilyl)ethane (**14**) have such high boiling points that they cannot be removed effectively by distillation or freeze-drying. Curve (2) in Figure 3 is the SEC chromatogram of the ω,ω,ω-pentachlorosilyl-functionalized, 3-arm star polystyrene (**17**) and excess 1,2-bis(trichlorosilyl)ethane (**14**) after end-functionalization and freeze-drying. The chromatogram shows a small peak due to the coupled polymer at 20.6 mL retention volume next to the main peak, another small peak due to the linear polystyrene from excess *sec*-BuLi at 22.7 mL, and a new peak at 27.7 mL. The new peak at 27.7 mL corresponds to the excess linking agent (**14**) which remained with the functionalized polymer. This excess 1,2-bis(trichlorosilyl)ethane was removed using a new method recently developed by our group.[47] The solution with the ω,ω,ω-chlorosilyl-functionalized, 3-arm star polystyrene, **17**, and excess 1,2-bis(trichlorosilyl)ethane, **14**, was treated with anhydrous methanol. Before the treatment, triethylamine was added to scavenge the hydrochloric acid byproduct of the reaction to eliminate unwanted side reactions that can be caused by the hydrochloric acid.[47] The SEC chromatogram (3) in Figure 3 is for the precursor (**18**) for the 13-end branched PS after methoxysilyl functionalization and precipitation. The peak that had appeared in SEC

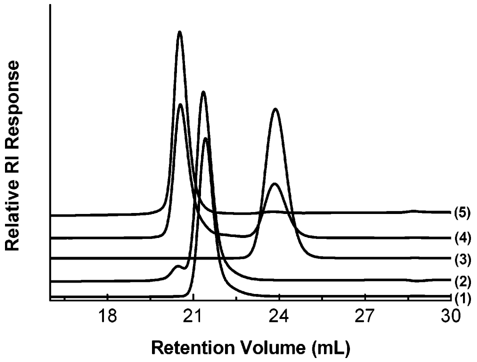


Figure 1. SEC chromatograms for various stages of the synthesis of the 6-end pom-pom polystyrene: curve (1), precursor polystyrene (**7**) before end-capping with excess tetrachlorosilane; curve (2), after freeze-drying of the end capped precursor polystyrene with excess tetrachlorosilane; curve (3), arm PS-*b*-oligoBD after end-capping with BD units; curve (4), after 1 week linking reaction between α,ω-chlorosilyl-functionalized polystyrene and PS-*b*-oligoBDLi; curve (5), after fractionation.

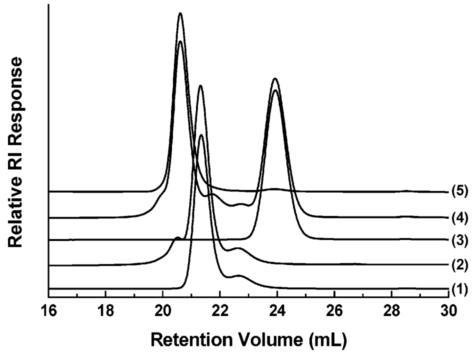


Figure 2. SEC chromatograms for various stages of the synthesis of the 6 end branched polystyrene: curve (1), three-armed star polystyrene before the end-capping with excess methyltrichlorosilane; curve (2), after the freeze-drying of the mixture of end capped precursor polystyrene and excess methyltrichlorosilane; curve (3), arm PS-*b*-oligoBD after end-capping with BD units; curve (4), after 1 week linking reaction between ω,ω,ω-dichlorosilyl-functionalized polystyrene and PS-*b*-oligoBDLi; curve (5), after fractionation.

Table 1. Molecular Weight Characterization of Precursor Polystyrenes for Each Branched Polystyrene

	precursor PS			
polymer	M_n (calcd)	$M_n{}^a$ (g/mol)	$M_w{}^a$ (g/mol)	$M_w/M_n{}^a$
6-pom	18 000	18 200	18 400	1.01
6-branch	15 000	18 100	18 500	1.02
9-branch	15 000	17 700	18 200	1.03
13-branch	15 000	17 700	18 200	1.03

[a] Determined by SEC coupled with light scattering (±5%).

chromatogram (2) of Figure 3 at a retention volume of 27.7 mL is no longer seen in chromatogram (3). It has been shown previously that the functionalization from chlorosilyl into methoxysilyl goes to completion.[47]

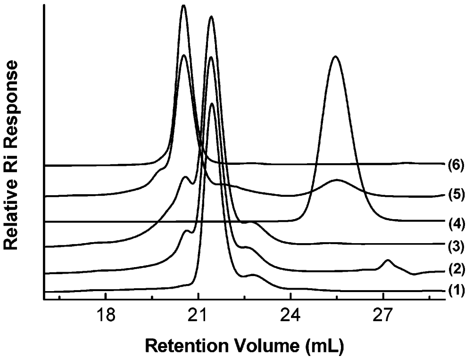


Figure 3. SEC chromatograms for various stages of the synthesis of the 13-end branched polystyrene: curve (1), three-armed star polystyrene before end-capping with excess 1,2-bis(trichlorosilyl)ethane; curve (2), after freeze-drying of end capped precursor polystyrene with excess 1,2-bis(trichlorosilyl)ethane; curve (3), ω,ω,ω-methoxysilyl-functionalized polystyrene after functionalization and precipitation into anhydrous methanol with TEA; curve (4), arm PS-*b*-oligoBD after end-capping with BD units; curve (5), after 3 weeks linking reaction between ω,ω,ω-methoxysilyl-functionalized polystyrene and PS-*b*-oligoBDLi; curve (6), after fractionation.

Preparation of Living Arm Polystyrenes and Linking Reactions. Poly(styryl)lithiums (**20** in Scheme 5) for the arms to be attached to the linear and star-branched polystyrene precursors were synthesized by the *sec*-butyllithium-initiated polymerization of styrene in benzene. An aliquot was removed from the reactor and terminated with methanol (**21**) for SEC analysis. The molecular weights of the arm polystyrenes were varied from 6100 g/mol for 6-arm star polystyrene to 1200 g/mol for the targeted 15-end branched polystyrene to achieve the same overall molecular weight for each molecule in the series (see Table 2). Each arm was then end-capped using 2 equiv of butadiene to convert the chain ends to less-hindered butadienyllithium chain ends (**22**).[49] The crossover reaction was investigated using UV−vis spectroscopy. In the UV−vis absorbance spectra, the poly(styryl)lithium (PSLi) peak at 334 nm disappeared, and a new peak at 290 nm, corresponding to poly(butadienyl)lithium (PBDLi), was observed after adding the butadiene. Correspondingly, the solution changed from dark red (PSLi) to light yellow (PBDLi). This indicates that the poly(styryl)lithium was completely end-capped by the butadiene. An aliquot of each end-capped polymer was terminated with methanol (**23**) and analyzed by SEC, NMR, and MALDI−TOF mass spectrometry. The molecular weights of the arm polystyrenes for each branched polymer increased slightly after the crossover reaction (see Table 2). Curve (3) in Figures 1 and 2 and curve (4) in Figure 3 are the chromatograms of PS-*b*-oligo(butadiene)s (PS-*b*-BDs) with different molecular weights, **23**, in Scheme 5.

The mass spectra of the arm polymer for the 6-end pom-pom polymer before and after the crossover reaction are shown in Figure 4. In the mass spectra of the unfunctionalized arm polystyrene (**21**), shown in Figure 4a,b, each major peak was assigned to a homopolystyrene with a different number of repeating units [e.g., *sec*-Bu-$(C_8H_8)_{27}$-H·Ag^+, calcd monoisotopic mass 2974.7 Da, *m/z* observed = 2974.7]. In Figure 4b, the first major peak was assigned to the unfunctionalized arm polystyrene containing 27 units of styrene, and the second major peak was assigned to the arm polystyrene having 28 units of styrene. After the crossover reaction (**23**), peaks appeared in the spectrum separated by 54.0 *m/z* units, as shown in Figure 4c, confirming the incorporation of butadiene units. The first big peak in the inset in Figure 4d was assigned to arm precursors containing 27 units of styrene and one unit of BD [i.e., C_4H_9-$(C_8H_8)_{27}$-C_4H_7·Ag^+, calcd monoisotopic mass 3028.7 Da, *m/z* observed = 3029.1], and the smaller peak at higher *m/z* was assigned to arm precursors also having 27 polystyrene units, but having two units of BD [i.e., C_4H_9-$(C_8H_8)_{27}$-C_8H_{13}·Ag^+, calcd monoisotopic mass 3082.8 Da,

Scheme 5. Anionic Synthesis of Poly(styryl)lithium (20) Arms for Each Branched Polymer, the Crossover Reaction of 20 with Two Units of Butadiene, and the Linking Reactions between the Precursor Polymers (9, 15, 16, and 18) and Excess PS-*b*-oligo(butadienyl)lithium (22)

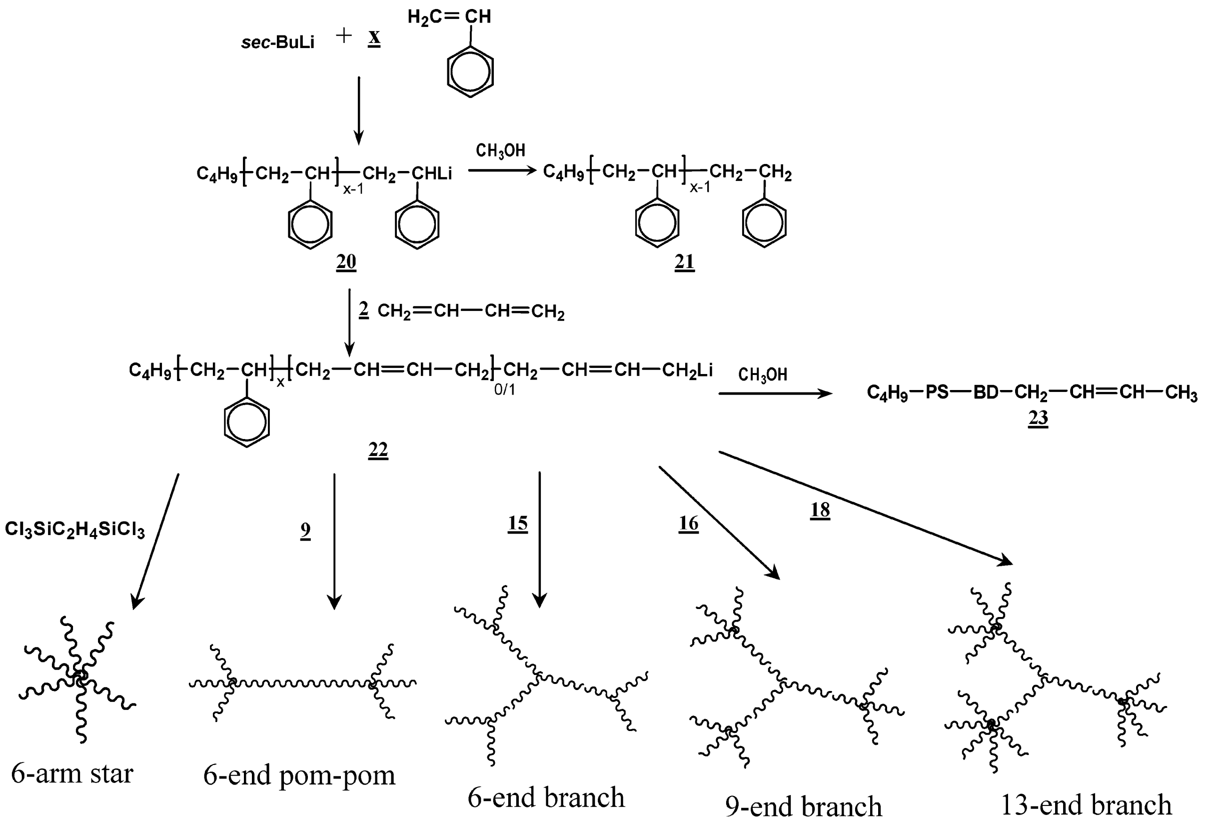


Table 2. Molecular Weight Characterization and Butadiene Unit Determination for Arm Polystyrenes before and after the Butadiene End-Capping

	before end-capping (PS)		after end-capping (PS-*b*-BD)			
					no. BD units	
arm polymer	M_n[a] (g/mol)	M_w/M_n[a]	M_n[a] (g/mol)	M_w/M_n[a]	NMR[b]	mass[c]
6-star	6100	1.02	6200	1.02	1.1	1.3
6-pom	3500	1.03	3800	1.02	2.1	1.7
6-branch	2900	1.03	3000	1.03	1.6	1.5
9-branch	2300	1.04	2400	1.03	1.4	1.5
13-branch	1200	1.04	1300	1.05	1.3	1.2

[a] Determined by SEC coupled with light scattering (see ref 49) (±5%). [b] Determined by ^{1}H NMR (300 MHz) (±5%). [c] Determined by MALDI−TOF mass spectrometry (see ref 49) (±2%).

m/z observed = 3083.2]. Furthermore, there was no peak corresponding to arm precursor containing 28 units of styrene with no BD units [i.e., C_4H_9-$(C_8H_8)_{28}$-H·Ag$^+$, calcd monoisotopic mass 3078.8 Da, not observed] between the two peaks. This meant that the number of butadiene units attached to each poly(styryl)lithium was exactly one or two. The average number of BD units per arm was estimated from the relative intensities of the two peaks, and the values are summarized in Table 2 where they are compared with the values determined by ^{1}H NMR. After the crossover reaction, new peaks assignable to the protons on the double bonds of the BD units appeared in the ^{1}H NMR spectra of all arm polymers in the region δ 4.8−5.6 ppm. This region included peaks for the protons from −C***H***=C***H***− units in the oligomeric butadiene chain having *cis*-1,4- and *trans*-1,4-microstructures 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 the resonances 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 peaks in the δ 5.03−5.6 ppm region. In the spectra, the peak assignable to the CH$_2$= protons in 1,2-microstructural units was not separated from the peak for the −CH= protons in the *cis*-1,4-, *trans*-1,4-, and 1,2-microstructural units. Allowing for the overlap of the peaks, the best estimate of the amount of 1,2-microstructure was 2−7 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− moieties in 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 results of this NMR determination of the butadiene units per molecule for each arm polymer were in good agreement with those of MALDI−TOF mass spectrometry (±0.2 BD units; see Table 2).

The linking reaction between each chlorosilyl-end-functionalized precursor polystyrene (**9**, **15**, and **16** in Scheme 5) for the 6-end pom-pom, 6-end branched, or 9-end branched polymer and an excess of the corresponding polystyrene-*b*-oligo(butadienyl)lithium (PS-*b*-oligoBDLi) (**22**) was carried out in benzene for 1 week

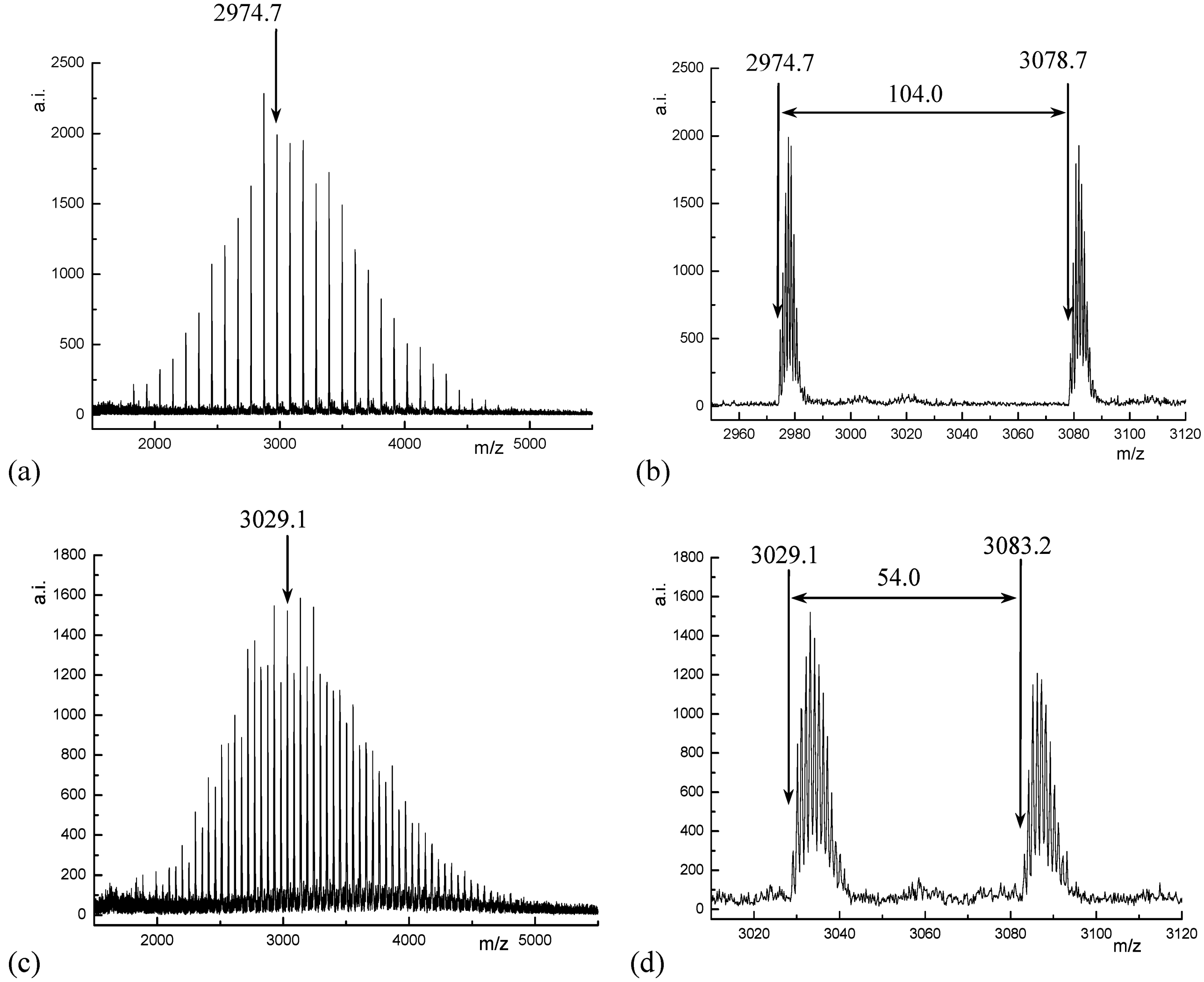


Figure 4. Comparison of MALDI−TOF mass spectra: (a) entire spectrum of the unfunctionalized arm polystyrene for the 6-end pom-pom polymer (**11**); (b) enlargement of *m/z* = 2960−3120 region corresponding to polystyrenes with 27 styrene units (left major peak) and with 28 styrene units (right major peak); (c) entire spectrum of the butadiene end-capped arm polystyrene for the 6-end pom-pom polymer (**13**); and (d) enlargement of *m/z* = 3020−3120 region corresponding to polystyrenes with 27 styrene units and one (left major peak) or two (right major peak) BD units.

at 40 °C in the presence of triethylamine. After 1 week of linking reaction, there was no further change with time in the chromatograms shown as curves (4) in Figures 1 and 2. Both chromatograms, after methanolysis, contain two major peaks. The first peak at 20.4 mL retention volume corresponds to the 6-end pom-pom polystyrene in Figure 1 and to the 6-end branched polymer in Figure 2. The second peaks at 23.6 mL (Figure 1) and 24.0 mL (Figure 2) correspond to the excess PS-*b*-oligoBD (**23**). The small peaks next to the primary peaks are due to coupled polymer and linear polymer contained in the precursor polymer.

The linking reaction between the methoxysilyl-functionalized precursor polystyrene (**18**) for the targeted 15-end branched polymer and excess PS-*b*-oligoBDLi (**22**) was allowed 3 weeks to reach a point beyond which no further linking occurred. The methoxy groups on the methoxysily end-functionalized precursor polymer are not as reactive as the chlorides on the chlorosily end-functionalized precursor polymers, and thus the reaction with the methoxy groups takes longer.[47] Curve (5) in Figure 3 is the SEC chromatogram for the targeted 15-end branched polymer formed after 3 weeks of reaction.

All branched polymers were separated from excess arm polymer by fractionation[50] using toluene as a good solvent and methanol as a poor solvent. Curves (5) in Figures 1 and 2 and curve (6) in Figure 3 are the SEC chromatograms obtained after the fractionations. Each SEC chromatogram taken after fractionation showed a single narrow peak indicating that the desired branched polymer was successfully separated from both excess arm polymer and the more highly branched polymer resulting from coupling.

Characterization of Branched Polystyrenes. After fractionation, the molecular weight of each branched polystyrene was characterized using SEC coupled with light scattering. The overall molecular weights of all branched polymers and an analogous linear polymer, listed in Table 3, were controlled to be about 36 000 g/mol. The observed polydispersity (M_w/M_n) of each branched polymer was ≤1.04. The number of end groups (f) was calculated from the molecular weights of the arm polymers, precursor polymer, and branched polymer, except for the 6-arm star polymer and the linear polymer, using the following equation:

$$f = \frac{M_{n,\text{branched}} - M_{n,\text{precursor}}}{M_{n,\text{arm}}} \qquad (1)$$

The calculated number of end groups based on molec-

Table 3. Molecular Characterization of Branched Polystyrenes

	final polystyrene			
polymer	M_n[a] (g/mol)	M_w[a] (g/mol)	M_w/M_n[a]	f[b]
linear	40 000	40 800	1.02	2.0
6-star	36 300	37 800	1.04	6.0
6-pom	40 500	41 700	1.03	5.8
6-branch	35 800	36 500	1.02	5.9
9-branch	38 900	39 700	1.02	9.0
13-branch	34 200	35 600	1.04	13.0

[a] Determined by SEC coupled with light scattering (±5%). [b] Arm functionality calculated using eq 1 (±5%).

Table 4. Dilute Solution Properties of Branched Polystyrenes

polymer	$[\eta]$[a] (cm^3/g)	g'[b] (expt)	g' (calcd)	$D_0 \times 10^7$[e] (cm^2/s)	R_h[f] (Å)
linear	20.2			8.3_7	46.7
6-star	10.2	0.51	0.51[c]	10.7_2	36.5
6-pom	17.5	0.87		9.0_3	43.3
6-branch	12.8	0.64	0.60[d]	9.6_6	40.5
9-branch	11.7	0.58	0.55[d]	10.6_2	36.8
branch	9.6	0.47	0.47[d]	10.8_1	36.2

[a] Determined in toluene at 35 °C (±0.5). [b] Branching factor; $g'=[\eta]_{\text{star}}/[\eta]_{\text{linear}}$ (±0.04). [c] Reference 56. [d] Calculated using eq 3. [e] Diffusion coefficient at infinite dilution determined by dynamic light scattering in toluene at 25 °C. [f] Calculated using eq 4.

ular weights in Table 3 compared well with the target number of end groups except for the end-branched polymer, which had a target of 15 arms and end groups based on the 15 silyl chloride functional groups in the star precursor, **18**. The steric hindrance generated during the formation of this highly branched star limited the arm functionality to 13 during the synthesis. Thus, such well-defined branched polymers can be successfully synthesized by anionic polymerization using multifunctional initiators as described herein.

The structural differences in the polymers arising from the differences in their topologies were probed using measurements of intrinsic viscosity. The intrinsic viscosities of all branched polymers and the linear analogue are listed in Table 4. Among the polymers with 6 chain ends, the intrinsic viscosity was lowest for the 6-arm star-branched polystyrene, next lowest for the 6-end branched polystyrene, and largest for the 6-end pom-pom polystyrene. The 6-arm star is most compact because it contains a single junction point. Though the pom-pom polymer has two junctions, it is not the next smallest in size due to the long linear portion in the center of the molecule. The linear precursor polymer was 6 times longer than the arm polymer. Thus, the linear character of the 6-end pom-pom strongly manifests itself, and its size is closer to that of the linear polymer. Among the 6-end, 9-end, and 13-end branched polymers which have four junction points, the intrinsic viscosity decreased with increasing number of end groups. Generally, the nature of the branching in a branched polymer is characterized in terms of the parameter g', which is defined as

$$g' = \frac{[\eta]_b}{[\eta]_l} \tag{2}$$

where $[\eta]_b$ is the intrinsic viscosity of the branched polymer and $[\eta]_l$ is the intrinsic viscosity of the corresponding linear polymer with the same molecular weight. For a regular 6-armed star-branched polymer, the theoretical model by Stockmayer and Fixman[56] predicts a g' value of 0.51. This is in good agreement with the experimentally determined value (0.51) in Table 4. We are unaware of a theoretical prediction for a 6-end pom-pom polymer to which the experimental value (0.87) may be compared. An empirical equation for g' for randomly branched polymers with a certain average number of trifunctional branch units was developed by Zimm and Stockmayer:[57]

$$g' = [(1 + M/7)^{1/2} + 4M/9\pi]^{-1/2} \tag{3}$$

where M is the average number of branch units. Even though eq 3 may not be expected to exactly apply for regularly end-branched polymers, the values in Table 4 calculated using eq 3 were relatively close to the experimentally determined values. The g' value for the 13-end branched polymer was the smallest among those for end-branched polymers having four junction points.

The hydrodynamic radius, R_h, of each branched polystyrene in toluene was determined from dynamic light scattering measurements of the translational diffusion coefficient at infinite dilution, D_0, by applying the Stokes–Einstein equation:[58]

$$R_h = \frac{k_B T}{6\pi\eta_0 D_0} \tag{4}$$

where k_B is Boltzmann's constant and η_0 is the solvent viscosity. The diffusion coefficient depends on the concentration, c, as $D(c) = D_0(1 + k_D c + ...)$. Thus, D_0 could be determined as the value of the intercept from an extrapolation on the plot of $D(c)$ against concentration for the concentration going to zero. In these measurements, nine concentrations from 4.5 to 100 mg/mL were used. The diffusion coefficients and hydrodynamic radii determined using eq 4 are presented in Table 4. The hydrodynamic radii vary in a manner consistent with the intrinsic viscosity results. The 6-arm star-branched polymer was the smallest among the three with 6-end groups, and the 13-end branched polymer was smallest among the three with four junction points.

Finally, the effect of branching on the glass transition temperatures of the polymers was investigated. All of the values of T_g and width of the transition, ΔT_g, in Table 5 were measured with the same instrumentation and protocol and may be readily compared with one another. To determine the width, a line was drawn tangent to the curve at T_g. Then the width was taken as the difference between the temperatures of intersection of this line with the solidus and liquidus lines. The value of T_g for the linear chain is in good agreement with literature values.[59,60] Measurement of an additional linear polystyrene standard (8.9×10^5 g/mol, Polymer Source, Inc., $M_w/M_n = 1.04$) provided the value of T_g for infinite molecular weight, $T_{g,\infty}$ (100 °C). The variations in the values of T_g seem reasonable. First, we note that the T_g's of all branched polymers are significantly lower than the T_g of the linear chain analogue. We have to qualify this observation with the distinction that the linear polymer does not present an exact analogue for comparison with either the star or the other branched polymers due to subtle differences in the way the molecules were synthesized. The 6-arm star contains a core that is reasonably flexible, and the

Table 5. Glass Transition Temperatures[a] and Widths of Transitions[b] of Arm Polystyrenes before and after BD End-Capping, Precursor Polystyrenes, and Branched Polystyrenes

	arm PS												
		before end-capping		after end-capping		precursor PS			branched PS				
polymer	M_n[c] (g/mol)	T_g (°C)	ΔT_g (°C)	T_g (°C)	ΔT_g (°C)	M_n[a] (g/mol)	T_g (°C)	ΔT_g (°C)	M_n[c] (g/mol)	total BD (wt %)[d]	T_g (°C)	ΔT_g (°C)	$T_{g,calc}$[e] (°C)
linear									40 000		98	5	
6-star	6100	85	4	78	8				36 300	1.1	86	9	94
6-pom	3500	72	4	61	6	18 200	94	4	40 500	1.5	87	7	91
6-branch	2900	67	5	64	6	18 100	92	5	35 800	1.4	83	9	92
9-branch	2300	61	5	57	6	17 700	92	6	38 900	1.8	79	8	91
13-branch	1200	32	4	30	6	17 700	92	6	34 200	2.6	76	8	87

[a] Measured at a heating rate of 10 °C/min using DSC (±1 °C). [b] ΔT_g as defined in the text. [c] Determined by SEC coupled with light scattering (±5%). [d] Calculated using BD wt % = 100 × [54 × BD unit/M_n of branched PS] (±5%). [e] T_g expected on the basis of BD content alone. Calculated using eq 5.

T_g of a linear PS containing such a connecting unit would be reduced relative to that of a conventional linear PS. The pom-pom and all end-branched stars each contain a central unit (due to the initiator structure) that is comparatively rigid, and the presence of this stiff unit would tend to increase the value of T_g for all of these polymers in the absence of BD end-capping of the arms. The linear chain has no "core" unit that is analogous.

A second general observation is that the three molecules having 6 ends have T_g's that vary over a 4 °C range. It is not possible to explain the three values of T_g by considering only the number of chain ends. Our third general observation is that when the number of branch points is held constant among the three end-branched star polymers, the value of T_g does decrease with increasing number of chain ends. Also, these changes are much more subtle than are the changes in the T_g's of the respective arms of these end-branched stars. That is, the T_g's of the end-branched stars decrease from 83 to 76 °C as the number of ends increases from 6 to 13, while the T_g's of the corresponding arms decrease from 64 to 30 °C. Our final observation is that incorporation of BD units in a chain increases the width of the transition. The widths for the linear arms before end-capping are about 4−5 °C. The widths after end-capping are larger. While the widths are even larger (7−9 °C) for the complete branched chains, it is difficult to separate an effect due to branching alone from the effect due to inclusion of BD units.

In surveying the data, there is no simple, consistent correspondence to be seen between the T_g of a given branched chain and the T_g of either its precursor or the end-capped arms used to make the branched molecule. In recent work by Lee et al.,[49] it was observed that the T_g of the arm of a 4-arm PS star was the same as the T_g of the star in the case that the arm was end-capped with BD. This suggested that the BD units might be serving to dynamically decouple the arm from the rest of the star. If that were generally true, then we should have seen here an equivalence of the T_g's of the end-capped arm for the 6-arm star and of the star itself. However, this is not observed, suggesting that increasing the functionality may limit the degree to which the arm may be decoupled from the rest of the star.

There are at least three characteristics of each branched molecule that may impact its value of T_g: the weight fraction of BD units, the number of chain ends, and the number of branch points. Thus, it is reasonable to suppose that a proper accounting of the T_g values measured here can only be attained when all three effects are accounted for, but we can consider how far we may get with simpler approaches. First we consider the copolymer effect arising from the BD units used to cap the arms. For linear polymers, the effect on T_g of including BD units randomly in a poly(styrene-*co*-butadiene) copolymer may be predicted well using an empirical copolymer equation[61]

$$\frac{1}{T_g} = \frac{w_{PS}}{T_{g,PS}} + \frac{w_{PB}}{T_{g,PB}} \tag{5}$$

where w_i is the weight fraction of BD or styrene units. $T_{g,PS}$ and $T_{g,PB}$ are taken as the T_g of a linear chain of the same overall molecular weight as that of the branched chain ($T_{g,PS}$ = 98 °C for linear PS and $T_{g,PB}$ = −102 °C[59] for linear PB at the same overall molecular weight (38 000 g/mol); both measured here). If one ignores the architecture of each chain and simply predicts the T_g that would be expected for each molecule due to the total composition of BD units in the chain, one obtains the values listed in the tenth column of Table 5. All calculated T_gs were up to 11 °C higher than the experimentally determined values. One reason for this could be that the BD units are *not* distributed randomly in the molecules. They are always located in a very particular spot—the point at which an arm links to a core or branch point. Nonetheless, it is also likely that the branching and chain end effects (architecture effects) are important as well.

Next we consider how successfully we can quantitatively rationalize the experimentally measured T_g values using a free-volume approach that accounts for the effect of chain end free volume on T_g.[62] Already the observation that the T_g's of the three different molecules with six ends are distinct is sufficient to suggest that this approach cannot be fully satisfying, but we consider how far it may be taken. Fox and Flory[62] proposed on the basis of a chain-end free volume theory that the value of T_g should vary with molecular weight as

$$T_g = T_{g,\infty} - \frac{K}{M_n} \tag{6}$$

where $T_{g,\infty}$ is the value of T_g at infinitely high M_n, M_n is the total molecular weight of the polymer, and K is a constant characteristic of a particular polymer. Specifically, K is related to the chain-end free volume variation with molecular weight. For a branched polymer,

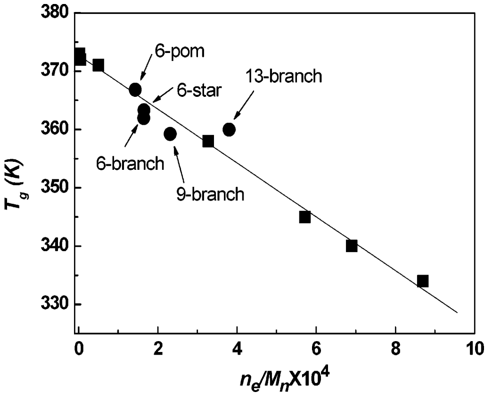


Figure 5. Comparison of glass transition temperatures of linear and branched polystyrenes as a function of n_e/M_n. Data points for linear chains (■) reflect the actual values measured. For the data from branched chains (●) an attempt has been made to correct for the presence of BD units by adjusting the value of the T_g for each by the magnitude of the effect anticipated by eq 5. The solid line has been obtained by fitting the T_g data for the linear polymers using eq 7 with $K' = 4600$.

eq 6 can be expressed as[63]

$$T_g = T_{g,\infty} - K' \frac{n_e}{M_n} \tag{7}$$

where n_e is the number of chain ends per molecule and K' is a constant that depends on the density, the chain-end free volume, and the free volume expansion coefficient. $T_{g,\infty}$ was determined from a measurement of a monodisperse linear polymer with a molecular weight of 8.9×10^5 g/mol and found to be 100 °C. Since n_e and M_n are known from the molecular characterization data in Table 3, a value of K' can be extracted by using eq 7 to fit the T_g value for all polymers. However, we could not fit all of the T_gs using one value of K'. If the manner in which each chain was branched were insignificant, one could expect to be able to reconcile all the data for the branched chains, including linear chains, with a single value of K', but this is not the case.

Finally, we attempt to account simultaneously for the presence of BD units and the free volume of chain ends. We do this by first estimating the value of T_g by just accounting for the number of chain ends, as done in the previous paragraph. This must be done using the same value of K' for all the branched chains. Then this value of T_g is further corrected for the presence of BD units in the polymer, as described above. Figure 5 displays T_gs for all of the linear polymers and the branched polymers after correcting the experimentally measured values for the presence of BD units. The K' value for the fit of the T_g data from the linear polymers was 4600, which compared well with the literature value of 5000.[62] The corrected T_g of the 6-star having one branch point and the corrected T_g of the 6-pom molecule having two branch points, but also a long linear portion, fall also reasonably close to the solid line. However, the T_gs of the 6-end, 9-end, and 13-end branched polymers with four branch points do not fall onto the solid line. Probably, the branch points affect the glass transitions of branched polymers. Thus, these results highlight the need for detailed theoretical consideration of the role of both branching (i.e., tethering at junctions) and chain ends in determining T_g. It would also be interesting to make measurements of T_g's for a series of polymers in which the molecules have the same architecture, but different molecular weights or different numbers of BD units. A study of this sort is underway. Investigations into the influences of the number of chain ends and number of branch points on the bulk thermodynamics and interfacial segregation of binary blends of linear PS and the branched polystyrenes described herein should soon be completed.

Conclusions

The use of trifunctional and difunctional initiators prepared by the stoichiometric addition reaction of *sec*-BuLi with 1,3,5-tris(1-phenylethyenyl)benzene and 1,3-bis(1-phenylethenyl)benzene, respectively, provided the precursor polymers needed to make a series of well-defined branched polymers suited to studying systematically the effects of branching and chain ends on polymer behavior. The precursor polymers for end-branched, star-branched polystyrenes with 6-, 9-, and 13-end branches were synthesized using a trifunctional initiator. The 3-arm precursor star polymer then was end-functionalized with an excess of the appropriate linking agent, purified, and then reacted with excess living arm polymer. The most highly branched polymer with 13-end groups was synthesized using a recently developed methoxysilyl functionalization and precipitation method, which addresses the challenge represented by removal of the excess, low volatility linking agent of high functionality. The precursor polymer for 6-end pom-pom polystyrene was synthesized using a dilithium initiator and was end-functionalized with the linking agent to create 6-end arms.

The properties of the end-branched, star-branched polystyrenes, all having four junction points, but with 6, 9, or 13 end groups, were compared to study the effect of chain ends. Comparison among the polystyrenes all having 6-end groups, but having a number of branch points equal to 1, 2, or 4, was used to elucidate the impact of changing the number of branch points. The branching factor g' and hydrodynamic radius decrease with increasing number of branch points among the polymers having six ends and also decreases with increasing number of end groups among the polymers having four branch points. The values of T_g vary among the polymers in a manner reflecting the influence of not only the number of chain ends but also the chain topology and the inclusion of butadiene units to facilitate linking.

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