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Star-*block*-Linear-*block*-Star Triblock (Pom-Pom) Polystyrene by Convergent Living Anionic Polymerization

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ABSTRACT: Star-*block*-linear-*block*-star triblock polystyrene polymers with identical stars at each end of a linear block (pom-pom polymers) were synthesized by the convergent living anionic polymerization method. The sequential synthesis involved first the formation of a living anionic polystyrene star with a hyperbranched core via continuous addition of coupling agent, 4-(chlorodimethylsilyl)styrene, to living polystyrene chains. Subsequent addition of styrene monomer to the living polystyrene star anions produced star-*block*-linear diblock polystyrene anions that were then coupled with dichlorodimethylsilane to make the architectural triblock. The obtained pom-pom polymers were purified by fractionation. Gel permeation chromatography−multiangle laser light scattering characterization clearly showed the molecular weight changes due to the progression of polymerization. The star-*block*-linear-*block*-star triblock copolymers were characterized by NMR (^{1}H and ^{29}Si) spectroscopy and dilute solution viscometry. The architectural triblock copolymers demonstrate interesting dilute solution properties.

Introduction

The designed synthesis of polymers with complex structures, especially where polymer segments of different branch architecture are combined in the same molecule, can result in materials with unique properties. A greater understanding of the effect of branching on properties can also be gained by the synthesis of these complex structures.

Recently, dendritic blocks have been combined with linear blocks in order to produce AB[1−7] and ABA architectural block copolymers.[8−10] The ABA type copolymers, where the A group represents the dendritic block and the B group the linear block, have attracted attention as interesting materials. Unfortunately, the chemical composition difference between the dendritic blocks and linear block causes difficulty for the study of the potential unique properties based solely on topology.

Some other examples of architectural block copolymers have also been reported in recent years. H-shaped polymers[11−14] and super-H-shaped polymers (or bridged star polymers)[15−17] are examples where branching has been controlled to produce unique materials. The dilute solution properties and melt rheology of H-shaped polymers have been investigated and show differences from their linear and star analogues.[11,18] Each of these structures is characterized by a single linear polymer segment that bridges together either trifunctional branch points in the case of H-shaped polymers or tetrafunctional branch points in the case of super-H-shaped polymers. Such polymers have sometimes been designated as A_nBA_n block copolymers, where n indicates the number of arms in the star. These structures have been synthesized by different multistep procedures that typically involve the synthesis of the separate segments, followed by functionalization, and subsequent coupling. Extensive postsynthesis purification is also required to remove residual low molecular weight blocks.

The triblock structures can be categorized as pom-pom polymers, which is a designation that has been given to multiarmed stars that are connected by a linear block.[19−21] Pom-pom polymers have been theoretically examined for their effect on melt rheology, but only a few models of coupled higher order stars other than super-H-shaped polymers have been synthesized.[22,23] Because of the difficulty in synthesis and the difficulty in obtaining large amounts of material by the complicated coupling techniques, little information is known about the properties related to these theoretical structures.

We have recently developed a one-pot synthetic technique, convergent living anionic polymerization, that can be used to make polymers with controlled branching.[24,25] The technique is based on what others have demonstrated with direct macromonomer formation[26,27] and limited branching reactions.[28−34] This technique involves the slow addition of a dual functional coupling agent such as 4-(chlorodimethylsilyl)styrene (CDMSS) or vinylbenzyl chloride (VBC) to a solution of living polymer anions. The coupling agent is functionalized with one group that can quantitatively couple with the living chain end and a vinyl functionality that allows quantitative addition and the preservation of the living chain end. The slow addition of the coupling agent results in, first, the nucleophilic substitution to make a macromonomer and subsequently the attack at the vinyl group to couple two chains. Continued reaction with additional coupling agent results in the synthesis of polymeric stars with a hyperbranched core. The stars can be synthesized to contain a single living chain end at the core by adding a less than stoichiometric amount of coupling agent. Using this living chain end, subsequent polymerization of added monomer can be done to produce an architectural diblock.[35] Since the diblock continues to be living, coupling with a difunctional reactant should allow the facile synthesis of architectural triblocks. Since the end blocks are multiarmed stars, the architectural triblock copolymers are most closely related to a super-H-shaped or a pom-pom architecture. The core of the star is hyperbranched, and therefore the materials can also be related to the ABA dendritic−linear hybrids described in the literature. We herein report results for the synthesis and characteriza-

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tion of star-*block*-linear-*block*-star triblock (pom-pom) polystyrene by convergent living anionic polymerization.

Experimental Section

Materials. Styrene (99%), *p*-chlorostyrene (97%), and dichlorodimethylsilane (99%) were obtained from Aldrich Chemical Co. Reagents were dried over calcium hydride and distilled under argon or under reduced pressure immediately before use. *sec*-Butyllithium in a mixture of cyclohexane and heptane was kindly donated by FMC, Lithium Division, or purchased from Aldrich Chemical Co. and used as received. The effective molarity of the solutions were determined to be 1.10 M (used for experiments 1−4) and 1.30 M (used for experiments 5−7) by repeated initiation and polymerization of styrene and the subsequent analysis of the molecular weights by GPC. HPLC grade (99.9+%) tetrahydrofuran (THF) was obtained from Fisher Scientific, dried over sodium metal, and distilled from sodium benzophenone ketyl under argon immediately prior to use. HPLC grade cyclohexane (99%) from Fisher Scientific was purified by repeated washings with H_2SO_4 and water and distilled from sodium metal. 4-(Chlorodimethylsilyl)styrene (CDMSS) was synthesized as previously reported.[25] CDMSS was dried over calcium hydride and distilled under reduced pressure immediately before use. HPLC grade toluene (99.99%) from EM Science and reagent grade methanol (99.8%) from Aldrich Chemical Co. were used as received. All glassware, glass syringes, and needles were oven dried at 150 °C for at least 24 h and cooled under argon. The glassware was further flame-dried under an argon purge after assembly. Gas-tight syringes were prepared by washing with dilute *sec*-butyllithium solution followed by washing with dry cyclohexane.

Polymerization. Polymerizations were conducted at room temperature. A typical polymerization procedure for experiments 1−4 is as follows (experiment 2): Styrene (2.5 mL, 21.8 mmol) was added by syringe to 100 mL of cyclohexane in a 250 mL round-bottom flask sealed with a rubber septum under an argon atmosphere. *sec*-BuLi (2.5 mL, 2.75 mmol) was then added. After 2 h an aliquot was removed and precipitated into argon-purged methanol. THF (3.0 mL) was then added to the reaction mixture. A solution of CDMSS in cyclohexane (approximately 0.50 M) was added by syringe pump using a gas-tight syringe. The addition rate of CDMSS solution was 1.0 mL/h over the course of 4.5 h to introduce a total of 4.5 mL of solution. Thirty minutes after complete addition, an aliquot was removed and precipitated in argon-purged methanol. To the living polymer solution, styrene (2.0 mL, 17.5 mmol) was added slowly by syringe pump using a gas-tight syringe. The solution was allowed to react for an additional hour, and then the reaction mixture was again sampled. A 1.0 mL aliquot of dichlorodimethylsilane was diluted in 10.0 mL of THF (approximately 0.75 M) and added into the living anion solution at a rate of 0.2 mL/h by syringe pump using a gas-tight syringe until the reaction solution turned colorless. The reaction mixture was then precipitated into methanol, filtered, washed with methanol, and dried to a constant weight at room temperature in a vacuum oven. The total yield of polymer was quantitative. ^{1}H NMR ($CDCl_3$): δ 0.1 (s, $-Si-(CH_3)_2$); δ 1.3−2.3 (m, $-CH(CH_3)CH_2CH_3$ and $-CH(Ph)-CH_2-$); δ 6.4−7.2 (m, $Ph-H$).

A series of polymerizations (experiments 5−7) were done using the same living star solution to produce polymers with identical star blocks while varying the linear block; the procedure is as follows: Polymerizations were conducted at room temperature. Styrene (30.0 mL, 262 mmol) was added via syringe to 500 mL of cyclohexane in a 1000 mL round-bottom flask sealed with a rubber septum under an argon atmosphere. *sec*-BuLi (4.50 mL, 5.85 mmol) was then added. After 2 h, an aliquot was removed and precipitated into argon-purged methanol. THF (18.0 mL) was then added to the reaction mixture. A solution of CDMSS in cyclohexane (approximately 0.50 M) was added by syringe pump using a gas-tight syringe. The addition rate of CDMSS solution was 2.0 mL/h over the course of about 4 h to introduce 8.2 mL of solution. After 30 min, an aliquot was removed and precipitated in argon-purged methanol. The reaction solution was separated into three parts by transfer under an inert argon atmosphere into separate 500 mL round-bottom flasks using a double-ended needle. Each of the solutions was diluted with approximately 150 mL of cyclohexane and 5.0 mL of THF. Using a gas-tight syringe and a syringe pump, styrene monomer (9.0 mL, 78.7 mmol, to experiment 5; 16.0 mL, 140 mmol, to experiment 6; and 24.0 mL, 210 mmol, to experiment 7) was slowly added to each of the living anion solutions. One hour after addition, an aliquot was removed from each reaction flask. A 0.5 mL aliquot of dichlorodimethylsilane was diluted in 20 mL of cyclohexane (approximately 0.20 M), and the solution was added by syringe pump using a gas-tight syringe into the living anion solutions at a rate of 0.2 mL/h until the reaction solution turned colorless. The addition times were about 5, 3, and 4 h for experiments 5, 6, and 7, respectively. The reaction mixtures were then precipitated into methanol, filtered, washed with methanol, and dried to a constant weight at room temperature in a vacuum oven. The polymer yield was quantitative after considering sample aliquots.

Fractionation. Toluene/methanol was used as solvent/nonsolvent pairs for fractional precipitation of the polystyrene star-*block*-linear-*block*-star triblock samples. All fractional precipitations were performed in a 500 mL separatory funnel.

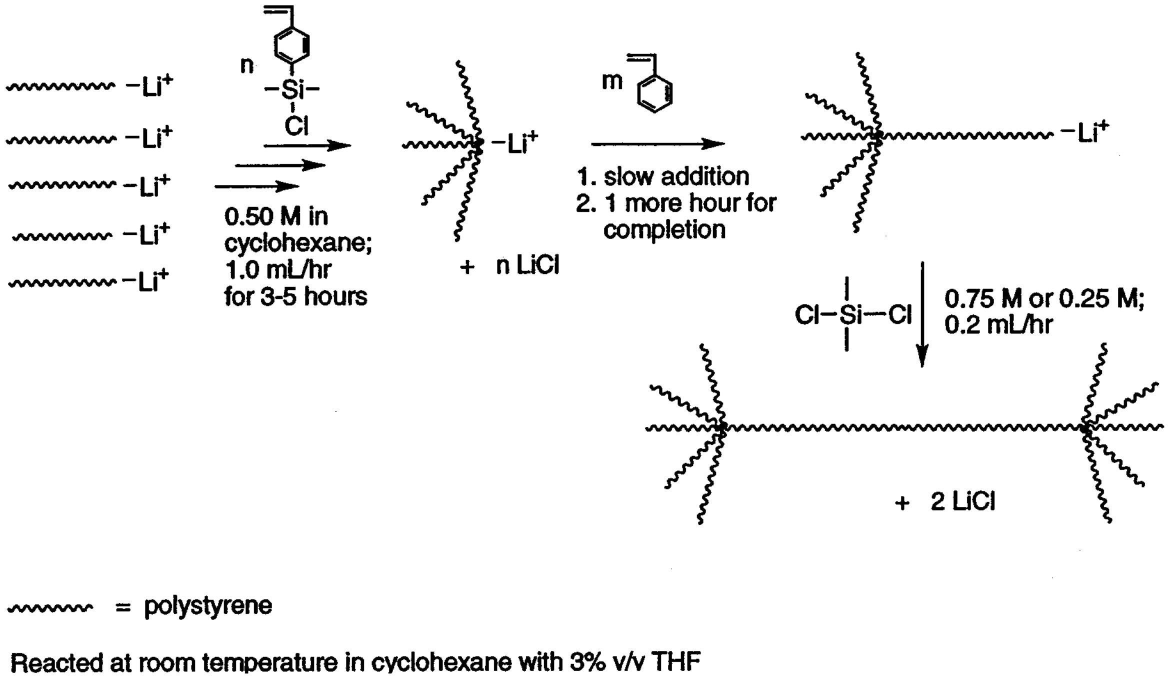
A typical procedure for fractional precipitation is as follows (experiment 2): 3.5 g of polystyrene star-*block*-linear-*block*-star triblock was dissolved in 180 mL of toluene. Methanol was then added dropwise until the solution became slightly turbid. Another 2−3 mL of methanol was added beyond the cloud point, and the solution was subsequently warmed until it became clear. Upon slow cooling to room temperature, a concentrated layer containing high molecular weight component separated from the bulk solution. The concentrated layer was carefully separated and collected into a vial. This fractionation procedure was repeated two more times on the bulk solution, and the three concentrated layers were combined for further fractional precipitation. This whole procedure was repeated to remove more low molecular weight component. The three new concentrated layers were combined and carefully separated into three fractions by this factional precipitation method, and the middle fraction was used as pure polystyrene star-*block*-linear-*block*-star triblock samples. The mass recovery of pure star-*block*-linear-*block*-star triblock was 23%.

Characterization. Molecular weights were determined by gel permeation chromatography (GPC) using a Hewlett-Packard model 1084B liquid chromatograph equipped with a calibrated RI (Waters R401) detector and a Wyatt Technology miniDAWN multiangle laser light scattering (MALLS) detector (λ = 633 nm, three detector angles: 45°, 90° and 135°). Elutions for experiments 1−4 were carried out with two Hewlett-Packard Plgel 5 μm Mixed-D columns (mixture of pore sizes: 50, 100, 500, 10, and 10^4 Å) at ambient temperature with THF at a flow rate of 0.70 mL/min. Elutions for experiments 5−7 were carried out in THF at a flow rate of 1.0 mL/min with one Plgel 5 μm Mixed-D and one Plgel 5 μm Mixed-C column (mixture of pore sizes: 50, 100, 500, 10^3, 10^4, and 10^6 Å) in series. The molecular weight characterization software (Astra 5.2) was supplied by Wyatt Technology. The refractive index increment (dn/dc) used for the samples was 0.193 mL/g.[25,36]

^{1}H and ^{29}Si NMR spectroscopy were performed on samples dissolved in deuterated chloroform on a Chemagnetics CMX Infinity 400 instrument. For ^{29}Si NMR, a small amount of Cr(acac)$_3$ (0.1%) was used to decrease the long spin−lattice relaxation time.[37] Sample concentration was 150 mg/mL in $CDCl_3$. The frequency was 79.48 MHz, spinning speed was 15 Hz, pulse delay was 15 s, and the total number of scans was 2048. Tetramethylsilane (TMS) was used as an external reference before and after each measurement, and the chemical shift difference for TMS was less than 0.02 ppm during each measurement.

Intrinsic viscosities of polymer samples were measured in THF at 30 °C using a size 50 Cannon-Ubbelohde viscometer. At least four different concentrations of each sample were measured. The reduced viscosity and the inherent viscosity

Scheme 1. Reaction Sequence for the Synthesis of Star-*block*-Linear-*block*-Star Triblock (Pom-Pom) Polystyrene



were plotted to zero concentration to obtain the intrinsic viscosity as the average of the two intercepts.

Results and Discussion

Star-*block*-linear-*block*-star, or pom-pom, polystyrenes were synthesized by sequential convergent coupling, followed by monomer addition, and then termination by coupling (Scheme 1). The addition of reactants was conducted using syringe transfer techniques, and the rate of addition was controlled by a syringe pump. Polymerizations were performed at room temperature for convenience, and the slow addition of all reactants avoided the possible temperature increases caused by exothermic anionic substitution and propagation reactions.

The one-pot procedure allows the control over a number of variables. First, the length of the initial chains, which become the arms of the star, can be controlled by varying the molar ratio of styrene to *sec*-butyllithium. Second, the number of arms can be controlled by the amount of CDMSS added relative to the initial chain ends. The length of the bridging block can also be controlled by varying the amount of styrene monomer relative to the star macroinitiator.

In the first step, living linear polystyrene chains were prepared in cyclohexane. The living chains were sampled by the removal of an aliquot, and after termination of the living chain end and isolation by precipitated in methanol, the molecular weights were characterized by GPC-MALLS. Experiments were performed to determine whether any low molecular weight material was being fractionated during the isolation step. Comparison between isolation by precipitation and by evaporation of the solvent yielded the same molecular weight and polydispersity values for the linear chains and therefore showed that no polymer was removed during precipitation.

THF (approximately 3% v/v) was introduced to the bulk reaction solution in order to increase the reaction rate, and the living chains were then coupled by reaction with slowly added CDMSS in a convergent process as previously reported.[25] While THF is known to undergo degradation reactions in the presence of alkyllithiums,[38-41] we have previously demonstrated the lack of any significant side reactions during the time frame of our polymerizations at room temperature with up to 20 vol % THF.[25] We have examined the use of smaller amounts of THF to achieve the same rate effects and have determined that approximately 3% v/v THF works well in these reactions with CDMSS as coupling agent. We have performed reactions in the absence of any added THF, but the polydispersity of the resulting star is slightly larger than if THF is added. This observation is related to the rate of addition to the double bond relative to the substitution of the chloride in a nonpolar solvent. Therefore, small amounts of THF were added to the polymerizations.

The reaction of a solution of living polystyryllithium with slowly added CDMSS occurs by first terminating one chain in the formation of macromonomer, and then another chain can quickly add to the double bond of the macromonomer. This series of reactions can be repeated as more CDMSS is added. In this way, the core of the forming star has either a single living anion or a transient vinyl functionality. Upon a stoichiometric addition of slowly added CDMSS, the stars become functionalized with a vinyl group.[42] If the addition is stopped prior to a stoichiometric amount, a single living chain end will remain at the core. This is in contrast to star formation with divinylbenzene where the same number of living chain ends exist as the number of arms.[43,44] The average number of generations of the resulting hyperbranched core can be determined using eq 1, where M_{initial} is equal to the molecular weight of the initial chains and M_{branch} is equal to the molecular weight of the residue from CDMSS (161.30 g/mol). The number of arms in the star is then equal to 2^G.

$$G = \frac{\log(M_{\text{star}}) - \log(M_{\text{initial}} + M_{\text{branch}})}{\log 2} \qquad (1)$$

Molecular weights of the initial chains (M_{initial}) and the stars (M_{star}) were determined by GPC-MALLS

Table 1. Characterization of Star-Shaped Polystyrene with Hyperbranched Core; Effect of Arm Length on Average Number of Arms[a]

expt	[St]/[BuLi]	M_n[b] of initial chain (g/mol)/PDI	addition rate of CDMSS (mmol/h)/BuLi (mmol)	M_n[b] of PS star (g/mol)/PDI	av no. of arms (*f*)[c]
A	10.0	900/1.14	0.50/2.60	11500/1.18	11
B	25.0	2060/1.03	0.20/1.10	18600/1.21	8.4
C	40.0	4600/1.03	0.50/2.20	31800/1.16	6.7
D	50.0	5600/1.07	0.50/2.60	34500/1.17	6.0
E	200	20700/1.03	0.05/0.33	95900/1.14	4.6
F	200	26500/1.03	0.13/0.65	121000/1.22	4.5

[a] All reactions were done at room temperature by procedure described previously[25] with 3% v/v THF added before the addition of 0.50 M CDMSS solution in cyclohexane. Addition of CDMSS completed in the time range of 4−5 h. [b] Determined by GPC-MALLS. [c] Determined by eq 1, number of arms = 2^G.

analysis of extracted samples using a literature[36] value for the refractive index increment (d*n*/d*c*) of 0.193 mL/g. Although the d*n*/d*c* value could vary for the different samples, especially at low molecular weights, the d*n*/d*c* value was found to be constant. The intensity of the light scattering signal is greatly decreased at low molecular weights; therefore, molecular weight values for initial chains were compared to those obtained relative to polystyrene standards, and number-average molecular weights agreed within 5%. Absolute molecular weights from MALLS characterization are required for determining the molecular weight of the branched structures, and so molecular weight values from MALLS characterization were used in all cases.

Experiments were performed to determine the maximum number of arms that can be coupled together by CDMSS through this process (Table 1). The addition rate and the length of the initial chains were studied as variables. It was previously demonstrated that using short arms (~1000 g/mol) at a reasonably fast addition rate of CDMSS over the course of approximtely 5 h stars can be synthesized with up to an average of 11 arms, corresponding to an average generational growth of about 3.4 for the hyperbranched core.[25] Keeping the polymer concentration constant and the relative addition rates constant (i.e., the moles of CDMSS per hour to the initial moles of living chain ends), the number of arms that can be coupled into the star decreases with increasing molecular weight. Under the given reaction conditions, the ultimate average number of arms that can be obtained is about 11 arms from 1000 g/mol chains, 6−7 arms using approximately 5000 g/mol chains, and 4−5 arms using approximately 20 000 g/mol chains. The reason for the decrease in the average number of arms with the molecular weight is speculated to be a combination of effects. Steric hindrance due to the length of the arm most likely has the greatest effect, although the decreased diffusion of the longer arms, and any increased solution viscosity due to the longer arms is anticipated to also affect the coupling. In all cases, the polydispersity of the resulting stars remains relatively low, presumably due to the effects on the reaction rate kinetics as reported previously.[25] Further experiments are being done to optimize the synthesis of multiarmed stars with higher molecular weight arms.

Given the maximum number of arms that can be coupled, the number of generations of the core, and therefore the number of coupled arms, can be controlled by stopping the addition of CDMSS before a stoichiometric amount is added. To form an *f*-armed star, (1 − 1/*f*) of the stoichiometric amount of CDMSS is needed, and the resulting living anion concentration is therefore 1/*f* of the initial concentration of living anions. As CDMSS is added and star is formed, the concentration of living anions decreases, and the red color of the polystyryllithium solution fades. While this work has relied on the offset of stoichiometry and the qualitative color change associated with star formation to control the number of arms in the star, UV−vis spectrosopy of the reaction solution could be used to determine the concentration change of the living anions[45] and therefore control the number of arms.

Experiments were run to make stars with different molecular weight arms of the star and different numbers of arms while retaining a single living chain end. Experiments 1−4 maintained arms of approximately 1000 g/mol while varying the number of arms in the star. Experiments 5−7 used arms of 4400 g/mol that were coupled to form 5-armed stars. The experimental details and the GPC-MALLS characterization results are presented in Table 2.

The stars retain a living chain end and were used as a macroinitiator for more styrene monomer. The length of the linear polystyrene block can be controlled by the stoichiometric ratio of monomer to star-shaped macroinitiator, and different length chains were readily produced. The living site of this macroinitiator is polystyryllithium, and previous experiments,[35] as well as this current work, show by GPC-MALLS molecular weight characterization that the diblock has a relatively low polydispersity, which means the macroinitiator can initiate the polymerization of styrene in an acceptably short period of time despite the increased steric hindrance associated with the branching.

After sampling for GPC-MALLS molecular weight analysis, the living star-*block*-linear diblock was coupled with dichlorodimethylsilane as a difunctional coupling agent. The coupling efficiency of polystyryl anions to chlorosilane compounds have previously been shown to have difficulty reaching 100% in hydrocarbon solvents even with added THF.[46,47] The difficulty in knowing the number of living chains, and therefore the amount of coupling agent required, necessitated the slow addition of the dichlordimethylsilane. By maintaining a deficiency of coupling agent, it was anticipated that the formation of a silyl chloride terminated diblock in the presence of living diblocks would allow coupling to proceed to the greatest extent. Table 3 presents the characterization results for the polymerization of the diblock and the coupling to the triblock.

The progression of the reactions are clearly demonstrated by the representative GPC chromatograms in Figures 1, 2, 3, and 4 for four different experiments (experiments 1, 2, 4, and 5, respectively). For each of the figures, the peak at the highest elution volume corresponds to the initial linear chains (peak a). The peak at the next highest elution volume (peak b) corresponds to the star. The star-*block*-linear diblock is measured at the lower elution volume (peak c), and the coupled triblock is measured at the lowest elution volume (peak d) on the chromatogram. From these figures, the efficiency of the reaction sequence can be evaluated. With no fractionation performed on the samples, minimal amounts of initial chain and star remain in the final product of any of the experiments. The amount of residual diblock, however, was found to increase as the molecular weight increased. The in-

Table 2. Characterization of Living Stars[a]

expt	[St]/[BuLi]	M_n[b] of initial chain (g/mol)/PDI	addition rate of CDMSS (mmol/h)/BuLi (mmol)	total amount of CDMSS added (mmol)	stoichiometric fraction of CDMSS added $(1 - 1/f)$[c]	M_n[b] of PS star (g/mol)/PDI	av no. of arms (f)[d]
1	8.0	1000/1.05	0.5/2.75	1.69	0.62	2700/1.22	2.5
2	8.0	830/1.14	0.5/2.75	2.25	0.82	6400/1.22	6.5
3	8.0	960/1.09	0.5/2.75	2.25	0.82	6800/1.19	6.1
4	8.0	990/1.03	1.5/11.0	2.45	0.89	10400/1.14	9.0
5	45.0	4400/1.07	1.0/5.85	4.10	0.70	22900/1.26	5.0
6	45.0	4400/1.07	1.0/5.85	4.10	0.70	22900/1.26	5.0
7	45.0	4400/1.07	1.0/5.85	4.10	0.70	22900/1.26	5.0

[a] Addition of CDMSS completed in the time range of 3−5 h. [b] Determined by GPC-MALLS. [c] Fraction relative to initial number of living chain ends. [d] Determined by eq 1, number of arms = 2^G.

Table 3. Characterization Results for Diblock and Triblock

expt	M_n[a] of diblock (g/mol)/PDI	M_n[a,b] of triblock (g/mol)/PDI	wt fraction of diblock residue[c]	M_n[a,d] of triblock (g/mol)/PDI	yield after fractionation (%)
1	4920/1.11	9400/1.09	0.04	11500/1.09	22
2	11600/1.11	19900/1.12	0.17	27200/1.02	23
3[e]	N/A	24100/1.09	N/A	32700/1.02	15
4	48200/1.04	66300/1.14	0.42	93800/1.04	21
5	50600/1.10	92700/1.16	0.09	115000/1.04	33
6	88800/1.06	146000/1.16	0.22	188000/1.05	41
7	111000/1.04	164000/1.15	0.35	228000/1.05	33

[a] Determined by GPC-MALLS. [b] Before fractionation (peak includes residual diblock). [c] Weight fraction of diblock responsible for lowering the molecular weight from the theoretical molecular weight of triblock (i.e., $2M_n$ of diblock). [d] After fractionation (residual diblock and lower molecular weight triblock removed). [e] Did not sample at diblock stage to reduce the possible termination caused by sampling.

crease in residual diblock is presumed to be the effect of the continuous slow addition process for the addition of dichlorodimethylsilane as well as the increase in solution viscosity that occurs for the higher molecular weight polymers. Slower addition of dichlorodimethylsilane or the addition of an exact stoichiometry should improve the results, although the higher molecular weight also results in fewer living chain ends and therefore a greater susceptibility to termination with electrophilic impurities. For the low molecular weight samples, the amount of residual diblock is similar to that found for linear triblocks formed by coupling with dichlorodimethylsilane,[47,48] but the high molecular weight sample from experiment 4 contains approximately 42 wt % diblock.

While this technique has advantages of producing relatively pure star-*block*-linear-*block*-star triblock polystyrene by a simple one-pot procedure without the need for extensive fractionation, fractionation was required in order to obtain characterization results on pure materials. Each of the triblock samples was therefore purified by fractional precipitation using toluene and methanol as solvent and nonsolvent, respectively. The results of the fractionation for all of the samples are detailed in Table 3 and for experiments 1, 2, 4, and 5 are shown as an inset in each of the figures (peak e in Figures 1, 2, 3, and 4, respectively). The fractionation procedure effectively removed residual diblock in all cases. Lower molecular weight triblock was also removed. Although the content of low molecular weight residues is not very large in any of the samples, loss of material occurred during purification since purified triblock samples were a priority over maximizing the yield. The mass recovery of purified triblock samples varied from 15% to 41%. Since some of the lower molecular weight triblock was removed by fractional precipitation, the average number of arms in the pom-pom polymers obtained after fractionation is actually slightly higher than that calculated by the synthesis procedure.

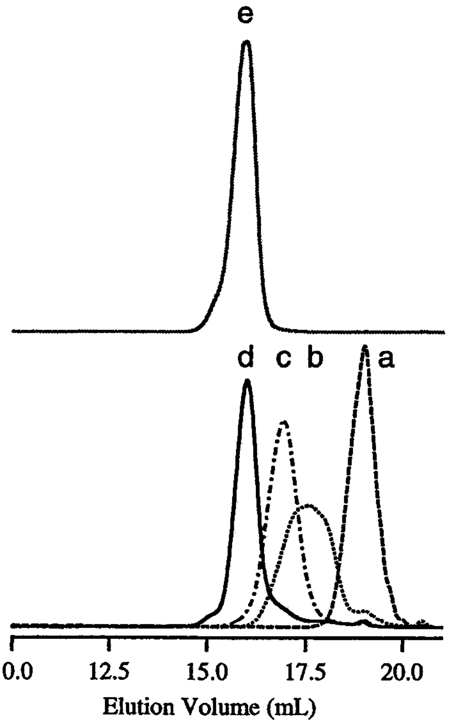


Figure 1. GPC chromatograms for experiment 1: (a) initial chain; (b) star; (c) star-*block*-linear diblock; (d) star-*block*-linear-*block*-star triblock (pom-pom); (e) triblock after fractionation.

^{1}H NMR spectroscopy of the polymers at different stages of synthesis shows little information. The initial oligomers, stars, star-*block*-linear diblock, and final star-*block*-linear-*block*-star triblock copolymer show typical resonances for polystyrene. The Si-methyl protons from CDMSS, however, are observed in the star, diblock, and triblock at a chemical shift around 0.1 ppm.

During the synthesis of star-*block*-linear-*block*-star triblock polystyrenes, two kinds of coupling agents were used: CDMSS to form the living star and dichlorodi-

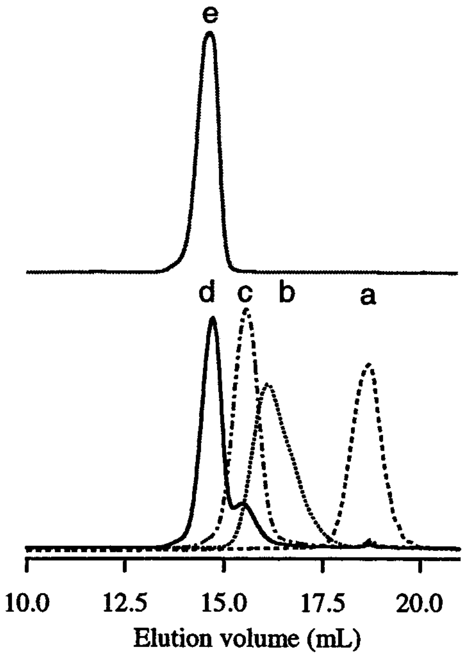


Figure 2. GPC chromatograms for experiment 2: (a) initial chain; (b) star; (c) star-*block*-linear diblock; (d) star-*block*-linear-*block*-star triblock (pom-pom); (e) triblock after fractionation.

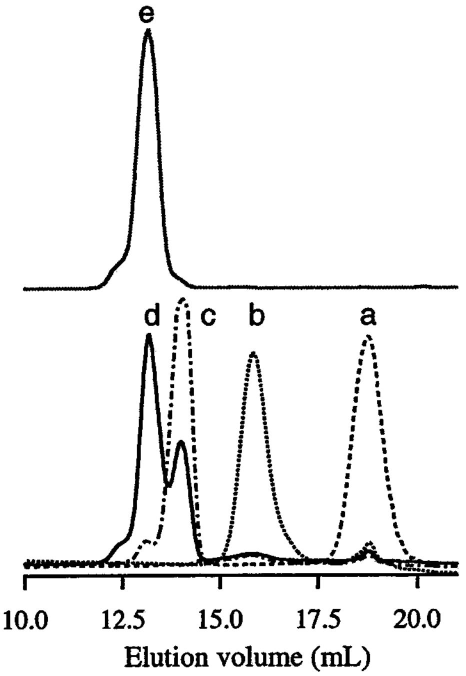


Figure 3. GPC chromatograms for experiment 4: (a) initial chain; (b) star; (c) star-*block*-linear diblock; (d) star-*block*-linear-*block*-star triblock (pom-pom); (e) triblock after fractionation.

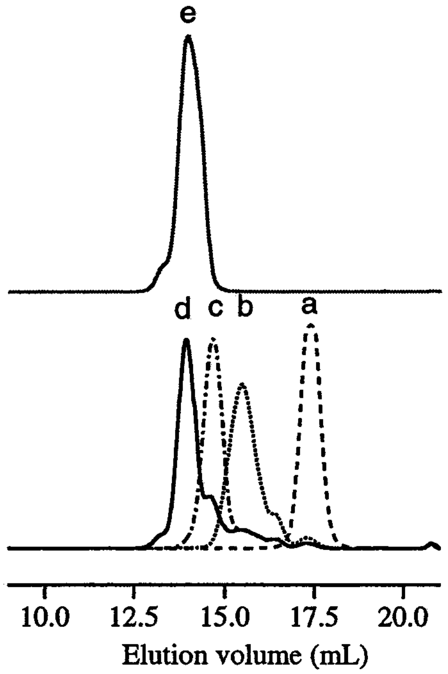


Figure 4. GPC chromatograms for experiment 5: (a) initial chain; (b) star; (c) star-*block*-linear diblock; (d) star-*block*-linear-*block*-star triblock (pom-pom); (e) triblock after fractionation.

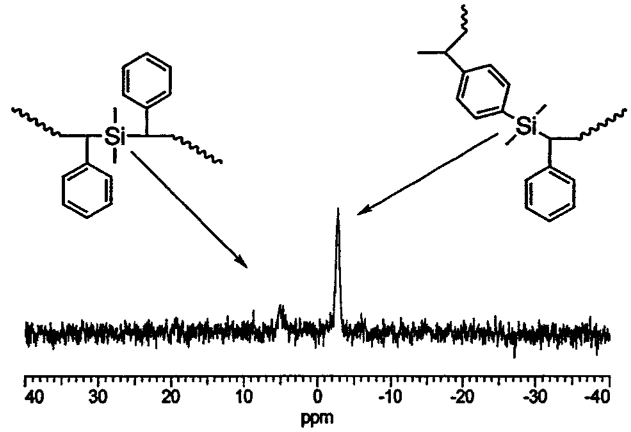


Figure 5. ^{29}Si NMR spectrum for star-*block*-linear-*block*-star triblock (pom-pom) polystyrene (experiment 1): 150 mg/mL in CDCl$_3$; 25 °C; Cr(acac)$_3$ concentration approximately 0.1%; frequency 79.48 MHz; spinning speed 15 Hz; pulse delay 15 s; total number of scans 2048; TMS used as external reference.

methylsilane to couple the living star-*block*-linear diblock. Two types of silicon atoms with different chemical environments are therefore expected, but the concentration of the coupling agent residues in the samples is very low. The triblock sample from experiment 1, which is the lowest molecular weight sample and therefore has the greatest concentration of Si from the two coupling agents, was analyzed by ^{29}Si NMR (Figure 5). Two peaks are observed in the spectrum. One peak is observed at −2.7 ppm and is attributed to the CDMSS residue at the core of the polystyrene star. The chemical shift is equivalent to what we reported previously for star and dendritic polystyrene (−2.8 ppm).[25] Another small peak is observed at 5.2 ppm and is attributed to the residue from dichlorodimethylsilane. Although the signal-to-noise ratio for this peak is low, the peak is found reproducibly at this chemical shift value. The peaks are relatively broad (about 2−2.5 ppm) and the low resolution is attributed to the long spin−lattice relaxation time of silicon,[37] low abundance of ^{29}Si, and the low silicon composition in the polymer.

The intrinsic viscosity reflects the chain conformation of the polymer in dilute solution. Star polymers resemble their linear chain analogues but have more compact structures leading to smaller hydrodynamic volumes. For star polymers with a given number of arms, a double-logarithmic plot of the intrinsic viscosity

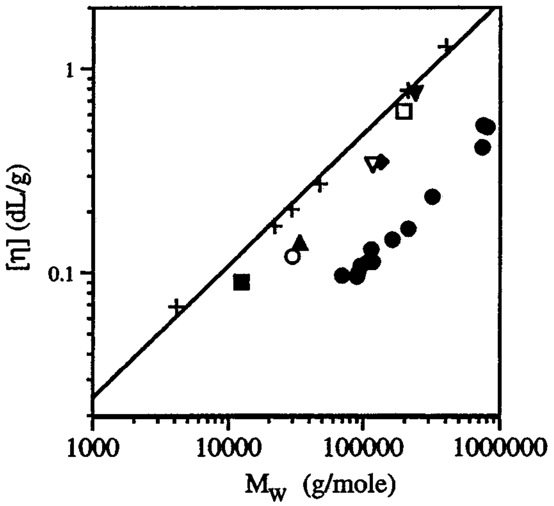


Figure 6. Intrinsic viscosity vs molecular weight relationship for linear (+),[53] dendritic (●),[25] and star-*block*-linear-*block*-star triblock (pom-pom) polystyrene (■, ○, ▲, ▽, ◆, □, ▼ for experiments 1−7, respectively).

as a function of the molecular weight results in straight lines which run parallel to the corresponding molecular weight dependence of the linear chains both in Θ-solvents and in good solvents.[49−51] Similar results are observed for H-shaped polymers.[11] This can be described by the contraction parameter, g', given in eq 2, as being constant for stars with a given number of arms.

$$g' = [\eta]_{\text{branched}} / [\eta]_{\text{linear}} \tag{2}$$

The star-*block*-linear-*block*-star triblock copolymers synthesized here contain two identical stars connected by a linear block. The double-logarithmic plots of the intrinsic viscosity as a function of the molecular weight for linear polystyrene, dendritic (hyperbranched) polystyrene,[25] and the star-*block*-linear-*block*-star polystyrenes are compared in Figure 6. At the same molecular weight, the intrinsic viscosity of the star-*block*-linear-*block*-star triblock is lower than that of the linear polystyrene but significantly greater than that of the dendritic polystyrene. This result is expected, since the triblock polystyrenes are more highly branched than linear polystyrene but less branched than the dendritic polystyrene samples. In the star-*block*-linear-*block*-star samples from experiments 1−4, the molecular weight of the arms remain relatively constant (~1000 g/mol), but the number of arms in the star, the length of the linear block, and the relative composition of star and linear blocks varies between samples. The contraction parameter, g', for these samples varies as a function of both the weight fraction of linear material and the total number of arms (Table 4). For example, samples from experiments 1 and 2 have the same weight fraction of linear block (0.53), but g' changes from 0.75 to 0.57 as the total average number of arms changes from 5 to 13. The samples from experiments 5−7 contain the same terminal star blocks (10 total average number of arms) but contain different lengths, and therefore different weight fractions, of the bridging linear block. The contraction parameter changes form 0.65 to 0.92 as the weight fraction of the linear block goes from 0.60 to 0.80. Samples with a wide variety of compositions and relative architectures can be made by this technique, and the intrinsic viscosity behavior reflects the variety in structure.

Table 4. Characterization of Star-*block*-Linear-*block*-Star Triblock Polystyrene

expt	$[\eta]^{\text{THF}}_{30°\text{C}}$ (dL/g)[a]	$[\eta]^{\text{THF}}_{30°\text{C}}$ (dL/g) linear polystyrene[b]	g' ($[\eta]_{\text{branched}}$/ $[\eta]_{\text{linear}}$	av no. of arms in triblock[c]	wt fraction of linear block[c]
1	0.09	0.12	0.75	5.0	0.53
2	0.12	0.21	0.57	13	0.53
3	0.14	0.23	0.61	12	0.58
4	0.34	0.46	0.74	18	0.78
5	0.35	0.52	0.67	10	0.60
6	0.62	0.72	0.86	10	0.76
7	0.77	0.82	0.94	10	0.80

[a] After fractionation. [b] Calculated based on $[\eta] = (2.29 \times 10^{-4})M_w^{0.667}$ for linear polystyrene—obtained from linear polystyrene standards at 30 °C in THF.[52] [c] Removal of lower molecular weight triblock by fractionation means the actual number of arms is higher than this value. [d] Based on the theoretical average triblock structure ($2M_n$ of diblock).

Conclusions

The technique of convergent living anionic polymerization has been expanded to produce star-*block*-linear-*block*-star (pom-pom) polystyrenes. The one-pot procedure allows control over the average number of arms of the star block and the length of the linear segment that bridges the stars. The A_nBA_n type star-*block*-linear-*block*-star triblock polymers produced by the one-pot, sequential monomer addition followed by coupling contain minimal contamination from the previous blocks. Although the amount of residual diblock increased in the samples with an increase in the molecular weight of the samples being coupled, purified star-*block*-linear-*block*-star triblock polymers can be obtained by fractionation. Characterization by dilute solution viscometry reflects the altered hydrodynamic volumes of the architectural copolymers compared with linear and other branched architectures. Triblock copolymers with varied molecular weight and number of arms as well as with variation in the length of the linear bridge are being investigated to produce materials for further examination of physical properties. Furthermore, the synthesis procedure is being reinvestigated in order to improve the coupling of diblock into triblock.

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Supporting Information Available: GPC chromatograms of all experiments and a representative intrinsic viscosity plot. This material is available free of charge via the Internet at http://pubs.acs.org.

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