$((PS)_nPS)_m$ Star-Shaped Polystyrene with Star-Shaped Branches at the Terminal Chain Ends by Convergent Living Anionic Polymerization

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Received January 27, 2003; Revised Manuscript Received May 29, 2003

ABSTRACT: Radially linked star-*block*-linear polystyrenes, star-shaped polymers with star-shaped branching at the ends of each arm, were synthesized by the convergent living anionic polymerization method. These novel structurally modified polymers were synthesized by sequential addition of a specific coupling agent, 4-(chlorodimethylsilyl)styrene (CDMSS), styrene, and CDMSS again to a solution of living polystyrene. Through a convergent process, the addition of the coupling agent to the living polystyrene solution resulted in star-shaped polymers with a hyperbranched core containing a single living site, which was used to initiate styrene to obtain living star-*block*-linear polystyrene diblock polymers. The living diblock was radially linked by the addition of CDMSS through another convergent process. The resulting polymers were purified by fractionation. The success of the synthesis was demonstrated by the molecular weight progression (gel permeation chromatography with multiangle laser light scattering detection). Glass transition temperature behavior relates to the end-group concentration combined with the effect of the branch points. Dilute solution properties studied by viscometry demonstrate that the polymers have lower intrinsic viscosity values than regular star-shaped polymers.

Introduction

Star-shaped polymers are the simplest type of branched polymer, with polymer chains connected at a single branch point. The synthesis of basic star-shaped polymers has been extended in recent years to the formation of polymers with more complex architectures.[1] The chemical compositions or molecular weights of the star arms have been varied to make asymmetric stars,[2,3] and the arms of stars have been modified with functional end groups or with dendritic peripheries.[4−9] Branching also has been introduced into the arms of star-shaped polymers to result in “umbrella stars”,[10,11] which are copolymers based on a central star with several branches grafted to the end of each arm, “dendrimer-like stars”,[12−17] which are star-shaped polymers with several generations of dendritic branching on each arm, and “comb stars”[18] or “star combs”[19] where the arms of the star consist of a comb-branched polymer. Many other types of complex-branched polymer architectures exist, such as “arborescent”[20,21] and “dendrigraft”[22] polymers, but are based more on a graft polymer architecture rather than on the basic star polymer architecture.

Although different polymerization mechanisms have been used to synthesize star-shaped polymers,[23] living anionic polymerization has great advantages over other polymerization methods for the preparation of star-shaped polymers or copolymers with well-defined structures and low degrees of heterogeneity.[24] Both “core first” and “arm first” methods have been used to synthesize star-shaped polymers by living anionic polymerization.[1,24,25] In the “core first” method, star-shaped polymers are synthesized by growing arms from a multifunctional initiator and in the “arm first” method by linking the preformed arms to a multifunctional linking agent. One advantage of the “arm first” method is that the molecular weights of the star and the precursor arms can be characterized independently, so the number of arms can be readily determined. Multifunctional silyl halides and divinyl compounds have been successfully used as the two main types of coupling agents to prepare star-shaped polymers by the “arm first” method. Multifunctional silyl halides work by effectively terminating multiple chains as they are coupled to the reactive core to result in the termination of all living chains. Divinyl compounds form star-shaped polymers through the addition of living polymeric chains to the vinyl groups without termination to result in a cross-linked core that contains as many living anions as arms that are coupled.

We have recently developed a novel method to synthesize star-shaped polymers.[26−28] The technique involves reactions of living linear chains with a bifunctional reactant, 4-(chlorodimethylsilyl)styrene (CDMSS), which contains a silyl chloride group capable of quantitatively terminating a living chain and a polymerizable vinyl group that is capable of addition and maintaining a living reaction site. We have demonstrated that macromonomers can be formed and subsequently polymerized in situ by anionic polymerization. The controlled addition of the coupling agent to living chains allows the reaction to proceed in a convergent fashion to form star-shaped polymers with a hyperbranched core. The molecular weight of the stars and the arms can be characterized independently; therefore, the average number of arms can be readily determined. Whereas multifunctional silyl halides form stars by terminating each living site at the core of the star and divinyl compounds result in the same number of living sites as arms attached, convergent living anionic polymerization results in only one living anion on the star during the synthesis. The proposed mechanism and a kinetic model of this method have been reported.[27]

We have been investigating this technique to synthesize polymers with more complex architectures. The addition of coupling agent, with or without comonomer, can be stopped before the complete addition of the

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10.1021/ma034108l CCC: $25.00

stoichiometric amount of CDMSS to retain a living anion at the focal point. Functionalizing the living site with a vinyl group can produce star-shaped or dendritic macromonomers, which have been used to synthesize graft copolymers.[29] By adding new monomers to the living site, dendritic-*block*-linear diblock copolymers, star-*block*-linear diblock copolymers,[30] and star-*block*-linear-*block*-star triblock (pom-pom) copolymers have been synthesized.[31]

The development of this technique is continuing in order to synthesize other polymer architectures. This paper presents more complete results than previously communicated[32] on the synthesis and characterization of a novel structure that is prepared by radially linking living star-*block*-linear diblock polymers. The reaction produces a polymer that can be described as a star-shaped polymer with star-shaped branching on the terminal chain ends of each arm. The final structures are designated as $((PS)_nPS)_m$, where the n refers to the average number of arms in the terminal star and the m refers to the number of core arms, following the type of nomenclature used by Hadjichristidis and others.[1-3] The structure of the polymer somewhat resembles star-shaped polymers with dendrimer peripheries[8,9] and umbrella-star structures.[10,11] Other structures with star-shaped branching at the terminal ends of a star have also recently been reported, either by using some aspects of the same procedure to produce well-defined copolymers with two chains extending from the star arms[33] or by growing two polymer chains from the terminal ends of a star.[34] The structures presented here are unique as a result of the versatility of the in situ polymerization, the control of the average number of arms attainable in both the inner and outer stars, and the all polystyrene composition.

Experimental Section

Materials. Styrene (99%, inhibited with ~10−15 ppm 4-*tert*-butylcatechol), *p*-chlorostyrene (97%, inhibited with ~500 ppm 4-*tert*-butylcatechol), 1,2-dibromoethane (99%), 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 molarities of the solutions were determined to be 1.10 M (used for experiments 1−5) and 1.30 M (used for experiments 6−11) by repeated initiation and polymerization of styrene and the subsequent analysis of the molecular weights by gel permeation chromatography coupled with multiangle laser light scattering (GPC-MALLS). HPLC grade (99.95%) tetrahydrofuran (THF) was obtained from EM Science, dried over sodium metal, and distilled from sodium benzophenone ketyl under argon. Cyclohexane (99%) from Fisher Scientific was purified by repeated washings with H_2SO_4 and water and then distilled from sodium metal. 4-(Chlorodimethylsilyl)styrene (CDMSS) was synthesized as previously reported.[27] CDMSS was dried over calcium hydride and distilled under reduced pressure immediately before use. High-purity toluene (99.99%) from EM Science and reagent grade methanol (98%) from Aldrich Chemical Co. were used as received for fractionation and precipitation. 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. Gastight syringes (Hamilton Co., #1005 and #1010) were prepared by sequentially washing with dilute *sec*-butyllithium solution and purified cyclohexane.

Polymerization. All polymerizations were carried out at room temperature using a slow addition technique by using gastight syringes and a syringe pump. A typical polymerization procedure for the synthesis of a radially linked star-*block*-linear polymer, $((PS)_nPS)_m$, is described as follows (experiment 1):

Initial Chain, (PS). Styrene monomer (2.5 mL, 21.8 mmol) was charged 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 (5 mL solution) was removed and precipitated into argon-purged methanol.

Initial Star, $(PS)_n$. THF (3 mL) was added to the reaction mixture. A solution of CDMSS in cyclohexane (approximately 0.50 M) was then added by syringe pump using a gastight syringe at a rate of 1.0 mL/h. 3.8 mL of CDMSS/cyclohexane mixture was added over a course of approximately 4 h. One hour after the complete addition, an aliquot (5 mL solution) was removed and precipitated into argon-purged methanol.

Star-block-Linear Diblock, $(PS)_nPS$. Styrene monomer (8.0 mL, 69.8 mmol) was added slowly over 0.5 h using a gastight syringe with the addition rate controlled by a syringe pump. One hour after complete addition, an aliquot (5 mL solution) was removed and precipitated into argon-purged methanol.

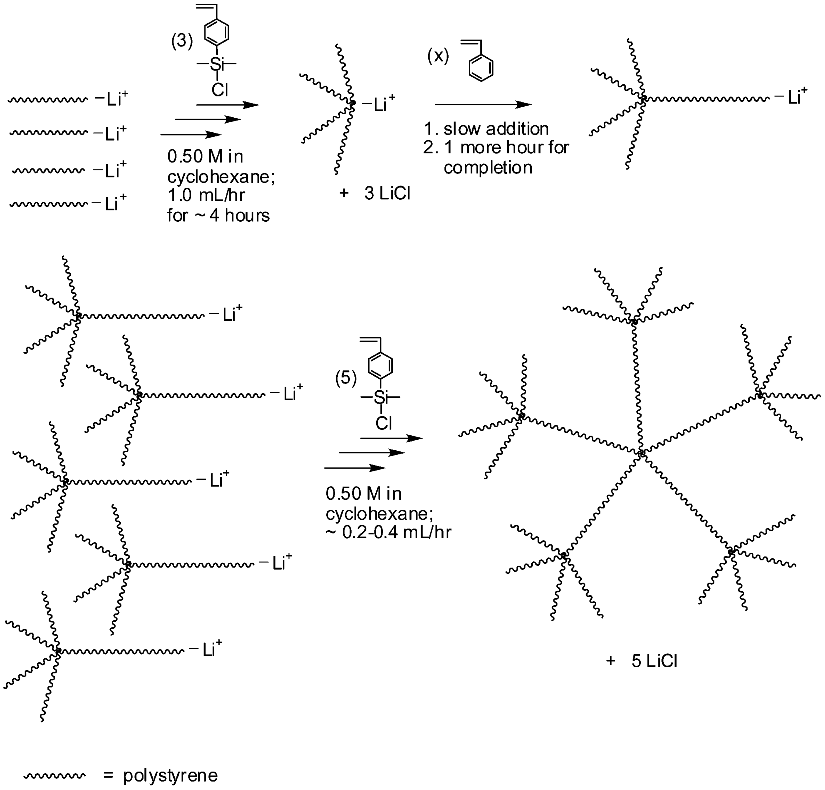
Radially Linked Star-block-Linear Polymer, $((PS)_nPS)_m$. CDMSS in cyclohexane (approximately 0.50 M) was added slowly using a gastight syringe at a rate of 0.4 mL/h until the reaction solution turned colorless. A total of about 2.0 mL CDMSS/cyclohexane mixture was added over a course of 5 h. The polymer was isolated by precipitation into methanol followed by filtration, washing with methanol, and drying at room temperature under vacuum. The yield of the final product was quantitative after considering the removed aliquots. ^1H NMR ($CDCl_3$): δ 0.1 ppm (s, $-Si-(CH_3)_2$); δ 1.3−2.3 ppm (m, $-CH(CH_3)CH_2CH_3$ and $-CH(Ph)-CH_2-$); δ 6.4−7.2 ppm (m, $Ph-H$). ^{29}Si NMR ($CDCl_3$, with ~0.1 wt % $Cr(acac)_3$): −2.7 ppm (s, $-Si(CH_3)_2-Ph$).

In several of the experiments, the star-shaped macroinitiators, $(PS)_n$, produced during the first convergent process were split into separate reaction flasks before continuing the syntheses in order to produce different samples with final structures that contained the same star terminal groups. Experiments 5−7 used the same initial stars, and experiments 8−10 used the same initial stars.

Fractional precipitation was performed on all final samples to carefully remove low molecular weight materials. Toluene/methanol was used as the solvent/nonsolvent pair in this work. Selection for the high molecular weight fraction, rather than a high yield, was the focus of the fractionation, and the resulting yield of the desired portion after fractionation varied between samples from 52 to 72%. An example procedure is given for the polymer from experiment 1. 8.6 g of crude polystyrene sample was dissolved in 430 mL of toluene to make an approximately 2% w/v solution. Methanol was added dropwise using a pipet until the solution turned slightly turbid. 5−6 mL of methanol was then added, and the turbid solution was sufficiently warmed until it became clear. After slowly cooling the solution to room temperature, a concentrated layer containing high molecular weight component was separated from the bulk solution. The procedure was repeated two more times on the bulk solution to obtain two more high molecular weight fractions. The low molecular weight component remaining in the bulk solution was recovered by rotary evaporation of the solvent. The three fractions with high molecular weight component were combined and dissolved in toluene, and the whole fractional precipitation procedure was repeated one more time to remove more low molecular weight material. The recovered mass of purified $((PS)_nPS)_m$ for this particular sample was 4.7 g, which gave a yield of 55%, while the total mass recovery was approximately 95%.

Characterization. Molecular weights and molecular weight distributions 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 ($\lambda = 690$ nm, three detector

Scheme 1. Reaction Sequence for the Synthesis of Radially Linked Star-*block*-Linear Polystyrene, $((PS)_nPS)_m$ Polymers



Reacted at room temperature in cyclohexane with 3% v/v THF

angles: 45°, 90°, and 135°). Elutions for experiments 1−4 were carried out with two Hewlett-Packard Plgel 5μ Mixed-D columns (linear range of molecular weight: 200−400 000 g/mol) at ambient temperature with THF at a flow rate of 0.70 mL/min. Elutions for experiments 5−10 were carried out in THF at a flow rate of 1.0 mL/min with one Plgel 5μ Mixed-D and one Plgel 5μ Mixed-C column (linear range of molecular weight: 200−2 000 000 g/mol) in series. The molecular weight characterization software (Astra 1.5.0b2) was supplied by Wyatt Technology. The refractive index increment (d*n*/d*c*) used for the samples was 0.193 mL/g.[27,35]

^1H 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 wt %) was used to decrease the long spin−lattice relaxation time.[36,37] Sample concentrations were approximately 150 mg/mL in $CDCl_3$. The chemical shift of tetramethylsilane (TMS) was measured before and after each polymer sample, and the chemical shift difference for TMS was less than 0.02 ppm for all experiments.

Glass transition temperatures (T_g) were measured on a Perkin-Elmer DSC-7 instrument using Pyris software. The samples were dried under vacuum at 100 °C for 24 h. Heating rates were 10 °C/min, and measurements were carried out under nitrogen purge. T_g was taken at the midpoint of the heat capacity change as determined by the baseline tangents.

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

Results and Discussion

Polymer Synthesis. Polystyrene with a radially linked star-*block*-linear architecture, $((PS)_nPS)_m$, was synthesized by the method depicted in Scheme 1.

The synthetic method involves four steps including two similar processes of convergent living anionic polymerization. In the first step, living polystyrene chains were synthesized by initiating styrene monomers with *sec*-BuLi. In the second step (first convergent process), the preformed linear living polystyrene chains were coupled by reaction with slowly added CDMSS to form a star-shaped polymer as previously reported.[27,31] The addition was stopped prior to a stoichiometric amount of CDMSS (relative to the initial living chains) to maintain a living site at the focal point. In the third step, the living star-shaped polymer was used as a macroinitiator for styrene monomer to grow a polystyrene chain. This step can be considered as growing a polymer arm from the core of the star as is done in “core first” methods; therefore, the synthesis of the star-*block*-linear diblock, $(PS)_nPS$, provides a method to synthesize asymmetrical star-shaped polymers.[2,3] The final step, or the second convergent process, involves the slow addition of CDMSS to couple the star-*block*-linear diblock living chains in a radial fashion around a new hyperbranched core to form $((PS)_nPS)_m$. A stoichiometric equivalent of CDMSS relative to the number of living diblock chains is added in this step in order to couple the chains and terminate the polymer with the formation of a vinyl functional group at the core of the coupled structure. Polymers were produced sequentially in the same reaction pot. At each reaction stage, the reaction solution was sampled and characterized by GPC-MALLS; therefore, the progression of the molecular weight could be followed.

This synthesis method allows the control of several variables. First, the length of the arms of the initial star can be controlled by varying the molar ratio of monomer to initiator. Second, the average number of arms of the

Table 1. Synthesis of $((PS)_nPS)_m$ Polymers: Characterization of Chain Lengths and Arm Numbers

exp[a]	[St]/[BuLi]	M_n of initial chains[c] (g/mol)/PDI	addition rate of CDMSS[b] (mmol/h)/BuLi (mmol)	M_n of $(PS)_n$, initial stars[c] (g/mol)/PDI	n^d (av no. of initial star arms)	M_n of $(PS)_nPS$,[c] star-*b*-linear diblock (g/mol)/PDI	M_n of $((PS)_nPS)_m$,[c,e] radially linked diblock (g/mol)/PDI	$m^{d,e}$ (av no. of core arms)
1	8.0	980/1.10	0.50/2.75	2810/1.24	2.6	10600/1.02	70200/1.13	6.5
2	8.0	1010/1.08	0.50/2.75	3250/1.22	2.9	16200/1.01	105000/1.16	6.5
3	8.0	1090/1.04	0.50/2.75	4320/1.29	3.6	21300/1.01	121000/1.16	5.6
4	8.0	1090/1.04	0.50/2.75	3650/1.26	3.0	19400/1.01	139000/1.13	7.2
5	10.0	1210/1.10	1.0/5.85	5060/1.36	3.8	15900/1.09	98100/1.15	6.2
6	10.0	1210/1.10	1.0/5.85	5060/1.36	3.8	27800/1.04	167000/1.17	6.0
7	10.0	1210/1.10	1.0/5.85	5060/1.36	3.8	50300/1.02	262000/1.19	5.2
8	49.0	4430/1.05	1.0/5.85	18900/1.26	4.2	25000/1.18	145000/1.15	5.8
9	49.0	4430/1.05	1.0/5.85	18900/1.26	4.2	37600/1.09	178000/1.17	4.7
10	49.0	4430/1.05	1.0/5.85	18900/1.26	4.2	59200/1.03	288000/1.15	4.9

[a] All reactions were done at room temperature in cyclohexane with 3% v/v THF. [b] Addition of CDMSS (approximately 0.50 M in cyclohexane) was completed in the time range of 4−5 h. [c] M_n and PDI were determined by GPC-MALLS. [d] Determined by eq 1, the number of arms $f = 2^G$; eq 1 for calculation of the number of arms, m, of $((PS)_nPS)_m$ is slightly modified to $G = [\log(M_{star}) - \log(M_{initial} + M_{branch})]/\log 2$ to account for the final stoichiometric addition of coupling agent. [e] After fractionation.

initial star can be controlled by the amount of CDMSS added relative to the amount of living chains. Third, the length of the linear block can be controlled by the stoichiometric amount of styrene added relative to the concentration of living stars. Finally, adjusting the amount of CDMSS added in the final step can accomplish some control of the coupling of the star-*block*-linear diblocks as in the synthesis of the initial star.[30,31] More details concerning each step of the procedure are described as follows.

Living linear polystyrene chains were prepared in cyclohexane by initiating styrene monomer with *sec*-BuLi at the desired monomer/initiator molar ratio. Relatively short (<5000 g/mol) living chains were targeted in this work. An aliquot of reaction solution was removed, terminated with argon-purged methanol, and isolated by precipitation in methanol. The molecular weights were characterized by GPC-MALLS, and the results for 10 different experiments are presented in Table 1. The number-average molecular weights of initial chains for experiments 1−7 were approximately 1000 g/mol and for experiments 8−10 were around 4400 g/mol.

THF (approximately 3% v/v) was introduced to the bulk reaction solution to increase the reaction rate, and the living chains were then coupled by reaction with slowly added CDMSS in a convergent process.[31] A living star-shaped polymer with a desired average number of arms was obtained by adding less than the stoichiometric amount of CDMSS relative to the amount of living chains. The determination of the maximum number of arms under the given reaction conditions and the relationship between the desired number of arms of living star and the amount of CDMSS added were discussed previously.[31] The molecular weights of the living stars were characterized by GPC-MALLS, and the results are presented in Table 1. Using the molecular weight of the initial living chains, the average numbers of arms (f) in the stars were calculated using eq 1[27]

$$G = \frac{\log(M_{star} + M_{branch}) - \log(M_{initial} + M_{branch})}{\log 2}; \quad f = 2^G \qquad (1)$$

where M_{star} is the molecular weight of the living star, $M_{initial}$ is the molecular weight of the initial living chains, and M_{branch} is the molecular weight of the branching unit. The average numbers of arms for the initial stars varied from 2.6 to 4.2, depending on the amount of CDMSS added. While the number of arms coupled in the star is an average number, the polydispersity is relatively low.

The stars, which retain a living site at the focal point, were used as macroinitiators to polymerize more styrene monomer to synthesize the star-*block*-linear diblocks, $(PS)_nPS$. The length of the linear block can be controlled by the stoichiometric amount of styrene added relative to the concentration of living stars. The styrene monomer was added slowly to prevent any possible temperature increase caused by the exothermic polymerization. Previous work demonstrated that the initiation efficiency of the living star is essentially quantitative and fast despite the possible steric hindrance effects at the living focal point, and GPC-MALLS characterization has demonstrated that the diblocks have relatively low polydispersities.[30,31]

The diblocks were sampled and characterized by GPC-MALLS by removing an aliquot from the reaction solutions after completion of polymerization. The number-average molecular weights of the star-*block*-linear diblocks, $(PS)_nPS$, varied from 10 600 to 59 200 g/mol.

The living star-*block*-linear diblocks were coupled through the formation of a new hyperbranched core to form the final structure, $((PS)_nPS)_m$, by slowly adding CDMSS into the reaction solution. The addition of the CDMSS in the convergent process is similar to that in the synthesis of the initial living stars, but a final stoichiometric amount of CDMSS was added to produce the maximum number of arms of the final structure.

The crude $((PS)_nPS)_m$ polymers synthesized by convergent living anionic polymerization contain a small amount of low molecular weight components: diblocks, initial stars, and initial chains. The low molecular weight components are a result of incomplete coupling and some premature termination during the sequential synthesis using syringe techniques. A fractional purification procedure was performed on the crude $((PS)_nPS)_m$ polymers to remove the low molecular weight contaminants. The molecular weights of the radially linked star-*block*-linear polymers, $((PS)_nPS)_m$, after fractionation were characterized by GPC-MALLS. The average number of arms of the final, radially linked architectural block copolymers was calculated by the same method used for the initial stars, with the molecular weight of the diblock used in the calculation instead of the molecular weight of the initial linear chains. The average number of star-*block*-linear arms, m in $((PS)_nPS)_m$, in the final structure varied from 4.7 to 7.2. The

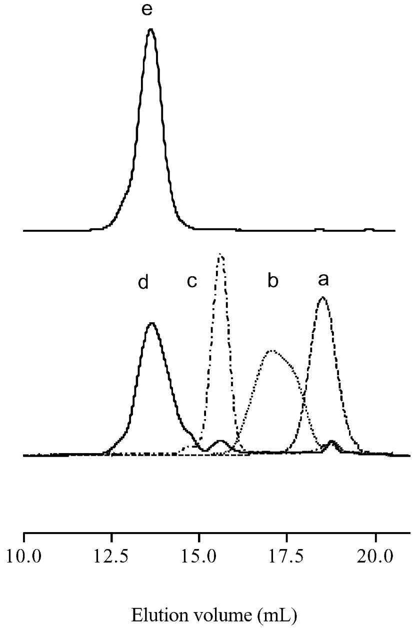


Figure 1. GPC chromatograms for experiment 1: (a) initial chain; (b) initial star; (c) star-*block*-linear diblock; (d) radial star-*block*-linear polystyrene; (e) purified radial star-*block*-linear polystyrene.

molecular weight characterization results for the star-*block*-linear diblocks and radially linked star-*block*-linear polystyrenes are presented in Table 1.

The progression of the synthesis is demonstrated by the changes in elution volume in the GPC chromatograms for aliquots of the reaction mixture at different stages of the polymerization. The GPC chromatograms for the synthesis of radially linked star-*block*-linear polystyrene, $((PS)_nPS)_m$, from experiment 1 are shown in Figure 1. From high elution volume to low elution volume, (a) corresponds to the polystyrene initial chain, PS, (b) to the initial star, $(PS)_n$, (c) to the star-*block*-linear diblock, $(PS)_nPS$, and (d) to the radially linked star-*block*-linear polystyrene, $((PS)_nPS)_m$. The polydispersity remains relatively low at each stage of the reaction. Although some residual initial chain, initial star, and star-*block*-linear diblock in the as prepared crude materials are observed in the GPC chromatograms, the amount is negligible. A small amount of material with low coupling efficiency (triblocks or 3-armed stars) is observed as a shoulder on the peak of (d) the radially linked star-*block*-linear polymer, but most of the sample contains stars of higher order. This method is useful for preparing unique branched materials without the need for fractionation; however, to obtain only the desired branched polymer for characterization of its properties, any residual low molecular weight material was removed through purification by fractional precipitation. The GPC chromatogram of purified (fractionated) material is shown (e) above the unpurified peak at the same elution volume scale. Samples from other experiments show similar GPC chromatograms (see Supporting Information).

Glass Transition Temperature. Roovers and Toporowsky studied the glass transition temperatures (T_g) of 4- and 6-armed star-shaped polystyrene and found that the T_g depends on the concentration of chain ends but can also be influenced by the presence of the branch point.[38] We reached similar conclusions on the T_g behavior for star-shaped polymers with a hyperbranched core and dendritic polystyrenes.[27] The results were successfully explained by Fox–Flory chain end free volume theory,[39,40]

Table 2. Glass Transition Temperature Characterization for $((PS)_nPS)_m$ Polymers

exp	T_g (°C)	M^a (per 2 chain ends) (g/mol)	exp	T_g (°C)	M^a (per 2 chain ends) (g/mol)
1	100	8300	6	102	14 700
2	101	11 100	7	103	26 500
3	102	12 000	8	102	11 900
4	102	12 900	9	103	18 000
5	99	8330	10	105	28 000

[a] Calculated by $2M_n$/the average number of chain ends of the polymer.

$$T_g = T_{g,\infty} - K/M \tag{2}$$

where K is a constant related to the nature of the end group, density of the bulk polymer, free volume expansion coefficient, and structural features,[41] and $T_{g\infty}$ is the glass transition temperature at infinite molecular weight where the effect of end groups is reduced to zero. For branched polymers, M can be considered to be equal to the number-average molecular weight divided by one-half the number of the end groups so that a direct comparison can be made to linear polymers.[27] The branch points can also have an effect on the T_g by reducing the free volume as observed in polymers with entanglements[41] and chemical cross-links.[42]

The T_g's were characterized for the fractionated $((PS)_nPS)_m$ polymer samples from each experiment and were found to range from 99 to 105 °C (Table 2). The T_g's are comparable to or higher than that of high molecular weight linear polystyrene; however, the end groups should lower the T_g in line with chain end free volume theory. The T_g vs M relationship is shown in Figure 2, where T_g was measured by DSC and M was calculated by the number-average molecular weight divided by half the number of total chain ends (the average number of arms of the core times the average number of initial star arms). The T_g behavior for linear polystyrene[43] and dendritic polystyrene[27] is shown for comparison. The T_g's for the $((PS)_nPS)_m$ polymer samples are somewhat higher than those observed for dendritic polystyrenes of comparable M. The branch points are proposed to have a significant effect on increasing the T_g. The higher functionality of the branch points for the $((PS)_nPS)_m$ polymers vs the trifunctional branch points of the dendritic polystyrenes may account for the higher T_g's compared to the dendritic samples, although other differences in the structures also exist.

Intrinsic Viscosity. Star-shaped polymers have more compact structures than linear polymers of the same composition, resulting in smaller hydrodynamic volumes.[44–47] A shrinking or contraction factor, g', given by eq 3, has been described for star polymers and has been experimentally determined in good solvents to be dependent on the number of arms (f) in the star according to eq 4.[46]

$$g' = [\eta]_{\text{branched}}/[\eta]_{\text{linear}} \tag{3}$$

$$\log g'_{\text{regular stars}} = 0.36 - 0.80 \log f \quad (f \geq 6) \tag{4}$$

The radially linked star-*block*-linear diblock copolymers, $((PS)_nPS)_m$, are star-shaped polymers but are more complex with star-shaped branching at the ter-

Table 3. Characterization of Intrinsic Viscosities of $((PS)_nPS)_m$ Polymers

exp	structure	$[\eta]_{((PS)_nPS)_m 30°C}^{THF}$ (dL/g)	g' [a] ($[\eta]_{((PS)_nPS)_m}/[\eta]_{linear}$)	$g'_{regular\ star}$ [b]	g'' [c] ($[\eta]_{((PS)_nPS)_m}/[\eta]_{regular\ star}$)
1	$((PS)_{2.6}PS)_{6.5}$	0.18	0.43	0.51	0.84
2	$((PS)_{2.9}PS)_{6.5}$	0.26	0.46	0.51	0.90
3	$((PS)_{3.6}PS)_{5.6}$	0.29	0.47	0.58	0.81
4	$((PS)_{3.0}PS)_{7.2}$	0.27	0.40	0.47	0.85
5	$((PS)_{3.8}PS)_{6.2}$	0.24	0.44	0.53	0.83
6	$((PS)_{3.8}PS)_{6.0}$	0.34	0.44	0.55	0.80
7	$((PS)_{3.8}PS)_{5.2}$	0.62	0.58	0.61	0.95
8	$((PS)_{4.2}PS)_{5.8}$	0.27	0.39	0.56	0.70
9	$((PS)_{4.2}PS)_{4.7}$	0.36	0.44	0.66	0.67
10	$((PS)_{4.2}PS)_{4.9}$	0.57	0.52	0.64	0.81

[a] Calculated based on $[\eta]_{linear} = (2.29 \times 10^{-4})M_w^{0.667}$ for linear polystyrene—obtained from linear polystyrene standards at 30 °C in THF.[24] [b] Equation 4: $\log g'_{regular\ star} = 0.36 - 0.80 \log f$. [c] Determined from ratio of $g'/g'_{regular\ star}$.

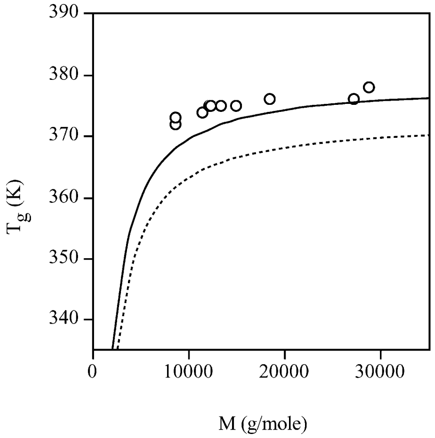


Figure 2. T_g vs M ($2M_n$/number of chain ends) for $((PS)_nPS)_m$ (○), linear polystyrene (dashed line), and dendritic polystyrene (solid line).

minal ends of each arm. A more compact structure in solvent and a lower g' value than that of a regular star with the same number of core arms and molecular weight is expected. The intrinsic viscosities of the $((PS)_nPS)_m$ polymers were measured in a good solvent (THF) at 30 °C. The intrinsic viscosities of linear polymers with the same molecular weight as the $((PS)_nPS)_m$ polymers were calculated on the basis of the intrinsic viscosity–molecular weight relationship, $[\eta] = (2.29 \times 10^{-4})M_w^{0.667}$, which was established by measuring the intrinsic viscosity of linear polystyrene standards in THF at 30 °C.[28] The intrinsic viscosity contraction factor, g', was calculated from eq 3, and the g' values expected for regular star-shaped polymers with the same number of core arms were calculated using eq 4. The characterization results are presented in Table 3.

The more compact structure of the $((PS)_nPS)_m$ polymers relative to regular star-shaped polymers of the same molecular weight could be described by another contraction factor, given by eq 5.

$$g'' = g'/g'_{star,\ calculated} = [\eta]_{((PS)_nPS)_m}/[\eta]_{regular\ star} \quad (5)$$

The contraction factor, g', has been shown to decrease to a plateau value with an increase in molecular weight (plateau around 10^5 g/mol),[48] and some of the polymers here may not be of high enough molecular weight to compare quantitatively. Furthermore, some of the samples are slightly below the threshold number of arms given in eq 4, which would result in slightly lower than calculated g' values[46] and therefore slightly larger than calculated g'' values.

For all of the radially linked star-*block*-linear polystyrenes obtained in this work, the g' values are lower than those calculated for regular star polymers with the same number of core arms. The relative amount of contraction of the polymers as a result of the star branching at the terminal ends of the arms is reflected in the g'' values. While the effect of the star branching on the terminal ends diminishes for polymers with long linear blocks (e.g., experiment 7), the effect is greatest for polymers where the segment density is increased closer to the core, i.e., when the linear block is relatively short. This is not unexpected given that g' decreases with an increase in the number of core arms for regular stars. In all cases, however, the amount of contraction is not nearly as great as if all arms were attached directly to the core. For example, summing the outer star arms and the linear blocks, the polymer from experiment 8 is made up of a total of 30.2 chain segments of approximately equivalent molecular weight. This polymer has the lowest g' value of 0.39, but the g' value is not as low as that calculated for a polymer with 30.2 chains emanating directly from the core (calculated to be 0.15 using eq 4).

Further determination of the intrinsic viscosity behavior based on the structure is difficult, given the differences in length and number of the star arms along with the changes in length of the linear block for the synthesized structures. Further evaluation of the solution properties and polymer dimensions dependent on chain architecture is in progress.

Conclusions

This work demonstrates a relatively simple method to synthesize star-shaped polymers with controlled star-shaped branching on the terminal ends of the arms. Living anionic polymerization combined with controlled functionalization of the growing chain end can result in a variety of chain architectures as demonstrated in this paper. The sequential addition of coupling agent, monomer, and the coupling agent again to preformed living polystyrene chains in a one-pot process resulted in living star-shaped polystyrene, living star-*block*-linear polystyrene, and ultimately radially linked star-*block*-linear polystyrene or $((PS)_nPS)_m$ polymers. The structure of the $((PS)_nPS)_m$ polymers can be varied by controlling the arm length of the initial star, the average number of the arms in the initial star, the length of the linear block of the star-*block*-linear diblock arm, and the number of the diblock arms in the final products.

The thermal properties of the polymers have been examined by differential scanning calorimetry to show that the T_g is affected by both the number of chain ends and the nature and number of branch points.

The $((PS)_nPS)_m$ polymers in a good solvent demonstrate lower intrinsic viscosities than their linear analogues as well as lower intrinsic viscosities compared to stars with the same number of core arms. However, the intrinsic viscosities are not as low as that expected for star polymers with the same overall number of arms emanating directly from the core due to the flexible linear block which allows a relative expansion of the structure.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research, and to the NSF for a CAREER award to D.M.K. (Grant DMR-9985221). Support from Kraton Polymers is also gratefully acknowledged.

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

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MA034108L