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Trifunctional Organolithium Initiator Based on 1,3,5-Tris(1-Phenylethenyl)benzene. Synthesis of Functionalized, Three-Armed, Star-Branched Polystyrenes

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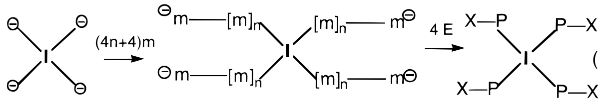
ABSTRACT: A novel hydrocarbon-soluble, trifunctional organolithium initiator for anionic polymerization has been developed on the basis of the addition of 3 mol of *sec*-butyllithium with 1,3,5-tris(1-phenylethenyl)-benzene. Well-defined, three-armed, star-branched polystyrenes have been synthesized using this initiator in benzene solution with stoichiometric amounts of tetrahydrofuran. The efficiency of the initiation reaction was evaluated by a combination of UV−visible spectroscopy and size-exclusion chromatography analysis. The minimum arm molecular weight for complete initiation was found to be about 5.7×10^{3} g /mol for this initiator system. The structures of the star-branched polymers were investigated by molecular weight characterization, intrinsic viscosity, and the corresponding values of g′ (0.80−0.81); these stars were also compared with an analogous symmetrical, three-armed, polystyrene star prepared by the end-linking reaction of 3 mol of poly(styryl)lithium with 1,3,5-tris(1-phenylethenyl)benzene as the linking reagent. Carbonation of a freeze-dried sample of a living three-armed, *ω,ω,ω*-tris[poly(styryl)-lithium] star prepared with the trifunctional initiator produced the corresponding *ω,ω,ω*-tricarboxyl-functionalized star with a functionality of 2.9_5.

Introduction

One of the major goals of synthetic polymer chemistry is to prepare polymers with control of the major variables affecting polymer properties. These variables include molecular weight, molecular-weight distribution, copolymer composition and microstructure, tacticity and diene microstructure, chain-end functionality, branching, and morphology. Anionic polymerization has approached the goal of synthesizing polymers with well-defined structures and low degrees of compositional heterogeneity in monomer−initiator−solvent systems that proceed in the absence of chain termination and chain-transfer reactions.[1,2]

The methodology of living anionic polymerization, especially alkyllithium-initiated polymerizations of styrene and diene monomers, is particularly suitable for the preparation of star-branched polymers and copolymers with well-defined structures. Since these living polymerizations generate stable, anionic polymer chain ends when all of the monomer has been consumed, postpolymerization reactions with a variety of multifunctional linking agents provide an elegant methodology for the preparation of regular, star-branched polymers.[1−6] In principle, for a regular star polymer, each arm is of uniform composition with precise molecular weight and narrow molecular-weight distribution (i.e., with low degrees of compositional heterogeneity).[5] Typical linking agents include multifunctional silyl and tin halides, multifunctional alkyl halides, divinylbenzenes, and multifunctional esters.[1] Recently, these linking methods have been extended to the preparation of heteroarm, star-branched polymers (i.e., star polymers in which the arms differ in either molecular weight or composition (also referred to as miktoarm star polymers)). The procedures for the preparation of heteroarm stars include living linking reactions with divinylbenzenes, 1,3-bis(1-phenylethenyl)benzene, 1,1-diphenylethylene-functionalized macromonomers, and also stepwise addition reactions with multilfunctional silyl halides.[1,7]

An alternative procedure for the preparation of star-branched polymers involves the use of multifunctional initiators. Thus, in principle, an initiator (**I**) of functionality **z** will generate star-branched polymers with **z** arms as shown schematically in eq 1 for **z** = 4 and monomer m. The advantages of the multifunctional initiator approach are primarily a consequence of the fact that the star polymer retains the carbanionic living chain ends of the arms after the monomer has been consumed. As a consequence of the living nature of this method, it is possible to prepare star polymers with a variety of chain-end functional groups (X, eq 1) by deliberate termination with various electrophilic species (E, eq 1). Furthermore, by sequential monomer addition it is possible to prepare new star-block copolymers that cannot be prepared by the end-linking procedures. For example, sequential polymerization of a styrene or diene monomer could be followed by polymerization of an alkyl methacrylate to form the outer block; such a polymer cannot be prepared directly by end-linking chemistry because the propagating ester enolate anion for an alkyl methacrylate polymerization is too stable to initiate styrene or diene polymerization.



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Unfortunately, the potential for new polymer syntheses using multifunctional initiators has not been realized because well-behaved, well-defined multifunctional initiators have not been available, especially for use in

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hydrocarbon media. Many multifunctional initiators have been prepared in polar solvents such as tetrahydrofuran which result in polydienes with a low 1,4-microstructure and high T_g values. A generally useful multifunctional initiator should utilize lithium as the counterion and should be soluble in hydrocarbon solvents so that polydienes can be prepared with a high 1,4-microstructure.[1]

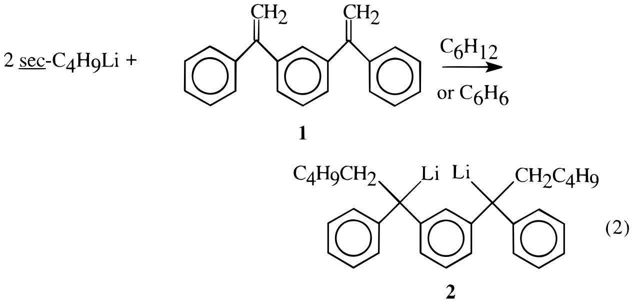
For example, Fijumoto and co-workers[8] prepared a trifunctional anionic initiator in THF from 1,3,5-tris(α-methoxybenzyl)benzene by reaction with a sodium/potassium alloy. The polymerization of α-methylstyrene at −78 °C in THF/diglyme produced a mixture of a base polymer, dimer, and star; the maximum content of the star polymer in the mixture was only 35%.

Hogen-Esch and co-workers[9] have described a trifunctional initiator on the basis of the metalation of 1,3,5-tris[2-(2′-pyridyl)ethyl]benzene by an α,*ω*-dipotassio-α-methylstyrene oligomer. The resulting anion was used to initiate polymerization of 2-vinylpyridine and 4-vinylpyridine at various temperatures in THF. In all cases, the unreacted initiator remained after polymerization and the polymer exhibited a broad molecular-weight distribution.

Gordon and co-workers[10] reported the preparation of a trifunctional initiator by trimetalation of 1,3-cycloheptadiene using Lochmann's base (n-C_4H_9Li/KO-*t*-Bu, 1/1) in pentane. Polymerization of styrene using this initiator was effected in THF; only simple SEC characterization was reported. A similar metalation of mesitylene (1,3,5-trimethylbenzene) reportedly formed a mixture of trifunctional, difunctional, and monofunctional carbanions.[11]

Anionic initiators such as butyllithium and naphthalene radical anions react with divinylbenzene by concurrent polymerization and branching reactions to form a compositionally heterogeneous, multifunctional initiator which can be described as a living microgel. For example, using the ratio [DVB]/[BuLi] = 2, the microgel exhibited $M_n = 1.9 \times 10^3$ g/mol and $M_w/M_n = 16.8$ and polymerized styrene to form a star polymer with a calculated star arm functionality of 6.[12] Rempp and co-workers[13,14] have recently extended this "core-first" method for preparation of star-branched polymers by preparing a "plurifunctional" initiator by potassium naphthalene-initiated polymerization of divinylbenzene in THF at −40 °C with [DVB]/[BuLi] = 0.5−3. Star polymers with arm functionalities varying from 8 to 42 were reported. However, the polydispersities were observed to be relatively broad as expected for a process which generates a random distribution of core sizes and functionalities.

An alternative approach for the preparation of hydrocarbon-soluble, multifunctional organolithium initiators is based on the addition of alkyllithium compounds to 1,1-diphenylethylene. 1,1-Diphenylethylene and its derivatives can be classified as nonhomopolymerizable monomers; they undergo monoaddition reactions with a variety of alkyllithium compounds and polymeric organolithium compounds.[15,16] This chemistry is the basis of a methodology for preparing polymers with chain-end and in-chain functional groups in quantitative yield.[17] The precedent for the preparation of a multifunctional initiator is provided by the fact that the reaction of 2 mol of *sec*-butyllithium with 1,3-bis(1-phenylethenyl)benzene (**1**) forms a hydrocarbon-soluble, dilithium initiator (**2**) as shown in eq 2.[18−20] This initiator produces narrow, monomodal molecular-weight-distribution polybutadienes and polystyrenes in the presence of lithium *sec*-butoxide or THF, respectively.[18] This dilithium initiator has been used to synthesize ABA triblock copolymers by a simple two-step procedure.[19,21] These previous results suggested that the chemistry of the facile, quantitative addition of organolithium compounds to diphenylethylene compounds could be extended to the preparation of a trilithium initiator (**4**) by the addition of 3 mol of *sec*-butyllithium to 1,3,5-tris(1-phenylethenyl)benzene (**3**) (see eq 3), the trifunctional analogue of 1,3-bis(1-phenylethenyl)benzene (see eq 2), which is the precursor for the analogous dilithium initiator.



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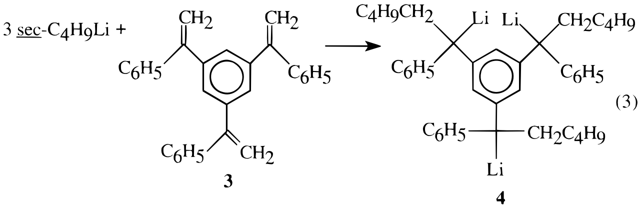

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Herein are reported the results of a systematic study of the reaction of *sec*-butyllithium with **3** to form a hydrocarbon-soluble, trifunctional initiator **4** and the use of this initiator to prepare well-defined, three-armed star-branched polystyrenes and their corresponding trifunctional chain-end functionalized derivatives.

Experimental Section

Materials. Styrene, benzene, and tetrahydrofuran (Fisher) were purified as described previously.[22−24] Solutions of *sec*-butyllithium (FMC, Lithium Division, 12.0 wt % in cyclohexane) were used for initiation after double-titration analysis.[25] The amount of non-carbon-bound lithium was determined to be <1% by double titration analysis.[25] A cylinder of carbon dioxide (Air Products, 99.99% pure, <2 ppm H_2O) was connected directly to a vacuum line via Cajon Ultra-Torr fittings and flexible steel tubing.

1,3,5-Tris(benzoyl)benzene, mp 113−114 °C [lit[26] mp 113−115 °C], was synthesized in 73% yield by a Friedel−Crafts reaction of 1,3,5-benzenetricarbonyl trichloride (Aldrich, 98%) with aluminum chloride in benzene followed by recrystallization in methanol. This compound showed only one peak by HPLC analysis. 1,3,5-Tris(1-phenylethylene)benzene was synthesized in 57% yield from 1,3,5- tris(benzoyl)benzene via the Wittig reagent[27] generated from methyltriphenylphosphonium iodide and methyllithium in THF using a procedure analogous to that reported by Schulz and Höcker[28] for the synthesis of 1,3-bis(1-phenylethenyl)benzene (**1**). Silica gel chromatography with toluene as the eluent was used to purify the crude product. The first eluted portion was collected and showed one spot by TLC analysis. Recrystallization in methanol produced pure samples of **3**: mp 90−91 °C [lit[26] mp 89−91 °C; lit[29] mp 97−99 °C]. ^1H NMR ($CDCl_3$): δ 7.36 (m, 18 H, arom CH), 5.47 ppm (m, 6H, $=CH_2$).[29] Only one peak appeared by SEC analysis of **3**. The FTIR carbonyl absorption at 1670 cm^{-1}, characteristic of the precursor 1,3,5-tris(benzoyl)benzene was not observed in the FTIR spectrum of **3**. Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.56; H, 6.41.[29]

Trifunctional Initiator Preparation and Polymerization. The addition reactions of *sec*-butyllithium with **3** 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.[30] To obtain precise stoichiometric control, *sec*-butyllithium was added stepwise to a benzene solution of **3** at room temperature. Following each addition, SEC analysis using a UV detector was used to monitor the extent of the addition reaction after removing a sample from the reaction and quenching it with degassed methanol. The addition of *sec*-butyllithium was continued until stoichiometric addition was achieved, as indicated by SEC analysis. The concentration of the initiator solution was determined by titration with *sec*-butanol using the method of Watson and Eastham.[31] The concentration of the initiator solution was 2.3×10^{-2} M; this solution was distributed into calibrated ampules which were sealed under high-vacuum conditions.

Polymerization was carried out using standard high-vacuum techniques.[32] Styrene (17.7 g, 0.17 mol) was polymerized in benzene (190 mL) using the trilithium initiator **4** (5.9×10^{-4} mol, 0.0295 M in 20 mL of benzene) either in the presence of THF ([THF]/[RLi] = 20) or in the absence of THF. Polymerizations proceeded for 50 min in an ice−water bath in the presence of THF and overnight at room temperature in the absence of THF. The polymerizations were monitored by UV−vis spectroscopy via a UV cell attached to the reactor. The resulting solution was split into ampules, sealed under high vacuum, and stored in a freezer. Deliberate termination was effected using ampules of degassed methanol.

For linking reactions, a stoichiometric amount of a solution of *sec*-butyllithium-initiated poly(styryl)lithium ($M_n = 8.5 \times 10^3$ g/mol; $M_w/M_n = 1.05$) in benzene was added stepwise (aliquot 1, 0.7 equiv; aliquots 2 and 3, 0.10 equiv; aliquot 4, 0.05 equiv; aliquots 3 and more, 0.01−0.005 equiv) to a benzene solution of **3** in the glovebox. Six hours after the addition of an aliquot, a sample was removed from the reactor, terminated with degassed methanol, and analyzed by SEC. After stoichiometric addition was achieved, the reaction was terminated with degassed methanol.

All polymers were isolated by precipitation of their benzene solutions into excess methanol, followed by precipitation, filtration, and drying under vacuum. The star polymer from the linking reaction of PSLi with **3** was purified (i.e., separated from an unlinked precursor) by fractionation of a toluene solution of the product mixture. Methanol was added until the mixture turned cloudy; the solution was then heated slightly until clear and left undisturbed at room temperature. The lower layer was separated and the polymer isolated by precipitation into methanol.

Functionalization. Carboxylations were performed by attaching the polymerization reactor to the vacuum line by heat-sealing and introducing gaseous CO_2 into the unstirred reactor through a breakseal.[22,33,34] For functionalizations in the presence of THF or after end-capping the polymer chain ends with 1,1-diphenylethylene,[34] these reagents in ampules were added to the reactor prior to addition of gaseous CO_2. For solid-state carboxylations,[33] the benzene solution of the living polymer was frozen using a dry ice−isopropyl alcohol bath and then the benzene was removed by sublimation into a liquid nitrogen-cooled receiver. After carbonation, solutions of polymeric carboxylate salts were hydrolyzed with methanol containing aqueous HCl (1 N) followed by precipitation into methanol. The concentration of carboxylic acid chain ends was determined by titration of a solution of 0.5 g of the functionalized polymer in 30 mL of THF with 0.01 N KOH in methanol to the phenolphthalein end point.[35]

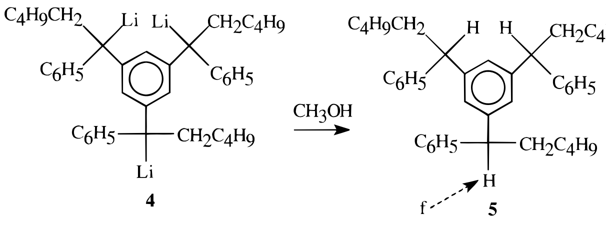
Characterization. Size-exclusion chromatographic (SEC) analyses of polymers were performed at a flow rate of 1.0 mL/min in THF at 30 °C using a Waters HPLC component system (RI or Hewlett-Packard 1040 diode array detector) equipped with ultra-micro-styragel columns (two 500, two 10^3, 10^4, and 10^5 Å) after calibration with standard polystyrene samples (Polymer Laboratories). The number-average molecular weights of star-shaped polymers were determined using membrane osmometry (membrane osmometer 503, Mechrolab Inc.) or by VPO (Knauer vapor pressure osmometer) at 37 °C in toluene. The weight-average molecular weights of these polymers were determined by coupling a Chromatix KMX-6 photometer with a Waters 150C instrument and interfacing the two with a digital computer. The intrinsic viscosities of star-shaped polymers were measured in THF at 30 °C using an Ubbelohde-type viscometer. Both ^{1}H (200 MHz) and ^{13}C (50 MHz) NMR spectra were measured in deuterated chloroform using a Varian Gemini-200 spectrometer. UV−vis absorption spectra of the initiator **4** and polymeric organolithiums were obtained using a Hewlett-Packard 8452A diode array spectrophotometer with a 0.1-cm UV cell attached to the polymerization reactor. Solutions were diluted in the UV cell by condensing the solvent from the reactor to obtain on-scale absorbances.

Results and Discussion

Initiator Preparation and Stoichiometric Control. The preparation of a useful trifunctional organolithium initiator by the addition of 3 mol of *sec*-butyllithium with 1,3,5-tris(1-phenylethenyl)benzene (**3**) (see eq 3) requires careful attention to stoichiometric control. If an excess of *sec*-butyllithium is used, either multimodal distributions or broad molecular distributions are obtained. If an excess of **3** is present, multimodal SEC behavior is observed with a high-molecular-weight peak [M_n (observed) > M_n (stoichiometric)] corresponding to branching functionalities greater than 3.[18,36] Thus, it was essential to prepare the pure trilithium initiator with precise stoichiometric control.

The addition products from the reaction of *sec*-butyllithium with **3** in benzene were carefully monitored by SEC. As soon as the first aliquot of *sec*-butyllithium (1.5 equiv) was added to **3**, a dark reddish color was observed, corresponding to the diphenylalkyllithium active centers (λ_{max} = 450 nm). Figure 1 shows the SEC−UV traces of the methanolysis products during the stepwise addition of *sec*-butyllithium. When less than the stoichiometric amount of *sec*-butyllithium had been added, a multimodal distribution was observed. From Figure 1, it was possible to detect the peaks corresponding to the monoaddition (23.2-min retention time), diaddition (22.5-min retention time), and triaddition (21.5-min retention time). When the stoichiometric point was reached, only one peak, corresponding to the triaddition (21.5-min retention time) was observed.

Titration results and the initial [**3**] indicated that the ratio of **3** to *sec*-butyllithium was 1:3. ^{1}H NMR analysis (Figure 2) of the methanolysis product of **4** (**5**, eq 6) indicates that all of the double bonds in **3** (δ = 5.47 ppm) had reacted with *sec*-butyllithium and a resonance is observed at 3.9 ppm which is characteristic of the tertiary 1,1-diphenylalkyl CH proton (see label f in eq 4). This ^{1}H NMR spectrum is very similar to the reported ^{1}H NMR spectrum of the methanolysis product from the analogous difunctional initiator, **2**.[18]



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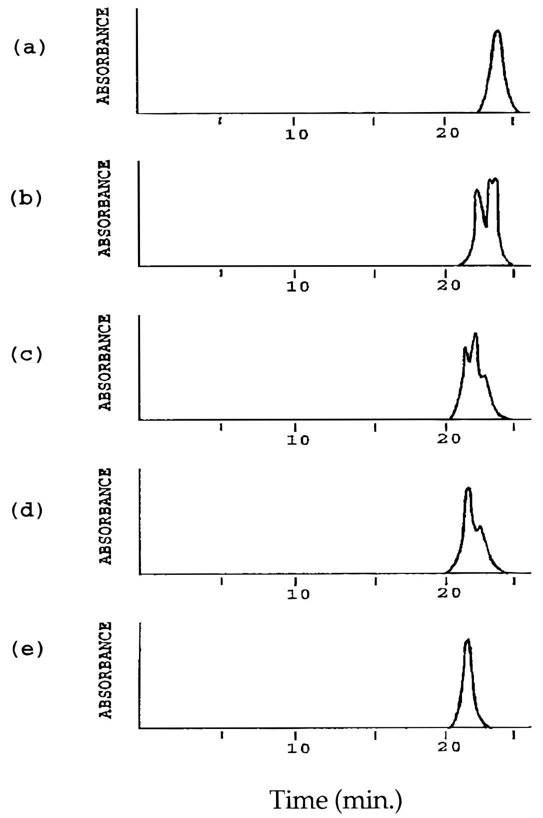


Figure 1. SEC chromatograms of the methanolysis products resulting from stepwise addition of *sec*-butyllithium (BuLi) to 1,3,5-tris(1-phenylethenyl)benzene (**3**) in benzene: (a) **3** before the addition of BuLi; (b) after addition of 50 mol equiv of BuLi; (c) after addition of 70 mol equiv of BuLi; (d) after addition of 90 mol equiv BuLi; (e) after addition of stoichiometric amount of BuLi.

The observed stoichiometric addition of *sec*-butyllithium to 1,3,5-tris(1-phenylethenyl)benzene, **3**, is somewhat surprising in view of the expected high anionic charge density at the three 1-phenylalkyl anions attached to a single benzene ring. The meta orientations of all of the anionic centers would be expected to minimize the charge overlap in the delocalized structures. That the delocalization is not negligible can be deduced from a comparison of the UV−vis absorptions for the difunctional initiator, **2** (λ_{max} = 438 nm[18,37]), compared to the trifunctional initiator **4** (λ_{max} = 450 nm), described herein.

Polymerization of Styrene Initiated by 4: Preparation and Characterization of Three-Armed, Star-Branched Polystyrenes. The initiation of styrene polymerization in benzene using the trifunctional organolithium initiator **4** was monitored by UV−vis spectroscopy. The crossover reaction from the tris(1,1-diphenylalkyllithium), **4**, with styrene to form poly(styryl)lithium active centers (i.e., initiation) was investigated by UV−vis spectroscopy by monitoring the decrease in absorbance corresponding to the initiator at 450 nm and the appearance of the poly(styryl)lithium absorbance at 334 nm.[38] After the addition of the styrene monomer [M_n (calc) = 30 × 10^3 g/mol] to the initiator **4** ([Li] = 9 × 10^{-3} M), a new peak was observed at 332 nm, corresponding to poly(styryl)lithium. After 12 h and complete consumption of the styrene monomer, the absorption peak corresponding to residual 1,1-diphenylalkyllithium initiator sites remained at 450 nm in the UV−vis spectrum of the products. This inefficient initiation process precludes the use of this initiator for the preparation of well-defined, star-branched polystyrenes under these conditions since it would be expected that mono-, di-, and trifunctional initiating species would all be growing in the reaction mixture to form a heterogeneous product with no control of the molecular weight.

The SEC chromatogram of the polymer prepared from initiator **4** in benzene solution exhibited a monomodal polymer peak centered at an elution volume of 29 mL; however, the molecular-weight distribution was quite broad (M_w/M_n = 1.55) as shown in Table 1 (sample 1). This type of inefficient initiation of styrene polymerization was also observed previously for the analogous dilithium initiator, **2**, in benzene.[18] However, for initiator **2**, bimodal molecular-weight distributions were observed.[18] Consistent with the UV−vis spectroscopic results, it was also determined that a small peak observed in the SEC chromatogram at an elution volume of approximately 45.5 mL corresponded to the hydrolysis product, **5**, from the residual initiator.

Consistent with inefficient initiation by the initiator, **4**, in benzene, the observed number-average molecular weight [M_n(obs) = 74 000 g/mol] is more than twice as large as the calculated value [M_n(calc) = 30 000 g/mol] (see Table 1). The calculated molecular weight is based on the ratio of g of monomer/mol of initiator (**4**),[1] assuming that all of the lithium initiation sites are active. Further aspects of the characterization of this polymer will be deferred for later discussion.

Previous studies using the dilithium initiator, **2**, suggested that inefficient initiation was a result of strong intermolecular association effects of the initiator with other molecules of the initiator.[18] If strong association or cross association of organolithium chain ends is the cause of the inefficient initiation observed with the initiator, **4**, it was deduced that the addition of a Lewis base such as THF might promote efficient initiation, since it is known that THF and other Lewis bases promote the dissociation of organolithium aggregates to form either unassociated species or aggregates with lower average degrees of association.[1,39−42] The amount of THF added was minimized, however, since it is known that simple and polymeric organolithium compounds react with THF by transferring a proton to the organolithium reagent and forming a molecule of ethylene and the lithium enolate of acetaldehyde.[1,41,43] To minimize or avoid this reaction, the amount of THF added to the preformed trifunctional initiator prior to the addition of the styrene monomer corresponded to [THF]/[RLi] = 20.

The crossover reaction from the tris(1,1-diphenylalkyl lithium) initiator, **4**, with styrene to form poly(styryl)lithium chain ends in the presence of THF was investigated by UV−vis spectroscopy. After the addition of THF ([THF]/[RLi] = 20) to the initiator, **4** ([Li] = 9 × 10^{-3} M), the initiator peak shifted from 450 to 480 nm. This bathochromic shift of the absorption peak is consistent with the formation of more dissociated ionic species in the Winstein spectrum,[44] such as solvent-separated ion pairs.[1,45] More dissociated ionic species are generally more reactive than the less dissociated analogues.[1,45] After the addition of the styrene monomer [M_n(calc) = 30 × 10^3 g/mol], the decrease in the absorbance of the initiator, **4** at 480 nm and the appearance of the poly(styryl)lithium absorbance at 332

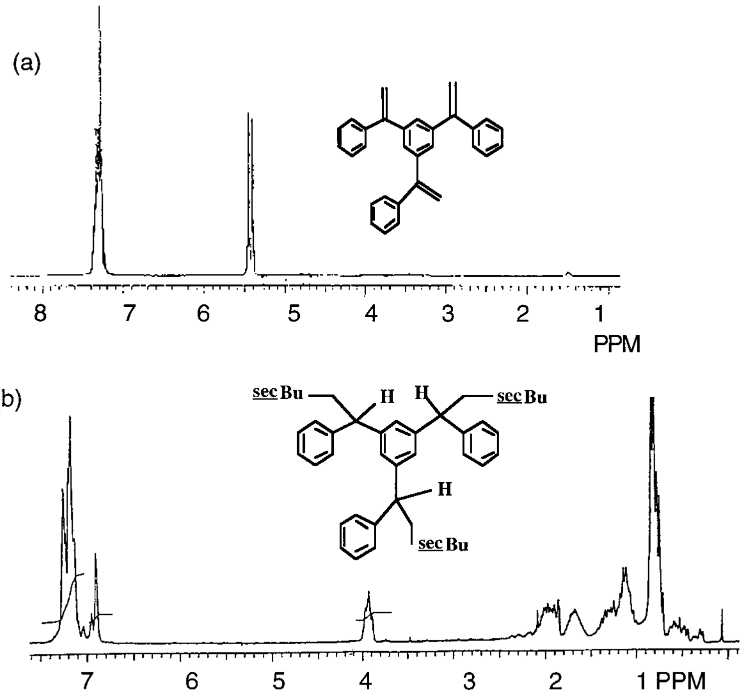


Figure 2. (a) ^{1}H NMR spectra of 1,3,5-tris(1-phenylethenyl)benzene (**3**) and the methanolysis product of the trifunctional initiator (**4**).

Table 1. Characterization Data of Three-Armed, Star-Branched Polystyrenes Synthesized in Benzene and in Benzene with Added THF with Initiator 4 and Also Prepared by the End-Linking of PSLi with 3

	molecular weight × 10^{-3} g/mol						
		SEC[a]			absolute		
sample	M_n (calcd)	M_n	M_w	M_w/M_n	M_n[b]	M_w[c]	M_w/M_n
1[d]	30	74	88	1.20	78	123	1.55
2[e]	30	32	34	1.07	32	33	1.03
3[e]	7.5	14	17	1.26			
4[e]	15	16	17	1.07	17		
5[f]	26	28	29	1.04	29	30	1.03

[a] Based on polystyrene standards. [b] From membrane osmometry. [c] From light scattering. [d] Prepared using initiator **4** in benzene. [e] Prepared using initiator **4** in benzene in the presence of THF: [THF]/[RLi] = 20. [f] Prepared by end-linking of **3** with poly(styryl)lithium ($M_n = 8.5 \times 10^3$ g/mol; $M_w/M_n = 1.05$). Sample characterized after fractionation.

nm were monitored and the results are shown in Figure 3. In contrast to the initiation reaction in benzene solution without THF, the initiation reaction was completed within 5–8 min after the addition of the monomer as deduced by the complete disappearance of the absorption corresponding to the trifunctional initiator, **4**, at 480 nm. At this point, the reaction medium was dark yellow–orange, compared to the dark reddish color of the trilithium initiator. The polymerization was completed after 50 min in an ice–water bath.

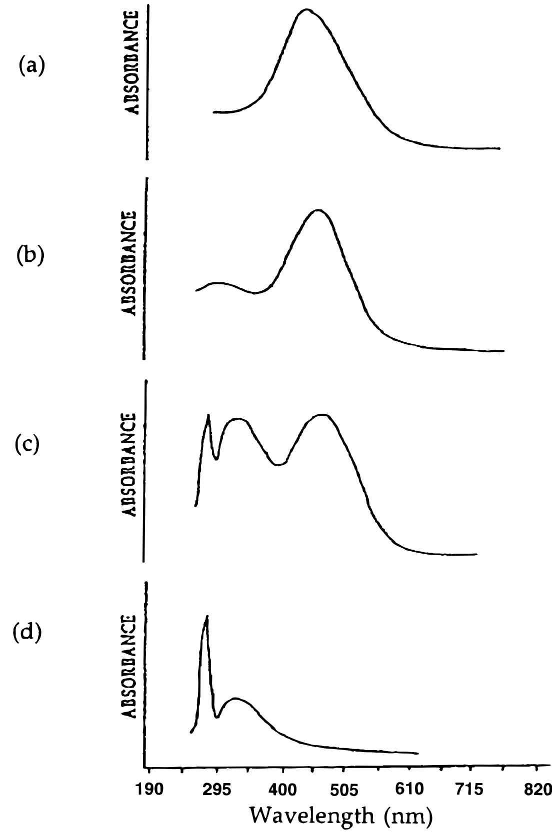


Figure 3. UV–visible absorption spectra recorded during the crossover reaction from the trifunctional initiator (**4**) to styrene in the presence of THF in benzene (THF]/[Li] = 20): (a) trifunctional initiator (**4**); (b) **4** after the addition of THF; (c) upon addition of styrene; (d) 5–8 min after addition of styrene.

The polymer prepared in the presence of THF exhibited a monomodal SEC chromatogram (see Figure 4). Furthermore, no evidence for the presence of a residual initiator was detected in this chromatogram in contrast to the chromatogram of the polymer prepared in benzene solution. The results of SEC analysis and molecular-weight characterization of the resulting polymer (sample 2) prepared in the presence of THF ([THF]/[RLi] = 20) are listed in Table 1. The observed number-average molecular weight (SEC or membrane osmometry) was in good agreement with the molecular weight calculated on the basis of the initiator stoichiometry.[1] This result is consistent with quantitative initiation of styrene polymerization by the initiator, **4,** to form the corresponding tris[poly(styryl)lithium], **6** (eq 5). The

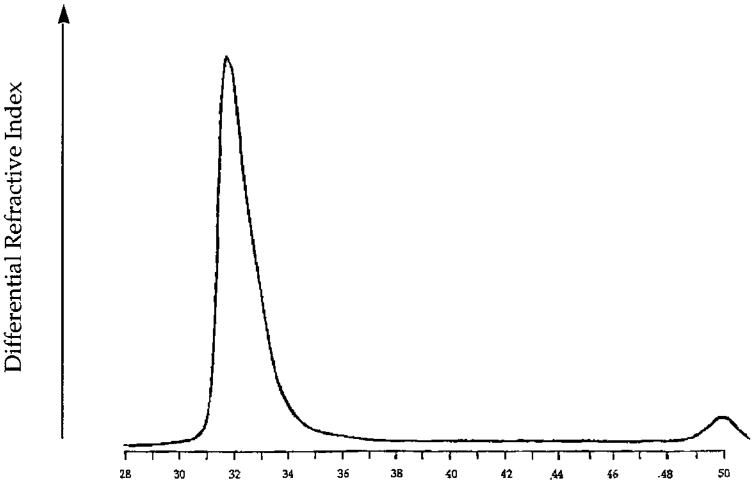
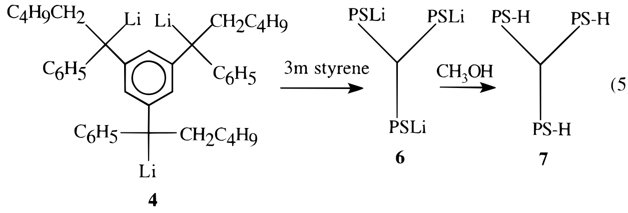


Figure 4. SEC chromatogram of the three-armed star polystyrene (sample 2, Table 1) synthesized in the presence of THF ([THF]/[Li] = 20) in benzene at 4 °C.



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observed narrow molecular-weight distribution ($M_w/M_n < 1.1$)[46] (SEC and absolute determination, see Table 1), shows that the rate of initiation is competitive with or faster than the rate of propagation.[1] Thus, it can be concluded that initiator **4** is an efficient and highly reactive initiator for the polymerization of styrene in the presence of THF to form three-armed, star-branched polystyrenes **7**.

The previous characterization data are necessary but not sufficient to conclude that **4** is a useful trifunctional initiator for the preparation of well-defined, three-armed, star-branched polystyrenes. It must be demonstrated that the resulting polymers are indeed star-branched and contain three arms of uniform size. Branched polymers generally have higher chain segment density, smaller radii of gyration, and lower hydrodynamic volumes compared to linear polymers with the same composition and molecular weight.[3-6] These differences are manifested in lower intrinsic viscosities and longer retention volumes by SEC analysis.[3] One means of characterizing the nature of the branching in star polymers is in terms of the parameter g' which is defined in eq 6, where $[\eta]_b$ is the intrinsic

$$g' = \frac{[\eta]_b}{[\eta]_l} \qquad (6)$$

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, three-armed, star-branched polymer, theoretical models by Zimm and Kilb[47] and Stockmayer and Fixman[48] predict g' values of 0.91 and 0.85, respectively.[6] In practice, reported values of g' range from 0.8 to 0.94;[6] a recent review suggests that the average values (±5%) of g' are 0.84 and 0.87 for a good solvent and a theta solvent, respectively.[4] It has been demonstrated that g' is sensitive to the asymmetry of the arms. It appears that as the disparity between the arms increases, g' increases; for example, a well-defined ($M_w/M_n = 1.02$) hetero, three-armed, star-branched polystyrene with arm molecular weights of 5 400, 15 300, and 36 200 g/mol exhibited a g' value of ≈0.92.[49]

Table 2. Dilute Solution Properties of Star-Branched Polystyrenes Prepared with the Trifunctional Initiator, 4, and by End-linking of PSLi with 3 (See Table 1 for Molecular Weight Characterization Data)

sample	$[\eta]_{star}$[a] (dL/g)	g'[b]
1[c]	0.335	0.78
2[d]	0.184	0.81
4[d]	0.117	0.81
5[e]	0.168	0.80

[a] Determined in THF at 30 °C. [b] $g' = [\eta]_{star}/[\eta]_{linear}$, where $[\eta]_{linear} = (1.28 \times 10^{-4})M_n^{0.721}$ in THF (ref 50). [c] Prepared using initiator **4** in benzene. [d] Prepared using initiator **4** in benzene in the presence of THF: [THF]/[RLi] = 20. [e] Prepared by end-linking of **3** with poly(styryl)lithium ($M_n = 8.5 \times 10^3$ g/mol; $M_w/M_n = 1.05$). Sample characterized after fractionation.

To obtain evidence regarding the uniformity of the arms in the resulting polymers, the intrinsic viscosities of these star polymers prepared with initiator **4** have been measured ($[\eta]_b$) and compared with the corresponding viscosities of linear polystyrenes ($[\eta]_l$) with the same molecular weight to obtain values of g' (eq 6). The viscosity measurements and the calculated values of g' are listed in Table 2. The value of g' in Table 2 for the star-branched polystyrene prepared in the presence of THF (0.81, for sample 2) is consistent with the average value of 0.84 (±5%)[4] observed for regular, three-armed star-branched polystyrenes (i.e., stars with monodisperse arms of equal length).[5] However, it should be noted that g' provides only indirect evidence regarding the uniformity of the arms.[3]

The value of g' observed for the star polymer prepared in the absence of THF is significantly lower than the values observed for regular, three-armed, star-branched polymers[4] and also lower than the value determined for the star polymer prepared in the presence of THF. For a monodisperse, heteroarm, star-branched polymer (i.e., a star molecule with well-defined arms of unequal length) it would be expected that g' would increase as discussed previously.[49] The lower value of g' observed for this polymer, compared to values observed for regular, three-armed, star-branched polymers, is consistent with the studies of Burchard[51-53] which showed that the size parameter g decreases for arms having a

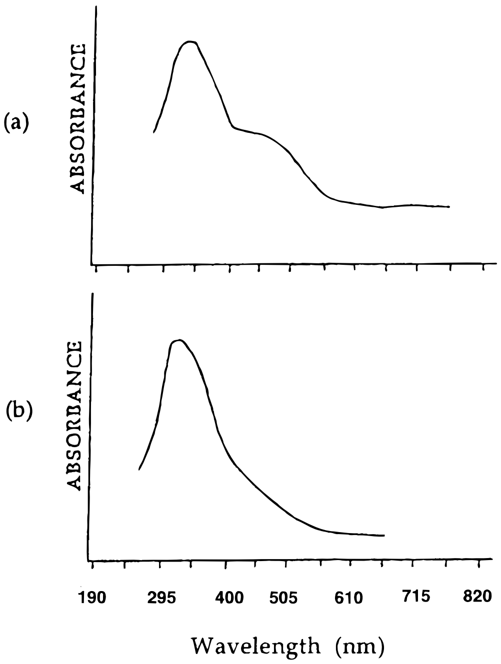
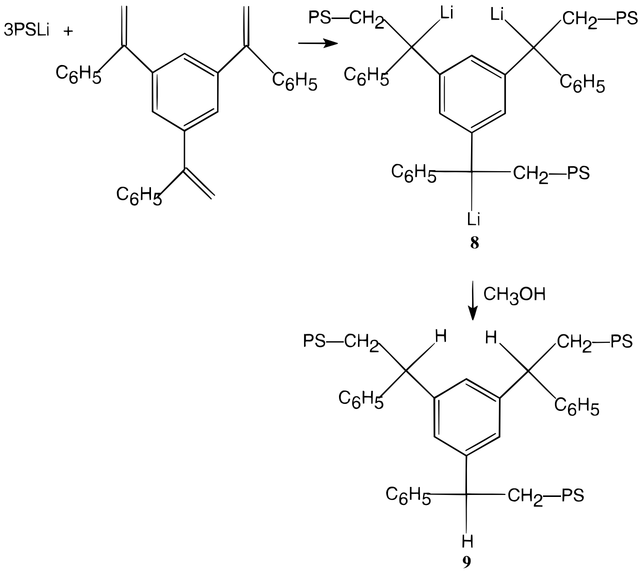


Figure 5. UV−visible absorption spectra of the crossover reaction from the trifunctional initiator **4** to styrene in the presence of THF in benzene ([THF]/[Li] = 20) after complete consumption of styrene: (a) sample 3, Table 1 [M_n(calcd) = 7.5 × 10^3 g/mol]; (b) sample 4, Table 1 [M_n(calcd) = 15 × 10^3 g/mol].

most probable molecular-weight distribution relative to the corresponding regular star polymers with monodisperse arms.[5] These results suggest that not only is the initiation process for initiator **4** in benzene inefficient (i.e., no control of M_n and incomplete consumption of initiator) but also the arm lengths are not uniform (i.e., they are polydisperse). In contrast, the results for the star polymer prepared in the presence of THF are consistent with the formation of a regular, star-branched polymer with uniform arm lengths.

*Limitations of Synthesis of Three-armed, Star-Branched Polystyrenes Using Initiator **(4)**: Minimum Arm Molecular Weight.* Although the initiator, **4**, has been shown to be effective for the synthesis of three-armed, star-branched polymers with arm molecular weights corresponding to M_n = 10 × 10^3 g/mol (sample 2, Table 1), it was important to determine the minimum arm molecular weight for a complete crossover to the styrene monomer for all three initiating sites. Therefore, the preparation of two lower molecular weight star polymers [M_n (calc) < 30 000 g/mol] was attempted with initiator **4** in benzene under optimized conditions ([THF]/[Li] = 20). The M_n(calcd) of sample 3 was 7.5 × 10^3 g/mol ([Li] = 9 × 10^{-3} M, [styrene] = 0.21 M) and the M_n(calcd) of sample 4 was 15 × 10^3 g/mol ([Li] = 9 × 10^{-3} M, [styrene] = 0.42 M). The crossover reactions from initiator **4** to the corresponding growing poly(styryl)lithium arms for these experiments were monitored by UV−visible spectroscopy (see Figure 5). UV−visible spectroscopic analysis revealed that the UV−visible absorption corresponding to residual 1,1-diphenylalkyllithium initiator sites (λ_{max} = 480 nm) was still observed after all of the styrene monomer was consumed for sample 3 (Figure 5a), but not for sample 4 (Figure 5b). Thus, the crossover reactions from the trifunctional initiator, **4**, to styrene were complete (i.e., initiation) in sample 4, but not in sample 3. The molecular-weight characterization data for both of these samples are shown in Table 1. The molecular weight of sample 4, M_n(VPO) = 17 × 10^3 g/mol was in good agreement with M_n(calcd) as shown in Table 1; in addition, the molecular-weight distribution for this polymer was narrow. On the other hand, analogous to sample 1, sample 3 had a much higher molecular weight than M_n(calcd) because of inefficient initiation; analogous to sample 1 also, the molecular-weight distribution was broad (see Table 1). Furthermore, the g' value of sample 4 was 0.81 (see Table 2). As discussed previously, this value is consistent with experimental data[4] for regular, three-armed, star-branched polymers (i.e., stars with monodisperse arms of equal length).[5]

Scheme 1



These results indicate that there is a minimum arm molecular weight which is required to achieve complete crossover to styrene for all of the initiating sites in the trifunctional initiator, **4**. This critical arm molecular weight is in the range of 5000−5700 g/mol, corresponding to star molecular weights of 15 000−17 000 g/mol. When three-armed star polystyrenes had calculated molecular weights higher than 15 × 10^3 g/mol, regular, well-defined, three-armed, star-branched polystyrenes were prepared. If the calculated molecular weights are lower than this value, there is insufficient monomer to ensure that all of the initiating sites can crossover to poly(styryl)lithium before all of the monomer is consumed.

End-Linking of Poly(styryl)lithium with 3: Preparation and Characterization of Regular, Three-Armed Star-Branched Polystyrene. Postpolymerization end-linking reactions of living polymeric organolithium compounds with multifunctional electrophilic compounds provide an elegant methodology for the preparation of regular, star-branched polymers with low degrees of compositional heterogeneity.[1,3−6] An alternative, versatile procedure utilizes living linking reactions of polymeric organolithium compounds with linking agents having two or more reactive vinyl substituents which can undergo facile addition reactions with polymeric carbanions, but which do not polymerize or oligomerize anionically due to steric hindrance.[15,16] Based on previous work with the double diphenyethylene derivative, **1**,[36,37,54] it was deduced that 1,3,5-tris(1-phenylethenyl)benzene, **3**, could function as a trifunctional living linking reagent by reaction with 3 mol

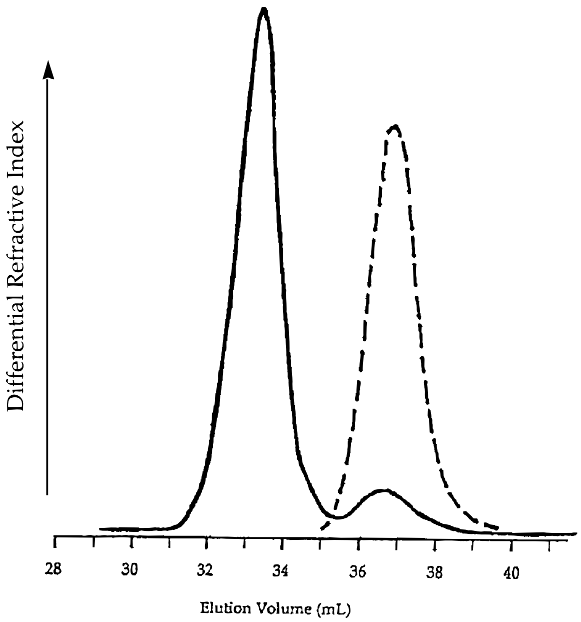


Figure 6. SEC chromatogram of the three-armed, star-branched polystyrene from the linking reaction of PSLi ($M_n = 8.5 \times 10^3$ g/mol) with **3**: dashed line (- - -) corresponds to the base polymer and the solid line (—) corresponds to the linked, three-armed, star-branched polymer (sample 5, Table 1).

of poly(styryl)lithium to form the corresponding regular, three-armed, star-branched polystyrene, **9**, with low degrees of compositional heterogeneity (see Scheme 1). An additional benefit of the investigation of this linking reaction was that the regular, star-branched polymer from linking could be compared with the product from the initiation of styrene polymerization using the analogous trifunctional initiator, **4**.

The linking reaction of **3** with poly(styryl)lithium ($M_n = 8.5 \times 10^3$ g/mol; $M_w/M_n = 1.05$) in benzene was effected in a glovebox by stepwise addition of aliquots of the PSLi solution corresponding to 0.7 equiv (1), 0.1 equiv (2), 0.05 equiv (1), and 0.005 equiv (1 or more). The progress of the addition reaction was monitored by removing samples, quenching with methanol, and product analysis by SEC. A slight excess of PSLi was used to ensure that the products corresponded to only the three-armed star and unlinked star (i.e., no coupled, dimer product). An SEC of the final product mixture is shown in Figure 6. The star polymer fraction at a lower elution volume corresponds to more than 90% of the mixture. This result attests to the high reactivity of **3** with respect to the addition of PSLi for the preparation of the three-armed star polymers, **9**. It is noteworthy that Pennisi and Fetters[55] stated that poly(styryl)lithium is unable to undergo complete reaction with a stoichiometric quantity of chlorosilanes containing 3−4 chlorines/silicon atom, presumable because of steric hindrance. It appears that no such limitation is encountered with the use of **3** as a linking agent. It is important to note that the product of this linking reaction, **8**, retains the stoichiometry of the carbanions (i.e., it is a living trilithium star which, analogous to trifunctional initiator **4**, could be used to initiate polymerization of the added monomer from the trilithium core branch point to generate hetero-, six-armed, star-branched polymers).[54]

The pure star polymer was isolated by fractionation and the SEC of the purified product is shown in Figure 7. The molecular-weight characterization data for this star polymer are shown in Table 1 (sample 5). It can be concluded that **3** is a useful trifunctional linking agent for polymeric organolithium compounds on the basis of the correspondence between the calculated and observed molecular weight and the narrow molecular-weight distribution of the star polymer prepared by linking of 3 mol of poly(styryl)lithium with **3**.

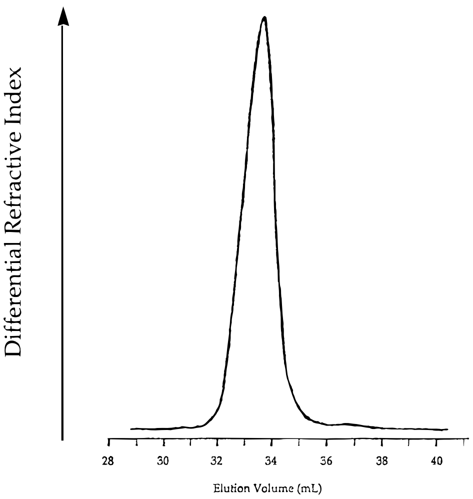


Figure 7. SEC chromatogram of the fractionated, three-armed, star-branched polystyrene from the linking reaction (sample 5, Table 1).

It was of interest to compare the value of the size parameter, g', for this regular, three-armed, star-branched polystyrene (sample 5, Table 1) prepared by end-linking of well-defined poly(styryl)lithium arms with the g' value for the analogous polystyrene star with comparable molecular-weight parameters [M_n(linked with **3**) = $0.91M_n$ (initiated with **4**); see Table 1] prepared using initiator **4** (sample 2, Table 1). The solution property data for these polymers are shown in Table 2. The g' values are very similar for these two polymers. This comparison provides further evidence to conclude that the use of the trifunctional initiator **4** results in regular, well-defined, three-armed, star-branched polymers, analogous to the star polymers prepared by traditional postpolymerization, end-linking chemistry of monodisperse living polymers.[1,3−6]

Preparation of ω,ω,ω-Trifunctional, Star-Branched Polystyrenes by Postpolymerization Functionalization Reactions of Living Star Polymers 6: Carbonation. The trifunctional initiator method has an important advantage over traditional end-linking chemistry for preparation of star polymers. Since each branch chain end is still a living, reactive carbanionic center after all of the monomer has been consumed, the addition of a different monomer will form block copolymer arms[1] or deliberate termination with electrophilic reagents will form multifunctional, chain-end functionalized stars.[17] It was of interest, therefore, to investigate the chain-end carboxylation[22,33,34] of the living, star-branched polymer to demonstrate the ability to form multifunctional, ω,ω,ω-end-functionalized, star-branched polymers and to prove that the living polymers, **6**, are indeed trifunctional.

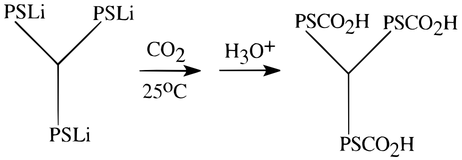
A solution of three-armed, star-branched ω,ω,ω-tris-[poly(styryl)lithium], **9** [M_n(VPO) = 17×10^3 g/mol; $M_w/M_n = 1.07$; [Li] = 9×10^{-3} M] prepared in the presence of THF ([THF]/[Li] = 20] was carboxylated by the introduction of gaseous carbon dioxide into an unstirred solution of the polymer in a 50/50 benzene/THF (v/v)

Table 3. SEC Analysis and Chain-End Titration of Products from Carboxylation of Three-Armed Tris[poly(styryl)lithium] (9)[a]

sample	dimer (wt %) from SEC	functionality from titration[b]
A[c]	12	2.7_5
B[d]	11	2.8_1
C[e]	2	2.9_5

[a] M_n(VPO) of base three-armed polystyrene = 17 × 10^3 g/mol; M_w/M_n = 1.07. [b] Carboxyl functionality determined by KOH titration;[35] theoretical functionality = 3.0. [c] Carboxylation in 50/50 THF/benzene (v/v) as the solvent. [d] Carboxylation of adduct of **9** and 3 equiv of 1,1-diphenylethylene. [e] Carboxylation of powder from freeze-drying of benzene solution of **6**.

mixture (eq 7); this procedure provides quantitative carboxylation of poly(styryl)lithium.[22] The SEC chromatogram of the products of this carboxylation reaction showed evidence for the presence of significant amounts of higher molecular weight products (12 wt %). In accord with this observation, the results of end-group titration (see Table 3) indicate that the carboxyl-group functionality of the polymeric product corresponds to only 2.8 functional groups/molecule. Even though this carboxylation was effected in the presence of a large amount of THF (50 vol %), significant amounts of side reaction products were formed.



6 **10** (7)

Another effective procedure for the quantitative carboxylation of poly(styryl)lithium chain ends is to endcap the chain end with 1,1-diphenylethylene to convert it into the corresponding polymeric 1,1-diphenylalkyllithium.[34] The yields of carboxyl-functionalized polymers obtained for this procedure were reported to be >99% even in the absence of added Lewis bases.[34] However, end-capping of **6** with 1,1-diphenylethylene prior to carboxylation was no more effective than the THF addition procedure. The amount of dimer formation was 11 wt % and carboxyl-group functionality by titration corresponded to only 2.8 carboxyl groups/molecule.

Another surprisingly effective procedure for carboxylation of poly(styryl)lithium involves freeze-drying of a benzene solution of the living polymer and introduction of gaseous carbon dioxide into the porous product.[33,34] Fortunately, this procedure worked well for the star-branched, ω,ω,ω-tris[poly(styryl)lithium] as shown by the SEC chromatogram in Figure 8(2% dimer fraction) and the titration data in Table 3 (2.9_5 functional groups/star molecule). These results confirm the expectation that the initiation of styrene polymerization by the trifunctional organolithium initiator, **4**, forms the corresponding three-armed, star-branched polymer with three active styryllithium chain ends which can participate in efficient chain-end functionalization reactions, such as carboxylation, to form the corresponding ω,ω,ω-trifunctional, star-branched polystyrenes (eq 7).

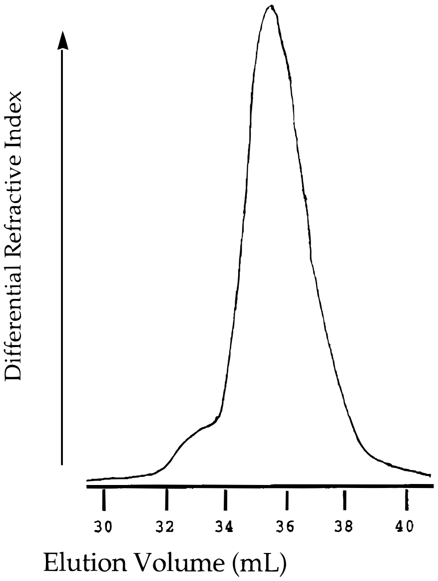


Figure 8. SEC chromatogram of chain-end carboxylation of ω,ω,ω-tris[poly(styryl)lithium] after freeze-drying of benzene solution (sample C, Table 3).

Conclusions

The addition of 3 equiv of *sec*-butyllithium to 1,3,5-tris(1-phenylethenyl)benzene produces a hydrocarbon-soluble, trilithium initiator which initiates styrene polymerization in the presence of stoichiometric amounts of THF to form well-defined, three-armed, star-branched polystyrenes provided that M_n(calc) > 15 000 g/mol. The star polymer product from this initiator is a living ω,ω,ω-tris[poly(styryl)lithium] which can react with additional monomers or can be functionalized with electrophilic terminating agents. The living linking of 3 equiv of poly(styryl)lithium to 1,3,5-tris(1-phenylethenyl)benzene produces the corresponding regular, three-armed, star-branched polystyrene efficiently.

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