Anionic Synthesis of Heteroarm, Star-Branched Polymers. Scope and Limitations

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ANIONIC SYNTHESIS OF HETEROARM, STAR-BRANCHED POLYMERS. SCOPE AND LIMITATIONS

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ABSTRACT

The scope and limitations of the following methods for the synthesis of heteroarm star-branched polymers are presented: (a) divinylbenzene linking reactions; (b) coupling reactions with macromolecular silyl halides; and (c) 1,1-diphenylethylene-based living linking reactions. The methodology of using 1,3-*bis*(1-phenylethenyl)benzene to prepare A_2B_2 hetero 4-armed stars is reviewed, and the synthesis of well-defined (polystyrene)$_2$(1,4-polybutadiene)$_2$ heteroarm stars is described. The synthesis of well-defined ABC heteroarm star polymers using macromonomers functionalized with 1,1-diphenylethylene groups is described.

INTRODUCTION

Advances in understanding and predicting polymer structure–property relationships require the availability of polymers with well-defined structures and low degrees of compositional heterogeneity [1, 2]. Living anionic polymerization provides one of the most versatile and elegant methodologies for the controlled synthesis of polymers with well-defined structures [3–8]. For example, a variety of well-defined, star-branched polymers have been prepared by reaction of living anionic polymers with multifunctional, electrophilic linking agents [9–12]. One of the challenges in anionic synthesis has been to prepare star-branched polymers in which the arms differ in either molecular weight or composition, i.e., heteroarm, star-

branched polymers. In the following sections the basic methods which have been used for the synthesis of heteroarm, star-branched polymers will be critically discussed.

Three general methods have been described for the preparation of heteroarm, star-branched polymers [12–31]:

1. Divinylbenzene linking reactions
2. Coupling reactions with macromolecular silyl halides
3. 1,1-Diphenylethylene-based living linking reactions

Each method has its own advantages and drawbacks, and these will be discussed in the following sections.

1. Divinylbenzene Linking Reactions [9–12].   Divinylbenzenes (DVB) react with polymeric organolithium compounds by simultaneous DVB homopolymerization and branching (linking) reactions with the resulting poly(4-vinylstyrene) blocks to produce star-branched polymers which retain the carbanionic active centers as illustrated in Scheme 1 for *para*-DVB. The "polymerization" linking process has been described as formation of a microgel nodule which serves as the branch point for the star-shaped polymer [9]. In principle, j molecules of divinylbenzene could link together $(j + 1)$ polymer chains [9]; although the number of arms in the star depends on the ratio of DVB to polymeric organolithium compound, the degree of linking obtained for this reaction is a complex function of reaction variables [9–12]. Although narrow monodisperse anionic polymers can be prepared for the arms, because of the random nature of the linking reaction the star-branched polymers prepared by the DVB method are polydisperse with M_w/M_n not more than 1.5 [11].
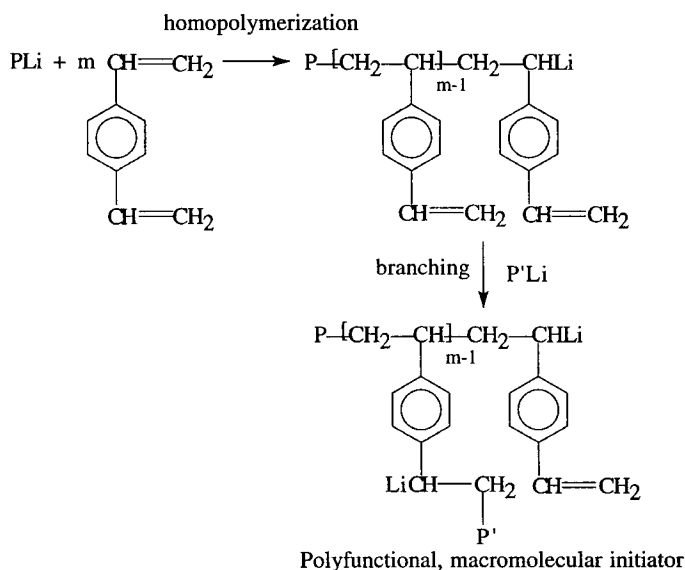

SCHEME 1.

Eschwey and Burchard [23] recognized that the DVB-linked product could function as a polyfunctional, macromolecular initiator. Thus, after DVB linking of short poly(styryl)lithium chains, additional styrene or isoprene monomer was added to double the number of arms, in principle. Preliminary viscosity and light-scattering data were consistent with heteroarm, star polymer formation. It has been reported that initiation is slow and incomplete with both styrene and diene monomers using this type of polyfunctional anionic initiator [9], presumably because of steric effects, but association phenomena could also inhibit efficient initiation [32].
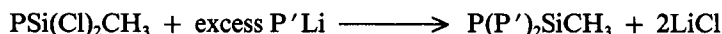
This "core-first" heteroarm star synthesis method based on DVB linking of poly(styryl)lithium has been applied to the synthesis of *star*-polystyrene–*star*-poly-(*n*-butyl methacrylate) [24] and *star*-polystyrene–*star*-poly(*t*-butyl methacrylate) [25, 26]. Although the final molecular weights were consistent with the expected star structures, no demonstration of the uniformity of the branches was provided. Furthermore, the authors assume that the polymers possess equal number of branches of either type. Independent work in these laboratories with trifunctional anionic macromolecular initiators suggests that it is difficult to obtain uniform growth of poly(alkyl methacrylate) arms under analogous conditions.

Thus, the DVB linking methodology for the synthesis of heteroarm, star-branched polymers presents an interesting technology. However, it lacks the precision and control necessary for the synthesis of polymers with well-defined structures and low degrees of compositional heterogeneity.

2. Coupling Reactions with Macromolecular Silyl Halides [9–11].   General methods for the preparation of regular star polymers have been developed based on linking reactions of polymeric organolithium compounds with multifunctional electrophilic species such as silicon tetrachloride:

$$4PLi + SiCl_4 \longrightarrow P_4Si + 4LiCl$$
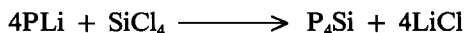
In general, for a given multifunctional silicon halide, the efficiency of the linking reaction decreases in the order poly(butadienyl)lithium > poly(styryl)lithium > poly(isoprenyl)lithium. Pennisi and Fetters [17, 27] have prepared asymmetric, three-armed star polystyrenes and polybutadienes using the reactions shown below:

$$PLi + excess\ CH_3SiCl_3 \longrightarrow PSi(Cl)_2CH_3 + LiCl + CH_3SiCl_3$$

$$PSi(Cl)_2CH_3 + excess\ P'Li \longrightarrow P(P')_2SiCH_3 + 2LiCl$$

This synthesis relies on the inability of poly(styryl)lithium to undergo complete reaction with a stoichiometric amount of chlorosilanes due to steric hindrances. The first step utilized a 10-fold excess of methyltrichlorosilane to prevent coupling reactions; this was removed by freeze-drying and heat treatment of the methyldichlorosilane end-functionalized polystyrene. In the second step, a 20% excess of polymeric organolithium compound was reacted with the functionalized polystyrene; these reactions required days for completion even in the presence of added Lewis base promoter. Fractionation was required to remove the excess nonlinked polymer chains. A similar approach was used to synthesize an A_2B star, $Ps(PI)_2$, which is a

model graft copolymer, poly(isoprene-*graft*-polystyrene) [28]. The second step of coupling poly(isoprenyl)lithium with the functionalized polystyrene was conducted at 40°C for 72 hours.

This methodology has recently been extended to the preparation of A_2B_2, ABCD, and ABC heteroarm star polymers [29, 30]. The ABC star terpolymer was prepared by reaction of poly(isoprenyl)lithium with an excess of methyltrichlorosilane followed, after removal of the excess methyltrichlorosilane, by a stoichiometric addition (titration) of poly(styryl)lithium and finally by a small excess of poly(butadienyl)lithium [29]. The resulting star polymer was fractionated to remove the unlinked polymer fraction; the final product exhibited a narrow molecular weight distribution ($M_w/M_n = 1.03$). The extension of this methodology based on differential reactivity to the synthesis of ABCD four-armed, star-branched polymers is problematic [30]. The fourth linking reaction with poly(butadienyl)lithium was reported to require 2 months for completion. The product was multimodal and characterized by SEC and light scattering. After fractionation, a narrow molecular weight distribution product was obtained ($M_w/M_n = 1.06$). However, all of the precursor arms had narrow molecular weight distributions and approximately the same molecular weight; therefore, the fact that the overall composition was as predicted does not convincingly demonstrate that the molecules are compositionally homogeneous. Unfortunately, polymers obtained at intermediate stages were not separately characterized. It remains to be convincingly demonstrated that this is a reliable method for the synthesis of a wide variety of well-defined, compositionally homogeneous, heteroarm, star-branched polymers.

3. *1,1-Diphenylethylene-Based Living Linking Reactions* [20–22].

A living linking agent is a species which can react with polymers which have carbanionic chain-ends to generate a linked polymer product which retains the active center stoichiometry. The general reaction scheme is

$$n\text{P}^1\text{Li} + \text{C} \longrightarrow (\text{P}^1)_n\text{C(Li)}_n \xrightarrow{m\text{M}_2} (\text{P}^1)_n\text{C(P}^2)_n$$
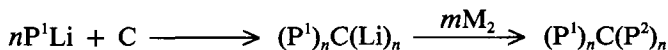
where C is a living linking agent with a linking functionality of n, P^1Li is a living carbanionic polymer chain, and M_2 is a second monomer which can be anionically polymerized by the active carbanionic centers in the living linked product. It is obvious from the reaction scheme that the use of living linking agents provides a method for preparing heteroarm star-branched polymers. Several criteria must be satisfied for a species to be useful as a living linking agent:

1. The living linking agent must react quantitatively with living carbanionic chain ends without oligomerization
2. The coupled product must retain the active centers stoichiometrically
3. The living coupled product must be capable of reinitiating polymer chain growth rapidly (relative to propagation) and stoichiometrically

Generally, living linking agents have two or more reactive vinyl substituents which can undergo addition reactions with polymeric carbanions, but which do not polymerize anionically due to steric hindrance. Divinylbenzenes and *m*-diisopropenylbenzene could be regarded as potential living linking agents; however, the homopolymerization and oligomerization, respectively, of these divinyl compounds

limit their effectiveness for the synthesis of well-defined star-branched polymers as discussed for DVB in the first section of this paper.

We have developed methods for the synthesis of hetero 4-armed star-branched homopolymers and copolymers [20, 21] and symmetric 3-armed star polymers [31] utilizing 1,1-diphenylethylene-derived living linking agents. As an extension of these investigations, a hetero 3-armed star-branched polymer was prepared using a 1,1-diphenylethylene-functionalized macromonomer [22]. Herein, we present a critical review of the scope and limitations of the use of 1,1-diphenylethylene-derived, living linking agents for the synthesis of heteroarm, star-branched polymers with well-defined structures and low degrees of compositional heterogeneity.

EXPERIMENTAL

Materials

Styrene, isoprene, benzene, and tetrahydrofuran (Fisher) were purified as described previously [33–35]. 1,3-Butadiene (99%, Air Products) was stored with stirring first over freshly crushed calcium hydride (Alfa) and then over sodium dispersion (Alfa) at temperatures below $-20°C$; t-butylbenzene (Pfaltz & Bauer) was purified using the same procedure as described for benzene. Solutions of sec-butyllithium (FMC, Lithium Division, 12.0 wt% in cyclohexane) were used for initiation after double titration analysis [36]. 1,3-Bis(1-phenylethenyl)benzene [MDDPE] was synthesized by the Friedel–Crafts reaction of isophthaloyl chloride with benzene followed by Wittig synthesis of the diolefin using procedures analogous to those described by Schulz and Höcker [37]; mp 46–47.5 (lit. [37], mp 46°C). 1,4-Bis(1-phenylethenyl)benzene [PDDPE] was synthesized by the Friedel–Crafts reaction of terephthaloyl chloride with benzene followed by Wittig synthesis of the diolefin according to procedures analogous to those reported by Höcker and Lattermann [38]; mp 136.5–137.2°C (lit. [38], mp 137°C). Both double diphenylethylenes exhibited only one peak by HPLC analysis.

sec-Butyllithium-initiated polymerizations were carried out at room temperature using both Schlenk-type equipment [39] and standard high vacuum techniques [40]. The linking reactions of polymeric organolithium compounds with MDDPE and PDDPE and crossover reactions of the resulting living linked products with styrene or butadiene monomer were effected using the procedures described previously in detail [20–22].

Characterization

Size-exclusion chromatographic (SEC) analyses of polymers were performed at a flow rate of 1.0 mL·min^{-1} in tetrahydrofuran at 30°C by using a Waters HPLC component system (RI or Hewlett Packard 1040 diode array detectors) equipped with ultra-μ-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 the star-branched polymers were determined using either membrane osmometry (Membrane Osmometer model 503, Mechrolab Inc.) at 37°C in toluene, vapor pressure osmometry (VPO) (Knauer Type 1100) at 45°C in toluene, or using a Universal calibration curve [41] generated from SEC elution

volumes and intrinsic viscosities calculated using the Mark–Houwink constants ($K = 1.03 \times 10^{-4}$, $a = 0.731$) [42–44] for linear polystyrene standards. The intrinsic solution viscosities of the star-branched polymers were measured in THF at 30°C using an Ubbelohde-type viscometer. Both ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra were measured in deuterated chloroform using a Varian Gemini-200 spectrometer. UV-Vis absorption spectra of the macromonomers and the living polymers were obtained using a Hewlett-Packard 8452A Diode array spectrophotometer with a 2.0 cm or 0.1 cm UV cell, respectively.

RESULTS AND DISCUSSION

Four-Armed Star Polymers

The methodology of using 1,3-*bis*(1-phenylethenyl)benzene (MDDPE) to prepare hetero 4-arm star polymers via anionic polymerization was previously introduced [20]. This process involves two reactions: a coupling reaction and a crossover reaction to a second monomer. This reaction sequence is outlined in Scheme 2. In the first step, two living carbanionic polymer chains are coupled with the living
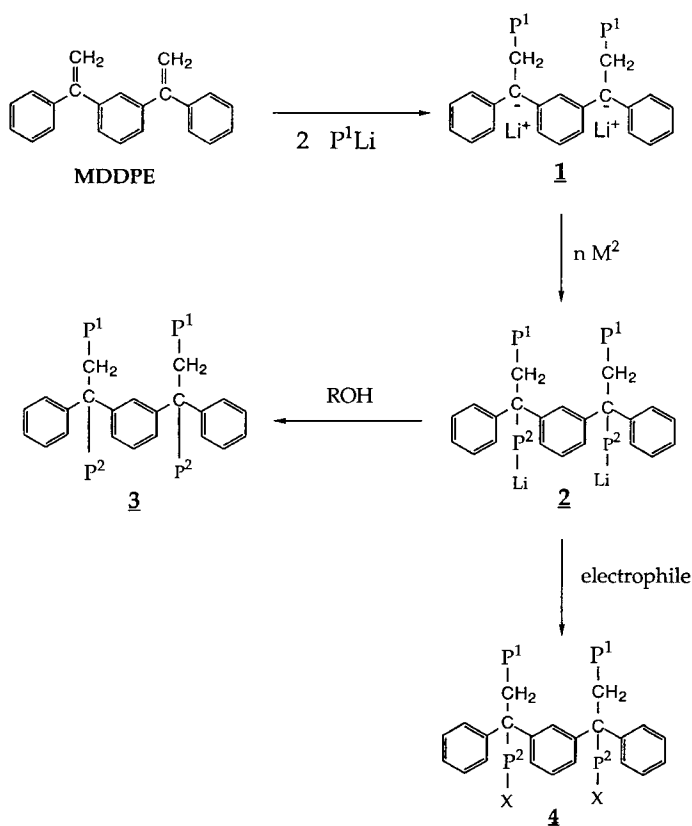
SCHEME 2.

coupling agent, MDDPE, to generate the corresponding dianion, $[(P^1)_2$ MDDPE-$(Li)_2]$ (1). In the second step, this polymer dianion (1) reinitiates the polymerization of a second monomer to generate two new polymer chains, thus forming a hetero 4-arm star branched homopolymer or block copolymer (3). Functionalized hetero-arm, star-branched polymers (4) can be prepared by quenching the dianion (2) with an appropriate electrophilic species [45].

Coupling Reactions

The coupling reactions were monitored using UV-visible spectroscopy by observing the increase in absorbance of the corresponding diphenylalkyllithium species (1) at 438 nm. Size exclusion chromatography (SEC) was also used to evaluate the efficiency of the coupling reaction; SEC was also useful to follow the course of the coupling reaction as shown in Fig. 1. The coupling reaction of PSLi of various molecular weights with MDDPE in benzene is a very efficient reaction when the stoichiometry of the reaction is carefully controlled by determining the exact chain-end concentration. Coupling reactions of MDDPE with poly(styryl)lithium produced the coupled product in excellent yield (>96%) as shown in Table 1; the efficiency decreased slightly with increasing molecular weight.

The high reactivity of the second diphenylethylene unit in MDDPE with respect to formation of the coupled product (1) is further exemplified by the observation that, using cyclohexane as solvent at room temperature, the addition reaction of poly(styryl)lithium (M_n = 3600 g/mol) with excess MDDPE ([MDDPE]/[PLSi] = 4) proceeds to give the dimeric adduct in 87% yield [46]. It should be noted that these results and previously published data [19–21] stand in sharp contrast to the results of Ikker and Möller [47] who reported an inability to obtain high coupling efficiencies for the reactions of poly(styryl)lithium with MDDPE in benzene using the cryptand [2.1.1].

One limitation of this methodology as a general procedure for synthesis of a wide variety of A_2B_2 star-branched polymers is the relative unreactivity of poly(die-
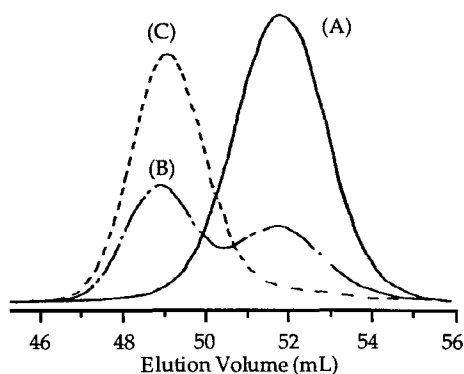

FIG. 1. SEC chromatograms of the coupling reaction of MDDPE with poly(styryl)-lithium (M_n = 1000 g/mol) in cyclohexane: base polymer (A), 55% coupling (B), and 100% coupling (C).

TABLE 1.   Molecular Weight Characterization Data and
Coupling Efficiencies in the Reaction of Stoichiometric Amounts
of PSLi with MDDPE in Benzene as Determined by SEC

PS		(PS)$_2$		
M_n, g/mol	M_w/M_n	M_n (coupled), g/mol	M_w/M_n	Coupling efficiency, %
1,800	1.06	3,700	1.05	99
3,000	1.04	6,300	1.04	99
4,600	1.04	9,650	1.04	97
9,800	1.02	23,500	1.02	96
14,600	1.03	30,250	1.03	96

nyl)lithium compounds in addition reactions with 1,1-diphenylethylene units [48]. It is necessary to add a small amount of THF ([THF]/[PLi] = 40) to accelerate the addition reaction; the coupling efficiency of poly(butadienyl)lithium ($M_n = 1.9 \times 10^3$ g/mol) with MDDPE in cyclohexane was >99% in the presence of added THF. Unfortunately, the required addition of a Lewis base to promote this dienyllithium coupling reaction limits the possibility of further diene polymerization for the second type of arms because only relatively high 1,2-diene microstructure, and consequently higher T_g diene blocks, would result [49]. A further complication in the observed coupling reaction of poly(butadienyl)lithium with MDDPE is that unpolymerized butadiene monomer can cause the formation of small amounts of high molecular weight components in the coupled product because the butadiene will copolymerize with 1,1-diphenylethylene units to generate branch functionalities higher than 2.

A second limitation with respect to the coupling reaction is the requirement that the living carbanionic polymers utilized must be sufficiently reactive to undergo facile addition reactions to 1,1-diphenylethylene units. In practice, this means that the first arms are limited primarily to styrene- and diene-type monomers.

Crossover Reactions

Of critical importance for the synthesis of heteroarm star-branched polymers was the determination of reaction conditions which would accelerate the rate of the crossover reaction of the diphenylalkyllithium sites with monomer (initiation) (k_2) relative to the rate of propagation (k_p), as described by the relative rate constant ratio, $k_2/k_p = R$. The values of R for crossover to styrene monomer in benzene were determined to be 0.07 and 0.10 at 25°C and 5°C, respectively. The analogous value of R at 25°C in cyclohexane was 0.12. Using the molecular weight distribution as an approximate experimental criterion for R, it was found that the narrowest molecular weight distributions for the polymers obtained by crossover experiments of polymeric diphenylmethyllithiums with styrene were obtained at 5°C (versus 25 or 45°C) in cyclohexane (versus benzene). Diphenylalkyllithium can initiate styrene monomer polymerization with a reasonably rapid rate, even though it is slower

than its homopolymerization rate ($R < 1$). Stoichiometry is very important; when excess MDDPE was present in the crossover reaction, the star polymer product exhibited multimodal distribution in SEC (with branching functionality greater than 4 arms). Even under stoichiometric coupling reaction conditions, the star-branched polymer obtained from the crossover reaction with styrene to form growing polystyrene arms with $M_n = 3.0 \times 10^3$ g/mol in each arm in cyclohexane solution showed bimodal molecular weight distribution as illustrated in Fig. 2; the degree of bimodality reflects the relative number of molecules growing by propagation with two reactive sites versus one reactive site. Whenever bimodality was observed, the UV-visible spectrum showed the existence of residual absorption for unreacted diphenylalkyllithium sites at 438 nm.

It was considered that the observed bimodality resulted from unusual chain-end association behavior for these dilithium species in hydrocarbon solution. Analogous to other polymeric organolithium compounds [7], the dilithium adduct would be expected to be aggregated at least into dimers in hydrocarbon solution. A cyclic dimeric ring form has been suggested by Szwarc and coworkers [50] for these difunctional diphenylalkyllithium aggregates. The unique association behavior of these species may complicate the crossover reaction compared to monofunctional diphenylalkyllithium species which, although also dimeric in hydrocarbon solution [7], exhibit no analogous inefficient crossover reactions to styrene monomer.

Addition of THF to a coupled product (2) prior to addition of styrene produces narrow molecular weight distribution, star-branched polymers even for polystyrene growing arm molecular weights as low as 3.0×10^3 g/mol as shown in Fig. 3. However, when the growing arm molecular weight was only 2×10^3 g/mol, the presence of residual diphenylalkyllithium species was detected by UV-visible absorption at 438 nm [20]. Thus, the minimum arm lengths required for complete crossover to styrene monomer in the presence of THF are 3×10^3 g/mol.

As discussed previously in connection with the coupling reaction of poly(butadienyl)lithium with MDDPE, the required addition of THF was not a satisfactory solution to prevent bimodal molecular weight distributions for the crossover reaction to form elastomeric polydiene blocks because it is known that diene microstructure is dramatically changed from high 1,4- to high 1,2-microstructure for alkyllithi-
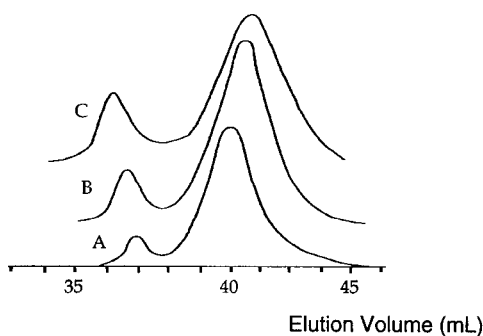

FIG. 2. SEC chromatograms of four-arm, star-branched polystyrene, [PS(M_n = 3000 g/mol)]$_2$-MDDPE-[PS(M_n = 3000 g/mol)]$_2$, prepared in cyclohexane: (A) at 5°C, (B) at 25°C, and (C) at 45°C.
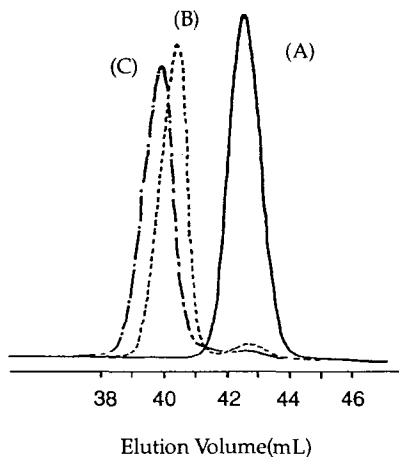
Elution Volume(mL)

FIG. 3.   SEC chromatograms of base polystyrene, M_n = 12,000 g/mol (A); coupled product, $(PS)_2$-MDDPE (B); and $(PS)_2$-MDDPE-$(PS)_2$ star polymer with arm-out, M_n (PS) = 3000 g/mol (C).

um-initiated diene polymerization in the presence of small amounts of THF [49]. It was found that the addition of sufficient amounts of lithium sec-butoxide ([sec-BuOLi]/[PLi] = 1) to the living coupled product (1) prior to addition of butadiene monomer produced monomodal, heteroarm star-branched polymers even with relatively low molecular weights for the polybutadiene arm which grows out from the coupled product; however, the molecular weight distribution was somewhat broad. This effect of lithium alkoxides was first observed for the dilithium initiator formed by the addition of 2 moles of sec-butyllithium to MDDPE [32]. In the presence of less lithium sec-butoxide than the equimolar amount, bimodal molecular weight distributions were obtained. Polymer products with minimum PB arm molecular weights (M_n = 10.0 × 10³ g/mol) exhibited a reasonably narrow molecular weight distribution without significant effect on polybutadiene microstructure as shown by the characterization data in Table 2.

There are fewer restrictions on the monomers which can be used in the crossover reaction than for the linking reaction. In essence, any monomer which undergoes living anionic polymerization can be added to the dilithium adduct (1) to grow arms and form heteroarm star-branched polymers with well-defined structures and low degrees of compositional heterogeneity. Since the growing arms are living, block copolymer arms can also be prepared, and these polymers exhibit unique and interesting physical and rheological properties [51].

Three-Armed Star Polymers

As discussed previously, MDDPE reacts rapidly with two equivalents of an organolithium compound in hydrocarbon solution to form the corresponding dilithium adduct. In fact, it has been reported that the rate constants of the first and second addition step for MDDPE with sec-BuLi are both 1.98 × 10⁻² L/mol·s in toluene [52]; for PDDPE the rate constant for the first addition is 2.06 × 10⁻² L/

TABLE 2. Molecular Weight Characteristics and Microstructures of Star-Branched $(PS)_2$–MDDPE–$(PB)_2$ Styrene–Butadiene Block Copolymers Prepared in Cyclohexane in the Presence of Lithium *sec*-Butoxide
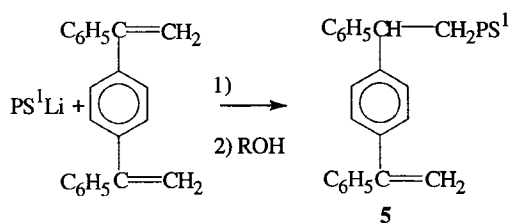
| No. | $M_n \times 10^{-3}$ g/mol | | M_w/M_n | Microstructure of PB block | |
	Calcd.	^{1}H-NMR[a]		1,4-	1,2-
S-1	2^2–2.5^2	8.7	1.14	85	15
S-2	2^2–10^2	24.5	1.05	90	10
S-3	10^2–11.5^2	42.5		92	8

[a]Calculated using the polystyrene molecular weight (SEC) and the relative integration areas for the aromatic protons relative to the vinyl protons from the diene units.
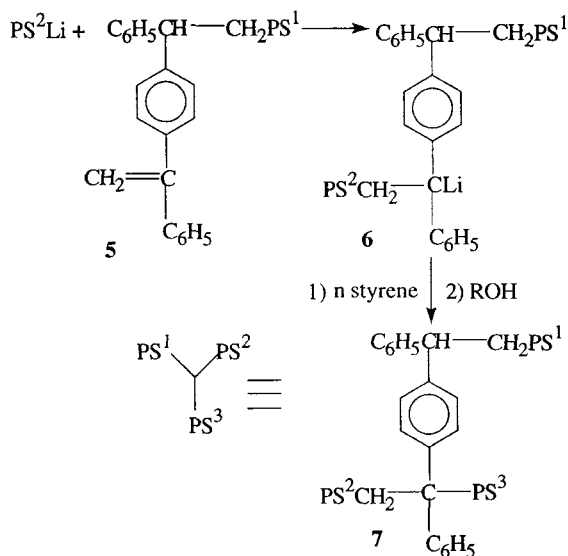
mol·s and that for the second addition is 1.51×10^{-3} L/mol·s [52]. However, McGrath and coworkers [53] reported that the monoadduct of MDDPE and *sec*-butyllithium could be prepared in THF at $-78°C$. Similar observations confirming the dramatic effect of solvents on the course of these addition reactions were made by Ma [54] for the corresponding reaction with poly(styryl)lithium. These results suggested that it might be possible to prepare a macromonomer with a terminal 1,1-diphenylethylene functionality by addition of one equivalent of polymeric organolithium with either MDDPE [1,3-*bis*(1-phenylethenyl)benzene] or PDDPE [1,4-*bis*(1-phenylethenyl)benzene] as illustrated in Scheme 3.

A general method for the synthesis of a nonhomopolymerizable macromonomers based on the 1,1-diphenylethylene functionality and their use for the rational synthesis for hetero 3-armed, star-branched polymers have been reported [22, 46]. The procedure is illustrated in Scheme 4 for synthesis of a 3-armed, heteroarm, star-branched polymer with three polystyrene arms with different molecular weights.

Although the addition reactions of poly(styryl)lithium with both MDDPE and PDDPE were investigated for preparing these macromonomers, PDDPE exhibited less tendency to form the corresponding diadduct in both hydrocarbon solution and in the presence of THF. Presumably dimer formation is less favorable in the case of the *para*-substituted PDDPE compared to the *meta*-substituted MDDPE because

SCHEME 3.

PS^2Li + $C_6H_5\overset{|}{C}H$—CH_2PS^1 $\longrightarrow$ $C_6H_5\overset{|}{C}H$—CH_2PS^1

(ring) CH_2=$\overset{|}{C}$ $\overset{|}{C_6H_5}$

5

PS^2CH_2—$\overset{|}{C}Li$ $\overset{|}{C_6H_5}$

6

1) n styrene | 2) ROH

$C_6H_5\overset{|}{C}H$—CH_2PS^1

PS^2CH_2—$\overset{|}{C}$—PS^3 $\overset{|}{C_6H_5}$

7

PS^1 $\diagdown$ $\diagup$ PS^2 $\overset{|}{PS^3}$ ≡

SCHEME 4.

the negative charge in the monoadduct can be delocalized into two aromatic rings and the remaining vinyl group. As discussed previously, even with a fourfold excess of MDDPE, the addition of poly(styryl)lithium in benzene at room temperature produced the dimer in 87% yield [46]. In contrast, with only a twofold excess of PDDPE, the corresponding reaction with poly(styryl)lithium produced only 7% dimer.

The results of investigations of optimum reaction conditions for the synthesis of the 1,1-diphenylethylene-functionalized macromonomer using PDDPE are listed in Table 3. The yield of the desired 1,1-diphenylethylene-functionalized macromonomer (**5**) increased with increasing reaction temperature; however, the amount of dimer formation also increased with increasing reaction temperature.

For the synthesis of 3-armed, heteroarm, star-branched polymers, the first step involves the addition of a polymeric organolithium compound, e.g., poly(styryl)lithium, with the macromonomer, **5**, to form the corresponding coupled product, **6**, a diphenylalkyllithium. For stoichiometric amounts of polymer lithium and macromonomer, it was found that the efficiency of this coupling reaction is >96%. This result also shows that the vinyl functionality of the macromonomer is >96%. Finally, the third arm is formed by addition of monomer, e.g., styrene, in the presence of THF to promote the crossover reaction. SEC analyses of the heteroarm star polymer product showed that each of these steps proceeds efficiently to give the expected products; only relatively small amounts of nonstar product were observed which corresponds in retention volume to the small amount of unreacted macromonomer and a small amount of polystyrene corresponding to the second arm. A narrow molecular weight distribution star product (M_w/M_n = 1.02) was easily obtained by one fractionation step. The SEC curves for each component in this star polymer synthesis and for the fractionated star polymer are shown in Fig. 4.

TABLE 3. Reaction Conditions for the Synthesis of Macromonomers (5) by Reaction of Poly(styryl)lithium (M_n = 5.4 g/mol) with Two Equivalents of PDDPE in t-Butylbenzene

Reaction temp., °C	Reaction time, h	[THF]	Diadduct, %	Functionality UV[b]	NMR[c]
5–8[a]	1.0	20 × [PLi]	1.40	0.98	0.98
25[a]	11.0	None	6.50	—	—
25	1.5	10 × [PLi]	3.06	0.93	0.90
−15	5.0	20 × [PLi]	1.65	0.88	0.84
−65	5.0	20 × [PLi]	0.30	0.84	0.80

[a]Benzene was used as the solvent.
[b]Number of C=C groups per chain as determined by UV absorbance at 260 nm.
[c]Number of C=C groups per chain as determined by ^{1}H NMR.

The limitations of this star polymer synthesis are analogous to those discussed for the hetero 4-armed star polymers. Only reactive polymeric organolithiums will react with the 1,1-diphenylethylene-functionalized macromonomer. However, any monomer which undergoes living anionic polymerization can be added to the coupled lithium adduct (6) to grow an arm and form heteroarm star-branched polymers with well-defined structures and low degrees of compositional heterogeneity. With respect to the macromonomer, although the methodology shown in Scheme 3 is
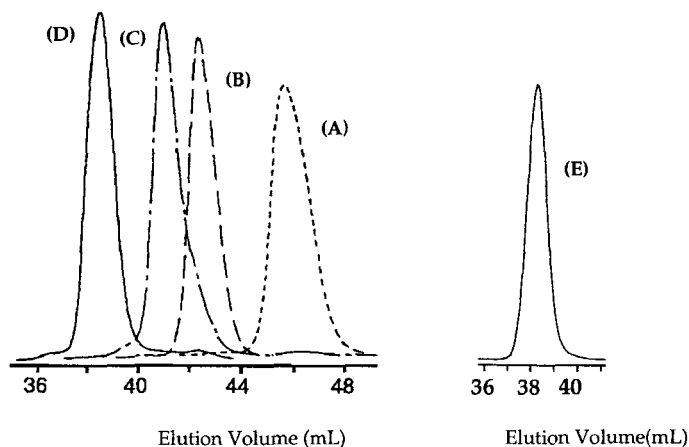

FIG. 4. SEC chromatograms of (A) polystyrene macromonomer (M_n = 5.4 × 10³ g/mol); (B) polystyrene base polymer (M_n = 15.3 × 10³ g/mol) for the second arm; (C) coupled product of PSLi with polystyrene macromonomer (M_n = 20.6 × 10³ g/mol); (D) hetero 3-armed star polymer PS(1)-PDDPE-branch-PS(2)PS(3) [M_n(calc.) = 50 × 10³ g/mol]; and (E) fractionated star polymer.

limited to reactive chain ends, any synthetic methodology which generates a 1,1-diphenylethylene functionality at the terminus of a polymer chain can be used to synthesize the macromonomer. Thus, work is in progress to prepare poly(ethylene oxide)-based 1,1-diphenylethylene macromonomers for heteroarm, star polymer synthesis.

It is of interest to utilize controlled syntheses of heteroarm star-branched polymers to explore the structure–property relationships for branched polymers. Because the radius of gyration of a branched polymer is smaller than that of a linear polymer of the same molecular weight, it is observed that the intrinsic viscosity of a branched polymer is also smaller than that of a linear polymer [9–11]. This relationship is usually expressed in terms of the g' value, which is defined by the intrinsic viscosity ratio of the branched to the corresponding linear polymer of the same molecular weight ($[\eta]_b/[\eta]_l$) [9, 11]. For the 3-armed polystyrene regular star polymers that have three arms with the same nominal molecular weights, g' values vary in the 0.84–0.90 and 0.81–0.88 ranges in θ solvent and good solvent, respectively [27]. For the hetero, 3-armed star polystyrene with arm molecular weights (M_n) of 5.4×10^3, 15.3×10^3, and 36.2×10^3 g/mol, the g' value was determined to be 0.92. Thus, even though this value is higher than expected for a regular 3-armed star polymer, it is still significantly smaller than the corresponding linear polymer as monitored by the g' value.

For 4-armed polystyrene regular star polymers that have four arms with the same nominal molecular weights, g' values vary in the 0.75–0.82 and 0.68–0.72 ranges at 35°C in a θ solvent and good solvent, respectively [55]. For a 4-armed, heteroarm star polystyrene with two arms with $M_n = 12 \times 10^3$ g/mol and two arms with $M_n = 3 \times 10^3$ g/mol, the value of g' was determined to be 0.81. This large effect of small branches once again indicates the sensitivity of viscosity measurements to branching effect.

Rheological investigations of such well-defined heteroarm star polymers will provide insight into the effects of branching on flow, especially in media which are simultaneously good and poor solvents for different types of arms. Another goal will be to determine the critical position and length of a branch required to produce observable changes in the rheological properties of polymers.

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REFERENCES

[1] L. J. Fetters and E. L. Thomas, "Model Polymers for Materials Science," in *Material Science & Technology*, Vol. 12, VCH Verlagsgesellschaft, Weinheim, Germany, 1993, p. 1.

[2] P. Rempp and J. E. Herz, "Model Polymers," in *Encyclopedia of Polymer*

Science and Engineering, Supplement Volume, 2nd ed. (J. I. Kroschwitz, Ed.), Wiley-Interscience, New York, 1989, p. 493.

[3]   P. Rempp and P. Lutz, *Makromol. Chem., Macromol. Symp.*, *67*, 1 (1993).

[4]   S. Bywater, in *Encyclopedia of Polymer Science and Engineering*, Vol. 2, 2nd ed., Wiley-Interscience, New York, 1985, p. 1.

[5]   P. Rempp, E. Franta, and J.-E. Herz, *Adv. Polym. Sci.*, *86*, 145 (1988).

[6]   M. Morton, *Anionic Polymerization: Principles and Practice*, Academic Press, New York, 1983.

[7]   R. N. Young, R. P. Quirk, and L. J. Fetters, *Adv. Polym. Sci.*, *56*, 1 (1984).

[8]   M. Szwarc, *Adv. Polym. Sci.*, *49*, 1 (1983).

[9]   B. J. Bauer and L. J. Fetters, *Rubber Chem. Technol.*, *51*, 406 (1978).

[10] S. Bywater, *Adv. Polym. Sci.*, *30*, 89 (1979).

[11] J. Roovers, "Branched Polymers," in *Encyclopedia of Polymer Science and Engineering*, Vol. 2, 2nd ed. (J. I. Kroschwitz, Ed.), Wiley-Interscience, New York, p. 478.

[12] D. Rein, P. Rempp, and P. J. Lutz, *Makromol. Chem., Macromol. Symp.*, *67*, 237 (1993).

[13] H.-B. Gia, R. Jerome, and P. H. Teyssie, *J. Polym. Sci., Polym. Chem. Ed.*, *18*, 3483 (1980).

[14] I. M. Khan, Z. Gao, K. Khougaz, and A. Eisenberg, *Macromolecules*, *25*, 3002 (1992).

[15] A. Takano, M. Okada, T. Nose, and T. Fujimoto, *Ibid.*, *25*, 3596 (1992).

[16] T. Fujimoto, H. Zhang, T. Kazama, Y. Isono, H. Hasegawa, and T. Hashimoto, *Polymer*, *33*, 2208 (1992).

[17] R. W. Pennisi and L. J. Fetters, *Macromolecules*, *21*, 1094 (1988).

[18] F. Afshar-Taromi and P. Rempp, *Makromol. Chem.*, *190*, 1791 (1989).

[19] S. J. Wright, R. N. Young, and T. G. Croucher, *Polym. Int.*, *33*, 123 (1994).

[20] R. P. Quirk and F. I. Hoover in *Recent Advances in Anionic Polymerization* (T. E. Hogen-Esch and J. Smid, Eds.), Elsevier, New York, 1987, p. 393.

[21] R. P. Quirk, B. Lee, and L. E. Schock, *Makromol. Chem., Macromol. Symp.*, *53*, 201 (1992).

[22] R. P. Quirk and T. Yoo, *Polym. Bull.*, *31*, 29 (1993).

[23] H. Eschwey and W. Burchard, *Polymer*, *16*, 180 (1975).

[24] C. Tsitsilianis, P. Chaumont, and P. Rempp, *Makromol. Chem.*, *191*, 2319 (1990).

[25] C. Tsitsilianis, S. Graff, and P. Rempp, *Eur. Polym. J.*, *27*, 243 (1991).

[26] C. Tsitsilianis, P. Lutz, S. Graff, J.-P. Lamps, and P. Rempp, *Macromolecules*, *22*, 5897 (1991).

[27] N. Khasat, R. W. Pennisi, N. Hadjichristidis, and L. J. Fetters, *Ibid.*, *21*, 1100 (1988).

[28] J. W. Mays, *Polym. Bull.*, *23*, 247 (1990).

[29] H. Iatrou and N. Hadjichristidis, *Macromolecules*, *25*, 4649 (1992).

[30] H. Iatrou and N. Hadjichristidis, *Ibid.*, *26*, 2479 (1993).

[31] R. P. Quirk, S.-H. Guo, M. Alsamarraie, and F. I. Hoover, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, *29*(2), 298 (1988).

[32] R. P. Quirk and J.-J. Ma, *Polym. Int.*, *24*, 197 (1991).

[33] R. P. Quirk and W. C. Chen, *Makromol. Chem.*, *183*, 2071 (1982).

[34] R. P. Quirk and P.-L. Cheng, *Macromolecules*, *19*, 1291 (1986).

[35] R. P. Quirk and M. Alsamarraie, *Ind. Eng. Chem.*, *Prod. Res. Dev.*, *25*, 381 (1986).

[36] H. Gilman and F. K. Cartledge, *J. Organomet. Chem.*, *2*, 447 (1964).

[37] G. G. H. Schulz and H. Höcker, *Makromol. Chem.*, *178*, 2589 (1977).

[38] H. Höcker and G. Lattermann, *Ibid.*, *158*, 191 (1972).

[39] D. F. Shriver and M. A. Drezdzon, *The Manipulation of Air-Sensitive Compounds*, 2nd ed., Wiley-Interscience, New York, 1986.

[40] M. Morton and L. J. Fetters, *Rubber Chem. Technol.*, *48*, 359 (1975).

[41] Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci.*, *Part B*, *5*, 753 (1967).

[42] K. A. Boni, F. A. Sliemers, and P. B. Stickney, *J. Polym. Sci.*, *Part A-2*, *6*, 1567 (1968).

[43] L. H. Tung and R. J. Runyon, *J. Appl. Polym. Sci.*, *17*, 1589 (1973).

[44] L. H. Tung, *Ibid.*, *24*, 953 (1979).

[45] R. P. Quirk, in *Comprehensive Polymer Science. First Supplement* (S. L. Aggarwal and S. Russo, Eds.), Pergamon Press, Oxford, UK, 1992, p. 83.

[46] R. P. Quirk and T. Yoo, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, *34*(2), 578 (1993).

[47] A. Ikker and M. Möller, *New Polym. Mater.*, *4*, 35 (1993).

[48] H. Yuki, *Prog. Polym. Sci. Jpn.*, *3*, 141 (1972).

[49] T. A. Antkowiak, A. E. Oberster, A. F. Halasa, and D. P. Tate, *J. Polym. Sci., Polym. Chem. Ed.*, *10*, 1319 (1972).

[50] A. Yamagishi, M. Szwarc, L. Tung, and G. Y.-S. Lo, *Macromolecules*, *11*, 607 (1978).

[51] R. P. Quirk and B. Lee, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, *32*(3), 607 (1991).

[52] E. Leitz and H. Höcker, *Makromol. Chem.*, *184*, 1893 (1983).

[53] A. D. Broske, T. L. Huang, R. D. Allen, J. M. Hoover, and J. E. McGrath in *Recent Advances in Anionic Polymerization* (T. E. Hogen-Esch and J. Smid, Eds.), Elsevier, New York, 1987, p. 363.

[54] J.-J. Ma, Ph.D. Thesis, University of Akron, 1991.

[55] J. E. L. Roovers and S. Bywater, *Macromolecules*, *7*, 443 (1974).