Polymer Bulletin 31, 29–36 (1993)

Polymer Bulletin

Anionic synthesis of ω-1,1-diphenylethylene-terminated polystyrene macromonomers. Rational synthesis of ABC hetero three-armed-star-branched polymers

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Summary

Polystyrene macromonomers with terminal 1,1-diphenylethylene functionality were prepared by the reaction of one equivalent of poly(styryl)lithium with 1,4-*bis* (l-phenylethenyl)benzene (**PDDPE**). The macromonomer functionalities were determined by ^{1}H NMR [δ(vinyl CH_2) = 5.4 ppm] and UV spectroscopy (λ_{max} = 260 nm). The stoichiometric linking reaction of poly(styryl)lithium (M_n = 15.3 x 10^3g/mol) with an ω-1,1-diphenylethylene-terminated polystyrene macromonomer (M_n= 5.4 x 10^3 g/mol) followed by addition of styrene monomer has been used to prepare a hetero three-armed, star-branched polymer with M_n =5.8x10^4 g/mol (5,400-15,300-37,300). The g' value ($[\eta]_b/[\eta]_l$) was equal to 0.92.

Introduction

Well-defined branched polymers are useful to elucidate the effects of branching on solution, melt and bulk properties and to test theoretical models (1-4). Living anionic polymerization has provided a versatile methodology for the controlled synthesis of star-branched polymers (2,3,5,6). However, few procedures are available for the controlled synthesis of hetero-armed star polymers in which the arms differ in molecular weight or composition (7-14). Herein we report a general method for the synthesis of a non-homopolymerizable macromonomers based on the 1,1-diphenylethylene functionality and their use for the rational synthesis for hetero 3-armed, star-branched polymers.

Experimental

Materials

Styrene, benzene and tetrahydrofuran (Fisher) were purified as described previously (15,16); 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 (17). **PDDPE** was synthesized by the Friedel-Crafts reaction of terephthaloyl chloride with benzene followed by Wittig synthesis of the diolefin according to the procedures of Höcker and Lattermann (18);mp 136.5-137.2°C[lit(18) mp 137°C]. This material exhibited only one peak by HPLC analysis

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Preparation of macromonomers

sec-Butyllithium-initiated polymerizations of styrene in benzene or t-butylbenzene (10 wt % monomer) were effected at room temperature using either Schlenk-type equipment (19), high vacuum techniques (20) or an Argon atmosphere glovebox (21). After removing an aliquot for characterization, the poly(styryl)lithium solution was added into either t-butylbenzene or benzene with THF as the polar additive. The reactions of this poly(styryl)lithium solution with a two-fold excess of **PDDPE** were effected at various temperatures with stirring for 1.5-5 hr in a glass reactor. After the addition reaction was complete as determined by UV spectroscopy, the resulting polymer solution was quenched with methanol and then precipitated two times into methanol to remove the unreacted, excess **PDDPE** and solvent. The polymers were filtered and dried in vacuum at 25°C.

Preparation of 3-arm star polymer using macromonomer

Poly(styryl)lithium (M_n=15.3x10^3 g/mole) was prepared in t-butylbenzene using sec-butyllithium- initiated polymerization in the Argon atmosphere dry box. A t-butylbenzene (10 mL) solution of 1.35 g of freeze-dried macromonomer (5.4x10^3 g/mole), prepared at -65 °C in the presence of THF ([THF]/[PLi] = 20), was added portionwise to a solution of poly(styryl)lithium(15.3x10^3 g/mole) in t-butylbenzene at room temperature. After approximately 6 hours, an aliquot (1mL) was removed from the reactor, terminated with methanol and analyzed by SEC. This process was repeated until the correct stoichiometric balance was obtained. The star polymer was prepared by addition of 5.5mL of styrene monomer in the presence of THF ([THF]/[PLi] = 20) to the living coupled product; after 1.5 hours the polymerization was terminated by addition of degassed methanol. The star polymer was purified by fractionation with mixtures of toluene and methanol.

Characterization

Size-exclusion chromatographic (SEC) analyses of polymers were performed at a flow rate of 1.0 mL min^{-1} in THF at 30 °C by using a waters HPLC component system (RI or Hewlett Packard 1040 diode array detectors) equipped with ultra-μ-Stragel columns (two 500, two 10^3, 10^4 and 10^5 Å) after calibration with standard polystyrene samples (Polymer Laboratories). The number average molecular weight of the star-branched polymer was determined using a membrane osmometer (Membrane Osmometry model 503, Mechrolab Inc.) at 37°C in toluene and from the universal calibration curve (22) generated from SEC elution volumes and intrinsic viscosities calculated using the Mark-Houwink constants (K=1.03x10^{-4}, a = 0.731) (23-25) for linear polystyrene standards. The intrinsic solution viscosity of the star-branched polymer was 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 using a Varian Gemini-200 spectrometer. Deuterated chloroform was used as the solvent. UV-Vis absorption spectra of the macromonomers and the living polymers were obtained using a Hewlett-Packard 8452A Diode array spectrophotometer with a 1.0 cm or 0.1 cm UV cell, respectively.

Results and Discussion

Divinylidene compounds such as 1,3-bis(1-phenylethenyl)benzene, not being anionically homopolymerizable, add 2 moles of sec-butyllithium (sec-BuLi) in hydrocarbon solution to form difunctional initiators for anionic polymerization (26). For 1,3-bis(1-phenylethenyl)benzene (**MDDPE**) , the rate constants of the first and second addition step of sec-BuLi are both 1.98×10^{-2} L/mol s in toluene (27); for the **PDDPE** the rate constant for the first addition is 2.06×10^{-2} L/mol s and that for the second additon is 1.51×10^{-3} L/mol s in toluene (27). Broske and coworkers (28) reported that the monoadduct of **MDDPE** and sec-butyllithium could be prepared in THF at -78°C. Similar observations were made by Ma (29,30) for the corresponding reaction with poly(styryl)lithium. These results suggested that it might be possible to prepare macromonomer with a terminal 1,1-diphenylethylene functionality by addition of one equivalent of polymeric organolithium with either **MDDPE** or **PDDPE**.

Although the addition reactions of poly(styryl)lithium with both **MDDPE** and **PDDPE** were investigated for preparing 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 the negative charge in the monoadduct can be delocalized into all three aromatic rings and the remaining vinyl group. For example, even with a four-fold excess of **MDDPE**, the addition of poly(styryl)lithium in benzene at room temperature produced the dimer in 87% yield . In contrast, with only a two-fold excess of **PDDPE**, the reaction with poly(styryl)lithium produced only 7% dimer.

The addition reaction of poly(styryl)lithium with **PDDPE** [see eq (1)] was investigated under a variety of experimental conditions to obtain the maximum yield of macromonomer and the minimum amount of diadduct. The results are shown in Table 1; the amount of dimer formation was determined by SEC analysis. In benzene at room temperature the monoaddition reaction is complete in less than 2 hours; in the presence of THF, the reaction is complete in approximately one hour.

By comparison of the ^{1}H-NMR spectra of the base polystyrene and the corresponding 1,1-diphenyethylene macromonomer (see Figure 1), it was observed that the macromonomer exhibited characteristic resonance peaks for the terminal diphenyl alkyl methine proton and vinyl protons at $\delta = 3.5$ppm and 5.4 ppm, respectively. The NMR double bond functionality results listed in Table 1 were determined by integrating the peak area for the vinyl protons ($\delta = 5.4$ppm) relative to the area for the aromatic protons ($\delta = 6.2\text{-}7.4$ ppm) . The double bond functionality in the macromonomer was also evaluated by UVspectroscopy. The 1,1-diphenylethylene group exhibits a strong absorbance ($\varepsilon = 11.8 \times 10^4$) at 260nm; in contrast, unfunctionalized polystyrene exhibits only a weak absorbance at this wavelength ($\varepsilon = 182$). Thus, the observed absorbance at 260nm was used to estimate the functionality after correction for the absorbance of the base polystyrene and the results are also listed in Table 1.

The yield of the desired 1,1-diphenylethylene-functionalized macromonomer (**1**) increased with increasing reaction temperature; however, the amount of dimer

Table 1

Reaction conditions for the synthesis of macromonomers 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 (hr.)	[THF]	diadduct (%)	Functionality UV[b]	Functionality NMR[c]
5-8[a]	1.0	20 x [PLi]	1.40	0.98	0.98
25[a]	11.0	none	6.50	-	-
25	1.5	20 x [PLi]	3.06	0.93	0.90
-15	5.0	20 x [PLi]	1.65	0.88	0.84
-65	5.0	20 x [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 260nm. [c]Number of C=C groups per chain as determined by ^{1}H NMR.

formation also increased with increasing reaction temperature. The macromonomer with the highest functionality (0.98) and minimum dimer (1.4%) was obtained in benzene at 5-8°C.

These macromonomers have been used to develop a general synthesis for hetero 3-armed star polymers as shown in Scheme 1. The first step involved the coupling reaction of poly(styryl)lithium (M_n = 15.3 g/mol) with the polystyrene macromonomer (**1**, M_n = 5.4 g/mol) to form the corresponding diphenylalkyllithium adduct, **2**. In this reaction, the stoichiometric balance is very important because any excess macromonomer will result in the formation of star polymer with arm functionality higher than 3. From the SEC results

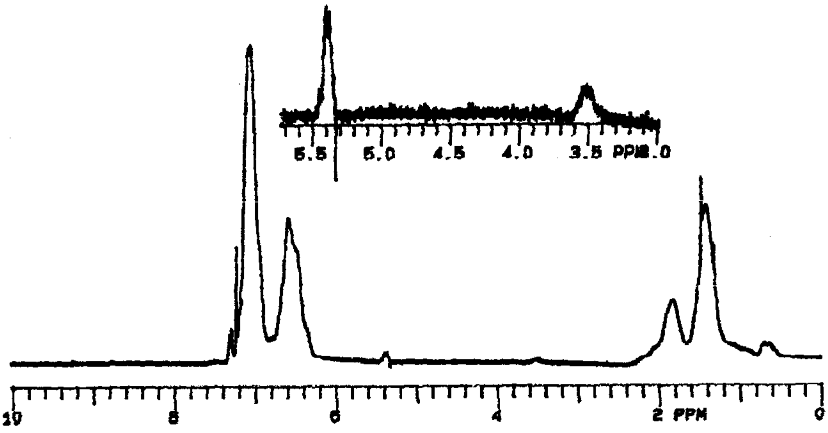
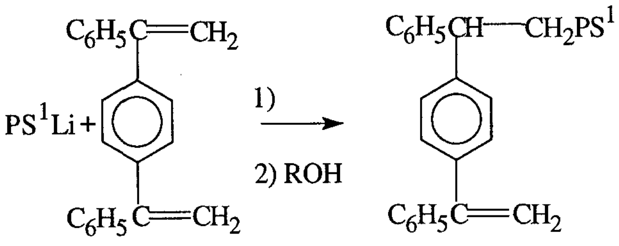


Figure 1:
^{1}H NMR spectrum of polystyrene macromonomer (**1**) (M_n = 5.4x10^3 g/mole).



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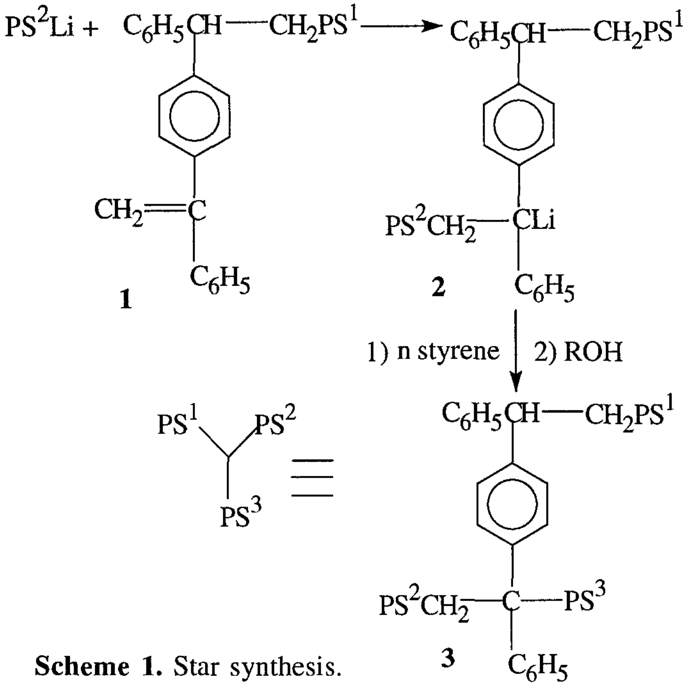
(1)

shown in Figure 2, the amount of the unreacted macromonomer (unfunctionalized polystyrene) was approximately 4.2% for the macromonomer that was prepared at -65 °C (see Table 1); this corresponds to an effective macromonomer functionality of 95.8% which is higher than the functionalities obtained by UV(84%) and NMR(80%) methods (see Table 1).



Scheme 1. Star synthesis.

The crossover reaction to form the third arm of the star (3) was carried out by adding styrene monomer in the presence of THF (20x[PLi]) for 1.5 hours; the amount of styrene added was calculated to result in an arm molecular weight corresponding to M_n = 30 x 10^3 g/mol. The SEC chromatograms corresponding to the macromonomer, the coupled product and the final hetero 3-armed star polymer (3) are compared in Figure 3. The overall efficiency of this star polymer synthesis is apparent from these results. There are only relatively small quantities of non-star polymers in the final product corresponding vide infra) to the unfunctionalized macromonomer and to polystyrene with molecular weight corresponding to the second arm polystyrene homopolymer. The higher molecular weight portion is ascribed to dimer formation resulting from oxygen contamination in glovebox. It was expected that these factors would result in some differences between the observed molecular weight and the calculated molecular weight for the star product.

The characterization data for the final star-branched polymer are listed in Table 2. The number average molecular weights determined by both membrane osmometry and using the universal calibration method (U.C.) (22) are higher than the molecular weight predicted from the arm molecular weights and the stoichiometry of the final polymerization to grow the third arm [M_n(calc) = 50 x 10 ^{3} g/mol]. This is presumably a consequence of the fact that perfect stoichiometry was not obtained as evidenced by the two bumps in the SEC curve for the final star polymers (see Figure 3) corresponding to arm-1 and arm-2; another factor is the fact that the final arm molecular weight is very sensitive to the number of moles of active polymeric lithium initiator. Given these

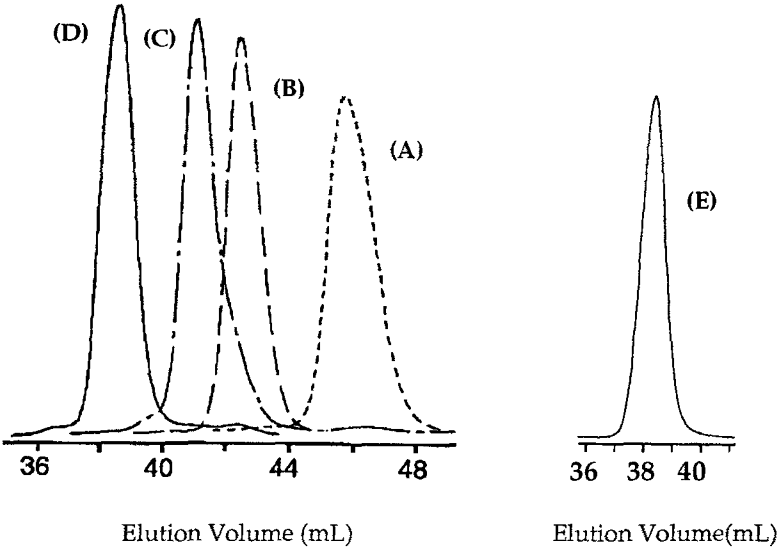


Figure 2:
SEC chromatograms of (A) polystyrene macromonomer (M_n = 5.4x10^3 g/mol); (B) polystyrene base polymer (M_n = 15.3x10^3 g/mol) for second arm; (C) coupled product of PSLi with polystyrene macromonomer (M_n = 20.6x10^3 g/mol) ; (D) hetero 3-armed star polymer PS(1)-PDDPE-branch-PS(2)PS(3) [M_n(calc.) = 50x10^3 g/mol] and (E) fractionated star polymer.

Table 2

Characterization data for polystyrene arms, coupling product and 3-arm polystyrene

polymer	Molecular weight characterization data			
	M_n (g/mol)			M_w/M_n^{c}
	SEC	U. C.^{a}	M. O.^{b}	
arm 1	5.4 x10^3	-	-	1.03
arm 2	15.3 x10^3	-	-	1.02
coupled product (**3**)	20.6x10^3	-	-	1.04
3- arm star	53.7 x10^3	55.4 x10^3	58.3 x10^3	1.02

^{a}Universal calibration curve method (22). ^{b} Membrane osmometry. ^{c} SEC.

variables, the discrepancy between the observed and calculated final molecular weight (15%) is not surprising. This discrepancy does not contribute to compositional heterogeneity, however, since the molecular weight distribtuion of the final star-branched polymer is quite narrow (M_w/M_n = 1.02).

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 (1-3). 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 ($[\eta]_b/[\eta]_l$) (1-3). For the 3-armed polystyrene regular star polymer that has the same arm size, g' values vary in the range of 0.84-0.90 and 0.81-0.88 in θ solvent and good solvent, respectively (8). However the g' value of the hetero 3-armed polystyrene star polymer prepared is higher than that of the regular star polymer. The application of this methodology for the synthesis of ABC star polymers is in progress.

Table 3 :

Calculation of g' values

molecular weight (g /mole)	$[\eta]_l$ ^{a} (dL/g)	$[\eta]_b$ ^{b} (dL/g)	g'
55.4 x 10^3	0.302	0.285	0.94
58.3 x 10^3	0.316	0.285	0.90

^{a}From the equation $[\eta]_l = 1.03 \times 10^{-4} M_n^{0.731}$(23-25) ^{b}Measured in THF at 30°C.

Acknowledgment

This research was supported by National Science Foundation Grant DMR-9014502. The authors thank FMC, Lithium Division, for providing samples of sec-butyllithium.

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Accepted May 10, 1993 K