Synthesis of Well-Defined Multifunctionalized Polystyrenes with Benzyl Bromide Moieties by a Novel Iterative Divergent Approach

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Summary: Well-defined chain-end-functionalized polystyrenes with two, four, eight, sixteen, and thirty-two benzyl bromide moieties were synthesized by the methodology based on a novel iterative divergent approach. In this methodology, the entire iterative synthetic sequence involves only two sets of the reactions: a coupling reaction of the terminal benzyl bromide moieties with the functionalized anion prepared from 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene and *sec*-BuLi and a transformation reaction of the introduced *tert*-butyldimethylsilyloxymethyl groups into bromomethyl functions by treatment with LiBr-$(CH_3)_3SiCl$. The iteration started with chain-end-functionalized polystyrene with one benzyl bromide moiety and could be repeated five times. All iterations proceeded quantitatively to afford chain-end-functionalized polystyrenes with a definite number of benzyl bromide moieties up to thirty-two.

Introduction

Functionalized 1,1-diphenylethylene derivatives (F-DPE) are now often utilized as convenient and versatile chain-functionalized agents of living anionic polymers.[1-12] For instance, chain-end-functionalized polymers are readily synthesized by the monoaddition reaction of living anionic polymers to F-DPE. Highly reactive anionic initiators like organolithium compounds quantitatively react with F-DPE in a monoaddition manner to generate new functionalized 1,1-diphenylalkyl anions. They can be used as functional initiators in the anionic polymerization to afford functionalized polymers at their initiating chain-ends. Moreover, in-chain-functionalized polymers can be synthesized by the reaction of living anionic polymers with F-DPE derivatives, followed by anionic polymerization of additional monomers to extend another polymer chains.[12] This method is named by Quirk as "*living functionalization reaction*" and becomes very important procedure for in-chain-functionalized polymers difficult to be synthesized by any other methods.[1] For such functionalizations, monoaddition nature of F-DPE derivatives toward anionic species and subsequent polymerization of additional monomers with the generated 1,1-

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diphenylalkyl anions after the monoaddition reactions are utilized.

Recently, we have successfully synthesized well-defined chain-end- and in-chain-functionalized polystyrenes with a definite number of benzyl halide moieties by the methodology in which the above-mentioned procedures are further extended.[13-17] The methodology involves the diverse modes of addition and coupling reactions of polystyryllithium with either 1,1-bis(3-methoxymethylphenyl)ethylene (**1**) or 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**2**) and subsequent transformation reactions into benzyl halides. In general, the benzyl halide can be introduced in numbers from one to four at chain-ends or in-chain. By using dianionic species and α,ω-dihaloalkanes prepared from **1** and potassium naphthalenide, it is possible to introduce up to eight benzyl chlorides at chain-ends and sixteen benzyl chlorides in chains at the present time.[18], [19]

Herein, we will present a more efficient methodology based on a novel iterative divergent approach for the synthesis of chain-end-functionalized polystyrenes with a large number of benzyl bromide moieties up to thirty-two.

Experimental

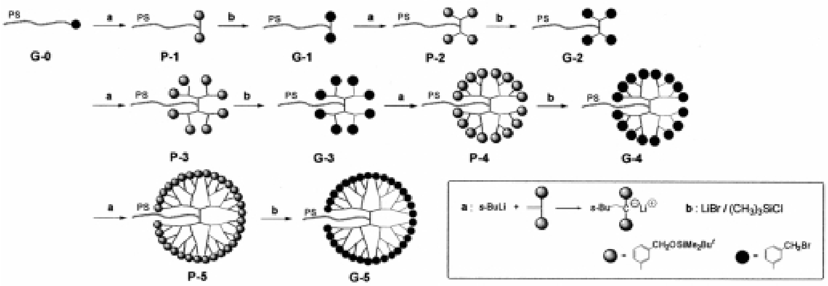
Synthesis of chain-end-functionalized polystyrene with two benzyl bromide moieties (G-1) was synthesized by the following reaction steps: At first, the reaction of **G-0**[14] (4.76 g, 1.07 mmol in THF, 47mL) with a 1.2-fold excess of the functionalized 1,1-diphenylalkyllitium prepared from *sec*-BuLi (1.29 mmol in heptane, 1.3mL) and 1.1-fold excess of **1** (1.42 mmol in THF, 1.4mL) was carried out in THF at −78 °C for 1 h. The reaction was terminated with degassed methanol and the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The resulting polymer, **P-1**, was purified by repeated reprecipitation from THF to methanol twice and freeze-drying from its benzene solution for at least 24 h for the next reaction. Secondly, a solution of **P-1** (4.89 g, 1.00 mmol) in $CHCl_3$ (30 mL) was added drop-wise into a 1:1 mixture of LiBr (8.68 g, 100 mmol) and $(CH_3)_3SiCl$ (10.9 g, 100mmol) in a mixed solvent of CH_3CN (30 mL) and $CHCl_3$ (120 mL) at 40 °C for 5 h. The reaction mixture was then poured into water to precipitate the polymer, **G-1**. It was purified by repeated reprecipitation twice and freeze-dried and characterized.: ^1H NMR ($CDCl_3$) δ 7.2-6.2 (m, 216H, Aromatic), 4.39-4.34 (m, 4H, $-C\boldsymbol{H}_2Br$), 2.5-1.2 (m, 130H, $C\boldsymbol{H}_2-C\boldsymbol{H}-$), 0.8-0.5 (m, 12H, $-CH(C\boldsymbol{H}_3)CH_2C\boldsymbol{H}_3$). Found: C, 88.50; H, 7.76; Br, 3.57. Calc. for $C_{356}H_{360}Br_2$:

C, 89.10; H, 7.56; Br, 3.33%. IR (KBr, cm^{-1}): 1208s(-CH$_2$Br). Similarly, chain-end-functionalized polystyrenes with four (**G-2**), eight (**G-3**), sixteen (**G-4**), and thirty-two (**G-5**) benzyl bromide moieties were synthesized. Their spectroscopic data are as follows: **G-2**: ^{1}H NMR (CDCl$_3$) δ 7.2-5.9 (m, Aromatic), 4.40-4.34 (m, 8H, -C$\boldsymbol{H}_2$Br), 3.4-3.0 (m, 6H, -(Ph)$_2$C-C$\boldsymbol{H}_2$-Ph-), 2.5-1.2 (m, C$\boldsymbol{H}_2$-C$\boldsymbol{H}$-), 0.8-0.4 (m, 24H, -CH(C$\boldsymbol{H}_3$)CH$_2$C$\boldsymbol{H}_3$). Found: C, 86.32; H, 7.62; Br, 5.96. Calc. for $C_{400}H_{410}Br_4$: C, 86.71; H, 7.46; Br, 5.83%. IR (KBr, cm^{-1}): 1208s(-CH$_2$Br). **G-3**: ^{1}H NMR (CDCl$_3$) δ 7.2-5.8 (m, Aromatic), 4.36-4.32 (m, 16H, -C$\boldsymbol{H}_2$Br), 3.5-2.7 (m, 8H, -(Ph)$_2$C-C$\boldsymbol{H}_2$-Ph-), 2.5-1.2 (m, C$\boldsymbol{H}_2$-C$\boldsymbol{H}$-), 0.8-0.4 (m, 48H, -CH(C$\boldsymbol{H}_3$)CH$_2$C$\boldsymbol{H}_3$). Found: C, 83.11; H, 7.55; Br, 9.72. Calc. for $C_{476}H_{498}Br_8$: C, 83.35; H, 7.32; Br, 9.33%. IR (KBr, cm^{-1}): 1208s(-CH$_2$Br). **G-4**: ^{1}H NMR (CDCl$_3$) δ 7.2-5.7 (m, Aromatic), 4.35 (s, 32H, -C$\boldsymbol{H}_2$Br), 3.5-2.6 (m, 30H, -(Ph)$_2$C-C$\boldsymbol{H}_2$-Ph-), 2.4-1.2 (m, C$\boldsymbol{H}_2$-C$\boldsymbol{H}$-), 0.8-0.2 (m, 96H, -CH(C$\boldsymbol{H}_3$)CH$_2$C$\boldsymbol{H}_3$). Found: C, 79.39; H, 7.76; Br, 13.13. Calc. for $C_{636}H_{682}Br_{16}$: C, 79.52; H, 7.16; Br, 13.32%. IR (KBr, cm^{-1}): 1208s(-CH$_2$Br). **G-5**: ^{1}H NMR (CDCl$_3$) δ 7.2-5.5 (m, Aromatic), 4.33 (s, 64H, -C$\boldsymbol{H}_2$Br), 3.5-2.6 (m, 62H, -(Ph)$_2$C-C$\boldsymbol{H}_2$-Ph-), 2.4-1.2 (m, C$\boldsymbol{H}_2$-C$\boldsymbol{H}$-), 0.8-0.3 (m, 192H, -CH(C$\boldsymbol{H}_3$)CH$_2$C$\boldsymbol{H}_3$). Found: C, 76.00; H, 7.00; Br, 17.00. Calc. for $C_{956}H_{1049}Br_{32}$: C, 76.05; H, 7.00; Br, 16.95%. IR (KBr, cm^{-1}): 1208s(-CH$_2$Br). ^{1}H NMR (CDCl$_3$) δ 4.33 (s, 64H, -CH$_2$Br). IR (KBr, cm^{-1}): 1208s(-CH$_2$Br).

Results and Discussion

For the synthesis of chain-end-functionalized polystyrenes with a definite number of benzyl bromide moieties, we have presented a more effective methodology based on a novel iterative divergent approach using **2**. By developing this methodology, a large number of benzyl bromide moieties up to thirty-two could successfully be introduced at the polystyrene chain-end. The synthetic procedure is outlined in Scheme 1.

Scheme 1



Basically, only two sets of reactions are needed for the entire iterative synthetic sequence: a coupling reaction of the terminal benzyl bromide moieties with the functionalized anion prepared from **2** and *sec*-BuLi and a transformation reaction of the introduced *tert*-butyldimethylsilyloxymethyl groups into bromomethyl functions by treatment with a 1:1 mixture of LiBr and $(CH_3)_3SiCl$. The iteration starts with chain-end-functionalized polystyrene with one benzyl bromide moiety synthesized according to our procedure previously reported.[14]

First of all, chain-end-functionalized polystyrene with one benzyl bromide moiety was reacted with a 1.2-fold excess of the functionalized anion prepared from **2** and *sec*-BuLi. The reaction was complete within 1 h in THF at −78 °C. The *tert*-butyldimethylsilyloxymethylphenyl groups thus introduced at the chain-end were transformed into benzyl bromide functions by treatment with LiBr-$(CH_3)_3SiCl$ at 40 °C for 5 h. The resulting polymer **(G-1)** was characterized by various analytical methods including IR, elemental analysis, ^1H NMR, SEC, and vapor pressure osmometry (VPO). The results are summarized in Table 1.

Table 1. Synthesis of chain-end-functionalized polystyrenes with two, four, eight, sixteen, and thirty-two benzyl bromide moieties[a)]

Polymer	M_n (kg/mol)				M_w/M_n [b)]	Benzyl bromide functionality[c)]		
	calcd	SEC[b]	^1H NMR	VPO		calcd	NMR	E. A.
G-1	4.7_9	4.2_3	4.7_5	4.8_0	1.04	2	2.0_0	2.1_4
G-2	5.4_7	4.9_6	5.6_4	5.4_2	1.04	4	3.9_2	4.0_9
G-3	6.8_5	5.6_0	6.9_5	6.7_8	1.03	8	8.0_8	8.3_3
G-4	9.5_9	7.0_5	9.9_4	9.6_4	1.04	16	$15._9$	$15._8$
G-5	$15._0$	8.5_4	$15._6$	$14._8$	1.03	32	$32._0$	$32._1$

[a)] Yields of polymers were 100% in all cases.

[b)] $M_{n(SEC)}$ and M_w/M_n values were estimated from SEC calibration relative to standard polystyrenes.

[c)] Functionalities of benzyl bromide moiety were determined by ^1H NMR and elemental analysis, respectively.

The IR spectrum of **G-1** exhibited an absorption peak at 1208 cm^{-1} characteristic to the C-Br bond, while two peaks at 1254 and 836 cm^{-1} for the Si-C bond in the prepolymer **(P-1)** completely disappeared. The ^1H NMR of **G-1** showed a resonance at 4.37 ppm assigned to the bromomethylene protons, whereas two resonances at 0.91 and 0.06 ppm characteristic to methyl protons of the *tert*-butyldimethylsilyl group and a resonance at 4.58 ppm for the silyloxymethylene protons observed in **P-1** completely disappeared. The degree of benzyl bromide-functionalization was determined by ^1H NMR to be 2.0_0. For this determination, two resonances at 4.37 ppm for the bromomethylene protons and

and 0.70 ppm for methyl protons of the initiator fragment were used. The results of elemental analysis (C, H, Br) for **G-1** were quite consistent with the assigned structure (see experimental section).

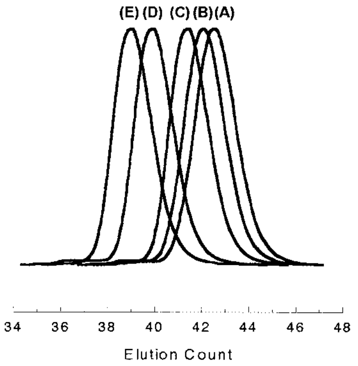


Figure 1 SEC Chromatograms of **G-1(A)**, **G-2(B)**, **G-3(C)**, **G-4(D)**, and **G-5(E)**

Figure 1(A) presents the SEC trace of **G-1**, which shows a symmetrical monomodal peak with remaining molecular weight distribution very narrow, the M_w/M_n being 1.04. The observed M_n value by SEC relative to polystyrene (4.2_3 kg/mol) was however somewhat smaller than the calculated value (4.7_9 kg/mol) based on the ratio of [M]/[I]. The absolute M_n value was therefore determined by VPO. The determined value (4.8_0 kg/mol) was in a fair agreement with the calculated value. Moreover, the M_n value (4.7_5 kg/mol) estimated by ^{1}H NMR also agreed well with the calculated value. All of the analytical results clearly indicate that the resulting polymer, **G-1**, is the expected chain-end-functionalized polystyrene with two benzyl bromide moieties as well as well-controlled chain length. The results also confirm that two reactions quantitatively proceed as desired.

Since **G-1** had the same end groups as the starting polymer, the same reaction sequence could be repeated in the second iteration. The resulting polymer (**G-2**) showed the well-defined chain-end-functionalized polystyrene with four benzyl bromide moieties on the basis of the analytical results (also see Table 1). With use of **G-2** as a starting polymer, the same reaction sequences were successively repeated in the third, fourth, and fifth iterations. The analytical results of the resulting polymers all, **G-3**, **G-4**, and **G-5**, clearly indicate the desired structures as expected. Thus, we were able to achieve the synthesis of chain-end-functionalized polystyrenes with eight, sixteen, and thirty-two benzyl bromide moieties.

As shown in Figure 1(A) ~ 1(E), all of the resulting polymers exhibit monomodal SEC peaks with narrow molecular weight distributions. In all cases, their M_n values observed by SEC were somewhat smaller than those calculated, presumably due to the dendritic structures of the benzyl bromide moieties introduced at the chain-ends. On the other hand, the observed M_n values by VPO and ^{1}H NMR agreed quite well with calculated in all polymer samples. The numbers of the benzyl bromide moieties were observed by both ^{1}H NMR and elemental analysis to be eight, sixteen, and thirty-two within analytical errors. These results again confirm that all of the iterations proceed quantitatively.

Thus, the procedure based on the iterative divergent approach is especially effective for the synthesis of chain-end-functionalized polystyrenes with a large number of benzyl bromide moieties. It maintains the following features that make it well suited for the requisite numbers of benzyl bromide moieties: (1) Only two sets of the reactions are needed in each iteration. (2) These reactions proceed efficiently and quantitatively. Accordingly, the expected functionalized polystyrenes from **G-1** to **G-5** are readily synthesized. Moreover, they are quantitatively end-functionalized and precisely controlled with respect to chain length. (3) At each stage in the iteration, the number of the benzyl bromide moieties doubles and successively increases from two, four, eight, sixteen, to thirty-two. (4) The iteration may possibly be further continued from **G-5**. (5) Since the reactions are always carried out on the polymer chains, all of the resulting functionalized polymers can be easily isolated and purified only by reprecipitation two or three times. (6) The introduced benzyl bromide moieties are, needless to say, highly reactive electrophiles, which can readily be transformed into a wide variety of other functional groups.

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